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A TREATISE ON CHEMISTRY.

VOL. III.—PART I.

A

TREATISE ON CHEMISTRY.

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VOLUME III.

THE CHEMISTRY OF THE HYDROCARBONS AND THEIR DERIVATIVES,

OR

ORGANIC CHEMISTRY.

PART I.

> "*Chymia, alias Alchemia et Spagirica, est ars corpora vel mixta, vel composita, vel aggregata etiam in principia sua resolvendi, aut ex principiis in talia combinandi.*"—STAHL, 1723.

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A TREATISE ON CHEMISTRY.

ORGANIC CHEMISTRY.

ORGANIC CHEMISTRY,

OR THE CHEMISTRY OF THE HYDROCARBONS AND THEIR DERIVATIVES.

HISTORICAL INTRODUCTION.

1 Many of the most important chemical facts known to the ancients have their place in the Organic portion of our science. Thus, for example, the only acid with which the ancients were acquainted was an organic substance, viz., vinegar or dilute acetic acid, and the name of this body and the idea of acidity were expressed by closely related words, ὄξος, *acetus*, vinegar; and ὀξύς, *acidus*, acid.[1]

Again, the first reagent of any kind which we find described is also an organic body, namely the extract of gall-nuts with which, as Pliny states, the ancients were accustomed to ascertain whether verdigris was adulterated with green vitriol.

The first rude attempts at distillation were also made with an organic body, viz., turpentine; whilst the first salts which were artificially prepared were organic ones, being those obtained by the action of vinegar on the alkalis. The mode of preparing soap by the action of fats upon the alkalis was also known in early times. In addition to a knowledge of the fats and oils, the ancients were acquainted with various resins, and colouring matters, as well as with sugar and gum. They likewise understood the preparation of wine from grape-juice, and certain nations, especially the Egyptians, Gauls and Germans, were accustomed to prepare beer from malted grain.

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[1] See Vol. ii. part i. p. 32.

As the direction in which the science first developed itself was that of alchemy, the object of which was the conversion of the baser metals into gold and silver, it is natural that attention was in the first place paid rather to the properties of mineral substances than to those of organic bodies. Nevertheless improvements in general chemical processes, especially that of distillation, gradually led to the discovery of definite organic compounds such as spirit of wine (*aqua vitæ*) and certain of the essential oils. The action of heat upon bodies when air is excluded was also studied in early times. Thus the products of the dry distillation, as we now term this process, of bodies such as cream of tartar were investigated, and the action of acids upon spirits of wine and other organic substances was likewise examined.

Later on, towards the sixteenth century, the cultivators of this science, as we have seen,[1] exhibited activity mainly in two directions, in the first place in the prosecution of the branch science of metallurgy, and secondly, in the development of iatro-chemistry. In these branches, and especially in the latter, it was, however, the inorganic division of the science which made the most rapid strides, because, in opposition to the practice of the old school, the use of metallic preparations as medicines was largely introduced. At the same time the study of organic compounds, and especially of the active principles of organic bodies, was not entirely neglected. Thus during this period benzoic acid, succinic acid, wood-vinegar, milk-sugar, and various ethers were discovered.

In the succeeding epoch, when the true function of chemistry had become fully recognised, inorganic compounds still claimed the more immediate attention of chemists, not only because they are more stable than organic bodies, but also because in the latter case it had not as yet proved possible, as it had in the case of inorganic bodies, to determine their composition by synthesis as well as by analysis.

2 From this period it is that we may date a distinct separation of mineral chemistry from that portion of the science which is concerned with the study of substances formed in vegetable and animal organisms. For a long time chemical compounds were grouped together according to their physical properties, and the common names at present in use for many substances remind one of this bygone classification. Thus, for instance, olive oil and other vegetable and animal oils were placed

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[1] Vol. i. p. 8, "Historical Introduction."

together with oil of vitriol and with oleum tartari (deliquesced carbonate of potash). Alcohol again (spirit of wine) was classed with stannic chloride (fuming spirit of Libavius), with ammonia (spirit of hartshorn), and with nitric acid (spirit of nitre), &c. Common butter was placed in the same group as antimony trichloride (butter of antimony) and other semi-solid metallic chlorides. Colourless solid bodies which were soluble in water, and possessed a peculiar taste were all classed together as salts, even sugar being placed in this group.

3 In the year 1675 Nicolas Lémery published his *Cours de Chymie.* In this work the aim of chemistry is defined to be a knowledge of the various substances "qui se rencontrent dans un mixte," understanding by this term all growing or increasing natural products. Lémery distinguished these bodies as mineral, vegetable, and animal products. In the first group he placed the metals, minerals, earths, and stones; in the second, plants, resins, the different kinds of gums, fungi, fruits, acids, juices, flowers, mosses, manna, and honey; and under the third head he described the various parts of animal bodies.

Although Lémery's system of classification was generally accepted, the founders of the phlogistic theory endeavoured to show that the observed differences depended on a variation in the composition of the bodies classed under each head. Thus Becher in 1669 had argued that the same elements occur in the three natural kingdoms, but that they are combined together in a simpler manner in mineral substances than they are in vegetable and animal bodies. Stahl, on the other hand, asserted in 1702, that in vegetable as well as in animal substances the watery and combustible principles predominate, and that these make their appearance when such an organic substance is heated out of contact with air, water and combustible charcoal being formed.

At this time, as well as during the preceding period, the investigation of organic compounds was carried on mainly with a view either to the preparation of medicines, or to the improvement of technical processes, such as that of dyeing. Only towards the close of the phlogistic period did organic chemistry begin to make real progress, and it is from this time forward that the scientific investigation of organic bodies can be said to have commenced.

4 The early ideas of van Helmont and afterwards of Stahl, that all organic substances can be resolved by the action of

heat into their ultimate constituents, viz., aqueous and combustible principles, were successfully combated by Boyle, who, in the *Sceptical Chemist* (1661), proved that this is not the case, inasmuch as the application of heat leads to different results according as air is permitted to have access or not, and that the various residues thus obtained in no way merit a uniform designation. The general reception of Boyle's views was slow but sure. Still it was not until Lavoisier's discovery in 1775 of the composition of carbon dioxide, and Cavendish's determination of that of water, that the fact of the existence of carbon and hydrogen in alcohol was ascertained (1784).

5 Amongst the early organic researches of a truly scientific character those of Scheele deserve the first mention, for he either discovered nearly all the most important vegetable acids, or suggested methods for their discrimination. Thus, he showed that the acid from lemons differs from that from grapes, whilst that contained in apples differs again from both of these. He proved that a fourth distinct acid is found in wood-sorrel, and pointed out that this can be obtained artificially by heating sugar with nitric acid. He likewise obtained gallic acid from gall-nuts, uric acid from urine, and lactic acid from sour cow's milk. By the oxidation of milk-sugar he prepared mucic acid, a substance altogether different from the acid obtained from cane-sugar. In the preparation of these and other acids Scheele employed methods many of which are in use at the present day. Scheele also showed that fatty oils and the solid fats contain the common principle glycerin, termed by him the sweet spirit of oils. This, he says, is connected with sugar not only on account of its sweet taste, but also because, like sugar, it is oxidized to oxalic acid by nitric acid.

Scheele's friend Bergman also assisted the progress of organic chemistry, whilst Rouelle who distinguished himself by researches on the hitherto neglected division of animal chemistry, discovered urea and hippuric acid.

6 Investigations such as these drew general attention to the subject of organic chemistry, and Lavoisier having established the true principle upon which the process of combustion depends, turned his mind to this interesting branch of the science, and ascertained the ultimate composition of certain organic compounds. He came to the conclusion that vegetable bodies are chiefly composed of carbon, hydrogen, and

oxygen, whilst the compounds of the animal kingdom contain in addition to these elements, nitrogen and not unfrequently phosphorus.[1]

The Lavoisierian system of chemistry was essentially the chemistry of oxygen and its compounds, and hence attention was naturally directed to the question whether a given compound is capable of combining, like an element, with oxygen, or whether it was already combined with this element. To that portion of a substance which combines with oxygen, Lavoisier, at the suggestion of Guyton de Morveau, gave the name of *la base* or *le radical*. This might either be an elementary substance, such as carbon, "le radical de l'acide carbonique," or a compound, such as, "le radical oxalique, tartarique," &c.

Respecting the difference between organic and inorganic compounds, he states that the oxidizable or acid-forming radicals of the mineral kingdom are almost always simple; those of the vegetable and especially of the animal kingdom are however generally composed of two substances, carbon and hydrogen, and these frequently contain nitrogen as well, and sometimes phosphorus.[2]

The observation that the elements can form different oxides led to the supposition that this might likewise be the case with organic radicals. Thus for example sugar was considered to be a neutral oxide, "d'un radical hydro-carboneux," whilst oxalic acid was supposed to be its higher oxide.

Amongst his more important investigations in the domain of organic chemistry Lavoisier's research on fermentation deserves especially to be mentioned, not only because he was the first to point out that sugar is decomposed into carbonic acid and alcohol, but especially because, in connection with this particular reaction, he for the first time enunciated the principle which underlies the whole of our science, viz., that the weight of the products of any chemical change is equal to the sum of the weights of the materials taking part in that change, and hence that all chemical decompositions may be expressed by equations, the truth of which can be ascertained by the analysis of the original compound, and controlled by that of the products of decomposition.

On this point Lavoisier's own words may be quoted: "We may consider the substances submitted to fermentation and the

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[1] Lavoisier's *Elements of Chemistry* (1787), Kerr's Translation, pp. 173, 174.

[2] *Ibid*, p. 261.

products resulting from that operation as forming an algebraic equation; and, by successively supposing each of the elements in this equation unknown, we can calculate their values in succession, and then verify our experiments by calculation and our calculations by experiment, reciprocally. I have often successfully employed this method for correcting the first results of my experiments, and so to direct me in the proper road for repeating them to advantage."[1]

It must, however, be especially borne in mind that Lavoisier did not distinguish organic chemistry as a special branch of the science; still less did he, as has been stated, define this portion of chemistry as the chemistry of compound radicals.[2] Thus for example he arranged all the acids together, dividing them like Lémery into mineral, vegetable, and animal. His more immediate followers also adopted this course, and it was at that time only occasionally that we find organic bodies classed together in a group.

7 By degrees, as substances common to both the animal and the vegetable world were discovered, the distinction between animal and vegetable chemistry disappeared, and the consequent fusion, widening the area covered by the general term organic, gradually led to a distinct separation into Inorganic and Organic chemistry. At the same time no exact limit could be said to exist between these two divisions of the science. One reason for this was that several compounds were found to exist which from their origin must be considered as organic, but which yielded on analysis results proving that they exactly obey the laws of constant and multiple proportion, laws supposed at that time to apply only to compounds belonging to the mineral kingdom. In the majority of instances, on the other hand, organic bodies appeared not to obey these laws.

8 For the purpose of obtaining more satisfactory information on this question, Berzelius, in 1814, proposed to investigate the composition of such substances more accurately than had hitherto been done. That this was much needed is clear when we remember that Proust, so late as 1803, stated that acetic acid contained nitrogen, and that Dalton changed his formula for alcohol from $2\,C + H + O$ in 1803, to $3\,C + H$ in 1810.

With this view Berzelius improved the processes of organic analysis, and then ascertained that all organic compounds,

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[1] Lavoisier, *Elements*, p. 197.

[2] Kopp, *Entwickelung der Chemie in der neuerem Zeit*, p. 521.

although in most cases possessing a somewhat complicated composition, obey the laws of constant and multiple proportions applicable to inorganic compounds. Agreeing with the views of Lavoisier, Berzelius explained the difference existing between these two great divisions by stating that whilst in inorganic nature every oxidized compound contains a *simple radical*, organic bodies consist of oxides of *compound radicals*. In the case of vegetable substances the radical usually consists of carbon and hydrogen, whilst in the case of animal substances it consists of carbon, hydrogen, and nitrogen.[1]

9 Berzelius, however, did not experimentally investigate these compound radicals, although the discovery of cyanogen by Gay-Lussac in 1815 served as an excellent example of the existence of such a series of bodies. The cyanogen compounds were, however, at that time almost invariably placed amongst inorganic bodies, for, as has been stated, the limit between inorganic and organic chemistry was not clearly defined. Thus Gmelin in 1817, in the first edition of his great handbook, states that a clear distinction ought to be made between the two classes of compounds, but that this distinction can be more readily felt than strictly defined. He laid down that Inorganic compounds are characterised by their binary constitution, the most simple consisting of compounds of two elements, a basic oxide or an acid (that is what we now term an acid-forming oxide), which can again unite to form a binary compound of a higher order, namely, a salt. Organic bodies, on the other hand, are at least ternary compounds, or are composed of three simple substances, generally united together in less simple proportions than is the case in inorganic bodies. Accordingly, Gmelin describes marsh gas, olefiant gas, cyanogen, &c., in the inorganic portion of his handbook. He likewise adds that organic compounds cannot, like inorganic compounds, be artificially built up from their elements.

About the same time Berzelius again enforced this distinction between inorganic and organic bodies, asserting, like Gmelin, that the first could, whilst the latter could not, be artificially produced. He assumed that in living structures the elements obey totally different laws from those which regulate the formation of compounds belonging to the inanimate world. Thus in the Introduction to his *Traité*[2] he says: "Dans la nature

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[1] Berzelius, *Lehrbuch*, 2te Aufl. 1817, vii. 544.

[2] *Ibid*, French edition, 1840. v. p. 1.

vivante les éléments paraissent obéir à des lois tout autres que dans la nature inorganique; les produits qui résultent de l'action réciproque de ces éléments, diffèrent donc de ceux que nous présente la nature inorganique." Organic bodies were thus believed to be the special product of the so-called vital force. He admits that the bodies occurring in nature may be converted into other organic compounds by chemical decompositions, but none can be built up from their elements.

10 In the year 1828 came Wöhler's memorable discovery of the artificial formation of urea. Cyanate of ammonia, which was considered to be a truly inorganic compound, is easily converted without change of composition into urea, a product of animal life. This first artificial production of a body hitherto only produced within the animal organism was however incomplete, for up to that time the cyanogen compounds had not been prepared from their elements. Again, this formation remained for a long time the only one of its kind, and the belief in the existence of a peculiar vital force still retained a firm footing. Besides, it was believed that urea, a substance so easily decomposed into carbon dioxide and ammonia, and moreover only excreted by the animal body, must be looked upon as standing half way between organic and inorganic compounds, and it was thought that it would still remain impossible to prepare artificially any of the other more complicated organic substances.

At the present day the belief in a special vital force has ceased to encumber scientific progress. We now know that the same laws of combination regulate the formation of chemical compounds both in animate and in inanimate nature. So soon as the constitution of any product of the organic world has been satisfactorily ascertained we look forward with confidence to its artificial preparation.

11 A modification of the early theory concerning the composition of organic compounds, by which they were supposed to consist of the aqueous and the combustible principles, and to which allusion has been made, took place in 1815, in consequence of the experiments of Gay-Lussac, who found that the weight of a volume of alcohol vapour is equal to the sum of the weights of one volume of aqueous vapour and one of olefiant gas; one volume of ether vapour being equal to one volume of the first and two of the latter constituent. At the same time Robiquet and Colin had shown that hydrochloric ether (ethyl chloride)

may be considered to be a compound of hydrochloric acid with olefiant gas.

Founded upon this observation Dumas and Boullay[1] proposed a theory according to which many derivatives of alcohol may be considered to be compounds in which olefiant gas is contained, in the same way as ammonia is present in the ammoniacal salts. Berzelius,[2] who was originally opposed to this view, adopted it at a later period, and proposed that the name Ætherin should be given to olefiant gas, C_2H_4. The following table is taken from Dumas and Boullay's memoir, the formulæ being however altered in accordance with the modern atomic weights:

Hydrochlorate of bicarburetted hydrogen, C_2H_4, HCl.	Ammonia hydrochloride, NH_3, HCl.
Nitrite of bicarburetted hydrogen, C_2H_4, HNO_2.	Ammonia nitrite, NH_3, HNO_2.
Sulphate of bicarburetted hydrogen, C_2H_4, H_2SO_4.	Acid ammonia sulphate, NH_3, H_2SO_4.
Alcohol, C_2H_4, H_2O.	Aqueous Ammonia, NH_3, H_2O.
Ether, $(C_2H_4)_2$, H_2O.	

Not only did they apply this system of classification to other derivatives of alcohol but they attempted to extend their theory to all organic compounds. Although it was found possible to arrange a certain number of organic bodies according to this system, the ætherin theory did not command general recognition, partly because a large number of organic bodies could not thus be classed, and partly because, in many instances, facts were against the theory. Thus, for example, although alcohol could be converted into ether or olefiant gas by the withdrawal of the elements of water, it was not possible to obtain this or any of the other ætherin compounds by the juxtaposition of their supposed proximate constituents, such a synthesis being possible in the case of the ammoniacal salts.

12 The classical research of Liebig and Wöhler[3] on the radical of benzoic acid published in 1832 was welcomed by Berzelius as the dawn of a new era.

In this celebrated investigation the authors proved that bitter-almond oil, benzoic acid, and a number of compounds obtained from these, may all be supposed to contain a group of atoms or, as they expressed it, "zusammengesetzter Grundstoff," or

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[1] *Ann. Chim. Phys.* xxxvii. 15.

[2] *Ann. Pharm.* iii. 286.

[3] *Ann. Pharm.* iii. 249, 282.

compound radical, to which they gave the name benzoyl, the termination "yl" being derived from the Greek ὕλη, matter.

It has been already stated that Berzelius, like Lavoisier, considered that organic compounds containing oxygen must be looked upon as the oxides of hydrocarbon radicals. The radical benzoyl, C_7H_5O, however, contains oxygen, and hence the predominating influence which this element had hitherto been supposed to exert from this time forward ceased, and oxygen was placed on a footing of equality with the other elements.

The radical theory was now enlarged both by Berzelius and Liebig, although neither of them agreed in the special views which the other advocated. Whilst both opposed the ætherin theory, according to which alcohol and ether must be considered to be compounds of olefiant gas and water, Berzelius considered the above compounds as oxides of two different radicals, whereas Liebig[1] in a memoir, properly deemed another pillar of the radical theory, showed that both compounds contain the same radical for which he proposed the name of *ethyl*. According to his view ether is the oxide, and alcohol the hydrate of this oxide. The compounds obtained by the action of acids on alcohol he considered to be saline compounds of the base ethyl oxide. A similar constitution was ascribed to the other alcohols and their derivatives, so that each contains a radical which plays a part similar to that played by potassium or any other metal in its salts. It is interesting to remember that so long ago as the year 1834 Liebig asserted that it would probably be found possible to isolate these radicals by the decomposition of their chlorides or iodides.

Alcohols on oxidation yield monobasic acids; methyl alcohol, or wood-spirit, yields formic acid, CH_2O_2, ethyl alcohol, or spirit of wine, being similarly converted into acetic acid, $C_2H_4O_2$. The analogy between these acids and monobasic benzoic acid was not far to seek, and thus the existence in these acids of the oxygenated radicals CHO and C_2H_3O was assumed.

Berzelius, however, took exception to this view and asserted that benzoyl, although in many respects acting like a simple body, must be regarded as the oxide of the body C_7H_5. Like other oxides benzoyl can unite with more oxygen to form an acid. Hence formic acid contains the radical formyl, CH, and acetic acid the radical acetyl, C_2H_3. Liebig afterwards adopted this view, finding that by this means it became possible to group

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[1] *Ann. Pharm.* ix. 1.

a large number of compounds round a common centre. Thus he supposed that vinyl chloride (monochlorethene), C_2H_3Cl, discovered by Regnault, may be looked upon as acetyl chloride, and that aldehyde, C_2H_4O, (which he prepared about this time), as well as acetic acid may be regarded as the hydrates of two distinct acetyl oxides.[1] In a similar way he considered chloroform (which he had also just discovered) to be the chloride of formyl, assuming that it stands to formic acid in the same relation as phosphorus trichloride does to phosphorous acid.

In 1837 Dumas adopted these ideas and in his own name, as well as in that of Liebig, explained the formation of so large a number of naturally occurring organic compounds from so small a number of elements, by the fact that these unite together and give rise to various radicals which sometimes play the part of chlorine and oxygen, and sometimes that of a metal. Radicals such as cyanogen, ethyl, benzoyl, &c., may be said to constitute the elementary bodies of organic chemistry, their elementary components being only recognised when the organic nature of the compound is entirely destroyed.

The discovery and isolation of these radicals was the task which Dumas and Liebig in conjunction with their younger colleagues set themselves to perform.[2]

13 The essential idea of the chemical constitution of organic compounds conceived by Berzelius was a dualistic electro-chemical one, analogous to that which he upheld in inorganic chemistry, the difference being that organic radicals play a part similar to that played by the elements in the inorganic portion of the science. According to him the radicals are divided, like the elements, into electro-positive or base-forming, and electro-negative or acid-forming radicals. In the former division are classed metals, hydrogen, and the alcohol radicals; in the latter the elements of the chlorine group, oxygen, benzoyl, &c.

"By the comparison of the behaviour of inorganic with that of organic compounds," says Liebig,[3] "we are led to recognise

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[1] In order to understand the above relations it must be borne in mind that the *equivalent* weights, $H=1$, $O=8$, $C=6$, &c., were then employed in place of the *atomic* weights which we now use. We thus have the formulæ: water, HO; ether, C_4H_5O; alcohol, C_4H_5O, HO; aldehyde, C_4H_3O, HO; acetic acid, $C_4H_3O_3, HO$; chloroform, C_2HCl_3; formic acid, C_2H_3O, HO. In the sequel the use of these old equivalent weights will be indicated by the symbols of the elements being printed in italics.

[2] *Compt. Rend.* v. 567.

[3] *Ann. Pharm.* xxv. 3.

the existence of certain component parts which do not undergo alteration in a series of compounds, and can be replaced by elementary bodies; of component parts which combine with elements to form compounds in which the elements can be replaced by others; of component parts, therefore, which take the position of simple bodies and play the part of elements. In this way the idea of compound radicals has arisen.

Hence, we term cyanogen a radical—(1) because it is an unchanging constituent in a series of compounds; (2) because it may be replaced in these compounds by simple bodies; and (3) because in its compounds with elementary bodies these latter can be set free and replaced by their equivalents of other simple bodies. Of these three conditions, at least two must be fulfilled if the radical is to be considered as a true one.

This definition of a compound radical is fully accepted at the present day.

14 The new era welcomed by Berzelius thus appeared to open brightly, but these hopes were apparently not destined to be realized, for whilst Liebig and Berzelius continued to uphold their new views, the latter, indeed, defining organic chemistry as the chemistry of compound radicals,[1] Dumas put forth ideas which appeared to him to be inconsistent with the radical theory. Much difficulty had been experienced in explaining, according to the radical theory, a large group of bodies, examined especially by the French chemists, and obtained by the action of chlorine on organic compounds. It had been noticed that in this reaction hydrogen is expelled, chlorine entering into combination, and this in equivalent quantities, one atom of chlorine being taken up for every atom of hydrogen which the body loses. These observations attracted but little attention until the year 1834, when Dumas found that hydrogen in oil of turpentine can be replaced atom for atom by chlorine, thus:

$$C_{10}H_{16} + Cl_2 = C_{10}H_{15}Cl + HCl.$$

He considered that these facts are based upon a law of nature, to express which he suggested the name of Metalepsy[2] (μετάληψις, an exchange). By the study of these phenomena Dumas arrived at his *empirical law of substitutions*,[3] namely:

(1) If the hydrogen contained in a hydrogenized body be

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[1] *Handbuch Org. Chem.* 1843, 1.

[2] *Mem. Acad. Scienc.* xv. 548.

[3] *Journ. de. Pharm. mai*, 1834.

withdrawn by the action of chlorine, bromine, iodine or oxygen, for every atom of the first, one atom of the elements of the chlorine group or half an atom of oxygen is substituted.[1]

(2) If the compound contain oxygen the same law holds good.

(3) If, however, the body contain water, the hydrogen of the water is first removed without substitution, and then the remaining hydrogen is substituted as in case No. 1.

This last statement was necessary because alcohol, which was considered to be a hydrate of ethylene, $C_2H_4H_2O$, is converted by chlorine into chloral, C_2HCl_3O. These rules are known as Dumas' theory of substitutions.

15 Laurent, amongst the younger chemists, especially devoted himself to the advancement of this subject. He found that the replacement of hydrogen by its equivalent of chlorine does not always take place, particularly in the case of oxygenated bodies, and that for this reason Dumas' third rule is incorrect. He also showed that in those cases in which substitution atom for atom takes place the physical and chemical properties of the substitution-product resemble those of the original body. Hence, he says, the chlorine takes up the position vacated by the hydrogen atom. In the new compound chlorine plays the part which hydrogen does in the original body.[2]

Dumas did not support this view. He states that his theory is purely empirical, and when Berzelius urged, against him instead of against Laurent, that he entirely ignored the electro-chemical difference between hydrogen and chlorine, Dumas replies that Berzelius attributes to him a view, namely, that the chlorine takes the actual place of the hydrogen, diametrically opposed to that which he has always held. He adds, moreover, that he will not hold himself responsible for alterations which Laurent had made in his theory.

In subsequent years the researches of Laurent, Regnault, and Malaguti, added a large number of substitution-products to those which were already known, and Dumas himself discovered trichloracetic acid, an instance in which, more than in any other, the substitution-product exhibits analogy with the original substance, so that at last Dumas not only adopted Laurent's views but expanded them considerably.

16 Before we proceed to the further consideration of the progress made in this direction it becomes necessary to mention

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[1] Dumas at that time employed the now universally adopted atomic weight for oxygen.

[2] *Ann. Chim. Phys.* [2], lvi. 140.

a theory of chemical constitution brought forward by Laurent in 1836. This theory, termed the *nucleus theory*, has indeed never been generally adopted, although Gmelin made use of it in his handbook with certain alterations, as a foundation for a classification of organic compounds.

According to this theory each organic compound contains a group of atoms termed a nucleus or germ. Primary nuclei consist of carbon and hydrogen, and in these the hydrogen may be replaced by other elements or by groups of atoms. In this case derivative- or secondary-nuclei are produced, and these exhibit both in composition and in chemical properties a striking analogy to the primary nuclei. Other atoms may be attached to this nucleus, or they may quite surround it, and when these are removed the primary nucleus makes its appearance. Laurent further assumed that organic compounds always contain an even number of atoms, and hence the formulæ which he adopts are frequently double of those which are now employed.

17 In the year 1839,[1] Dumas developed the substitution theory to a *theory of chemical types*, the principles of which he thus enunciated:—

(1) The elements of a compound body can, in many instances, be replaced, either by other elements in equivalents, or by compound bodies which are capable of playing the part of simple ones.

(2) When such a substitution takes place in equivalent proportions, the body which is formed by such a substitution retains its *chemical type*, and the element which has entered into the compound *plays the same part* as the element which has been withdrawn.

In addition to the chemical types, in which Dumas included the following,

$C_2H_4O_2$	Acetic acid
$C_2H_3ClO_2$	Chloracetic acid
C_2H_4O	Aldehyde
C_2HCl_3O	Chloral
$CHCl_3$	Chloroform
$CHBr_3$	Bromoform
CHI_3	Iodoform,

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[1] *Comptes Rendus*, viii. 609.

he adopted Regnault's suggestion respecting the existence of molecular or mechanical types, according to which, two substances belong to the same type when substitution has taken place, provided that the number of elementary atoms remains constant. Under this he included compounds which contain the same number of atoms but possess different properties, such, for instance, as alcohol and acetic acid.

Dumas pointed out, moreover, that the properties of a compound depend rather upon the arrangement of its parts than upon their special nature. He compared chemical compounds to a solar system of which the constituent parts are held together by their mutual attractions. The system remains the same if the atom of one element be replaced by that of another.

As the best proof of the truth of his ideas, Dumas laid weight upon the fact that acetic acid, $C_4H_4O_4$, and trichloracetic acid, $C_4HCl_3O_4$, possess the closest resemblance in chemical properties.

Berzelius, who, as we have seen, opposed the theory of substitutions, pointed out the dissimilarity between the two bodies and insisted on the fact that their essential properties are distinctly different. He considered acetic acid as a hydrated oxide of a hydrocarbon-radical termed acetyl, C_4H_3, whereas trichloracetic acid is a copulated compound of oxalic acid and chloride of carbon:

Acetic acid . . .	$C_4H_3,O_3 + HO.$
Trichloracetic acid . .	$C_2Cl_3 + C_2O_3 + HO.$

The constitution of other substitution-products was viewed by Berzelius in a similar light, although for this purpose he was obliged to double and sometimes to treble the simplest formulæ of many compounds, and thus so to complicate the subject that his theory was not generally accepted.

18 Liebig opposed the views of Berzelius, which he said depended on a number of considerations which have no foundation in fact. He pointed out that even in inorganic chemistry the metal in permanganic acid can be replaced by chlorine without altering the form of the substance, although no two substances are more unlike than chlorine and manganese. Facts like these, he says, must simply be accepted. If manganese can be replaced by chlorine, why should a similar replacement of hydrogen appear incredible?[1]

In another place[2] Liebig remarked that Berzelius was the first

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[1] *Ann. Pharm.* xxxi. 119 (foot note). [2] *Ann. Pharm.* xxxii. 72 (foot note).

to adopt the view that organic acids, ethers, and so forth, are the oxides of compound radicals, and he admits that this view illumined many a dark chapter in organic chemistry. The analogy which Berzelius first pointed out between organic and inorganic compounds ought however, he continues, not to be carried on beyond a certain point, for if the principles of inorganic chemistry be consequently followed out in organic chemistry, the effect is rather that of complication than of simplification.

At the same time Liebig did not hesitate to attack the French chemists,[1] who went too far for him, and when Dumas assumed that the carbon in organic substances could be replaced, he turned upon him, and in a satirical vein, in a letter dated from Paris, and signed (*anglice*) S. Windler,[2] relates how not only all the hydrogen and all the metal in acetate of manganese has been substituted atom by atom for chlorine, but how at last even the carbon has been in like manner replaced, and that the final product, although consisting of nothing but chlorine, possessed the chief characteristic properties of the original salt!

19 Facts bearing out the truth of the law of substitutions, so far at any rate as the replacement of hydrogen is concerned, rapidly increased; but a still more important discovery was that of reverse substitutions, that is, the production of the original body from the substitution-product.

In 1842 Melsens showed that by the action of potassium amalgam trichloracetic acid can be converted into acetic acid. Such observations did not however convince Berzelius, who now looked upon acetic acid as an oxalic acid copulated with methyl, $C_2H_3 + C_2O_3 + HO$; explaining in the same way the constitution of other compounds capable of undergoing substitution. He supposed that all these contained a group consisting of carbon and hydrogen, and termed by him the *copula*, in which the hydrogen is replaced by chlorine, etc.

In 1845 Hofmann discovered the chlorinated anilines,[3] and, as Liebig in a note to this important investigation expressed his conviction in the truth of the newer views more strongly than before, Berzelius replied that all organic bases must be regarded as copulated ammonias. Aniline is the compound $C_{12}H_4 + N_3H$, and chloraniline is $C_{12}H_3Cl + NH_3$. Both contain ammonia as a basic constituent. The composition of the copula is a matter of indifference.

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[1] *Ann. Pharm.* xxiv. 1.

[2] *Ann. Chem. Pharm.* xxxiii. 308.

[3] *Ann. Chem. Pharm.* liii. 8; *Chem. Soc. Mem.* ii. 266.

In the assumption of the copula, the dispute with Laurent as to whether chlorine could replace hydrogen and fulfil its functions had been overlooked. That which was held to be absurd was at once accepted as a simple and clear expression of fact. Berzelius however continued in opposition. His formulæ gradually became more and more complicated, and he was compelled to adopt more and more doubtful hypotheses. Thus, for example, he represented dichlorformic ether, a compound obtained by Malaguti by acting with chlorine on ethyl formate, as being copulated of anhydrous formic acid, formyl chloride, anhydrous acetic acid, and acetyl chloride, giving it the formula $2\,C_2HO_3 + C_2HCl_3 + 2\ C_4H_3O_3 + C_4H_3Cl_3$; whilst now, according to the new atomic weights, the formula is written $C_3H_4Cl_2O_2$. We need not, therefore, be surprised to find that after Berzelius's death the supporters of his views experienced great difficulty in rebuilding the radicals from the copulæ.

20 The radical theory had meanwhile received most valuable support from Bunsen's classical researches on the cacodyl compounds. He showed that these contain a common group of atoms, cacodyl (afterwards called arsendimethyl, $(CH_3)_2As$,) a body which exactly acts as a metal, and can exist in the free state.[1]

Soon afterwards Kolbe and Frankland succeeded in preparing from the compounds of the alcohol radicals the hydrocarbons which, according to their empirical formulæ, must be considered as the free radicals. The isolation of the alcohol radicals as well as of cacodyl was naturally welcomed by the followers of the radical theory, inasmuch as it placed that which had hitherto only been a hypothesis in the rank of known facts.

The question formerly much discussed respecting the possibility of the existence of a radical containing oxygen was again taken up. Berzelius had denied the possibility of the existence of such a body, and in 1843 he argued that this view is as incorrect as that which assumes sulphurous acid (sulphur dioxide) to be the radical of sulphuric acid, or manganese peroxide to be that of manganic acid. He adds: "an oxide cannot be a radical; the very definition of the word radical is that it is a body which combined with oxygen forms an oxide."

But as soon as the upholders of the radical theory adopted the theory of substitutions they were obliged to admit that the electro-negative element, chlorine, is capable of taking the place of electro-positive hydrogen without any great alteration

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[1] *Ann. Chem. Pharm.* xlii. 14; *Phil. Mag.* [3] xx. 313, 382, 395.

occurring in the nature and properties of the compound; and when this had been once admitted, the possibility that oxygen may also replace hydrogen could no longer be denied.

21 The further development of the doctrine of substitutions and of the theory of types led to a clearer understanding of the terms equivalent, atom, and molecule.

In this direction the development of the theory of polybasic acids had an especial value. It has been already remarked (Vol. ii. p. 35) that according to the dualistic view the neutral or normal salts of the oxyacids must be regarded as compounds of a basic oxide with an acid, or rather with an acid-forming oxide, whilst the acid salts must be considered to be compounds of a neutral salt with a hydrated acid. Hence in those days the following formulæ were in vogue:

Hydrated sulphuric acid	$HO.SO_3$
Neutral sulphate of potash	$KO.SO_3$
Acid sulphate of potash	$KO.SO_3 + HO.SO_3$

According to these formulæ the acid salt contains twice as much acid as the normal or neutral salt.

Phosphoric acid and citric acid formed, however, exceptions to this rule, for these were considered as tribasic acids, and their formulæ as well as those of their salts are not divisible by three:

Phosphoric Acid.	Acid Salts.		Neutral Salts.
$PO_5.\,3HO.$	$PO_5.\,2HO.\,NaO.$	$PO_5.\,HO.\,2NaO.$	$PO_5.\,3NaO.$
Citric Acid.			
$C_{12}H_5O_{11}.\,3HO.$	$C_{12}H_5O_{11},\,2HO.\,NaO.$	$C_{12}H_5O_{11}.\,HO.\,2NaO.$	$C_{12}H_5O_{11}.\,3NaO.$

According to Berzelius the only reason for considering an acid to be polybasic is that its formula is not thus divisible.[1]

After the publication of Graham's classical investigations on the various modifications of phosphoric acid and its salts, Liebig[2] in 1838 proposed his theory of polybasic acids founded upon a complete investigation of the salts of a number of organic acids. He showed that many organic acids resemble phosphoric and citric acids inasmuch as one equivalent of these can take up from one to three equivalents of a base. Such acids he considered to be polybasic, even if their formulæ were divisible. And he considered the capability of forming certain double salts to be the special characteristic of this class of acids.

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[1] Kekulé, *Lehrb.* i. 80.

[2] *Ann. Pharm.* xxvi. 13

The theory of polybasic acids was further developed by Laurent and Gerhardt, the latter pointing out that the property of forming two or more ethers was peculiar to these bodies. Whilst Laurent added that the same holds good for their amides. Both of these investigators, whose names will always be honourably associated in the history of the science, laboured incessantly to combat the views concerning the constitution of chemical compounds which they deemed incorrect, and to replace them by others which are more in harmony with ascertained facts.

22 The interesting speculations of Laurent and Gerhardt concerning the relative magnitudes of the atom and molecule went far to settle our views on these points, and the arguments which they made use of for this purpose hold good at the present day.

Laurent founded his conclusions especially on chemical analogies, and upon the similarity observed in corresponding chemical reactions. Thus, for instance, he showed that a molecule of chlorine must consist of two atoms, inasmuch as when it acts upon organic compounds either two, four, or six atoms, and never one, three, or five atoms take part in the reaction. He came to the same conclusion by comparing the action of chlorine with that of cyanogen chloride, benzoyl chloride, and similar compounds. All these substances exhibit strictly analogous metamorphoses, pointing to the conclusion that if the molecule of these chlorides consists of two parts, the same must also hold good in the case of chlorine itself.

Gerhardt, on the other hand, starting from Avogadro's law, was led to a clear comprehension of the idea of an atom as being the smallest portion of an element which is contained in the molecule of any one of its compounds.

The labours of these two great investigators met, however, with but slight consideration during their lifetime. Laurent died early, and even Gerhardt only lived long enough to enjoy the partial recognition of their views which soon afterwards became general. When Gerhardt first proposed the doubling of the atomic weights, or rather of the equivalent weights, then in use, for oxygen, sulphur, and carbon, Berzelius did not think the proposal worthy even of mention in his Jahresbericht.

For the purpose of obtaining a sound experimental basis for their theoretical views Laurent and Gerhardt published many valuable experimental investigations. Little consideration was, however, paid to these results when they were correct, and when (as was sometimes the case) they were incorrect, they were criticised with no sparing hand. Whilst recognising their great power of arranging facts from a general point of view, we must admit that they frequently made assertions which rested more on a theoretical than an experimental basis, and hence their views were frequently criticised, especially by Liebig[1] as unscientific. Uninfluenced, however, by these attempts to discredit their work, and fully convinced of the truth of their ideas, they returned Liebig's sarcasm with interest.

23 In looking back on these discussions we seem to enter a bygone age. Berzelius endeavoured to throw ridicule on the existence of oxygenated radicals by saying that sulphur dioxide may as truly be considered as the radical of sulphuric acid. At the present day we actually adopt this view, considering this acid as a compound of sulphur dioxide (sulphuryl) with the semi-molecule of hydrogen peroxide (hydroxyl), for both of these groups of atoms fulfil the conditions which Liebig defined as characteristic of a compound radical.

The employment of empirical, or unitary formulæ as they were called, in opposition to dualistic, was a step in the right direction; for every compound consisting of more than two elements is now considered as a chemical whole, and not as made up of several constituents. The unitary system also clearly points out the general analogies of similar substances, and enables the facts to be brought into direct comparison, instead of viewing the constitution by the deceitful mirror of inherited hypotheses.[2]

Certain groups of substances can thus be considered from the same point of view, and their composition indicated by general formulæ such as $C_mH_nO_c$, the adoption of which led to the taunt that Laurent and Gerhardt were creating a sort of chemical algebra. The use of such formulæ, however, soon proved that the mutual relations of various compounds could not be thus so clearly exhibited as by the formulæ of the radical theory. Accordingly Laurent and Gerhardt made use of the so-called synoptical formulæ, in which the group of atoms remaining behind in a number of chemical metamorphoses was written in a separate position from the other constituents, or sometimes marked by a separate sign, the method of representation at one time falling into the radical and at another time into the nucleus theory.

24 Important progress was next made by the amalgama-

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[1] *Ann. Chem. Pharm.* lvii. 93, 358, and lviii. 227.

[2] Kekulé, *Lehrb.* i. 84.

tion of the two theories of types and radicals. Dumas had already pointed out that hydrogen can not only be replaced by elements such as chlorine, but also by certain groups of atoms, such as NO_2; and that these may be designated as compound radicals. Gerhardt revived this view in 1839, but not exactly in the sense of the radical theory, according to which theory the radicals are closed groups of atoms and form the proximate constituents of compounds. Here, however, it must be noticed that Liebig[1] had already pointed out that a radical is not to be considered as an unalterable quantity, and that it was not necessary that the existence of the radical must precede the formation of an organic compound.

Gerhardt did not assume that a substitution must occur when an element is replaced by a compound body, but rather that a combination of the two residues takes place to form a chemical unit, and not a copulated compound. The group of atoms which can be assumed to be a radical was termed "le rest" or "le restant." Then came his "théorie des residus" according to which such a residue possesses indeed the composition of a compound radical, but is not contained as such in the compound. Thus, for instance, the radical theory considers ethyl nitrate as nitrate of ethyl oxide, and the formula is written, with equivalent weights, $C_4H_5O.NO_5$; this ether is obtained by the action of nitric acid on alcohol:

$$C_2H_6O + HNO_3 = C_2H_5NO_3 + H_2O.$$

According to Gerhardt the reaction which here takes place is that the one compound gives up an atom of hydrogen, and the other the group or residue OH, and that these unite together to form water, whilst the two other residues form the chemical unit, ethyl nitrate.

Gerhardt's theory of residues soon replaced the radicals of the old theory, and their assumption in the new theory of types brought about the union of the two theories. This was more especially effected by the discovery of the compound ammonias made by Wurtz[2] in 1849. Liebig[3] had foreseen the possible existence of such compounds, inasmuch as he predicted that by uniting the alcohol radical with amidogen, NH_2, compounds would be obtained possessing the characteristic properties of ammonias. Wurtz also assumed a corresponding

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[1] *Ann. Pharm.* xiv. 166; xviii. 323.

[2] *Comptes Rendus*, Aout. 13, 1849; *Phil. Mag.* [3] xxxv. 34.

[3] *Handwörterb.* i. 698.

constitution of these compounds, and he wrote the formula ethylamine (ethyliaque) $C_2H_5.NH_2$. Still, this may be also considered, according to Berzelius's views, as a copulated ammonia, $C_2H_4 + NH_3$. Indeed Hofmann,[1] in his investigations on aniline, originally adopted this view, although he soon discovered facts which rendered it untenable. He showed that ethylamine is a substituted ammonia, $(C_2H_5)H_2N$, inasmuch as the second and third atom of hydrogen can also be replaced by the alcohol radical, and the compounds thus obtained still retain their characters as ammonias.

25 The discovery of the compound ammonias may certainly be regarded as the foundation of our present theory. From this time forward organic compounds have been arranged on the *types* of certain simple inorganic bodies. Thus, for instance, it was assumed that in ammonia the hydrogen could be not only replaced atom for atom by metals (Laurent), but also by compound radicals.

In 1850 Williamson[2] showed, in an analogous way, that the alcohols and ethers may be considered to be built up on the type of water. When in one molecule of the latter one atom of hydrogen is replaced by an alcohol radical an alcohol is obtained. By the replacement of the second an ether is formed. This view he further expanded, inasmuch as he represented acetic acid as water in which an atom of hydrogen was replaced by the group C_2H_3O, for which he proposed the name of oxygen-ethyl, or othyl, in order to distinguish it from the word acetyl, already given by Berzelius to a radical containing no oxygen. At the same time he pointed out that by the replacement of the second atom of hydrogen by an oxygenated radical, compounds must be obtained which stand in the same relation to the fatty acids as ether does to alcohol. These bodies, the anhydrous acids, or anhydrides, were soon afterwards discovered by Gerhardt.[3]

For many years after this, chemists were accustomed to class organic compounds on the type of simple inorganic substances and thus arose Gerhardt's well-known theory of types, according to which the organic compounds of ascertained constitution may all be classed under four types: (1) that of hydrogen; (2) that of hydrochloric acid; (3) that of water, and (4) that of ammonia. Accordingly, we have the following:

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[1] *Quart. Journ. Chem. Soc.* i. 285, ii. 334.

[2] *British Association Reports*, 1850, part ii. p. 65; *Chem. Soc. Journ.* (1852), iv. 229.

[3] *Quart. Journ. Chem. Soc.* v. 127; *Ann. Chim. Phys.* [3], xxxvii. 285.

GERHARDT'S TYPES.

I.		II.		III.		IV.	
Hydrogen	$\left.\begin{matrix}H\\H\end{matrix}\right\}$	Hydrochloric Acid	$\left.\begin{matrix}H\\Cl\end{matrix}\right\}$	Water	$\left.\begin{matrix}H\\H\end{matrix}\right\}O$	Ammonia	$\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N$
Ethyl Hydride	$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}$	Ethyl Chloride	$\left.\begin{matrix}C_2H_5\\Cl\end{matrix}\right\}$	Ethyl Alcohol	$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O$	Ethylamine	$\left.\begin{matrix}C_2H_5\\H\\H\end{matrix}\right\}N$
Diethyl	$\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}$	Acetyl Chloride	$\left.\begin{matrix}C_2H_3O\\Cl\end{matrix}\right\}$	Ethyl Ether	$\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O$	Diethylamine	$\left.\begin{matrix}C_2H_5\\C_2H_5\\H\end{matrix}\right\}N$
Acetyl Hydride (Aldehyde)	$\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}$	Benzoyl Chloride	$\left.\begin{matrix}C_7H_5O\\Cl\end{matrix}\right\}$	Acetic Acid	$\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O$	Triethylamine	$\left.\begin{matrix}C_2H_5\\C_2H_5\\C_2H_5\end{matrix}\right\}N$
Acetyl Methide (Acetone)	$\left.\begin{matrix}C_2H_3O\\CH_3\end{matrix}\right\}$	Cyanogen Chloride	$\left.\begin{matrix}CN\\Cl\end{matrix}\right\}$	Acetic Anhydride	$\left.\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\right\}O$	Acetamide	$\left.\begin{matrix}C_2H_3O\\H\\H\end{matrix}\right\}N$

The organic bromides and iodides are of course classed in the second division, whilst many sulphur compounds are found in the third, and bodies containing phosphorus and arsenic are arranged in the fourth class. This system was further developed by the classification of many inorganic bodies, such as the oxyacids which are ranged under the type of water.

26 A further advance in the theory of types was made by its application to the classification of polybasic acids, such as sulphuric acid. In the memoir already referred to, Williamson had placed this acid under the double water type, inasmuch, as he assumed, that it might be considered as two molecules of water joined together by the replacement of two atoms of hydrogen by a group of atoms, whilst a monobasic acid belongs to the type of one molecule of water. In a similar way the other dibasic acids and their salts may be arranged:

Type.	Acetic Acid.	Nitric Acid.
$\left.\begin{matrix}H\\H\end{matrix}\right\}O$	$\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O$	$\left.\begin{matrix}NO_2\\H\end{matrix}\right\}O$
Type.	Sulphuric Acid.	Succinic Acid.
$\begin{matrix}\left.\begin{matrix}H\\H\end{matrix}\right\}O\\\left.\begin{matrix}H\\H\end{matrix}\right\}O\end{matrix}$	$\begin{matrix}H\\SO_2\\H\end{matrix}\begin{matrix}\}O\\\}O\end{matrix}$	$\begin{matrix}H\\C_4H_4O_2\\H\end{matrix}\begin{matrix}\}O\\\}O\end{matrix}$

Williamson[1] then showed in 1854 that chloroform may be considered as the trichloride of the radical CH. When it is heated with sodium ethylate, $C_2H_5.ONa$, it yields tribasic formic ether, $CH(OC_2H_5)_3$, and this belongs to the type of three molecules of water exactly as chloroform is classed under the type of three molecules of hydrochloric acid:

Type.	Chloroform.	Type.	Tribasic formic ether.
$3HCl$	$CH.Cl_3$	$3H_2O$	$\left.\begin{matrix}CH\\(C_2H_5)_3\end{matrix}\right\}O_3$

This view of the constitution of chemical compounds was further developed by Odling,[2] and applied by him to a large number of organic as well as inorganic compounds. They were then adopted by Gerhardt in 1856, and published in his Treatise on Organic Chemistry.[3]

27 As the possibility of the replacement of several hydrogen atoms by a radical was first observed in the case of polybasic

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[1] *Proc. Roy. Soc.* vii. 135.

[2] *Quart. Journ. Chem. Soc.* vii. 1.

[3] *Traité Chim. Org.* iv. 581, &c.

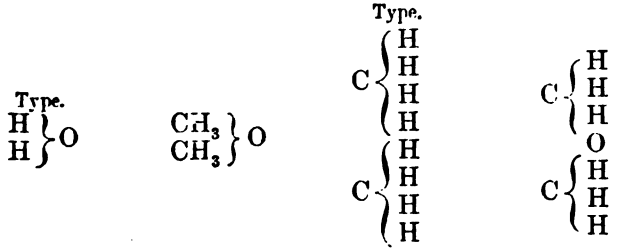
acids, the radicals themselves were termed in the first case polybasic, and this expression was afterwards changed to *polyatomic radicals.* This latter term is, however, not wholly free from objection, and at present the proposal of Erlenmeyer to employ the word *polyvalent* is generally adopted.[1]

The theory of polyvalent radicals soon received valuable support from Berthelot's investigation of glycerin and its derivatives, the constitution of these compounds being first clearly pointed out by Wurtz. Indeed this chemist must be considered to be one of the originators of the new theory of types, not only on account of the above-mentioned views, but especially by his valuable discoveries of the glycols or divalent alcohols.

According to this theory, as we have seen, the radicals are not to be considered as closed groups of atoms, or even as bodies capable of isolation, but rather as the residues of molecules which remain unaltered throughout a certain number of reactions. Gerhardt first pointed out that most chemical decompositions may be regarded as double substitutions, and he added that if the substances which exchange their positions in such a reaction are compound bodies instead of being elementary ones, they are then termed radicals.

28 These typical formulæ were not intended to indicate the arrangement of the atoms; they were in no sense constitutional formulæ, but were formulæ of decomposition used by common consent, and expressing a certain number of reactions. One of these compounds may, therefore, be represented on various types.

Thus, for instance, methyl ether, C_4H_6O, was usually supposed to belong to the water type, but it may also belong to the fourth type of marsh gas, which Kekulé added to Gerhardt's three original types. Under this latter assumption it would consist of two molecules of marsh gas held together by one atom of dyad oxygen:



Type. $\left.\begin{matrix}H\\H\end{matrix}\right\}O$ $\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\}O$ Type. $\begin{matrix}C\left\{\begin{matrix}H\\H\\H\\H\end{matrix}\right.\\C\left\{\begin{matrix}H\\H\\H\\H\end{matrix}\right.\end{matrix}$ $\begin{matrix}C\left\{\begin{matrix}H\\H\\H\end{matrix}\right.\\O\\C\left\{\begin{matrix}H\\H\\H\end{matrix}\right.\end{matrix}$

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[1] Lothar Meyer, *Mod. Theor. der Chemie*, 3rd Ed. p. 140.

By replacing the hydrogen in ammonia by methyl, methylamine, CH_5N, is produced; this may be regarded as a substituted ammonia, but it may also be looked upon as marsh gas in which hydrogen has been replaced by the monad group, NH_2; and lastly, it may be represented as having been formed by the union of two monad residues, and hence may be classed in the type of hydrogen; thus:

$$N\left\{\begin{array}{l}CH_3\\H\\H\end{array}\right. \qquad C\left\{\begin{array}{l}H\\H\\H\\NH_2\end{array}\right. \qquad \left\{\begin{array}{l}CH_3\\NH_2\end{array}\right.$$

Olefiant gas combines with bromine to form ethylene dibromide, $C_2H_4Br_2$. In this the bromine can be replaced by hydroxyl when ethylene alcohol (ethyl glycol) is formed. These two compounds may be typically regarded as follows:

Ethylene dibromide $\left.\begin{array}{l}C_2H_4\\Br_2\end{array}\right\}$ $\qquad C_2H_4\left\{\begin{array}{l}Br\\Br\end{array}\right.$

Ethylene alcohol $\left.\begin{array}{l}C_2H_4\\H_2\end{array}\right\}O_2$ $\qquad C_2H_4\left\{\begin{array}{l}OH\\OH\end{array}\right.$

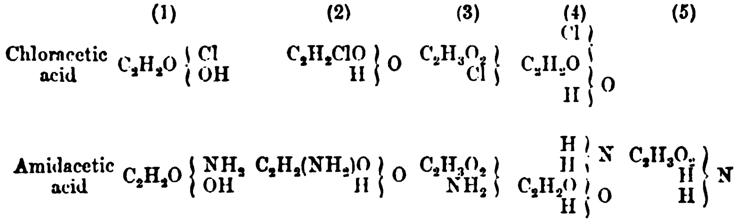
By the action of hydrochloric acid on the latter body the hydroxyl is first replaced by chlorine when ethylene chlorhydrate is formed, and this, on oxidation, yields monochloracetic acid.

29 Hence ethylene chlorhydrate may be considered as a chlorinated ethyl alcohol. It may, therefore, be regarded on the *mixed types* of water and hydrochloric acid, the two molecules being united by the replacement of one atom of hydrogen in each by the dyad radical C_2H_4 (formula No. 1). Or we may consider it to be a compound of ethylene with chlorine and hydroxyl; or again it may be represented on the type of water (formula No. 2), or on the mixed type of hydrochloric acid and water (formula No. 3).

$$\overset{(1.)}{C_2H_4\left\{\begin{array}{l}Cl_2\\OH\end{array}\right.} \qquad \overset{(2.)}{\left.\begin{array}{r}C_2H_4Cl\\H\end{array}\right\}O} \qquad \overset{(3.)}{\begin{array}{l}\left.\begin{array}{r}Cl\\C_2H_4\end{array}\right\}\\ \left.\begin{array}{r}\\H\end{array}\right\}O\end{array}}$$

When chloracetic acid, also obtained by the action of chlorine on acetic acid, is treated with ammonia, amidacetic acid,

$C_2H_3NH_2O_2$, is formed. This, like the compounds from which it is produced, is monobasic. It presents, however, certain analogies with the compound ammonias just as chloracetic acid exhibits properties analogous to those of ethyl chloride, and hence the formulæ of these compounds may be written in different ways:

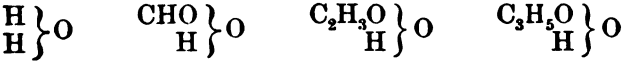


$$\begin{array}{cccccc}
 & (1) & (2) & (3) & (4) & (5) \\
\text{Chloracetic acid} & C_2H_2O\left\{\begin{array}{l}Cl\\OH\end{array}\right. & \left.\begin{array}{r}C_2H_2ClO\\H\end{array}\right\}O & \left.\begin{array}{r}C_2H_3O_2\\Cl\end{array}\right\} & \begin{array}{l}\left.\begin{array}{r}Cl\\C_2H_2O\end{array}\right\}\\ \left.\begin{array}{r}H\end{array}\right\}O\end{array} & \\
\text{Amidacetic acid} & C_2H_2O\left\{\begin{array}{l}NH_2\\OH\end{array}\right. & \left.\begin{array}{r}C_2H_2(NH_2)O\\H\end{array}\right\}O & \left.\begin{array}{r}C_2H_3O_2\\NH_2\end{array}\right\} & \begin{array}{l}\left.\begin{array}{r}H\\H\end{array}\right\}N\\ \left.\begin{array}{r}C_2H_2O\\H\end{array}\right\}O\end{array} & \left.\begin{array}{r}C_2H_3O_2\\H\\H\end{array}\right\}N
\end{array}$$

The first of these formulæ point out that these compounds contain the dyad radical $C_2H_2O_2$. The second and third formulæ show that we have to do with substitution-products of acetic acid. These may be regarded as compounds of a monad radical, inasmuch as amidacetic acid is formed from chloracetic acid, one atom of chlorine being replaced by the monad-amido group. The fourth series of formulæ constructed on the mixed type of water and hydrochloric acid, indicate the water-ammonia type; whilst in the fifth case amidacetic acid is represented as a compound ammonia. Which of these formulæ is to be preferred depends upon which of the relations of the compounds it is especially desired to lay weight. It is usual to choose those by which the more important reactions are most clearly represented.

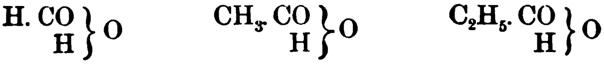
30 In 1838 Gerhardt pointed out that by the action of sulphuric acid on various compounds bodies are formed in which the characteristic properties of the constituents are not reproduced. In order to distinguish combinations of this kind from ordinary compounds, he termed them *copulated compounds.* The original views thus propounded by him were afterwards considerably enlarged and modified by Berzelius, who, although he at first ridiculed Gerhardt's idea of copulated compounds, afterwards, as we have seen, adopted the name. With the notion of these copulated compounds that of *copulated radicals* is intimately connected.

According to this view many radicals are supposed to be made up of several simpler radicals. Thus, for instance, many monobasic acids which belong to the type of water may be written, first of all, according to the water type:



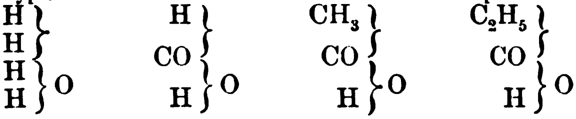
$$\begin{array}{cccc}\text{Type.} & \text{Formic Acid.} & \text{Acetic Acid.} & \text{Propionic Acid.}\\ \left.\begin{matrix}H\\H\end{matrix}\right\}O & \left.\begin{matrix}CHO\\H\end{matrix}\right\}O & \left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O & \left.\begin{matrix}C_3H_5O\\H\end{matrix}\right\}O\end{array}$$

But these compounds are frequently found to decompose in such a way that the group carbonyl, CO, is liberated as CO_2, together, in the case of formic acid, with hydrogen, and, in the case of the others, with an alcohol radical. The radicals of these acids may, therefore, be looked upon as containing carbonyl, and either hydrogen or an alcohol radical. This is represented in the following formulæ:



$$\begin{array}{ccc}\text{Formic Acid.} & \text{Acetic Acid.} & \text{Propionic Acid.}\\ \left.\begin{matrix}H.CO\\H\end{matrix}\right\}O & \left.\begin{matrix}CH_3.CO\\H\end{matrix}\right\}O & \left.\begin{matrix}C_2H_5.CO\\H\end{matrix}\right\}O\end{array}$$

The employment of the intermediate types led to the representation of these acids together with other compounds, as containing copulated radicals thus:



$$\begin{array}{cccc}\text{Type.} & \text{Formic Acid.} & \text{Acetic Acid.} & \text{Propionic Acid.}\\ \begin{matrix}\left.\begin{matrix}H\\H\end{matrix}\right\}\\\left.\begin{matrix}H\\H\end{matrix}\right\}O\end{matrix} & \left.\begin{matrix}\left.\begin{matrix}H\\CO\end{matrix}\right\}\\H\end{matrix}\right\}O & \left.\begin{matrix}\left.\begin{matrix}CH_3\\CO\end{matrix}\right\}\\H\end{matrix}\right\}O & \left.\begin{matrix}\left.\begin{matrix}C_2H_5\\CO\end{matrix}\right\}\\H\end{matrix}\right\}O\end{array}$$

The followers of Berzelius, especially Frankland and Kolbe,[1] considered these acids as conjugate compounds, but as these chemists did not recognise any oxygenated radicals, they looked upon acetic acid as the hydrate of a compound of oxygen with acetyl containing methyl and carbon, and they expressed the constitution of acetic acid by the formula $HO, (C_2H_3)C_2, O_3$, without admitting the new atomic weights.[2]

The development of the theory of types played an important part in the history of the science. Instead of supporting the view of the unalterability of the radicals, it led to the notion that the residue consists of groups of atoms which, in a certain series of metamorphoses, remain unaltered, whilst under other circumstances they may undergo change. It also threw a new

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[1] *Chem. Soc. Mem.* iii. 390.

[2] The reader will find a full account of the new theory of types as well as of copulated radicals in Kekulé's *Lehrbuch der organischen Chemie*, and in his memoir "on the so-called copulated compounds and the theory of polyatomic radicals."—*Ann. Chem. Pharm.* civ. 129.

light upon facts in other directions, explaining certain analogies and differences, and thus rendering possible a general view respecting the behaviour of the atoms in compounds.[1]

31 Before however we can enter into this question we must refer to another point and once more look back to the time when Williamson applied the theory of types to inorganic compounds, and showed that the existence of compound radicals must be assumed in these just as much as in organic substances.

Even before this time many salts, such as those of ammonium and those of uranyl, had been considered to contain compound radicals, but the number had then so largely increased that organic chemistry could not be correctly defined to be the chemistry of compound radicals.

All the organic compounds formed in nature contain carbon and hydrogen. Most contain oxygen as well, and many nitrogen. According to the older views it was, however, supposed that the hydrogen was, in many compounds, as, for instance, in oxalic acid, combined with oxygen to form water. Thus carbon was in some cases found to be the only remaining constituent, and this fact was pointed out by Gerhardt, in 1846.

Hence, organic chemistry was defined as the chemistry of the carbon compounds, as well as that of the radicals containing carbon. According to this definition, however, many compounds of this element must be considered to belong to organic chemistry although they are not formed from the bodies of vegetables or animals and occur in the mineral kingdom. Such bodies are carbon dioxide and marsh gas. This difficulty of classification has been avoided in various ways. Thus, Gmelin[2] in his Handbook says: "Carbon is the only element which is essential to organic compounds; every one of the other elements may be absent from particular compounds, but no compound which in all its relations deserves the name of organic is destitute of carbon. . . . If we were to regard as organic, those carbon compounds which have hitherto been classed amongst inorganic substances, namely carbonic oxide, carbonic acid, sulphide of carbon, phosgene, cast-iron, &c., we might define organic compounds simply as the *compounds of carbon*. But organic compounds are still further distinguished by containing more than one atom of carbon. . . . *Hence the term organic compounds includes all primary compounds*

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[1] Lothar Meyer, *Mod. Theor. der Chemie*, 3rd Ed. p. 150.

[2] *Handbook*, vii. 4 and 5.

containing more than one atom of carbon. By primary compounds we mean such as are not, like bi-carbonate of potash, made up of other compounds."

In order to understand this definition it must be remembered that in those days, the atomic weight of carbon was supposed to be only half as great as that which is at present assigned to it, and this remark applies also to oxygen, sulphur, and several other elements. Thus the following formulæ were then employed: carbonic oxide, CO; carbonic acid, CO_2; phosgene gas, $COCl$; and carbon disulphide, CS_2; whilst to the organic compounds of most simple constitution, the following formulæ were assigned: methyl alcohol, $C_2H_4O_2$; formic acid, $C_2H_2O_4$; hydrocyanic acid, C_2HN; chloroform, C_2HCl_3.

As soon, however, as it appeared that the atomic weights of the above elements must be doubled, and that the molecule of carbon dioxide or carbon disulphide contained exactly the same number of atoms of carbon as one molecule of methyl alcohol or of formic acid, either Gmelin's definition could no longer hold good, or the latter compounds must be considered to belong to inorganic chemistry, or, in the third place, the oxides and the sulphide of carbon must be considered to be organic compounds.

On this question Kekulé remarks: "We must come to the conclusion that the chemical compounds of the vegetable and animal kingdom contain the same elements as those of inanimate nature. We know that in both cases the same laws of combination hold good, and hence that no differences exist between organic and inorganic compounds, either in their component materials, in the forces which hold these materials together, or in the number and the mode of grouping of their atoms. We notice continuous series of chemical compounds whose single members, especially when only those which lie close together, are compared, exhibit strong analogy, and between which no natural division is perceptible. If, however, for the sake of perspicuity a line of demarcation is to be drawn, we must remember that this boundary is an empirical rather than a natural one, and may be traced at any point which seems most desirable. If we wish to express by organic chemistry that which is usually considered under the name, we shall do best to include all carbon compounds. We, therefore, define organic chemistry as the chemistry of the carbon compounds, and we do not set up any opposition between inorganic and organic bodies. That to which the old name of organic chemistry has been given, and which we express by the more distinctive term of the chemistry of the carbon compounds, is merely a special portion of pure chemistry, considered apart from the other portion only because the large number and the peculiar importance of the carbon compounds renders their special consideration necessary."[1]

Other chemists have expressed themselves in a similar way. Thus Butlerow states that a division of the kind is needed both in the interest of the student as well as in that of the scientific investigator. The carbon compounds exhibit certain peculiarities in consequence of which their investigation demands special methods, which are not necessary in the case of the other elements.[2] Another reason for treating the carbon compounds separately is the enormous mass of material which presents itself for investigation, so that although such a division is an artificial one, it is one which is extremely useful.[3]

32 The distinction between these classes of carbon compounds is, however, one which up to the present time has never been carried out in every detail. Thus, no chemist has ever thought it advisable to omit such substances as the oxides and the sulphide of carbon from the inorganic portion of his work, or to class substances like carbonate of lime, or spathic iron-ore, or even cast-iron, under the head of organic compounds. Hence we find a description of the oxides of carbon, of carbon disulphide, and of their various derivatives, generally placed in the divisions both of inorganic and of organic chemistry. In the same way the cyanogen compounds are frequently described both in inorganic and in organic treatises. The explanation being, that these bodies contain only one atom of carbon, and that they are in many respects analogous to the compounds of the elementary bodies. Wood-spirit and formic acid, on the other hand, which also only contain one atom of carbon in the molecule, are never considered as inorganic compounds, for they are closely connected with alcohol, acetic acid, and other bodies containing a larger number of carbon atoms, whose peculiar properties orginally led to the distinction between the two great branches of pure chemistry.

33 This peculiarity depends upon the fact that they are

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[1] *Lehrbuch d. org. Chemie*, i. 11.

[2] Butlerow, *Lehrb. d. org. Chem.* 5.

[3] Erlenmeyer, *Lehrb. d. org. Chem.* p, 5.

carbon compounds, for carbon possesses properties by which it is distinguished from all other elements. In the first place we have to remember that hydrogen is found in all organic bodies in addition to carbon; in most others oxygen occurs; and in many nitrogen is also contained. Others again consist of carbon, hydrogen, and nitrogen only.

The number of these bodies is enormously large. Carbon yields more compounds than all the other elements taken together. Moreover, the number of atoms contained in the molecule may be very considerable. Thus, for instance, oil of turpentine consists of carbon and hydrogen, and contains 26 atoms; cane-sugar, which in addition contains oxygen, contains 45; and stearin, also an oxygenated body, contains 173 atoms.

Kekulé,[1] who first pointed out that carbon is a tetrad element, showed at the same time that the existence of so large a number of carbon compounds may be explained by the fact that the atoms of this element have the power of combining one with another. A similar view was also put forward shortly afterwards by A. S. Couper.[2]

The atoms of other polyvalent elements, such as oxygen, sulphur, &c., are indeed found to combine with one another, but the number which can be thus connected together is in their case a very limited one. With carbon, however, such a limit to the power of combination has not yet been reached. A large number of its atoms are capable of uniting to form a chain which in many reactions behaves as if it were a chemical unit.

Still more clearly however is carbon distinguished from all the other elements by the fact that in such a chain of atoms *all the free combining units can be saturated by hydrogen.* Hence the existence of a large number of hydrocarbons becomes possible. These are all volatile, whilst amongst the hydrogen compounds of the other elements only those of the chlorine, oxygen, nitrogen, boron, and silicon groups are volatile, and in the case of each of these (with the exception of phosphorus) only one hydride is known.

The hydrocarbons are however not only the simplest, but at the same time, on theoretical grounds, the most important, compounds of this element, especially because all the other compounds may be derived from these by the replacement of hydrogen by other elements. In the organic compounds

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[1] *Ann. Chem. Pharm.* civ. 129; cvi. 129; *Lehrbuch*, i. 161.

[2] *Phil. Mag.* [4], xvi. 104.

occurring in nature we usually find a portion of the hydrogen replaced by oxygen or by nitrogen, or by both of these elements. Some few are found to contain sulphur. All the elements may be made to combine with carbon compounds, but it is only in a few instances that all the hydrogen in the hydrocarbon can be replaced by another element. This explains the fact which has already been mentioned, that by far the larger proportion of carbon compounds contain hydrogen, or a residue of the hydrocarbon from which they all are derived.

34 Hence we may define that portion of our science which is usually denoted as organic chemistry as being *the chemistry of the hydrocarbons and their derivatives.* The characteristic nature of this definition is seen from the fact that, when the general chemical constitution of a carbon compound has been rightly ascertained, it can be converted into the corresponding hydrocarbon, or, inversely, it may be prepared from this latter compound.

In employing this definition, we do not draw any distinctive line between organic and inorganic chemistry, for the simpler carbon compounds which have already been described in the inorganic portion of this work, such as carbon dioxide, carbon oxychloride, sulphide of carbon, hydrocyanic acid, &c., all of which contain one atom of carbon, may be looked upon as direct derivatives of a hydrocarbon, namely, marsh gas, CH_4. From this they can all be prepared, and into this they can all be converted. When this gas is burnt in the air, water and carbon dioxide are formed, the monad hydrogen being replaced by dyad oxygen. Marsh gas can also be directly converted into carbon disulphide, and when the vapour of the latter body is passed together with sulphuretted hydrogen over red-hot metallic copper, the sulphur is substituted by hydrogen, and the hydrocarbon, marsh gas, is formed. If this latter compound be treated with chlorine, the first product which is obtained is methyl chloride, CH_3Cl, and when this is heated with caustic potash, wood-spirit, or methyl alcohol, CH_4O, is obtained:

$$CH_3Cl + KOH = CH_3.OH + KCl.$$

When this alcohol is oxidised, formic acid is produced, two atoms of hydrogen being replaced by one atom of oxygen. By the further action of chlorine on methyl chloride the successive replacement of all the hydrogen by chlorine takes place, the last product but one being chloroform, $CHCl_3$; and if this substance be heated with ammonia, hydrocyanic acid is obtained, three atoms of chlorine being replaced by one atom of triad nitrogen:

$$CHCl_3 + 4\ NH_3 = CHN + 3\ NH_4Cl.$$

As all the cyanides can be derived from hydrocyanic acid, they may be all considered as derivatives of marsh gas. The carbonates may be similarly considered to be derived from marsh gas, for we must assume in the aqueous solution of carbon dioxide the existence of carbonic acid, $CO(OH)_2$, that is to say, marsh gas, in which one-half of the hydrogen has been replaced by oxygen, and the other two by hydroxyl. Indeed the various varieties of cast-iron may even be regarded as derivatives of hydrocarbons, inasmuch as when cast-iron is dissolved in hydrochloric or sulphuric acid the carbon which is combined with the iron gives rise to hydrocarbons in which the hydrogen may be said to have replaced iron.

35 Only one single carbon compound is known for which the corresponding hydrocarbon does not exist. This is the simplest of all carbon compounds, viz. carbon monoxide. All endeavours to isolate the hydrocarbon CH_2 have as yet proved abortive, and there are good reasons for believing that the existence of such a body in the free state is not possible. No other hydrocarbon except marsh gas is known which contains only one atom of carbon. On the other hand, we are acquainted with three which contain two atoms of carbon:

Ethane, C_2H_6. Ethylene, C_2H_4. Ethine, C_2H_2.

In order to explain the constitution of these substances it is assumed that in ethane the two carbon atoms are connected together singly; in ethylene by double linking; whilst in ethine or acetylene the three combining units of the two carbon atoms are supposed to be linked together.

A large number of carbon atoms may be combined together in a similar way, and thus the above hydrocarbons form the first members of groups of which each is distinguished from the preceding by an increment of CH_2. The composition of these may be expressed by the following general formulæ:

Series.	C_nH_{2n+2}.	C_nH_{2n}.		C_nH_{2n-2}.	
Methane	$C\,H_4$	——		——	
Ethane	C_2H_6	Ethylene	C_2H_4	Ethine	C_2H_2
Propane	C_3H_8	Propylene	C_3H_6	Propine	C_3H_4
Butane	C_4H_{10}	Butylene	C_4H_8	Butine	C_4H_6
Pentane	C_5H_{12}	Pentylene	C_5H_{10}	Pentine	C_5H_8
Hexane	C_6H_{14}	Hexylene	C_6H_{12}	Hexine	C_6H_{10}
&c.		&c.		&c.	

Besides these, other groups, such as C_nH_{2n-4} and C_nH_{2n-6} &c., are known. The first members of these naturally contain more than two atoms of carbon.

36 Other carbon compounds can be derived from these various series. Thus, for instance, just as by the action of chlorine on marsh gas methyl chloride is obtained, so the other members of the marsh gas series yield chlorides of monad radicals having the general formula $C_nH_{2n+1}Cl$ in which chlorine can be easily replaced by hydroxyl, and thus a series of hydroxides are obtained to which the names of alcohols have been given, and to which the general formula $C_nH_{2n+2}O$ is applicable.

When methyl chloride is heated with ammonia, a strong base is obtained, which has received the name of methylamine:

$$CH_3Cl + NH_3 = CH_3NH_2 + HCl.$$

And by a similar reaction with the other chlorides a series of such bases or amines is obtained having the general formula $C_nH_{2n+3}N$.

Moreover, as methyl alcohol gives rise to formic acid by oxidation, so these other alcohols yield a series of acids having the general formula $C_nH_{2n}O_2$, obtained by the replacement of two atoms of hydrogen in the alcohol by one of oxygen. Many of these acids are found in fats and oils, and hence they are termed the fatty acid series, or the adipic series of acids. Thus we obtain the following series from the marsh gas hydrocarbons:

Chloride.		Alcohol.		Amine.		Fatty Acid.	
Methyl chloride	$C\,H_3Cl$	Methyl alcohol	$C\,H_4O$	Methylamine	$C\,H_5N$	Formic acid	$C\,H_2C_2$
Ethyl chloride	C_2H_5Cl	Ethyl alcohol	C_2H_6O	Ethylamine	C_2H_7N	Acetic acid	$C_2H_4O_2$
Propyl chloride	C_3H_7Cl	Propyl alcohol	C_3H_8O	Propylamine	C_3H_9N	Propionic acid	$C_3H_6O_2$
Butyl chloride	C_4H_9Cl	Butyl alcohol	$C_4H_{10}O$	Butylamine	$C_4H_{11}N$	Butyric acid	$C_4H_8O_2$
Pentyl chloride	$C_5H_{11}Cl$	Pentyl alcohol	$C_5H_{12}O$	Pentylamine	$C_5H_{13}N$	Pentylic acid	$C_5H_{10}O_2$
Hexyl chloride	$C_6H_{13}Cl$	Hexyl alcohol	$C_6H_{14}O$	Hexylamine	$C_6H_{15}N$	Hexylic acid	$C_6H_{12}O_2$

In addition to these, a large number of other derivatives of the above hydrocarbons is also known, and these again yield other groups which can all be arranged in corresponding series. All the hydrocarbons contain an even number of atoms of hydrogen; this being owing to the tetrad nature of carbon. For the same reason it also follows *that the sum of the atoms of monad and triad elements which are contained in a molecule of a carbon compound is always an even number.*

37 In 1842 Schiel[1] remarked that the alcohol radicals form a very simple and regularly graduated series of bodies, of which the properties as well as the composition exhibit corresponding regular gradations. He gave the following description, the old equivalents being used:

$C_2H_2 = R$

RH	Methyl.
R_2H	Ethyl.
R_3H	Glyceryl
R_4H	?
R_5H	Amyl.
$R_{16}H$	Cetyl.
$R_{24}H$	Cerotyl.

He also predicted the existence of other series. Shortly afterwards, Dumas[2] showed that the fatty acids form a similar series, and that in these, as Schiel had pointed out in the case of the alcohols, the boiling-point regularly rises with the increment C_2H_2.

In his *Précis de Chimie organique*, published in 1844, Gerhardt collected together a large number of such groups, and was the first to give to these the name of *homologous series*, whilst he classed the bodies obtained from one another by definite chemical metamorphoses, such, for instance, as ethyl chloride, ethyl alcohol, acetic acid, &c., as *heterologous series.*

This classification into homologous and heterologous series Gerhardt compares to the arrangement of a pack of cards. The cards of each suit being placed in regular order in a vertical line, those of equal value in the different suits will be found in a horizontal row. These latter correspond to the homologous series, whilst the first represent

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[1] *Ann. Chem. Pharm.* xliii. 107.

[2] *Ibid.* xlv. 330.

the heterologous series. If one card be wanting, its place is nevertheless indicated, and, although absent, we know its exact character. In the same way with organic compounds. When the series is not complete, the composition of the missing substance can not only be predicted, but even its more important properties indicated. Of its possible existence there can be no doubt, and if it is desired to complete the series, this can be done by employing suitable reactions.

If we compare the various members of one such series of homologous bodies together, thus, for example, those of the marsh gas hydrocarbons, C_nH_{2n+2}, we find, in the first place, that they differ from one another in *physical* properties. The lowest members are gases at the ordinary temperature; the members next following are liquids whose boiling-points increase with their molecular weights, whilst the highest members are solid bodies, which are volatilised only at a high temperature. The same holds good with the other series. Their lowest members are either gases or volatile liquids; the highest, on the other hand, are solid bodies either only volatilised with difficulty or undergoing decomposition when heated.

We next observe that the *chemical* character of each group depends essentially upon the mode in which the carbon atoms are connected with one another, as well as with the rest of the elements contained in the molecule. For this reason the corresponding members of each homologous series closely resemble one another in their chemical relationships. One result of this is that whilst the comparatively limited number of compounds which the other elements form renders it possible that the nature and composition of the compound can be determined by a few reactions, this, on the other hand, is only exceptionally possible in the case of the carbon compounds. In most instances it is necessary for this purpose not only to prepare the body in the pure state, but also to determine its physical and chemical characters, and then to pass on to the determination of its quantitative composition. Not only do newly discovered bodies require this complete treatment, but frequently this is the only mode by which substances which have long been known can be satisfactorily recognised. Hence we shall now pass on to describe the methods which have been employed, and are still in use, for the *ultimate analysis* of the carbon compounds.

ULTIMATE ORGANIC ANALYSIS.

DETERMINATION OF CARBON AND HYDROGEN.

38 The first successful analysis of an organic compound was carried out by Lavoisier, and the principle upon which he founded his method for the determination of carbon and hydrogen is the same as that which is employed for a like purpose at the present day. The body to be analysed is completely burnt, the quantity of carbon dioxide and water thus produced being accurately determined.

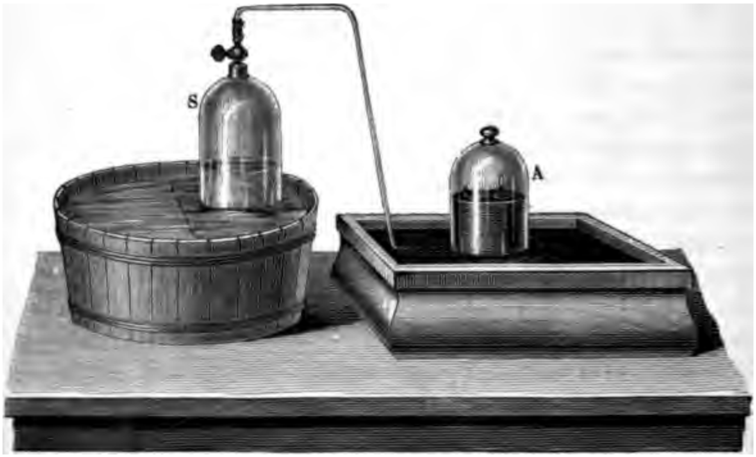

Fig. 1.

Lavoisier's Method. The apparatus used by Lavoisier[1] for this purpose is shown in Fig. 1. The glass bell-jar A, carefully

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[1] *Mem. Acad.* 1781 (published in 1784), and *ibid.* 1784 (published in 1787).

calibrated and standing over mercury, contains common air. Into this is brought a weighed lamp fed with the alcohol or oil to be analysed; on the wick a small piece of phosphorus is placed, and this can be inflamed by contact with a warm bent wire. The bell-jar S contains a measured volume of oxygen standing over water. By lowering this, the oxygen can be passed over into the vessel A for the purpose of completing the combustion. As soon as this is effected, the carbon dioxide formed by the combustion is absorbed by caustic potash, and from the volume of this gas, together with that of the air which remains behind after the combustion, and from the volume of unburnt oxygen, Lavoisier calculated the composition of the alcohol or oil which had undergone combustion in the lamp. In this way, however, he arrived at altogether erroneous results, inasmuch as he was not acquainted with the exact composition of either carbon dioxide or water, and the numbers which he used for the specific gravities of the various gases employed were by no means accurate. Nevertheless, if his results be recalculated with the adoption of correct constants, it appears that his analyses were at least as accurate as those of many chemists who in the following years occupied themselves with the subject.

Lavoisier even then observed that the indirect determination of water by the subtraction of the weight of carbon dioxide from the sum of the weights of the burnt substances and the oxygen employed for the combustion might with advantage be replaced by a direct determination of this substance. Later on, indeed, he described an apparatus for the burning of large quantities of oil, in which both the water and carbon dioxide formed are weighed. This method has a special interest, as the arrangement of the apparatus closely resembles that in use at the present day.[1] The apparatus used is shown in Fig. 2. The combustion takes place in A, and the oil for the lamp is introduced at *a*. The gas-holder (P) is filled with oxygen, and this gas passes through *b*, and is dried in the tube *p*. The products of combustion pass through *c* into the absorption-apparatus. The greater portion of the water collects in the bottle (*f*), and that which escapes is deposited in the spiral tube (*h*), whilst the last traces are taken up in the tube *k*, which contains a "deliquescent salt." The gases then pass through a system of bottles (FF), of which only two are represented in the

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[1] Lavoisier's *Elements* (Kerr's translation), 503.

figure, although Lavoisier employed eight or nine. These, with the exception of the last, contain caustic potash, lime-water being placed in the last one in order that the complete absorption of the carbon dioxide may be recognised by the

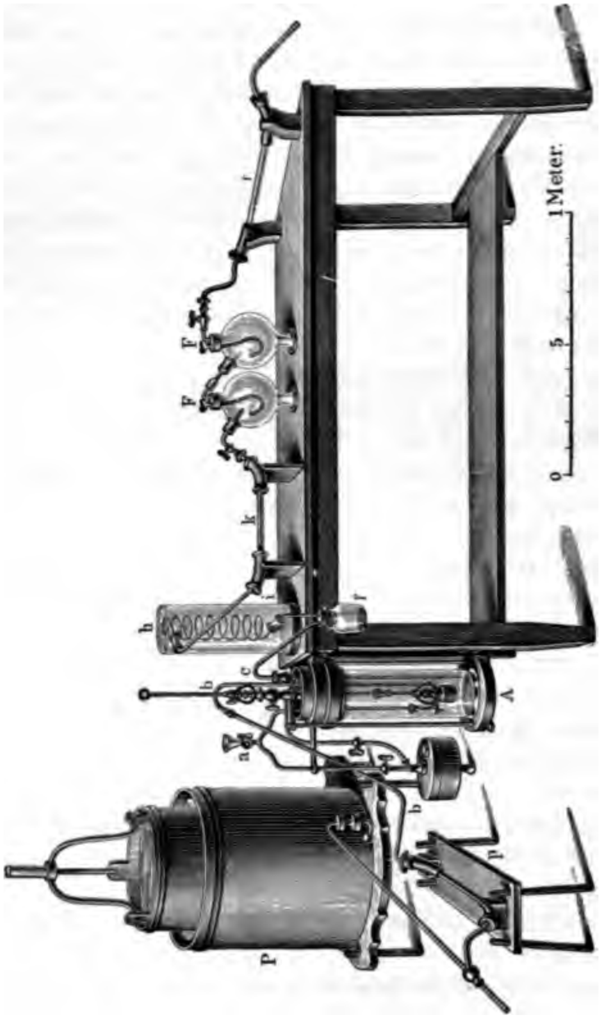

FIG. 2.

non-turbidity of the lime-water. The first experiments made with this apparatus did not yield very satisfactory results, and his endeavours to improve the method were cut short by his untimely execution in May, 1794.

combustion was effected in an apparatus the construction of which is shown in Fig. 3. The closed lower end of the hard glass tube AA, 2 dcm. in length and 8 mm. in diameter, is placed upon a charcoal fire, or strongly heated by an alcohol lamp (H). The upper end of this combustion-tube is closed with a stopcock, which, however, is not bored through, but has a cavity bored into the stopper. A pill is placed in this cavity, and the stopcock turned, when the pill falls into the red-hot tube. By repeating this operation, all the air contained in the combustion-tube is driven out by the side tube. A weighed quantity of the pills is then gradually added, and the whole of the gas generated collected in a graduated jar over mercury. The excess of oxygen is determined by adding a certain volume of hydrogen and exploding the mixture, and then the carbon dioxide is absorbed by caustic potash, and thus the volumes of the two gases are ascertained. These volumes, together with the weight of the substance burnt, give data for ascertaining the quantity of water formed. In this way Gay-Lussac and Thénard analysed no less than fifteen organic substances free from nitrogen, and four substances containing this element. In the latter case they took the precaution of avoiding a large excess of oxygen in order to prevent the formation of the oxides

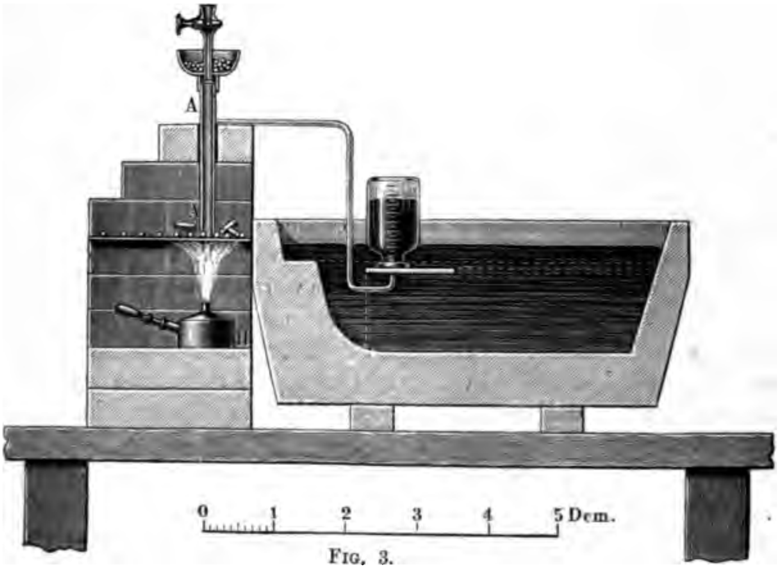

FIG. 3.

of nitrogen. Some of the analyses thus conducted are fairly accurate, when the calculations are corrected, this being necessary because at that time neither the true composition of carbon dioxide nor that of water was known. Thus corrected, Gay-Lussac and Thénard's numbers for the percentage composition of sugar are as follows. The results calculated from the formula are added for the sake of comparison.

	Found.	Calculated.
Carbon	41·36	42·10
Hydrogen	6·39	6·44
Oxygen	51·14	51·46
	98·89	100·00.

This method, however, did not yield satisfactory results in the case of very volatile bodies, and the composition of these substances had to be determined, as before, by eudiometric methods.

We are indebted to Saussure for improving this branch of analysis, and for determining accurately the composition of several compounds, such as that of alcohol.[1] He also analysed non-volatile bodies, some of them with great exactitude, by combustion in oxygen, determining the volume of this gas needed for the combustion, as well as that of the carbon dioxide formed.[2]

41 *Berzelius's Method.* Saussure's method would probably have come into general use had not Berzelius[3] published in 1814 his much more exact method for the analysis of organic bodies. It has already been stated in the introduction that Berzelius began this investigation with the view of ascertaining whether organic bodies obey the same laws of chemical combination as those which regulate the formation of inorganic substances. Adopting Lavoisier's plan, he absorbed the water and carbon dioxide formed by the decomposition, determining their amounts gravimetrically. Like Gay-Lussac and Thénard, he employed potassium chlorate as an oxidising agent, reducing the violence of its action by mixing it with ten times its weight of common salt. At the closed end of his glass combustion-tube he placed some of this mixture of

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[1] *Ann. Chim.* lxxviii. 57.

[2] *Bibl. Britan.* lvi. 333.

[3] Thomson's *Ann. Phil.* [4], 401.

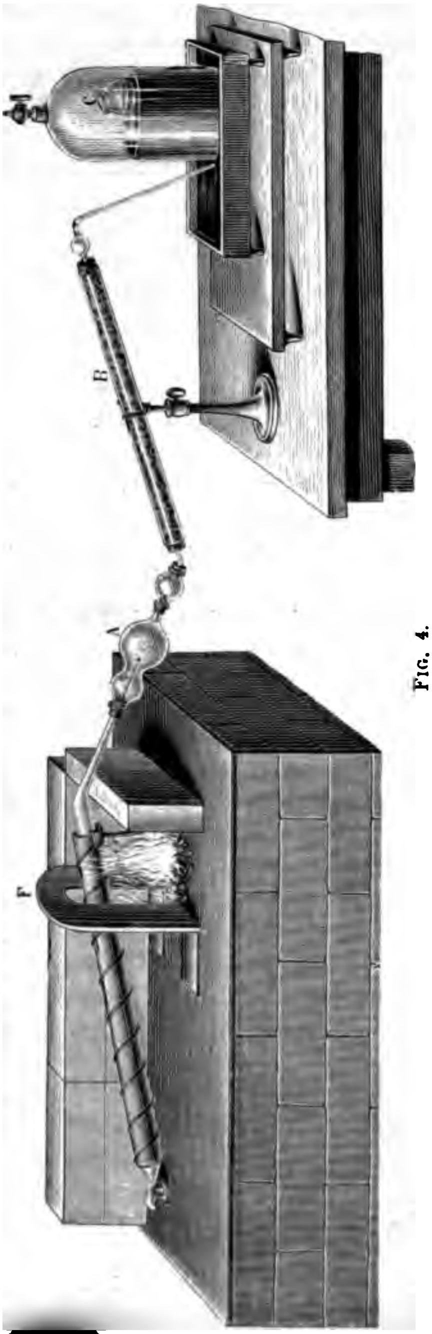

Fig. 4.

common salt and potassium chlorate; then came an intimate mixture of the substance with the same oxidising material, whilst the front portion of the tube was filled with the oxidising substance alone. The open end of the tube was drawn out to a long point and the whole placed in a furnace (Fig. 4), in which it was heated by charcoal and placed in the position indicated in the figure. For the sake of precaution the tube was surrounded by a coating of copper foil fastened with iron wire. The open end was then connected with a light glass rereceiver (A), which in its turn was joined to the tube B, containing calcium chloride, which served to absorb the water not condensed in A. The carbon dioxide formed, together with the excess of oxygen, was collected over mercury in the bell-jar containing a small glass vessel filled with caustic potash. In carrying out the experiment, the front end of the tube was first heated, and the fire gradually extended to the further end, the screen F being gradually pushed back. The oxygen evolved at the end of the operation served for the purpose of driving the combustion-products left in the tube through the absorption vessels. The increase in the weight of the vessels A and B gave the weight of the water formed, and that of the vessel C the amount of carbon dioxide. This method is not applicable to the case of nitrogenous bodies, inasmuch as oxides of nitrogen are then formed which are absorbed by the caustic potash. Besides, the method is liable to various other errors which render an exact determination of hydrogen and carbon impossible. If we desire to obtain an idea of the accuracy of this process, the analytical numbers obtained by Berzelius must be recalculated, inasmuch as inexact

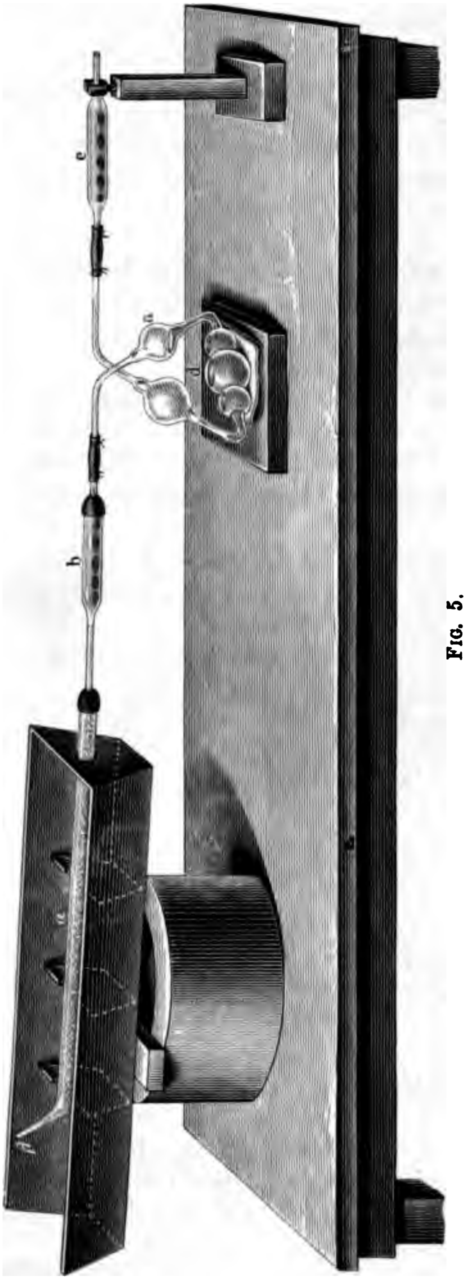

FIG. 5.

atomic weights were employed by him. If this be done, we obtain the following numbers for the percentage composition of sugar:

Carbon	42·7
Hydrogen	6·5
Oxygen	50·8
	100·0

42 *Liebig's Method.* To Liebig belongs the singular honour of having so completely perfected and simplified the process of organic analysis that his method is used at the present day almost unaltered. The labour which this investigation involved was however so great that it was many years (1823–1830) before it was completed, and the potash apparatus in the form in which it is now used, was not described until 1831.[1] From this time forward he was able, with the help of his pupils, to carry out the numerous important investigations which gave to the Giessen laboratory a world-wide reputation.

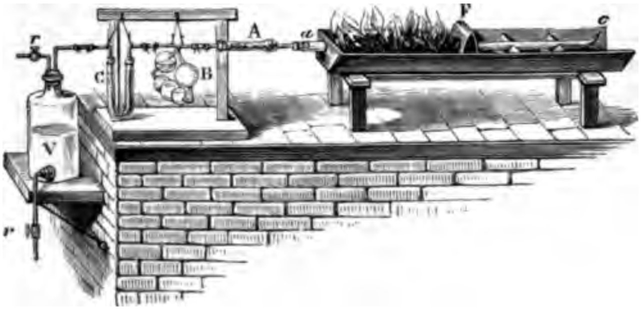

FIG. 6.

As an oxidising agent, Liebig employed cupric oxide, CuO, a substance which had been used by Gay-Lussac and Thénard in their analyses of nitrogenous substances. This compound is also employed for the qualitative detection of carbon and hydrogen, inasmuch as, when, in the perfectly dry state, it is ignited with an organic substance, the above elements unite with its oxygen to form carbon dioxide and water, the presence of which can be readily detected.

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[1] *Pogg. Ann.* xxi.

Liebig's original combustion apparatus is shown in Fig. 5, whilst Fig. 6 exhibits the form in which at a later time it became generally adopted. It consists of the combustion-tube (Fig. 7) made of difficultly fusible glass, drawn out at the closed end to a fine point. This is filled in different ways according to the nature of the body undergoing combustion. If it be a solid, not too volatile or hygroscopic, the following method described by Liebig[1] may be used:—A small quantity of finely-divided, and previously ignited, black oxide of copper which has been cooled in a closed vessel is first brought into the combustion-tube to the point *c*; some more of this oxide is then placed in a small porcelain mortar, and to this from 0·2 to 0·3 gram of the substance is added. This is then covered with more oxide, and well mixed by means of the pestle. The mixture is next filled into the combustion-tube up to the point *b*, and the mortar rinsed out with more oxide, and this also brought into the tube, which is then filled, though not completely, from the point *a* with pure copper oxide. The length of the last layer of pure oxide depends on the combustibility and volatility of the substance. If an easily volatile substance

FIG. 7.

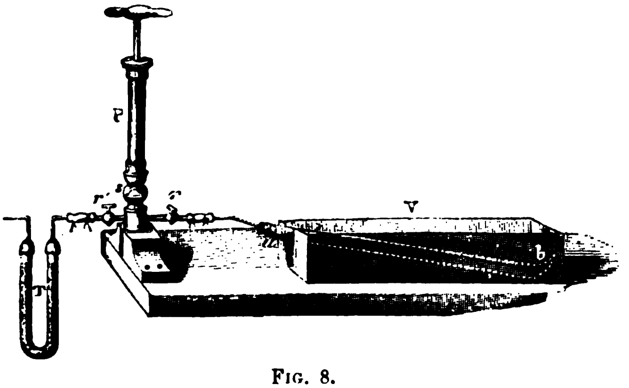

FIG. 8.

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[1] For further details of this method we must refer to Fresenius's *Quantitative Analysis*, p. 455, § 174, sixth ed.

has to be burnt, or one which, on heating, gives off large quantities of combustible vapours, the column of oxide must be longer than in other cases. The tube is then laid flat on the table and gently tapped, so that a free passage for the products of combustion is left above the surface of the copper oxide.

Inasmuch as copper oxide is a very hygroscopic substance and may, therefore, have absorbed moisture from the air during the process of mixing, this moisture must be removed when an exact determination of the hydrogen is required. For this purpose the tube, prepared in the way described, is placed in connection with the exhausting syringe (P, Fig. 8), the second opening of which is joined to a U-tube (T) containing chloride of calcium. The combustion-tube (*ab*) is warmed in a water-bath or sand-bath, then exhausted, and dry air allowed to enter, and this operation repeated several times.

43 In order to avoid this tedious dessicating process, the substance may, according to Bunsen's proposal, be mixed with the oxide of copper in the tube itself. This is effected by means of a copper- or brass-wire bent at the end like a corkscrew (Fig. 9), a vertical and, at the same time, a rotatory motion being given to the wire. The tube is then placed in the combustion-furnace,

FIG. 9

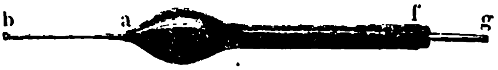

FIG. 10.

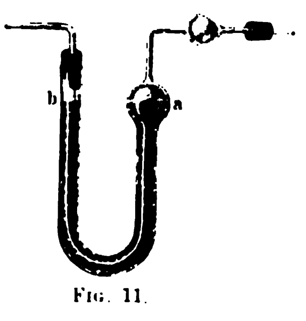

FIG. 11.

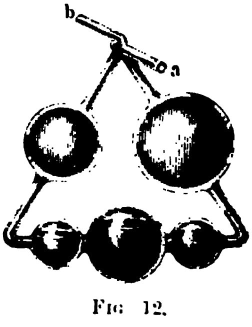

FIG. 12.

closed by a soft bored cork, through which passes the end of the chloride of calcium tube (Fig. 10), this being employed for the absorption of the water produced. Another form of such a tube is shown in Fig. 11. The carbon dioxide is collected in a Liebig's potash-bulb filled with a concentrated solution of caustic potash (Fig. 12). Another form of this apparatus is shown in Fig. 13. All these forms of bulbs are so arranged that the gas passes in single bubbles through the various bulbs, thus remaining for a considerable time in contact with the caustic potash. In order to be sure that the carbon dioxide is completely absorbed (for this gas is, to begin with, mixed with a large quantity of air), and also to prevent the exit air from carrying away aqueous vapour from the caustic potash solution, a few pieces of solid potash are placed in the U-tube (C) (Figs. 6 and 14) connected to and weighed with the potash-bulbs. The bulbs are then connected by means of the U-tubes to an aspirator (V) (Fig. 6), the stopcock remaining open.

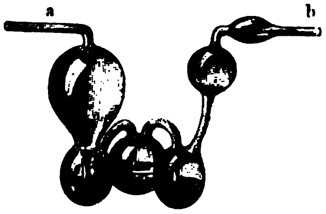

FIG. 13.

In carrying out the combustion, the first point to be ascertained is that the apparatus is perfectly air-tight. This is usually done by first placing the Liebig's bulbs in a slanting position with the larger bulb uppermost, warming this until a sufficient quantity of air has escaped through the liquid. When the air in the apparatus cools, the liquid rises in the bulb, and there assumes a higher level than in the other part of the apparatus. If this level remains constant for a considerable time, we may conclude that all the parts of the apparatus are tight, and the combustion itself can now be commenced.

The next operation is to surround the front part of the tube with red-hot charcoal, care being taken that the end of the tube carrying the cork is placed in such a position that in the first place no water condenses on it, and in the second that the cork does not become over-heated and charred. In order to keep the hot charcoal in its right place, and to prevent the further portions of the tube from becoming heated before the proper time, the iron screen F (Fig. 6) is used. This is gradually pushed back as the front portions of the tube have become red-hot. More charcoal is now added, and the process is continued until the whole of the layer of copper oxide is red-hot. The portion containing the substance is now very carefully and gradually heated, so that whilst the combustion is going on, not more than one or two bubbles of gas pass every second through the potash-bulbs. When the whole of the tube has been surrounded by red-hot charcoal, and as soon as the evolution of gas ceases, the potash-bulbs are placed in a vertical position, the charcoal removed from the drawn-out end of the tube, and the screen placed in front of the point. Owing to the gradual cooling, and to the absorption of carbon dioxide, the potash solution will now be seen to pass back into the large bulb. When this is filled with liquid, and the pressure within the apparatus being, therefore, somewhat less than the atmospheric pressure, the pointed end of the tube is broken by means of pliers. The potash-apparatus is now brought back into its original slanting position, and, by means of the aspirator, air is drawn through the apparatus in order to allow the whole of the carbon dioxide and aqueous vapour to pass through the absorption vessel. In order to be quite sure that in this operation none of the carbon dioxide produced by the combustion of the charcoal finds its way into the combustion-tube, a long, closely-fitting glass tube is dropped over the open point of the combustion-tube. Sometimes, instead of connecting the tube with an aspirator, air is drawn through the potash-bulbs by the mouth, by means of a bulb-tube and caoutchouc. The arrangement, when this plan is adopted, is shown in Fig. 14. As soon as the bubbles passing through the potash-apparatus no longer diminish in size, the current of air is stopped, and the absorption vessels are removed, placed in the balance case, and, after they are completely cold, their weight ascertained.

Difficultly volatile and non-volatile liquids are weighed out in short glass tubes open at one end. These are dropped into the combustion-tube containing some copper oxide, more oxide added, and then the liquid allowed to run out of the tube into the oxide of copper by carefully sloping the tube. Volatile liquids must be weighed out into a small weighed glass bulb having long ends. One end is then broken off, and the end, together with the bulb, allowed to fall into the combustion-tube, which is then filled with oxide of copper. The front of the tube is first heated to redness, and afterwards the portion in which the bulb is placed, so that the liquid is driven out into the oxide of copper. The combustion is then allowed to proceed in the ordinary way.

In his analyses of sugar, Liebig obtained the following results, which agree sufficiently well with the theoretical numbers when they are re-calculated with the present atomic weights :

Carbon	41·71
Hydrogen	6·45
Oxygen	51·84
	100·00

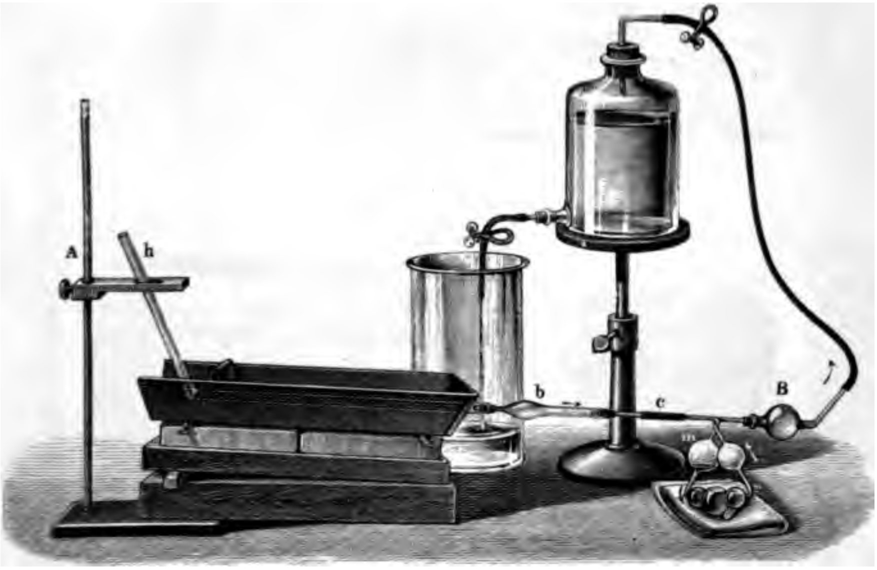

FIG. 14.

44 *Gas Combustion-furnaces.* The use of charcoal has the advantage that the temperature at the various parts of the tube can be readily controlled, either by removing or by fanning the burning charcoal. On the other hand, its employment is accompanied by several disadvantages, which led to the proposal to replace charcoal by alcohol lamps. A furnace of this kind constructed by Hess came into use, but was soon superseded by gas combustion-furnaces when Bunsen introduced his non-luminous gas-burner. An old form of gas-furnace introduced by

v. Babo is shown in Fig. 15. Erlenmeyer's furnace exhibited in Fig. 16 is much used at the present day. Its arrangement is readily understood by reference to the figure. In order to protect the combustion-tube from the direct action of the flame, it is generally placed in a trough made either of fireclay, or of iron lined with some calcined magnesia, and, for the purpose of throwing the hot gases of the flame on to the top of the tube, tiles are placed on the sides and top of the furnace. Erlenmeyer's furnace does not burn much gas, but great care must be taken in heating the tube, as it easily cracks unless the temperature be very gradually raised.

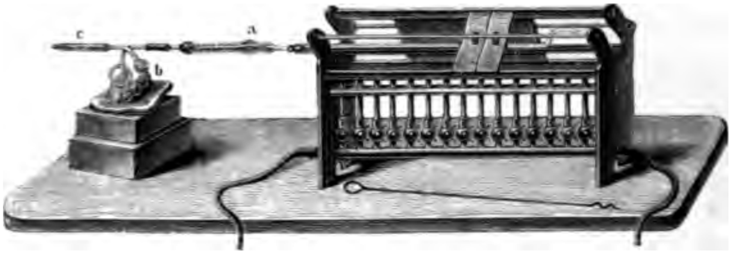

FIG. 15.

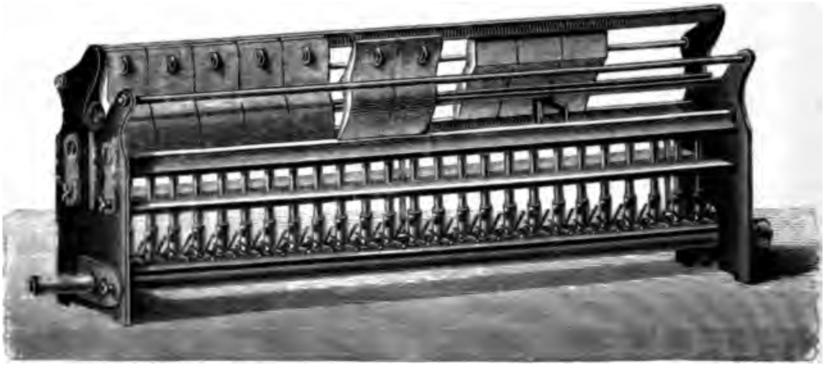

FIG. 16.

This risk is much lessened in Hofmann's form of furnace[1] (Figs. 17 and 18), in which a well-diffused radiant heat, similar

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[1] *Quart. Journ. Chem. Soc.*, xi. 30.

to that obtained from red-hot charcoal, is produced by the ignition of heated fireclay cylinders. The hollow cylinders are fixed upon fish-tail gas-burners, and are closed at the top, the sides being punctured with a large number of small openings, at which the gas burns mixed with air. In order to concentrate the heat, plates of fireclay are placed at the sides and top of the furnace.

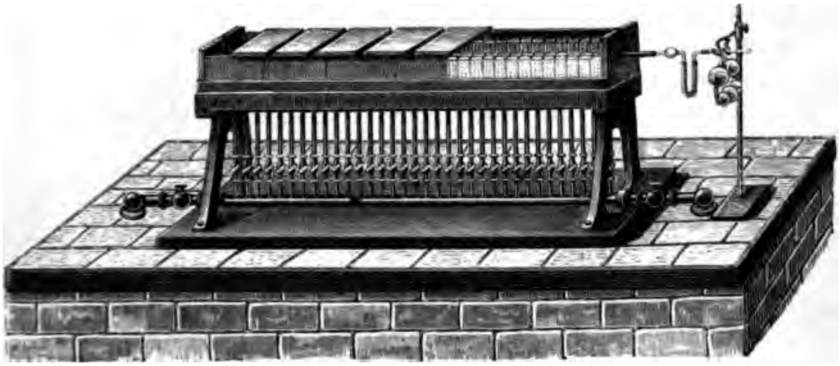

Fig. 17.

Another form of combustion-furnace now much in vogue is that proposed by Glaser[1] and shown in Fig. 19. It was first described by Donny, and the combustion-tube is heated by means of perforated pieces of iron shown in the figure, forming a trough in which the combustion-tube lies wound round with iron gauze. The tube is heated partly by conduction from the hot iron and partly by the gas which burns through the perforations. Perforated clay covers are employed for raising and equalising the temperature.

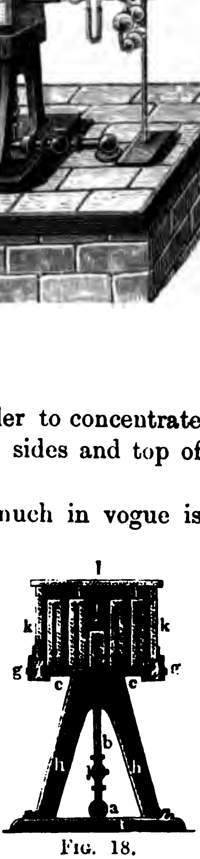

Fig. 18.

45 *Combustion in a Current of Oxygen.* When the combustion is performed according to Liebig's original method, it sometimes happens, especially in the case of bodies rich in carbon, that some of the carbon is deposited on the upper part of the tube or even upon the reduced metallic copper, and this is only incompletely burnt when air is passed over it. In order to avoid

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[1] *Ann. Chem. Pharm.* Suppl. vii. 213.

this source of error, some pieces of fused potassium chlorate, or better, perchlorate, may be placed at the end of the tube, from which a current of oxygen is evolved at the end of the operation. When every precaution is taken, the combustion carried out in this way yields satisfactory results. Thus, for example, the percentage of carbon ought never to be more than 0·1 to 0·05 below the theoretical amount, whilst the hydrogen should not be more than about 0·2 per cent. in excess of theory. By this plan, however, a new tube must be employed for each combustion, and hence it was long ago proposed to conduct the combustion in a stream of air or oxygen, and this method is now generally adopted. Fig. 19 shows the arrangement of an apparatus for carrying out a combustion of this kind. A tube open at both ends is used; one end is connected with the absorption-tubes, and the other with a drying apparatus (A), through which either dry air or dry oxygen can be passed. The part of the tube near the calcium chloride tube is filled to two-thirds of its length with granulated copper oxide, behind which the substance to be analysed is placed in a platinum or porcelain boat. In front of, and in connection with the absorption-tubes, is placed an aspirator (B), in order to ensure the passage of the products of combustion through the absorption-tubes, and to prevent them by any chance from passing into the drying apparatus. After the copper oxide has been heated to redness, the substance is gradually ignited, a slow current of air being at the same time passed through the apparatus from the gas-holder, in order to carry the products of the combustion into the absorption-tubes. As soon as the whole tube is red-hot, the current of air is changed for one of oxygen. By this means any carbon left in the platinum boat is completely burnt, and all the reduced copper is re-oxidised. This method is very convenient, as after each combustion the apparatus is in exactly the same state as it was before the experiment; and as soon as it has cooled down a new combustion may be commenced.

According to this plan the whole of the apparatus is well dried before the combustion, and hence we might suppose that the hydrogen determination would be more correct than by the older process in which the hygroscopic copper oxide is exposed to the air. Experience has, however, shown that this is not the case, although no satisfactory explanation for the fact has been given.[1]

[1] Lieben, *Liebigs Ann.* clxxxvii. 112.

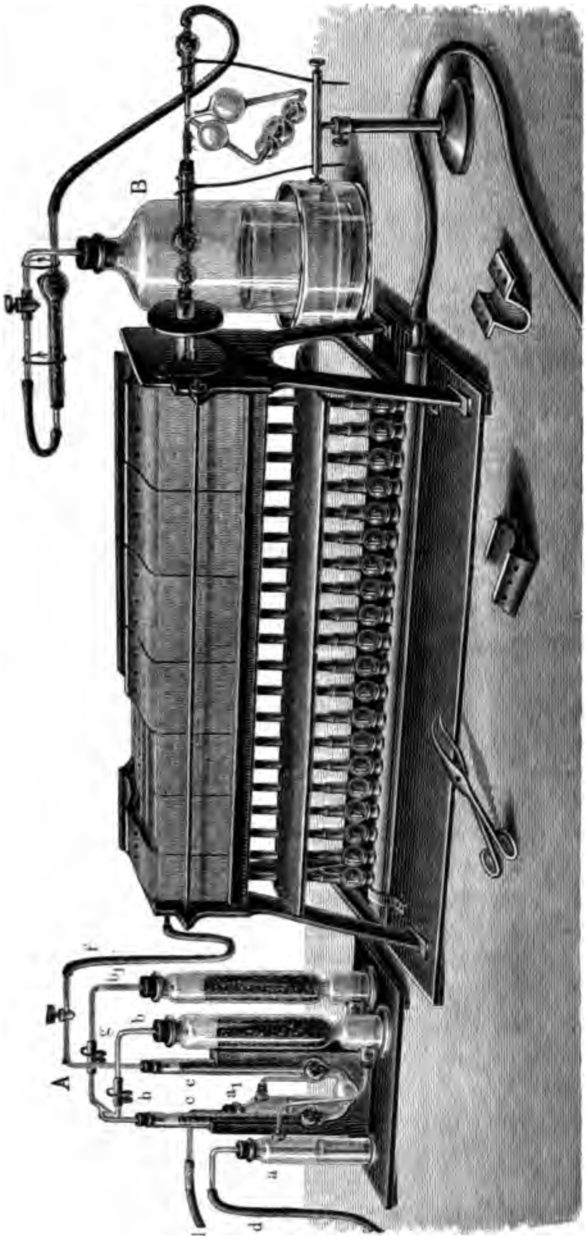

FIG. 19.

Another similarly unexplained occurrence in such combustions is that that the first analyses are almost always incorrect, and hence this method is to be recommended chiefly when a large number of analyses have to be made quickly one after the other. It is then advisable to make several combustions of some such substance as sugar, for the purpose of getting the tube into order, and as soon as a correct analysis is obtained the apparatus is known to be in the right condition. In view of the fact that the current of gas is constantly passing through the tube, this method requires much more continued attention than the combustion in closed tubes; and this is especially the case when easily volatile bodies, or bodies which evolve a large quantity of gaseous products, are burnt. On the other hand, the passage of a current of oxygen at the end of the operation is a guarantee of the complete combustion of the substance. For the above reasons combustions are carried out in some laboratories in a closed tube, and at the end of the operation a current of oxygen is passed over it, the end of the tube being drawn out in the form shown in Fig. 20. The tube is filled, as in Liebig's or Bunsen's method, with the oxide of copper substance, and the combustion carried on in the way already described. As soon as no further bubbles are seen to pass through the potash apparatus the burners at the end of the tube are turned down, and this end when cold joined to an oxygen gasometer by a caoutchouc tube. The closed end of the combustion-tube is then broken by squeezing with pliers, and the oxygen allowed to pass slowly through the tube until the whole of the air has been displaced.

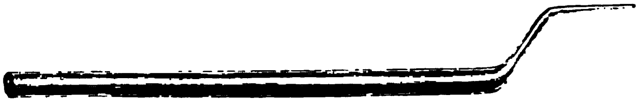

FIG. 20.

46 *Combustion of nitrogenous substances.* It has already been mentioned that in the combustion of nitrogenous bodies, oxides of nitrogen may be formed; these will be partly absorbed by the water and partly carried forward into the potash. It is to Gay-Lussac that we owe the suggestion of a method by means of which carbon and hydrogen contained in nitrogenous bodies can be accurately determined. As has been stated, he employed copper oxide as an oxidising agent, and in order to prevent the formation of oxides of nitrogen finding their way into the measuring apparatus he filled the front part of the tube with copper turnings. Gay-Lussac carried on his combustion as we do now, and in 1815 he succeeded in determining the composition of hydrocyanic acid, cyanogen gas, uric acid, &c. At a later date this method was perfected in the classical investigation by Gay-Lussac and Liebig on the fulminates.

If a nitrogenous substance has to be analysed, the tube is filled in the usual way, a layer, of from 15 to 20 centimetres in length, of metallic copper being placed in the front of the tube. For this purpose either copper turnings may be employed, or the metal obtained by reduction of the oxide in hydrogen. Sometimes a spiral of copper wire, or, more conveniently, a cylinder of rolled-up copper gauze is used. The metal must be heated to bright redness before the combustion of the substance is commenced, in order to insure the complete decomposition of any oxides of nitrogen which may pass over.

47 *Combustion of Bodies containing Sulphur.* Carbon compounds containing sulphur yield on combustion sulphur dioxide, and this would of course be absorbed by the caustic potash. In order to prevent this, Liebig and Wöhler[1] proposed to place a small tube containing dried lead dioxide or manganese dioxide between the chloride of calcium tube and the potash-bulbs. In passing over these oxides, the sulphur dioxide is oxidised, the sulphate of lead or of manganese being formed. Carius[2] proved, however, that when a substance which contains much sulphur is thus burnt, the oxides of sulphur are not wholly absorbed, and Bunsen has observed that the above peroxides may absorb some carbon dioxide. Hence it is advisable to burn bodies containing sulphur by means of lead chromate, a substance which was first used in organic analysis by Berzelius[3] in 1838 for the purpose of preventing the formation of carbon monoxide in the combustion. If care be taken not to heat the front part of the tube too strongly the whole of the sulphur dioxide remains, in this case, in the combustion-tube in the form of lead sulphate.

48 *Use of Lead Chromate in Combustions.* Lead chromate is also employed in several other cases instead of copper oxide.

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[1] *Ann. Pharm.* xxvi. 270.

[2] *Ann. Chem. Pharm.* cxvi. 28.

[3] *Pogg. Ann.* xliv. 391

For the purpose of preparing this compound a solution of lead acetate is mixed with one of potassium dichromate, the precipitate well washed, and the dried substance fused at as low a temperature as possible, and powdered after cooling. Lead chromate possesses an advantage over copper oxide in not being hygroscopic. It also fuses readily, and hence it is especially valuable for the analysis of bodies very rich in carbon, or of those from which carbon readily separates, and in these cases it is advisable to add to it a small quantity of potassium dichromate. It is also used for the combustion of organic salts of the alkalis and alkaline earths, as these when heated in an atmosphere of carbon dioxide leave a residue of carbonates.

When the same lead chromate has been frequently employed for combustion, and a large quantity of chromic oxide and metallic lead has been formed, it may readily be oxidised by moistening with nitric acid, drying and fusing.

If an organic substance containing an element of the chlorine group be burnt with copper oxide it may happen that a portion of the chlorine is set free and this may condense in the absorption-tubes. In order to avoid this, lead chromate is used, in which case the haloid salt of lead is formed. Such a combustion may however be carried on with copper oxide if a spiral of metallic copper be placed in the front of the tube, and if this be heated not too strongly. As the above cuprous compounds are however tolerably easily volatile, they are sometimes carried forward into the chloride of calcium tube.[1] Moreover these halogen elements may be given off from the cuprous salt when oxygen is passed over the substance. Hence it is better in such cases to employ a spiral of fine silver wire or silver foil instead of copper.[2]

When a compound containing mercury is to be burnt, a copper spiral is also placed in front of the tube and this must be only very gently heated, otherwise the deposited mercury may be volatilised and pass into the weighed tube.

49 *Organic Analysis by means of Platinum.* This metal in its finely-divided state is well known to possess the power of condensing oxygen in large quantity, and of giving it up again to combustible bodies. Upon this fact F. Kopfer[3] has founded a method of analysis capable of very general application, and

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[1] Stadeler. *Ann. Chem. Pharm.* lxix. 335.

[2] Kraut, *Zeitschr. anal. Chem.* ii. 242.

[3] *Journ. Chem. Soc.* xxix. 660.

characterised by its exactitude, especially in the determination of hydrogen, as well as by its simplicity and convenience. The combustion is carried on in a current of oxygen gas in a tube open, at both ends about 1·5 cm. in diameter, Fig. 21. At a_1, $a_{,2}$ and a_3 are placed plugs of asbestos wound round with fine platinum wire, of which the end ones sit loosely in the tube, whilst a_2 is fastened more firmly, and this, in order to prevent the passage being stopped by volatile bodies, has a prismatic form. The space between a_1 and a_2 is filled with an intimate mixture of about 10 grams of platinum-black[1] and the requisite quantity of freshly ignited and woolly asbestos. This mixture, which is easily obtained by simply shaking up the two materials in a bottle together, possesses a large amount of

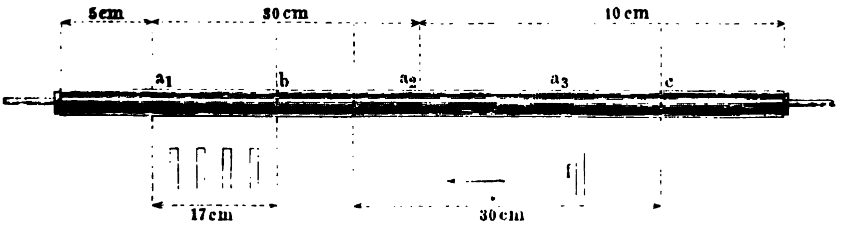

FIG. 21.

surface for the mass of the body, and therefore acts very quickly. Between a_2 and a_3 is placed the boat or tube containing the substance. The combustion-tube between a_1 and *b* is surrounded with a double cover of brass wire gauze, whilst that between *b* and *c* is placed in a trough of double wire gauze. Either air or oxygen may be employed for the purpose of carrying on the combustion. For purifying and drying the gas Kopfer used a very convenient apparatus. The gases pass first through a Liebig's potash-bulb containing a fifty per cent. solution of caustic potash, and from this so small a quantity of water evaporates that for the purpose of drying only short chloride of calcium tubes are employed, and these may be used for a length of time. The combustion furnace is composed of

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[1] In order to prepare this substance, a quantity of platinum chloride containing about 10 grams of metal is heated to boiling with 25 grams of pure caustic potash, dissolved in 400 cc. of water. This is then added to a boiling solution of 10 grams of grape sugar in 400 cc. of water and the whole boiled for a few minutes.

two moveable boxes of sheet iron of which the first carries four burners, and the last only one (*f*), moveable in a slot (Fig. 22). In order to carry out the combustion the tube is first filled with oxygen, and then the current so regulated that two bubbles pass through per second. At this point the four front burners are lighted, and the substance heated, beginning from *c* (Fig. 22). in the direction shown by the arrow, for the purpose of allowing the greater part of the volatile products to condense between a_2 and *b*, a small portion only, passing over the heated platinum and being completely burnt. The position of the burner *f* is then so placed that the combustion goes on regularly. When a quantity of carbon has separated out, or when difficultly volatile substances have sublimed between the parts *a* and *b*, a piece of wire gauze is placed over the tube, and this portion is heated to redness. When the combustion is complete, the oxygen is replaced by air, and a new analysis may then be begun as soon as the tube has cooled. In the case of very easily oxidisable substances a very vigorous combustion often takes place about a_2, the platinum-black being thereby heated to redness. In such a case the oxidation must be regulated by pushing the burner in the opposite direction to that shown by the arrow.

Should the substance contain the elements of the chlorine group, fifteen grams of thin silver foil cut into small four-sided pieces must be mixed with the platinum-asbestos. After the combustion it is then ignited in a current of hydrogen in which the tube is allowed to cool, and lastly it is heated in a rapid current of air when the apparatus is ready to be employed for a new analysis.

Compounds which contain nitrogen or sulphur are burnt by bringing into the front part of the tube a layer of lead dioxide[1] about 10 cm. long, and surrounded by an air-bath, the bottom of which consists of three pieces of brass wire gauze, and the top of which contains two such layers whereby the temperature is regulated. This is shown in Fig 23. It is then heated for an hour to a temperature of 150° to 200°, pure carbon dioxide passed through, and lastly this replaced by dry air. During the combustion the lead dioxide is kept at the same temperature, when the sulphur is entirely held back in the form of

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[1] This is best obtained by boiling pure red lead with nitric acid. The residue is first washed with hot dilute nitric acid, and then with hot water, and, after drying on a water-bath, is broken into small pieces.

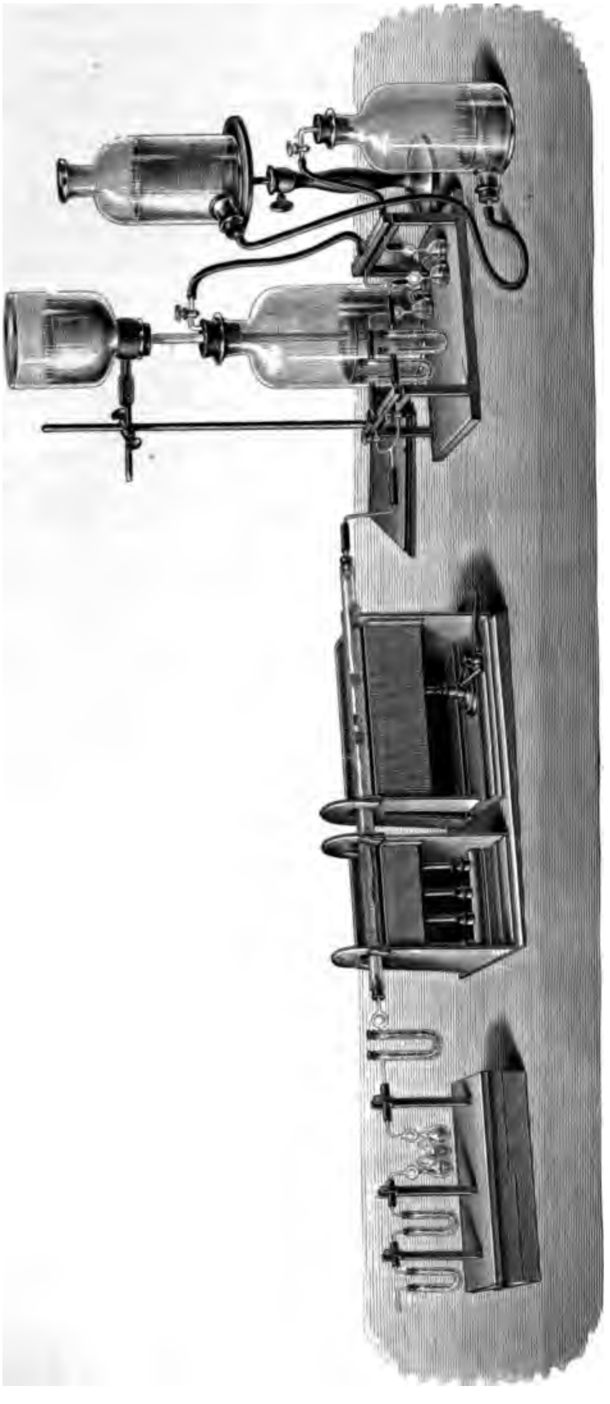

FIG. 21.

sulphate, and nitrogen in the form of nitrate. If, in addition to these, the substance contains the elements of the chlorine group, asbestos containing silver foil must likewise be employed.

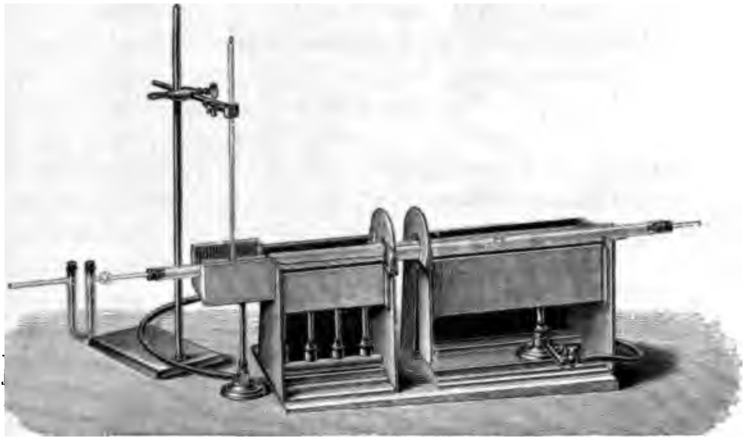

Fig. 23.

DETERMINATION OF NITROGEN.

50 *Detection of Nitrogen.* Many organic bodies containing nitrogen, when heated with an alkali, evolve either ammonia or a compound ammonia. The presence of these substances may be detected by their smell, by their alkaline reaction, and by their property of yielding a thick cloud when brought into contact with hydrochloric acid. The presence of nitrogen can thus be readily detected. If however the quantity of nitrogen be but small it may thus escape detection. Moreover a large number of carbon compounds exist of artificial origin, obtained by the action of nitric acid or of the oxides of nitrogen, and these do not, as a rule, yield ammonia when ignited with an alkali.

The smallest trace of nitrogen can however be detected in every case by a method proposed by Lassaigne.[1] For this purpose the body is heated in a small tube with metallic sodium. If the substance be explosive it must be mixed beforehand with

[1] *Compt. Rend.* 1843, 387.

dry carbonate of soda. In most cases a slight detonation takes place with separation of carbon. The mixture is then heated more strongly in order to volatilise the sodium, the mass allowed to cool, the residue dissolved in water and filtered. The filtrate which contains cyanide of sodium is then mixed with a solution of ferrous sulphate which has undergone partial oxidation in the air, and acidified with dilute sulphuric acid. If a large quantity of nitrogen be contained in the organic body, an immediate precipitate of Prussian blue is thrown down. If, however, only small traces of nitrogen be present, the acidified liquid becomes green, and after a time a blue flocculent precipitate is observed.

51 *Estimation of Nitrogen.* For the purpose of determining nitrogen quantitatively, two methods are employed. It may be obtained either in the form of ammonia or of a compound ammonia, or it may be liberated and the volume of nitrogen gas determined.

Will and Varrentrapp's Method. The first method, for which we are indebted to the above-named chemists,[1] is by far the simplest, and it is, therefore, employed in all those cases in which it is possible to do so. It depends on the fact already mentioned, first observed by Dumas, that nitrogenous bodies when heated with an alkali form ammonia, the carbon being oxidised and the nascent hydrogen uniting with the nitrogen.

$$C + 4KOH = CO_2 + 2K_2O + 4H.$$

If an excess of hydrogen be formed at the same time, it is either evolved as such or in the form of hydrocarbons. Wöhler and Liebig proposed to employ this for the determination of nitrogen, and the above-named pupils of Liebig worked out the process in the exact form in which it is now so much used. Soda-lime is employed as the alkali, as it does not attack the glass. This is obtained by slaking two parts of quicklime with a solution of one part of caustic soda and gently igniting the mixture. In the process of analysis, soda-lime is brought into a small combustion tube (*a*, Fig. 24), and the substance well mixed with it in the tube, which is then filled up to the end with pure soda-lime. The tube is then tapped so as to open a

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[1] *Ann. Chem. Pharm.* xxxix. 257.

channel at the top, and attached to the bulb-apparatus (*b*), containing dilute hydrochloric acid, so arranged that the liquid can neither be blown out by the rapid current of gas nor drawn back into the tube, if an absorption should take place. Another bulb-apparatus which perhaps secures this end more certainly has been proposed by Arendt and Knop, and shown in Fig. 25.

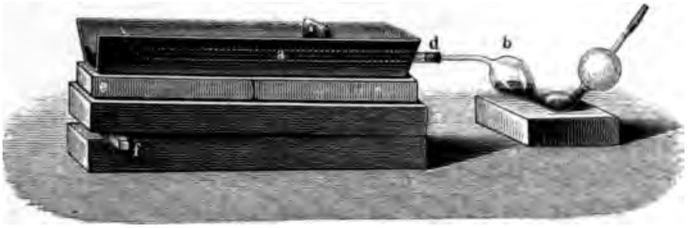

FIG. 24.

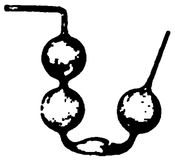

FIG. 25.

When the whole apparatus is arranged, the front layer of soda-lime is ignited, and the mixture of the substance with soda-lime is then gradually heated. At the end of the operation the point is broken, and air drawn through the apparatus either by means of the mouth or by an aspirator, in order to bring the whole of the ammonia into the hydrochloric acid. The residue left in the tube should be white, and to effect this, the tube requires to be pretty strongly heated so that any carbon containing nitrogen, or any cyanogen compounds, may be completely burnt.

Nitrogenous liquids are weighed out in bulb-tubes and treated in the same way as in the carbon and hydrogen determination. In place of soda-lime a mixture of equal parts of powdered quicklime and soda may, in many cases, be employed.[1] In case of bodies which contain large quantities of nitrogen, and which therefore evolve a large quantity of ammonia, it may happen that, in spite of all care, the acid passes back into the red-hot tube. This may be prevented simply by mixing the substance with some sugar in order that the ammonia may be diluted with hydrogen or some hydrocarbon. The hydrochloric acid is then evaporated on a water-bath with an excess of platinic chloride, and the residue thrown on to a filter and washed with

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[1] Johnson, *American Chemist*, iii 161.

ether to which only a few drops of alcohol have been added, because Hofmann has shown that the double platinum salts of the compound ammonias are frequently rather soluble in alcohol. The residue on the filter is then dried at 100° and weighed. It is then ignited and the weight of the residual platinum obtained. From this it is easy to calculate the quantity of nitrogen, because all these platinum double salts contain two atoms of nitrogen to one atom of the platinum. The comparison of the weight of the double salt with that of platinum is in many cases of importance, for by this means we ascertain whether ammonia or a compound ammonia has been formed.

52 *Liebig's Relative Method.* It has already been stated that Gay-Lussac was the first to employ copper oxide and metallic copper in the analysis of nitrogenous compounds. He collected the products of combustion over mercury, and determined the volume of the carbon dioxide and that of the free nitrogen by absorbing the first of these gases with alkali. Gay-Lussac and Liebig, in their investigation on fulminic acid, perfected this method, and the latter founded on this his method for the relative determination of nitrogen. For this purpose an unweighed quantity of the body, mixed with about fifty times its weight of oxide of copper, is brought into the combustion-tube, which is closed at the end and half filled with the mixture. In the next fourth part of the tube, pure oxide of copper is added, the last quarter being filled with metallic copper and the open end of the tube being furnished with a gas-delivery tube. The metallic copper is first heated to redness; next the further portion of the combustion-tube is heated, in order to expel the whole of the air contained in the tube by means of the gases evolved during the combustion; the ignition is slowly carried forward, and the gases are collected in small graduated tubes over mercury, as shown in Fig. 26. In order to ascertain the

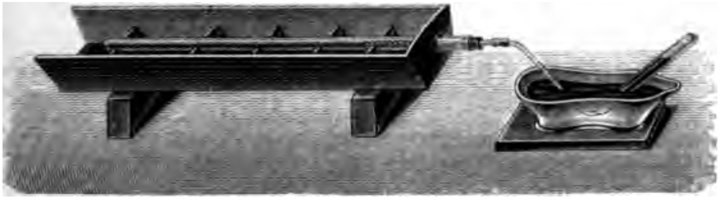

FIG. 26.

relation between the carbon dioxide and nitrogen in this gaseous mixture, the tubes are brought one after the other into a cylinder filled with mercury (Fig. 27), and fixed in such a position that the level of the mercury inside and outside the tube is the same. The volume of the gaseous mixture is then read off, a small quantity of caustic potash solution blown into the tube by means of the pipette (Fig. 28), and after this has been moved slowly up and down in the tube, the whole of the carbon dioxide is absorbed. As soon as this is effected, the level of the mercury inside and outside is again equalised, and the volume of the nitrogen read off, and thus the relation between it and the carbon dioxide ascertained. The first tube may contain a small quantity of air; the later ones, on the other hand, ought, if the experiment has been properly conducted, to yield identical results.

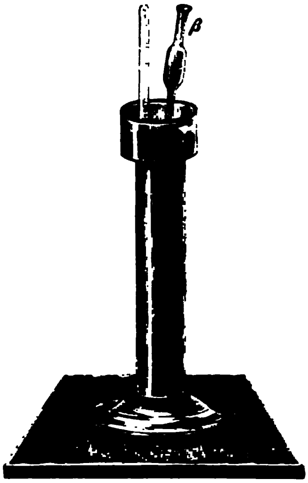

FIG. 27.

FIG. 28.

If the amount of carbon contained in the substance has been previously determined by combustion-analysis, it is easy to ascertain the absolute amount of nitrogen from the relative volumes of the carbon dioxide and nitrogen. This method of Liebig's for the relative determination of nitrogen is simply and easily carried out, but only yields, as he himself remarks, accurate results when the substance does not contain more than four atoms of carbon to one of nitrogen. Moreover, it possesses the disadvantage common to the other relative methods,[1] that the determination of the nitrogen is entirely dependent on that of the carbon.

53 *Bunsen's Relative Method.* Bunsen [2] has proposed another method of nitrogen determination especially valuable for the

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[1] Marchand, *Journ. Pr. Chem.* xli. 177: Gottlieb, *Ann. Chem. Pharm.* lxxviii. 241; Simpson, *ibid.* xcv. 63.

[2] *Handwörterbuch.* Suppl. 200.

analysis of such a substance as gun-cotton, in which the nitrogen can in fact not be determined by any other method. For this

Fig. 29.

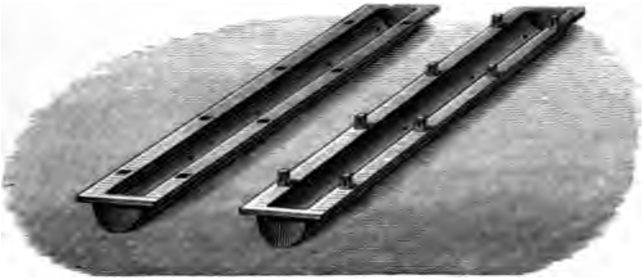

Fig. 30.

Fig. 31.

purpose about five grams of copper oxide and from 0·3 to 0·4 gram of the substance mixed with some metallic copper are placed in a combustion-tube closed at one end, about 50 centimetres in length, and having a diameter of about 3 centimetres. The other end of the tube is then drawn out to a fine but strong point, as shown in Fig. 32, which is carefully fused after the whole apparatus has been filled with dry hydrogen, and this gas has then been removed for the most part by means of an air-pump, the arrangement for this purpose being represented in Fig. 29. The tubes are then placed in an iron trough (Figs. 30 and 31), filled with a paste of plaster of Paris and water, and when after the lapse of about an hour this has set, the whole is heated to dull redness. After cooling, the drawn out end is broken under an eudiometer, and the gas determined by eudiometric methods.

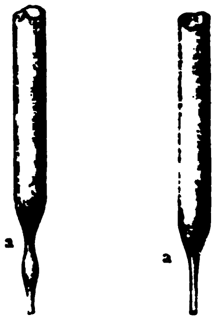

FIG. 32.

In order to carry out these operations successfully, a considerable amount of practice and great manual dexterity are needed; and hence, in those cases to which the easy method of Varrentrapp and Will is inapplicable, the process which is usually adopted is the method of the absolute determination of nitrogen, known as Dumas's method.

54 *Dumas' Absolute Method.* Into a combustion-tube, closed at one end, a compound is first brought which easily gives off carbon dioxide on heating. For this purpose either copper carbonate or white-lead may be employed. Then comes a short layer of copper oxide, then the mixture of the substance with copper oxide, and next a long layer of pure copper oxide, and lastly, in the front part of the tube, a spiral of metallic copper. By heating the further end of the tube the whole of the air is completely driven out, being replaced by carbon dioxide, and this operation may be hastened by adopting Bunsen's suggestion of placing the tube in connection with an air-pump. The combustion-tube is then fitted with a gas-delivery tube, in order to enable the products of combustion to pass into the graduated cylinder over mercury (Fig. 33). When the whole tube has been ignited, the gaseous products of combustion contained in the tube are driven forward by the evolution of carbon dioxide from the material placed at the end, the whole of this latter gas being absorbed by the caustic potash solution contained in the

receiver, so that the residual gas consists of pure nitrogen. In order to determine the volume of this latter, the measuring tube is withdrawn from the mercury by means of a small dish filled with mercury placed underneath, and brought into a high cylinder filled with water. The dish is then removed, and the cylinder allowed to remain in position until it has attained the temperature of the surrounding air. As soon as the level of the water has become constant, the height of the meniscus is read off, and from this the volume of gas determined.

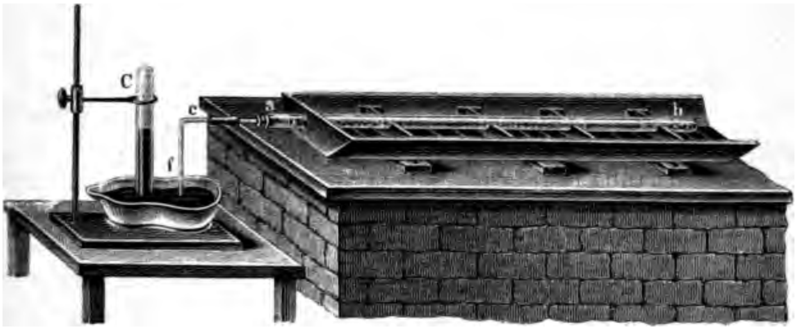

FIG 33.

A disadvantage attaches to this process, inasmuch as in the analysis of bodies rich in carbon it may easily happen that a separation of carbon takes place, which may still contain nitrogen, and if this be deposited on the upper portions of the combustion-tube or on the metallic copper, it cannot be completely burnt. In addition to this, some quantity of carbon monoxide may possibly be formed.

55 *Simpson's Method.*[1] This method is not open to the above objections, and yields accurate results. It is, in fact, a modification of Dumas' method, and is now frequently employed. For the purpose of evolving carbon dioxide, Maxwell Simpson recommends the use of carbonate of manganese, but in place of this it is more convenient to employ magnesite in lumps about the size of a pea. A layer of about 10 centimetres of this is placed at the end of the tube, then a mixture of mercuric oxide and copper oxide, this mixture being separated from the magnesite by a plug of asbestos. In other respects the tube is

[1] *Chem. Soc. Journ.* vi. 289.

filled as described under Dumas' method. The copper spiral should be about 20 centimetres in length, for the purpose not only of decomposing the whole of the oxides of nitrogen which are formed, but also to absorb any excess of oxygen which may come off. The portion of the tube containing the carbonate is first gently heated, and as soon as the evolution of gas becomes rapid, the front part of the tube containing the copper spiral is heated until all the air is driven out of the apparatus, which is readily ascertained by collecting the gases from time to time in a test-tube over mercury and adding a small quantity of caustic potash. As soon as the absorption is complete, the combustion may be proceeded with. The further end of the tube is allowed to cool, and the tube slowly heated from the front towards the back. The gases evolved are collected over mercury in a pear-shaped vessel (Fig. 34) containing caustic potash. As soon as the whole tube is red-hot, and no further evolution of gas is noticed, the gases contained in the tube are swept forward by re-heating the carbonate contained at the closed end. The nitrogen is next transferred to an accurately calibrated eudiometer, by a process which is rendered sufficiently evident by Fig. 35, and as soon as the caustic potash solution is seen to ascend into the capillary gas-delivery tube, no more mercury is poured in, and thus the exact volume of nitrogen evolved is brought into the eudiometer.

Zulkowsky[1] has recently described another simpler collecting apparatus, which avoids the use of mercury, and renders it possible to work rapidly. It consists of two tubes of about 58 centimetres in length (A and B, Fig. 36), of which the former is graduated, and serves for collecting and measuring the gas, whilst the latter is open at the bottom, and serves for filling in the caustic potash. Both tubes are held by means of supports (K_1 and K) in a vertical position, and are connected with one another by the caoutchouc tube. Two small tubes (c and c_1) are fused on to these tubes. The first of these is connected by means of a caoutchouc tube with the combustion-tube, and can be closed by the pinchcock *f*. The second small tube serves for letting out the caustic potash, and is also furnished with a pinchcock (*e*). The small bulbs *g* contain a few drops of mercury, and serve as a safety valve, in order to prevent the caustic potash solution from passing back into the combustion-tube in

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[1] *Liebig's Annalen*, clxxxii. 296.

case of a slow evolution of gas. When a nitrogen determination has to be made, the measuring tube is taken out of the clamp

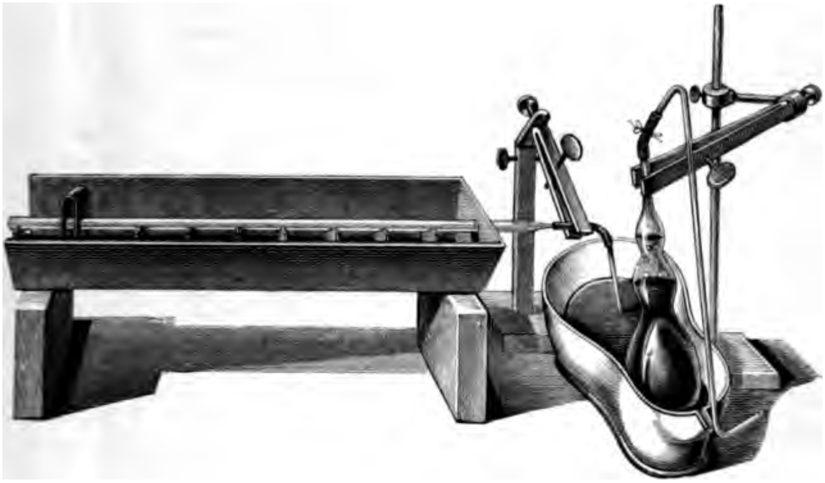

FIG. 34.

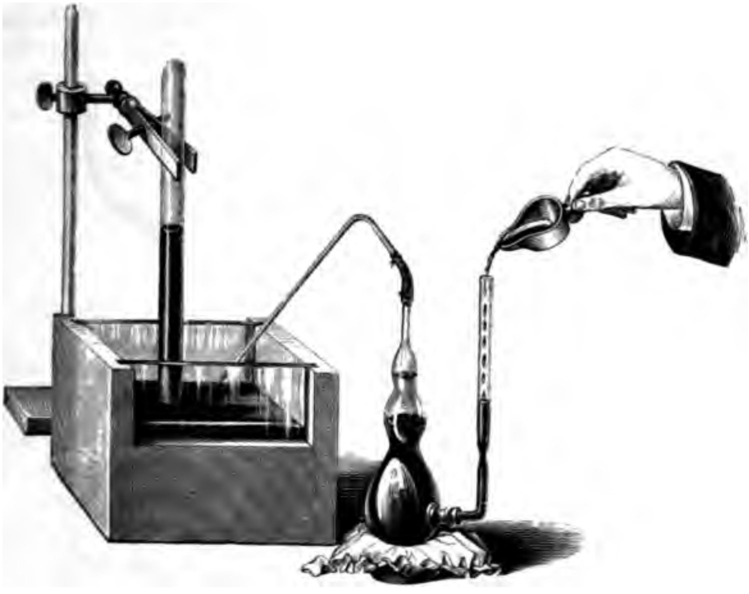

FIG. 35.

K, and brought into the position shown in the right-hand figure. Caustic potash is then poured in, and if the caoutchouc tube *h* be wide enough, this readily flows down so as to fill the whole of the tube. The apparatus is now connected with the combustion-tube, and the hinder portion of that tube heated so as to drive out the air. This is collected in the measuring tube,

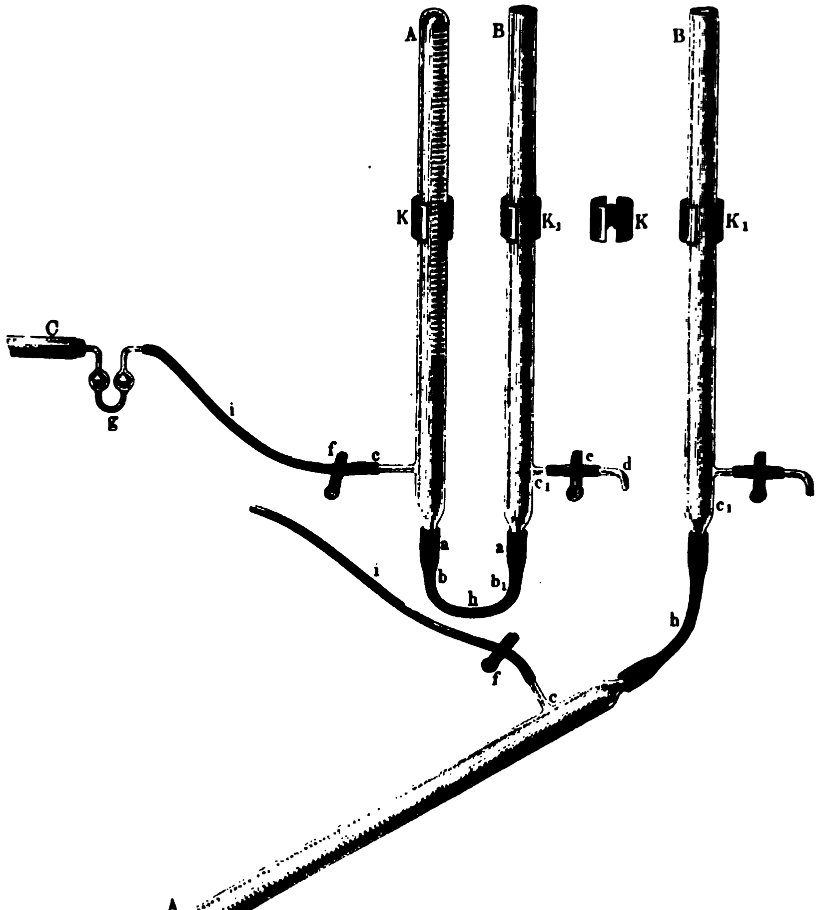

Fig. 36.

and is from time to time allowed to pass out by bringing it into the position shown at the right hand of the figure. As soon as the whole of the air has been driven out, the combustion is carried on in the usual way. The nitrogen is collected in the measuring tube, and the caustic potash is driven into the second tube, from which, in order to diminish the pressure, it is from time to time drawn off. When the combustion has been completed, the apparatus is disconnected from the combustion-tube, and brought into a situation where the temperature is tolerably constant, allowed to stand, the temperature of the caustic potash then determined, and the level of the liquids in the two tubes equalised by allowing the solution to flow out through the tube c_1. The volume of the gas, thus placed under the atmospheric pressure, is then read off.

In some rare cases the formation of nitric oxide cannot be altogether avoided in Dumas' process. It is then necessary to collect the gas over ferrous sulphate, and to allow for the volume of this gas thus absorbed.[1]

Several suggestions have been made for the purpose of determining nitrogen together with carbon and hydrogen in a single combustion. The method proposed for this purpose by Pflüger[2] can here be only shortly mentioned. He carries on the combustion in a vacuous space, and determines gravimetrically the quantity of water formed, whilst that of the carbon dioxide and nitrogen is ascertained by volumetric measurements.

DETERMINATION OF CHLORINE, BROMINE, AND IODINE.

56 These elements may be determined easily and rapidly by igniting the substance with pure quicklime. For this purpose, a narrow combustion-tube about 45 centimetres long is closed at one end, and into this some quicklime is brought, and then the substance either mixed beforehand with lime or weighed out in a small bulb, and this is dropped on to the lime. A channel is next made at the top by tapping the horizontal tube, and then the mixture, commencing at the open end, is heated. When the whole has been ignited and allowed to cool, the contents of the tube are brought into a flask containing water. Care must be taken that the material is not thrown out by the violent slaking of the lime. The whole is then

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[1] Frankland, *Ann. Chem. Pharm.* xcix. 350.

[2] Pflüger's *Arch. ges. Phys.* 1878, 117.

made slightly acid with dilute nitric acid, and the tube washed out first with water and then with dilute nitric acid. After filtering and washing the residue, the halogens are precipitated by silver nitrate in the slightly acidified solution.

It sometimes happens in the analysis of compounds containing iodine that this element separates out on the addition of nitric acid. In this case it is, therefore, better to dissolve out with water, to wash, and to add silver nitrate to the filtrate, and then to dissolve out the residue in acid, and add the filtrate to the first liquid.

The decomposition of very volatile bodies which contain chlorine or bromine may be readily effected according to Piria's plan, which has been somewhat improved by Hugo Schiff.[1] The substance is placed in a small platinum crucible with a mixture of 1 part of anhydrous sodium carbonate and from 4 to 5 parts of lime. It is then covered with a large crucible, and the two brought into such a position that the small crucible lies in the large one with its mouth downwards. The space between the two crucibles is then filled up with the alkaline mixture, the cover placed on the larger crucible, and the whole heated to redness. Substances containing iodine cannot however be analysed according to this method, as calcium iodate is formed, but the determination of iodine may be carried out if sodium carbonate alone be employed.

57 *Carius's Method.* In this method,[2] which is applicable to all cases in which the haloid element is easily removed, the substance is weighed out in thin glass bulbs. The form of bulb for solid bodies is seen in Fig. 37, whilst Fig. 38 exhibits that in which liquids are contained. These bulbs are then brought into a glass tube half filled with a solution of silver nitrate in nitric acid having a specific gravity of 1·2. The open end of the tube is then drawn out to a capillary point and the liquid boiled until all air has been expelled. After this the point is fused and allowed to cool (Fig. 39). The bulb is then broken by shaking the tube, and the whole heated gradually in an air-bath (Fig. 40), to a temperature varying, according to the nature of the substance, from 150° to 200°. In the case of bodies rich in carbon which undergo oxidation with difficulty, nitric acid of specific gravity 1·4 must be used, and a small quantity of

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[1] *Liebigs Ann.* cxcv. 293.

[2] *Ann. Chem. Pharm.* cxvi. 1 ; cxxxvi. 129.

potassium dichromate added. As soon as the whole of the organic substance has disappeared, the tube is allowed to cool, the capillary end is carefully softened in the gas-flame so that a very small opening appears, through which the carbon dioxide formed is allowed to escape, but so that the liquid is not thrown forward. The haloid salts of silver which are formed in this decomposition are then brought on to a filter, together with the remains of the glass bulb, and these are weighed together.

FIG. 37.

FIG. 38.

FIG. 39.

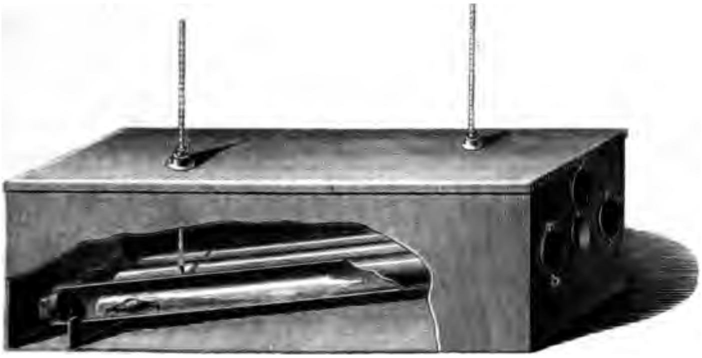

FIG. 40.

DETERMINATION OF SULPHUR.

58 For the purpose of determining sulphur in compounds which are not volatile, these are fused, according to Liebig's proposal,[1] with caustic potash and nitre in a silver basin, and the mass allowed to cool as soon as it has become white. It is then dissolved in water, acidified with nitric acid, precipitated with barium chloride, and the precipitate treated in the usual way.

Volatile sulphur compounds are oxidised by a method analogous to that described for chlorine compounds. They are placed in a combustion-tube with a mixture of sodium carbonate and nitre, or, according to Kolbe's[2] process, with potassium chlorate.

Debus's[3] method may also be employed, in which a mixture of carbonate of soda and potassium dichromate is used, or that proposed by Otto, in which pure cupric chromate is employed. In all these cases sulphates are obtained, and their amount determined in the usual way.

Another good method is that proposed by Russell.[4] In a combustion-tube closed at one end, from two to three grams of mercuric oxide are brought; then a mixture of the substance with mercuric oxide and sodium carbonate, and lastly only the latter substance. The combustion-tube is then furnished with a gas-delivery tube, in order to condense the vapours of mercury and of water, and the combustion is carried on as usual from back to front. After the ignition the contents of the tube are thrown into water, and the solution acidified with hydrochloric acid. In order to ascertain that no sodium sulphide has been formed, a drop or two of mercuric chloride is added. If no dark precipitate is formed, the solution is precipitated with sodium carbonate.

Lastly a method has been suggested by Carius depending on the fact that the substance can be oxidised in a closed tube with nitric acid, sulphuric acid being formed. Sometimes it is necessary to add a small quantity of potassium dichromate.

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[1] *Handwörterbuch*, i. 887.

[2] *Handwörterbuch*, Suppl. 205.

[3] *Ann. Chem. Pharm.* lxxvi. 90.

[4] *Quart. Journ. Chem. Soc.* vii. 212.

DETERMINATION OF PHOSPHORUS.

59 Organic substances containing phosphorus are ignited with sodium carbonate and nitre or potassium chlorate, in order to form a phosphate. They may also be oxidised with fuming nitric acid, when phosphoric acid is obtained. According to Carius a useful oxidising mixture is sulphuric acid and iodate of silver, the two being heated with the substance to 180°. After the liquid has cooled and is diluted with water, it is filtered, and some sulphurous acid added to the filtrate, in order to precipitate any dissolved silver iodate, and thus a solution of phosphoric acid is obtained, which (as in the other cases) is determined in the usual way.

DETERMINATION OF OTHER ELEMENTS.

60 In order to determine any of the other elements (with the exception of oxygen), it is usually necessary to ignite the organic substance either by itself or mixed with nitre, or else to destroy the substance completely by heating it with nitric acid. The element which it is then desired to determine is brought into solution in the usual way and determined by suitable methods.

In the case of salts of organic acids, the metal may generally be determined as in its organic compounds. In some instances, indeed, the method employed may be simpler. This is the case in the organic compounds of gold, platinum, and silver, which only require to be ignited in order to leave the metal in the pure state in a condition in which it may be weighed.

The salts of other metals leave on ignition a residue of oxide or carbonate, or sometimes of the metal mixed with carbon. These are then brought into solution and determined in the usual way.

DETERMINATION OF OXYGEN.

61 This element is very seldom determined directly, its amount being usually obtained after the percentage of all the other elements has been determined, for if these numbers do not add up to 100, the difference is usually taken to be the percentage of oxygen. It is however in this case absolutely necessary that we should know positively what other elements are present, and that the amount of each of these should be determined as accurately as possible, for if one be overlooked, the results of the analysis will, of course, lead to totally incorrect formulæ.

A classical example of this kind of error is that of the analysis of taurine, a crystalline compound occurring in the animal kingdom. The formula $C_2H_7NO_5$ was long adopted as expressing the composition of this substance, until Redtenbacher found that the body contained sulphur. The reason of the non-detection of the sulphur was, that both in constitution and in properties taurine differed from all the sulphur compounds then known. Moreover, the apparent truth of this formula could be upheld with some show of reason, inasmuch as the atomic weight of sulphur is double that of oxygen, and when the amount of the sulphur was ascertained, the formula of the substance was shown to be $C_2H_7NO_3S$. A method for the direct determination of oxygen is, therefore, much to be desired, not only for the purpose of avoiding errors of this kind, but also because such a determination would serve as a valuable control of the correctness of the analysis.

Unfortunately, none of the various methods which have been as yet proposed for this purpose have come into general use, and the reader is referred to the original papers in which these proposals are described.[1]

CALCULATION OF ANALYSES.

62 *Percentage Composition.* When a substance has been completely analysed, its percentage composition is calculated. The following examples illustrate the nature of this simple operation.

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[1] Wanklyn and Frank, *Phil. Mag.* [4] xxvi. 554; Baumhauer, *Zeitsch. anal. Chem.* 1866, 114; Ladenburg, *Ann. Chem. Pharm.* cxxxv. 1; Mitscherlich, *Ann.* cxxx. 536; Cretier, *Zeitsch. anal. Chem.* 1874, 1.

Example No. 1. 0·146 of a volatile liquid burnt with copper oxide yielded 0·449 of carbon dioxide and 0·2135 of water.

Now as 43·89 parts by weight of carbon dioxide contain 11·97 parts by weight of carbon, and as these numbers stand almost exactly in the proportion of 11 to 3, the quantity of carbon may be obtained by the fraction—

$$\frac{0{\cdot}449 \times 3 \times 100}{0{\cdot}146 \times 11} = 83{\cdot}87.$$

For the purpose of obtaining the percentage of hydrogen we have the following expression:

$$\frac{0{\cdot}2135 \times 100}{0{\cdot}146 \times 9} = 16{\cdot}25.$$

Hence the compound is a hydrocarbon having the composition—

Carbon	83·87
Hydrogen	16·25
	100·12.

Example No. 2. 0·2607 of aurin, a red colouring matter, yielded 0·7515 carbon dioxide: and 0·1152 water.

Hence 100 parts contain

Carbon	78·61
Hydrogen	4·91.

But, as these numbers do not add up to 100, and as the qualitative analysis has shown that it contains nothing but carbon, hydrogen, and oxygen, inasmuch as the substance, when heated, yields water on decomposition, it follows that the percentage composition is:

Carbon	78·61
Hydrogen	4·91
Oxygen	16·48
	100·00.

Example No. 3. (1) 0·3827 of caffeine yielded 0·6948 of carbon dioxide and 0·1800 water. (2) By Will and Varrentrapp's method, 0·1350 of caffeine yielded 0·2750 of platinum.

It has already been stated that one atom of platinum corresponds to two atoms of nitrogen, and hence the percentage of nitrogen is:

$$\frac{0{\cdot}2750 \times 28 \times 100}{0{\cdot}1350 \times 196{\cdot}7} = 28{\cdot}99.$$

If now the amount of carbon and hydrogen be calculated from the above analytical results, numbers are obtained which do not add up to 100, and as no other element can be detected, the difference between the amount thus found and 100 must be the quantity of oxygen caffeine contains. Hence the percentage composition of the substance is:

Carbon	49·51
Hydrogen	5·22
Nitrogen	28·99
Oxygen	16·28
	100·00.

In a determination of the nitrogen contained in caffeine according to Liebig's relative method, it was found that the gaseous mixture consisted of one volume of nitrogen to four volumes of carbon dioxide. Hence caffeine must contain one atom of nitrogen to every two atoms of carbon, and the percentage of nitrogen is found by the equation:

$$\frac{49{\cdot}51 \times 14}{24} = 28{\cdot}88.$$

If the amount of nitrogen be determined as gas, the volume of the dry gas is ascertained at 0° and 760° from the well-known formula:

$$V' = \frac{V(p - f)}{760\,(1 + 0{\cdot}003665 \times t)},$$

when f signifies the tension of the vapour of water. As we know that 1 cbc. of nitrogen under the above conditions weighs 0·00125 gram, it is easy to determine the weight of nitrogen contained in 100 parts of the compound.

CALCULATION OF FORMULÆ.

63 Having ascertained the percentage composition, the next point to determine is the formula of the compound. In the case of inorganic compounds the numerical relation in which

the various constituent atoms stand to one another can be readily ascertained. In the case, however, of the much more complicated compounds of the organic branch of the science, this cannot be so readily done. Thus, for instance, in the case of caffeine we have:

$$\frac{49{\cdot}51}{12} = 4{\cdot}13$$

$$\frac{5{\cdot}22}{1} = 5{\cdot}22$$

$$\frac{28{\cdot}99}{14} = 2{\cdot}07$$

$$\frac{16{\cdot}28}{16} = 1{\cdot}02.$$

These numbers stand in the relation of 4, 5, 2, 1. As, however, the sum of the monad atoms must be an even number, we are obliged to take as the simplest formula $C_8H_{10}N_4O_2$.

If, according to the same plan, we calculate the formula of the volatile hydrocarbon whose analysis has been given in Example No. 1, we find that this is a paraffin, but which of the paraffins it is remains doubtful, for, as the following calculated results show, this compound may be one of at least three; inasmuch as the composition of each of these bodies does not differ from that of the other, more widely than the results of several analyses of one and the same substance are often found to do.

	Hexane.	Heptane.	Octane.
Carbon . .	83·72	84·0	84·21
Hydrogen .	16·28	16·0	15·79
	100·00	100·00	100·00.

Again, in other cases, analysis gives no assistance whatever in the determination of the formula. Thus, for instance, a very large number of different formulæ may be found which will agree sufficiently well with the experimental results in the case of aurin (Example No. 2). Of these, we will here give only three:

	$C_{13}H_{10}O_2$.	$C_{19}H_{14}O_3$.	$C_{25}H_{18}O_4$.
Carbon . .	78·79	78·62	78·53
Hydrogen .	5·05	4·83	4·71
Oxygen . .	16·16	16·55	16·76
	100·00	100·00	100·00.

Molecular Formulæ. It is, however, not necessary merely to determine the simplest formula of a compound, but, if possible, its molecular formula, and this can readily be accomplished if we can determine its molecular weight.

The only perfectly reliable method for this purpose, in cases in which the body can be volatilised without decomposition, is to ascertain its vapour density. Hence we now proceed to describe the various methods which have been employed for this purpose.

DETERMINATION OF VAPOUR DENSITY.

64 By the density or specific gravity of a gas or vapour is meant the weight of a given volume compared with the same volume of air taken as the unit.

Two methods for determining vapour density were, until recently, in common use, and although they are neither of them now employed in organic chemistry, their description is still of interest from an historical point of view.

The principle of the first method, which we owe to Gay-Lussac,[1] consists in determining the volume of a given weight of vapour; whilst that of the second method, proposed by Dumas,[2] consists in the determination of the weight of a given volume of vapour, and this process is still employed for determining the vapour density of difficultly volatile liquids. Although the first is the older of the two methods, the second or Dumas' method is the simpler, and it, therefore, will be first described.

Dumas' Method. A thin glass bulb or globe of from 200 to 300 cbc. capacity, having its neck drawn out and bent as shown in Fig. 41, and filled with dry air, is carefully weighed, the temperature of the balance-case being ascertained. A quantity of the liquid under examination, varying according to the capacity of the globe, is then introduced, such a quantity being however always taken that the vapour evolved is sufficient in quantity to expel the whole of the air. The bulb containing the liquid is then heated in an iron vessel which is filled, according to the volatility of the substance, either with water, oil, or paraffin (Fig. 42), the temperature being raised to a point

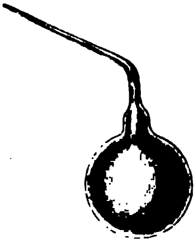

FIG. 41.

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[1] Biot, *Traité de Phys.* i. 291.

[2] *Ann. Chim. Phys.* (1827) xxxiv. 326.

at least from 30° to 50° above the boiling-point of the liquid, the reason for this precaution being that vapours obey the laws of gaseous expansion and pressure more exactly at temperatures considerably removed from their boiling-points than at lower temperatures.

When no further vapour issues from the drawn-out point, as may be seen by holding a flame in front of the opening, the capillary tube is sealed as close as possible to the surface of the liquid. At the same time the temperature of the bath is read off by means of a thermometer placed in the heated liquid at a height corresponding to the centre of the globe. The globe is next removed, carefully cleaned, and again weighed when cold, together with the drawn-off point. It is then only necessary to determine the volume of the globe. For this purpose the sealed end is broken under mercury, and, if the experiment has been successfully carried out, the whole of the bulb will be filled by the mercury with the exception of the small volume occupied by the condensed liquid, and this volume is usually so small that it may be disregarded. If, however, it is desired to determine this amount, the condensed liquid is allowed to pass into the narrow neck of the bulb, and this then replaced by mercury. In

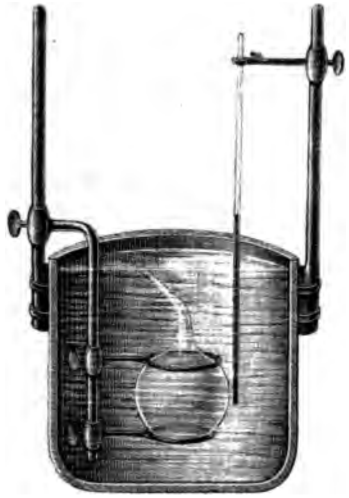

FIG. 42.

case the whole of the air has not been completely removed by the vapour, a bubble of air remains, and its volume may be ascertained by passing it into a graduated tube over mercury. To determine the volume of the mercury contained in the globe, it is poured into a carefully graduated cylinder or else weighed. This weight in grams divided by 13·59 gives the volume of the mercury in cubic centimeters. The calculation is simple, especially if no residual air occurs, and this may be readily avoided by taking enough substance. The following are the experimental data:

Weight of the globe with air at t° $= g$.
„ „ vapour at $T^\circ = G$.
Capacity of globe . . . . $= C$.

The weight of the vacuous globe is found from the following formula, inasmuch as 1 cbc. of air at 0° and 760° weighs 0·001293 grm. The height of the barometer may, in this case, be neglected, as the variation is very slight during the progress of the experiment. The weight of the air contained in the globe is:

$$\frac{C \times 0{\cdot}001293}{1 + 0{\cdot}003665 \times t} = x.$$

The vacuous globe will, therefore, weigh $g - x$, and that of the vapour $G - (g - x) = y$. We have now to find what an equal volume of air at the same temperature weighs. We have thus the equation:

$$\frac{C \times 0{\cdot}001293}{1 + 0{\cdot}003665 \times T} = z.$$

The vapour density (D) is therefore:

$$D = \frac{y}{z}.$$

The calculation is considerably simplified if we make use of a table showing the weight of 1 cbc. of air at different temperatures. The following table is sufficiently accurate for ordinary use. This table may be also employed in the calculation of vapour density according to other methods. It gives the value for every 10°; the intermediate values can easily be obtained by interpolation.

$t°$.	n.	$t°$.	n.
0	0·001293	170	0·000796
10	0·001243	180	0·000779
20	0·001205	190	0·000762
30	0·001165	200	0·000746
40	0·001128	210	0·000730
50	0·001093	220	0·000715
60	0·001060	230	0·000701
70	0·001029	240	0·000688
80	0·001000	250	0·000674
90	0·000972	260	0·000662
100	0·000946	270	0·000650
110	0·000921	280	0·000638
120	0·000898	290	0·000626
130	0·000876	300	0·000616
140	0·000854	310	0·000605
150	0·000834	320	0·000595
160	0·000815		

The following formula may be used with this table:

$$D = \frac{G - g + Cnt}{CnT}.$$

The following example serves to show the limits of error accompanying the determination of vapour density by this method.

Example of Dumas' Method. A volatile hydrocarbon (hexane, C_6H_{14}) of the paraffin series, of which the analysis has been given, yielded the following results:

$g = 23{\cdot}449$
$t° = 15°{\cdot}5$
$G = 23{\cdot}720$
$T° = 110°$
$C = 178$ cbc.

The density calculated from these numbers is 2·986, whilst that required by the formula is 2·979.

65 *Gay-Lussac's Method.* In this process the graduated and calibrated glass tube C (Fig. 43) is employed, filled with mercury, and placed in an iron vessel containing this metal. The substance is contained in a very thin bulb or small stoppered tube of known weight (Fig. 44); this is then filled with the liquid, again weighed, and then passed up to the top of the divided tube. Surrounding this is a wide glass cylinder open at both ends and filled with water. The iron vessel is now heated by gas or charcoal. The expansion due to the heat either causes the bulb to burst or drives the stopper out of the tube, and the liquid is soon thus completely converted into vapour. To effect an equal distribution of temperature the water is continually stirred. As soon as the temperature at which the determination has to be made is reached, the volume of the vapour, the temperature of the water, and the height of the barometer are read off; whilst, at the same time, the temperature of the air and the difference between the height of the mercury inside and outside the tube are ascertained.

FIG. 43.

FIG. 44.

Example of Gay-Lussac's Method. A determination of the vapour density of pentane, C_5H_{12}, made by this method, gave the following results:

Weight of pentane	0·101
Temperature of air	16°
Temperature of vapour . . .	91°
Volume of vapour	59·5 cbc.
Height of barometer	752 mm.
Difference of level	220 mm.

The pressure inside the tube was consequently equal to that of a column of mercury of 752° mm. at 16° minus that of a column of 220° mm. at 91°. In order to be able to substract one from the other, these values must first be reduced to the same temperature. As the co-efficient of expansion of mercury for 1° is 0·00018, the heights at 0° will be:

$$\frac{752}{1+(0{\cdot}00018 \times 16)} = 749{\cdot}9$$

$$\frac{220}{1+(0{\cdot}00018 \times 91)} = 216{\cdot}4.$$

The pressure inside the graduated tube was therefore:

$$749{\cdot}9 - 216{\cdot}4 = 533{\cdot}5.$$

59·5 cbc. of pentane weigh, at 91° and under a pressure of 533·5 mm. of mercury, 0·101 gram. Under the same conditions an equal volume of air weighs:

$$\frac{0{\cdot}001293 \times 59{\cdot}5 \times 533{\cdot}5}{760 \times 1+(0{\cdot}003665 \times 91)} = 0{\cdot}0405.$$

Hence the vapour density of pentane is:

$$\frac{0{\cdot}101}{0{\cdot}0405} = 2{\cdot}493,$$

and this agrees well with the theoretical value 2·494.

Gay-Lussac's method possesses the great advantages of requiring very small quantities of the substance, and of enabling several determinations to be made at any temperature under 100°. On the other hand, it is not well adapted to the case of substances possessing high boiling-points, inasmuch as the cylinder must then be filled with oil or paraffin, and a constant temperature of the column cannot in this case be easily attained. Poisonous mercurial vapours are also given off during the process, and this renders the method dangerous in the case of bodies requiring high temperatures. In order to overcome this objection, Natanson has constructed an air-bath in which only the upper part of the tube is heated, but this modification has not come into general use.

66 *Hofmann's Method.* Hofmann[1] conceived the happy idea of employing a wide barometer-tube in place of the short tube used by Gay-Lussac, and of heating this by the vapour of a

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[1] *Ber. Deutsch. Chem. Ges.* i. 198.

liquid boiling at a constant temperature. The apparatus is shown in Fig. 45. The graduated barometer-tube (*a*), more than 1 meter in length, is filled with dry mercury and placed in a mercurial trough. Outside this a wide glass tube (*b*) is placed, closed at its upper end by a well-fitting cork, through which the tube *d* passes for the entrance of the heated vapour. The condensed liquid and the excess of vapour pass away through the tube *c* into the condenser (*g*). A very small stoppered bottle whose weight is known, having a capacity of from 0·05 to 0·1 cbc. (Fig. 46), is filled with a known weight of the substance. The bottle thus filled is passed up to the top of the

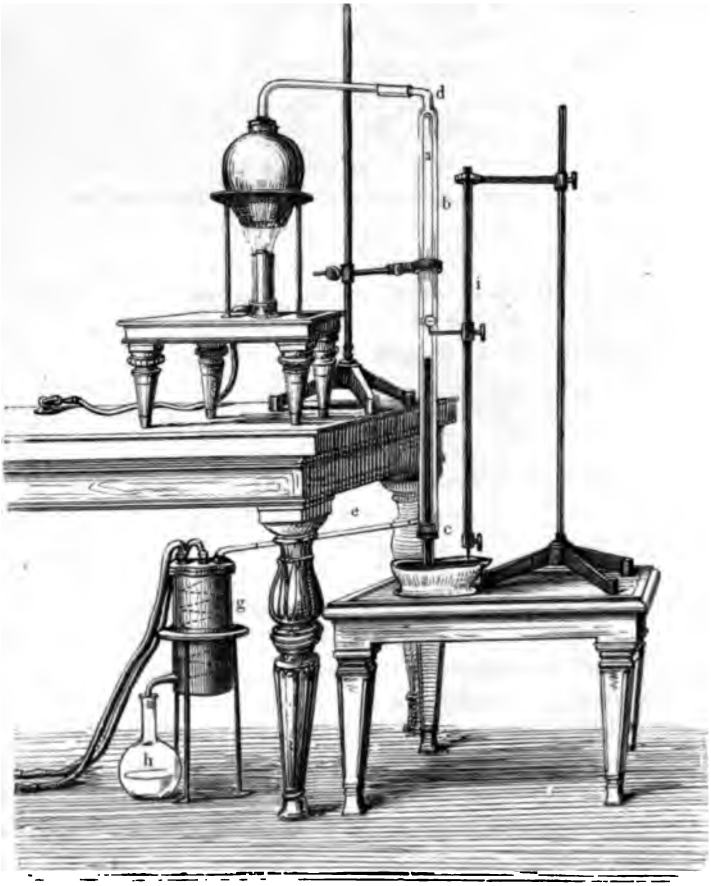

FIG. 45.

mercury in the barometer, and in the case of the more volatile liquids this usually displaces the stopper at once, and in other cases it is easily driven out when the substance becomes heated. The copper vessel (*f*) serves to contain the liquid of constant boiling-point, and by this means the barometer-tube is easily brought up to a constant temperature. As soon as the meniscus of the mercury is seen to remain unchanged, the volume of the vapour and the height of the mercurial volume are read off by means of a pendulum cathetometer (*i*). In many cases water may be employed as the heating liquid, inasmuch as the vaporisation of the substance takes place under diminished pressure, and bodies which boil up to 180° can be completely volatilised at 100°.[1]

FIG. 46.

For the purpose of determining the vapour density at higher temperatures, Hofmann makes use of the following substances:

	Boiling-point.
Aniline	181°·5
Toluidine	202
Ethyl benzoate	212
Amyl benzoate	261.

Of course other bodies may be employed provided their boiling-points do not lie too near that of mercury.

The calculation is carried out in a similar way as in Gay-Lussac's method, but inasmuch as the lower portion of the mercurial column is not surrounded by vapour, two calculations are necessary in order to reduce the height of this column to 0°. In addition to this, the tension of the vapour of mercury must also be taken into account when high temperatures are necessary. For this purpose the well-known table of Regnault[2] is employed, the following extract from which is sufficient for most purposes:

Temperature.	Tension of Vapour.	Temperature.	Tension of Vapour.
160°	5·9 mm.	220°	34·70 mm.
170	8·09	230	45·35
180	11·00	240	58·82
190	14·84	250	75·75
200	19·90	260	96·73
210	26·35	270	123·01

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[1] Schröder, *Ber. Deutsch. Chem. Ges.* iv. 472.

[2] *Phil. Mag.* [4] xx. 227.

67 Another great improvement suggested by Hofmann[1] is that of using a plain tube instead of a graduated and calibrated one. Not only are these plain tubes cheaper than the calibrated ones, but they are also much less liable to fracture, inasmuch as all glass tubes in which divisions have been etched are liable to crack when exposed to rapid changes of temperature. For this purpose, a tube as cylindrical as possible is chosen, and when the mercurial column has become stationary, the pendulum cathetometer is placed in position. The apparatus is then allowed to cool, and, after removing the outer glass tube, a slip of paper is placed at the point where the meniscus stood. After the volume of the vapour has been thus determined, the tube is dismounted and filled with mercury up to the mark, and then the mercury weighed on a pair of common scales capable of turning with half a grain. From the weight of the mercury the volume of gas in cubic centimeters is obtained.

In the apparatus above described, two calculations, as we have seen, are necessary in order to obtain the height of the mercury at 0°. This, however, does not give a strictly correct result, inasmuch as the column of mercury which is not surrounded by vapour does not possess the same temperature throughout its length. The temperature of that portion near the cork is necessarily higher than that of the air. In cases where the temperature is not high this difference is of little moment, but at a high temperature it may become of consequence. In order to avoid this error, Wichelhaus[2] has proposed to substitute Hofmann's barometer-tube by a syphon barometer. The apparatus, however, thus becomes much more complicated and liable to fracture; moreover, the height of the outside tube requires to be greater, and this necessitates the employment of a larger quantity of vapour in order to obtain a constant temperature. Another disadvantage involved in the employment of a syphon barometer is that only one experiment can be made with the same material, for when the tube cools, air enters into the vacuous space. By the use of a straight tube, on the other hand, the volume of the vapour may not only be redetermined at the same temperature, but its volume at different temperatures may be ascertained.

Hofmann has, therefore, improved his apparatus by allowing the outer tube to dip into the reservoir of mercury at the bottom, a small tube being sealed on at a distance of from 2 to 3 mm.

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[1] *Ber. Deutsch. Chem. Ges.* ix. 1304.

[2] *Ber. Deutsch. Chem. Ges.* iii. 166.

from the surface of the mercury, by means of which the excess of vapour and products of condensation can be withdrawn.

Lastly he obtained the same result in a still simpler manner. The barometer-tube stands upon a thick plate of caoutchouc lying at the bottom of the mercurial trough, and this plate is fastened to an iron disc furnished with a handle which is bent so as to come out of the mercury. In one side of this plate a groove is cut by means of which the mercury in the tube is brought in contact with that in the trough. When the vapour passes through the outer tube, which only needs to be 40 cm. longer than the barometrical column, the mercury which it contains flows out into the trough, and as soon as the volume of the vapour has become constant, the caoutchouc plate is pushed back so that the mouth of the tube is closed, and thus the mercury in the tube is separated completely from that in the trough. This is done by means of the handle, so that the level of the mercury remains unaltered. As soon as the cathetometer has been placed in position, the whole is allowed to cool, and the height of the mercury is determined at the temperature of the air, the calculation being then carried out as already described.

Further modifications of the apparatus have been made by J. W. Brühl[1] and C. Engler.[2]

As the substances employed for the preparation of vapour at higher temperatures than the boiling-point of aniline are costly, it became advisable to use as small a quantity of these as possible. This is arranged for by Hofmann,[3] inasmuch as the condensed liquid is allowed to run back again into the boiler. By means of such an arrangement a constant temperature can be attained in from twenty to twenty-five minutes and maintained for several hours, with a volume of from 100 to 150 cbc. of liquid.

As an example of the calculation in Hofmann's method we may take the vapour density determination of ethyl-propinyl ether, C_5H_8O :

Weight of substance, 0·0518 = S.
Volume of the vapour, 52·5 cbc. = v.
Temperature of the vapour, 100° = T.
Temperature of the air, 15° = t.
Height of barometer, 752°·5 mm. = H.
Height of mercurial column, 484 mm. = h.
Reduced pressure, 275 mm. = h'.

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[1] *Ber. Deutsch. Chem. Ges.* ix. 1368 ; xii. 197.

[2] *Ibid.* ix. 1419.

[3] *Ber. Deutsch. Chem. Ges.* 1876, ii. 1304. *Chem. Soc. Journ.* 1877, i. 33.

Hence the vapour density is obtained by the following formula:

$$\frac{S \times 760 \times (273+T)}{0{\cdot}001293 \times 273 \times v \times d} = D.$$

Found.	Calculated.
2·895	2·909.

Hofmann's method soon almost entirely superseded the two older methods, Dumas' being employed only for the determination of the vapour density of substances which have a high boiling-point, and for this purpose improvements were made in the method by Troost and Deville,[1] as well as by Bunsen.[2] Dumas' method is also subject to the serious disadvantage, that the greater portion of the material employed, frequently more than 3 grams, is lost during the operation, and this, in the case of expensive preparations, is a matter of serious inconvenience. In order to overcome this difficulty, various suggestions have been made, by means of which the escaping vapours could be caught and condensed, but this leads to complications which destroy the simplicity of the method.

Habermann[3] has lately made another suggestion. He connects the fine neck of the globe with a Bunsen filter-pump in order to produce a vacuum, whereby the substance, as in Hofmann's method, boils at a lower temperature. By this method not less than 1 gram of the substance must be employed, and this can readily be condensed in a bulb-tube placed between the globe and the pump. By this means, however, Habermann has only been able to determine the vapour density of such substances as boil below 250°.

68 *Victor Meyer's Methods. Method No.* 1. Victor Meyer[4] has recently worked out a plan by means of which, without employing a greater quantity of the substance than that used in Gay-Lussac's or Hofmann's process, the vapour density of high boiling bodies may be determined at a temperature of 448°, the boiling-point of sulphur. He employs Wood's fusible metal as the liquid over which to collect the gas, and makes use of the bulb-tube shown in Fig. 47. In carrying out the experiment, about 50 mgrm. of the substance are allowed to

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[1] *Ann. Chim. Phys.* [3] lviii. 257.

[2] *Ann. Chem. Pharm.* cxli. 273.

[3] *Liebigs Annalen*, clxxxvii. 341.

[4] *Ber. Deutsch. Chem. Ges.* 1876, ii. 1216.

vaporise in a vessel completely filled with the liquid alloy, the volume of vapour being ascertained from the weight of the metal which flows out.[1] A substance which is solid at the ordinary temperature is weighed out in a short glass tube sealed up at one end, Fig. 48 (*a*), whilst liquids are enclosed in small stoppered bottles, which differ from those used by Hofmann by being slightly curved in order that they may more readily pass up into the bulb-tube, Fig. 48 (*b*). The whole apparatus is then heated to 100°, and afterwards placed on a large balance and weighed to within a decigram.

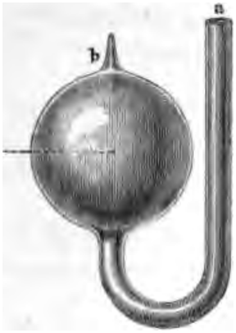

FIG. 47.

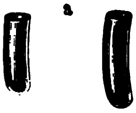

FIG. 48 (*a*).

FIG. 48 (*b*).

The apparatus must then be heated in the vapour of sulphur. This is accomplished in a cast-iron crucible of 400 cbc. capacity, which is loosely covered (Fig. 49). The crucible contains from 120 to 130 grams of sulphur, and is heated by means of a powerful burner. After about twenty minutes, when the sulphur is boiling rapidly and the current of vapour passes out between the cover and the crucible, the boiling is allowed to go on for about four minutes, the burner then turned out and the bulb-tube lifted out of the crucible. The vapour contained in the bulb at the moment the bulb is withdrawn from the crucible is under the pressure of the atmosphere plus that of the short column of fusible metal in the bent tube. The height of the column has therefore to be ascertained. For this purpose a finely drawn-out glass tube, having a drop of sealing wax at the

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[1] Similar methods for lower temperatures, by making use of mercury, had been formerly suggested: Hofmann, *Ann. Chem. Pharm.* Suppl. i. 10; Wertheim, *ibid.* cxxiii. 173; cxxvii. 81; cxxx. 269; W. Marshall Watts, *Laboratory*, i. 225.

end, is brought on to the glass at the height of the meniscus in the inner tube. This leaves a mark by means of which the height can be ascertained. For the special precautions which the author recommends, the original paper must be referred to.

FIG. 49.

The following formula serves for the calculation:[1]

$$D = \frac{S \times 760(1 + 0{\cdot}003665 \times 444{\cdot}2)}{0{\cdot}001293\,[P + \frac{2}{3}p]\left[\left(\frac{a}{9{\cdot}608} + \frac{q}{13{\cdot}6}\right)(1 + 346{\cdot}2 \times 0{\cdot}0000303) - \frac{r}{9{\cdot}158}\right]}.$$

By collecting the constants, we obtain the equation:

$$D = \frac{S \times 1543500}{[P + \frac{2}{3}p]\left[\left(\frac{a}{9{\cdot}608} + q \times 0{\cdot}07\right)1{\cdot}01 - \frac{r}{9{\cdot}158}\right]}.$$

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[1] *Ber. Deutsch. Chem. Ges.* x. 2070.

In these formulæ:

S = Weight of the substance.
P = Height of barometer reduced to 0°.
p = Pressure of column of metal, which is two-thirds that of mercury.
a = Weight of alloy employed.
9·608 = Specific gravity of alloy at 100°.
9·158 = Ditto at 448°.
q = Weight of mercury contained in small bottle.
r = Weight of the remaining alloy.

As the tube containing the substance is very small, q may be neglected.

The vapour density of methyl-anthracene, a body boiling at a higher point than mercury, was thus ascertained:

S = 0·0360.
a = 283·33.
r = 168·9
P = 722·5 mm.
p = 34·0 mm.

	Found.	Calculated.
Vapour density . .	6·57	6·63.

FIG. 50.

69 *Method No.* 2. In order to determine the vapour density of bodies boiling below a temperature of 350°, V. Meyer[1] has proposed a method by means of which the molecular weight may be determined with great simplicity and ease. The vessel in which the substance is placed is filled with mercury, as shown in Fig. 50. It is made of thin glass, and has a capacity of 35 cbc. This is filled according to the method already described, but at the ordinary temperature, at which it is weighed. It is then hung by a thin wire in the boiling flask (Fig. 51), the neck of which being long does not require any condensing arrangement, and it is then heated to the boiling-point of water, aniline, or any other higher boiling liquid. When no more mercury is seen to flow out, the apparatus is removed and

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[1] *Ber. Deutsch. Chem. Ges.* 1877, ii. 2068.

after cooling weighed again. In order to determine the excess of pressure in the side-tube, the capillary tube is opened, and the whole is filled with mercury, and the point marked on the wider tube.

Fig. 51.

In the calculation the following data are required:

S = Weight of substance.
T = Temperature of vapour.
t = „ „ air.
P = Barometric pressure reduced to 0°.
p = Excess of pressure in the side-tube.
s = Tension of mercury vapour.
a = Weight of mercury employed.
r = Weight of remaining mercury.
q = Weight of mercury contained in the small bottle.

The last number is required only in very exact determinations. The calculation is effected by the following formula:

$$D = \frac{S \times 760\,(1 + 0{\cdot}003665\,T)\,13{\cdot}59}{(P + p - s,\ 0{\cdot}001293\,(a+q)\,\{1 + 0{\cdot}0000303\,[T - t]) - r)\,(1 + 0{\cdot}00018\,[T - t])\,(1 \times 0{\cdot}00018)}.$$

13·59 is the specific gravity of mercury at 0°.
0·0000303 is the coefficient of expansion of glass.
0·00018 ditto of mercury, which above 240° rises to 0·00019.

The constants in the above formula are:

$$\frac{760 \times 13{\cdot}59}{0{\cdot}001293} = 7988000.$$

The temperature of the vapour does not need to be determined, as the boiling-point of the liquid employed is known. In the case, however, of bodies whose boiling-points approach that of mercury, it is necessary to determine the temperature, as, according to the recent experiments of Naumann, it appears that the boiling-points of liquids which are not miscible undergo considerable depression. Thus he finds that diphenylamine, which boils at a temperature of 310° by itself, boils at 290° when mixed with mercury.

The vapour density of benzoic acid was in this way determined in the vapour of diphenylamine with the following results:

S = 0·0603.
a = 471·7 grams.
r = 66·4 grams.
q = 1 gram.
P = 726 mm.
p = 21 mm.
T = 290°.
t = 15°·2.
s = 165·7 mm.

	Found.	Calculated.
Vapour density	4·20	4·22.

70 *Method No. 3.* Victor and Carl Meyer[1] have recently described an easy method for determining the vapour density of bodies of low, as well as those possessing a very high, boiling-point.

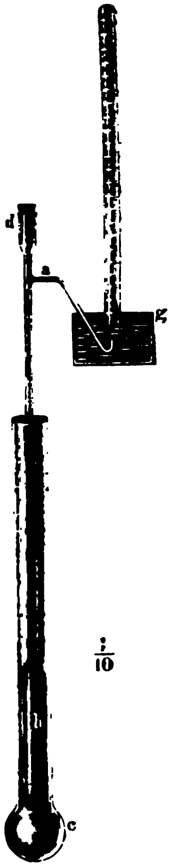

FIG. 52.

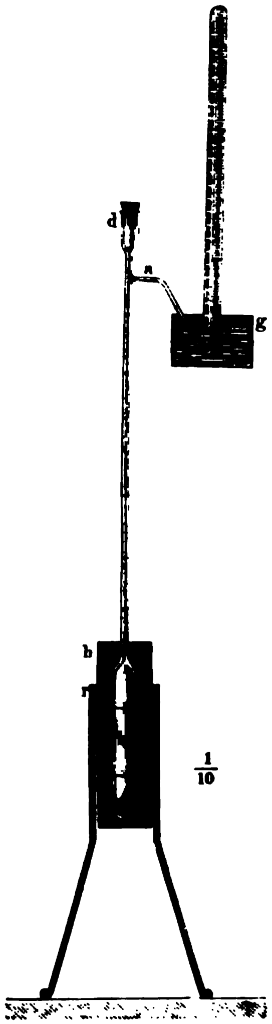

FIG. 53.

This is especially valuable for bodies boiling above 448°, and for such as attack mercury or fusible metal. The temperature to

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[1] *Ber. Deutsch. Chem. Ges.* 1878, ii. 2253.

which the vapour is heated does not require to be determined, nor is it necessary to know the volume of vapour at that temperature, as both of these values are eliminated in the expression for the density. The only observation which is required is the volume of the vapour in the form of its equal volume of air measured at the atmospheric temperature. The apparatus is shown in Fig. 52. It consists of the boiling flask *c*, in which is placed the glass *b*, having a capacity of about 100 cbc.; and on to this is fused a tube 600 mm. in length, closed with a caoutchouc stopper (*d*), and furnished with a short capillary gas-delivery tube (*a*). The substance employed for heating purposes may be any of those already mentioned.

If it be necessary to work at a temperature above 310°, a bath of molten lead (Fig. 53) is employed, which can be heated to a temperature sufficiently high for the complete volatilisation of the substance. This point is easily ascertained by dipping a thin tube containing a small quantity of the body into the lead and seeing whether it boils quickly. The experiment is commenced by heating the empty vessel *b* (at the bottom of which a small plug is contained) in the long tube or in the lead bath. The tube is closed by the stopper *d*, and the gas-delivery tube dips in the water of the trough. As soon as the temperature becomes constant, and when, therefore, no further evolution of air is observed, the stopper is quickly removed, and a weighed quantity of the substance (such in amount that its vapour does not occupy more than half the volume of the vessel *b*) thrown in and the cork quickly replaced, the graduated cylinder filled with water having been placed over the end of the gas-delivery tube. The substance at once evaporates, and in fifteen seconds displaces its own volume of air which collects in the cylinder. As soon as no further bubbles are emitted, the tube is removed into a larger cylinder filled with water, the levels of the liquids brought to the same point, and after a time the volume of the air read off, the temperature of the water and the height of the barometer being at the same time observed. These observations yield sufficient data for the calculation:

S = Weight of substance.
t = Temperature of the water.
B = Barometric pressure reduced to 0°.
w = Tension of vapour of water.
V = Volume of air.

The vapour density is calculated by the formula:

$$\frac{S \times 760\,(1 + 0{\cdot}003665t)}{(B - w)\,V \times 0{\cdot}001293},$$

or, by collecting the constants:

$$\frac{S\,(1 + 0{\cdot}003665t) \times 587780}{(B - w)\,V}.$$

As examples we may quote the following:

(1) Chloroform, $CHCl_3$, in water vapour.

$S = 0{\cdot}1008$ $t = 16^\circ{\cdot}5$ $B = 707{\cdot}5$ mm. $V = 22$ cbc.

	Calculated.	Found.
Vapour density . .	4·13	4·13.

(2) Benzoic acid, $C_7H_6O_2$, in diphenylamine vapour.

$S = 0{\cdot}0855$ $t = 16^\circ$ $B = 717{\cdot}8$ mm. $V = 17{\cdot}8$ cbc.

	Calculated.	Found.
Vapour density . .	4·22	4·24.

(3) Diphenylamine, $C_{12}H_{11}N$, in lead bath.

$S = 0{\cdot}0905$ $t = 17^\circ$ $B = 714{\cdot}8$ mm. $V = 13{\cdot}6$ cbc.

	Calculated.	Found.
Vapour density . . .	5·83	5·92.

The same experimenters have employed this method for the determination of the vapour density of inorganic compounds which volatilise at a red-heat or even at a higher temperature. For this purpose the glass vessel is replaced by one of porcelain or platinum heated in a suitable gas-furnace.[1]

The literature of the subject must be referred to for further information respecting the subject of vapour density determination.[2]

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[1] *Ber. Deutsch. Chem. Ges.* 1879, 1112.

[2] Grabowski, *Ann. Chem. Pharm.* cxxxviii. 174; Landolt, *Ber. Deutsch. Chem. Ges.* v. 497; Goldschmidt and Ciamician, *ibid.* x. 641; Hofmann, *ibid.* ix. 962; xi. 1684; Pfaundler, *ibid.* xii. 165.

DETERMINATION OF MOLECULAR FORMULÆ.

71 (A) *Molecular Formulæ of Volatile Bodies.*—When the percentage composition and the vapour density of a compound are known, the molecular formula can be readily ascertained. Hydrogen is 14·435 times lighter than air, and hence the molecular weight of a substance is obtained by multiplying its vapour density by twice 14·435.

Example No. 1. Thus, for instance, the molecular weight of the above-mentioned paraffin is $2{\cdot}986 \times 28{\cdot}87 = 86{\cdot}2$, or in round numbers 86. Now, as the percentage composition of this body is known, the amount of carbon and hydrogen contained in 86 parts can be readily found.

$$\frac{83{\cdot}87 \times 86}{100} = 72{\cdot}13 \text{ carbon.}$$

$$\frac{16{\cdot}25 \times 86}{100} = 13{\cdot}97 \text{ hydrogen.}$$

If we divide the numbers thus obtained by the atomic weights, we find that the hydrocarbon is hexane, C_6H_{14}. The want of exact agreement between the numbers thus obtained and those calculated from the formula is explained by the fact that the above numbers contain the experimental errors due both to the analysis and to the vapour density determination. This error may be partially eliminated if we compare the theoretical composition and vapour density, directly with the numbers found by experiment:

	Found.	Calculated.
Carbon	83·87	83·72
Hydrogen	16·25	16·28
	100·12	100·00
Vapour density . .	2·986	2·979.

The numbers thus found are seen to agree well with the calculated values.

Example No. 2. Methyl-anthracene gave on analysis the following percentage composition:

Carbon	93·92
Hydrogen	6·23
	100·15.

Its vapour density is 6·57, and hence its molecular weight is 190, and the amount of carbon and hydrogen contained in 190 parts is:

Carbon	178·5
Hydrogen	11·8.

These numbers, divided by the approximate atomic weights, give:

$$\frac{178·5}{12} = 14·9,$$

$$\frac{11·8}{1} = 11·8,$$

showing that methyl anthracene possesses the formula $C_{15}H_{12}$. This corresponds to a theoretical vapour density of 6·63, and a percentage composition of:

Carbon	93·75
Hydrogen	6·25
	100·00.

Example No. 3. As a last example of this kind we may take ethyl propenyl ether, whose vapour density determination has been already given. Ultimate analysis gave:

Carbon	71·26
Hydrogen	9·55
Oxygen	19·19
	100·00.

Its molecular weight is 28·87 × 2·895 = 83·6.

$$\frac{83·6 \times 71·26}{100} = 59·60 \text{ carbon.}$$

$$\frac{83·6 \times 9·55}{100} = 7·98 \text{ hydrogen.}$$

$$\frac{83·6 \times 19·19}{100} = 16·0 \text{ oxygen.}$$

Hence the molecular formula is C_5H_8O, and this corresponds to:

C_5	60	71·43
H_8	8	9·53
O	16	19·04
		100·00.

72 (B) *Molecular Formulæ of Acids.* Many carbon compounds are acids whose molecular weight, whether they be volatile or not, may be readily ascertained by determining in the first place whether the acid is monobasic or polybasic, and then analysing one of its salts. As a rule the silver salts are employed for this purpose because they are easily obtained anhydrous and in the pure state, and because they leave a residue of pure silver on ignition.

Example No. 4. The composition of monobasic melissic acid, according to analysis, is as follows:

Carbon	79·61
Hydrogen	13·48
Oxygen	6·91
	100·00.

Ignition of the silver salt showed that it contained 19·3 per cent. of silver. Hence the molecular weight of this salt is:

$$\frac{100 \times 107{\cdot}7}{19{\cdot}3} = 558.$$

This salt differs from the acid by containing one atom of silver in place of one atom of hydrogen. Hence the molecular weight of the acid is:

$$(558 - 107{\cdot}7) + 1 = 451{\cdot}3,$$

or the even number 452 may be taken as representing the molecular weight of the acid. The weight of carbon, hydrogen, and oxygen contained in the molecule will then be respectively:

$$\frac{79{\cdot}16 \times 452}{100} = 357{\cdot}8,$$

$$\frac{13{\cdot}48 \times 452}{100} = 60{\cdot}9,$$

$$\frac{6{\cdot}91 \times 452}{100} = 31{\cdot}2.$$

Hence the formula is $C_{30}H_{60}O_2$, and this gives:

C_{30}	360	79·64
H_{60}	60	13·28
O_2	32	7·08
	452	100·00.

The calculated percentage of silver, namely, 19·28, in the above salt, agrees with that which has already been described.

Example No. 5. Analysis of silver benzoate gave the following results:

Carbon	36·68
Hydrogen	2·19
Silver	47·16
Oxygen	13·97
	100·00.

Benzoic acid is likewise monobasic, and the molecular weight of its silver salt as calculated, as in the last example, is 228·4, that of the acid being 120·7. If the quantities of the various elements contained in 228·4 parts of the salt be next calculated, the formula $C_7H_5AgO_2$ is obtained. Hence the acid is $C_7H_6O_2$, as is shown by the following comparison of the theoretical with the analytical results:

		Calculated.	Found.
C_7	84	36·73	36·68
H_5	5	2·19	2·19
Ag	107·7	47·09	47·16
O_2	32	13·99	13·97
		100·00	100·00.

Example No. 6. Meconic acid, a compound found in opium, is a polybasic acid. On adding silver nitrate to its aqueous solution, a white silver salt is precipitated, but when the same reagent is added to a solution of the acid previously neutralised by ammonia, a yellow silver salt is obtained. The composition of the acid and of the two silver salts is found by experiment to be:

	Meconic Acid.	White Silver Salt.	Yellow Silver Salt.
Carbon . . .	42·0	20·2	15·9
Hydrogen . .	2·0	0·5	0·2
Oxygen . . .	56·0	27·0	21·9
Silver . . .	—	52·3	62·0
	100·0	100·0	100·0.

If in the first analysis the numbers be divided respectively by the atomic weights of the elements, we obtain the following relation between the number of atoms of the constituents of the acid:

$$\frac{42}{12} = 3\cdot5,$$
$$\frac{2}{1} = 2\cdot0,$$
$$\frac{56}{16} = 3\cdot5.$$

The most simple formula of meconic acid deduced from these numbers is $C_7H_4O_7$, but whether this, or a multiple of it, expresses the molecular weight cannot be decided by the results of analysis. In the two salts different quantities of hydrogen are replaced by silver. The white salt contains for every seven atoms of carbon:

$$\frac{0\cdot5 \times 84}{20\cdot2} = 2\cdot1 \text{ parts, or 2 atoms of hydrogen,}$$
$$\frac{52\cdot3 \times 84}{20\cdot2} = 217\cdot0 \text{ parts, or 2 atoms of silver.}$$

In the yellow salt we find:

$$\frac{0\cdot2 \times 84}{15\cdot9} = 1\cdot05 \text{ part, or 1 atom of hydrogen,}$$
$$\frac{62\cdot0 \times 84}{15\cdot9} = 327\cdot5 \text{ parts, or 3 atoms of silver.}$$

From this we conclude that the acid is tribasic, and that the formula $C_7H_4O_7$ represents a molecule. A further confirmation of this conclusion is found in the fact that acid salts containing only one atom of a monad metal are known.

The molecular formulæ of the above compounds are therefore:

Meconic acid . .	$C_7H_4O_7$,
White salt . . .	$C_7H_2Ag_2O_7$,
Yellow salt . . .	$C_7HAg_3O_7$.

In certain instances, an acid, whose molecular formula has to be determined, may be known to belong to a given homologous series. In this case, in order to determine its molecular formula, we only need to determine the quantity of silver, or of any other metal, contained in one of its salts.

Example No. 7. An acid, which from its derivation and chemical relations undoubtedly belongs to the group of fatty acids, gives a silver-salt which yields, on ignition, 45·51 per cent. of metal. Hence the molecular weight of the acid is 130. The general formula, however, of the fatty acid series is $C_nH_{2n}O_2$ and the value of n is ascertained by the equation:

$$14n + 32 = 130$$
$$\therefore n = 7.$$

Hence the molecular formula of the acid is $C_7H_{14}O_2$.

73 (C) *Molecular Formulæ of Bases.* Many carbon compounds exist which contain nitrogen, and which act as bases, combining like ammonia with acids. Some of these bases are monacid, others are polyacid. In order to find the molecular weight of such a compound, it is only necessary to ascertain the quantity of acid contained in an anhydrous normal salt, or, better still, to find the quantity of platinum present in the double salt formed by the combination of the hydrochloride with platinic chloride, and which, like ammonium platinic chloride, contains two molecules of hydrochloric acid to each molecule of platinic chloride.

Example No. 8. Caffeine is a monacid base; its platinum double salt contains two molecules of caffeine and two molecules of hydrochloric acid combined with one molecule of platinic chloride, and 100 parts of this compound leave, on ignition, 24·6 per cent. of platinum. Consequently the amount of the platinum salt which contains one atom, or 196·7 parts of platinum, is:

$$\frac{196{\cdot}7 \times 100}{24{\cdot}6} = 799{\cdot}6.$$

The molecular weight of caffeine is found from this by the equation:

$$2n + (2 \times 36{\cdot}5) + 338{\cdot}3 = 799{\cdot}6$$
$$\therefore n = 194.$$

As the percentage composition of this base is known, its molecular formula can easily be found:

$$\frac{194 \times 49{\cdot}51}{100} = 96{\cdot}1 \text{ of carbon,}$$

$$\frac{194 \times 5{\cdot}22}{100} = 10{\cdot}1 \text{ of hydrogen,}$$

$$\frac{194 \times 28{\cdot}99}{100} = 56{\cdot}2 \text{ of nitrogen,}$$

$$\frac{194 \times 16{\cdot}28}{100} = 31{\cdot}58 \text{ of oxygen.}$$

One molecule of caffeine, therefore, consists of:

$$\frac{96{\cdot}1}{12} = 8{\cdot}0 \text{ atoms of carbon,}$$

$$\frac{10{\cdot}1}{1} = 10{\cdot}1 \text{ atoms of hydrogen.}$$

$$\frac{56{\cdot}2}{14} = 4{\cdot}0 \text{ atoms of nitrogen,}$$

$$\frac{31{\cdot}58}{16} = 1{\cdot}97 \text{ atom of oxygen.}$$

Its molecular formula is therefore $C_8H_{10}N_4O_2$, corresponding to a molecular weight of 194, or more exactly of 193·78.

In the determination of the molecular weight of an organic base we also often know beforehand to which homologous series it belongs. In such a case, the determination of the platinum in the double salt is sufficient to determine the formula.

Example No. 9. A compound ammonia, having the general formula $C_nH_{2n+3}N$ forms a double salt, 100 parts of which, on ignition, leave a residue of 33·62 of platinum.

As the platinum double salt possesses the formula $(C_nH_{2n+3}N,ClH)_2 + PtCl_4$, the molecular weight of the base is easily found to be 86, and hence we have the equation:

$$12\,n + 2\,n + 3 + 14 = 86$$
$$\therefore\; n = 4{\cdot}93.$$

Hence the base possesses the formula $C_5H_{13}N$, and has a molecular weight of 86·86.

74 (D) *Molecular Formulæ of Non-volatile and Neutral Bodies.* Most carbon compounds, however, neither act as acids nor as bases, and if they are not volatile without decomposition, and do not enter into combination to form distinct compounds with other elements by means of which the molecular weight can be ascertained, the molecular formulæ can be ascertained, in many cases at least, by a careful examination of their chemical metamorphoses.

Example No. 10. Numerous analyses of cane-sugar have shown it to possess the following percentage composition:

Carbon	42·10
Hydrogen	6·44
Oxygen	51·46
	100·00.

As in the case of aurin, this result may be expressed by a number of different formulæ. In order to obtain a clue as to which of these is the correct one, we must consider certain general properties of the body. In the first place, cane-sugar when boiled with sulphuric acid is converted into equal quantities of two other kinds of sugar possessing an identical composition, but distinguished by certain chemical as well as by certain physical properties. These two varieties of sugar are known as grape-sugar and fruit-sugar. That they are formed from cane-sugar by addition of the elements of water, is proved by analysis, which gives for the new sugars the following composition:

Carbon	40·00
Hydrogen	6·67
Oxygen	53·33
	100·00.

On dividing these numbers by the respective atomic weights of the elements, the following numbers are obtained:

$$\frac{40}{12} = 3{\cdot}33 \text{ carbon.}$$

$$\frac{6{\cdot}67}{1} = 6{\cdot}67 \text{ hydrogen.}$$

$$\frac{53{\cdot}33}{16} = 3{\cdot}33 \text{ oxygen.}$$

Hence these two kinds of sugar contain two atoms of hydrogen for every one atom of carbon and one atom of oxygen, and the simplest formulæ for them is CH_2O. This, however, cannot possibly represent the molecular formula of the compound, inasmuch as such a simple body must either be a gas or, at any rate, a very volatile substance. Neither of these kinds of sugar belong to either of the above categories, for on heating they decompose, leaving a residue of carbon. The molecular formula must therefore be a multiple of the simplest formula. Both these sugars yield, on fermentation, equal molecules of alcohol, C_2H_6O, and carbon dioxide, CO_2; hence we may conclude that the molecular formula cannot be less than $C_3H_6O_3$. Both, moreover, combine with nascent hydrogen to form manna-sugar, or mannitol, which possesses the following composition:

Carbon	39·56
Hydrogen	7·69
Oxygen	52·75
	100·00.

As mannitol stands in such a close relationship to grape-sugar, fruit-sugar, and cane-sugar, it may be well to calculate how many atoms of hydrogen and oxygen these compounds contain for every 3 atoms of carbon. Thus we find for cane-sugar, $C_3H_{5\cdot5}O_{2\cdot75}$, and for mannitol, $C_3H_7O_3$. Hence, the simplest formulæ of these two bodies, consistent with the foregoing reactions, are, cane-sugar, $C_{12}H_{22}O_{11}$, mannitol, $C_6H_{14}O_6$; and those of the two other descriptions of sugar, $C_6H_{12}O_6$. That this formula for mannitol is its molecular formula, may be seen from the following considerations. An exact investigation of this body has shown that it contains six hydroxyls, or that it is an alcohol of an hexad radical. Hence it possesses the formula $C_6H_8(OH)_6$. This may be further proved by a few simple reactions. The six hydroxyls may be replaced by six of hydrogen, hexane, C_6H_{14}, being thus formed, and this is the original hydrocarbon of mannitol. It might, notwithstanding, be supposed that as mannitol is not volatile without decomposition its molecular weight might be a multiple of the above numbers. This supposition, however, is impossible, as no hydrocarbon can contain a larger proportion of hydrogen than is contained in a hydrocarbon of the series C_nH_{2n+2}. As the three other sugars are so clearly connected with mannitol, we may assume that the above simple formulæ likewise represent the molecular formulæ of these compounds.

Example No. 11. As a last example of the method by which the molecular formula of a non-volatile compound may be determined, we will take that of aurin, the analysis of which has already been given. This compound is formed when a mixture of oxalic acid, $C_2H_2O_4$, and phenol, C_6H_6O, is warmed with sulphuric acid; water and formic acid, CH_2O_2, being at the same time produced. As oxalic acid easily splits up on heating into formic acid and carbon dioxide, we must assume that the latter compound, in the nascent state, acts upon phenol yielding aurin and water. If we represent this reaction by an equation, we find that of the three formulæ which we have already given for aurin, the second one explains the decomposition most readily:

$$3\,C_6H_6O + CO_2 = C_{19}H_{14}O_3 + 2H_2O.$$

That this, the simplest formula, is at the same time the molecular formula, has been proved, or at any rate rendered extremely probable, not only by the fact that aurin can be converted into the hydrocarbon triphenylmethane, $C_{19}H_{16}$, whose derivative it is, but also that aurin can be prepared from this hydrocarbon by the replacement of two atoms of hydrogen by one atom of oxygen and two atoms of hydrogen by two of hydroxyl.

In the numerous cases to which none of these means for ascertaining the molecular weight of a substance apply, we must be content to make use of the simplest formula, although it must be remembered that in certain cases even the simplest formula cannot be obtained.

EMPIRICAL AND RATIONAL FORMULÆ.

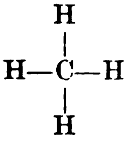
75 *Law of the Linking of Atoms.* By an empirical formula is understood one which simply expresses the composition of the body. If at the same time it represents the molecular weight, it is termed an empirical-molecular formula. Besides these, *rational formulæ* are employed, especially in organic chemistry, this name having been first made use of by Berzelius. Such formulæ are intended to indicate the chemical nature of the compound, and to express the relations in which it stands to other bodies, or, in other words, to point out either the compounds from which it has been derived or those into which it can be resolved. For the true aim of chemistry, as Kekulé justly remarks, is not so much the study of the existing substance as that of its past history and its future development. In the historical introduction reference has been made, not only to the growth of rational formulæ, but likewise to the influence which the theory of types has exerted on our knowledge of the peculiar

relations of the atoms in combination and in decomposition. It was formerly supposed that the several constituent atoms of the molecule were held together by the attraction which one of them exerted upon all or upon a large number, and that these, in their turn, exerted a corresponding attraction and thus held each constituent in its place. Chemists have, however, now come to the conclusion that this attraction is only exerted between the atoms severally. The atoms may thus be represented as forming a chain, one atom being linked on to the other, so that when one of them is removed without altering the position of the others, the chain is broken.

It next remains to notice how this law of the linking of atoms[1] may be explained from the known constitution of the carbon compounds.

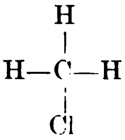
76 *Carbon is a tetrad element,* and, therefore, one atom of carbon unites with four atoms of hydrogen, giving rise to methane or marsh-gas, CH_4, the simplest of the hydrocarbons. This hydrogen may be replaced by other monad elements or residues. Thus by the action of chlorine we obtain methyl chloride, CH_3Cl, which, on uniting with ammonia, yields methylamine, CH_3NH_2, and on treatment with caustic potash is converted into methyl alcohol, CH_3OH. If two atoms of hydrogen in this latter body be replaced by oxygen we obtain formic acid, $COH.OH$. These formulæ may be graphically represented according to A. S. Couper's suggestion,[2] as follows, each atom being connected with another by means of a line indicating the mode in which the attraction acts:

Methane.



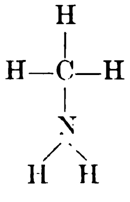
$$\begin{array}{c} H \\ | \\ H-C-H \\ | \\ H \end{array}$$

Methyl Chloride.

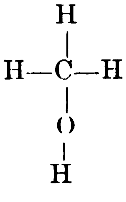


$$\begin{array}{c} H \\ | \\ H-C-H \\ | \\ Cl \end{array}$$

Methylamine.

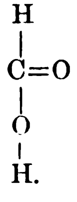


Methyl Alcohol.



$$\begin{array}{c} H \\ | \\ H-C-H \\ | \\ O \\ | \\ H \end{array}$$

Formic Acid.



$$\begin{array}{l} H \\ | \\ C=O \\ | \\ O \\ | \\ H. \end{array}$$

The simplest mode in which two carbon atoms can combine together is when one combining unit of the one atom is linked by one combining unit to the other atom. Six free

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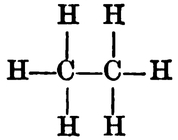
[1] L. Meyer, *Modern. Theor.* 3te Aufl. 151.

[2] *Phil. Mag.* [4], xvi. 104.

combining units then remain, or a hexad group is formed capable of combining with hydrogen to form ethane, possessing the following graphical formula:



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & — & C & — & C & — & H \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

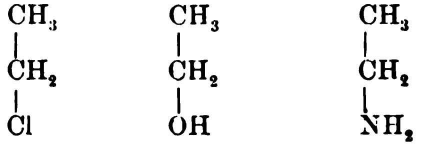
More than two carbon atoms can combine together in a similar way, and the valency of such a group will be increased by two units for every atom of carbon which thus becomes attached. If n atoms of carbon unite together, the number of free combining units will be represented by

$$2+n(4-2)=2+2n.$$

If the whole of these units be saturated by hydrogen, members of the homologous series, C_nH_{2n+2}, known as the paraffin series, are formed. In these, just as in marsh-gas, one atom of hydrogen may be replaced by monad elements or residues, and thus the homologous series of chlorides, alcohols, and amines, which have been already described, may be obtained.

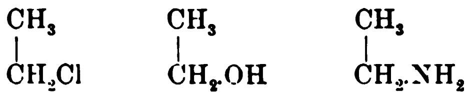
77 *Derivatives of Ethane.* Ethane, C_2H_6, forms the following derivatives: ethyl chloride, C_2H_5Cl; ethyl alcohol, $C_2H_5.OH$; ethylamine, $C_2H_5.NH_2$. The graphical formulæ of these are readily obtained, and may shortly be written in three different ways, as follows:

(1)



$$\begin{array}{c} CH_3 \\ | \\ CH_2 \\ | \\ Cl \end{array} \qquad \begin{array}{c} CH_3 \\ | \\ CH_2 \\ | \\ OH \end{array} \qquad \begin{array}{c} CH_3 \\ | \\ CH_2 \\ | \\ NH_2 \end{array}$$

(2)



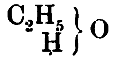
$$\begin{array}{l} CH_3 \\ | \\ CH_2Cl \end{array} \qquad \begin{array}{l} CH_3 \\ | \\ CH_2.OH \end{array} \qquad \begin{array}{l} CH_3 \\ | \\ CH_2.NH_2 \end{array}$$

(3) $CH_3.CH_2Cl$ $CH_3.CH_2.OH$ $CH_3.CH_2.NH_2$.

Ethyl alcohol, on oxidation, yields acetic acid, one atom of oxygen replacing two atoms of hydrogen.

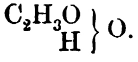
The question now occurs, which two of the six atoms are thus replaced? This point is determined on ascertaining that acetic acid like alcohol contains the radical hydroxyl, a fact with which the originators of the theory of types were acquainted, for they assumed that both these compounds were obtained from water by the replacement of one atom of hydrogen by a radical:

Ethyl Alcohol.



$$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O$$

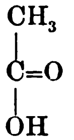
Acetic Acid.



$$\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O.$$

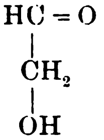
These formulæ indicate that both compounds contain an atom of hydrogen capable of acting differently from the other atoms of the same element, inasmuch as this particular one can be readily replaced by monad elements or groups. Besides, we know that the hydroxyl can be replaced by chlorine when these and similar compounds are acted on by phosphorus pentachloride, ethyl chloride, C_2H_5Cl, and acetyl chloride, C_2H_3OCl, being formed, whilst by the process of reverse substitution the chlorine in these bodies may be readily replaced by hydroxyl. Hence it follows that the true constitution of acetic acid can only be represented by one of the following constitutional formulæ:

(1)



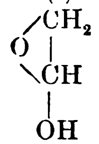
$$CH_3-C{=}O-OH$$

(2)



$$HC{=}O-CH_2-OH$$

(3)



In order to ascertain which of these is to be accepted, two general methods are employed. The molecule may either be decomposed by simple reactions into smaller molecules of well-known constitution, or it may be built up from such molecules.

78 *The First or Analytical Method. Example* 1. When acetic acid is heated with an alkali, marsh-gas and a carbonate are obtained:

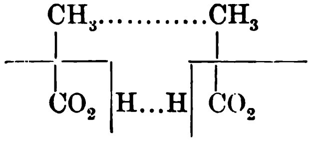
$$C_2H_3O_2Na + NaOH = CH_4 + Na_2CO_3.$$

Example 2. When a galvanic current is passed through a concentrated solution of potassium acetate, acid potassium carbonate, free hydrogen, and ethane are produced:

$$2\,C_2H_3O_2K + 2H_2O = 2\,KHCO_3 + H_2 + C_2H_6.$$

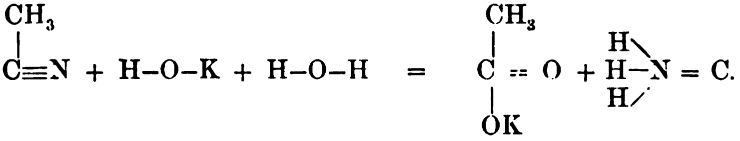
The change which takes place in this reaction is easily explained. When the salt undergoes electrolytic decomposition, it first yields the metal potassium and a residue, $C_2H_3O_2$. But the metal at once decomposes water, and the residue yields carbon dioxide and methyl, $C_2H_3O_2 = CO_2 + CH_3$. The latter body cannot, however, exist in the free state, and hence two molecules combine to form ethane, C_2H_6.

The most probable conclusion to be drawn from these decompositions is that one atom of carbon of the acetic acid is linked directly with carbon, and hence its constitution is represented by the first of the above three constitutional formulæ. The decomposition by electrolysis being represented in the following way:



$$\begin{array}{c|c|c} CH_3 \ldots\ldots & \ldots\ldots & CH_3 \\ | & & | \\ \hline | & & | \\ CO_2 & H \ldots H & CO_2 \end{array}$$

79 *The Second or Synthetic Method.* That acetic acid possesses the above constitution and contains the group methyl, is moreover ascertained by the fact that it can be synthetically obtained from the methyl compounds. Thus, when methyl iodide is heated with potassium cyanide, methyl cyanide, $CH_3.CN$, is obtained, and this, when boiled with a solution of caustic potash, yields potassium acetate and ammonia



$$\begin{matrix} CH_3 \\ | \\ C \equiv N \end{matrix} + H{-}O{-}K + H{-}O{-}H \;=\; \begin{matrix} CH_3 \\ | \\ C = O \\ | \\ OK \end{matrix} + \begin{matrix} H\diagdown \\ H{-}N \\ H\diagup \end{matrix} = C.$$

By the action of chlorine upon acetic acid, monochloracetic acid, $C_2H_3ClO_2$, is formed. This is a monobasic acid, like acetic acid itself, and it is converted by means of phosphorus pentachloride into monochloracetyl chloride, $C_2H_3Cl.OCl$, and from this we conclude that it also contains the group hydroxyl, and that the substitution has taken place in the methyl group. Its constitution, as well as that of acetic acid, may, therefore, be represented by the following formulæ:

	Acetic Acid.	Chlor-acetic Acid.
(1)	$CH_3.CO.OH$	$CH_2Cl.CO.OH.$
(2)	$\left.\begin{matrix} CH_3.CO \\ H \end{matrix}\right\} O$	$\left.\begin{matrix} CH_2Cl.CO \\ H \end{matrix}\right\} O.$

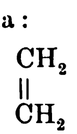
Such or similar formulæ were formerly used, but whilst Berzelius's school intended by the use of these formulæ to indicate that methyl is a copulated oxalic acid, the upholders of the theory of types distinctly stated that such rational formulæ are to be considered not as constitutional formulæ, but as formulæ of decomposition, simply indicating the chemical metamorphoses of the substance in question and its relationships to other substances, but in no way indicating the constitution or position of the atoms.

All the formulæ for acetic acid which have been mentioned indicate (1) that it contains two atoms of carbon connected together by the simplest method of linking; (2) that one of these atoms is combined with three atoms of hydrogen; and (3) that the other is so connected with two atoms of oxygen that one of the atoms of this latter element is linked to carbon with both its combining units, the other being connected with only one combining unit, its second combining unit being saturated with hydrogen.

80 *Non-Saturated Compounds.* If we remove two atoms of hydrogen from ethane, ethylene or olefiant gas, C_2H_4, is produced, and this substance is sharply distinguished from ethane. The latter, like all paraffins, is attacked by chlorine and bromine only in daylight, and with the formation of substitution-products, whilst ethylene and its homologues unite directly in the dark with two atoms of the above halogens. Hence we may assume that the latter hydrocarbon belongs to the class of unsaturated compounds or contains free combining units. In this case the constitution of ethylene may be represented by the following formulæ:

$$\begin{array}{c}CH_3\\ |\\ =CH\end{array}\qquad\qquad \begin{array}{c}-CH_2\\ |\\ -CH_2\end{array}$$

It is, however, as we shall see later, much more probable that the two carbon atoms are connected together by two combining units of each, and that the constitution is expressed more correctly by the formula:



$$\begin{array}{c}CH_2\\ \|\\ CH_2\end{array}$$

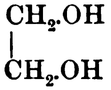
The easy combination of ethylene with the elements of the chlorine group can in this case be readily explained by the tendency which the carbon atoms exhibit to combine in the simplest possible way. However this may be, it can be easily shown that the first of the above formulæ does not indicate the constitution of ethylene.

The bromine in ethylene dibromide, $C_2H_4Br_2$, can readily be replaced by hydroxyl, and by the action of hydrochloric acid on the glycol, $C_2H_4(OH)_2$, thus produced, ethylene chlorhydrin, C_2H_4ClOH, is formed. This substance on oxidation yields monochloracetic acid, $C_2H_2ClO.OH$. Hence it follows that the above compounds possess the following constitutional formulæ:

Ethylene Dibromide.

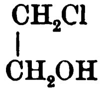
$$\begin{array}{l} CH_2Br \\ | \\ CH_2Br \end{array}$$

Ethylene Alcohol or Glycol.



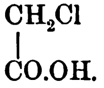
$$\begin{array}{l} CH_2.OH \\ | \\ CH_2.OH \end{array}$$

Ethylene Chlorhydrin.



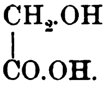
$$\begin{array}{l} CH_2Cl \\ | \\ CH_2OH \end{array}$$

Mono-chlor-acetic acid.



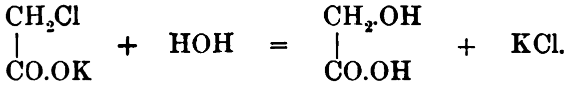
$$\begin{array}{l} CH_2Cl \\ | \\ CO.OH. \end{array}$$

By a moderate oxidation ethylene alcohol can be converted into glycollic acid, $C_2H_4O_3$, by replacement of two atoms of hydrogen by one atom of oxygen. This reaction is exactly parallel to the formation of acetic acid from ethyl alcohol, and hence the following formula must be given to glycollic acid:



$$\begin{array}{l} CH_2.OH \\ | \\ CO.OH. \end{array}$$

The truth of this is easily proved by the fact that glycollic acid is also formed when a salt of chloracetic acid is boiled with water:



$$\begin{array}{l} CH_2Cl \\ | \\ CO.OK \end{array} + HOH = \begin{array}{l} CH_2.OH \\ | \\ CO.OH \end{array} + KCl.$$

Glycollic acid contains two hydroxyls in different positions; one of these may be termed the alcoholic hydroxyl, because it occupies the same position as the hydroxyl in alcohol, whilst the other playing the part of the hydroxyl in acetic acid, and capable of having its hydrogen replaced by metals, is, on this account, called the basic hydroxyl.

As we may assume that analogous constitution gives rise to analogous properties, we may predict that glycollic acid will act partly as an alcohol and partly as an acid. This is found to be the case. Exactly as we obtain ethyl chloride by acting on and this was confirmed by the discovery in the following year by William Henry of the existence of a similar hydrocarbon in coal-gas. Dalton states "that the hydrocarbon contained in oil-gas is a compound *sui generis* consisting of the elements of olefiant gas united in the same proportion, but differing in the number of atoms, most probably the atom of the new gas consisting of two of olefiant gas."

This hypothesis was soon proved by Faraday to be correct. In the year 1825 he published a communication "On certain new compounds of carbon and hydrogen obtained by the decomposition of oil by heat."[1] At that time a Portable Gas Company was established in London for supplying the public with the gas obtained from the distillation of oil, and pumped under a pressure of 30 atmospheres into portable vessels. A considerable quantity of a liquid was in this way condensed, and this liquid was examined by Faraday. It readily evaporates under the atmospheric pressure, and, like olefiant gas, has the power of uniting with its own volume of chlorine to form an oily liquid. Its specific gravity proved to be double that of olefiant gas, and its chloride contains twice as much carbon and hydrogen as Dutch-liquid, this being the name which was at that time given to the oil of olefiant gas from its discoverers.

Shortly before this, Liebig[2] had shown that the salts of fulminic acid possess exactly the same composition as the corresponding salts of cyanic acid. In a note to his memoir[3] Faraday refers to this discovery, and adds the following remark:—"In reference to the existence of bodies composed of the same elements, and in the same proportion, but differing in their qualities, it may be observed that, now we are taught to look for them, they may probably multiply upon us."

Notwithstanding these early observations, many chemists believed that some error had been made in the analyses of these substances. Thus, Berzelius was unable to conceive that bodies could exist having the same composition but possessing totally different properties. When, however, Wöhler proved in the year 1828, that ammonium cyanate can be converted into urea, and when Berzelius himself ten years later showed that racemic acid and tartaric acid have the same composition, the fallacy of the old axiom became evident, and it was generally acknowledged that chemical compounds possessing the same qualitative

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[1] *Phil. Trans.* 1825, 440.

[2] *Ann. Chim. Phys.* xxiv. 298.

[3] *Loc. cit.* p. 460.

and quantitative composition need not necessarily exhibit the same physical and chemical properties.[1]

Berzelius himself admitted that the doctrine of isomerism had now been completely confirmed, inasmuch as the same number of the same elementary atoms arranged in different ways not only may give rise to compounds having a dissimilar crystalline form, but exhibiting distinct chemical properties. To compounds of the latter kind Berzelius gave the name of *isomers* (from ἰσομερής; ἴσος equal; μέρος, a share or portion), and soon afterwards he divided these, on the one hand, into those to which we now give the name of *polymeric* compounds, because they possess a different molecular weight, and, on the other, into those termed *metameric* bodies, which, with an equal molecular weight, exhibit different properties.

Since Berzelius's time a large number of such bodies have been discovered. The radical theory and the theory of types are capable of explaining many cases of isomerism, but it was not until the doctrine of the linking of atoms was established that a clear light was thrown on this subject.

The causes which can produce isomerism are numerous, and hence we must divide isomeric bodies into different groups.

82 *Isomerism in the Restricted Sense.* The compounds classed under this head all contain carbon atoms in direct combination, and their isomerides have the same molecular weight.

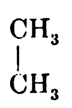
Let us in the first place investigate the cause of those cases of isomerism which can be predicted by theory, and notice how far these predictions have been found to agree with the facts.

The simplest hydrocarbons are those of the series C_nH_{2n+2}. It is clear that in this series, cases of isomerism can only occur when the carbon atoms are combined in different ways with one another. Hence the three first terms of the series cannot give rise to isomeric forms, and the following substances are the only ones known:

Methane.

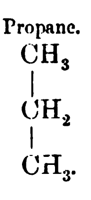
CH_4

Ethane.



$$\begin{array}{c}CH_3\\|\\CH_3\end{array}$$

Propane.



$$\begin{array}{c}CH_3\\|\\CH_2\\|\\CH_3.\end{array}$$

The fourth term, C_4H_{10}, of the series is derived from propane

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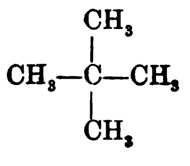
[1] *Pogg.* xix. 326.

by the substitution of one atom of hydrogen by methyl. This replacement may, however, take place either at the end of the chain of carbon atoms or in the central carbon group. Hence two isomerides exist and both of these are known:

Butane.

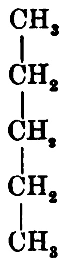
$CH_3-CH_2-CH_2-CH_3$

Isobutane.



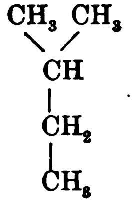
Three isomerides of the next member of the group, C_5H_{12}, are possible, and these are all of them known:

Pentane.

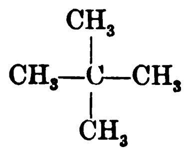


$CH_3-CH_2-CH_2-CH_2-CH_3$

Isopentane.



Tetramethylmethane.



The number of possible isomerides increases rapidly as we ascend the series. This is seen by the following table:[1]

No. of carbon atoms	1	2	3	4	5	6	7	8	9	10	11	12	13
No. of possible isomeric paraffins	1	1	1	2	3	5	9	18	35	75	159	357	799

Of these, however, only a relatively small number has as yet been prepared.

When an atom of hydrogen in a paraffin is replaced by a monad element or radical, the compounds of the alcohol radicals are obtained. In this case isomerism commences in the third series, and two propyl alcohols, C_3H_8O, are known, viz.:

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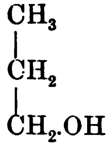
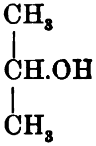
[1] Cayley, "On the analytical forms called trees, with applications to the theory of chemical combinations," *Brit. Assoc. Rep.* 1875, 257. Recalculated by Dr. Hermann of Würtzburg, the two last are 355 and 802.

Primary
Propyl alcohol.



$$\begin{array}{l} CH_3 \\ | \\ CH_2 \\ | \\ CH_2.OH \end{array}$$

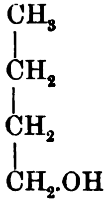
Secondary
Propyl alcohol.



$$\begin{array}{l} CH_3 \\ | \\ CH.OH \\ | \\ CH_3 \end{array}$$

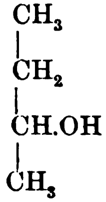
Four butyl alcohols, $C_4H_{10}O$, can in like manner exist according to theory. These are all of them known, viz.:

(1)
Primary
Normal.



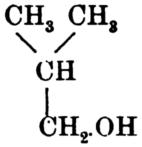
$$\begin{array}{l} CH_3 \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CH_2.OH \end{array}$$

(2)
Secondary
Normal.

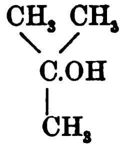


$$\begin{array}{l} CH_3 \\ | \\ CH_2 \\ | \\ CH.OH \\ | \\ CH_3 \end{array}$$

(3)
Iso-alcohol.



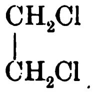
(4)
Tertiary.



Nine pentyl alcohols, $C_5H_{12}O$, can exist according to theory, of which only seven are as yet known.

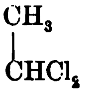
If two atoms of hydrogen in a paraffin be replaced, isomeric compounds are obtained in the second term of the series. Thus we have:

Ethylene Chloride.



$$\begin{array}{l} CH_2Cl \\ | \\ CH_2Cl \end{array}$$

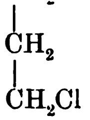
Ethidene Chloride.



$$\begin{array}{l} CH_3 \\ | \\ CHCl_2 \end{array}$$

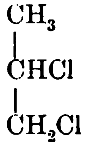
The chloride $C_3H_6Cl_2$ can exist according to theory in four modifications:

(1)
Trimethene
Chloride.



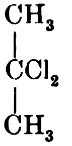
$$\begin{array}{l} CH_2Cl \\ | \\ CH_2 \\ | \\ CH_2Cl \end{array}$$

(2)
Propylene
Chloride.



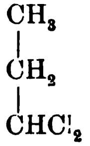
$$\begin{array}{l} CH_3 \\ | \\ CHCl \\ | \\ CH_2Cl \end{array}$$

(3)
Propidene
Chloride.



$$\begin{array}{l} CH_3 \\ | \\ CCl_2 \\ | \\ CH_3 \end{array}$$

(4)
Propionene
Chloride.



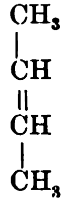
$$\begin{array}{l} CH_3 \\ | \\ CH_2 \\ | \\ CHCl_2 \end{array}$$

In the case of the hydrocarbons, C_nH_{2n}, a larger number of isomerides can exist than is possible in the case of the marsh-gas series. Thus, for example, we know only two butanes but three butylenes:

α-Butylene.

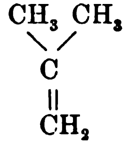
$$\begin{array}{l} CH_3 \\ | \\ CH_2 \\ | \\ CH \\ \| \\ CH_2 \end{array}$$

β-Butylene.



$$\begin{array}{l} CH_3 \\ | \\ CH \\ \| \\ CH \\ | \\ CH_3 \end{array}$$

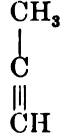
Isobutylene.



It has already been stated that the hydrocarbons of the series C_nH_{2n} have been assumed to contain free combining units. If this were the case, four propylenes and eight butylenes must exist. If, however, these hydrocarbons be supposed to contain two carbon atoms having a double linking, only one propylene and three butylenes can exist, and this has been proved to be the fact.

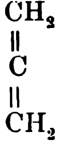
In the case of the hydrocarbons of the series C_nH_{2n-2}, a still larger number of cases of isomerism are possible. Thus, for instance, we have two substances having the formula C_3H_4.

Allylene.



$$\begin{array}{l} CH_3 \\ | \\ C \\ ||| \\ CH \end{array}$$

Iso-allylene.



$$\begin{array}{l} CH_2 \\ \| \\ C \\ \| \\ CH_2 \end{array}$$

A large group of carbon compounds are derived from benzene, C_6H_6. In these the carbon atoms are linked together in a peculiar way, the nature of which will be hereafter explained. The homologues of this series are formed by the replacement of one or more atoms of hydrogen by alcohol radicals, and hence a variety of isomerides is formed, such as the following:

(1) Ethyl-benzene. $C_6H_5.C_2H_5$

(2) Dimethyl-benzene. $C_6H_4\begin{cases} CH_3 \\ CH_3 \end{cases}$

(1) Propyl-benzene. $C_6H_5.C_3H_7$

(2) Isopropyl-benzene. $C_6H_5.CH(CH_3)_2$

(3) Methyl-ethyl-benzene. $C_6H_4\begin{cases} CH_3 \\ C_2H_5 \end{cases}$

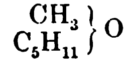
(4) Trimethyl-benzene. $C_6H_3\begin{cases} CH_3 \\ CH_3 \\ CH_3 \end{cases}$

The foregoing cases do not, however, exhaust the number of existing isomeric bodies, inasmuch as two or more atoms of hydrogen in the benzene may be replaced, and this replacement may take place in different positions in the molecule. Thus, as will be seen hereafter, there may be three isomerides having the composition of dimethyl-benzene, of methyl-ethyl-benzene, and of trimethyl-benzene; thus four hydrocarbons having the formula C_8H_{10} exist, and eight having the formula C_9H_{12}.

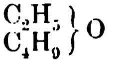
In these compounds, moreover, not only the hydrogen in the alcohol radical, but that in the benzene residue may be replaced in different positions, and thus the existence of a still larger number of isomerides in the benzene derivatives becomes possible.

83 (2.) *Metamerism.* The compounds classed under this head possess the same molecular weight, but contain two or more carbon groups connected together with a divalent or polyvalent radical. The number of bodies which may thus be grouped together is very large. A few simple examples will here suffice. If an atom of hydrogen in an alcohol be replaced by an alcohol-radical, an oxide or ether is obtained. Thus the following substances can be obtained, all having the composition $C_6H_{14}O$.

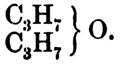
(1)
Methyl-pentyl ether.


$$\left.\begin{matrix}CH_3\\C_5H_{11}\end{matrix}\right\}O$$

(2)
Ethyl-butyl ether.


$$\left.\begin{matrix}C_2H_5\\C_4H_9\end{matrix}\right\}O$$

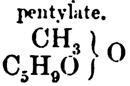
(2)
Dipropyl ether.


$$\left.\begin{matrix}C_3H_7\\C_3H_7\end{matrix}\right\}O.$$

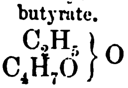
Inasmuch, however, as the radical propyl can exist in two isomeric forms, butyl in four, and pentyl in nine, it is possible, according to theory, that sixteen ethers having the above general formula may exist.

The so-called compound ethers or ethereal salts form a very important class of isomeric bodies. Thus, for example, the following compounds of the general formula $C_6H_{12}O_2$ are known:

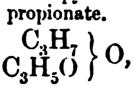
(1)
Methyl pentylate.


$$\left.\begin{matrix}CH_3\\C_5H_9O\end{matrix}\right\}O$$

(2)
Ethyl butyrate.


$$\left.\begin{matrix}C_2H_5\\C_4H_7O\end{matrix}\right\}O$$

(3)
Propyl propionate.


$$\left.\begin{matrix}C_3H_7\\C_3H_5O\end{matrix}\right\}O,$$

and in this case the variety of constitution exhibited by the radicals leads to the formation of eight distinct isomerides.

As a last example the amines having the general formula C_3H_9N may be cited:

(1) Propylamine.	(2) Isopropylamine.	(3) Methylethylamine.	(4) Trimethylamine.
$N\begin{cases}C_3H_7\\H\\H\end{cases}$	$N\begin{cases}CH(CH_3)_2\\H\\H\end{cases}$	$N\begin{cases}CH_3\\C_2H_5\\H\end{cases}$	$N\begin{cases}CH_3\\CH_3\\CH_3.\end{cases}$

The two first substances are isomeric compounds, the others metameric.

84 (3.) *Polymerism.* This division contains compounds possessing the same composition, but differing in molecular weight. The hydrocarbons of the series C_nH_{2n} may serve as an example:

Ethylene	C_2H_4
Propylene	C_3H_6
Butylene	C_4H_8
Pentylene	C_5H_{10}.
&c.	

The following compounds are also polymeric:

Acetylene	C_2H_2
Benzene	C_6H_6
Styrolene	C_8H_8
Dihydronapthalene	$C_{10}H_{10}$
Tetrahydroanthracene	$C_{14}H_{14}$
Distyrolene	$C_{16}H_{16}$.

As another series we have:

Formyl aldehyde	CH_2O
Acetic acid	$C_2H_4O_2$
Lactic acid	$C_3H_6O_3$
Grape sugar	$C_6H_{12}O_6$.

And again:

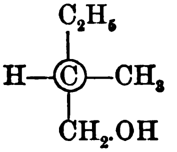
Acetaldehyde	C_2H_4O
Butyric acid	$C_4H_8O_2$
Paraldehyde	$C_6H_{12}O_3$.

85 (4.) *Physical Isomerism.* A number of bodies are known which according to their general deportment must be considered to possess the same chemical constitution, but which exhibit certain distinct differences in physical properties. Thus, they may crystallize in different systems or possess different melting points. These substances can readily be converted from the one into the other modification, and their isomerism is probably

due to a different arrangement of their molecules, analogous to the dimorphous and trimorphous inorganic compounds.

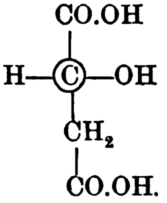
Many carbon compounds possess the property of rotating the plane of polarization, and such compounds generally exist in two or three modifications, assuming distinct optical properties, as for instance that of turning the plane of polarization more or less either to the right or to the left. In the case of crystallizable compounds this difference is rendered evident in the existence of hemihedral faces, which in one modification lie to the right in reference to the other faces, and in another modification lie to the left, so that the one crystal is the reflected image of the other. In the case of liquids a similar difference in molecular structure is exhibited in the phenomenon known as *circular polarization*, a property which is possessed by a large number of organic liquids. It has been pointed out by van't Hoff[1] and Le Bel,[2] that all optically active bodies contain one or more assymetric carbon atoms. By this is meant a carbon atom connected with four dissimilar groups of atoms, as shown by the following examples:

Optically active amyl alcohol.



$$\begin{array}{c} C_2H_5 \\ | \\ H-C-CH_3 \\ | \\ CH_2.OH \end{array}$$

Malic acid.



$$\begin{array}{c} CO.OH \\ | \\ H-C-OH \\ | \\ CH_2 \\ | \\ CO.OH. \end{array}$$

Hence we may conclude that optical isomerism is probably caused by different relative arrangement of the atoms which form the molecule. Further information on this point will be given under special heads.

86 (5.) *Unexplained Isomerism.* Lastly, cases of isomerism occur for which, up to the present, we have no sufficient explanation. Many cases of this kind have been long observed, but some of these have disappeared on finding that the differences were merely due to impurities contained in the substances.

On the other hand, cases are known of distinctly pure substances differing in their chemical properties and yet possessing the same constitutional formulæ. This, however, is not any

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[1] *La Chimie dans l'Espace.*

[2] *Bull. Soc. Chim.* [2], xxii. 337.

contradiction to the law of the linking of atoms, as might be supposed, but simply points to the conclusion that graphical formulæ cannot represent the arrangement of the atoms in space, about which, in fact, nothing is known. These rational formulæ possess a somewhat similar meaning to the parallelogram of forces in mechanics. They simply serve to give us a notion of the attraction which the single atoms in the molecule exert upon one another.

Compounds in which the isomeric relations cannot yet be explained, can as a rule be readily transformed one into the other.

CLASSIFICATION OF THE CARBON COMPOUNDS.

87 The carbon compounds may be classed in different groups according to the mode of linking of the carbon atoms.

I. *The Fatty Group.* To this belong all compounds in which the carbon atoms are connected together by a single linking as in the paraffins and their derivatives. The group receives its name from the fact that several of its compounds, such as the acids of the series $C_nH_{2n}O_2$ and others, occur in the fats of animals and plants. A characteristic property of these substances is that their chemical metamorphoses are principally brought about by substitution, that is, by one atom or group of atoms being removed and other groups occupying their places. For this reason the members of the fatty group have also been termed *saturated compounds.*

II. *Compounds containing relatively less hydrogen than the foregoing.* These contain carbon atoms united by double or triple linkage. The hydrocarbons which belong to this group form the following series:

$$C_nH_{2n}$$
$$C_nH_{2n-2}$$
$$C_nH_{2n-4}$$
$$C_nH_{2n-6}.$$

These compounds, as well as their substitution-products, are termed *unsaturated compounds,* as they possess the characteristic property of combining directly with hydrogen or with the elements of the chlorine group or their hydracids, and thus become *saturated compounds by addition.* This is caused by the rupture of one of the links of a doubly-linked carbon atom. The inverse operation can also be carried out, and the various hydrocarbons of this group can readily be obtained by the removal of hydrogen or chlorine from the saturated fatty compounds.

III. *The Aromatic Group.* The compounds belonging to this group are relatively much richer in carbon than those of the fatty group. In many chemical metamorphoses, however, they resemble the members of the latter group, as for example in their power of readily forming substitution derivatives. Only in rare instances do they yield additive products, and these, it is important to note, are not fatty bodies. Thus, for instance, the simpler hydrocarbons belonging to this series and having the general formula C_nH_{2n-6} are isomeric with the compounds of the second group of bodies, containing relatively less hydrogen. But whilst these latter by the addition, for example, of bromine, yield octobromides, $C_6H_6Br_8$, only six bromine atoms can be added to the simplest aromatic hydrocarbon yielding the hexbromide, $C_6H_6Br_6$. Hence we conclude that these compounds, rich in carbon, consist of groups of *closed chains*, each containing six atoms of carbon. The name aromatic group has been given to these because many of the bodies belonging to the group are contained in ethereal oils, balsams, gum-resins, and other bodies possessing an aromatic smell.

IV. *Compounds of Unknown Constitution.* A number of the compounds occurring in the vegetable and animal organism, possess constitutions so complicated that their determination has hitherto not proved possible. Indeed, not many years have elapsed since this remark applied to by far the larger number of organic compounds. By degrees, however, this group is becoming smaller, and in process of time it will doubtless entirely disappear.

88 *Different Methods of Classification.* Each of these chief groups contains several subdivisions, and these may be arranged in different ways. Perhaps the most systematic method of arrangement would be to commence each group with a discussion of the hydrocarbons, and then to follow on with a description of the series of substances obtained by the replacement of one, two, three, or more of the constituent atoms of hydrogen. Such a method of classification, however, labours under the

disadvantage that compounds which stand as a rule closely together, as, for example, the alcohols $C_nH_{2n+2}O$ and the acids $C_nH_{2n}O_2$, are thus found widely separated, whilst other groups possessing but little analogy, except in their empirical formulæ, are brought into proximity.

Hence it is desirable, alike for the sake of perspicuity as for the purpose of showing the genetic relationships existing between different bodies, to depart, in many cases, from such a systematic treatment and to arrange the compounds according as they are derived one from the other.[1]

FATTY BODIES AND COMPOUNDS CONTAINING RELATIVELY LESS HYDROGEN THAN THESE.

89 *Hydrocarbons of the Series* C_nH_{2n+2} *or the Paraffin Series.* Before the year 1848 none of the hydrocarbons belonging to this class were distinctly known, with the single exception of marsh-gas, the first term of the series. Chemists had, however, met with other members of the series, and had examined their properties, but their true nature was not fully understood. In the above year the investigations of Kolbe[2] on the electrolysis of the fatty acids, and those of Frankland[3] on the action of zinc on the iodides of the alcohol radicals, opened a new field of investigation which soon yielded a rich harvest. The hydrocarbons thus obtained were considered, from their mode of production, as the free radicals of the alcohols.[4] Gerhardt, however, proposed to double their formulæ in order to bring them into co-ordination with Avogadro's law, and he considered the so-called radicals to be homologues of marsh-gas. Hofmann[5] also gave his adhesion to this duplication of the formulæ, pointing out that the adoption of Kolbe and Frankland's formulæ led to an increment in the boiling point for each increment of CH_2, double that known to exist in other homologous series.

Together with the radicals Frankland discovered what he believed to be a distinct series of hydrocarbons. These were obtained by the replacement of the iodine in the iodide of the

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[1] Kekulé, *Lehrbuch*, i. 225.

[2] *Ann. Chem. Pharm.* lxix. 279; *Chem. Soc. Journ.* ii. 157.

[3] "On the Isolation of the Organic Radicals," *Chem. Soc. Journ.* ii. 263; iii. 30; iii. 322.

[4] Gerhardt and Laurent, *Compt. Rend.* 1849, 19; 1850, 11.

[5] *Chem. Soc. Journ.* ii. 121 (1850).

alcohol radical by hydrogen. He assumed these *hydrides* to be the true homologues of marsh-gas, and according to the views first expressed by Brodie,[1] these were believed to stand in the same relation to the radicals as the alcohols to their ethers:

Ethyl hydride.	Ethyl.
$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}$	$\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}$
Ethyl alcohol.	Ethyl ether.
$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O$	$\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O.$

Brodie likewise predicted the existence of mixed radicals, bodies standing in the same relation to the simple radicals as Williamson's mixed ethers do to common ether:

Ethyl ether.	Ethyl.
$\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O$	$\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}$
Ethyl-amyl ether.	Ethyl-amyl.
$\left.\begin{matrix}C_2H_5\\C_5H_{11}\end{matrix}\right\}O$	$\left.\begin{matrix}C_2H_5\\C_5H_{11}\end{matrix}\right\}.$

Such mixed radicals were soon afterwards isolated by Wurtz, who obtained them by the action of sodium on a mixture of the two iodides, as well as by the electrolysis of a mixture of two of the fatty acids. It was at this time generally believed that a real difference existed between the hydrides and radicals, the molecule of the latter being supposed to consist of two atoms. Still it seemed remarkable that the isomeric members of two such differently constituted groups not only do not differ in physical properties, but even exhibit a close analogy in their chemical characters. Indeed this similarity led Greville Williams,[2] who discovered many of the hydrocarbons of this group in the products of distillation of Boghead cannel, to consider them as radicals, chiefly because the several members differed from one another by the increment C_2H_4.

The chemical reactions of the radicals were at that time but incompletely known. One point, however, was ascertained, namely, that when acted upon by chlorine the radicals did not yield, as might have been expected, two molecules of the corresponding chloride, but two or more of the atoms of hydrogen of the hydrocarbon were found to be replaced by chlorine.

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[1] *Chem. Soc. Journ.* iii. 405 (1851).

[2] *Phil. Trans.* 1857, 447.

The next point requiring examination was the action of chlorine upon the hydrides. Dumas had already found that the first substitution-product of marsh-gas is the compound CH_3Cl, and Berthelot had shown that this substance is identical with methyl chloride. On the other hand, Frankland and Kolbe had obtained from ethyl hydride the chloride C_2H_5Cl, a substance which they believed differed from ethyl chloride.[1]

90 It was not until the year 1862 that our knowledge of this point became precise. In that year Pelouze and Cahours[2] showed that American petroleum consists almost entirely of a mixture of homologous hydrocarbons of the series C_nH_{2n+2}, and Schorlemmer[3] found the same in the distillation-products of cannel coal. The examination of these latter products showed that their monochlorinated substitution-products are really the chlorides of the alcohol radicals from which the alcohols and their other derivatives can be prepared, and hence that the hydrocarbons themselves are hydrides.

The next question was to ascertain precisely the nature of the action of chlorine upon the radicals themselves, and Schorlemmer[4] found that the two following:—

$$\begin{array}{cc} \text{Ethyl-amyl} & \text{and Di-amyl.} \\ \left.\begin{array}{l} C_2H_5 \\ C_5H_{11} \end{array}\right\} & \left.\begin{array}{l} C_5H_{11} \\ C_5H_{11} \end{array}\right\} \end{array}$$

yielded, respectively, chloride of heptyl, $C_7H_{15}Cl$, and chloride of decatyl, $C_{10}H_{21}Cl$; and from these the corresponding alcohols were prepared.[5]

He further proved that the radical methyl, or di-methyl, as it was afterwards called, is identical with hydride of ethyl, inasmuch as not only did the existence of the differences which had been previously observed between their physical properties prove to be a fallacy, but both bodies were converted on treatment with chlorine into ethyl chloride. About the same time Schöyen[6] showed that Frankland's di-ethyl was converted by chlorine into butyl chloride.

From this time forward the supposed distinction between radicals and hydrides may be said to have completely broken

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[1] *Chem. Soc. Journ.* i. 60.

[2] *Ann. Chim. Phys.* [4], i. 1; *Ann. Chem. Pharm.* cxxiv. 289; cxxvii. 190; cxxix. 87.

[3] *Chem. Soc. Journ.* xv. 419 (1862).

[4] *Chem. Soc. Journ.* xvi. 425.

[5] *Proc. Roy. Soc.* xiv. 164.

[6] *Ann. Chem. Pharm.* cxxx. 233; cxxxi. 76; cxxxii. 231.

down, and it was acknowledged that in the formation of the radicals two carbon atoms are combined exactly in the same way as they are connected together in the other compounds. That, for instance, in the radical di-methyl, the two carbon atoms are connected together exactly in the same way as the two carbon atoms are linked together in the ethyl compounds.

The lower members of this series are very volatile liquids. The boiling point rises with each increment of CH_2, and the highest members are crystalline solids. A mixture of these latter substances was discovered in the year 1830 by Reichenbach[1] in wood-tar. This was believed by him to be a definite chemical compound, to which he gave the name of *paraffin*, from *parum affinis*, its most important characteristic being its inactive properties. For a long time it was believed that paraffin belonged to the series of hydrocarbons, C_nH_{2n}, for in those days, as has been stated, the only member of the series C_nH_{2n+2} known was marsh-gas. Moreover the percentage compositions of the higher members of these two groups exhibit differences so slight that they fall within the errors of analysis, and it becomes impossible thus to determine to which of the two groups a substance belongs. This can, however, be readily ascertained when the substances are treated either with chlorine or bromine. These elements combine directly with the group C_nH_{2n}, but act with difficulty on the group C_nH_{2n+2}, giving rise to substitution-products. In addition to this, the members of the first of these groups are easily attacked by oxidizing agents, whilst those of the latter group are only oxidized with difficulty even by the most energetic reagents. In this respect paraffin distinctly belongs to the latter class.[2] On these grounds Henry Watts[3] has suggested that the name of paraffin should be made generic, and applied to all the members of this series of these hydrocarbons.

The paraffins are not attacked in the cold either by chromic acid, concentrated nitric acid, or sulphuric acid, or even by a mixture of the two latter acids, but if they are heated with dilute nitric acid, with chromic acid, or with a mixture of manganese dioxide and dilute sulphuric acid, they are slowly oxidized, the greater portion being completely converted into

[1] *Jahrb. Chem. Phys.* (Schweigg-Seidel) xxix. 436.
[2] *Chem. Soc. Journ.* xv. 419.
[3] Fownes, *Manual of Chemistry*, Tenth Edition, 518.

carbon dioxide and water. By the action of nitric acid, small quantities of the fatty acids as well as succinic acid and nitrates are produced, whilst by oxidation with chromic acid a small quantity of acetic acid is formed.[1] Chlorine, in the daylight, attacks these hydrocarbons but slowly. The liquid becomes warm, hydrochloric acid is evolved, and monochlorides are first produced. These, however, are readily converted, in the presence of nascent chlorine, into higher substitution-products. But the formation of this latter class of bodies may be prevented to a great extent by passing chlorine into the vapour of the slowly boiling hydrocarbon instead of into the liquid itself.[2] The explanation of this being that the monochlorides are less volatile than the hydrocarbons from which they are produced, so that they condense as soon as they are formed, and thus the chlorine comes almost exclusively in contact with the vapour of the hydrocarbon. The apparatus must, however, be protected from the direct sunlight, as otherwise complete decomposition takes place with evolution of light and heat and deposition of carbon.

When the monochlorides are treated with chlorine, further substitution takes place, but it is only in the case of the two lowest terms of the series that the whole of the hydrogen can be replaced by chlorine. Propane, C_3H_8, can be converted into hexchlorpropane, $C_3H_2Cl_6$; and hexane yields hexchlorhexane, $C_6H_8Cl_6$ as an end product, and even these are formed with difficulty. For in order to obtain these bodies, the decomposition must not only be carried on in the sunlight, but as soon as the action of the chlorine becomes feeble, iodine must be added.[3] The action of this latter element depends upon the formation of iodine chloride, which readily decomposes into its elements the liberated chlorine in the nascent or atomic condition acting more energetically than the same element in the molecular state. Then the nascent iodine combines anew with chlorine, and thus it plays a similar part to that of the oxides of nitrogen in the sulphuric acid manufacture. The chlorination of the paraffins can, however, be carried out further by heating the chlorinated products in closed tubes, together with chloride of iodine, under increased pressure. Propane thus treated yields in the first place octochlorpropane, C_3Cl_8, and this, by further action of chloride of iodine, is converted into hexchlorethane,

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[1] Schorlemmer, *Ann. Chem. Pharm.* cxlvii. 214.

[2] Schorlemmer, *Phil. Trans.* 1871.

[3] Schorlemmer, *Proc. Roy. Soc.* xviii. 29.

C_2Cl_6, and tetrachlormethane, CCl_4. Under the same conditions hexane yields, together with the two latter compounds, hexchlormesol, C_4Cl_6, and hexchlorbenzol, C_6Cl_6.[1]

Bromine likewise yields substitution-products. but not so readily as chlorine,[2] but by the action of excess of bromine under the influence of heat and pressure, substitution-products are formed similar to those which are obtained by the action of chloride of iodine.

CONSTITUTION OF THE PARAFFINS.

91 The paraffins whose constitution is known may be classed under four groups.

(1) *The Normal Paraffins.* In these the carbon atoms are connected together by simple linkage, no one atom being connected with more than two others. Of these the following have been examined :

		Boiling point.			Boiling point.
Methane	CH_4	gas	Heptane,	C_7H_{16}	98°·4
Ethane	C_2H_6	gas	Octane,	C_8H_{18}	125°
Propane	C_3H_8	gas	Nonane,	C_9H_{20}	148°
Butane	C_4H_{10}	1°	Dodecane,	$C_{12}H_{26}$	202°
Pentane	C_5H_{12}	38°	Hecdecane,	$C_{16}H_{32}$	278°.
Hexane	C_6H_{14}	70°			

(2) *Isoparaffins.* These contain an atom of carbon connected with three other carbon atoms, the other carbon atoms being joined by single linkage. The following members of this series are known :

Boiling point.

Trimethylmethane, $\mathrm{CH}\left\{\begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_3}\\ \mathrm{CH_3}\end{matrix}\right.$ −17°

Dimethylethylmethane, $\mathrm{CH}\left\{\begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_3}\\ \mathrm{C_2H_5}\end{matrix}\right.$ +30°

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[1] Krafft and Merz, *Ber. Deutsch. Chem. G s.* viii. 1296 ; Krafft, *ib.* ix. 1085 ; x. 801.

[2] Schorlemmer, *Phil. Trans.* for 1877, p. 49.

Methyldiethylmethane,	$CH\begin{cases}CH_3\\C_2H_5\\C_2H_5\end{cases}$	60°
Dimethylpropylmethane,	$CH\begin{cases}CH_3\\CH_3\\C_3H_7\end{cases}$	62°
Dimethylbutylmethane,	$CH\begin{cases}CH_3\\CH_3\\C_4H_9\end{cases}$	91°
Triethylmethane,	$CH\begin{cases}C_2H_5\\C_2H_5\\C_2H_5\end{cases}$	96°
Dimethylheptylmethane,	$CH\begin{cases}CH_3\\CH_3\\C_7H_{15}\end{cases}$	155°.

(3) *Mesoparaffins.* In these two or more carbon atoms occur, each connected with three other atoms of carbon. The name of this class is derived from the fact that they stand between the foregoing class and the group next following (*μέσος*, middle).[1] The following terms of this series are known:—

	Boiling point.
Tetramethylethane $(CH_3)_2CH.CH(CH_3)_2$	58°
Tetramethylbutane $(CH_3)_2CH.CH_2.CH_2.CH(CH_3)_2$	109°
Pentamethylbutane $(CH_3)_2CH.CH(CH_3).CH_2.CH(CH_3)_2$ . . .	130°
Tetramethylhexane $(CH_3)_2CH.CH_2.CH_2.CH_2.CH_2.CH(CH_3)_2$ . .	122°.

(4) *Neoparaffins.* In these compounds one atom of carbon is connected with four other carbon atoms. From having been lately discovered they have received the above name. The following have been prepared:

		Boiling point.
Tetramethylmethane,	$C(CH_3)_4$	9°·5
Trimethylethylmethane,	$C\begin{cases}(CH_3)_3\\C_2H_5\end{cases}$	45°
Dimethyldiethylmethane,	$C\begin{cases}(CH_3)_2\\(C_2H_5)_3\end{cases}$	86°.

92 *Modes of Preparation.* Various methods may be employed for the preparation of the paraffins. Some of them consist in bringing together two alcohol radicals, and thus effecting direct

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[1] Odling, *Phil. Mag.* [5], i. 205.

synthesis, as in reactions 1 and 2. Another method, as in reactions 4, 5, and 6, is that of liberating the alcohol radical from a compound and bringing it into combination with hydrogen.

Paraffins are, therefore, obtained by the following reactions:

(1) An alcoholic iodide is heated with zinc to 150° (Frankland). In this reaction a compound of the radical with zinc is first formed, and this is decomposed by an excess of the iodide.

$$(a)\quad 2\,Zn + 2\,C_2H_5I = Zn(C_2H_5)_2 + ZnI_2$$

$$(b)\quad Zn(C_2H_5)_2 + 2\,CH_3I = 2\,C_4H_{10} + ZnI_2.$$

(2) Sodium acts in a similar way to zinc, but much more readily and at a lower temperature (Wurtz). If a mixture of two iodides, such as those of ethyl and amyl, be employed, the following reaction takes place:

$$C_2H_5I + C_5H_{11}I + 2Na = C_7H_{16} + 2NaI.$$

At the same time the hydrocarbons butane (diethyl) and tetramethylhexane (diamyl), $C_{10}H_{20}$, are formed by reactions which are readily understood.

These, however, are not the sole products either of this or of Frankland's reaction, inasmuch as a small portion of the paraffins decompose into lower members of the paraffin group and into the hydrocarbons of the series C_nH_{2n}. Thus by the action of zinc upon ethyl iodide, not only do we obtain butane, but also ethane and ethylene:

$$C_4H_{10} = C_2H_6 + C_2H_4.$$

The higher members of the series are especially apt to undergo such decompositions. Thorpe and Young[1] found that when solid "paraffin" is repeatedly distilled it yields liquid paraffins which, according to their boiling points, appear to be normal ones, the whole series, beginning with pentane and reaching up to $C_{17}H_{36}$, being present; and at the same time the corresponding hydrocarbons of the series C_nH_{2n} are produced.

(3) The paraffins may be obtained synthetically by the electrolysis of the fatty acids (Kolbe). The decomposition which here occurs will be fully described under the particular acids. The first paraffin obtained in this way was tetramethylbutane or dibutyl, formed from valerianic acid:

$$2\,C_4H_9.COOH = C_8H_{18} + 2CO_2 + H_2.$$

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[1] *Chem. Soc. Journ.* xxvi. 260.

(4) When an alcoholic iodide is heated with zinc and water to 150° a paraffin is produced, whose molecule contains the same number of carbon atoms as the iodide:

$$2\,C_2H_5I + 2\,Zn + 2H_2O = 2C_2H_6 + ZnI_2 + Zn(OH)_2.$$

In this case also, the zinc compound of the alcohol radical is first formed, and this is at once decomposed in contact with water. Hence pure paraffins can be readily obtained by bringing such a zinc compound into contact with water, which acts upon it with great energy:

$$Zn(C_2H_5)_2 + 2H_2O = Zn(OH)_2 + 2\,C_2H_6.$$

Certain of the other metallic compounds of the alcohol radicals are decomposed by water in the same way, others, again, such as the mercury compounds, do not act on water, but are easily attacked by acids:

$$Hg(C_2H_5)_2 + HCl = C_2H_6 + Hg(C_2H_5)Cl.$$

(5) Nascent hydrogen effects an inverse substitution in the iodides. Thus if hexyl iodide be brought in contact with zinc and hydrochloric acid, hexane is formed:

$$C_6H_{13}I + H_2 = C_6H_{14} + HI.$$

The following reactions, however, take place at the same time

$$(a)\quad 2\,C_6H_{13}I + Zn = C_{12}H_{26} + ZnI_2$$
$$(b)\quad C_{12}H_{26} = C_6H_{14} + C_6H_{12},$$

thus giving rise to small quantities of hexylene and dodecane.

(6) When an alcoholic iodide is heated with an excess of hydriodic acid a paraffin is formed together with free iodine. As hydriodic acid converts all the alcohols, even those of the polyvalent radicals, into iodides, the alcohols can be readily converted into paraffins. Thus when mannitol is heated with hydriodic acid the following reactions occur:

$$(a)\quad C_6H_8(OH)_6 + 11\,HI = C_6H_{13}I + 6\,H_2O + 5\,I_2$$
$$(b)\quad C_6H_{13}I + HI = C_6H_{14} + I_2.$$

Berthelot[1] has indeed shown that when a large excess of concentrated hydriodic acid is employed, and the mixture exposed

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[1] *Ann. Chim. Phys.* [4] xx. 392.

to a high temperature, almost every carbon compound can be converted into a paraffin or a mixture of these substances. Thus, for example, butyric acid and succinic acid treated in this way yield butane:

$$(a)\quad C_4H_8O_2 + 6\,HI = C_4H_{10} + 2\,H_2O + 3\,I_2$$

$$(b)\quad C_4H_6O_4 + 12\,HI = C_4H_{10} + 4\,H_2O + 6\,I_2.$$

and aniline by this treatment yields hexane:

$$C_6H_7N + 11HI = C_6H_{14} + NH_4I + 5I_2.$$

Wood, coal, and even charcoal thus treated yield mixtures of paraffins. Graphite, on the other hand, remains unchanged.

As free iodine may, in these cases, give rise to complications, it is advisable to add amorphous phosphorus in order to prevent the liberation of iodine.

(7) Paraffins are likewise formed when the fatty acids or acids of the series $C_nH_{2n-2}O_4$ are heated with alkalis. Acetic acid thus treated yields methane:

$$CH_3.CO.ONa + HONa = CH_4 + CO(ONa)_2,$$

whilst by heating suberic acid with baryta hexane is obtained:

$$C_6H_{12}(CO_2H)_2 + 2\,Ba(OH)_2 = C_6H_{14} + 2BaCO_3 + 2H_2O.$$

These reactions are, however, usually not simple ones, a larger or smaller quantity of bye-products being at the same time formed.

93 The hydrocarbons obtained by dissolving cast-iron in acids also contain paraffins. By dissolving a manganiferous spiegel-iron in dilute sulphuric acid, Cloëz obtained a liquid in which the series of paraffins from decane, $C_{10}H_{22}$, to hecdecane, $C_{16}H_{34}$, were contained.[1]

Paraffins are also formed by the direct distillation of wood, coal, bituminous shale, fatty oils, resins, animal matter, and other organic substances. It has already been stated that Reichenbach was the first to obtain the solid members of the series. In this way he also obtained a mixture of the lower members, which are usually liquids. To this mixture he gave the name of *eupion* (εὖ, good, and πιόν, fat). He observed that these liquids are not attacked by sulphuric or nitric acid, or even by potassium or the alkalis.[2] Frankland[3] then noticed that the

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[1] *Compt. Rend.* lxxxv. 1003.

[2] *Ann. Chem. Pharm.* xiii. 217.

[3] *Ib.* lxxiv. 57.

lower boiling portion of this probably consisted of pentane (amyl hydride).

Liquid paraffins occur together with solid products in very large quantities in the products of the distillation of coal or of bituminous shales containing large quantities of hydrogen, such as Boghead cannel (Greville Williams), and cannel coal (Schorlemmer). From their boiling-points, these all appear to belong to the normal series of paraffins, and in this respect resemble those obtained by the distillation of the lime-soap obtained from Menhaden oil (the oil of the fish *Alosa Menhaden*).[1]

Paraffins also occur in nature. Several are contained in the different kinds of petroleum. That which is now obtained in such enormous quantity from Pennsylvania consists almost exclusively of normal paraffins, containing, however, together with these, small quantities of isomerides, whose constitution has not yet been ascertained, as well as other series of hydrocarbons, such as the groups C_nH_{2n}, C_nH_{2n-6}, and probably also groups lying between these.[2]

Petroleum almost always contains solid paraffin. Canadian petroleum is especially rich in these solid products, as is also that obtained by the distillation of Boghead cannel. Indeed, this latter substance contains a portion of the solid paraffins already formed, as may be shown by extracting it from the mineral with ether.[3]

Similar compounds occur as minerals in the coal measures as well as in the deposits of brown-coal and bituminous shale. These are known under the names of ozokerite, hatchettite, mineral tallow, mineral wax, &c. A solid paraffin, which probably possesses the formula $C_{16}H_{34}$, is contained in the oil of roses, and separates out in the crystalline form on cooling the oil.

A very remarkable occurrence of normal heptane has lately been observed by Thorpe[4] in the resin from a Californian pine (*Pinus sabiniana*). This will be described more specially hereafter.

94 *Application of Paraffins.* Paraffin as obtained on the

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[1] Warren and Storer, *Mem. Amer. Acad.* ix. 208.

[2] Schorlemmer, *Phil. Trans.* 1871, vol. clxii. part i. p. 111 ; *Chem. Soc. Journ.* [2], viii. 216 ; Warren, *Silliman's Amer. Journ.* xl. 89, 216 ; Pelouze and Cahours, *Compt. Rend.* liv. 1241 ; *Ann. Chim. Phys.* [4], i. 5.

[3] Bolley, *Ann. Chem. Pharm.* cxv. 61.

[4] *Chem. Soc. Journ.* 1879.

manufacturing scale is not chemically pure. The commercial products always consist of mixtures of paraffins, and frequently contain hydrocarbons belonging to other series.

The tar obtained by the distillation of bituminous shale, Boghead cannel, brown-coal or peat, is worked up for a variety of products, of which the most important are: (1) naphtha, chiefly used as a solvent; (2) illuminating oils, known in commerce as kerosene, photogene, paraffin-oil, solar oil, mineral sperm-oil, &c.; (3) lubricating oils; and (4) solid paraffins, used for candle-making, &c.

In order to obtain these several products, the crude oil, after it has been separated from the watery products of distillation, is distilled a second time, when coke remains behind. The distillate is then treated with caustic soda in order to remove phenol (carbolic acid) and similar bodies which impart a disagreeable smell to the oil. Then it is brought in contact with sulphuric acid, which takes up certain basic compounds which also have a disagreeable odour, and at the same time decomposes other bodies which impart a dark colour to the oil. It is then washed with water and dilute soda-lye and rectified. The first product which comes over is the naphtha, the second distillate is the illuminating oil, and after this comes the portion which is employed either alone or mixed with other suitable oils for lubricating purposes. As soon as the distillate begins partially to solidify, the receiver is changed, the solid portions being allowed to separate out in a cool situation as long as they will crystallise. The liquid is then drawn off and used as a lubricant, and the solid mass freed from the adherent liquid, dried in a centrifugal sieve, and then pressed in hair mats placed between iron plates heated to between 35° and 40°. The solid mass is then melted and heated to 150°, when it is mixed with 2 per cent. of sulphuric acid in order to decompose all adherent impurities. It is next washed with hot water, and lastly crystallised from solution in the higher boiling portions of the naphtha. The mother-liquor is poured off from the crystals, and any adherent mother-liquor removed from the fused mass by treatment with superheated steam. The solid paraffin thus obtained is white and odourless. As it is a mixture of different compounds, the melting-point of the different kinds varies between 40° and 60°. When warmed in the air at a temperature above 120°, it begins to evaporate, and at the same time absorbs oxygen, and becomes yellow. When the mass is extracted with alcohol, the unaltered paraffin dissolves, a soft brown elastic mass remaining behind.[1]

Solid paraffin is also obtained in large quantities from the impure naturally occurring ozokerite or mineral wax. This is found at Borislav, in Gallicia, and elsewhere, in the form of a yellow solid of the hardness of common beeswax, which is purified by a process similar to that just described.

Solid paraffin is chiefly used for the manufacture of candles. It is also used in chemical works and laboratories in place of oil for obtaining constant high temperatures, and for the purpose of rendering caoutchouc joints tight.

95 *Petroleum* (*oleum petræ*), also known as rock-oil or naphtha. Herodotus states that a substance known as *pissasphaltum* was obtained from the island of Zante, and was used for the purpose of embalming. Plutarch mentions the occurrence of the burning oil at Ecbatana, and Dioscorides, as well as Pliny, state that the rock-oil from Agrigentum in Sicily was used for illuminating purposes.

Other localities in which springs of rock-oil occur have been known for many centuries. These natural oils remained, however, for a long time almost unused, only small quantities of the product coming into the market, and being chiefly employed either for medicinal purposes or as lubricants. These substances were not introduced on the large scale until the year 1859, when the remarkable petroleum industry of the United States arose, and the demand thus aroused soon stimulated the production in other countries.

Petroleum is an unpleasant-smelling substance which, according to its place of occurrence, is either a colourless or yellowish liquid, usually possessing a bluish lustre, or a brown or black semi-solid buttery mass, gradually approaching in appearance the various minerals known as mineral-pitch, asphalt, or mineral resin, which have been formed either by the volatilization of the liquid hydrocarbons or by their gradual oxidation. The different kinds of petroleum are all mixtures of a number of hydrocarbons occurring in varying proportions.

Petroleum is found in almost all the geological formations from the oldest up to the most recent of the stratified rocks. The oil-region of Pennsylvania is a narrow band about 60 miles in length, lying between Pittsburg and Lake Erie. It occurs,

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[1] Bolley, *Schweiz. Polyt. Zeitsch.* xiii. 65.

like the Canadian deposits, in the Devonian formation.[1] These latter extend over a large area, lying between Lake Erie and the River Hudson. The deposits in Ohio, Virginia, Tennessee, Kentucky, and California are of less magnitude.

A variety of theories have been broached to explain the origin of the petroleum springs.[2] That which is generally received is that petroleum is a product of decomposition of organised material. On the other hand, Byasson[3] and Mendelejeff[4] are of opinion that it is produced by the infiltration of water into the interior of the earth, where, coming in contact with molten iron or other metals containing combined carbon, it forms petroleum exactly as a similar mixture of hydrocarbons is obtained by the solution of cast-iron in dilute acids. This hypothesis is rendered somewhat more probable by the observation made by Silvestri[5] of the occurrence of petroleum in certain lavas of Etna. This amounts to 1 per cent. of the solid lava, and consists partly of liquid products boiling from 79° to 400°, and partly of solid paraffins.

In addition to the above-mentioned sources of petroleum, the following rock-oil springs are of importance. Those already mentioned, situated in the island of Zante; those in the Crimea and the Caucasus, where at Baku, on the west shore of the Caspian, the sacred fire has burnt for an unknown period, and where, especially in summer, the springs are so powerful that a jet of oil issues to a height of 30 feet. Other well-known sources of petroleum occur in Persia, Burmah, India, China, in Trinidad, Barbadoes, &c. In Europe petroleum is also found in Italy, Gallicia, Bavaria, Hanover, Holstein, and Alsace.

96 *The Petroleum and Paraffin Oil Manufacture* took its rise in England about the year 1847, when a spring of dense petroleum, having a specific gravity of 0·9, was discovered in a coal mine at Alfreton, in Derbyshire, by Dr. Lyon Playfair, who communicated the fact to Mr. James Young and Mr. Meldrum. In conjunction with Mr. Meldrum, Mr. Young succeeded in rendering this available for a period of two or three years. After this period the spring was exhausted, and it became necessary to seek for a source from which a material similar to petroleum could be obtained. Common coal, such as that from which Reichenbach

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[1] *Die Petroleumindustrie Nordamerikas*, Wien, 1877.

[2] *Neues Handwörterbuch*, iii. 39.

[3] *Monit. Scientif.* 1876, 1077.

[4] *Rèvue Scientif.* 1877, 409.

[5] *Gaz. Chim. Ital.* 1877, 1; *Zeitsch. Kryst.* i. 402.

first obtained paraffin oil and paraffin, yields, however, so small an amount of tar products on distillation that it was impossible to employ this as a source of petroleum. Mr. Binney found another natural source of petroleum in a peat bog at Down-holland, and he endeavoured, unsuccessfully, to obtain this substance artificially by the destructive distillation of the peat. Another material was, however, discovered, somewhat approximating to coal, or intermediate between bituminous shale and what is commonly known as coal, at Bathgate, in Scotland, and this was being introduced for gas-making under the name of Boghead gas-coal just about the time when the exhaustion of the petroleum spring in Derbyshire caused Messrs. Binney and Young to search for another source of paraffin for the preparation of lubricating and burning oils. After many trials with other materials Mr. Young, in 1850, became acquainted with the Boghead or Torbane Hill mineral, and found that it yielded on distillation an unusually large amount of paraffin. He at once obtained a patent (No. 13,292) for the manufacture of oils from it, and thus founded the well-known works at Bathgate, which exist to the present day, for the preparation of paraffin oils and solid paraffin.

97 *American Oil-wells.* The occurrence of petroleum in Pennsylvania had long been known, and the Indians were in the habit of employing it as a medicine for outward application. At the beginning of this century a gallon of this rock-oil cost upwards of £4, but in the year 1843 its price had sunk to five shillings. The first proposition to employ bore-holes for obtaining a supply of the petroleum was made by G. H. Bissel, and on the 27th August, 1859, Mr. Drake opened the first bore-hole at Titusville. This gave a daily yield of 880 gallons of oil. Shortly afterwards the oil mania broke out, and this reached its maximum in the year 1861, when Funk bored the first flowing-well, which yielded daily about 10,000 gallons, and shortly afterwards another spring which yielded over 100,000 gallons per diem. Since this time a large number of equally fruitful wells have been bored.

Crude petroleum was first worked up for illuminating oil, which, as soon as improved lamps for burning petroleum were introduced, became widely used throughout Europe, thus giving rise to the petroleum industry in Canada, Gallicia, and other places. The oil wells of Pennsylvania yield annually over twenty million of gallons of oil.

The oil is accompanied by a considerable quantity of gaseous products. These chiefly consist of hydrogen, marsh-gas, and ethane.[1] The amount of the gas thus evolved is in some localities so large that it is used not only at the spot where it issues for heating and illuminating purposes, but is carried in pipes for very considerable distances serving to heat boilers, blast-furnaces and puddling-furnaces, &c.

The following description from the pen of Professor Lawrence Smith[2] gives some idea of the size of these gas-springs:—"The principal oil-wells are found in Butler county, Pennsylvania, lat. 40° 30′, long. 80°. Wells of minor importance are also found in the neighbouring counties. The two most productive wells are those of Burns and Delameter, about 30 miles from Pittsburg. Their depth is about 1,600 feet, for they are bored down to the fourth layer of sand. The Burns well has never given oil, but the one at Delameter was a petroleum well of 1,600 liters; it now gives gas at such a pressure that plummet-lines weighing 800 kilos can be drawn out of it with the hand. The Delameter well is situated in a valley surrounded by mountains, and furnishes heat and light to the whole neighbourhood. A large number of pipes diverge from this well; one conducts the gas direct to the cylinder of an engine which, with this pressure alone, acquires an enormous speed. Another pipe feeds a flame capable of reducing as much iron-ore as half the blast-furnaces of Pittsburg can put out in a day. Twenty yards further on is the mainpipe of the wells; from a pipe 3 inches in diameter issues a flame 40 feet high, the noise of which shakes the hills. For a distance of 50 feet round the earth is burnt up; but further off the vegetation is tropical, and enjoys a perpetual summer. On a calm night the noise can be heard at a distance of 15 miles; at 4 miles the noise is like that of a train passing near, whilst close by it resembles that of a thousand locomotives blowing off steam. At the distance of a furlong the noise is like the continued roar of artillery, the human voice can scarcely be heard, and the flame reaches a height of 70 feet. In winter the surrounding mountains are covered with snow, but on two acres around the well the grass is green, except in the immediate neighbourhood, where the soil resembles lava."

The oil, which either flows from the wells or is pumped up, also contains gaseous paraffins in solution, especially ethane,

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[1] Sadtler, *American Chemist*, 1876, p. 98; Fouqué, *Compt. Rend.* lxvii. 1045.

[2] *Journ. Chem. Soc.* 1879, i. p. 287.

propane, and butane.[1] These gases, which are given off in the distillation of the crude oil, are again condensed by pressure, and the liquor obtained, consisting mainly of butane, is termed *cymogene*, and is employed for the production of artificial cold. The products boiling at about 18° are known as *rhigolene*, and it has been suggested to employ this as an anæsthetic agent.

The products boiling up to about 170° are distinguished as gazoline, naphtha, and benzine, ligroin, or petroleum-spirit. These are partly used for illuminating purposes, specially constructed lamps being employed for burning them; or they are used for saturating air or hydrogen, the mixture of vapour and gas being burnt in an ordinary gas-burner. Another use of petroleum-spirit is as a substitute for turpentine, as a solvent for india-rubber, and for oil in the woollen manufacture, &c.

The oil boiling above 170° is termed "standard kerosene," or "mineral sperm" oil, having a "flashing-point" of 150° F., and is used for burning in the ordinary paraffin lamps.

According to the Act passed in 1871 "for the safe keeping of petroleum,"[2] no oil can be sold which evolves combustible vapour at a temperature of 100° F. (37°·8 C.).

At the request of the Government, Professor Abel has lately investigated the various methods in use for determining the "flashing-point" of petroleum. He finds these to yield unsatisfactory results, and he proposed a new system of testing which has now been adopted by Government, and embodied in an Act of Parliament. A standard apparatus for this purpose is placed in charge of the Weights and Measures Office, and every apparatus has to be stamped and tested so as to be identified as a legal apparatus. The flashing-point of 73° as furnished by the new test is equivalent to the minimum flashing-point of 100° as obtained by the older methods.

Preparation of the Normal Paraffins from Petroleum. It has already been mentioned that Pennsylvanian petroleum, as well as the lighter oils obtained from Boghead coal and cannel, contain the normal paraffins. In order to obtain these in the pure state, Greville Williams decomposes the mixtures which are contained in the petroleum by carefully treating the oil with concentrated nitric acid, when the other hydrocarbons, &c., are partly oxidised and partly converted into heavy volatile nitro-compounds. As, however, concentrated nitric acid acts very violently on the mixture, and sometimes may even cause

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[1] Ronalds, *Journ. Chem. Soc.* xviii. 54.

[2] 34 & 35 Vict. c. 105.

the ignition of the oil, it is better first to shake the oil repeatedly with concentrated sulphuric acid until the substance is no longer coloured, and then to act on the residue with concentrated nitric acid, or with a mixture of the commercial acid and sulphuric acid. When no further action takes place, the oil is separated from the acid, washed with water and caustic soda solution, and dried over solid caustic potash. It is then distilled in order to separate it from any adherent nitro-compounds, and repeatedly rectified over sodium, when it may be separated into its constituents by repeated fractional distillation. As this process is very often employed for the separation and purification of volatile bodies, we shall here shortly describe it.

FRACTIONAL DISTILLATION.

98 When a mixture of two liquids whose boiling-points do not lie close together is subjected to distillation, a large portion of the more volatile body comes over at the beginning; but the boiling-point gradually rises, and more and more of the vapour of the less volatile mixes with that of the more volatile compound. It is only when the difference between the boiling-points of the two bodies is very considerable that it is possible to effect an almost complete separation by one distillation. In such a case, when the operation is carried on very slowly, the more volatile body distils at a nearly constant temperature; and as soon as all has passed over, the thermometer rises rapidly to the boiling-point of the less volatile compound. But in most instances it is impossible to obtain even an approximate separation by one distillation only. By collecting separately the portions distilling between certain intervals of temperature, say between each 5° or 10°, the first will consist chiefly of the lower boiling body, and the last of the less volatile substance, whilst the composition of the greater portion, boiling between these two points, remains very similar to that of the original mixture.

The following example shows how imperfectly even bodies whose boiling-points do not lie close together can be separated by one distillation. A mixture of 100 grams of ethyl alcohol (boiling-point 78°·4) and 100 grams of amyl alcohol (boiling-point 132°) was distilled from a long-necked flask, and the distillate collected in seven fractions, the composition of which was found by optical analysis to be as follows:

Boiling-point . . .	80°-90°	90°-100°	100°-110°	110°-120°	120°-130°	130°-131°	131°-132°
Weight of fraction . .	47	45	25	14	18	11	36
Per cent. of ethyl alcohol .	88·1	82	61·5	52·1	18·4	4·5	0·2
Per cent. of amyl alcohol .	11·9	18	38·5	47·9	81·6	95·5	99·8
	100·0	100	100.0	100·0	100·0	100·0	100·0

Four grams of pure amyl alcohol remained in the flask.

It is not difficult to explain why, in such a distillation, the less volatile body distils so much below its boiling-point. As is well-known, all volatile bodies evaporate below their boiling-points, and this takes place with the greater facility the higher the tension of the vapour and the quicker the surrounding atmosphere is changed. Now these conditions are fulfilled on boiling a mixture of two liquids; the vapour of the lower boiling body carries that of the less volatile substance with it on passing through the mixture, and being quickly condensed, a new atmosphere is constantly formed.

In ordinary cases such mixtures contain more than two compounds. Thus the so-called fusel-oil is a mixture of several homologous alcohols. In order to isolate from such mixtures tolerably pure compounds, the different fractions obtained in the first distillation must again be submitted to the same operation, and those portions which distil between the same intervals of temperature collected separately, and this process repeated until bodies with a nearly constant boiling-point have been obtained. A complete separation, however, cannot be effected in this way; since the substances obtained by this method, although they may have a constant boiling-point, are never perfectly pure, and require to be afterwards treated by some different process to ensure their perfect purity.

99 The apparatus used for the purpose of fractional distillation in the laboratory is that suggested by Würtz and shown in Fig. 54. The flask A contains the boiling mixture; the vapours of the hydrocarbons pass into the bulb-tube *c*, in which a thermometer is placed, and the less volatile portions are here partly condensed as the vapour comes in contact with a large surface cooled by the atmosphere. The vapour which is not

condensed passes next into the Liebig's condenser, C, surrounded by cold water, and from this the liquid can be collected in various fractions in the receiver B.

Linnemann[1] has improved on this method, inasmuch as he places cups of platinum gauze in the upright tube through which the vapour passes (Figs. 55 and 56). The liquid condenses on these, and falls back through the meshes. The vapours are thus washed by the liquid, and come in contact with a column of liquid whose temperature is always lower than that of the mass of the liquid in the flask. When this apparatus is in use, the tube and bulbs gradually become filled with liquid and all the vapour is condensed. It is therefore necessary to remove the flame from time to time in order that the liquid may flow back again. In this way the process of distillation is rendered slower, and an improvement has been introduced by the attachment of side-tubes to the bulbs (Figs. 57 and 58), down which the condensed liquid flows regularly back into the flask.

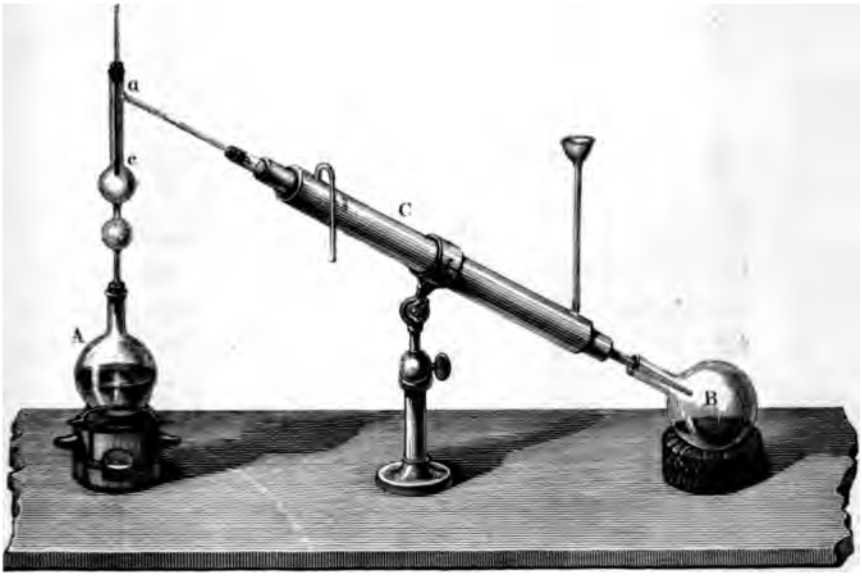

FIG. 54.

100 An apparatus somewhat different from this has been employed by Warren[2] in the fractional distillation of tar-oils and

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[1] *Ann. Chem. Pharm.* clx. 195.

[2] *Ann. Chem. Pharm.* Suppl. iv. 51.

petroleums. This permits a complete control over the temperature of the vapour, accomplished by an air-bath (*a a*, Fig. 59), round


Fig. 55.


Fig. 56.

Fig. 57.

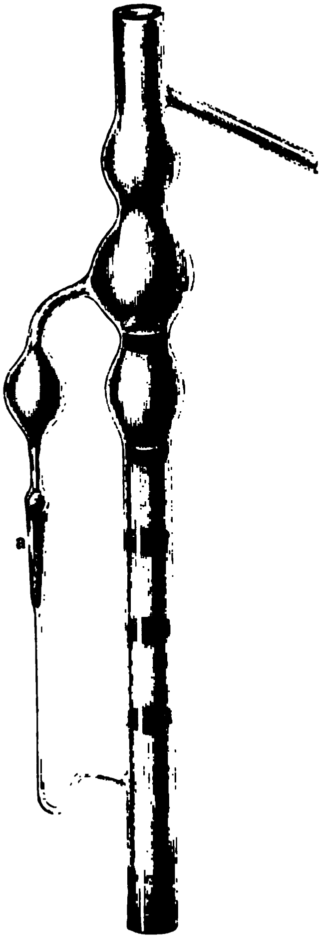

Fig. 58.

which a spiral tube is placed, connected with the boiling-flask. The temperature of this air-bath is regulated by a lamp. The liquid used for heating the air-bath may be either water, oil, or fusible metal, and into this the thermometer (*t*) is placed. The boiling of the liquid and the temperature of the bath are so regulated that the liquid boils somewhat rapidly. In distilling petroleum the difference in temperature between the boiling liquid and the air-bath was, to begin with, about 35° or even more. This difference became gradually smaller as the various fractions were redistilled, until at last it almost disappeared. An apparatus of a similar kind, but on a larger scale, as used by Warren, is shown in Fig. 60.

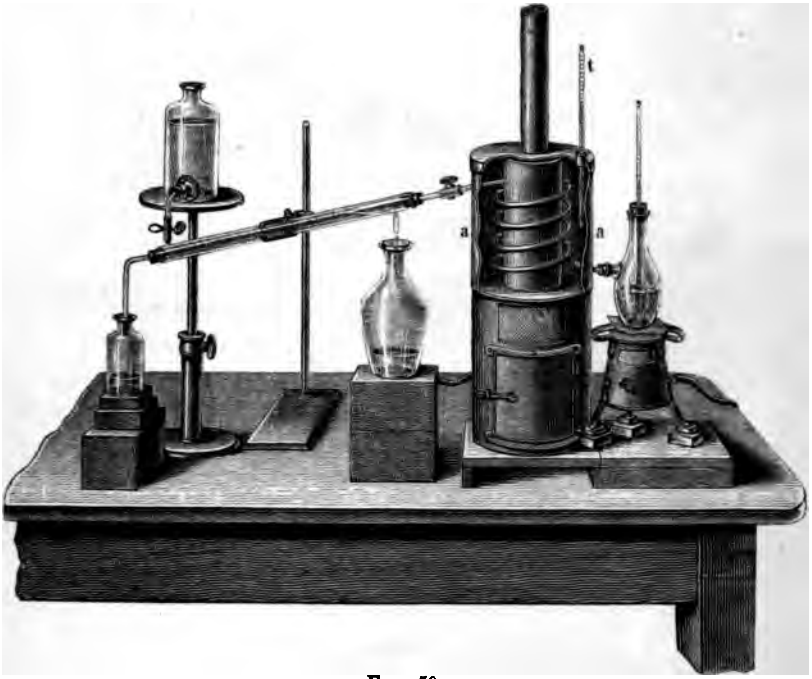

FIG. 59.

101 Even the approximate separation of volatile substances cannot, however, always be carried out by fractional distillation, even when the boiling-points are considerably removed from one another. Thus, for example, if a mixture of aniline boiling at 182° and water be distilled, the aniline distils over first. In such a case the boiling-point of the mixture is frequently lower than that of the more volatile body. Pierre and Puchot[1] found

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[1] *Compt. Rend.* lxxiii. 599, 788.

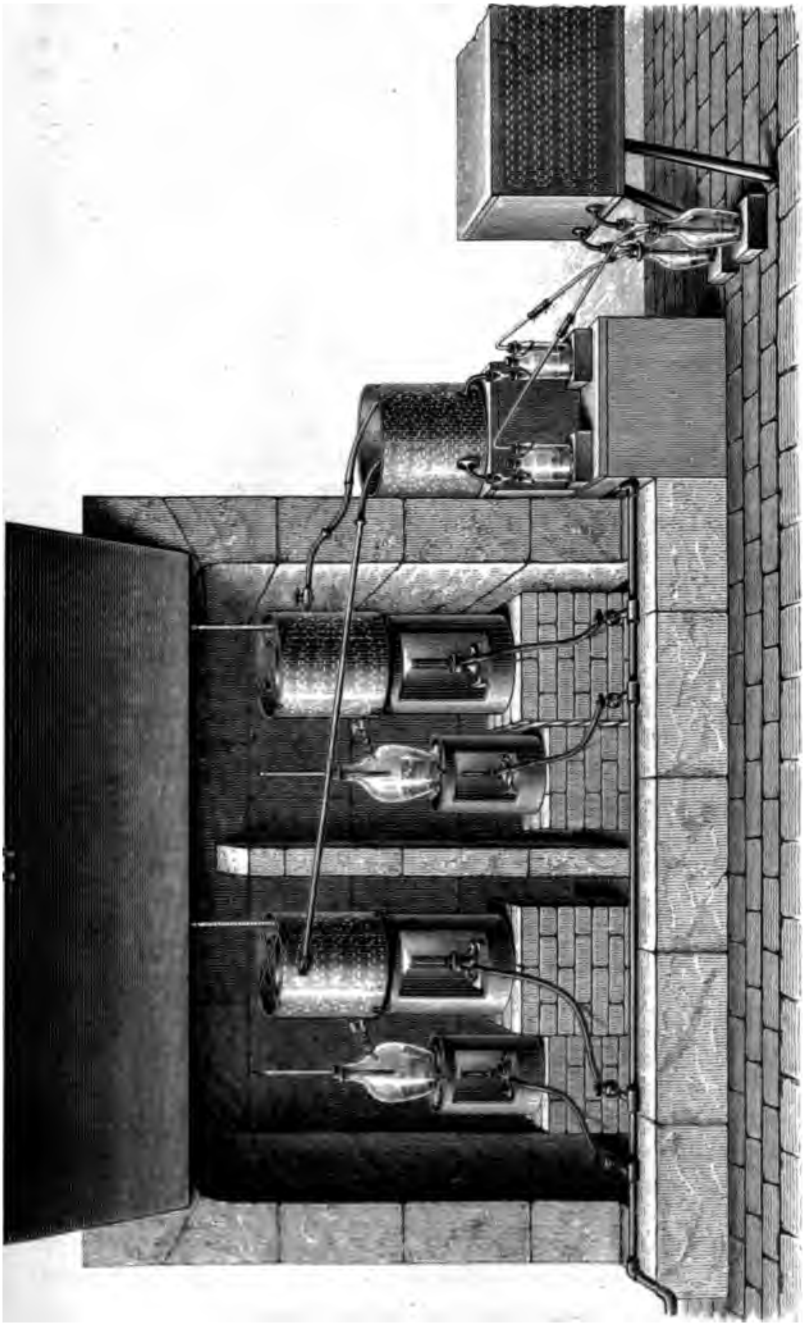

FIG. 60.

that a mixture of water and of amyl alcohol, which boils at 132°, begins to boil at 96°, and the distillate contains 2 volumes of water to 3 of amyl alcohol. Similar observations have been made with other mixtures.

Wanklyn[1] has shown that, when a mixture of equal parts by weight of two liquids of different boiling-points is distilled, the quantity of each constituent in the distillate is proportional to the product of its vapour density and vapour tension at the temperature of ebullition of the fraction. Hence, if the vapour tensions and vapour densities of the two liquids are proportional, the mixture will distil unchanged. Berthelot has confirmed this conclusion. He found that a mixture of 90·9 parts of carbon disulphide, which boils at 46°, and 9·1 parts of ethyl alcohol, boiling at 78°·4, possesses a constant boiling-point of 78°·4, and distils without undergoing any alteration in composition. Thorpe[2] has added another example in corroboration of this conclusion, as he observed that, when a mixture of equal volumes of carbon tetrachloride, boiling at 76°·6, and methyl alcohol, boiling at 65°·2, is distilled, 46·5 per cent. of the whole boils between 55°·6 and 59°, that is to say, nearly 10° lower than the boiling-point of the most volatile constituent. The distillate contains, to 1 part of methyl alcohol, 3·61 parts of tetrachloride of carbon, and by multiplying the vapour tensions of the two liquids at 55°·7 by their vapour densities almost exactly the same relation is obtained:

$$\frac{372{\cdot}4 \times 76{\cdot}69}{487{\cdot}4 \times 15{\cdot}97} = 3{\cdot}67.$$

When the residue is distilled further, almost pure tetrachloride of carbon comes over first, and afterwards pure methyl alcohol.

A striking lecture experiment, illustrating the effect of the admixture of the two liquids, is to fill three barometer tubes with mercury and to pass up into the first a few drops of methyl alcohol, into the second a few drops of carbon tetrachloride, and into the third a small quantity of a mixture of methyl alcohol and carbon tetrachloride in the proportion of 3 cbc. of the former to 5 cbc. of the latter. In the first tube the mercury will be depressed about 80 mm., in the second 70 mm., whilst in the third it will sink through 130 mm. (Thorpe).

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[1] *Phil. Mag.* [4] xlv. 129.

[2] *Journ. Chem. Soc.* 1879, 544.

THE COMPOUNDS OF THE MONAD ALCOHOL RADICALS.

C_nH_{2n+1}.

102 In the following chapter will be found a short description of the chief families of the above compounds, arranged in the order in which their chemical history will be considered in the sequel.

These compounds are derived from the paraffins by the substitution of one atom of hydrogen by other atoms or groups of atoms. They may, therefore, be regarded as compounds of monad radicals, to which the name of *the alcohol radicals* has been given, because the alcohols were the first compounds of these bodies which were studied, and even to the present day these bodies are employed as the point of departure for the preparation of the other compounds.

The Alcohols are hydroxides, and in many cases exhibit analogous properties to the hydroxides of the metals. Hence Liebig, when he established the radical theory, compared ethyl alcohol to caustic potash. The latter substance was then supposed to be a compound of potassium oxide with water, or hydrated potash, and alcohol was accordingly considered as the hydrate of ethyl oxide. According to the theory of types, it was considered as water, in which 1 atom of hydrogen is replaced by ethyl, but it may just as truly be considered to be ethane, in which 1 atom of hydrogen has been replaced by hydroxyl, or, in other words, it is formed by the union of two monad residues, ethyl, C_2H_5, and hydroxyl, OH.

Ethereal Salts or Compound Ethers. The alcohols are converted by the action of acids into compound ethers, the alcohol radical replacing, either partially or wholly, the hydrogen of the acid:

$$(a)\quad C_2H_5.OH + HCl = \overset{\text{Ethyl chloride.}}{C_2H_5Cl} + H_2O.$$

$$(b)\quad C_2H_5.OH + HO.NO_2 = \overset{\text{Ethyl nitrate.}}{C_2H_5O.NO_2} + H_2O.$$

$$(c)\quad C_2H_5.OH + \left.\begin{matrix}HO\\HO\end{matrix}\right\}SO_2 = \overset{\text{Hydrogen ethyl sulphate.}}{\left.\begin{matrix}HO\\C_2H_5O\end{matrix}\right\}SO_2} + H_2O.$$

Other modes of formation of compound ethers may be mentioned:

(*a*) A silver salt is heated with an alcoholic iodide:

$$Ag_2CO_3 + 2C_2H_5I = (C_2H_5)_2CO_3 + 2\ AgI.$$

(*b*) Absolute alcohol is acted on by an acid chloride:

$$POCl_3 + 3HO.C_2H_5 = PO(OC_2H_5)_3 + 3HCl.$$

$$SiCl_4 + 4HO.C_2H_5 = Si(OC_2H_5)_4 + 4HCl.$$

(*c*) A salt of the corresponding acid is distilled with a salt of ethyl—sulphuric acid, or other corresponding alcoholic sulphate:

$$KClO_4 + K(C_2H_5)SO_4 = C_2H_5.ClO_4 + K_2SO_4.$$

The alcohols can again be obtained from the ethereal salts or compound ethers by heating them with an alkali, thus:

$$C_2H_5O.NO_2 + KOH = C_2H_5OH + KO.NO_2.$$

Haloid Ethers. The compounds of the alcohol radicals with the elements of the chlorine group are termed haloid ethers. These are formed in a variety of ways. Thus, for example, the chlorides and bromides are obtained by the action of the corresponding haloid elements on the paraffins, and also by the action of the corresponding phosphorus compounds on the alcohols:

(*a*) $C_2H_5.OH + PCl_5 = C_2H_5Cl + POCl_3 + HCl.$

(*b*) $C_2H_5.OH + PBr_5 = C_2H_5Br + POBr_3 + HBr.$

When an excess of alcohol is present, the hydracid formed as well as the phosphoryl compound react upon it, the amount of the haloid ether being increased:

$$3C_2H_5OH + POCl_3 = 3C_2H_5Cl + PO(OH)_3.$$

In this case, however, the free phosphoric acid acts upon another portion of the alcohol, and a phosphate is produced.

In order to prepare the iodides, the alcohols are heated with concentrated hydriodic acid, or, better, they are treated directly with iodine and amorphous phosphorus:

$$5C_2H_5OH + 5I + P = 5C_2H_5I + H_3PO_4 + H_2O.$$

The alkalis usually act on the haloid ethers in a different way, and instead of obtaining the alcohol, the hydracid is separated and an olefine formed. Hence, in this case, freshly precipitated moist silver oxide is usually employed, and this acts as if it were the hydroxide AgOH.

The alcohols may also be readily obtained from the haloid ethers by converting the latter into the ethereal salts of organic acids and then decomposing these by alkalis. The same end may likewise be attained by heating the haloid ethers with water under pressure:[1]

$$C_4H_9Cl + H_2O = C_4H_9OH + HCl.$$

This reaction serves as a striking example of the influence of mass, for whilst fuming hydrochloric acid easily converts butyl alcohol into the chloride and water, exactly the opposite reaction takes place in presence of a large quantity of water, inasmuch as a weak acid does not attack the alcohol. Hence it follows that, when an alcohol is heated with an acid, not in excess, a condition of equilibrium is attained when the acid becomes so dilute that its action ceases.

103 *Simple and Mixed Ethers* are formed when the hydrogen of an alcoholic hydroxyl is replaced by an alcohol radical. Hence these bodies are oxides of the radical, standing in the same relation to the alcohols as potassium oxide does to caustic potash.

These bodies can be obtained by a variety of reactions:

(1.) The alkali-metals dissolve in alcohols with evolution of hydrogen. Sodium and ethyl alcohol thus form sodium ethylate, $C_2H_5.ONa$, and if this be warmed with ethyl iodide, ethyl oxide or diethyl ether is obtained:

$$\left.\begin{matrix}C_2H_5\\Na\end{matrix}\right\}O + \left.\begin{matrix}C_2H_5\\I\end{matrix}\right\} = \left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O + NaI.$$

Ethers which contain the same radical twice are termed *simple ethers*, whilst those which contain two different alcohol radicals are termed *mixed ethers*. If in the above reaction ethyl iodide be replaced by methyl iodide, methyl-ethyl ether, $\left.\begin{matrix}CH_3\\C_2H_5\end{matrix}\right\}O$, is obtained.

(2.) Ethers are also formed when the alcohols are heated with concentrated sulphuric acid. In this case the alcoholic hydrogen sulphate is first formed, and this is decomposed by the excess of alcohol, as follows:

$$SO_2\left\{\begin{matrix}OC_2H_5\\OH\end{matrix}\right. + \left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O = \left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O + SO_2\left\{\begin{matrix}OH\\OH.\end{matrix}\right.$$

The mixed ethers may also be obtained in this way. Thus

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[1] Niederist, *Liebigs Ann.* clxxxvi. 388; cxcvi. 349.

methyl-ethyl ether is obtained by heating hydrogen ethyl sulphate with methyl alcohol.

(3.) When an alcohol is heated with an iodide, an ether is also formed, and this occurs when concentrated hydriodic acid is heated with an excess of alcohol, the following reactions taking place:

$$(1)\ C_5H_{11}.OH + HI = C_5H_{11}I + H_2O.$$

$$(2)\ C_5H_{11}I + C_5H_{11}OH = (C_5H_{11})_2O + HI.$$

A small quantity of hydriodic acid suffices to convert a large quantity of alcohol into ether. The reaction continues until a certain quantity of water is formed, when a condition of equilibrium is attained.

Hydrosulphides and Sulphides. The hydrosulphides are also termed the *thio-alcohols*, as they are obtained (1) from the alcohols by the substitution of sulphur for oxygen, thus by acting on the alcohols with phosphorus pentasulphide:

$$5C_2H_5OH + P_2S_5 = 5C_2H_5SH + P_2O_5.$$

Free phosphorus pentoxide is, of course, not formed, out the thio-phosphates, such as $(C_2H_5)_2HPO_2S_2$ and $(C_2H_5)_3\,PO_2S_2$.

(2.) The hydrosulphides are also formed by the action of an alcoholic chloride on potassium hydrosulphide:

$$C_2H_5Cl + KSH = C_2H_5.SH + KCl.$$

(3.) Also by heating a solution of the latter compound with potassium ethyl sulphate:

$$KSH + K(C_2H_5)SO_4 = C_2H_5.SH + K_2SO_4.$$

The thio-alcohols are, like many volatile sulphur compounds, distinguished by their disagreeable smell. They stand in the same relation to common alcohol as sulphuretted hydrogen does to water, and resemble this compound inasmuch as they act as weak acids, and as one atom of hydrogen can easily be replaced by metals. Amongst these metallic compounds those with mercury are the most characteristic. They are formed when a hydrosulphide is brought in contact with mercuric oxide:

$$2\,C_2H_5SH + HgO = (C_2H_5S)_2Hg + H_2O.$$

In consequence of this relation the thio-alcohols have been termed *mercaptans* (mercurium captans), and their metallic compounds *mercaptides*.[1]

The Sulphides or Thio-Ethers are always formed in the preparation of the mercaptans from the chlorides, the following reactions taking place:

$$(1)\ C_2H_5SH + KSH = C_2H_5SK + SH_2.$$

$$(2)\ C_2H_5SK + C_2H_5Cl = (C_2H_5)_2S + KCl.$$

Sulphine Compounds.[2] The sulphides unite with the iodides and bromides of the alcohol radicals to form crystallisable salts such as triethylsulphine iodide, $S(C_2H_5)_3I$. These substances are not attacked by alkalis, but when freshly precipitated silver oxide is added to their aqueous solutions, the corresponding hydroxides are formed, such as triethylsulphine hydroxide, $S(C_2H_5)_3OH$. These latter are difficultly crystallisable, they are deliquescent, and possess alkaline and caustic properties like caustic soda. They also resemble the alkaline hydroxides, inasmuch as they precipitate metallic salts, expel ammonia from its compounds, and form, with acids, neutral salts, amongst which the chlorides unite with platinum chloride to form soluble double salts, such as $[S(C_2H_5)_3Cl]_2 + PtCl_4$.

104 *Sulphonic Acids.* These acids are easily formed by oxidation of the mercaptans and other sulpho-compounds of the alcohol-radicals:

$$\underset{\text{Mercaptan.}}{C_2H_5.SH} + 3O = \underset{\text{Ethylsulphonic acid.}}{C_2H_5.SO_2.OH.}$$

They possess the same composition as the corresponding acid sulphites of the alcohol radicals, which, however, are not known in the free state, as they decompose with extreme ease, whilst the sulphonic acids are very stable and powerful acids. They may be heated pretty strongly without decomposition, are not altered by boiling caustic alkalis, and only oxidised by nitric acid with difficulty, forming the acid sulphates.

The sulphonates are also formed when an iodide is brought in contact with a solution of a normal sulphite:[3]

$$C_2H_5I + SO_3\left\{\begin{matrix}K\\K\end{matrix}\right. = SO_2\left\{\begin{matrix}C_2H_5\\OK\end{matrix}\right. + KI.$$

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[1] Zeise assumed the existence in these bodies of the radical C_2H_5S, to which he gave the name of mercaptum (*mercurio aptum*). See Berzelius, *Jahresber.* xiv. 334.

[2] v. Oefele, *Ann. Chem. Pharm.* cxxvii. 370; cxxxii. 82.

[3] Strecker, *Ann. Chem. Pharm.* cxlviii. 90; Hemilian, *ib.* clxviii. 185.

Phosphorus pentachloride converts them into sulphonic chlorides:

$$SO_2\left\{\begin{matrix}C_2H_5\\OK\end{matrix}\right. + PCl_5 = SO_2\left\{\begin{matrix}C_2H_5\\Cl\end{matrix}\right. + KCl + POCl_3.$$

And if this latter compound be treated with sodium ethylate the ethyl-ether of ethylsulphonic acid is produced:

$$SO_2\left\{\begin{matrix}C_2H_5\\Cl\end{matrix}\right. + NaOC_2H_5 = SO_2\left\{\begin{matrix}C_2H_5\\OC_2H_5\end{matrix}\right. + NaCl.$$

This ether is isomeric with ethyl sulphite, which is formed by the action of thionyl chloride on ethyl alcohol:

$$SO\left\{\begin{matrix}Cl\\Cl\end{matrix}\right. + 2HOC_2H_5 = SO\left\{\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix}\right. + 2HCl.$$

Cold caustic potash converts the latter compound into alcohol and potassium ethyl sulphite, $SO\left\{\begin{matrix}OC_2H_5\\OK\end{matrix}\right.$, which is isomeric with potassium ethyl sulphonate, from which it differs, inasmuch as its aqueous solution is easily decomposed with formation of hydrogen-potassium sulphite and alcohol. The rational constitution of this compound is not known. The easy conversion of mercaptan into sulphonic acid renders it very probable that in the latter the alcohol radical is in direct linking with sulphur.

The alcohol radicals also form compounds with *selenium* and *tellurium*, the more important of which will be hereafter described.

105 *The Compound Ammonias or Amines* are formed by heating the haloid ethers, or the nitrates of the alcohol radicals, with ammonia under pressure, when the following consecutive reactions take place:

Primary Monamines.

$$(1)\quad C_2H_5Cl + N\left\{\begin{matrix}H\\H\\H\end{matrix}\right. = N\left\{\begin{matrix}C_2H_5\\H\\H\end{matrix}\right. + HCl.$$

Secondary Monamines.

$$(2)\quad C_2H_5Cl + N\left\{\begin{matrix}C_2H_5\\H\\H\end{matrix}\right. = N\left\{\begin{matrix}C_2H_5\\C_2H_5\\H\end{matrix}\right. + HCl.$$

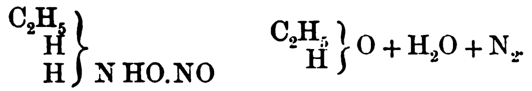
Tertiary Monamines.

$$(3)\quad C_2H_5Cl + N\left\{\begin{matrix}C_2H_5\\C_2H_5\\H\end{matrix}\right. = N\left\{\begin{matrix}C_2H_5\\C_2H_5\\C_2H_5\end{matrix}\right. + HCl.$$

The amines containing the lower members of the series of alcohol radicals are gaseous at the ordinary temperature; the higher ones are mostly liquids. They possess a peculiar ammoniacal smell, but generally this is accompanied by a fish-like odour. They precipitate many metallic salts, and combine directly with acids to form crystallisable compounds. Their chlorides unite with platinum chloride, like sal-ammoniac, whilst their sulphates yield alums with aluminium sulphate.

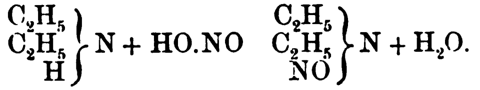
The three groups into which they may be divided are distinguished by the following reactions.

(1.) The *primary amines* are converted into alcohols by means of nitrous acid. If a solution of hydrochloride of ethylamine be warmed with silver nitrite, the following reaction takes place :



$$\left.\begin{matrix}C_2H_5\\H\\H\end{matrix}\right\}N\ HO.NO \qquad \left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O + H_2O + N_2.$$

(2.) The *secondary amines* under similar circumstances give rise to nitroso-products:



$$\left.\begin{matrix}C_2H_5\\C_2H_5\\H\end{matrix}\right\}N + HO.NO \qquad \left.\begin{matrix}C_2H_5\\C_2H_5\\NO\end{matrix}\right\}N + H_2O.$$

The nitroso-diethylamine thus obtained is again converted into diethylamine on heating with aqueous hydrochloric acid.

(3.) The *tertiary amines* are not affected by nitrous acid. They combine readily with the iodides of the alcohol radicals, giving rise to an iodide of a compound ammonium, such as tetramethylammonium iodide, $N(CH_3)_4I$. These decompose, on heating, into the compounds from which they have been formed, just as sal-ammoniac dissociates into hydrochloric acid and ammonia. In both cases re-combination takes place on cooling; and hence the compound ammonium iodides appear to distil without decomposition. They are not decomposed by alkalis. Moist silver oxide converts them into hydroxides, which are non-volatile, crystalline, very soluble bodies analogous in properties to the caustic alkalis. Thus they destroy animal matter such as the skin, saponify fats, precipitate many metallic compounds, &c., and form crystallisable salts with acids. Their chlorides yield, with platinum chloride, compounds analogous to ammonium-platinum chloride, and their sulphates give rise to alums.

It has already been stated that frequent cases of isomerism occur amongst the amines. Thus, for instance, the hydrogen atoms in ammonia may be replaced by one, two, or three radicals, and thus a variety of isomeric compounds result, and, by the above reactions, it is easy to distinguish whether we have to do with a primary, secondary, or tertiary compound. The simplest case in which isomerism can occur is that of (1) propylamine, (2) methylethylamine, and (3) trimethylamine. If these bodies be treated with ethyl iodide as long as this substance produces any action, the following compounds are formed:

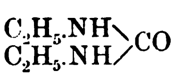
(1) Propyltriethylammonium iodide, $N(C_3H_7)(C_2H_5)_3I$.
(2) Methyltriethylammonium iodide, $N(CH_3)(C_2H_5)_3I$.
(3) Trimethylethylammonium iodide, $N(CH_3)_3(C_2H_5)I$.

It is only necessary to determine the quantity of iodine contained in the body formed to ascertain which of these compounds is under examination.

106 *Hydrazine Compounds.* Just as the *amines* are derived from ammonia, NH_3, so the hydrazines are derived from the as yet unknown body hydrazine or diamide, $H_2N - NH_2$. Compounds analogous to this are to be found in the liquid hydrogen phosphide $H_2P - PH_2$, and in dimethylarsine (cacodyl), $(CH_3)_2As - As(CH_3)_2$.

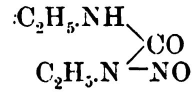
The hydrazine compounds as yet known are obtained by replacement of one or two atoms of hydrogen in hydrazine, $H_2N - NH_2$, by alcohol radicals. So far, only derivatives with one or with two alcohol radicals are known. In order to prepare mono-ethyl hydrazine, $H_2N - NH(C_2H_5)$, it is necessary to start from diethyl-urea, a secondary amine. This is treated with nitrous acid, giving rise to the nitroso-compound No. (1), and then this product is acted upon by nascent hydrogen, yielding the hydrazine-compound No. (2):

Diethylurea.



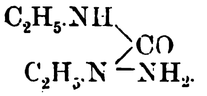
$$\begin{matrix} C_2H_5.NH \\ C_2H_5.NH \end{matrix} \Big> CO$$

(1).



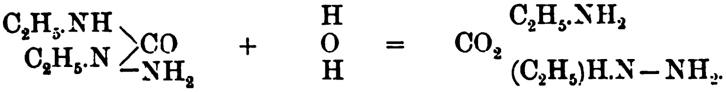
$$\begin{matrix} C_2H_5.NH \\ C_2H_5.N-NO \end{matrix} \Big> CO$$

(2).



$$\begin{matrix} C_2H_5.NH \\ C_2H_5.N-NH_2 \end{matrix} \Big> CO.$$

If the compound No. (2) be heated with alkalis or acids, it is decomposed like all ureas, yielding carbon dioxide, ethylamine, and ethyl hydrazine, as follows:



$$\begin{array}{l} C_2H_5.NH \\ C_2H_5.N \end{array}\!\!\begin{array}{l} >CO \\ -NH_2 \end{array} + \begin{array}{c} H \\ O \\ H \end{array} = CO_2 \begin{array}{l} C_2H_5.NH_2 \\ (C_2H_5)H.N-NH_2. \end{array}$$

Nitroso-amines containing acid radicals, *e.g.* like

$$\left.\begin{array}{l} C_2H_5 \\ C_2H_3O \end{array}\right\} N-NO,$$

give on reduction no corresponding hydrazines, but the amides are regenerated:

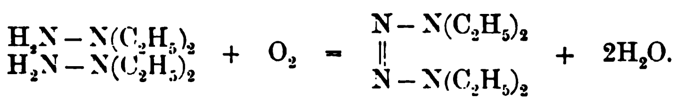
$$\left.\begin{array}{l} C_2H_5 \\ C_2H_3O \end{array}\right\} N-NO + 4H_2 = \left.\begin{array}{l} C_2H_5 \\ C_2H_5 \end{array}\right\} N-NH_2 + 2H_2O.$$

Hydrazines containing two radicals, or *Dihydrazines*, are obtained by the reduction, with zinc dust and acetic acid, of the nitroso-derivatives of secondary amines:

$$\left.\begin{array}{l} C_2H_5 \\ C_2H_5 \end{array}\right\} N-NO + 2H_2 = \left.\begin{array}{l} C_2H_5 \\ C_2H_5 \end{array}\right\} N-NH_2 + H_2O.$$

The hydrazines are volatile liquids possessing an ammoniacal odour, and uniting with acids to form salts.

Dihydrazines unite with the iodides of the alcohol radicals, giving rise to *azonium iodides*, such, for instance, as triethylazonium iodide $H_2N_2(C_2H_5)_3I$. These are converted into powerfully alkaline hydroxides by means of moist silver oxide. Weak oxidising agents resolve the dihydrazines into secondary amines with evolution of nitrogen, whilst stronger reagents give rise to *Tetrazones*, such as tetraethylazone, $N_4(C_2H_5)_4$:



$$\begin{array}{l} H_2N-N(C_2H_5)_2 \\ H_2N-N(C_2H_5)_2 \end{array} + O_2 = \begin{array}{l} N-N(C_2H_5)_2 \\ \| \\ N-N(C_2H_5)_2 \end{array} + 2H_2O.$$

The tetrazones are non-volatile, oily, alkaline liquids possessing a garlic-like smell.[1]

107 *Cyanides of the Alcohol Radicals.* These bodies are formed when an alcoholic iodide is heated with silver cyanide, or when a mixture of chloroform and an amine is treated with alcoholic potash:

$$CH_3NH_2 + CHCl_3 = CH_3.NC + 3HCl.$$

The compounds obtained in this way are usually termed

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[1] E. Fischer, *Liebigs Annalen*, cxc. 67. *Ibid.* cxcix. 281.

isocyanides or *carbamines*, in order to distinguish them from the isomeric compounds which had previously been prepared. They are poisonous liquids possessing a penetrating and highly unpleasant odour. Aqueous acids decompose them easily into formic acid and an amine:

$$CH_3NC + 2H_2O = CH_3NH_2 + COH.OH.$$

When heated in closed glass tubes, they are converted into the isomeric *nitrils*, which bodies are also formed, together with small quantities of the carbamines, by heating an iodide with potassium cyanide, or by heating the latter compound with a hydrogen sulphate of an alcohol radical:

$$NCK + \left.\begin{matrix}K\\C_2H_5\end{matrix}\right\}SO_4 = NC.C_2H_5 + K_2SO_4.$$

In this reaction a carbamine is doubtless first formed, and this is decomposed at the high temperature into a nitril.

The pure nitrils possess a strong but not unpleasant smell. They are not changed by the action of dilute aqueous acids, but are converted into the fatty acids and ammonia in the presence either of strong aqueous mineral acids or of caustic potash. Thus methyl cyanide or acetonitril, when treated in this way, yields acetic acid:

$$CH_3.CN + HCl + 2H_2O = CH_3.CO.OH + NH_4Cl.$$

On treatment with nascent hydrogen, the nitrils form amines:

$$CH_3.CN + 2H_2 = CH_3.CH_2.NH_2.$$

And this reaction proves that in the nitrils the cyanogen is linked with the alcohol radical by the carbon atom, whilst in the carbamines it is nitrogen which connects these two, acting in this case, as in sal-ammoniac and similar bodies, as a pentad. All these compounds decompose on heating, with formation of bodies in which nitrogen is triad. The pentad nitrogen in carbamine is also converted on heating into the triad form, and hence we may assume that the compound first decomposes into cyanogen and the alcohol radical, and that these then unite again:

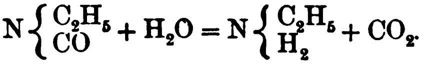
$$C{\equiv}N{-}CH_3 = N{\equiv}C\rightarrow \leftarrow CH_3.$$

Cyanates and Isocyanates. The cyanates of the alcohol radicals are very unstable liquids, formed by the action of cyanogen chloride on a solution of sodium in an alcohol:

$$NCCl + NaOC_2H_5 = NC.OC_2H_5 + NaCl.$$

These bodies are decomposed in contact with the alkalis into an alcohol and a cyanate. They undergo polymerisation with extreme ease, and give rise to crystalline *cyanurates*.

Isocyanates, Carbimides, or Carbonylamines, are bodies isomeric with the cyanates. They were formerly believed to be the true cyanates. They are, however, distinguished from these by the fact that alkalis decompose them into carbon dioxide and an amine:

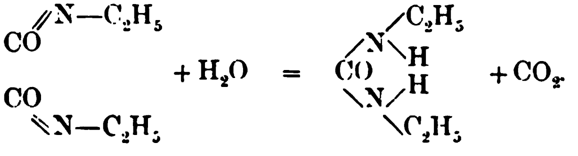


$$N\begin{cases} C_2H_5 \\ CO \end{cases} + H_2O = N\begin{cases} C_2H_5 \\ H_2 \end{cases} + CO_2.$$

This is the reaction by means of which the amines were discovered by Würtz. Aqueous acids also decompose them in the same way.

Ethyl carbimide is formed when potassium cyanate is distilled with potassium ethyl sulphate. Probably ethyl cyanate is first produced, but this is converted by molecular rearrangement into ethyl carbimide. The other carbimides are formed in a similar way. They are obtained from the carbamines by oxidation with mercuric oxide, and are volatile liquids possessing a penetrating smell which causes a flow of tears, and they are easily converted into crystalline *isocyanurates*.

108 *Compound-Ureas or Carbamides.* These bodies are derived from urea by the replacement of the whole or a portion of its hydrogen by alcohol radicals. They may be formed in several ways. Thus ethyl carbamide, $CO\begin{cases} NH.C_2H_5 \\ NH_2 \end{cases}$, is obtained by the action of cyanic acid on ethylamine, as also by treating ethyl carbimide with ammonia. If ethylamine be employed instead of ammonia, a symmetrical diethyl-carbamide is formed, which is also obtained by the decomposition of the carbimide with water:

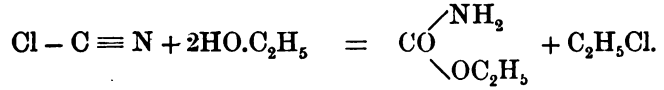


A compound isomeric with this may be prepared by acting with cyanic acid on diethylamine, whilst triethylcarbamide, $CO\begin{cases} NH.C_2H_5 \\ N(C_2H_5)_2 \end{cases}$, is formed from diethylamine and ethyl carbimide. The triamines do not undergo alteration when treated either with cyanic acid or with the carbimides, but the simple substituted carbamides are obtained by the action of diamines on carbonyl chloride. The compound ureas all unite with acids to form crystallisable salts.

Urethanes or Carbamic Ethers. Carbamic acid, $CO\langle^{NH_2}_{OH}$, is not known in the free state (Vol. I. p. 646), and only a few of its inorganic salts have been prepared, but many of its compound ethers, or the urethanes, are well-defined substances. They may be prepared in several ways. Thus, if ethyl carbonate be treated with aqueous ammonia, ethyl carbamate is formed:

$$CO\begin{cases} OC_2H_5 \\ OC_2H_5 \end{cases} + NH_3 = CO\begin{cases} NH_2 \\ OC_2H_5 \end{cases} + HO.C_2H_5.$$

By the prolonged action of ammonia, ethyl-urethane is converted into alcohol and urea, whilst, on the other hand, if pure alcohol be heated with urea to 100°, urethane is formed. These compounds are also formed by the action of cyanogen chloride upon an alcohol:

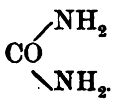


$$Cl - C \equiv N + 2HO.C_2H_5 = CO\begin{cases} NH_2 \\ OC_2H_5 \end{cases} + C_2H_5Cl.$$

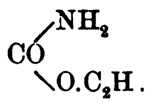
The urethanes are solid crystallisable compounds, which are decomposed by alkalis, with formation of ammonia, alcohol, and a carbonate.

Allophanates. The ethers of allophanic acid stand to biuret (Vol. I. p. 652) in the same relation as the urethanes (carbamic ethers) to urea, thus:

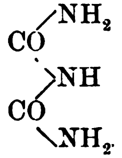
Urea.



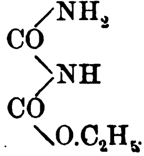
Urethane.



(Allophanic Amide).
Biuret.



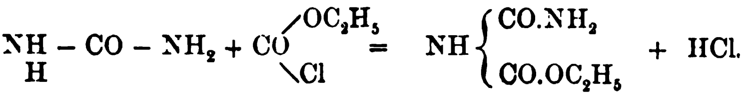
Allophanic
Ethylether.



These allophanic ethers are formed by the action of the vapour of cyanic acid upon the anhydrous alcohols, thus:

$$2CO.NH + C_2H_5.OH = NH \begin{cases} CO.NH_2 \\ CO.OC_2H_5. \end{cases}$$

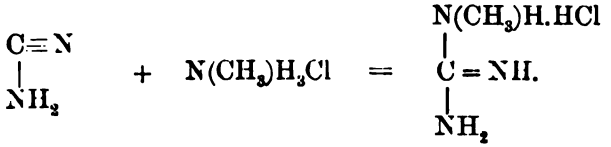
They may also be prepared by heating a chloro-carbonate with urea:



$$\underset{H}{NH} - CO - NH_2 + CO \begin{matrix} \diagup OC_2H_5 \\ \diagdown Cl \end{matrix} = NH \begin{cases} CO.NH_2 \\ CO.OC_2H_5 \end{cases} + HCl.$$

Free allophanic acid is not known, but in addition to the ethereal salts a few unstable compounds have been prepared, such as the following: $NH \begin{cases} CO.ONa \\ CO.OC_2H_5. \end{cases}$

Compound Guanidines. These bodies are formed by the action of cyanamide upon a hydrochloride of a monamine, as guanidine itself is obtained by the action of cyanamide upon an ammonium salt (Vol. I. p. 680):



$$\begin{matrix} C\equiv N \\ | \\ NH_2 \end{matrix} + N(CH_3)H_3Cl = \begin{matrix} N(CH_3)H.HCl \\ | \\ C = NH. \\ | \\ NH_2 \end{matrix}$$

Guanidines containing two alcohol radicals have, as yet, not been prepared, although some containing three such radicals have been obtained. These are formed with separation of carbon dioxide, when an isocyanuride is heated with an alcoholic solution of sodium ethylate, as also if a disubstituted thio-carbamine be heated with a monamine and mercuric oxide:

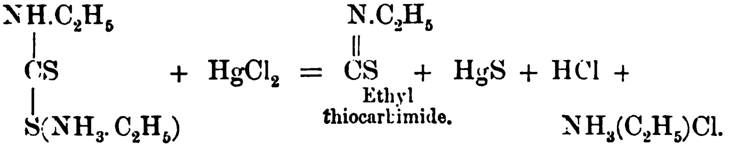
$$CS(NH.C_2H_5)_2 + H_2N.C_2H_5 + HgO = C(N.C_2H_5)(NH.C_2H_5)_2 + HgS + H_2O.$$

The compound guanidines resemble guanidine itself in acting as powerful bases.

109 *The Thiocyanates and Isothiocyanates.* The first of these classes of bodies is formed in a similar way to the other ethereal salts. Thus, for example, ethyl thiocyanate is obtained on heating potassium thiocyanate with ethyl iodide or potassium ethyl sulphate. They are most unpleasant-smelling liquids, which

are decomposed by alkalis with formation of alcohols and a thiocyante.

The isothiocyanates or *thiocarbimides* are also known as *mustard-oils*, because the oil of mustard belongs to this group, and the various members possess a similar strong pungent smell. They are formed by a general reaction. Thus ethyl mustard-oil, $SCNC_2H_5$, is obtained by mixing an alcoholic solution of ethylamine with carbon disulphide, when an ethyl-thiocarbimic acid is formed, and this, on heating with a salt of mercury or silver is converted into the thiocarbimide:



$$\begin{array}{l} NH.C_2H_5 \\ | \\ CS \\ | \\ S(NH_3.C_2H_5) \end{array} + HgCl_2 = \underset{\text{Ethyl thiocarbimide.}}{\begin{array}{c} N.C_2H_5 \\ \| \\ CS \end{array}} + HgS + HCl + NH_3(C_2H_5)Cl.$$

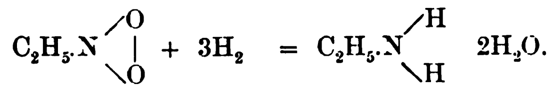
Iodine acts in a similar way with formation of iodic acid and free sulphur. Dilute sulphuric acid decomposes these mustard-oils with formation of an amine and carbonyl sulphide:

$$N\begin{cases} C_2H_5 \\ CS \end{cases} + H_2O = N\begin{cases} C_2H_5 \\ H_2 \end{cases} + COS.$$

Compound Thio-Ureas. These are formed by the action of ammonia or an amine on the mustard-oils. They are crystalline bodies forming salts with acids.

110 *The Nitro-Paraffins.* These compounds are isomeric with the nitrites of the alcohol radicals, and are formed together with the latter, when an alcoholic iodide is acted upon by silver nitrite. They act as weak acids, and contain one atom of hydrogen capable of replacement by a metal, whilst the nitrites are neutral bodies, and easily converted by alkalis into an alcohol and a nitrite. Nascent hydrogen converts the nitro-paraffins into compound ammonias, whilst the nitrites in the same way yield alcohols. This last reaction indicates the constitution of these two classes of compounds:

Nitro-ethane.



$$(1)\ C_2H_5.N\begin{array}{l} /O \\ \ \ | \\ \backslash O \end{array} + 3H_2 = C_2H_5.N\begin{array}{l} /H \\ \\ \backslash H \end{array}\ 2H_2O.$$

Ethyl nitrite.

$$(2)\ C_2H_5.O{-}NO + 3H_2 = C_2H_5.OH + NH_3 + H_2O.$$

Phosphorus Bases or Phosphines. These compounds are produced by the replacement of hydrogen in phosphuretted hydrogen (phosphine) by alcohol radicals. In their chemical properties these compounds exhibit great analogy with phosphine itself, and are classed as *primary*, *secondary*, and *tertiary* phosphines (the name having become generic). The last-named combine with the iodides of the alcohol radicals to form *phosphonium iodides*, which compounds, as well as the bodies derived from them, closely resemble the corresponding ammonium compounds.

The alcohol radicals also form corresponding compounds with *arsenic* and *antimony*, as well as with *boron*.

III *Compounds of the Alcohol Radicals with Silicon.* Silicon, like carbon, is a tetrad. The analogy of the compounds of these elements has already been pointed out in the first volume. Hence, it is not surprising that the compounds of silicon with the alcohol radicals exhibit a close similarity to the paraffins. For this reason silicon ethyl, $Si(C_2H_5)_4$, has been termed *siliconnonane*, SiC_8H_{20}, that is, it may be considered to be nonane in which one atom of carbon has been replaced by silicon.[1] Silicononane is not attacked by nitric acid. Chlorine gives rise to substitution-products, especially to silico-nonyl chloride, $SiC_8H_{19}Cl$, which compound can be converted into the alcohol, ethereal salts, and other derivatives, all containing silicon.

Compounds of the Alcohol Radicals with Metals. Only a few of the metals combine directly with the alcohol radicals. Of these, the more important are the metals of the magnesium group, aluminium, mercury, lead, and tin. The compounds thus formed are all liquids, and most of them volatile. Those of the magnesium group and aluminium inflame spontaneously when brought in contact with air, and are decomposed by water with the formation of the hydroxides of the metals, and the paraffins. The other compounds do not undergo alteration in the air, and are not decomposed by water; they are, however, attacked by acids. When the alkali metals act upon the zinc compounds, a portion of the zinc is replaced, and a body having a composition such as $NaC_2H_5 + Zn(C_2H_5)_2$ is formed. It has hitherto not proved possible to isolate the

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[1] The view held by Dumas that even carbon may undergo substitution, a view so powerfully ridiculed by Liebig, has thus proved to be true, although not exactly in the form anticipated by its author.

compound of the alcohol radical with the alkali metal from this zinc compound.

In general the metallic compounds of the alcohol radicals correspond to the chlorides of the metals, though this is not always the case, as is shown in the following table:

$NaCl$	NaC_2H_5.
$ZnCl_2$	$Zn(C_2H_5)_2$.
$HgCl_2$	$Hg(C_2H_5)_2$.
$PbCl_2$	——
——	$Pb(C_2H_5)_4$.
——	$Pb_2(C_2H_5)_6$.
Sn_2Cl_4	$Sn_2(C_2H_5)_4$.
——	$Sn_2(C_2H_5)_6$.
$SnCl_4$	$Sn(C_2H_5)_4$.

THE ALCOHOLS AND THEIR DERIVATIVES.

112 These compounds may be divided into three distinct classes or groups, primary, secondary, and tertiary alcohols and their derivatives.

Primary Alcohols and Fatty Acids. The primary alcohols, when slowly oxidised, first lose two atoms of hydrogen, and are converted into *aldehydes* (alcohol dehydrogenatum[1]), and these again readily pass into the fatty acids by the addition of one atom of oxygen, the acids being derived directly from the alcohols by the replacement of two atoms of hydrogen by one atom of oxygen:

$$\left.\begin{matrix} C_2H_5 \\ H \end{matrix}\right\} O \quad + \quad O_2 \quad = \quad \left.\begin{matrix} C_2H_3O \\ H \end{matrix}\right\} O \quad + \quad H_2O.$$

The reactions by which the constitution of the acetic acid thus formed has been elucidated, have already been referred to, namely, by the electrolysis of the acid and by its synthetical preparation from the methyl compounds. Thus we saw that, when an electric current is passed through a concentrated solution of potassium acetate, the salt which is best suited to the purpose, it first decomposes, like an inorganic salt, into

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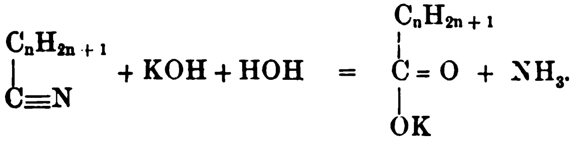
[1] Liebig, *Ann. Chem. Pharm.* xiv. 133.

$C_2H_3O_2 + K$. The liberated metal, however, at once acts upon the water, and hydrogen is evolved at the negative pole, whilst at the same time the group of atoms liberated at the other pole decomposes into carbon dioxide and methyl, CH_3, two of the latter groups uniting to form ethane, C_2H_6. All the other fatty acids decompose in a similar way according to the equation:

$$2\,C_nH_{2n}O_2 \;=\; H_2 \;+\; 2\,CO_2 \;+\; (C_{n-1}H_{2n-1})_2.$$

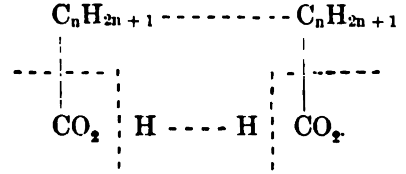
If $_{n-1}$ be written $_m$, we obtain for the hydrocarbon the expression $(C_mH_{2m+1})_2 = C_nH_{2n+2}$, which is the general formula for the paraffins.

The fatty acids can be obtained synthetically from the alcohols containing one atom less carbon by replacing the hydroxyl by cyanogen and thus obtaining the nitril, which, when boiled with caustic potash, yields the potassium salt of a fatty acid. This reaction is expressed by the following general equation:



$$\begin{matrix} C_nH_{2n+1} \\ | \\ C{\equiv}N \end{matrix} + KOH + HOH \;=\; \begin{matrix} C_nH_{2n+1} \\ | \\ C=O \\ | \\ OK \end{matrix} + NH_3.$$

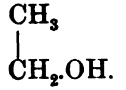
The following scheme represents the electrolysis of the fatty acids:



It is then clear that the fatty acids are compounds of the organic radicals with *carboxyl*, $HO-\overset{\uparrow}{C}=O$, this latter being formed from *methoxyl*, $HO-\overset{\uparrow}{C}H_2$, this latter group being characteristic of the primary alcohols.

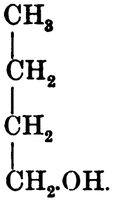
Hence a primary alcohol may be defined as a body derived from a paraffin by the replacement of an atom of hydrogen in the methyl group by hydroxyl. Or the alcohols may be considered as methyl alcohol in which one atom of hydrogen is replaced by an alcohol radical. Hence the following bodies are primary alcohols:

Ethyl alcohol.



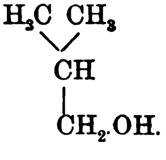
$CH_3-CH_2.OH.$

Butyl alcohol.

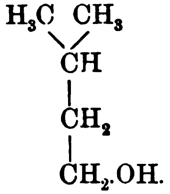


$CH_3-CH_2-CH_2-CH_2.OH.$

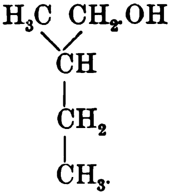
Isobutyl alcohol.



Inactive amyl alcohol.



Active amyl alcohol.



Kolbe[1] has proposed a general nomenclature for the alcohols, under which not only the primary but also the other groups may be classed, as derivatives of methyl alcohol. To this latter compound he gives the name of carbinol, and classes the primary alcohols as follows:

Ethyl alcohol	Methyl carbinol.
Butyl alcohol	Propyl carbinol.
Isobutyl alcohol.	Isopropyl carbinol.
Amyl alcohol (inactive)	Isobutyl carbinol.
Amyl alcohol (active)	Pseudobutyl carbinol.

This nomenclature has not been generally adopted, although the suggestion is not without merit.

The primary alcohols may not only be distinguished by their products of oxidation, but they likewise may be detected by the following very delicate reaction.[2] The alcohol is first converted into the iodide, and a few drops of this are brought into a distillation flask, having a capacity of a few cubic centimeters, in which a mixture of silver nitrite and white sand has previously been placed. As soon as the violence of the reaction has subsided, the liquid is distilled off, and the nitro-paraffin which has been formed is dissolved by shaking with caustic potash, and then dilute sulphuric acid added drop by drop, when a dark-red colouration takes place. This colour disappears as soon as the liquid becomes acid, but again makes its

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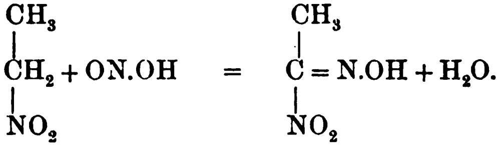
[1] *Zeitsch. Chem.* 1866, 118.

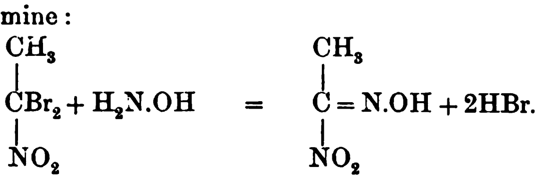
[2] V. Meyer, *Liebigs Annalen*, clxxx. 139.

appearance when the liquid is rendered alkaline by caustic potash. So far this reaction has only been applied, in the series of primary alcohols, as high as octyl-alcohol, and thus far with success.[1] This reaction depends on the formation of a *nitrolic acid* in the following way:



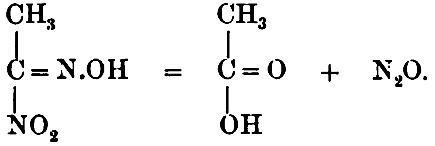
$$\begin{array}{l}CH_3\\ |\\ CH_2 + ON.OH\\ |\\ NO_2\end{array} = \begin{array}{l}CH_3\\ |\\ C = N.OH + H_2O.\\ |\\ NO_2\end{array}$$

A nitrolic acid is also formed when a nitro-paraffin is converted into the dibromo-compound, and this is acted upon by hydroxylamine:



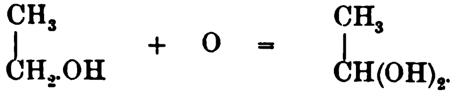
$$\begin{array}{l}CH_3\\ |\\ CBr_2 + H_2N.OH\\ |\\ NO_2\end{array} = \begin{array}{l}CH_3\\ |\\ C = N.OH + 2HBr.\\ |\\ NO_2\end{array}$$

The nitrolic acids are colourless, and crystallise well, forming with alkalis dark-red salts, which explains the production of the above reaction. They are extremely unstable compounds, decomposing easily with formation of a fatty acid. When heated with sulphuric acid, this simple decomposition takes place, pure nitrogen monoxide being evolved:



$$\begin{array}{l}CH_3\\ |\\ C = N.OH\\ |\\ NO_2\end{array} = \begin{array}{l}CH_3\\ |\\ C = O\\ |\\ OH\end{array} + N_2O.$$

113 *Aldehydes.* It has already been stated that these bodies occur as intermediate products in the oxidation of the alcohols to fatty acids. They are oxides of dyad radicals, and in their formation the first step is, in the cases of acetaldehydes, the production of ethidene alcohol:



$$\begin{array}{l}CH_3\\ |\\ CH_2.OH\end{array} + O = \begin{array}{l}CH_3\\ |\\ CH(OH)_2.\end{array}$$

This, however, like all other compounds containing two hydroxyl

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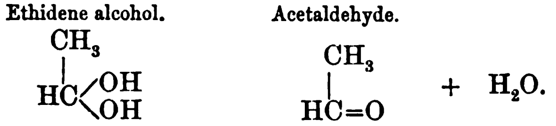
[1] Gutknecht, *Ber. Deutsch. Chem. Ges.* xii. 622.

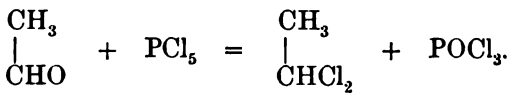
groups, combined with one carbon atom, splits up with separation of water, and we have the anhydride or oxide left; in the above case ethidene oxide or acetaldehyde being formed:



Ethidene alcohol. Acetaldehyde.

$$\begin{array}{l} CH_3 \\ | \\ HC\begin{cases} OH \\ OH \end{cases} \end{array} \qquad \begin{array}{l} CH_3 \\ | \\ HC{=}O \end{array} \quad + \quad H_2O.$$

That the above formula expresses the constitution of this compound is seen from the fact that by the action of phosphorus pentachloride it is converted into ethidene chloride or dichlorethane:



$$\begin{array}{l} CH_3 \\ | \\ CHO \end{array} + PCl_5 = \begin{array}{l} CH_3 \\ | \\ CHCl_2 \end{array} + POCl_3.$$

We may, however, acording to the theory of radicals and of types, consider aldehyde, $C_2H_3O.H$, as the hydride of an acid radical having the general formula $C_nH_{2n-1}O$. All the aldehydes are characterised by possessing a peculiar suffocating smell, whilst another peculiar characteristic of these bodies is that they unite with the hydrogen sulphites of the alkali-metals to form crystalline compounds, which are generally difficultly soluble, and are decomposed by acids with separation of the aldehyde, and hence this property is frequently made use of for the purification of these bodies.

On oxidation the aldehydes yield the fatty acids, and if freshly precipitated oxide of silver be employed as the oxidising agent, the following reaction takes place:

$$2\,CH_3.COH + 3Ag_2O = 2\,CH_3.CO.OAg + H_2O + 2\,Ag_2.$$

When heated with ammoniacal silver solution a similar reaction occurs, and if the aldehydes are soluble in water, metallic silver is deposited on the sides of the containing vessel in the form of a bright mirror.

114 *Haloid Compounds of the Acid Radicals.* The chlorides and bromides of the acid radicals are easily formed by the action of the chloride or bromide of phosphorus on the acid:

$$3\,CH_3.CO.OH + PCl_3 = 3\,CH_3.COCl + P(OH)_3.$$

These bodies are, as a rule, liquids which fume strongly in contact with the air, and possess a powerful acid smell, depending on the fact that they are rapidly decomposed by water into the corresponding fatty acid and the hydracids:

$$CH_3.COCl + H_2O = CH_3.CO.OH + HCl.$$

The iodides, which as yet have been but slightly investigated, are not formed by the action of iodide of phosphorus on the acids, inasmuch as a further decomposition takes place with separation of iodine. They may, however, be prepared from the anhydrides, and are decomposed by water in a similar way to the chlorides and bromides. The haloid compounds of the acid radicals can thus be distinguished from those of the alcohol radicals, and this explains the fact that the former cannot be obtained by the action of the hydracids on the acids as the alcoholic chlorides are prepared by the action of the hydracids on the alcohols. They may, however, be obtained in this way in presence of phosphorus pentoxide:[1]

$$CH_3.CO.OH + HCl + P_2O_5 = CH_3.COCl + 2\,HPO_3.$$

115 *Ethereal Salts or Compound Ethers.* The fatty acids are monobasic, and the one atom of hydrogen can be replaced not only by metals, but also by acid radicals, and thus the bodies formerly known as compound ethers are obtained. These are now generally termed the ethereal salts, and they may be prepared in a variety of ways:

(1.) An alcohol is brought in contact with an acid chloride:

$$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O + \left.\begin{matrix}C_2H_3O\\Cl\end{matrix}\right\} = \overset{\text{Ethyl acetate.}}{\left.\begin{matrix}C_2H_5\\C_2H_3O\end{matrix}\right\}O} + HCl.$$

(2.) An acid is allowed to act upon an alcohol:

$$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O + \left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O = \left.\begin{matrix}C_2H_5\\C_2H_3O\end{matrix}\right\}O + H_2O.$$

In this case the formation of the ethereal salt takes place slowly in the cold, but more quickly when heated. When a certain quantity of water is formed, the reaction becomes feeble, and at last stops. On the other hand, the ethereal salts are decomposed by water into the alcohol and the acid.

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[1] Friedel, *Compt. Rend.* lxviii. 1557.

(3.) When hydrochloric acid is passed into a mixture of the acid with alcohol, the formation of the ethereal salt takes place more perfectly and more quickly. This depends partly on the fact that hydrochloric acid acts as a hygroscopic agent, but partly, no doubt, because hydrochloric acid increases the yield by the formation of the acid chloride, which then acts according to equation No. 1, as these chlorides will attack the alcohol more readily than water. It is, moreover, possible that the alcohol is first converted into the chloride, which then acts again upon the acid:

$$\left.\begin{matrix}C_2H_5\\Cl\end{matrix}\right\} + \left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O = \left.\begin{matrix}C_2H_5\\C_2H_3O\end{matrix}\right\}O + HCl.$$

Indeed, perhaps the whole of these reactions come into play.[1]

(4.) Concentrated sulphuric acid acts in a similar way to hydrochloric acid. Hence the ethereal salts are frequently prepared by mixing the acid or an alkaline salt of the same with the alcohol and concentrated sulphuric acid and heating, or, again, a mixture of equal molecules of the acid and alcohol is allowed to run into a warm mixture of the alcohol with an excess of sulphuric acid, when the ethereal salt is formed together with water, and both distil over. The following equation represents the reactions which take place:[2]

$$(a)\ \left.\begin{matrix}C_2H_5\\O\end{matrix}\right\}O + \left.\begin{matrix}H\\H\end{matrix}\right\}SO_4 = \left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}SO_4 + H_2O.$$

$$(b)\ \left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}SO_4 + \left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O = \left.\begin{matrix}C_2H_5\\C_2H_3O\end{matrix}\right\}O + H_2SO_4.$$

(5.) Ethereal salts are lastly formed by heating the salt of a fatty acid with (*a*), a haloid ethereal salt, or (*b*), with a hydrogen sulphate of an alcohol radical:

$$(a)\left\{\begin{matrix}\left.\begin{matrix}C_2H_3O\\K\end{matrix}\right\}O + \left.\begin{matrix}C_2H_5\\I\end{matrix}\right\} = \left.\begin{matrix}C_2H_5\\C_2H_3O\end{matrix}\right\}O + KI.\\ \left.\begin{matrix}C_2H_3O\\Ag\end{matrix}\right\}O + \left.\begin{matrix}C_6H_{13}\\Cl\end{matrix}\right\} = \left.\begin{matrix}C_6H_{13}\\C_2H_3O\end{matrix}\right\}O + AgCl.\end{matrix}\right.$$

$$(b)\ \left.\begin{matrix}C_2H_5\\K\end{matrix}\right\}SO_4 + \left.\begin{matrix}C_4H_7O\\K\end{matrix}\right\}O = \left.\begin{matrix}C_2H_5\\C_4H_7O\end{matrix}\right\}O + K_2SO_4.$$

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[1] Demole, *Ber. Deutsch. Chem. Ges.* 1877, 1790; Henry, *ib.* 2041.

[2] Markownikoff, *Ber. Deutsch. Chem. Ges.* vi. 1176.

116 *Anhydrides or Oxides of the Acid Radicals.* These compounds stand in the same relation to the acids as the ethers of the alcohol radicals do to the alcohols.

They are formed by the action of the haloid salts of the acid radicals on the salts of the acids:

$$\left.\begin{array}{r}C_2H_3O\\ Cl\end{array}\right\} + \left.\begin{array}{r}C_2H_3O\\ Na\end{array}\right\}O = \left.\begin{array}{r}C_2H_3O\\ C_2H_3O\end{array}\right\}O + NaCl.$$

The anhydrides are insoluble in water, but when placed in contact with it, they decompose slowly in the cold, and more quickly when heated, yielding two molecules of the acid. This decomposition takes place more rapidly in presence of alkalis or in presence of alcohol, when an ethereal salt is formed:

$$\left.\begin{array}{r}C_2H_3O\\ C_2H_3O\end{array}\right\}O + 2\left.\begin{array}{r}C_2H_5\\ H\end{array}\right\}O = 2\left.\begin{array}{r}C_2H_5\\ C_2H_3O\end{array}\right\}O + H_2O.$$

Hydrochloric acid decomposes the anhydrides in the following way:

$$\left.\begin{array}{r}C_2H_3O\\ C_2H_3O\end{array}\right\}O + HCl = \left.\begin{array}{r}C_2H_3O\\ Cl\end{array}\right\} + \left.\begin{array}{r}C_2H_3O\\ H\end{array}\right\}O,$$

and the phosphorus compounds of the chlorine group act similarly:

$$3\left.\begin{array}{r}C_2H_3O\\ C_2H_3O\end{array}\right\}O + 2PI_3 = 6\left.\begin{array}{r}C_2H_3O\\ I\end{array}\right\} + P_2O_3.$$

117 *Thio-Compounds of the Acid Radicals. Thio-Acids* are formed by the action of phosphorus pentasulphide on the fatty acids:

$$5\left.\begin{array}{r}C_2H_3O\\ H\end{array}\right\}O + P_2S_5 = 5\left.\begin{array}{r}C_2H_3O\\ H\end{array}\right\}S + P_2O_5.$$

The phosphorus pentoxide which is thus formed acts on a portion of the thio-acid with formation of other products of uncertain composition.

The thio-acids which have hitherto been investigated are liquids possessing an unpleasant smell, and forming salts of which some, such as the lead and silver salts, are easily decomposed with formation of the sulphide of the metal.

The Thio-Anhydrides or Sulphides of the Acid Radicals are obtained by the action of sulphide of phosphorus on the oxides.

These are also unpleasant smelling liquids, which are decomposed by water in the following way:

$$\left.\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\right\}S + H_2O = \left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}S + \left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O.$$

The thio-acids also give rise to *compound thio-ethereal salts* obtained by heating the ordinary acid ether with sulphide of phosphorus, as also by decomposing the salts of the thio-acids with haloid ethers, and lastly by the action of the acid chlorides upon the mercaptides:

$$\left.\begin{matrix}C_2H_5\\Na\end{matrix}\right\}S + \left.\begin{matrix}C_2H_3O\\Cl\end{matrix}\right\}H = \left.\begin{matrix}C_2H_5\\C_2H_3O\end{matrix}\right\}S + NaCl.$$

118 *Amides.* The acid radicals are capable of replacing hydrogen in ammonia, thus giving rise to compound ammonias which, in order to distinguish them from the amines, are termed amides. In order to prepare these bodies the following reactions are employed:

(1.) The acid chloride or the anhydride is treated with dry ammonia:

(*a*) $C_2H_3OCl + 2NH_3 = C_2H_3O.NH_2 + NH_4Cl.$

(*b*) $(C_2H_3O)_2O + 2NH_3 = C_2H_3O.NH_2 + C_2H_3O_2NH_4.$

(2.) An ethereal salt is treated with alcoholic ammonia:

$$\left.\begin{matrix}C_2H_3O\\C_2H_5\end{matrix}\right\}O + NH_3 = C_2H_3O.NH_2 + C_2H_5.OH.$$

(3.) The ammonium salt of the acid is heated:

$$C_2H_3O.ONH_4 = C_2H_3O.NH_2 + H_2O.$$

When the amides are heated with phosphorus pentoxide they yield nitrils with liberation of water. Phosphorus pentasulphide also produces the same reaction:

$$5C_2H_3O.NH_2 + P_2S_5 = 5C_2H_3.N + 5H_2S + P_2O_5.$$

If the salt of a monamine be employed in reaction No. 3, instead of an ammonium compound, an amide is obtained in which one atom of hydrogen is replaced by an alcohol radi[illegible]

Such compounds are also formed by acting with a carbimide on a fatty acid:

$$N\left\{\begin{matrix}C_2H_5\\CO\end{matrix}\right. + \left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O = N\left\{\begin{matrix}C_2H_3O\\C_2H_5\\H\end{matrix}\right. + CO_2.$$

The amides containing two or three acid radicals have as yet been but slightly investigated. The first is formed when a nitril is heated with a fatty acid:

$$C_2H_3O.OH + C_2H_3N = N\left\{\begin{matrix}C_2H_3O\\C_2H_3O\\H\end{matrix}\right.$$

And if instead of the acid, the anhydride be employed, a triamide is produced:

$$(C_2H_3O)_2O + C_2H_3N = N(C_2H_3O)_3.$$

The anhydride and a carbimide yield the following reaction:

$$N\left\{\begin{matrix}C_2H_5\\CO\end{matrix}\right. + \left.\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\right\}O = N\left\{\begin{matrix}C_2H_3O\\C_2H_3O\\C_2H_5\end{matrix}\right. + CO_2.$$

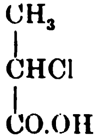
When ureas, thio-ureas, and similar compounds are treated with an acid chloride, one atom of hydrogen is also replaced by an acid radical.

119 *Substitution Products of the Fatty Acids.* Chlorine and bromine attack the fatty acids, especially when heated, or in presence of iodine, the hydrogen in the alcohol radical being replaced. Thus acetic acid yields:

Monochloracetic acid.	Dichloracetic acid.	Trichloracetic acid.
$CH_2Cl.CO_2H$	$CHCl_2.CO_2H$	$CCl_3.CO_2H$.

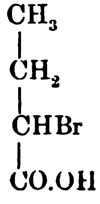
In the higher members, this substitution invariably takes place in connection with the carbon atom which is combined with the carboxyl. Thus propionic and butyric acids yield as first substitution products:

α Chlorpropionic acid.



$$\begin{matrix}CH_3\\|\\CHCl\\|\\CO.OH\end{matrix}$$

α Brombutyric acid.



$$\begin{matrix}CH_3\\|\\CH_2\\|\\CHBr\\|\\CO.OH\end{matrix}$$

Iodine does not form direct substitution products. In order to obtain these bodies the ether of the chlorinated or brominated acid must be heated with potassium iodide, and the acid set free from the product. When such an iodo-acid is heated with hydriodic acid, a fatty acid is again formed, from which it is seen why free iodine cannot act upon these bodies:

$$CH_2I.CO.OH + HI = CH_3.CO.OH + I_2.$$

SYNTHESIS OF THE PRIMARY ALCOHOLS AND THE FATTY ACIDS.

120 Whilst almost all the members of the homologous series of fatty acids have been long known, our knowledge respecting the corresponding alcohols has only recently been rendered complete.

As the alcohols may be so easily converted by oxidation into the fatty acids, a method of realising the inverse reaction, and of converting the acids into the alcohols, did not appear difficult of attainment. This problem attracted the attention of many chemists, but the first attempts proved abortive, and it was not until after Mendius[1] had discovered that the nitrils can unite with hydrogen to form the amines, that this question was solved. This method promised, moreover, likely to yield results of more general interest, inasmuch as it seemed that by this means the whole series of acids and alcohols could be synthetically built up. For Frankland and Kolbe,[2] as well as Dumas, Malaguti, and Leblanc,[3] had shown in 1847 that the nitrils or cyanides of the alcohol radicals can be converted into the fatty acids by boiling with potash, and Hofmann[4] had converted the amines into the corresponding alcohols by the action of nitrous acid.

Now the lowest member of the nitril series is hydrocyanic acid or formionitril, and this combines directly with hydrogen to form methylamine. But methyl alcohol can be obtained from this latter compound, and this again can be converted into methyl cyanide or acetonitril, which, in its turn, can be made to yield acetic acid and ethyl alcohol. Here, however, the simplicity of the reaction ends, for when the same operation is conducted in the next group, a mixture of isomeric alcohols is

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[1] *Ann. Chem. Pharm.* cxxi. 129.

[2] *Chem. Soc. Journ.* i. 60.

[3] *Compt. Rend.* xxv. 442, 656.

[4] *Chem. Soc. Journ.* iii. 231.

obtained, and these cannot readily be separated. The cause of this will be explained later on.

Other general methods may, however, be employed for the synthetical formation of the alcohols and acids corresponding to the normal paraffins.

In 1851 Williamson[1] showed that when a mixture of a formate and a salt of a fatty acid is heated, the aldehyde of the latter is produced:

$$\left.\begin{matrix} C_2HO \\ H \end{matrix}\right\} O + \left.\begin{matrix} CHO \\ H \end{matrix}\right\} O = \left.\begin{matrix} C_2H_3O \\ H \end{matrix}\right\} + CO_2 + H_2O.$$

Five years later this was confirmed by the experiments of Limpricht[2] and Piria,[3] and when Wurtz[4] in 1862 had discovered that the aldehydes combine directly with nascent hydrogen to form the alcohols, no further obstacles were seen to present themselves to a systematic construction of the homologous series of the acids and alcohols. Many unperceived difficulties were, however, met with in the practical carrying out of the process, and it was not until the year 1869 that Lieben and Rossi[5] sufficiently perfected the methods, by means of which, beginning with ordinary alcohol, the whole series of normal primary alcohols and the corresponding acids could be synthetically obtained.

Lieben and Rossi's Method. The first step of this process is the preparation of propionic acid from ethyl alcohol by means of acetonitril, and then heating its calcium salt with calcium formate. In this way propioaldehyde is obtained, and this combines directly with hydrogen to form propyl alcohol. From this latter propyl cyanide (butyronitril) can be prepared, and this again, in a similar way, yields butyr-aldehyde and butyl alcohol, &c.

Fatty acids are also formed by the action of carbon dioxide on the compounds of the alcohol radicals with the alkali metals (Wanklyn):[6]

$$C_2H_5Na + CO_2 = C_2H_5.CO_2Na.$$

Frankland and Duppa's Method. Another method discovered by Frankland and Duppa and improved by other chemists, not

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[1] *Chem. Soc. Journ.* iv. 138.

[2] *Ann. Chem. Pharm.* ci. 291.

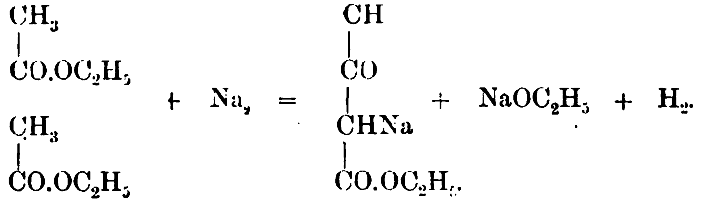
[3] *Ann. Chim.* xlviii. 113; *Ann. Chem. Pharm.* c. 104.

[4] *Compt. Rend.* liv. 914.

[5] *Ann. Chem. Pharm.* clviii. 137; clix. 58, 79; clxv. 109; clxvii. 293; Lieben and Janecek, *ib.* clxxxvii. 126.

[6] Wanklyn, *Chem. Soc. Journ.* xi. 103.

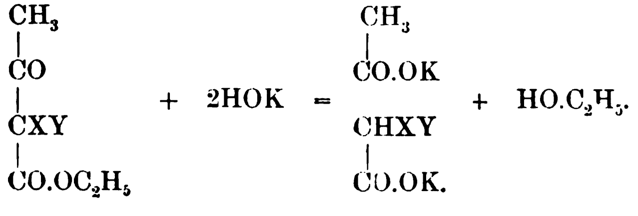
only enables us to prepare the fatty acids synthetically, but also the other series, and a variety of other compounds.[1] This depends upon the fact that the hydrogen of the methyl in acetic acid can be replaced by a carbon-containing radical. For this purpose, sodium is dissolved in acetic ether, when sodium aceto-acetic ether and sodium ethylate are formed:



$$\begin{array}{l} CH_3 \\ | \\ CO.OC_2H_5 \\ CH_3 \\ | \\ CO.OC_2H_5 \end{array} + Na_2 = \begin{array}{l} CH \\ | \\ CO \\ | \\ CHNa \\ | \\ CO.OC_2H_5 \end{array} + NaOC_2H_5 + H_2.$$

In this reaction, however, little or scarcely any hydrogen is evolved in the free state, as this, in the nascent condition, reduces a portion of the acetyl in the acetic ether to ethyl, forming sodium ethylate. If acetic acid be added to the solid product, aceto-acetic ether is formed. This possesses slightly acid properties due to the presence of two carbonyl groups, and when acted upon by sodium, yields the original compound in the pure state. The sodium in this body may readily be substituted by an alcohol radical on treatment with an alcoholic iodide, and in this compound the second atom of hydrogen can be substituted by sodium, and this in its turn again replaced by an alcohol radical.[2]

All these compounds, like acetic ether itself, are decomposed by concentrated caustic potash, in the following way:



$$\begin{array}{l} CH_3 \\ | \\ CO \\ | \\ CXY \\ | \\ CO.OC_2H_5 \end{array} + 2HOK = \begin{array}{l} CH_3 \\ | \\ CO.OK \\ \\ CHXY \\ | \\ CO.OK. \end{array} + HO.C_2H_5.$$

In these formulæ X and Y represent either hydrogen or an alcohol radical. It is clear that by this reaction not only homologous acids but many isomeric acids may be built up, as, for example, in the following instances:

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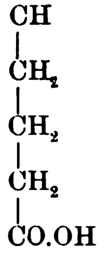
[1] Concerning the history of this subject, see Wislicenus' "Synthesis of Aceto-acetic Ethers," *Lieb. Ann.* clxxxvi. 161.

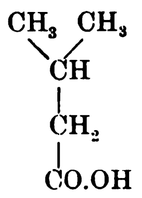
[2] On this subject see Conrad and Limpach, *Lieb. Ann.* cxcii. 153.

Pentylic acid.

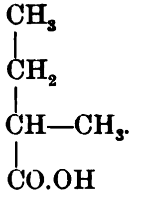


$$\begin{array}{l} CH \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CO.OH \end{array}$$

Valerianic acid.



Methyl-ethyl acetic acid.



$$\begin{array}{l} CH_3 \\ | \\ CH_2 \\ | \\ CH—CH_3. \\ | \\ CO.OH \end{array}$$

Pentylic acid is obtained by replacing one atom of hydrogen in acetic acid by the primary radical propyl, whereas secondary propyl yields valerianic acid. In order to obtain the third acid, sodium aceto-acetic ether is, in the first place, treated with iodide of ethyl, the ethyl compound is then acted upon by sodium, and the body thus obtained converted, by means of methyl iodide, into methyl-ethyl aceto-acetic ether, and this finally decomposed by caustic potash.

SECONDARY ALCOHOLS AND KETONES.

121 The secondary alcohols, the existence of which was predicted by Kolbe[1] in 1866, may be regarded as methyl alcohol, in which two atoms of hydrogen are replaced by alcohol radicals. The first of these secondary alcohols, C_3H_8O, was prepared by Friedel[2] by the action of hydrogen (2) on acetone, C_3H_6O, obtained on the dry distillation (1) of calcium acetate:

$$(1)\quad \left.\begin{array}{l} CH_3.CO.O \\ CH_3.CO.O \end{array}\right\} Ca \quad = \quad \begin{array}{l} CH_3 \\ CH_3 \end{array}\!\!>CO \quad + \quad CaCO^3.$$

$$(2)\quad \left.\begin{array}{l} CH_3 \\ CH_3 \end{array}\right\} CO \quad + \quad H_2 \quad = \quad \left.\begin{array}{l} CH_3 \\ CH_3 \end{array}\right\} CH.OH.$$

Other fatty acids yield *ketones* when treated in a similar way, and these are also formed, as Freund[3] has shown, when an acid chloride acts upon the zinc compound of an alcohol radical. Thus acetyl chloride and zinc ethyl give methyl-ethyl-ketone:

$$Zn(C_2H_5)_2 \ + \ 2\,ClCO.CH_3 \ = \ 2\,C_2H_5.CO.CH_3 \ + \ ZnCl_2.$$

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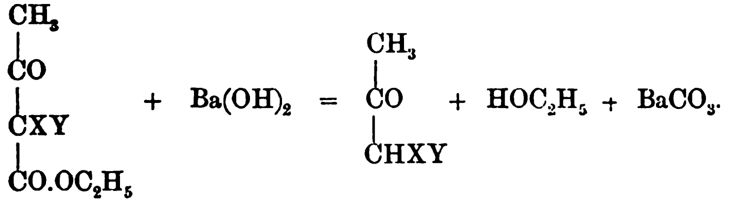
[1] *Zeitsch. Chem.* 1866, 118.
[2] *Compt. Rend.* lv. 53.
[3] *Ann. Chem. Pharm.* cxviii. 1.

The same compound, together with dimethyl ketone and diethyl ketone, is obtained when a mixture of calcium acetate and calcium propionate is heated. The formation of the ketone from the fatty acid is, therefore, exactly analogous to that of the aldehyde from a mixture of the salt of a fatty acid and a formate. Whilst just as the aldehydes were formerly considered to be hydrides of the acid radicals, so the ketones were looked upon as compounds of the latter with alcohol radicals.

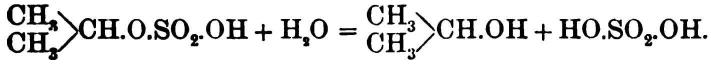
Another general method for the preparation of the ketones is the decomposition of the acet-acetic ethers by baryta water:



$$\begin{array}{l} CH_3 \\ | \\ CO \\ | \\ CXY \\ | \\ CO.OC_2H_5 \end{array} + Ba(OH)_2 = \begin{array}{l} CH_3 \\ | \\ CO \\ | \\ CHXY \end{array} + HOC_2H_5 + BaCO_3.$$

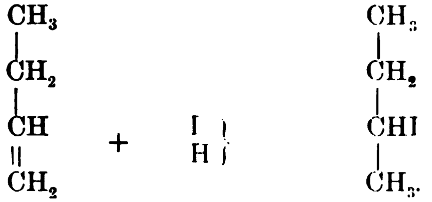
The ketones combine directly with nascent hydrogen with formation of secondary alcohols.

The secondary alcohols can also be obtained by various other reactions. Thus all the olefines which contain the groups $-CH=CH_2$ and $-CH=CH-$ dissolve in sulphuric acid with formation of an acid ethereal salt, which when heated with water yields the alcohol:

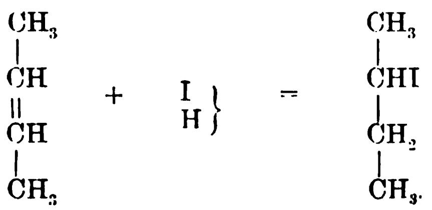


$$\begin{array}{l} CH_3 \\ CH_3 \end{array}\!\!>CH.O.SO_2.OH + H_2O = \begin{array}{l} CH_3 \\ CH_3 \end{array}\!\!>CH.OH + HO.SO_2.OH.$$

These olefines also combine with the hydracids to form the haloid ethereal salts:



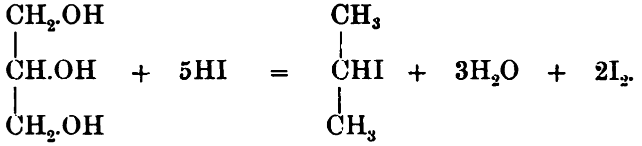
$$\begin{array}{l} CH_3 \\ | \\ CH_2 \\ | \\ CH \\ \| \\ CH_2 \end{array} + \left.\begin{array}{l} I \\ H \end{array}\right\} \qquad \begin{array}{l} CH_3 \\ | \\ CH_2 \\ | \\ CHI \\ | \\ CH_3. \end{array}$$



$$\begin{array}{l} CH_3 \\ | \\ CH \\ \| \\ CH \\ | \\ CH_3 \end{array} + \left.\begin{array}{l} I \\ H \end{array}\right\} = \begin{array}{l} CH_3 \\ | \\ CHI \\ | \\ CH_2 \\ | \\ CH_3. \end{array}$$

By the action of chlorine upon the paraffins, secondary as well as primary chlorides are formed, whilst with bromine only secondary bromides are produced.[1]

Secondary iodides are formed when the alcohols of polyvalent radicals are heated with concentrated hydriodic acid and amorphous phosphorus. Thus, glycerin, $C_3H_5(OH)_3$, yields secondary propyl iodide:



$$\begin{array}{l} CH_2.OH \\ | \\ CH.OH \\ | \\ CH_2.OH \end{array} + 5HI = \begin{array}{l} CH_3 \\ | \\ CHI \\ | \\ CH_3 \end{array} + 3H_2O + 2I_2.$$

Phosphorus is added for the purpose of preventing the liberation of iodine:

$$2\,C_3H_8O_3 + 2\,H_2O + P_2 + I_2 = 2\,C_3H_7I + 2H_3PO_4.$$

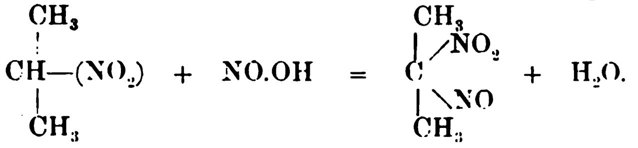
From these iodides, the alcohols may be obtained by the action of freshly precipitated oxide of silver.

The alcohols may likewise be obtained by heating the iodides with concentrated acetic acid and anhydrous acetate of lead in closed tubes, the ethereal acetates thus formed being decomposed by caustic potash. This latter reaction is also employed in order to convert the chlorides and bromides into alcohols.

By the action of silver nitrite on the secondary iodides, nitroparaffins are obtained. These dissolve in caustic potash, and when sulphuric acid is added to this solution a deep-blue colour is produced. When shaken with chloroform this coloured compound dissolves, and on evaporation of the dark-blue solution, colourless crystals of a *pseudo-nitrol* are obtained:

Iso-nitro propane.

Propyl-pseudonitrol or Nitro-nitroso-propane.



Small traces of a secondary compound can be recognised by this reaction, but it is only applicable to the lower terms of the series.[2] The pseudo-nitrols are colourless in the solid state,

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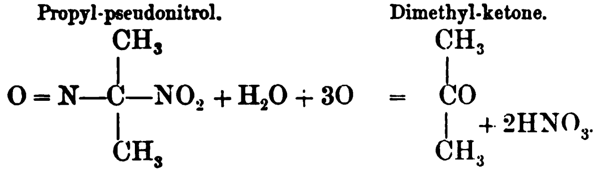
[1] Schorlemmer, *Phil. Trans.* clxii. (1872) 111 ; *Ib.* clxix. (1878) 40.

[2] Meyer and Locher, *Lieb. Ann.* clxxx 139.

but when fused or in solution they possess a deep-blue colour. On oxidation they first form ketones:



Propyl-pseudonitrol. Dimethyl-ketone.

$$O=N-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-NO_2 + H_2O + 3O = \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{CO}} + 2HNO_3.$$

The secondary alcohols also easily form ketones on oxidation, and these on further oxidation decompose in such a way that the carbonyl remains in combination with one alcohol radical, whilst the other yields oxidation products like its corresponding alcohol.[1] Hence dimethyl ketone yields acetic acid and formic acid, the latter however, readily undergoes decomposition into carbon dioxide and water. Diethyl ketone, $CO\left\{\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right.$, and methyl propyl ketone, $CO\left\{\begin{matrix}CH_3\\C_3H_7\end{matrix}\right.$, both yield acetic and propionic acids, whilst from methyl iso-propyl ketone, $CO\left\{\begin{matrix}CH_3\\CH(CH_3)_2\end{matrix}\right.$, first acetic acid and then dimethyl ketone is obtained, which latter is further oxidized as before described.

From this it would appear that the simplest alcohol radical always remains in combination with the carbonyl. This is, however, not always the case. Thus, for example, from trimethylcarbylmethyl ketone, $CO\left\{\begin{matrix}CH_3\\C(CH_3)_3\end{matrix}\right.$, we obtain trimethylacetic acid $\left\{\begin{matrix}C(CH_3)_3\\COOH\end{matrix}\right.$ and formic acid.

Hence, in many cases, the constitution of the secondary alcohols can readily be recognised by their products of oxidation. Thus, for example, a secondary alcohol is obtained from mannite, $C_6H_8(OH)_6$, which, when completely oxidized, yields acetic and butyric acids, and, therefore, must be considered as methyl butyl carbinol, $\left.\begin{matrix}CH_3\\C_4H_9\end{matrix}\right\}CO.OH$.

The ketones act in many respects, like aldehydes, as oxides of dyad radicals. Phosphorus pentachloride converts them into the dichlorides:

$$\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\}CO + PCl_5 = \left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\}CCl_2 + POCl_3.$$

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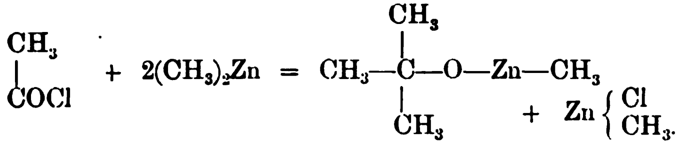
[1] Popoff, *Ann. Chem. Pharm.* clxi. 285.

Many ketones also combine with the hydrogen sulphites of the alkali metals to form difficultly soluble crystalline compounds which are decomposed again by an excess of acid or alkali. Hence this reaction is often employed for the purification of the ketones.

TERTIARY ALCOHOLS.

122 A general method for the preparation of these alcohols, the existence of which was also predicted by Kolbe, has been discovered by Butlerow.[1] This consists in placing an excess of the zinc compound of an alcohol radical in contact with the acid chloride for several days, when a crystalline mass is formed:



$$\begin{array}{l}CH_3\\|\\COCl\end{array} + 2(CH_3)_2Zn = CH_3\text{—}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}\text{—}O\text{—}Zn\text{—}CH_3 + Zn\begin{cases}Cl\\CH_3.\end{cases}$$

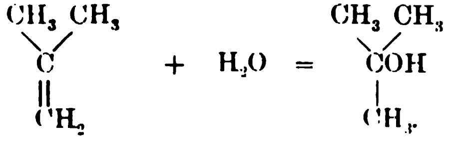
We may assume that as in the case already mentioned, (p. 182) a ketone is here first formed, and that this unites with one molecule of the zinc compound, in a similar way as it does with hydrogen to form a secondary alcohol. If the above compound be next treated with water, tertiary butyl alcohol, or trimethyl carbinol, is obtained, and this is the first member of this series:

$$(CH_3)_3C.O.ZnCH_3 + 2H_2O = (CH_3)_3C.OH + Zn(OH)_2 + CH_4.$$

The tertiary alcohols are also formed by the direct union with water of the olefines containing the groups

$$\begin{matrix}\text{—}C\\\text{—}C\end{matrix}\!\!>C=CH_2 \quad \text{and} \quad \begin{matrix}\text{—}C\\\text{—}C\end{matrix}\!\!>C=CH\text{—}$$

Thus:



$$\begin{array}{c}CH_3\ \ CH_3\\ \diagdown\ \diagup\\ C\\ \|\\ CH_2\end{array} + H_2O = \begin{array}{c}CH_3\ \ CH_3\\ \diagdown\ \diagup\\ COH\\ |\\ CH_3.\end{array}$$

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[1] *Zeitsch. Chem.* 1864, 385, 702.

This combination takes place with especial ease in presence of sulphuric acid or nitric acid.[1]

The same olefines readily unite with the hydracids to form tertiary haloid ethereal salts.

The tertiary alcohols are at once broken up on oxidation in such a manner that the carbon atom which holds the group together remains in connection with one alcohol radical forming a fatty acid, whilst the two other alcohol radicals yield the same oxidation products as their corresponding alcohols do. In this way ketones frequently occur as intermediate products. Thus trimethyl carbinol first yields formic acid and dimethyl ketone, and the latter readily splits up into water, carbon dioxide and acetic acid. This last product is also obtained from methyl diethyl carbinol, whilst propionic acid is also formed from the isomeric dimethyl propyl carbinol. It is a singular fact that in these oxidations a small quantity of a fatty acid is obtained which contains as much carbon in the molecule as the tertiary alcohol. This is, however, not difficult to explain. The tertiary alcohol easily decomposes into water and an olefine, and these latter, as we have seen, readily combine with water to form a tertiary alcohol. It is also possible that, under certain circumstances, a primary alcohol may be produced, and the formation of isobutyric acid from trimethyl carbinol may be explained by the following equations:

$$(CH_3)_2C(OH)CH_3 = (CH_3)_2C : CH_2 + H_2O.$$

$$(CH_3)_2C : CH_2 + H_2O = (CH_3)_2CH.CH_2OH.$$

Isobutyl alcohol is thus obtained, which, on oxidation, yields isobutyric acid.[2]

123 Tertiary nitro-paraffins are formed with difficulty. They do not possess any acid properties, and hence they do not dissolve in alkalis and do not give any reaction with nitrous acid.

The reason that these tertiary compounds do not act as acids is not far to seek. In order that a replacement by a metal can occur, the carbon compound must contain acid-forming or negative elements or radicals united to a carbon atom, which latter must also be united to an atom of hydrogen or hydroxyl.

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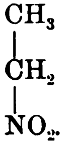
[1] Butlerow, *Lieb. Ann.* clxxx. 245.

[2] Butlerow, *Zeitsch. Chem.* 1871, 484; *Lieb. Ann.* clxxxix. 173.

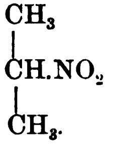
Hence acetic acid is an acid. Its anhydride (acetyl oxide) is, however, not an acid. The same reasoning applies to the nitro-paraffins.

Nitro-ethane.



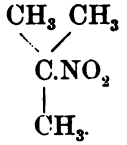
$$\begin{array}{l} CH_3 \\ | \\ CH_2 \\ | \\ NO_2. \end{array}$$

Secondary Nitropropane.



$$\begin{array}{l} CH_3 \\ | \\ CH.NO_2 \\ | \\ CH_3. \end{array}$$

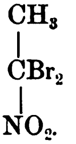
Tertiary Nitrobutane.



Bromnitro-ethane.

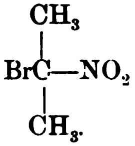
$$\begin{array}{l} CH_3 \\ | \\ CHBr \\ | \\ NO_2. \end{array}$$

Dibromnitroethane.



$$\begin{array}{l} CH_3 \\ | \\ CBr_2 \\ | \\ NO_2. \end{array}$$

Secondary Bromnitropropane.



$$\begin{array}{c} CH_3 \\ | \\ BrC—NO_2 \\ | \\ CH_3. \end{array}$$

The two first of these bodies only act as weak acids, whilst bromnitro-ethane, obtained by the replacement of hydrogen by negative bromine, is a strong acid. All the other compounds are, however, perfectly neutral.[1]

It has already been stated that a mixture of isomeric alcohols is obtained by the action of nitrous acid upon primary amines which contain more than two atoms of carbon. The fact that in this case the alcohols produced are not homogeneous had been overlooked, and it was thought that propylamine, for example, was converted by the above reaction into secondary propyl alcohol, and isobutylamine, in like manner, into tertiary butyl alcohol.[2] As soon, however, as the fact of the production of a mixture of alcohols became apparent, a somewhat far-fetched hypothesis was made use of, until at last a very simple explanation was found,[3] namely, that the reaction goes on quite normally up to a certain point, and that a primary alcohol is produced from propylamine, but another portion of the propylamine is converted into propylene, which is partly evolved as a gas and partly combines with water to form a secondary alcohol :

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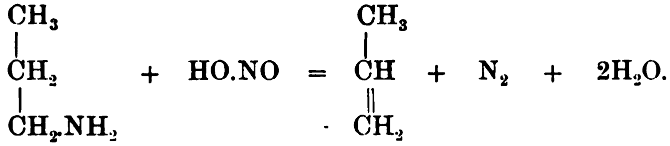
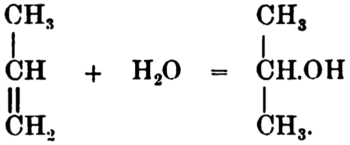
[1] V. Meyer, *Lieb. Ann.* clxxx. iii.

[2] Linnemann, *Ann. Chem. Pharm.* clxi. 45 ; clxii. 3.

[3] Meyer and Forster, *Deutsch. Chem. Ges. Ber.* ix. 535 ; Meyer, Barbieri, and Forster, x. 130.



$$\begin{array}{l} CH_3 \\ | \\ CH_2 \\ | \\ CH_2.NH_2 \end{array} + HO.NO = \begin{array}{l} CH_3 \\ | \\ CH \\ \| \\ CH_2 \end{array} + N_2 + 2H_2O.$$



$$\begin{array}{l} CH_3 \\ | \\ CH \\ \| \\ CH_2 \end{array} + H_2O = \begin{array}{l} CH_3 \\ | \\ CH.OH \\ | \\ CH_3. \end{array}$$

In a similar way isobutylamine yields isobutyl-alcohol, isobutylene, and trimethylcarbinol.

THE METHYL GROUP.

METHANE OR METHYL HYDRIDE, CH_4.

124 The existence of this substance was observed by the ancients, as Pliny noticed the occurrence, in several localities, of jets of combustible gases. In later times we find that Basil Valentine, in describing the outbreaks of fire which occur in mines, mentions a suffocating damp which is noticed before such an outbreak. He does not, however, appear to consider that the gases issuing in such emanations are combustible, but rather that the fire comes out of the rock and drives out the poisonous air. Libavius, likewise, gives an account of an explosive fire-damp; and during the seventeenth and eighteenth centuries a large number of descriptions are found of explosions which occur in mines, and especially in coal-pits. At the same time no distinct statement is made of the nature of this inflammable fire-damp, which, like other combustible gases, was not at that time distinguished from hydrogen.

Fire-damp as well as the gas of marshes was then considered to be poisonous, nor was it until the year 1776 that Volta[1] pointed out the inflammable nature of the latter gas. He showed that marsh gas differs from hydrogen, in requiring twice its volume of oxygen for combustion, as well as in giving rise to carbondioxide, whilst ordinary inflammable air needs only half its volume of oxygen for combustion and yields no carbondioxide. In 1785 Berthollet investigated the properties of marsh gas more accurately, and found that it contains both carbon and hydrogen, and that it usually occurs mixed with nitrogen. All the naturally occurring inflammable gases were, however, considered to be identical with the gases obtained artificially by the dry distillation of organic matter, as well as with the substance

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[1] *Sull' aria inflammabile nativa delle paludi.* Milano, 1777.

known as olefiant gas, until William Henry,[1] in 1805, proved that the gases obtained by the destructive distillation of coal, oil, and wax, contain two distinct gaseous hydrocarbons, viz., olefiant gas and carburetted hydrogen (marsh gas) mixed with carbonic oxide gas. Shortly afterwards Dalton,[2] Davy, and Berzelius confirmed the existence of two distinct gaseous compounds of carbon and hydrogen, which, from their difference in specific gravity, were termed light, and heavy, carburetted hydrogen, the former being marsh gas and the latter olefiant gas. The first of these was afterwards looked upon as methyl hydride, and the name methane given to it by Hofmann.

125 *Properties.* Methane is a colourless inodorous gas which, according to Cailletet, can be liquefied under a pressure of 180 atmospheres at a temperature of —11°. Its specific gravity was determined by Thomas Thomson[3] to be 0·555.

Marsh gas is not poisonous, and colliers who frequently breathe air containing 9 per cent. of this gas do not appear to suffer. When the percentage increases above this point, pressure on the forehead and eyes is noticed, which, however, disappears again on gaining the open air.

Methane is readily inflammable, burning with a slightly luminous flame, which in the upper part has a yellow, and in the lower a blue, colour. When mixed with double its volume of oxygen, and fired by an electric spark or by a flame, it explodes more violently than the same volume of electrolytic gas, and a mixture of marsh gas with from seven to eight volumes of air also explodes with great violence. Mixtures of air and marsh gas varying from this proportion burn with a weaker explosion, and if one constituent be present in large excess the electric spark does not explode the mixture (Davy).

Methane is but slightly soluble in water; its coefficient of absorption, according to Bunsen, for temperatures between 0° and 26° is obtained from the following interpolation formula:

$$c = 0{\cdot}05449 - 0{\cdot}0011807t + 0{\cdot}000010278t^2.$$

It is more soluble in alcohol, the following formula giving its solubility in that liquid between 2° and 24°:

$$c = 0{\cdot}522586 - 0{\cdot}0028655t + 0{\cdot}0000142t^2.$$

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[1] *Nicholson's Journal*, xi. p. 65.

[2] Vol. I. p. 612.

[3] *Nicholson's Journal*, 1807.

It has already been mentioned that methane occurs in nature.[1] Thus it forces its way out together with petroleum at various points on the earth's surface. The sacred fire at Baku consists of burning marsh gas containing admixtures of nitrogen, carbon dioxide, as well as of the vapour of petroleum (Hess). The gas issuing from the mud volcanoes at Bulganak, in the Crimea, on the other hand, consists, according to the analyses of Bunsen, of perfectly pure methane. It has already been stated in the first volume (p. 608) that the gases which escape in large quantities from the oil wells of Pennsylvania contain marsh gas and its homologues, together with hydrogen.

Marsh gas not only occurs in these sources and in very large quantities in the coal measures, but it is also found in many sulphur springs in the neighbourhood of active volcanoes, and it is likewise evolved in the boric acid fumeroles in Tuscany. Moreover, methane is a never-failing constituent in the products of the dry distillation of organic matter, and hence it is found in large quantities in coal gas.[2]

126 *Preparation.* Methane is obtained when either acetic acid or acetone is heated with an excess of caustic alkali. In order to prepare it, an intimate mixture of one part of sodium acetate and four parts of soda-lime is made and then heated in a flask or tube of hard glass, or, still better, in one of copper or iron, until the gas is evolved. In this way, however, the formation of a certain amount of free hydrogen (according to Kolbe[3] about eight per cent.), as well as of ethylene, cannot be avoided. This latter may be removed by passing the gas through U tubes containing pumice stone moistened with strong sulphuric acid.

According to C. A. Brindley the best mode of preparation is to mix 750 grams of caustic soda dissolved in 800 cbc. of water with 750 grams of acetate of soda, and, when this is dissolved, to add 1,250 grams of coarsely-powdered quick-lime. The mixture is then evaporated to dryness, and afterwards gradually heated to redness in an iron bottle. In this way 125 litres of marsh gas are obtained.

Methane is formed from acetic acid according to the following equation:

$$CH_3.CO.ONa + NaOH = CH_4 + CO(ONa)_2.$$

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[1] Vol. I. pages 608–10.

[2] Persoz, *Revue Scientif.* i. 51 ; Dumas, *Ann. Chim. Phys.* lxxiii. 92.

[3] *Ausf. Lehrb. Org. Chem.* i. 275.

In order to prepare it in the perfectly pure state, zinc methyl is decomposed with water.[1]

$$Zn(CH_3)_2 + 2HOH = Zn(OH)_2 + 2CH_4.$$

The synthetic formation of methane is of great theoretical interest. Berthelot[2] obtained it thus by passing a current of sulphuretted hydrogen, saturated with the vapour of carbon disulphide, over ignited metallic copper, when the following reaction takes place:

$$CS_2 + 2H_2S + 8\ Cu = CH_4 + 4\ Cu_2S.$$

By this means about one-fifth to one-third of the total hydrogen in the sulphuretted hydrogen is converted into marsh gas. In order to separate the methane, he agitated the gas with alcohol, in which, as has been stated, marsh gas is tolerably soluble. By warming the alcoholic solution the pure gas is driven off.

Methane is also formed by submitting a mixture of hydrogen and carbonic oxide gas to the action of electricity in an induction tube, round which the electricity passes:

$$CO + 3H_2 = CH_4 + H_2O.$$

After the induction current has acted for five hours, about 6 per cent. of marsh gas is produced.[3] Although methane can be produced in this way, it is decomposed into its constituents at once, when subjected to the direct action of the electric spark. This decomposition, however, is not a complete one. The action of the induction spark ceases after half an hour, the original volume does not become quite doubled,[4] whilst a certain proportion of acetylene is formed. This latter gas, together with naphthalene, $C_{10}H_8$, is also formed, according to Berthelot, when methane is exposed to a very high temperature, a portion of the gas being at the same time converted into its elementary constituents.

Like all the paraffins, methane is a very stable body, unacted upon by cold concentrated nitric acid, and even by fuming sulphuric acid at a temperature of 150°. On the other hand, chlorine attacks it so easily that when the mixed gases are

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[1] Frankland, *Phil. Trans.* 1853, cxlii. 417.

[2] *Compt. Rend.* xliii. 236.

[3] Brodie, *Proc. Roy. Soc.* xxi. 245.

[4] Buff and Hofmann, *Ann. Chem. Pharm.* cxiii. 129.

exposed to the sunlight an explosion may occur with separation of carbon, whilst in diffused daylight a series of substitution products is formed.

METHYL ALCOHOL,
CH_3OH.

127 Boyle, in his *Sceptical Chemist* (1661), constantly insists upon the fact that bodies cannot be resolved into their ultimate constituents by means of fire, a view which was generally held at that time, and one which was supported by a mass of strange experimental evidence, respecting the truth of which the cautious Boyle gives it as his opinion "that he that hath seen it hath more reason to believe it than he that hath not."[1] In particular he states that the volatile product obtained by the dry distillation of wood is not a simple body, but that it consists of an acid-, or acetous-, and an indifferent or an adiaphorous (from *ἀδιάφορος*, indifferent) spirit, which latter he showed to be inflammable.[2] These two products he separated as follows: "I took eight ounces of the rectified spirit of box (wood), wherein the acetous and neutral spirit remained confounded, as they had been in the first distillation; and having poured this upon a quantity of calcined coral, sufficient to satiate the acid corpuscles (which quickly fell to corrode it with noise and bubbles), we gently distilled it to dryness in a glass head and body, by which means we obtained of adiaphorous spirit but eight grains less than seven ounces and a half."

It was not until the year 1819 that this spirituous liquid again attracted the attention of chemists. Colin believed it to be acetone, whilst Döbereiner in 1821 stated that he found it to contain common alcohol. Upon this Taylor[3] remarked that so early as 1812 he had examined this body, to which he had given the name of pyroligneous ether, because it was a substance which, although it possesses great similarity with ordinary alcohol, still differs from this body, inasmuch as it does not yield sulphuric ether on treatment with sulphuric acid. This property was confirmed by Macaire and Marcet (1824), by Gmelin (1829), and by Liebig (1832). A complete investigation

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[1] Boyle, *Opera*, i. 486, footnote.

[2] "New Observations about the Adiaphorous Spirits of Woods and divers other bodies," *Opera*, i. 616.

[3] Tillochs, *Phil. Mag.* lx. 315.

of wood-spirit was made, in the year 1834, by Dumas and Péligot,[1] who were the first to point out the striking analogy existing between this body and common alcohol, an analogy which has exerted a marked influence on the progress of organic chemistry.[2] They gave to this compound the name of methyl alcohol (from *μέθυ*, wine; *ὕλη*, wood). Their analytical results, however, did not agree with those obtained by Liebig, and hence Berzelius suggested in 1839 that wood-spirit must contain different bodies, and this supposition was soon confirmed.

Methyl alcohol is also formed when wood is heated to the boiling-point of mercury, with an equal weight of caustic potash and a small quantity of water,[3] as well as when wood is heated with water to a temperature of 200°.[4] It is also produced in the dry distillation of other organic materials, and is likewise contained in the products of the action of heat on calcium formate $(CHO_2)_2Ca$.[5]

Methyl alcohol does not occur in the free state in nature, although the methyl ethereal salts are contained in a variety of plants. Thus, for instance, the wintergreen oil obtained from *Gaultheria procumbens*, a plant indigenous to New Jersey and various other parts of the United States, consists entirely of methyl salicylate, $CH_3C_7H_5O_3$.[6] This compound is also the chief constituent of the ethereal oils of other species of *Gaultheria*, as, for instance, the *G. punctata* and *leucocarpa*, which grow on the top of the extinct volcanoes of Java,[7] and also of the *Andromeda leschenaultii*, indigenous to the Neelgherry Hills.[8] The ethereal oils from the seeds of *Anthriscus cerefolium*, *Pastinaca sativa* and *Heracleum giganteum*, contain the ethereal salts of various alcoholic radicals, amongst which small quantities of a methyl compound, probably methyl butyrate, occur.[9]

128 *Commercial Preparation.* Methyl alcohol is prepared on the large scale from the aqueous liquid obtained in the dry distillation of wood. This contains a variety of other compounds, together with methyl alcohol and acetic acid. The most volatile

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[1] *Ann. Chim. Phys.* lviii. 5; lxi. 193.

[2] Kopp, *Geschichte der Chemie.* iv. 330.

[3] Péligot, *Ann. Chim. Phys.* lxxiii. 218.

[4] Greville Williams, *Chem. News.* xxvi. 231, 293.

[5] Lieben and Paterno, *Ann. Chem. Pharm.* clxvii. 293; Friedel and Silva, *Compt. Rend.* lxxvi. 1545.

[6] Cahours, *Compt. Rend.* xvi. 853; xxxix. 255.

[7] De Vrij, *Pharm. Journ. Trans.* [3], ii. 503; *Ber. Deutsch. Chem. Ges.* xii. 246.

[8] Broughton, *Pharm. Journ. Trans.* [3], ii. 281; Köhler, *Ber. Deutsch. Chem. Ges.* xii. 246.

[9] Gutzeit, *Liebig's Ann.* clxxvii. 344.

portions are first distilled over, and these repeatedly rectified over quicklime in order to remove as much as possible acetic acid, water, and tarry substances. The wood-spirit thus obtained contains together with methyl alcohol, acetone, allyl alcohol, methyl acetate, homologues, and condensation products of acetone, together with oily bodies and other compounds. The pure alcohol is obtained by first heating with caustic soda in order to convert the methyl acetate into alcohol. The disagreeable smelling impurities are then destroyed by a weak oxidising agent, and the product subjected to a systematic fractional distillation, for which purpose an arrangement is used similar to that employed in the rectification of common alcohol.[1] The product obtained in this way, freed as much as possible from acetons and allyl alcohol, constitutes the wood-spirit of commerce.

Methyl alcohol is now largely obtained as a by-product in the beetroot sugar industry. In this industry, as in the manufacture of cane-sugar, large quantities of molasses or treacle remain behind after the whole of the crystallisable sugar has been withdrawn. These molasses are invariably employed to yield ordinary alcohol by fermentation. Now the juice of the beet as well as that of cane-sugar contains, in addition to the sugar, large quantities of extractive and nitrogenous matter, together with considerable quantities of potash salts. In some sugar-producing localities the waste liquor or spent-wash from the stills, termed "vinasse" in French, is thrown away; but in France it has long been the custom of the distiller to evaporate these liquids to dryness and to calcine the mass in a reverberatory furnace, thus destroying the whole of the organic matter, but recovering the alkaline salts of the beetroot. In this way 2,000 tons of carbonate of potash are annually produced in the French distilleries. For more than thirty years the idea has been entertained of collecting the ammonia water, tar, gas, and oils, given off when this organic matter is calcined; but the practical realisation of the project has only quite recently been accomplished, and a most unexpected new field of chemical industry thus opened out through the persevering and sagacious labours of M. Camille Vincent[2] of Paris. In this process the spent-wash, after evaporation, is submitted to dry distillation. The distillate consists of a complex mixture of

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[1] *Ber. Entw. Chem. Ind.* ii. 277.

[2] *Compt. Rend.* lxxxiv. 214; *Bull. Soc. Chim.* [2], xxvii. 148; Expos. Univ. 1878, Prod. Chim. groupe 5, classe 47.

chemical products, resembling in this respect the corresponding product in the manufacture of coal-gas. It is, however, distinguished from this, and approximates in composition to the products of the dry distillation of wood, by containing not only ammoniacal salts, but especially trimethylamine, acetonitril, and methyl alcohol. The distillate having been neutralised by sulphuric acid, is evaporated in retorts, when the two latter compounds distil over. The nitril is decomposed by rectification over lime into acetic acid and ammonia, and the distillate contains dilute methyl alcohol, which may be dehydrated by a second treatment with caustic lime.

The best commercial wood-spirit contains about 95 per cent., the more common varieties 75 to 90 per cent. of the pure alcohol, whilst some samples may contain only from 35 to 40 per cent. of pure substance.[1] Besides water, it contains acetone and other bodies.

129 *Preparation of pure Methyl Alcohol.* In order to prepare pure methyl alcohol the method suggested by Wöhler[2] is best employed. This consists in preparing from the commercial article crystalline methyl oxalate, $(CH_3)_2C_2O_4$, a body which boils at 162°, is easy to purify, and is readily converted into oxalic acid and pure methyl alcohol by heating with water. According to Erlenmeyer[3] this ethereal salt is best obtained by dissolving anhydrous oxalic acid in boiling wood-spirit. The crystals which separate out on cooling are then washed with water by means of a filter-pump, until the liquid which runs off does not give the iodoform reaction. It is then boiled with water in a flask connected with a reversed Liebig's condenser, in order to decompose the ethereal salt completely, for which purpose the ebullition must continue for at least three hours; an addition of caustic soda facilitates the decomposition. According to Carius,[4] methyl benzoate, $CH_3.C_7H_5O_2$, may be employed instead of the oxalate. This is obtained easily by saturating a solution of benzoic acid in methyl alcohol with hydrochloric acid, and then removing the more volatile ethereal product by distillation. The residue is washed with water and then decomposed by heating with caustic soda.

It has already been mentioned that the ethereal oil of the *Gaultheria procumbens* chiefly consists of methyl salicylate,

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[1] Bardy and Bordet, *Bull. Soc. Chim.* xxxii. 4.

[2] *Ann. Chem. Pharm.* lxxxi. 376.

[3] *N. Rep. Pharm.* cx. 209.

[4] *Ann. Chem. Pharm.* cx. 209.

$CH_3.C_7H_5O_3$, boiling at 224°. This was formerly employed for the preparation of pure methyl alcohol. As salicylic acid is now prepared on a large commercial scale, the artificial salt may be made use of instead of benzoic acid for the purification of wood-spirit.

Purified wood-spirit, as we have seen, frequently contains acetone, a body boiling at 56°, or 9° lower than methyl alcohol. This compound may, however, be almost completely separated by fractional distillation, and the product thus obtained, termed in French *methylènes de queue*, easily yields pure methyl alcohol by converting it into methyl formate, $CH_3.CHO_2$, a body which boils at 32°, and which is readily decomposed by caustic soda.[1]

Pure methyl alcohol obtained according to one or other of these methods may be distilled from a water-bath in order to remove the water with which it is mixed, and then allowed to stand over ignited carbonate of potash for a long time, and afterwards rectified over either freshly burnt lime or anhydrous potassium ferrocyanide. The product thus obtained still contains small quantities of water which can only be got rid of by rectification over metallic sodium or phosphorus pentoxide.

130 *Properties.* Pure methyl alcohol is a colourless mobile liquid possessing a pure vinous smell similar to that of common alcohol and having a specific gravity of 0·8142 at 0° (Kopp). The boiling point as given by various observers varies from 58°·6 to 66°·5. This is partly to be explained by the fact that the early experimenters operated upon an impure compound, and partly also because the substance retains water with the greatest avidity. The perfectly anhydrous compound boils, according to Dittmar and Stewart[2] at 55°·1, whilst Kopp[3] formerly found the boiling point to be 54°·6 to 55°·2. The vapour density of methyl alcohol was first determined by Dumas and Péligot, and found to be 1·12.

Methyl alcohol is miscible with water in all proportions, a contraction and consequent evolution of heat occurring, this being greatest when the relation of one molecule of methyl alcohol to three of water is preserved. On ignition it burns with a pale blue flame, like common alcohol, which it also resembles, inasmuch as it acts as a solvent for many substances which are insoluble in water, such as fats and volatile oils,

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[1] Krämer and Grodzki, *Ber. Deutsch Chem. Ges.* ix. 1928; Bardy and Bordet, *Bull. Soc. Chim.* xxxi. 531.

[2] *Chem. News*, xxxiii. 35.

[3] *Ann. Chem. Pharm.* xciv. 257.

camphor, resins, &c. The alkalis and various salts are also soluble in this menstruum, whilst bodies which do not dissolve in common alcohol, such as potassium carbonate, potassium sulphate, &c., are likewise insoluble in methyl alcohol. Potassium and sodium dissolve in methyl alcohol with evolution of heat and liberation of hydrogen. Crystals separate out from such solutions which consist of compounds of the corresponding methylate with methylic alcohol. The potassium salt possesses the composition $CH_3OK + CH_3OH$.[1] These bodies are instantly decomposed by water, with formation of caustic potash and methyl alcohol. Anhydrous baryta dissolves in pure methyl alcohol with evolution of heat, and on evaporating the solution in a vacuum, crystals of $BaO + 2CH_4O$ are deposited (Dumas and Péligot). When thallium ethylate C_2H_5OTl, a liquid obtained by the action of ethyl alcohol on thallium is poured into excess of methyl alcohol, thallium methylate, CH_3OTl, separates out in the form of a white granular precipitate, which when ignited burns with a beautiful green flame. This compound is soluble in ether and alcohol, and is decomposed by water with formation of thallium hydroxide (Lamy). Anhydrous calcium chloride dissolves in methyl alcohol with evolution of heat. Six-sided tables of the compound $CaCl_2 + 4CH_4O$ separate out on cooling the concentrated solution. These are very deliquescent and quickly decomposed by water, but may be heated in dry air to 100° without losing methyl alcohol (Dumas and Péligot). Hence this compound was formerly used for the purification of wood-spirit.[2] The raw product was saturated with calcium chloride, and this then distilled on a water-bath until the excess of wood-spirit, acetone, and other easily volatile constituents had passed over. The residue was then heated with water and distilled, when the purified wood-spirit first came over, and this was afterwards dried as above described. Similar compounds with lithium and magnesium chlorides, containing respectively three and six molecules of methyl alcohol to one molecule of metallic chloride, have been prepared by Simon.[3]

Purified wood-spirit was formerly employed instead of spirit of wine as a source of heat, and as a solvent for various gums and resins. At the present day it is very largely used in the manufacture of aniline colours, and it is important for this

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[1] Wiedmann and Schweizer, *Journ. Pr. Chem.* xxiii. 6.

[2] Kane, *Phil. Mag.* [3], x. 45, 116.

[3] *Ber. Deutsch. Chem. Ges.* xii. 1281.

manufacture to be able to determine the quality of the commercial product by a simple method. If the substance should only contain water the matter is easy enough, for mixtures of methyl alcohol and of ethyl alcohol with water exhibit, as Deville[1] has proved, almost the same specific gravity for equal percentage mixtures, and hence tables made for the purpose of obtaining the strength of dilute spirit of wine may be employed for wood-spirit. Dupré[2] has also determined the specific gravity of dilute aqueous solutions of wood-spirit of various strengths. More commonly, however, acetone and other ketones are present, as well as water, in common wood-spirit, and this lowers the value of the commercial article, not only by dilution, but also because their presence acts prejudicially on the colour. For the purpose of analysing commercial wood-spirit it is usual to prepare methyl iodide from it, and determine from the quantity of this compound obtained, the value of the methyl alcohol. This method, first proposed by Krell,[3] has been worked out by Krämer and Grodzki,[4] as well as by Bardy and Bordet.[5]

METHYL OXIDE OR DI-METHYL ETHER, $(CH_3)_2O$.

131 This compound was first prepared in 1835 by Dumas and Péligot[6] by heating the alcohol with sulphuric acid, and termed by them hydrate of methylene. Ebelmen[7] afterwards showed that boron trioxide may be employed instead of sulphuric acid. It was then supposed that methyl oxide was formed by the withdrawal of the elements of water from the alcohol. This, however, is not the case, as will be afterwards explained (see Etherification, under "Ethyl Ether").

In order to prepare this compound, a mixture of thirteen parts of methyl alcohol and twenty of sulphuric acid is gently heated to a temperature of 140° in a flask provided with a reversed condenser. The gas which comes off is washed through caustic soda in order to remove sulphur dioxide and carbonic acid, and then passed into sulphuric acid, which absorbs 600 times its own volume. It appears that in this case the compound $H_2SO_4 + (CH_3)_2O$ or $SO(OH)_2(OCH_3)_2$ is

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[1] *Ann. Chim. Phys.* [3], v. 139.

[2] *Proc. Roy. Soc.*, xx. 336.

[3] *Ber. Deutsch. Chem. Ges.* 1873, 1310.

[4] *Ibid.* 1874, 1493.

[5] *Bull. Soc. Chim.* xxxii. 4.

[6] *Ann. Chim. Phys.* [2], lviii. 19.

[7] *Ibid.* [3], xvi. 138.

formed. This may be preserved without alteration, and when it is allowed to drop into an equal volume of water methyl oxide is evolved.[1]

Methyl ether is now prepared on a large scale for the production of artificial cold. For this purpose one part of sulphuric acid is mixed with rather more than one part of anhydrous wood-spirit, and the mixture, which must be of specific gravity 1·29, heated to a temperature of 125° to 128°, care being taken that the temperature does not rise above 130°. As soon as no more ether is evolved, the liquid is allowed to cool, and a sufficient quantity of wood-spirit added to the residue to bring up the specific gravity to 1·29. By repeating this operation, a large quantity of methyl ether can be obtained by the employment of a small quantity of sulphuric acid. The gas during its evolution is washed by passing through caustic soda solution and over chloride of calcium, and being thus freed from carbonic acid, sulphur dioxide, and water, is then condensed to a liquid by pressure.[2]

Methyl ether is an agreeably smelling gas which, when ignited, burns with a bluish flame, and which may be condensed by pressure or cold to a mobile liquid boiling at —21° (Berthelot). Methyl ether is readily soluble in wood-spirit, spirit of wine, and common ether; it is less soluble in water, which, however, absorbs at 18° about thirty-seven times its volume, acquiring a burning taste. If methyl oxide be brought in contact with dry hydrochloric acid in a freezing mixture, a colourless mobile fuming liquid is formed which begins to boil with decomposition from –3° to –1°, and which contains thirty-seven to thirty-nine per cent. of chlorine, nearly corresponding to the formula $(CH_3)_2O,HCl$.[3] Water decomposes it instantly into its constituents. By the action of chlorine on this ether, substitution-products are obtained, of which the first is monochlormethyl ether, CH_3OCH_2Cl, boiling at 59°·7, and the last perchlormethyl ether, $(CCl_3)_2O$, a liquid which on heating yields tetrachlor-methane, CCl_4, and carbonyl chloride, $COCl_2$.

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[1] Erlenmeyer and Kriechbaumer, *Deutsch. Chem. Ges. Ber.* vii., 699.

[2] Tellier, *Arch. Pharm.* x. 57.

[3] Friedel, *Compt. Rend.* lxxxi. 152.

ETHEREAL SALTS OF METHYL.

132 *Methyl Chloride*, CH_3Cl, was discovered by Dumas and Péligot, who prepared it by heating a mixture of one part of wood-spirit, two parts of common salt, and three parts of sulphuric acid. The compound thus obtained is, however, not pure, but contains methyl oxide and sulphur dioxide.

In order to prepare pure methyl chloride, zinc methyl is dissolved in double its weight of wood-spirit, and hydrochloric acid led into the boiling liquid contained in a flask furnished with a reversed condenser.[1] Methyl chloride is also obtained when the so-called basic cacodyl sesquichloride (Bunsen) and cacodyl dichloride (Baeyer) are heated. It is likewise formed as the first substitution-product when chlorine is allowed to act upon methane in diffused daylight (Dumas).

It was formerly believed that the body obtained by this last process was an isomeride of methyl chloride, as it was said to exhibit a peculiar reaction with water. Berthelot,[2] however, has shown that the substances obtained by these various processes are identical, and that the last preparation, like the chloride obtained in other ways, yields methyl alcohol when heated to 100° with caustic potash, whilst when treated with sulphuric acid and sulphate of silver or mercury, methyl sulphuric acid is formed, and this on heating with sodium acetate and acetic acid to 200° yields methyl acetate.

Methyl chloride has recently been obtained, as has been stated, on a large scale in the dry distillation of the beetroot "vinasses," which contains a large quantity of trimethylamine. This base is neutralised with hydrochloric acid and the concentrated solution heated to 260°, when a regular evolution of methyl chloride and trimethylamine commences:

$$3\ N(CH_3)_3\,ClH = 2CH_3Cl + 2N(CH_3)_3 + CH_3NH_2 + HCl.$$

The residue, which also contains hydrochloride of methylamine as well as sal-ammoniac, is either worked up for the methyl base, or by heating it to 300°, more methyl chloride can be obtained together with methylamine and ammonia. The methyl chloride thus obtained is separated from the alkaline compounds by

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[1] Groves, *Journ. Chem. Soc.* 1874, 641.

[2] *Ann. Chem. Pharm.* cv. 241; *Compt. Rend.* xlv. 916.

treatment with hydrochloric acid; and after drying over calcium chloride it is condensed by pressure and preserved in cylinders made of strong wrought iron or copper. A mobile ethereal-smelling liquid is thus obtained which boils at −23°,[1] and when ignited burns like other organic chlorine compounds, with a green bordered flame. Its specific gravity is as follows:

At −30° = 0·9990
−25° = 0·9915
− 0° = 0·9523
+ 15° = 0·9247

The tension of the vapour being:

At 0° = 2·48 Atmospheres.
15° = 4·11 „
20° = 4·81 „
25° = 5·62 „
30° = 6·50 „
35° = 7·50 „

The vapour density of methyl chloride was first determined by Dumas and Péligot and found to be 1·736. Methyl chloride is only slightly soluble in water, but dissolves readily in alcohol. The neutral solution is not precipitated by silver nitrate. It forms with water at 6° a solid hydrate which separates out in amorphous flakes when the gas is led into cold water, but may be obtained in large crystals by the cooling of the aqueous solution.

It has already been mentioned that methyl chloride obtained from marsh gas was formerly supposed to be an isomeric modification; this was not only because it was believed to be less soluble in water that the chloride obtained by other means, but also that it did not, like the latter, yield a hydrate. The observations upon which this conclusion was based no doubt depend on the fact that by the action of chlorine upon methane a mixture is obtained which contains not only unaltered marsh gas, but also higher substitution-products.

Methyl chloride is largely used for the preparation of various aniline colours, as well also as a means of producing artificial cold. For this latter purpose it will doubtless prove of great service both in the laboratory and on the larger industrial

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[1] Vincent and Delachanal, *Bull. Soc. Chim.* xxxi. 11.

[illegible] allowed to escape from the receiver [illegible] begins to boil, and in a few moments [illegible] the liquid is lowered by the ebullition to [illegible] boiling point of the chloride. The liquid [illegible] length of time in a quiescent state, and [illegible] freezing agent. By increasing the rapidity [illegible] by means of a current of air blown through [illegible] by placing the liquid in connection with

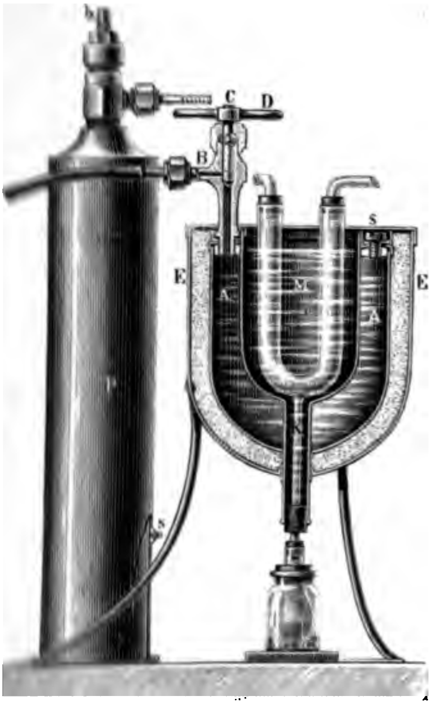

FIG. 61.

a good air pump the temperature of the liquid can in a few minutes be reduced to −55°, and large masses of mercury rapidly solidified. The construction of a small freezing machine employed by M. Camille Vincent is shown in Fig. 61. It consists of a double-cased copper vessel, between the two casings of which the methyl chloride (A) is introduced. The central space (M) is filled with some liquid such as alcohol, incapable of solidification. The chloride of methyl is allowed to enter from the cylindrical reservoir (P) by the screw tap (B), the screw (S) being left open to permit of the escape of the gas. As soon as the whole mass of liquid has been reduced to a temperature of −23°, ebullition ceases, the screw (S) may be replaced, and if a temperature lower than −23° be required, the tube (B) placed in connection with a good air-pump. By this simple means a litre of alcohol can be kept for several hours at temperatures either of −23° or —55°, and thus a large number of experiments can be performed for which hitherto the expensive liquid nitrous oxide or solid carbonic acid was required.

M. Vincent has recently constructed a much larger and more perfect and continuous form of freezing machine, in which, by means of an air-pump and a forcing pump, the chloride of methyl is evaporated in the freezing machine and again condensed in the cylinders. This enlarged form of apparatus will probably compete favourably with the ether and the sulphurous acid freezing machines now in use, as it can be simply constructed, and as the vapour and liquid do not attack metal and are non-poisonous, and the frigorific effects which it is capable of producing are most energetic.

133 *Methyl Bromide*, CH_3Br. This substance was first prepared by Bunsen,[1] by gently heating basic cacodyl superbromide, as $(CH_3)_2(OH)_2Br$. It is a colourless gas which at −17° condenses to a colourless liquid. Pierre[2] obtained it by acting with ordinary phosphorus on a well-cooled mixture of wood-spirit and bromine. According to him it is a sweetly smelling ethereal liquid which boils at + 13° and has a specific gravity at 0° of 1·664.

Amorphous phosphorus is now generally employed in this, as in the preparation of other bromides and iodides.[3] In this instance 133 grams of amorphous phosphorus and 800 grams of methyl alcohol are mixed in a large retort surrounded by ice-cold water and furnished with a reversed condenser. To this 800 grams of bromine is gradually added by means of a stoppered funnel. After leaving the amorphous phosphorus in contact for several hours, the liquid is distilled, and the vapour condensed in a receiver surrounded by a freezing mixture. The product is washed with alkaline water and dried over calcium chloride. The bromide thus obtained has a specific gravity of 1·73 at 0° and boils at 4.°5. Merrill explains the

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[1] *Ann. Chem Pharm.* xlvi. 44.

[2] *Ann. Chim. Phys.* [3], xv. 325.

[3] Merrill, *Journ. Pr. Chem.* [2], xviii. 293.

difference between his results and those before described, by the supposition that Pierre's compound contained water.

Pure methyl bromide has a pleasant ethereal smell, resembling that of chloroform, and a burning taste. Its vapour density is 3·253 (Bunsen). When a flame is brought near the gaseous compound it burns with a greenish-brown, slightly luminous flame, giving off vapours of bromine and hydrobromic acid. When the source of heat is removed the flame is at once extinguished. It forms with water a white crystalline hydrate which does not exist above 4° and probably consists of $CH_3Br + 20\,H_2O$ (Merrill).

134 *Methyl Iodide*, CH_3I, was first prepared by Dumas and Péligot by the action of iodine on common phosphorus and wood-spirit. This compound, like many iodides, easily undergoes double decomposition with other bodies, and therefore is largely used for the preparation of other methyl compounds. It has consequently been a matter of some importance to discover the most economical method of preparation.[1]

At the present day methyl iodide is prepared on a large scale by the use of commercial amorphous phosphorus. To a mixture of 35 parts of purified wood-spirit, 100 parts of iodine and 10 parts of amorphous phosphorus are gradually added:

$$10\,CH_3.OH + 5\,I_2 + P_2 = 10\,CH_3I + 2\,PO(OH)_3 + 2\,H_2O.$$

It is here seen that the phosphorus is in excess. A somewhat smaller quantity may be employed, but the excess appears to increase the rapidity of the reaction, and that which is not used can easily be regained. The mixture is allowed to stand over night, and then the methyl iodide distilled off, the distillate being washed with dilute caustic soda and dried over calcium chloride. Like the chloride and other methyl compounds, the iodide is largely employed in the manufacture of the various aniline colours.

Methyl iodide is a colourless, powerfully refracting liquid, having a specific gravity of 2·269 at 25° and boiling at 42°·5 (Linnemann). Its vapour density was found by Marchand to be 5·417.[2] It possesses a peculiar ethereal smell, and on exposure to light turns brown from liberation of iodine. When heated with sixteen times its volume of water for eight hours to 100° it

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[1] Landolt, *Ann. Chem. Pharm.* lxxxiv. 44; Hofmann, *Quart. Journ. Chem. Soc.* xiii. 69.

[2] *Journ. Prack. Chem.* xxxiii. 186.

is decomposed with formation of methyl alcohol and hydriodic acid.[1]

Methyl iodide can be inflamed only with difficulty, and burns when a flame is brought into its neighbourhood with a steel-grey coloured flame and with evolution of dense violet fumes of iodine.

Methyl Fluoride, CH_3F, was first prepared by Dumas and Péligot[2] in 1836, by heating potassium fluoride with potassium methyl sulphate. It is a colourless gas with an ethereal odour, which takes fire and burns with a blue flame with formation of hydrofluoric acid.

135 *Normal Methyl Sulphite*, $(CH_3)_2SO_3$, is formed by the action of thionyl chloride, $SOCl_2$, on wood-spirit. It is a pleasant smelling liquid boiling at 121°·5 and having a specific gravity at 16° of 1·0456.[3] Ebelmen and Bouquet found the vapour density to be 4·78. If a small quantity of caustic potash be added to its alcoholic solution, needles of potassium methyl sulphite, $K(CH_3)SO_3$ are deposited.

Hydrogen Methyl Sulphate, or Methyl Sulphuric Acid, $H(CH_3)SO_4$, was obtained by Dumas and Péligot by mixing one part of methyl alcohol with two parts of sulphuric acid, when the mixture becomes hot and the following reaction takes place :

$$CH_3.OH + H_2SO_4 = H(CH_3)SO_4 + H_2O.$$

A limit is placed on the reaction by the formation of water, and for this reason the liquid always contains free sulphuric acid and methyl alcohol. In order to remove these, the mixture is diluted with water, neutralised with barium carbonate, filtered, and sulphuric acid added to the solution until all the barium is thrown down. The filtrate, on evaporation in a vacuum, is said to yield methyl sulphuric acid in deliquescent crystals, although this statement is denied by Claesson.[4] He obtained the anhydrous acid by allowing methyl alcohol to drop into chlorsulphonic acid cooled by ice :

$$SO_2\left\}\begin{matrix}OH\\Cl\end{matrix}\right. + HO.CH_3 = SO_2\left\{\begin{matrix}OH\\OCH_3\end{matrix}\right. + HCl.$$

The product, which contains some free sulphuric acid together with hydrochloric acid and methyl chlorosulphonate,

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[1] Niederist, *Liebigs Annalen*, cxcvi. 349.

[2] *Ann. Chim. Phys.* [2], lxi. 193.

[3] Carius, *Ann. Chem. Pharm.* cx. 219 ; cxi. 97.

[4] *Journ. Pr. Chem.* N. F. xix. 231.

$SO_2Cl(OCH_3)$, is an oily liquid which does not adhere to glass and does not solidify at −30°. If its aqueous solution be allowed to evaporate in a vacuum no crystals are obtained. On heating methyl sulphuric acid with methyl alcohol, methyl oxide is formed, this substance being also produced, as has been stated, by the action of sulphuric acid upon the alcohol:

$$\left.\begin{matrix}CH_3\\H\end{matrix}\right\}O + SO_2\left\{\begin{matrix}OH\\OCH_3\end{matrix}\right. = \left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\}O + SO_2\left\{\begin{matrix}OH\\OH.\end{matrix}\right.$$

Methyl sulphuric acid is monobasic, forming salts, most of which crystallise well.

Potassium Methyl Sulphate, $2K(CH_3)SO_4 + H_2O$, forms deliquescent monoclinic tables.

Calcium Methyl Sulphate, $Ca(CH_3)_2(SO_4)_2$, crystallises in deliquescent octohedrons.

Barium Methyl Sulphate, $Ba(CH_3)_2(SO_4)_2 + 2H_2O$, forms monoclinic tables and possesses a sweet taste.

Lead Methyl Sulphate, $Pb(CH_3)_2(SO_4)_2 + H_2O$, crystallises in long prisms; it decomposes on heating into lead sulphate and normal methyl sulphate.

Normal Methyl Sulphate, $(CH_3)_2SO_4$. This compound, which has also been called sulphuric methyl ether, was prepared by Dumas and Péligot[1] by distilling 1 part of methyl alcohol with 8 to 10 parts of sulphuric acid. According to Claessen,[2] however, this method yields only a small product, as a large proportion of the alcohol is decomposed by the sulphuric acid with formation of sulphurous acid even when carefully heated. A better method is to heat anhydrous methyl sulphuric acid under diminished pressure to a temperature of 130° to 140°, when the sulphate distils over:

$$2\,H(CH_3)SO_4 = H_2\,SO_4 + (CH_3)_2SO_4.$$

It is a colourless liquid possessing a smell resembling peppermint and boiling at 187° to 188°, undergoing slight decomposition, but distilling unaltered in a vacuum. Its specific gravity is 1·327 at 18°. When heated with water it decomposes into methyl alcohol and methyl sulphuric acid, which on further boiling yields alcohol and free sulphuric acid.

Methyl Nitrite, CH_3NO_2, was first obtained by Strecker[3] by

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[1] *Ann. Chim. Phys.* lviii. 54.

[2] *Journ. Pr. Chem.* N. F. xix. 243.

[3] *Ann. Chem. Pharm.* xci. 76.

heating wood-spirit and nitric acid together with copper or arsenic trioxide. The nitrogen trioxide which is formed acts upon the alcohol as follows:

$$2\,CH_3.OH + N_2O_3 = 2\,CH_3.NO_2 + H_2O.$$

It is also produced when nitric acid acts upon brucine. It is an ethereal-smelling gas, which condenses at a low temperature to a colourless liquid boiling at − 12°.

136 *Methyl Nitrate*, $CH_3.NO_3$. According to Dumas and Péligot[1] this ether is formed in small quantity by heating nitric acid and methyl alcohol. A larger yield was obtained by adding a freshly-prepared mixture of sulphuric acid and wood-spirit to saltpetre, the heat evolved in the reaction being sufficient to vaporize the compound. The product obtained was, however, not pure. It began to boil at 60°, whilst the portion coming over at 66° possessed approximately the composition of the nitrate. That it chiefly consisted of this substance is seen by the fact that on the addition of alcoholic potash, crystals of nitre were rapidly formed. Carey Lea,[2] however, could not obtain methyl nitrate in this way. He succeeded in preparing it by employing the method suggested by Millon for the preparation of ethyl nitrate. Nitric acid alone acts chiefly as an oxidizing agent with formation of nitrous fumes, and converts the alcohol into nitrite. This action is, however, avoided by the addition of urea, which at once destroys the nitrous acid formed. In order to prepare methyl nitrate, 150 cc. of pure nitric acid, having a specific gravity of 1·31, are brought into a retort together with 40 grams of nitrate of urea, and to this 200 cc. of methyl alcohol are added and the mixture carefully distilled to one-third, 130 cc. of nitric acid and 170 cc. of wood-spirit are then added, and the mixture again distilled to one-third, and at last 10 grams of nitrate of urea, 110 cc. of nitric acid, and 150 cc. of methyl alcohol, and this is again distilled to one-third. The distillates are then mixed and shaken up with a solution of common salt, the ether which separates out being washed with a dilute solution of potassium carbonate. Methyl nitrate is also easily obtained by adding 2 parts of a cold solution of methyl alcohol and sulphuric acid to a cold mixture of 1 part of nitric acid and 2 parts of sulphuric acid.

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[1] *Ann. Chim. Phys.* lviii. 37.

[2] *Silliman's Am. Journ.* [2], xxxiii. 227.

Methyl nitrate is a liquid of an ethereal odour, which at 20° has a specific gravity of 1·182. When ignited it burns with a bright yellow flame, and its vapour explodes when heated above 150° with such force that a cast-iron boiler, in which a glass balloon containing 200 cc. of vapour was placed, was fractured by the explosion; whilst Dumas and Péligot found that when a flame was brought to the mouth of a glass bulb containing the vapour placed in a platinum crucible, not only was the bulb broken but the platinum crucible was torn to pieces. The liquid also detonates on percussion. If a piece of filter paper be impregnated with the liquid and then struck with a hammer on an anvil, an explosion takes place as violent as that caused by nitro-glycerin (Girard).

Carey Lea, in 1862, showed that this compound may be used instead of the much more expensive iodide of methyl in the preparation of iodine-violet and iodine-green, and for a long time it was employed for this purpose. It is, however, no longer used, owing to the series of fatal explosions which have resulted from its employment.

137 *Phosphite of Methyl.* As yet only the methyl phosphorous acid $P(OH)_2(OCH_3)$ is known. This is obtained by acting on methyl alcohol with phosphorous trichloride and forms a syrupy very acid liquid which cannot be prepared in the anhydrous state as on heating it decomposes into alcohol and phosphorous acid. It is monobasic and forms a series of salts which have been only slightly investigated.[1]

Phosphates of Methyl. The orthophosphate, $PO(OCH_3)_3$, has not been prepared. When phosphorous oxychloride acts on methyl alcohol, bibasic methyl phosphoric acid, $PO(OCH_3)(OH)_2$, and monobasic dimethyl phosphoric acid, $PO(OCH_3)_2(OH)$, are formed. Each of these yields a series of salts investigated by Schiff.[2] The free acids are only known in solution as thick acid liquids.

Methyl Arsenite, $As(OCH_3)_3$, is obtained by the action of sodium ethylate on arsenic tribromide, in the form of a liquid which boils at 128° to 129°, and is instantly decomposed by water into arsenic trioxide and methyl alcohol.

Methyl Arsenate, $AsO(OCH_3)_3$, is obtained by the action of methyl iodide on silver arsenate. It is a liquid which undergoes partial decomposition on distillation between 213° and

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[1] Schiff, *Ann. Chem. Pharm.* ciii. 164.

[2] *Ann. Chem. Pharm.* cii. 334.

[illegible] a vacuum without decomposition. [illegible] formation of arsenic acid and methyl [illegible]

[illegible] *yl.* The normal ether, or methyl ortho[illegible] prepared by Ebelmen and Bouquet[2] by [illegible] trifluoride into wood-spirit. The same com[illegible]ned when pure anhydrous methyl alcohol is [illegible] trioxide.[3] It is a powerfully-smelling liquid, and having a specific gravity of 0·94 at 0°. When [illegible] burns with a very brilliant green-coloured flame, [illegible] than that of the corresponding ethyl compound. [illegible]fore preferable to use wood-spirit instead of common [illegible] in testing for boric acid.

Mono-Methyl Borate, BO_2CH_3, is also formed by the action [illegible] boron trioxide on methyl alcohol, together with the normal ether. This is a syrupy liquid which also burns with a bright green flame and decomposes on heating into the ortho-ether and a glassy residue consisting of the compound $B_3O_5CH_3$. All these ethers decompose water with formation of methyl alcohol and boric acid, and for this reason methyl orthoborate becomes turbid on exposure to moist air.

139 *Methyl Orthosilicate*, $Si(OCH_3)_4$, is formed by the action of silicon tetrafluoride on anhydrous methyl alcohol. It is a liquid of ethereal odour, boiling at 120° to 122° and having a specific gravity at 0° of 1·0589. It is tolerably readily soluble in water, gelatinous silicic acid separating out from the solution after some weeks. If aqueous methyl alcohol be employed in the above reactions ethyl disilicate, $Si_2O(OCH_3)_6$, is formed. This is also a pleasantly-smelling liquid, boiling between 201° and 202°·5, and having a specific gravity at 0° of 1·1441.[4] The vapour density is 9·19.

140 *Carbonates of Methyl.* The normal ether $(CH_3)_2CO_3$ has not yet been prepared. If a solution of anhydrous baryta in methyl alcohol be treated with carbon dioxide a precipitate of pearly plates separates out. This consists of barium methyl carbonate, $Ba(CH_3)_2(CO_3)_2$, easily soluble in cold water. This solution gradually decomposes in the cold and more quickly on heating, with formation of barium carbonate, methyl alcohol, and carbon dioxide (Dumas and Péligot).

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[1] Crafts, *Bull. Soc. Chem.* xiv. 99.

[2] *Ann. Chim. Phys.* [3], xvii. 59.

[3] H. Schiff, *Ann. Chem. Pharm.* Suppl. Bd. v. 154.

[4] *Bull. Soc. Chim.* [2], iii. 356.

By acting on methyl alcohol with carbonyl chloride, methyl chlorocarbonate is formed:

$$CO\left\{\begin{matrix}Cl\\Cl\end{matrix}\right. + HO.CH_3 = CO\left\{\begin{matrix}Cl\\OCH_3\end{matrix}\right. + HCl.$$

This is an irritating-smelling liquid which is insoluble in water, but gradually decomposes in contact with this into carbon dioxide, hydrochloric acid, and methyl alcohol.

Methyl Carbamate, or Methyl Urethane, $CO\left\{\begin{matrix}NH_2\\OCH_3\end{matrix}\right.$. This was first obtained by Dumas and Péligot by dissolving the foregoing compound in aqueous ammonia. It is likewise formed by passing the vapour of cyanic acid into methyl alcohol.[1] In order to explain this reaction we must assume that the unstable cyanic acid decomposes into an isomeric carbimide and this acts as follows on the alcohol:

$$N\left\{\begin{matrix}CO\\H\end{matrix}\right. + HO.CH_3 = N\left\{\begin{matrix}CO.OCH_3\\H_2.\end{matrix}\right.$$

Methyl carbamate is also obtained by acting on methyl alcohol with cyanogen chloride.[2] It easily crystallizes in large deliquescent tables which melt at 55°, and the liquid boils at 177°.

Methyl Allophanate, $NH\left\{\begin{matrix}CO.NH\\CO.OCH_3\end{matrix}\right.$, is also formed together with urethane by the action of cyanic acid on wood-spirit. This compound stands in the same relation to biuret as urethane does to urea. It is difficultly soluble in water and crystallizes in needles.

Methyl Thiocarbonate, $(CH_3)_2CS_3$, is a yellowish disagreeably-smelling liquid boiling at about 250° and is obtained by distilling concentrated solutions of calcium methyl sulphite and potassium thiocarbonate (Cahours).

SULPHUR COMPOUNDS OF METHYL.

141 *Methyl Hydrosulphide or Methyl Mercaptan*, $CH_3.SH$, was discovered by Dumas and Péligot, who obtained it by heating potassium hydrosulphide with methyl sulphate. It was afterwards more thoroughly examined by Gregory,[3] who prepared it

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[1] Liebig and Wöhler, *Ann. Chem. Pharm.* liv. 370; Gerhardt and Laurent, *Compt. Rend.* xxiii. 457; Liebig, *Ann. Chem. Pharm.* lviii. 260.

[2] Echevarria, *Ibid.* lxxix. 110.

[3] *Ann. Pharm.* xv. 239.

by distilling concentrated solutions of potassium hydrosulphide and potassium methyl sulphate. It is a colourless unpleasantly-smelling liquid, boiling at 21° and quickly uniting with mercuric oxide to form mercury methyl mercaptide, $(CH_3S)_2Hg$, a compound which crystallizes from hot alcohol in glistening white plates.

Methyl Sulphide, $(CH_3)_2S$. In order to prepare this substance, Regnault[1] recommends a solution of caustic potash in methyl alcohol to be divided into two nearly equal parts. The smaller of these is saturated with sulphuretted hydrogen and then mixed with the other part, so that potassium monosulphide is formed together with a little free potash but no potassium hydrosulphide. This solution is then saturated with gaseous methyl chloride, the solution gently warmed whilst the gas is being passed in, and the volatile product collected in a reservoir surrounded with ice. The distillate, which consists of a mixture of methyl sulphide and methyl alcohol, is next washed with water which dissolves the alcohol, the sulphide remaining insoluble. This latter is again repeatedly washed with water, and at last dried over calcium chloride.

Methyl sulphide is a colourless mobile liquid possessing an extremely unpleasant odour. It boils at 41°, and has a specific gravity of 0·845 at 21°. When allowed to drop into dry chlorine gas it takes fire and burns with a red flame with separation of carbon. Substitution-products are however formed by a more gradual action of chlorine, the last of which, perchlormethyl sulphide, $(CCl_3)_2S$, is a red liquid which decomposes on heating.[2] Methyl sulphide combines with mercuric chloride, mercuric iodide, platinic chloride, and other haloid salts, and these compounds can be obtained beautifully crystallized from hot alcohol.[3]

142 *Dimethyl-Sulphine Compounds.* Methyl sulphide combines directly with bromine to form the dibromide, $(CH_3)_2SBr_2$, a compound which crystallizes from water in amber-yellow octohedrons. If methyl sulphide be dropped into well-cooled fuming nitric acid, and the solution allowed to evaporate, colourless deliquescent needles of the nitrate, $(CH_3)_2S(OH)NO_3$, are obtained. If these are decomposed by barium carbonate, or if the bromide be decomposed by freshly precipitated oxide of

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[1] *Ann. Chim. Phys.* [2], lxxi. 391.

[2] Riche, *Ann. Chim. Phys.* [3]. xliii. 292.

[3] Loir, *Ibid.* xxxix. 448; liv. 42.

[illegible] dimethyl-sulphine oxide, $(CH_3)_2SO$, is formed. This is soluble in water and alcohol, and on evaporation and cooling solidifies to a colourless and inodorous mass. If the nitrate be heated to 100°, dimethyl-sulphone $(CH_3)_2SO_2$, is formed. This is soluble in water and nitric acid, and crystallizes from the latter solution in prisms which melt at 109° although at 100° they begin to volatilize. The liquid boils at 238°.[1]

[illegible] *Trimethylsulphine Compounds.*[2] Methyl sulphide combines readily with methyl iodide to form $(CH_3)_3SI$, a compound crystallizing from aqueous solution in large colourless prisms, and from alcohol in rhombic tables which soon become brown on exposure to air. It is also formed when the sulphide or the mercaptan is heated to 100° with hydriodic acid:

$$(1)\quad 2(CH_3)_2S + HI = (CH_3)_3SI + CH_3SH.$$

$$(2)\quad 3CH_3.SH + HI = (CH_3)_3SI + 2H_2S.$$

It is likewise obtained by the action of methyl iodide on methyl thiocyanate.

The iodide is decomposed by moist silver oxide with formation of trimethylsulphine hydroxide, $(CH_3)_3SOH$. The solution of this compound is strongly alkaline, and on evaporation yields the base as an oil having the smell of an isonitril.[3] On neutralization with acids a series of trimethylsulphine salts are obtained, some of which may be prepared by the action of silver salts on the iodide (Letts). The chloride crystallizes in deliquescent prisms, and combines with platinic chloride to form the double salt, $2(CH_3)_3SCl + PtCl_4$, crystallizing from boiling water in yellowish-red combinations of the cube and octohedron. The free base rapidly absorbs carbon dioxide, giving rise to a crystalline carbonate. Its solution readily absorbs sulphuretted hydrogen with formation of the hydrosulphide, $S(CH_3)_3SH$, which exhibits all the reactions of the hydrosulphides of the metals. If the hydroxide be added to this solution, trimethylsulphine sulphide, $[(CH_3)_3S]_2S$, is produced. This solution decomposes on concentration with formation of three molecules of methyl sulphide. The aqueous solution of the sulphide exhibits the characteristic reactions of the sulphides of the alkali metals. Thus it dissolves antimony trisulphide, is coloured

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[1] Saytzeff, *Ann. Chem. Pharm.* cxliv. 148.

[2] Cahours, *Bull. Soc. Chim.* [2], iv. 40; *Ann. Chim. Phys.* [5], x. 13; Dehn, [illegible]

[3] Klinger, *Ber. Deutsch. Chem. Ges.* x. 1880.

deep violet by sodium nitroprusside, and is decomposed by acids with evolution of sulphuretted hydrogen.[1]

Methyl Disulphide, $(CH_3.)_2S_2$, is obtained by acting on methyl chloride with alcoholic solution of potassium disulphide. It is a yellowish unpleasantly-smelling liquid boiling at 112°. It is likewise obtained by employing a higher sulphide of potassium, when the trisulphide of methyl is formed at the same time. This body closely resembles the disulphide, but boils at 200°.

144 *Methyl Sulphonic Acid*, $CH_3.SO_3H$. This acid was discovered by Kolbe[2] in 1845, and originally termed methyl hyposulphuric acid. Berzelius and Marcet had found in 1813 that carbon disulphide on treatment with moist chlorine yielded the compound CCl_4SO_2, to which substance they gave the name of sulphite of chloride of carbon. This is also readily obtained by treating carbon dioxide with hydrochloric acid and manganese dioxide, and is, as Kolbe showed, trichlormethyl sulphonic chloride, $CCl_3.SO_2Cl$. If this is heated with baryta water, barium trichlormethyl sulphonate, $(CCl_3.SO_3)_2Ba$, is produced and the free acid can easily be obtained from this as a white deliquescent mass. It is easily reduced by nascent hydrogen, one atom of chlorine after the other being replaced by hydrogen, and thus methyl sulphonic acid is formed. The same substance is produced when methyl mercaptan, methyl disulphide, or methyl thiocyanate is heated with nitric acid. On evaporation on the water-bath the acid remains as a thick syrup which still may contain some free sulphuric acid. In order to obtain the pure acid, the barium salt is decomposed with sulphuric acid, or the lead salt with sulphuretted hydrogen. This substance has not been obtained in the crystalline state, but only as a strongly acid thick colourless inodorous liquid, which when heated above 130° becomes brown and begins to decompose. It may be boiled with ordinary nitric acid without undergoing change, and chlorine even in the sunlight does not act upon it. Its salts are all soluble in water and almost all crystalline.

Potassium Methyl Sulphonate, $CH_3.SO_3K$, is not only formed by neutralizing the acid with potash, but also by heating methyl iodide with an aqueous solution of normal potassium sulphite. It is easily soluble in water, and crystallizes from hot alcohol in finely interlaced threads. The double compound, $CH_3.SO_3K + CH_3.SO_3H$, separates in deliquescent prisms when a mixed

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[1] Crum-Brown and Blackie, *Chem. News*, xxxvii. 130 ; xxxix. 51.

[2] *Ann. Chem. Pharm.* liv. 174.

solution of the sulphonate and of the free acid is placed in a vacuum over sulphuric acid.

Barium Methyl Sulphonate, $(CH_3.SO_3)_2Ba + H_2O$, forms fine transparent rhombic tables which are unalterable in the air.

Lead Methyl Sulphonate, $(CH_3.SO_3)_2Pb + H_2O$, crystallizes in large prisms, also unalterable in the air.

Silver Methyl Sulphonate, $CH_3.SO_3Ag$, forms fine transparent tablets which have a sweet metallic taste, and remain unaltered on long exposure to the air.

Methyl Sulphonic Chloride, $CH_3.SO_2Cl$, was obtained by Carius[1] by acting on the acid with phosphorus pentachloride:

$$SO_2\left\{\begin{matrix}CH_3\\OH\end{matrix}\right. + PCl_5 = SO_2\left\{\begin{matrix}CH_3\\Cl\end{matrix}\right. + POCl_3 + HCl.$$

It is a powerfully-smelling liquid boiling at 150° to 153°. It is slowly decomposed by water into hydrochloric acid and methyl sulphonic acid. On heating with phosphorus pentachloride to 150°-160°, the following reaction occurs:

$$SO_2\left\{\begin{matrix}CH_3\\Cl\end{matrix}\right. + PCl_5 = SO_2Cl + CH_3Cl + POCl_3.$$

SELENIUM COMPOUNDS OF METHYL.

145 *Methyl Selenide*, $(CH_3)_2Se$. By distilling a solution of potassium methyl sulphate with potassium selenide, Wöhler and Dean obtained a reddish-yellow highly offensive liquid which, until recently, was held to be the above compound. It is, however, most probably the diselenide. Methyl monoselenide is obtained by heating potassium methyl sulphate with caustic potash and phosphorus pentaselenide:

$$\begin{gathered}P_2Se_5 + 10\,K(CH_3)SO_4 + 16\,NaOH = \\ 5\,(CH_3)_2Se + 5\,K_2SO_4 + 5\,Na_2SO_4 + 2\,Na_3PO_4 + 8\,H_2O.\end{gathered}$$

It is a colourless strongly refracting liquid, heavier than water, possessing a most unpleasant smell, and boiling at 58°·2. It decomposes in contact with water in the cold, and more quickly on boiling, with separation of selenium.

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[1] *Ann. Chem. Pharm.* cxiv. 140.

Methylseleni-nitrate, $(CH_3)_2Se(NO_3)OH$, is formed by dissolving the selenide in strong cold nitric acid. It crystallizes out from water in long prisms, melting at 90°·5, and volatilizing below 100°.

Methylseleni-dichloride, $(CH_3)_2SeCl_2$, is precipitated by hydrochloric acid from a concentrated solution of the nitrate. It crystallizes from alcoholic solution in mother-of-pearl scales, which have an unpleasant smell, and melt at 59°·5.

The corresponding bromide and iodide are known, and also *methylseleni-platinic chloride*, $2(CH_3)_2Se+PtCl_4$, obtained by the direct combination of its constituents, and crystallizing in yellow feathery needles from alcohol.[1]

Methyl Selenonic Acid, $CH_3.SeO_3H$, is obtained by oxidizing the diselenide with nitric acid. It crystallizes in prisms which melt at 122°, having an unpleasant smell and a metallic taste. It forms a series of crystalline salts.[2]

TELLURIUM COMPOUNDS OF METHYL.

146 *Methyl Telluride*, $(CH_3)_2Te$, was obtained by Wöhler and Dean[3] on distilling potassium telluride with a concentrated solution of potassium methyl sulphate. It is a light-yellow mobile liquid which boils between 80° and 82°, yielding a yellow vapour, and has a very unpleasant garlic-like odour, which is so persistent, that when working with the substance the breath becomes persistently tainted with the smell.

Methyl Tellurium Oxide, $(CH_3)_2TeO$. Methyl telluride dissolves in strong cold nitric acid with the formation of the nitrate, $(CH_3)_2Te(NO_3)OH$, which crystallizes in large colourless prisms. Hydrochloric acid throws down the chloride, $(CH_3)_2TeCl_2$, from this solution, in the form of a thick white precipitate, which crystallizes from solution in hot water in long thin prisms. When heated with water and freshly precipitated silver oxide, a solution of the oxide, or more probably of the hydroxide, $(CH_3)_2Te(OH)_2$, is obtained. A distinctly crystalline mass is produced on evaporation which deliquesces on exposure to air, and absorbs carbon dioxide. It possesses a

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[1] C. Loring Jackson, *Liebig's Annalen*, clxxix. 1.
[2] Wöhler and Dean, *Ann. Chem. Pharm.* xcvii. 6.
[3] *Ibid.* xciii. 233.

most unpleasant taste, but is odourless. Its solution turns red litmus-paper blue, and it liberates ammonia from sal-ammoniac at the ordinary temperature, and gives a blue precipitate with a solution of copper sulphate.

Sulphur dioxide precipitates methyl telluride from its solutions:

$$(CH_3)_2TeO + SO_2 + H_2O = (CH_3)_2Te + H_2SO_4.$$

The oxide forms, with acids, salts which have been examined by Wöhler and Dean, and also by Heeren.[1] They are, as a rule soluble in water, and crystallize well.

NITROGEN BASES OF METHYL.

METHYLAMINE, $N(CH_3)H_2$.

147 Methylamine was discovered by Wurtz,[2] in 1849, who obtained it by the action of caustic potash on methyl isocyanate, or isocyanurate (see p. 225). Hofmann[3] then prepared it by heating methyl iodide with ammonia, and Carey Lea,[4] as well as Juncadella,[5] showed that it is also easily obtained when methyl nitrate is used instead of the iodide. This base is also formed by various other reactions, of which the following are the most important.

Mendius[6] found that methylamine is produced when hydrocyanic acid is acted upon with dilute sulphuric acid and zinc; and Debus[7] showed that it is likewise produced when a mixture of hydrogen with the vapour of hydrocyanic acid is passed over platinum black heated to 110°; again Berthelot[8] obtained it by heating methyl alcohol with ammonium iodide to 100°, or with sal-ammoniac to 300°. According to Dusart and Bardy,[9] only a small quantity of the base is formed when sal-ammoniac alone is used, but if hydrochloric acid be added, and the mixture heated for thirty hours to a temperature of 205°-208°, a better yield is obtained. On the other hand, Weith[10] found that when an excess of methyl alcohol is employed, the sal-ammoniac can be completely methylated. On heating two grams of this salt with 12 cbc. of pure methyl alcohol

[1] *Chem. Centralb.* 1861, 916.

[2] *Ann. Chim. Phys.* [3], xxx. 443.

[3] *Phil. Trans.* 1851, p. 381.

[4] *Chem. News*, vi. 46.

[5] *Compt. Rend.* xlviii. 342.

[6] *Ann. Chem. Pharm.* cxxi. 139.

[7] *Chem. Soc. Journ.* xvi. 249.

[8] *Ann. Chim. Phys.* [3], xxxviii. 69.

[9] *Compt. Rend.* lxxiv. 189.

[10] *Ber. Deutsch. Chem. Ges.* viii. 458.

to 280°-285° for ten hours, methyl ether, hydrochloride of trimethylamine, and tetramethylammonium chloride were formed. On heating three grams of sal-ammoniac with 12 cbc. of methyl alcohol for six hours to the same temperature, hydrochloride of methylamine was obtained in addition to the above compounds.

Methylamine occurs in nature in *Mercurialis annua* and *M. perennis*,[1] being formerly known in the impure state as mercurialine. It is also found in herring brine, and occurs frequently as a product of the decomposition of the alkaloids, and similar compounds. It has likewise been observed by Anderson in the products of distillation of animal matter, and also of that of wood (Camille Vincent), and it is now obtained on the large scale in Vincent's process. It has already been stated (p. 202) that hydrochloride of trimethylamine decomposes, at a temperature of about 285°, into methyl chloride and trimethylamine which volatilize, and hydrochloride of methylamine, which remains behind. This is always mixed with some sal-ammoniac, from which it may, however, be separated by solution in absolute alcohol ; the spirit is then distilled off, and the residual salt decomposed with caustic soda.

Methylamine is a colourless gas condensing at a few degrees above 0°, to a mobile liquid which does not solidify on exposure to the temperature obtained by a mixture of ether and solid carbon dioxide. It has a strong ammoniacal, but also a slight fish-like smell, and is more soluble in water than is ammonia, which it resembles very closely. At 12°·5 one volume of water dissolves 1,150, and at 25°, 959 volumes of the gas. It is easily combustible, and may in this way readily be distinguished from ammonia. It burns with a bright yellow flame, forming water, carbon dioxide, and nitrogen. If an insufficient supply of air be present, small quantities of cyanogen and hydrocyanic acid are also formed. This latter compound is produced, together with ammonium cyanide, when the gas is led through a red-hot tube filled with pieces of porcelain. When it is heated with potassium, potassium cyanide is formed, with evolution of free hydrogen.

Like ammonia, the aqueous solution precipitates many metallic salts, and these precipitates partially dissolve in an excess of the reagent. Silver chloride also dissolves in excess

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[1] Schmidt, *Liebig's Ann.* cxciii. 73.

of methylamine. On the other hand, the hydroxides of cadmium, nickel, and cobalt do not do so, and these reactions serve as another means of distinguishing it from ammonia, and in addition we have the fact that aluminium hydroxide dissolves in methylamine but is insoluble in ammonia.

Hydrochloride of Methylamine or Methyl-ammonium Chloride, $N(CH_3)H_3Cl$, crystallizes from alcohol in large iridescent tablets which deliquesce on exposure to moist air. It forms with gold chloride the double salt $N(CH_3)H_3Cl+AuCl_3+H_2O$, which crystallizes in splendid large golden yellow needles, whilst the platinum salt, $[N(CH_3)\,H_3Cl]_2PtCl_4$, forms golden yellow scales or large hexagonal tables, soluble in water but insoluble in alcohol.

Sulphate of Methylamine or Methyl-ammonium Sulphate, $[N(CH_3)H_3]_2SO_4$, is easily soluble in water but insoluble in alcohol. It crystallizes in deliquescent stellar needles. It forms an alum with aluminium sulphate, $[N(CH_3)H_3]_2SO_4+Al_2(SO_4)_3+24H_2O$, which crystallizes in large regular octohedrons.

Nitrate of Methylamine or Methyl-ammonium Nitrate, $N(CH_3)H_3NO_3$, forms orthorhombic prisms which are deliquescent and easily soluble in alcohol.

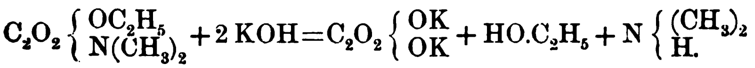
Carbonate of Methylamine or Methyl-ammonium Carbonate, $[N(CH_3)H_3]_2CO_3$, is produced on distillation of a mixture of calcium carbonate and hydrochloride of methylamine. It has, however, not yet been obtained in the pure state. It forms hard prisms which are very deliquescent, has a strongly alkaline reaction, and undergoes volatilization at the ordinary temperature of the air. At the same time, methylammonium-methylcarbamate is formed. This also is produced by the direct union of methylamine and carbon dioxide.

With platinous chloride, methylamine forms several compounds corresponding to certain of the platinammonias (Würtz).

DIMETHYLAMINE, $N(CH_3)_2H$.

148 This was discovered by Hofmann, who obtained it by heating methyl iodide with an alcoholic solution of ammonia, when the hydriodides of ammonia, methylamine, dimethylamine, and trimethylamine, as well as tetramethylammonium iodide are formed. The last salt is, however, soluble in alcohol, and it, therefore, can be readily separated from the other four. These are then distilled

with caustic potash, and the vapours led into a well-cooled tube, when trimethylamine, dimethylamine, and a portion of the methylamine are condensed, the remainder of the last-named substance passing forward with the ammonia, and being afterwards absorbed in hydrochloric acid. The mixture of the three bases is then treated with ethyl oxalate, $C_2O_4(C_2H_5)_2$, which does not act upon the trimethylamine, whilst the methylamine is converted into dimethyloxamide, $C_2O_2(NH.CH_3)_2$, and the dimethylamine into the ethyl ether of methyl oxamic acid. This latter can be separated by cold water from the difficultly soluble diethyl oxamide ; on distillation with caustic potash it is converted into potassium oxalate, alcohol, and dimethylamine :



$$C_2O_2\left\{\begin{matrix}OC_2H_5\\N(CH_3)_2\end{matrix}\right. + 2\,KOH = C_2O_2\left\{\begin{matrix}OK\\OK\end{matrix}\right. + HO.C_2H_5 + N\left\{\begin{matrix}(CH_3)_2\\H.\end{matrix}\right.$$

The alcoholic solution is neutralized with hydrochloric acid, evaporated down, and the residue, on distillation with potash, yields dimethylamine.

This base is also formed on distillation of the so-called sulphite of aldehyde-ammonia with lime. This product, however, was at one time supposed by Hofmann to be its isomeride, ethylamine.[1]

Dimethylamine also occurs in Peruvian guano[2] as well as in the products of distillation of wood (Camille Vincent). It is an ammoniacal-smelling, readily inflammable liquid boiling at between 8° and 9°.

Hydrochloride of Dimethylamine or Dimethyl-ammonium Chloride, $N(CH_3)_2H_2Cl$, is a white deliquescent mass crystallizing in scales, and forming with gold chloride, and platinum chloride, crystallizable compounds.

TRIMETHYLAMINE, $N(CH_3)_3$.

149 This occurs somewhat widely distributed in nature. Thus, for instance, it is found in various plants, as the *Chenopodium vulvaria*, *Arnica montana*, *Mercurialis annua*, the bloom of the hawthorn, that of the wild cherry, and of the pear, as well as in ergot, and other fungi parasitic on cereals. It also occurs in various animal liquids, and especially in herring-brine. It is likewise found as a product of decomposition of various

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[1] Gössmann and Petersen, *Ann. Chem. Pharm.* cii. 317.

[2] Lucius, *Ibid.* ciii. 105.

alkaloids, and amongst the products of the dry distillation of nitrogenous organic matter and of wood.

Before Hofmann's investigation on the amines it was believed that the base occurring in nature was the isomeride, propylamine. He prepared it first according to the method described, and afterwards he and Winkles[1] obtained it in larger quantity by distilling herring-brine, in which Wertheim[2] had first found it, together with lime.

It has lately been prepared in large quanties by Vincent in the distillation of the "vinasses" of the French beet-root sugar refineries. A solution of the sulphates of ammonia and trimethylamine is thus obtained from which the first salt can be partially separated by crystallization. The darkly-coloured mother-liquor is then distilled with lime, and the product passed into hydrochloric acid. This solution is then boiled down until the temperature reaches 140°. The sal-ammoniac present crystallizes out on cooling, and the mother-liquor is drawn off from this, and further evaporated until the boiling-point rises to 200°; the residue thus obtained consists of commercial hydrochloride of trimethylamine, from which the free base can be readily prepared by treatment with an alkali.

Trimethylamine is a mobile liquid boiling at from 9° to 10° and having a specific gravity of 0·673 at 0° (Blennard). It has a powerful and penetrating characteristic fish-like smell. It is very soluble in water and the concentrated aqueous solution, as well as the pure base, is easily combustible. Devillier and Buisine[3] found from 5 to 10 per cent. of this base in the commercial trimethylamine, together with 50 per cent. of dimethylamine, whilst the remaining, and about equal part, consisted of ethylamine, propylamine and iso-butylamine. According to Vincent[4] this depends upon the fact that the "vinasses" of different preparations do not always yield the same products, and that their relative amount depends upon the circumstances under which the distillation is conducted.

Trimethylamine is now used for the purpose of preparing pure potassium carbonate from potassium chloride, the process adopted being exactly similar to that described in Vol. II. Part I. p. 152 as the ammonia-soda process. The reason that ammonia cannot be employed in the preparation of potassium carbonate is that sal-ammoniac and hydrogen potassium

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[1] *Chem. Soc. Journ.* v. 288.

[2] *Wien. Akad. Ber.* vi. 113.

[3] *Compt. Rend.* lxxxix 48.

[4] *Ibid.* lxxxix. 238.

carbonate are about equally soluble in water, whilst the hydrochloride of trimethylamine is a much more soluble salt. In addition to this, it has been employed in medicine, and is said to have been of value in cases of acute rheumatism and gout.

Hydrochloride of Trimethylamine or Trimethylammonium Hydrochloride, $N(CH_3)_3HCl$, forms deliquescent crystals, and serves, as has been mentioned, for the preparation of methyl chloride. It unites with platinum chloride to form the compound $2N(CH_3)_3HCl + PtCl_4$, crystallizing in orange-coloured octohedrons. The sulphate forms, with aluminium sulphate, the alum $[N(CH_3)_3H]_2SO_4 + Al_2(SO_4)_3 + 24H_2O$, crystallizing in transparent octohedrons, possessing an astringent taste, and smelling of herring-brine. Trimethylamine combines with carbon disulphide, yielding, with considerable evolution of heat, the compound $CS_2,N(CH_3)_3$, which crystallizes in rhombic needles from alcoholic solution, and is decomposed by both alkalis and strong acids into its constituents. Dilute acids, on the other hand, unite with it to form salts. When it is brought in contact with an equal number of molecules of hydrochloric acid, the neutral compound, $CS_2,N(CH_3)_3,HCl$, is formed, which, when in contact with more acid, yields the compound $2CS_2,N(CH_3)_3, 3HCl$.

Nitric acid and sulphuric acid form corresponding compounds.[1]

TETRAMETHYLAMMONIUM COMPOUNDS.

150 The iodide, $N(CH_3)_4I$, as has been mentioned, is the chief product of the action of ammonia on methyl iodide, and is readily formed by the union of the latter compound with trimethylamine. It crystallizes from hot water in shining white needles, which possess an intensely bitter taste. On heating, it decomposes into trimethylamine and methyl chloride, which, however, reunite on cooling. The iodide possesses the property of yielding, with chlorine and iodine, several crystalline polychlorides and polyiodides, which easily undergo decomposition. When freshly precipitated silver oxide is added to a solution of the iodide, the hydroxide, $N(CH_3)_4OH$, is formed. This yields on evaporation in a vacuum, a crystalline mass, which rapidly absorbs water and carbon dioxide from the air. It acts as a powerful caustic, is strongly alkaline, and generally resembles the fixed caustic alkalis in its behaviour. On neutralization

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[1] Blennard, *Compt. Rend.* lxxxvii. 1040.

ether of cyanic acid. It is obtained by distilling a mixture of freshly-prepared potassium cyanide with potassium methyl sulphate, and it is a mobile liquid which has an excessively suffocating odour, its vapour vigorously attacking the mucous membranes. Aqueous acids and alkalis decomposes it with formation of carbon dioxide and methylamine:

$$N\begin{cases}CH_3\\CO\end{cases} + H_2O = N\begin{cases}CH_3\\H_2\end{cases} + CO_2.$$

When dry, ammonia acts upon methyl carbimide, *methyl urea* is formed, and this is likewise produced when the vapour of cyanic acid is passed over methylamine, or when a solution of potassium cyanate is evaporated with sulphate of methylamine. The formation from the carbimide occurs as follows:

$$CO.N(CH_3) + NH_3 = CO\begin{cases}N(CH_3)H\\NH_2.\end{cases}$$

Methyl urea forms long transparent prisms easily soluble in water, and combining with acids to form crystallizable salts (Würtz).

When methyl carbimide is brought in contact with water, *dimethyl-urea* is formed:

$$2\,CO.N(CH_3) + H_2O = CO\begin{cases}N(CH_3)H\\N(CH_3)H\end{cases} + CO_2.$$

The same compound is produced by acting on cyanic acid with methylamine. Dimethyl-urea forms crystals which melt at 100°, and it boils without decomposition at 270°. It is easily soluble in water, and combines with acids (Würtz).

Trimethyl Tricarbimide, $C_3O_3(NCH_3)_3$, is a polymeric modification of carbimide formed in the preparation of the latter compound, and also produced when this substance is allowed to stand. It is likewise obtained, as above described, from the cyanurate, as well as when potassium cyanurate is distilled with potassium methyl sulphate. It crystallizes in short prisms, which do not dissolve in cold water, are slightly soluble in hot water, and easily soluble in alcohol. They melt at 175° and boil at 271°.

Methyl Thiocyanate, $NC.SCH_3$, was first obtained by Cahours[1] on distilling a concentrated solution of equal parts of potassium thiocyanate and calcium methyl sulphate. It is a colour-

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[1] *Ann. Chim. Phys.* [3], xviii. 281.

less alliaceous-smelling liquid. At 0° its specific gravity is 1·088, and it boils at 133°.

Methyl Thiocarbimide or Methyl Mustard Oil, $CS.NCH_3$. When methylamine is brought in contact with carbon disulphide, methyl-thiocarbamic acid, $CS(NH.CH_3)SH$, is produced, the silver salt of which, when heated with water, decomposes as follows:

$$CS\left\{\begin{matrix}N(CH_3)H\\ SAg\end{matrix}\right. = 2N\left\{\begin{matrix}CH_3\\ CS\end{matrix}\right. + Ag_2S + H_2S.$$

Methyl thiocarbimide is a white crystalline solid, which melts at 34° and boils at 119°, and smells strongly of horse-radish. It combines with ammonia to form crystalline methyl thiocarbamide, $CS(NCH_3.H)NH_2$. The crystalline hydriodide is isomeric with methyl thiocarbamide iodide, $CS(NH_2)_2CH_3I$, obtained by the union of carbamide with methyl iodide. It possesses the characters of a sulphine compound, yielding with silver oxide and water a strongly alkaline hydroxide, $CS(NH_2)_2CH_3.OH$, which yields well crystallizable salts with acids.[1]

NITRO-COMPOUNDS OF METHYL.

152 *Nitro-Methane*, $CH_3.NO_2$, is formed when concentrated solutions of potassium nitrate and potassium chloracetate are boiled together:

$$CH_2Cl.CO_2K + KNO_2 + H_2O = CH_3NO_2 + KCl + HKCO_3.$$

The compound thus formed was termed by Kolbe[2] nitro-carbinol. About the same time V. Meyer and Stüber[3] obtained the same compound by acting on methyl iodide with silver nitrite, when a violent action occurs.

Nitro-methane is a heavy liquid, possessing a peculiar smell, and boiling at 101°. It acts as a weak acid, solidifying with an alcoholic soda solution to a mass of fine needles, having the composition $CH_2NaNO_2 + C_2H_6O$. These, when dried over sulphuric acid, fall to a light powder, which detonates on heating, and undergoes spontaneous decomposition when kept. Its concentrated aqueous solution is still more unstable, for

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[1] Bernthsen and Klinger, *Ber. Deutsch. Chem. Ges.* xi. 492.

[2] *Journ. Prac. Chem.* [2], v. 427.

[3] *Ber. Deutsch. Chem. Ges.* v. 514; *Liebig's Ann.* clxxi. [illegible]

after a few moments it suddenly suffers decomposition with evolution of heat.

The freshly prepared solution gives characteristic precipitates with many metallic salts. Of these, the yellow mercury compound is the most singular, as it is extremely explosive, detonating strongly if merely touched, when in the dry state, with a glass rod. Two milligrams of the compound when heated on a platinum cover explode with a noise equal to that of the discharge of a pistol.

On heating nitro-methane with fuming sulphuric acid, carbon dioxide and hydroxylamine are formed.[1]

$$CH_3\,NO_2 = CO + NOH_3.$$

When nitro-methane is dissolved in caustic potash, and some potassium nitrate added and then dilute sulphuric acid, a deep red solution is obtained, the colour of which disappears on addition of more sulphuric acid, and is reproduced on the addition of alkalis. This reaction depends on the formation of *methyl nitrolic acid*, $CH(NO_2)NOH$, of which the alkaline salts have a deep red colour (see p. 171). The free acid forms large glistening crystals, soluble in water, alcohol and ether. It is an extremely unstable body decomposing on standing. When heated to 64° it melts with evolution of red fumes, whilst formic acid remains behind. This latter compound is also formed on boiling with dilute sulphuric acid, when nitrogen monoxide is evolved.[2]

$$CH_2N_2O_3 = CH_2O_2 + N_2O.$$

If nitro-methane be heated with alcoholic solution of caustic soda, a crystalline mass of sodium methazonate is formed, which is permanent in the air and highly explosive.

Methazonic acid, $C_2H_4N_2O_3$, obtained from this, can be obtained from solution in ether or benzol in large crystals, which, on heating, decompose with explosive violence, and at the ordinary temperature undergo rapid change with formation of a red colour.[3]

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[1] Preibisch, *Journ. Prac. Chem.* [2], viii. 316.

[2] Meyer, *Liebig's Ann.* clxxv. 97; Tscherniak, *ibid.* clxxx. 166.

[3] Friese, *Ber. Deutsch. Chem. Ges.* ix. 394; Lecco, *ibid.* 705.

PHOSPHORUS COMPOUNDS OF METHYL.

153 Paul Thénard[1] in 1846 examined the properties of several volatile compounds containing phosphorus which he had obtained by acting on calcium phosphide with methyl chloride. Amongst these occurred trimethylphosphine, $P(CH_3)_3$, and tetramethyldiphosphine, $P_2(CH_3)_4$. In 1855 Cahours and Hofmann[2] investigated the substances obtained by the action of methyl iodide on sodium phosphide, and discovered, in addition to the two bodies just mentioned, tetramethylphosphonium iodide, $P(CH_3)_4I$. They likewise found that by this process explosive bodies are produced, and, for this reason, the investigation is not without danger. On this account they sought for and succeeded in finding a better method of preparation, which will afterwards be described.

Monomethylphosphine and dimethylphosphine were discovered by Hofmann in 1871.[3]

Methyl Phosphine, $P(CH_3)H_2$, is formed by the action of phosphonium iodide on methyl iodide in the presence of zinc oxide:

$$2\,CH_3I + 2\,PH_4I + ZnO = 2\,P(CH_3)H_3I + ZnI_2 + H_2O.$$

The secondary base is formed at the same time, according to the equation:

$$2\,CH_3I + PH_4I + ZnO = P(CH_3)_2H_2I + ZnI_2 + H_2O.$$

In order to prepare these compounds, the materials are mixed in the proportions indicated by the first equation, placed in carefully closed tubes, and then heated from six to eight hours to 100°. After this operation, the contents of the tubes form a crystalline mass consisting of the two double zinc salts. The primary base is obtained from these by decomposition with water, whilst the dimethylphosphine salt remains unaltered, but may be decomposed by alkalis.[4]

In order to prepare the free bases, the product of the reaction is brought into the vessel A, Fig. 62, filled with hydrogen, and water is allowed to drop upon the mass. Methyl phosphine gas

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[1] *Compt. Rend.* xxv. 289.

[2] *Phil. Trans.* 1857, 575; see also *Chem. Soc. Journ.* xiii. 289; xiv. 73, 316.

[3] *Proc. Roy. Soc.* xx. 221.

[4] Hofmann, *Ber. Deutsch. Chem. Ges.* iv. 605.

is then evolved with hissing and effervescence; this is allowed to pass through a spiral tube surrounded by a freezing mixture into the vessel H, also well cooled, in which it is condensed. When no evolution of gas takes place on further addition of water, the crystalline mass is heated until the whole is dissolved, when a sudden torrent of gas is frequently given off, and hence the receiver is connected with a condensing flask, K, containing concentrated hydriodic acid, in which any uncondensed gas which might otherwise escape is absorbed.

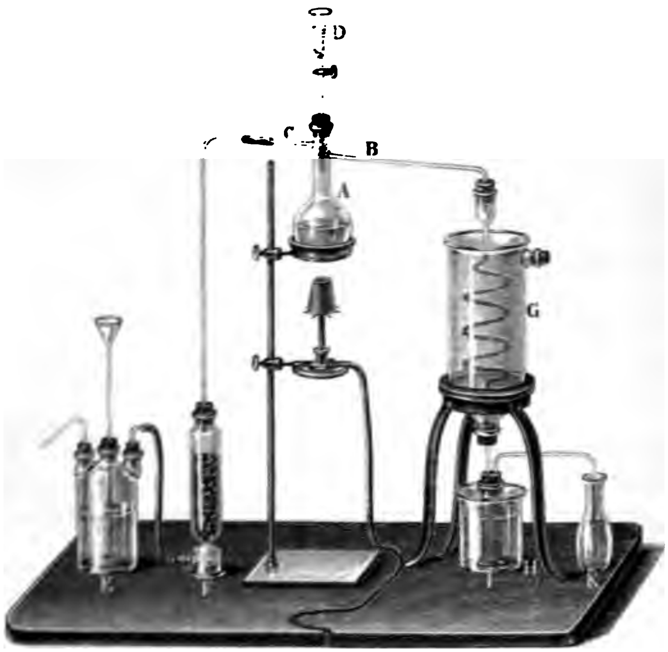

FIG. 62.

Methyl phosphine is a colourless gas, possessing an excessively powerful odour. It condenses on cooling or under pressure to a liquid boiling at −14°, and its vapour density is 1·687. On exposure to air, it evolves white fumes, and takes fire even when but slightly warmed. In contact with chlorine, bromine, or nitric acid, it burns with a bright flame. It forms with acids a well-defined series of salts which, like those of phosphuretted hydrogen, are decomposed by water, and possess moreover the singular property of bleaching vegetable colours like chlorine, a reaction which is not exhibited by the free base. This may be well shown by bringing a piece of litmus-paper, half moistened with water and half with acid, into the gas, when the latter half only will be bleached.

Methyl Phosphonium Chloride, $P(CH_3)H_3Cl$, is formed by the union of its two anhydrous constituents. It crystallizes in four-sided tables, which are so volatile that their ethereal solution evaporates as a whole.

Methyl Phosphonium Iodide, $P(CH_3)H_3I$, separates from concentrated hydriodic acid in large compact crystals, and can easily be obtained pure by sublimation.

Methyl Phosphinic Acid, $P(CH_3)O(OH)_2$, is obtained when the base is passed into concentrated nitric acid. It forms a hygroscopic, spermaceti-like, crystalline mass, which melts at 105°, is easily soluble in water, and possesses a purely acid taste. Being a dibasic acid, it yields two series of salts.[1]

Phosphorus pentachloride decomposes it into the chloride, $P(CH_3)OCl_2$, a white crystalline body which melts at 32° and boils at 163°, and is decomposed with explosive violence by water.[2]

This compound is isomeric with methylphosphorous acid, from which, however, it is sharply distinguished by its properties.

154 *Dimethylphosphine*, $P(CH_3)_2H$. If caustic soda solution be added to the liquid from which methyl phosphine has been obtained, the secondary base is liberated, and separates out in a layer on the top of the liquid. It is a colourless liquid, boiling at 25°, and taking fire instantly on exposure to the air, burning with a very luminous, phosphorus-like flame. If the atmosphere of hydrogen in which it is prepared contains even a trace of air, this is instantly observed by the formation of a white cloud, and dangerous explosions may ensue in the preparation of this body, unless great care be taken. It forms with acids easily soluble salts. The hydrochloride yields with platinic chloride a well crystallizable double salt.[3]

Nitric acid oxidizes the base to dimethylphosphinic acid, $P(CH_3)_2O.OH$, a white paraffin-like mass, melting at 76°, and volatilizing without decomposition. It is a monobasic acid, and yields a well-defined series of salts.[4] Phosphorus pentachloride

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[1] Hofmann, *Ber. Deutsch. Chem. Ges.* v. 104.

[2] *Ibid.* vi. 303.

[3] *Ibid.* iv. 610.

[4] *Ibid.* v. 108.

converts it into the chloride, $P(CH_3)_2OCl$, a crystalline body melting at 66°, and boiling at 204°, and being slowly decomposed by water.[1]

155 *Trimethyl Phosphine,* $P(CH_3)_3$, is obtained by acting on phosphorus trichloride with zinc methyl:

$$3\,Zn(CH_3)_2 + 2PCl_3 = 3ZnCl_2 + 2\,P(CH_3)_3.$$

The apparatus employed for preparing this substance is shown in Fig. 63. A pipette furnished with a stopcock contains phosphorus trichloride, and the retort a mixture of ether and zinc methide. This is connected with a bent tube, in which a few drops of phosphorus trichloride are placed, whilst to this is attached a cylinder (C) containing dry carbon dioxide, the whole of the apparatus being filled with the same gas before the beginning of the experiment from the evolution flask (A). The trichloride is then allowed to pass drop by drop into the retort, when a reaction takes place as violent as that observed when sulphur trioxide acts on caustic baryta, so that the zinc methyl is partly volatilized, and carried forward not only into the receiver but into the bent tube, where it meets with the phosphorus trichloride, and is absorbed. The drop of trichloride serves also as an indicator of the progress of the reaction. After a time the action becomes less violent, and when no further evolution of

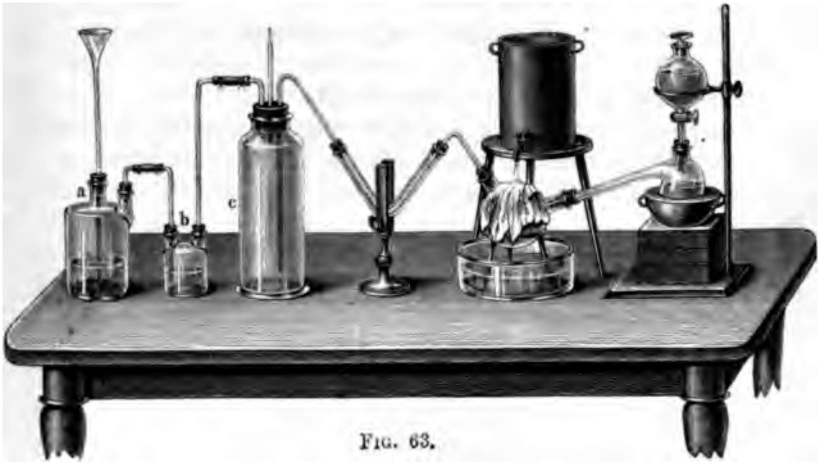

FIG. 63.

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[1] Hofmann, *Ber. Deutsch. Chem. Ges.* vi. 307.

heat takes place, it is complete. In the receiver and bent tube, and sometimes even in the cylinder (C), two layers of liquid are found, of which the upper one consists of a mixture of ether and phosphorus trichloride, which may again be employed in a second preparation of the base; the second and heavy layer is a compound of trimethylphosphine with zinc chloride. For the purpose of obtaining the free base, solid caustic potash is added to this liquid, and water gradually allowed to drop in, when so much heat is evolved that the base distils over; this then is dried over caustic potash and rectified. These operations must be carried on in an atmosphere of carbon dioxide.

Trimethylphosphine is also easily formed by heating methyl alcohol with phosphonium iodide in sealed tubes.[1]

$$3CH_3.OH + PH_4I = P(CH_3)_3HI + 3H_2O.$$

If it is desired to prepare it according to this process, two molecules of the iodide are added to only five molecules of alcohol in order to avoid the formation of tetramethyl phosphonium iodide. In this case, however, large quantities of phosphine are formed by a secondary reaction, and hence it is necessary to employ strong and well fused tubes, which must be heated for many hours to 180°. The product thus obtained yields the free base on treatment with caustic soda solution.

The formation of this compound by heating phosphonium-iodide with carbon disulphide to 150° is of great theoretical interest:[2]

$$3CS_2 + 4PH_4I = P(CH_3)_3HI + 3H_2S + 3PSI.$$

Trimethylphosphine is a light, mobile, powerfully refracting liquid, which boils at from 40° to 42°, and has a most indescribable and penetrating odour. It fumes in the air, and on exposure becomes surrounded by a crystalline crust of trimethylphosphine oxide, $P(CH_3)_3O$, and frequently takes fire. It also combines directly with sulphur, selenium, and the elements of the chlorine group, as well as with carbon bisulphide. The compounds thus obtained closely resemble the corresponding triethylphosphines.

156 *Tetramethylphosphonium Iodide*, $P(CH_3)_4I$, is formed by the union of methyl iodide with trimethylphosphine, and, together

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[1] Hofmann, *Ber. Deutsch. Chem. Ges.* iv. 205, 372.

[2] Drechsel, *Journ. Prac. Chem.* [2]. x. 180.

with the tertiary base, by heating methyl alcohol with phosphonium iodide:[1]

$$4\ CH_3.OH + PH_4I = P(CH_3)_4I + 2H_2O.$$

It crystallizes from hot alcohol in beautiful glistening white crystals, which assume a reddish colour on exposure to air. A strongly alkaline hydroxide is obtained by acting with moist silver oxide on its aqueous solution, and this decomposes on distillation into methane and trimethylphosphine oxide:

$$P(CH_3)_4OH = CH_4 + P(CH_3)_3O.$$

Tetramethyl Diphosphide, $P_2(CH_3)_4$. This compound, corresponding to liquid phosphuretted hydrogen, was, as has been stated, discovered by Paul Thénard, and then observed by Cahours and Hofmann. It is a thick, colourless liquid, possessing a most unpleasant smell, boiling at 250°, and taking fire on exposure to air.

ARSENIC COMPOUNDS OF METHYL.

157 In the year 1760, the French chemist Cadet observed that a mixture of equal parts of acetate of potash and white arsenic, when heated, yields, together with white arsenic and acetic acid containing arsenic, a heavy brownish-red liquid which has a most frightful smell, and fumes strongly in the air.[2] This fact was confirmed by Durande,[3] whilst Thénard[4] investigated this compound, which was termed *Cadet's fuming arsenical liquid*, and gave to it the name of "*acetite oleo-arsenical.*" It is, however, to the classical research of Bunsen,[5] carried on for many years under circumstances of no slight danger, that we owe an exact knowledge of the arsenical methyl compounds.

Bunsen showed that Cadet's liquid, as well as its numerous derivatives, contains a radical having the formula C_2H_6As, and that this substance, in its chemical relations, exhibits striking analogies with a metal. He succeeded in isolating this body, and as we have already seen, this discovery contributed largely to the development of the theory of compound radicals.

[1] Hofmann, *Ber. Deutsch. Chem. Ges.* iv. 205.

[2] *Mém. de Math. et Phys. Pres. des Savants Étrang.* iii. 633.

[3] *Nouveau Chim. Prac. Theor.* iii. 39.

[4] *Ann. de Chim.* lii. 54.

[5] *Ann. Chem. Pharm.* xxiv. 271; xxvii. 148; xxxi. 175; xxxvii. 1; xlii. 14; xlvi. 1; and *Chem. Soc. Mem.* 1841, i. 49; *Phil. Mag.* [3], xx. 180, 395; xxii. 180.

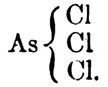
This body, like most of its compounds, possesses a frightfully offensive odour, so much so that the air of a room containing even a trace of the vapour is rendered so unbearable as frequently to cause vomiting. For this reason the name *cacodyl* (*κακώδης*, stinking) was given to this compound by Berzelius.

Various hypotheses have been put forward respecting the constitution of this radical. Kolbe[1] first suggested the view that it was *arsen-dimethyl*, $As(CH_3)_2$. This was rendered very probable by the experiments of Frankland,[2] and this view was afterwards corroborated by Cahours and Riche.[3] The latter also discovered *trimethylarsine* and the *tetramethylarsonium compounds.* But it is to Baeyer,[4] who at a later period, in a masterly investigation, first prepared the *arsen-monomethyl compounds,* that we are indebted for the full explanation of the relations which these various bodies bear to one another.

The arsenic compounds of methyl and of the other alcoholic radicals played an important part in the development of theoretical views, not only because they furnished us with the first example of an isolable organic radical, but also because they served Frankland[5] and Kekulé[6] as a means of more exactly illustrating the meaning of the term "chemical valency."

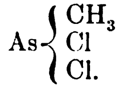
The arsenic compounds of methyl may be considered as being derived from arsenic trichloride by the partial or complete replacement of the chlorine by the alcohol radical:

Arsenic trichloride.



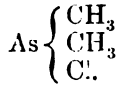
$$As\left\{\begin{matrix}Cl\\Cl\\Cl.\end{matrix}\right.$$

Arsen-methyl dichloride.



$$As\left\{\begin{matrix}CH_3\\Cl\\Cl.\end{matrix}\right.$$

Arsen-dimethyl chloride.



$$As\left\{\begin{matrix}CH_3\\CH_3\\Cl.\end{matrix}\right.$$

Trimethylarsine.

$$\left\{\begin{matrix}CH_3\\CH_3\\CH_3.\end{matrix}\right.$$

The chlorine of these compounds may be replaced by other elements or radicals, and for this reason arsen-monomethyl is

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[1] *Handwörterb.* iii. 442; iv. 222.
[2] *Journ. Chem. Soc.* ii. 297.
[3] *Compt. Rend.* xxxvi. 1001; xxxix. 541; *Ann. Chem. Pharm.* lxxxviii. 316, xcii. 361.
[4] *Ann. Chem. Pharm.* cvii. 257.
[5] *Phil. Trans.* 1852, p. 440; or *Experimental Researches*, 188.
[6] *Ann. Chem. Pharm.* cvi. 129.

considered as a dyad, and arsen-dimethyl as a monad radical. These arsenic compounds are, as Baeyer has shown, mutually convertible. They combine like phosphorus trichloride, with one molecule of chlorine, and the bodies thus obtained easily decompose with evolution of methyl chloride. The compound of arsen-monomethyl is, however, so unstable that it can only be preserved in a freezing mixture:

$$As(CH_3)_3Cl_2 = CH_3Cl + As(CH_3)_2Cl.$$
$$As(CH_3)_2Cl_3 = CH_3Cl + As(CH_3)Cl_2.$$
$$As(CH_3)\,Cl_4 = CH_3Cl + AsCl_3.$$

Trimethylarsine, $As(CH_3)_3$, is obtained, together with cacodyl and tetramethylarsonium iodide, by the action of sodium arsenide on methyl iodide (Cahours and Riche). It is produced on treating arsenic trichloride with zinc methyl:[1]

$$2AsCl_3 + 3Zn(CH_3)_2 = 2As(CH_3)_3 + 3ZnCl_2.$$

In place of arsenic trichloride, cacodyl iodide may be employed. It is, however, best prepared by distilling potash with tetramethylarsonium iodide or one of its double salts,[2] which will be described hereafter. It is a strongly refracting liquid, boiling at about 70°, and possessing a highly penetrating and disagreeable odour. It does not form salts with acids, but on exposure to air becomes heated, without taking fire, owing to its absorption of oxygen to form a crystalline oxide. It also unites directly with sulphur and the elements of the chlorine group, yielding crystalline compounds.

Tetramethylarsonium Compounds. The iodide, $As(CH_3)_4I$, is the chief product of the action of methyl iodide on sodium arsenide, and remains behind as a white crystalline mass when the trimethylarsine and cacodyl, which are formed at the same time, are removed by distillation in an atmosphere of carbon dioxide. It is also formed by the action of methyl iodide on cadodyl:

$$(CH_3)_4As_2 + 2CH_3I = (CH_3)_4AsI + (CH_3)_2AsI.$$

When treated with silver oxide, the aqueous solution yields the corresponding hydroxide, $As(CH_3)_4OH$. This substance has a strongly alkaline reaction, and, on evaporation, is deposited in the form of deliquescent tabular crystals. When

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[1] Cahours and Riche, *Comptes Rendus*, xxxix. 541.

[2] Cahours, *Comptes Rendus*, l. 1022.

arsenic is heated with methyl iodide to 200°, the compound $As(CH_3)_4I + AsI_3$ is obtained, crystallizing from hot alcohol in red glittering needles. On heating arsenide of zinc with methyl iodide to 180°, the double salt $As(CH_3)_4I + ZnI_2$ is obtained, and this separates from hot alcohol in white needles. A corresponding cadmium compound is also known.

When zinc methyl acts upon tetramethylarsonium iodide, and the product thus obtained is distilled, a considerable quantity of trimethylarsine passes over first, and then a liquid which, according to Cahours,[1] is *pentamethylarsine*, $As(CH_3)_5$. It is decomposed by iodine into methyl iodide and tetramethylarsonium iodide whilst hydrochloric acid yields the corresponding chloride, together with marsh gas. This singular body deserves further examination.

THE CACODYL OR DIMETHYLARSINE COMPOUNDS.

158 The point of departure of these bodies is Cadet's liquid, or *alcarsin*, as Bunsen termed it, giving it this name because he at first believed it might be considered as a polymeric alcohol, oxygen being replaced by arsenic.

According to Baeyer, the best mode of preparing this substance is to heat equal parts of white arsenic and anhydrous sodium acetate in a retort in quantities of about 3 kg. at a time, allowing the vapours to pass through a Liebig's condenser into a receiver containing water. Highly poisonous gases are thus given off, which must be allowed to pass up a flue into the open air. The heavy oily liquid consists chiefly of cacodyl oxide, which is formed according to the following equation:

$$4CH_3.CO_2K + As_2O_3 = [(CH_3)_2As]_2O + 2K_2CO_3 + 2CO_2.$$

In addition to this, some free cacodyl is formed by reduction, and this it is which gives to the crude product the property of spontaneous ignition. Acetic acid, acetone, marsh gas, ethylene, water, and arsenic occur as by-products. For the purpose of purification, the crude oil is distilled with several times its weight of hydrochloric acid and corrosive sublimate. In this way pure cacodyl chloride can be obtained, which may be converted into the pure oxide by distillation with caustic potash.

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[1] *Ann. Chem. Pharm.* cxxii. 338.

Cacodyl Oxide or Dimethylarsine Oxide, $\left.\begin{matrix}(CH_3)_2As\\(CH_3)_2As\end{matrix}\right\}O$. This is a colourless, heavy liquid, which is not soluble in water, but dissolves in alcohol and ether. It boils at about 150°, and solidifies a few degrees below −23°, forming a crystalline mass; it does not fume in the air, but its vapour, when mixed with air, explodes if heated above 50°. It possesses a frightfully irritating smell, destroying the mucous membrane and producing insensibility, and acts as a very powerful poison. Although it does not possess an alkaline reaction, it is a very strong base readily uniting with acids to form salts.

Cacodyl Chloride, $(CH_3)_2AsCl$. When the oxide is heated with hydrochloric acid alone, not only is the chloride formed but also the oxychloride in considerable quantity; the production of this latter being avoided by the employment of corrosive sublimate. Cacodyl chloride is a heavy, colourless, transparent liquid which boils at a temperature not far from 100°, yielding a vapour whose density is 4·56. The vapour ignites spontaneously on exposure to air, burning with a pale arsenic-like flame. Heated in oxygen it explodes most violently. It does not fume on exposure to air but absorbs oxygen, forming crystals the composition of which has not been ascertained. Its smell is very penetrating and stupefying, far surpassing in this respect the smell of the oxide. Inhaled in even moderate quantity it produces such inflammation of the mucous membrane of the nose that the vessels swell up, and the eyes are congested with blood. Cacodyl chloride forms double salts with various metallic chlorides such as sal-ammoniac. The platinum compound, $2\,(CH_3)_2AsCl + PtCl_4$, is obtained as a red precipitate by mixing alcoholic solutions of the chloride and platinum chloride. When this is dissolved in hot water yellow needles of cacoplatylchloride, $(CH_3)_4As_2O.PtCl_2 + H_2O$, and from this other cacoplatyl compounds can be obtained.

Cacodyl Trichloride, $(CH_3)_2AsCl_3$. Cacodyl monochloride takes fire in chlorine gas. If, however, it be dissolved in carbon disulphide and chlorine led on to the surface of the liquid the trichloride crystallizes out in transparent prisms which decompose at 40° into methyl chloride and methyl-arsen-dichloride.

The compounds of cacodyl with the other members of the chlorine group closely resemble the chlorides.

Cacodyl Cyanide, $(CH_3)_2As(CN)$, is formed by distilling the oxide with [illegible] acid, as well as by acting on the same substance with mercuric chloride. It crystallizes in large glistening four-sided prisms which can be sublimed. They melt at 33° and boil at about 140°. This compound is scarcely soluble in water though easily so in alcohol and ether. When heated in the air it takes fire and burns with a reddish-blue flame. This substance is extraordinarily poisonous, and for this reason its preparation and purification can only be carried on in the open air; indeed even under these circumstances it is necessary for the operator to breathe through a long glass tube open at both ends, and thus to ensure the inspiration of air free from impregnation with every trace of the vapour of this very volatile compound. If only a few grains of this substance be allowed to evaporate in a room at the ordinary temperature, the effect upon any one inspiring the air is that of sudden giddiness and insensibility amounting to complete unconsciousness. These symptoms, however, last only for a short time, and are without subsequent evil effects, provided the operator withdraws himself in good time from the action of the poison (Bunsen).

Cacodyl Sulphide, $\left.\begin{matrix}(CH_3)_2As\\(CH_3)_2As\end{matrix}\right\}S$, was obtained by Bunsen by distilling the chloride with a solution of barium hydrosulphide. It is a colourless liquid which does not fume in the air, and possesses a highly disagreeable and unpleasant smell, reminding one at the same time of mercaptan and alcarsin, and one which remains attached to articles with which it has been in contact for a great length of time. It boils far above 100°, but volatilizes together with aqueous vapour, and is very easily inflammable. It is decomposed by acids with evolution of sulphuretted hydrogen, and it yields, with solutions of various metallic salts, precipitates like those produced by sulphide of ammonium. It combines with sulphur to form the disulphide $(CH_3)_4As_2S_2$, crystallizing from alcohol in large clear rhombic tables possessing an unpleasant smell, and fusing at 50°.

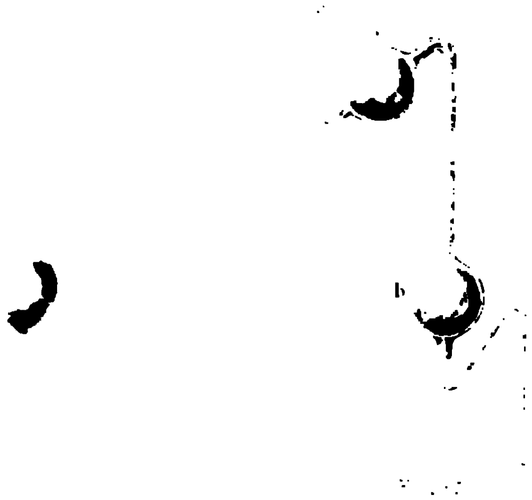
Cacodyl Selenide, $\left.\begin{matrix}(CH_3)_2As\\(CH_3)_2As\end{matrix}\right\}Se$, is obtained by distilling the chloride with sodium selenide. It is a yellow liquid which in smell resembles the sulphide, but, at the same time, has an aromatic odour. It behaves towards solutions of the metallic salts like the selenides of the alkali metals.

159 *Dicacodyl*, $(CH_3)_4As_2$. This is the free radical of the dimethylarsine compounds. It is easily formed by heating the chloride with zinc from 90° to 100°:

[illegible] Z [illegible]

[illegible] the [illegible] with [illegible] to the vapour [illegible]

[illegible] atmosphere [illegible] Fig. [illegible] The bulb [illegible] caustic potash, [illegible] dioxide. The [illegible]-pump into the



[illegible] by means [illegible] in the [illegible] the zinc. [illegible] the [illegible] A [illegible] of zinc [illegible] by [illegible] when [illegible] again [illegible]

Dicacodyl is a heavy, clear, mobile, strongly refracting liquid which smells like the oxide, and undergoes such a violent oxidation on exposure to air that when it is attempted to drop the liquid from a bottle the liquid takes fire before it leaves the glass. When air is allowed to come into contact with it slowly, it forms a thick white cloud, and is converted into cacodyl oxide and cacodylic acid. It boils at 170° and solidifies at −6°, forming large quadratic prisms. The vapour density of cacodyl chloride is 7·101. It burns in oxygen with a pale blue flame, and when thrown into chlorine burns with a bright light with deposition of carbon. Shaken up with chlorine water it forms cacodyl chloride. It also combines directly with sulphur and other elements yielding the compounds which have been already described, and for this reason Bunsen correctly observes that this radical in every respect plays the part of a simple electropositive element, and that it is indeed a *true organic element*.

With the haloid salts of the organic radicals it forms the arsenium compounds:

$$(CH_3)_4As_2 + 2\,C_2H_5Cl = (CH_3)_2(C_2H_5)_2AsCl + (CH_3)_2AsCl.$$

Cacodylic Acid or Dimethylarsenic Acid, $AsO(CH_3)_2OH$, is formed by the further oxidation of the oxide in the air. It may be obtained more rapidly by pouring water on the last-named compound mixed with mercuric oxide:

$$(CH_3)_4As_2O + 2\,HgO + H_2O = 2\,(CH_3)_2AsO.OH + 2\,Hg.$$

It is easily soluble in water, has an acid reaction, is odourless, and crystallizes from alcoholic solution in deliquescent oblique rhombic prisms. It is not attacked by fuming nitric acid or even by aqua regia, and according to Bunsen it is not poisonous, although the experiments of Lebahn and Schultz[1] have not altogether corroborated this statement, as they found that doses of four decigrams act fatally upon a rabbit. Phosphorus pentachloride decomposes cacodylic acid into arsendimethyl trichloride:

$$(CH_3)_2AsO.OH + 2\,PCl_5 = (CH_3)_2AsCl_3 + 2\,POCl_3 + HCl.$$

Concentrated hydrochloric acid converts cacodylic acid into the compound $(CH_3)As(OH)_2Cl$, to which Bunsen has given the name of cacodyl perchloride, as it is also obtained by the action

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[1] *Ber. Deutsch. Chem. Ges.* xii. 22.

of moist air on the trichloride. Water
mation of cacodylic acid. The salts of ca
in water and crystallize with difficu
$(CH_3)_2OAs.OAg$, separates out from ho
groups of needles.

MONOMETHYL ARSINE Co

160 Cacodyl trichloride decomposes, as
when heated to 40°-50° into methyl cl
dichloride, $As(CH_3)Cl_2$, which compound
heating cacodylic acid in a current of hy

$$As(CH_3)_2O.OH + 3\,HCl = As(CH_3)C$$

It is a heavy, mobile, strongly refractin
It does not fume in the air and is not d
which it dissolves with tolerable readine
body attack the mucous membrane in
manner. If even smelt, the eyes, the n
swell considerably, and a peculiar pierc
the throat (Baeyer). The crystalline tet
is formed when this body is treated wit
compound is stable only at a low tem
decomposes into methyl chloride and arse
dichloride be saturated under water wi
methylarsenoxide, $As(CH_3)O$, is formed w
evolved. Methylarsenoxide is soluble i
and carbon disulphide, and may be ob
solvent in large crystals, apparently cubi
the regular system. These melt at 95
asafœtida. In a short time they unde
porcelain-like mass, and in this respect
arsenic trioxide; indeed in its general pr
appears to hold a middle place betwee
cacodyl oxide. It forms with hydriodic ac
$As(CH_3)I_2$, crystallizing in long glitteri
sessing no smell, which melt at 25°,
without decomposition above 200°.

Methylarsensulphide, $As(CH_3)S$, is fo
sulphuretted hydrogen on the chloride, a
alcohol or carbon disulphide in glittering
which have a faint smell of asafœtida

Zinc-Methyl or Zinc Methide, $Zn(CH_3)_2$. This important body was discovered, together with its homologue, zinc-ethyl, in 1849, by Frankland.[1] By this discovery our science was enriched with a new class of bodies, not only of the highest importance for the development of our theoretical knowledge, but also serving as the means of preparing a number of highly interesting carbon compounds, such as those of the alcohol radicals, with boron, phosphorus, and silicon, the tertiary alcohols, and many other bodies, some of which have already been described, and many others which will be mentioned in the sequel.

Frankland obtained these zinc compounds by heating the corresponding iodides with zinc to a temperature of 150°, and subjecting the crystalline product of the reaction to dry distillation. In the case of methyl iodide the compound obtained is $Zn(CH_3)I$, and this when heated decomposes as follows:

$$2\,Zn\left\{\begin{matrix}CH_3\\ I\end{matrix}\right. = Zn\left\{\begin{matrix}CH_3\\ CH_3\end{matrix}\right. + Zn\left\{\begin{matrix}I\\ I.\end{matrix}\right.$$

He also found that this reaction easily takes place at 100° in the presence of anhydrous ether, but then the ether cannot readily be separated from the zinc-methyl. If, however, the compound thus obtained be repeatedly heated with zinc and methyl iodide, nearly pure zinc-methyl can be obtained.[2]

Butlerow, who has employed large quantities of zinc-methyl in his researches, found it advisable to employ granulated zinc which had previously been treated with acid. This was then quickly dried and placed with the iodide in sealed tubes, which were afterwards heated to 100° until the whole of the liquid had disappeared.[3]

Another method for the preparation of zinc-methyl in quantity consists in heating mercury-methyl, $(CH_3)_2Hg$, which can be readily prepared, with a large excess of zinc for twenty-four hours to 120°.[4]

It is, however, most readily obtained according to the process described by Gladstone and Tribe.[5] These observers found that when copper is present under certain conditions, the reaction takes place very readily. For this purpose they make use of a

[1] *Journ. Chem. Soc.* ii. 297.

[2] Wanklyn, *Journ. Chem Soc.* xiii. 124.

[3] *Zeitsch. f. Chem.* 1863, 497.

[4] Frankland and Duppa, *Journ. Chem. Soc.* xvii. 29.

[5] *Journ. Chem. Soc.* 1879, i. 107.

"copper-zinc couple," prepared in the following way: Thin zinc foil, of which about 9 square dm. weigh about 2 grams, is cut into small pieces. These are then brought into the flask which serves for the preparation of the zinc-methyl. Eighty-four cbc. of a solution of sulphate of copper containing 2 per cent. of the anhydrous salt is then poured in, and in this way a spongy coating of copper is deposited upon the zinc. The zinc sulphate formed is then poured off, the metal washed with water, alcohol, and afterwards with ether, and dried in a current of coal gas or hydrogen. To this, methyl chloride is then added, and the crystalline zinc methyl iodide is formed slowly at the ordinary temperature, but quickly when warmed. This is then distilled in an atmosphere of carbon dioxide, and thus pure zinc-methyl obtained. The same chemists have lately given a simpler method for preparing the "copper-zinc couple." Copper oxide is reduced in a current of hydrogen at as low a temperature as possible. One part of the metal thus obtained is brought into a flask with 9 parts of coarsely divided zinc filings, and the mixture, constantly shaken and turned round, is warmed over a gas-flame until the zinc filings begin to alter their form and become yellow. Then the powder is once more strongly shaken, and if the experiment succeeds the product must be a dark powder having a metallic lustre.[1]

In order to prepare zinc-methyl the apparatus shown in Fig. 66 is best employed. The flask (A) in which the mixture is contained is always connected to a reversed condenser, the upper end of which is placed in connection with a small bulb apparatus containing mercury, in order to prevent the access of air. Before the vessel is heated, the whole apparatus is filled with carbon dioxide. The end of the reaction is easily ascertained by no more methyl iodide running back. The flask is then connected with the upper end of the condenser and the zinc-methyl distilled off and collected in a receiver filled with carbon dioxide and shut off from the air by means of mercury.

165 *Properties.*—Zinc-methyl is a colourless, mobile, strongly refracting liquid, boiling at 46° and having a specific gravity at 10°·5 of 1·386. Its vapour density is 3·29 (Wanklyn). It has a strong disagreeable odour, and instantly takes fire when brought in contact with the air, burning with a bright greenish-blue flame with formation of thick clouds of zinc oxide. It burns

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[1] *Journ. Chem. Soc.* 1879, i. 567.

explosively in oxygen, and is decomposed with great violence by water with evolution of marsh gas:

$$Zn(CH_3)_2 + 2\,H_2O = 2\,CH_4 + Zn(OH)_2.$$

Hence it is necessary in the preparation to avoid the presence of all moisture.

According to Frankland, the accidental inhalation of its vapour produces symptoms of poisoning indicated by its powerful action on the nervous system. Friedel and Crafts[1] also considered it highly poisonous. On the other hand, Wanklyn and Butlerow[2] state that it is not poisonous. The latter chemist who, as has been said, has worked for a long time with this material, mentions that although it possesses an unpleasant smell, and for some time exerts a disagreeable sensation in the throat, and gives rise to difficulty of breathing and violent coughing when inhaled, these symptoms disappear after a few hours without any

FIG. 66.

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[1] *Bull. Soc. Chim.* 1865, ii. 357.

[2] *Ann. Chem. Pharm.* cxliv. 39.

visible effects remaining. By the action of methyl iodide or of zinc-methyl iodide at a high temperature, ethane is formed:

$$(1)\quad Zn\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\} + 2\,CH_3I = 2\,C_2H_6 + ZnI_2.$$

$$(2)\quad Zn\left\{\begin{matrix}CH_3\\I\end{matrix}\right. + CH_3 = C_2H_6 + ZnI_2.$$

It is therefore necessary in the preparation of zinc-methyl that an excess of metal should be present, but in spite of this almost always some quantity of ethane, as well as of marsh gas, is formed, inasmuch as it is impossible to obtain either the apparatus or the material absolutely dry.

When dry air is slowly brought in contact with zinc-methyl a crystalline mass smelling like camphor is obtained, having the composition $Zn(OCH_3)CH_3$. This is decomposed by water into methyl alcohol, marsh gas, and zinc hydroxide. The same compound is also formed when zinc-methyl is acted upon by a small quantity of methyl alcohol, whilst when an excess is employed a second solid compound, $Zn(OCH_3)_2$, is formed (Butlerow).

Iodine converts zinc-methyl first into zinc-methyl iodide, CH_3ZnI, a body already mentioned, and this on further treatment with iodine yields methyl iodide and zinc iodide. It has already been stated that the formation of zinc-methyl is assisted by the presence of ether, but that it is not possible to separate these two bodies by fractional distillation. This is not in consequence of the two substances boiling at nearly the same temperature, but because a distinct compound of the two is formed, having the composition $2\,Zn(CH_3)_2 + (C_2H_5)_2O$. Frankland has proved this by employing, instead of common ether, methyl ether, which boils at 21°, and he thus obtained the homologous compound $2\,Zn(CH_3)_2 + (CH_3)_2O$, which boils at the same temperature as zinc-methyl itself. Zinc-methyl readily absorbs sulphur dioxide with formation of methyl-zinc-sulphonate, $(CH_3.SO_2)_2Zn$, a compound examined by Hobson,[1] who described it first as zinc-methyl-dithionate. He also prepared a series of other salts by double decomposition. Zinc-methyl combines slowly with nitric oxide, giving rise to a colourless crystalline body having the composition $Zn(CH_3)_2(NO_2)_2$, which oxidizes so quickly on exposure to air that it readily takes fire. It is at once decomposed by water with formation of marsh gas,

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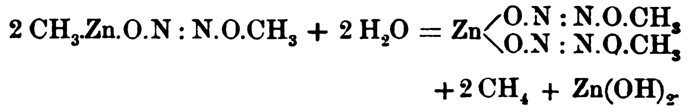
[1] *Journ. Chem. Soc.* x 243.

zinc hydroxide, and *zinc dinitromethylate*, $Zn(CH_3)_2(N_2O_2)_2 + H_2O$, which yields, with sodium carbonate, the corresponding sodium salt $Na(CH_3)N_2O_2 + H_2O$. This separates from its alcoholic solution in crystals which on heating deflagrate powerfully. The constitution of these singular bodies is not known. The following formulæ and equation may, however, probably express their composition:

$$Zn(CH_3)_2 + 2\,NO = CH_3.Zn.O.N{:}N.O.CH_3.$$



$$2\,CH_3.Zn.O.N : N.O.CH_3 + 2\,H_2O = Zn\begin{cases} O.N : N.O.CH_3 \\ O.N : N.O.CH_3 \end{cases} + 2\,CH_4 + Zn(OH)_2.$$

When sodium is allowed to act on an ethereal solution of zinc-methyl, sodium methyl, $NaCH_3$, is formed. This body has probably not yet been obtained in the pure state. Its existence is, however, proved by the products obtained by the action of carbon dioxide on this substance, when heat is evolved and sodium acetate is produced:[1]

$$NaCH_3 + CO_2 = NaCO_2.CH_3.$$

166 *Mercury-Methyl*, $Hg(CH_3)_2$, was discovered by Frankland, who obtained it by the action of light on methyl iodide in presence of mercury, when the crystalline compound, mercury methyl iodide, $Hg(CH_3)I$, is formed, and this, when heated with zinc-methyl, is converted into mercury-methyl. The same compound is obtained by the action of zinc-methyl on mercuric chloride, and Frankland and Duppa[2] discovered another very simple method by which this body can be obtained in any desired quantity. Sodium amalgam does not act upon methyl-iodide in the cold, but if methyl acetate be added, heat is evolved and mercury-methyl is formed:

$$2\,CH_3I + HgNa_2 = Hg(CH_3)_2 + 2\,NaI.$$

In order to prepare it according to this method sodium amalgam containing one per cent. of the alkali metal is gradually added to a mixture of ten volumes of methyl iodide and one volume of methyl acetate, and the mixture shaken. In the first instance it is necessary that this should be well-cooled, and as soon as a sufficient quantity of sodium methyl is formed to render the mass syrupy the volatile portion is distilled off on a

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[1] Wanklyn, *Proc. Roy. Soc.* (1859), x. 4.

[2] *Journ. Chem. Soc.* xvi. 415.

water-bath, and the amalgam again heated until no further action takes place. The products of the reaction are then distilled with water, and the mercury-methyl which passes over is shaken with caustic potash in order to decompose any ethyl acetate which may be present; then washed with water, and lastly dried over calcium chloride. The part which the ethyl acetate plays in the reaction is not understood, it appearing to undergo no alteration.

Mercury-methyl is a transparent liquid having a specific gravity of 3·069, boiling at 95°, and possessing a peculiar, rather sweetish odour, which becomes exceedingly unpleasant on long acquaintance. It is unalterable in the air, but can however be readily inflamed, and burns with a luminous flame, with evolution of mercury vapours. On heating with other metals the mercury can readily be replaced, and compounds are thus obtained which can only with difficulty be otherwise prepared. Unfortunately mercury-methyl is a very poisonous substance, and a prolonged inspiration of its vapour produces phenomena of chronic poisoning which are afterwards fatal.

According to unpublished experiments performed in the Physiological Laboratory of Owens College, Dr. Gamgee has found that, when an atmosphere saturated with mercuric methide is inhaled, the respiratory movements of both frogs and mammals cease. The action is apparently one exerted on the respiratory centre in the medulla oblongata. There is no paralysis of muscles or nerves. The heart is unaffected.

Mercury-Methyl Chloride, $Hg(CH_3)Cl$, is formed when methyl iodide is heated with an excess of corrosive sublimate. It is also obtained by the action of concentrated hydrochloric acid on mercury-methyl:

$$Hg\left\{\begin{matrix}CH_3\\CH_3\end{matrix}\right. + HCl = Hg\left\{\begin{matrix}CH_3\\Cl\end{matrix}\right. + CH_4.$$

It forms colourless crystals, and yields, by double decomposition with silver nitrate, the corresponding nitrate, which crystallizes in tablets and is very soluble in water.

Mercury-Methyl Iodide, $Hg(CH_3)I$, is easily obtained by the action of methyl-iodide on mercury in the sunlight, as well as by treating mercury-methyl in alcoholic solution with iodine:

$$Hg(CH_3)_2 + I_2 = Hg(CH_3)I + CH_3I.$$

It is soluble in water, and crystallizes in colourless tablets, having an unpleasant smell and taste. It melts at 143°, and volatilizes at a higher temperature. It sublimes, however, at the ordinary temperature of the air, and when it or the chloride is treated with moist silver oxide a solution of the hydroxide, having a strongly alkaline reaction, is obtained.

Mercury-Methyl Sulphate, $(HgCH_3)_2SO_4$, is obtained in the form of crystals, together with marsh gas, by the action of concentrated sulphuric acid on mercury-methyl.

The solutions of all these salts yield a yellow precipitate, with sulphide of ammonium, of *mercury-methyl sulphide* (Frankland.)

167 *Aluminium-Methyl*, $Al(CH_3)_3$. By heating methyl iodide with aluminium foil Cahours obtained a colourless liquid, which contains iodine, and is spontaneously inflammable, and this, when treated with zinc-methyl yielded aluminium-methyl. The same body is obtained more simply by heating aluminium with mercury-methyl. It is a colourless mobile liquid, crystallizing a few degrees above 0° to a mass of white tablets. It takes fire instantly on exposure to air, and is decomposed with great violence by water. Its vapour density at 160° corresponds nearly to the formula $Al_2(CH_3)_6$; it diminishes, however, when the temperature is raised, and at 220° closely corresponds to the formula $Al(CH_3)_3$.[1]

Lead-Methyl, $Pb(CH_3)_4$, was obtained by Cahours [2] by acting with methyl iodide on an alloy of lead and sodium, as well as by the action of zinc-methyl on chloride of lead:

$$2\,PbCl_2 + 2\,Zn(CH_3)_2 = Pb(CH_3)_4 + 2\,ZnCl_2 + Pb.$$

According to Butlerow,[3] who has carefully examined this substance, it is a mobile liquid, unalterable in the air, and having a slight smell resembling raspberries. It boils at 110°, and has a specific gravity at 0° of 2·034, its vapour density being 9·6. Methyl is withdrawn from this substance by the action of the haloid elements or their hydroxides, and crystalline salts of lead-trimethyl are formed. The iodide, $Pb(CH_3)_3I$, forms long colourless needles difficultly soluble in water. When this body is distilled with solid caustic potash the hydroxide, $Pb(CH_3)_3OH$, is obtained as a mustard-like smelling liquid, solidifying to acute prisms, and acting as a strong alkali (Cahours).

[1] Buckton and Odling, *Proc. Roy. Soc.* xiv. 19.
[2] *Ann. Chim. Phys.* [3], lxii. 285.
[3] *Zeitsch. Chem. Pharm.* 1863, 497.

168 *Tin Tetramethyl*, $Sn(CH_3)_4$, is produced when methyl iodide is heated together with an amalgam of tin and sodium. It is an ethereal-smelling liquid, boiling at 78°, and having a specific gravity at 13° of 1·187.[1] Its vapour density is 6·00. By the action of iodine *tin trimethyl iodide*, $Sn(CH_3)_3I$, is obtained, a liquid smelling like mustard-oil, boiling at 170°, and having at 0° a specific gravity of 2·1432. Caustic soda converts it into the corresponding hydroxide, $Sn(CH_3)_3OH$, which crystallizes in colourless prisms, slightly soluble in water, yielding a strongly alkaline solution, and gives rise to crystalline salts when brought into contact with acids. It is volatile without decomposition; but if it is heated for some time near its boiling-point it loses water and is converted into the oxide, $O\left\{\begin{array}{l}Sn(CH_3)_2\\Sn(CH_3)_2.\end{array}\right.$

Tin Dimethyl or Stanno-tetramethyl, $Sn_2(CH_3)_4$. According to Cahours this substance is formed in the reaction already described together with tin tetramethyl. Ladenburg, however, could only obtain a few drops of a liquid which was probably this compound.

Tin Dimethyl Iodide, $Sn(CH_3)_2I_2$, is formed together with zinc trimethyl iodide when tin foil is heated with methyl iodide to 160°. It crystallizes in yellow oblique rhombic prisms which melt at 22°, and dissolve in water and still more readily in alcohol. It boils at 228° and is decomposed by ammonia with formation of the amorphous oxide $Sn(CH_3)_2O$, which does not dissolve in water but is soluble in caustic potash and yields with acids a series of crystalline salts.

OTHER DERIVATIVES OF METHYL.

169 The methyl compounds are mono-substitution-products of methane. If, however, two or more atoms of hydrogen in this body be replaced, substances are obtained which may be regarded as compounds of dyad or polyvalent radicals. Though these belong to other groups of carbon compounds, yet they exhibit but slight analogy with other groups and are best considered in this place.

Dichlormethane or Methylene Dichloride, CH_2Cl_2, was first obtained by Regnault[2] by acting on methyl chloride with

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[1] Ladenburg, *Ann. Chem. Pharm.* Suppl. Bd. viii. 60.

[2] *Ann. Chim. Phys.* lxxi. 379.

chlorine in the sunlight. It was afterwards more thoroughly examined by Perkin[1] and Butlerow.[2] It is not only formed according to Regnault's process, but also by treating an alcoholic solution of chloroform with zinc and sulphuric acid (Geuther) or with zinc and ammonia (Richardson, Williams, Perkin) as also by the action of chlorine on di-iodomethane.

Dichlormethane is a colourless liquid boiling at 40° possessing a smell similar to that of chloroform and having a specific gravity at 0° of 1·360 and a vapour density of 3·012. The inhalation of its vapour produces the same effects as that of chloroform.

TRICHLORMETHANE OR CHLOROFORM, $CHCl_3$.

170 Chloroform was discovered in 1831 by Liebig,[3] who obtained it by the action of alkalis on chloral (trichloracetaldehyde) and by treating acetone and alcohol with bleaching powder. Almost at the same time Soubeiran[4] obtained it by the latter of these reactions and termed it *éther bichlorique*. This chemist was considered to be the discoverer of the substance until Liebig[5] put forward his claim as having first prepared the compound, although he originally believed it to be a new chloride of carbon. It is to Dumas[6] (1834) that we owe the recognition of the fact that the compound contains hydrogen, and the determination of its true formula.[7] Regnault then proved that it is the second substitution-product of methyl chloride.

Chloroform is likewise produced by the action of bleaching-powder on a large number of organic substances, but not on *pure* methyl alcohol, sodium acetate, or methyl oxalate, as was formerly believed to be the case.[8] (See Iodoform).

Preparation.—Chloroform is manufactured on the large scale by warming an aqueous solution of bleaching powder with alcohol. Many processes are given for its manufacture, all of which recommend that bleaching powder should be well stirred up to a thin paste with water, and this then heated with strong alcohol. A good yield is obtained when 10 parts of bleaching

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Journ. Chem. Soc. xxii. 260.

[2] *Zeitsch. Chem.* 1869, 276.

[3] *Pogg. Ann.* xxiii. 444; *Ann. Pharm.* i. 31, 198.

[4] *Ann. Chim. Phys.* [2], xlviii. 131; *Ann. Pharm.* i. 272.

[5] *Ann. Chem. Pharm.* clxii. 161.

[6] *Ann. Chim. Phys.* lvi. 115; *Ann. Pharm.* xvi. 164.

[7] *Ibid.* [2]. lxxi. 353.

[8] Belohoubek, *Wien. Akad. Ber.* lxvi. 188.

powder are rubbed up with 40 parts of hot water and 1 part of alcohol of specific gravity 0·834 added, the temperature of the mixture being 65°. A violent reaction then takes place, and the larger portion of the chloroform distils over without further heating, the rest being driven over by passing steam into the vessel. The chloroform is then washed with water and dried over calcium chloride, or rectified over concentrated sulphuric acid.

Of late years a large quantity of chloroform has been obtained by the action of caustic soda on chloral hydrate, which is now prepared on a commercial scale, formic acid being produced at the same time :

$$CCl_3.CH(OH)_2 + NaOH = CCl_3H + CHNaO_2 + H_2O.$$

The formation of chloroform from spirit of wine cannot be represented by means of a simple equation. Bleaching powder acts upon this substance both as a chlorinating and as an oxidizing agent. The mass froths strongly from evolution of carbon dioxide, and for this reason large vessels have to be used in its preparation. The following equation serves fairly to represent the principal reaction that takes place in the conversion of the alcohol into chloroform :

$$\begin{aligned}3\,C_2H_6O + 8\,Ca(OCl)_2 = {} & 2\,CHCl_3 + 3CaCO_3 + CO_2 \\ & + 8\,H_2O + 5\,CaCl_2.\end{aligned}$$

171 *Properties.*— Chloroform is a colourless mobile liquid, possessing a peculiar ethereal smell and a burning taste. It boils at 61° (Liebig, Regnault), and has a specific gravity at 0° of 1·5252. Its vapour density was determined by Dumas to be 4·20. Chloroform is almost insoluble in water, but is miscible in all proportions with ether, alcohol, and other organic liquids. It readily dissolves phosphorus, bromine, iodine, and many organic substances. For this reason it is employed in analytical processes, as well as in the preparation and purification of a large number of compounds. It is not inflammable, but colours the non-luminous flame green, and an alcoholic solution burns with a smoky flame, evolving fumes of hydrochloric acid.

This discovery of the anæsthetic properties of chloroform was made by Sir James Simpson of Edinburgh in 1848,[1] and since

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[1] "Anæsthetic and other Therapeutical Effects of the Inhalation of Chloroform," *Edin. Monthly Journ. of Med. Science*, viii. 415.

that time the inhalation of the vapour of chloroform has been largely practised for the purpose of procuring insensibility to pain in the case of surgical operations. Chloroform is likewise used as a medicine.

Chloroform used for medicinal purposes must, of course, be pure, and this is often not the case with the commercial article. It sometimes contains hydrochloric acid, and even free chlorine; the presence of both of these can be detected by the action of such impure chloroform upon litmus, as well as by the fact that it renders silver nitrate solution turbid, whilst the pure substance does not do so. If a cold solution of potassium dichromate in dilute sulphuric acid be coloured green by chloroform, the presence of alcohol or other easily oxidizable bodies is indicated. Pure chloroform is not coloured brown either by caustic potash or by sulphuric acid. It does not attack bright metallic sodium even at the boiling point, and if this metal should, under these circumstances, become covered with a white coating of chloride, the presence of other chlorine compounds, such as dichlorethane or ethylene dichloride, may be presumed. These same impurities may also be recognised, inasmuch as when heated with alcoholic potash the impure chloroform evolves a combustible gas, viz. ethylene. When chloroform is evaporated on a watch-glass without warming it or blowing air upon it, it ought not to leave a residue either of water or of bodies possessing a strong smell. Should the latter be found to be the case, the chloroform has been prepared from alcohol containing fusel oil.

It has already been stated that monamines can easily be detected by the help of chloroform (p. 162). So inversely the latter compounds may be employed for the detection of small quantities of chloroform. As the most easily obtainable amine, aniline is used for this purpose; a few drops of this liquid being heated with the substance under investigation together with alcoholic caustic soda solution. The characteristic smell of carbamine is observed, according to Hofmann, in solution containing one part of chloroform to 6,000 parts of water.

Chloroform undergoes a series of decompositions which will be described under the corresponding bodies, only a few of the more important being mentioned:

(1) When heated with concentrated sulphuric acid and potassium bichromate, carbonyl chloride, $COCl_2$ (see Vol. I., p. 621) is formed.

(2) When heated with alkalis chloroform is converted into

formic acid, and for this reason it was formerly termed formyl chloride:

$$CHCl_3 + 4\,KOH = CHO.OK + 3\,KCl + 2H_2O.$$

(3) When heated with alcoholic ammonia, ammonium cyanide is formed:

$$CHCl_3 + 5NH_3 = CN(NH_4) + 3\,NH_4Cl;$$

(4) On treatment with bromine, brom-chloroform, $CBrCl_3$, is produced as a colourless liquid boiling at 104°, which has a specific gravity at 0° of 2·060 (Paterno, Friedel, Silva).

172 *Tetrachlormethane or Carbon Tetrachloride*, CCl_4. This compound, the final product of the chlorination of marsh gas, was discovered by Regnault[1] in 1839, and obtained by the action of chlorine on chloroform in the sunlight. It is also formed when a mixture of carbon disulphide and chloroform is passed through a porcelain tube filled with pieces of porcelain heated to redness.[2] It is best prepared by acting with chlorine gas on a boiling mixture of sulphide of carbon containing some antimony pentachloride, the latter compound serving as a carrier of chlorine. The liquid is then distilled, and the portion boiling under 100° separated and treated with boiling caustic potash in order to remove chloride of silver, trichloride of antimony, and undecomposed carbon bisulphide.[3] Tetrachlormethane is also formed when chloroform is heated with chloride of iodine to 160°—170° (Hofmann).

It is a colourless liquid boiling at 78°, having a specific gravity at 0° of 1·6298, and possessing a smell similar to that of chloroform. Its vapour has a density of 5·24 (Kolbe).

Dibrommethane or Methene Dibromide, CH_2Br_2, is formed by the action of bromine on the corresponding iodide, and together with tribrommethane by acting with bromine on methyl bromide for some hours at a temperature of 150°. It is a liquid which boils at 80°–82° and at 11°·5 has a specific gravity of 2·0844,[4] its vapour density being 5·95 (Steiner).

173 *Tribrommethane or Bromoform*, $CHBr_3$. This compound was discovered by Löwig,[5] in 1832, who prepared it by decomposing bromal (tribrom-acetaldehyde) with aqueous alkalis.

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[1] *Ann. Chim. Phys.* lxxi. 377.

[2] Kolbe, *Ann. Chem. Pharm.* xlv. 41.

[3] Hofmann, *Chem. Soc. Journ.* xiii. 62.

[4] Steiner, *Ber. Deutsch. Chem. Ges.* vii. 507.

[5] *Ann. Pharm.* iii. 295.

Löwig considered it to be a bromide of carbon, but Dumas[1] ascertained its true composition, and obtained it by the action of bromide lime upon spirit of wine, or on acetone. It is also produced when bromine is added to alcohol, or better, when bromine is poured into an alcoholic solution of caustic potash. It is likewise found in crude bromine.[2] Bromoform smells and tastes like chloroform; it boils at 149°-150°, and has a specific gravity at 14°·5 of 2·775,[3] and a vapour density of 8·63 (Cahours).

Tetrabrommethane or Carbon Tetrabromide, CBr_4, was discovered by Bolus and Groves[4] and is formed by heating carbon disulphide, bromoform, iodoform or bromopicrin with bromine in presence of bromide of iodine or certain metallic bromides.

In order to prepare it, 2 parts of carbon bisulphide, 14 parts of bromine and 3 parts of iodine, are placed in a sealed tube and heated for 48 hours to a temperature of 250°, and then the contents of the tube distilled with caustic soda. When water is added to a mixture of bromoform and bromine, tetrabrommethane is also formed on exposing the mixture to daylight; but the reaction only takes place slowly, whereas if some caustic soda be added, it proceeds much more rapidly, inasmuch as the hydrobromic acid formed is at once neutralized.[5]

It crystallizes from hot alcohol in white glistening tablets, which have a sweetish taste, and an ethereal smell. It has a specific gravity at 14° of 3·42, fuses at 91°, and boils with partial decomposition at 189°·5. It may, however, be sublimed without change by careful heating.

174 *Di-iodomethane or Methylene Di-iodide*, CH_2I_2, was first prepared by Butlerow[6] by acting on sodium ethylate with iodoform. This chemist showed that the body formerly obtained by Brüning by the action of iodoform on caustic potash is identical with this compound. It is also formed when chloroform is brought in contact with concentrated hydriodic acid:[7]

$$CHCl_3 + 4\,HI = CH_2I_2 + 3\,HCl + I_2.$$

This body, which is used for the preparation of several other

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[1] *Ann. Chim. Phys.* [2], lvi. 120.

[2] Hermann, *Ann. Chem. Pharm.* xcv. 211.

[3] Schmidt, *Ber. Deutsch. Chem. Ges.* x. 193.

[4] *Chem. Soc. Journ.* xxiii. 154, 161; xxiv. 773.

[5] Habermann, *Ber. Deutsch. Chem. Ges.* vi. 549.

[6] *Ann. Chem. Pharm.* cvii. 110; cxi. 242.

[7] Lieben, *Zeitsch. Chem.* 1868, 712; Bljuducho, *Ibid.* 1871, 258.

compounds, is, however, best obtained by the following method proposed by Baeyer.[1] An upright condenser is fixed to a liter flask by means of a wide tube, the upper end of which is connected with a T-tube, so that the materials can be brought in by the one limb whilst the hydriodic acid formed can escape by the other. 200 grams of hydriodic acid, having a boiling point of 127°, are brought into the flask, and to this 50 grams of iodoform are added, and the mixture is then heated to the boiling point, and phosphorus added little by little until no further evolution of iodine takes place. Then 100 grams of iodoform and the necessary quantity of phosphorus are added alternately. The formation of the di-iodomethane is explained by the following reaction:

$$CHI_3 + HI = CH_2I_2 + I_2.$$

Di-iodomethane is a yellowish strongly refracting liquid, boiling with partial decomposition, at 181°, solidifying to glistening tablets at 2°, and possessing a specific gravity at 5° of 3·342.

175 *Tri-iodomethane or Iodoform*, CHI_3. This compound was discovered by Serullas[2] in 1822 and termed by him "carbide d'iode." It is to Dumas[3] that we are indebted for first pointing out that this compound contains hydrogen. There is no substance in which the hydrogen can be so readily overlooked as in this, for iodoform of all known compounds contains the relatively smallest quantity of this element, namely 0·26 per cent.

Iodoform is formed by the action of iodine upon alcohol in presence of the caustic alkalis or their carbonates. Instead of alcohol a number of other substances may be used; these will be mentioned hereafter. A number of processes are given for its preparation; the following, recommended by Filhol,[4] is usually employed. Two parts of crystallized carbonate of soda are dissolved in ten parts of water, one part of alcohol poured into the solution, and then one part of iodine gradually added to the liquid heated to 60°-80°, when iodoform gradually begins to separate out. The liquid is filtered, and the above mentioned quantity of carbonate of soda again added to the filtrate heated to 80°. Chlorine is then passed into the liquid, which is shaken from time to time, the object being to decompose the iodide of

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[1] *Ber. Deutsch. Chem. Ges.* v. 1094.

[2] *Ann. Chim. Phys.* [2], xx. 165; xxii. 172; xxv. 311; xxxix. 230.

[3] *Ibid.* lvi. 122.

[4] *Journ. Pharm.* vii. 267.

sodium which is formed, and to obtain the iodine in a finely divided state. When no more iodoform separates out the current of chlorine is stopped, the liquid allowed to stand until it becomes colourless, and then, on cooling, the iodoform collected on a filter and washed with cold water.

A good yield is also obtained by warming together the following constituents until the liquid becomes colourless: iodine, 32 parts; potassium carbonate, 32 parts; 95 per cent. alcohol, 16 parts; water 80 parts. The liquid is then poured off from the iodoform which is deposited, and the following is added to the liquid: potassium dichromate 2 to 3 parts, hydrochloric acid 16 to 24 parts. This serves to decompose the iodate and iodide and to liberate iodine. The whole is then neutralized by the addition of 32 parts of carbonate of soda, 6 parts of iodine, and 16 parts of alcohol, the liquid again poured off from the iodoform, and these operations repeated until the liquid contains too large a quantity of salt in solution.[1] The formation of iodoform is represented by the following equation:

$$CH_3.CH_2OH + 4I_2 + 6KOH = CHI_3 + CHKO_2 + 5KI + 5H_2O.$$

In addition to this, other products are formed, such as potassium iodate, acetic ether, &c.

Iodoform is insoluble in water, but dissolves readily in alcohol, crystallizing from this menstruum in large lemon-yellow bright six-sided tables which melt at 119° and sublime when strongly heated, undergoing partial decomposition with formation of iodine vapours. It may, however, be volatilized without decomposition in a current of steam. It possesses a saffron-like smell, and a sweet taste. In the pure state it does not undergo alteration on exposure to light, but its solution in bisulphide of carbon is excessively sensitive to light, quickly becoming coloured violet owing to separation of free iodine.[2]

It has already been mentioned that many other bodies, in addition to alcohol, yield iodoform. Amongst the simpler of these, ethyl ether and acetic acid have frequently been classed. Lieben,[3] in a very complete series of experiments, has, however, shown that these substances, if perfectly pure, do not yield the slightest trace of iodoform. On the other hand, the normal primary and secondary alcohols as well as their aldehydes

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[1] *Pharm. Journ. Trans.* [3], iv. 593.

[2] Humbert, *Journ. Pharm. Chim.* [3], xxix. 352.

[3] *Ann. Chem. Pharm.* Suppl. vii. 218 and 377.

and ketones all yield iodoform, but their isomerides do not. Hence the formation of iodoform serves as an excellent means in many cases for ascertaining the purity of these bodies, and also as a test for their presence even in very small traces. Thus, for example, if water containing only $\frac{1}{2000}$th part of alcohol be gently warmed with crystals of iodine, and then caustic soda added, and the liquid allowed to stand for some time, a distinct precipitate is observed, and this when examined under a microscope exhibits the six-sided tablets or stellar crystals characteristic of iodoform.

Iodoform possesses anæsthetic properties, acting especially on the muscles. It is used as a medicine and has been employed for outward application, especially in cases of cancer.

Chloriodoform, $CHICl_2$, is a yellow oily liquid, boiling at 131°, obtained by heating iodoform with the chlorides of lead, mercury or tin.

Tetra-iodomethane or Carbon Tetra-iodide, CI_4, was obtained by Gustavson[1] by acting on aluminium iodide with tetrachlormethane in presence of carbon disulphide. It crystallizes in large regular octohedrons, which decompose slowly in the air at the ordinary temperature, but quickly at 100°, into iodine and carbon.

176 *Chlornitromethane*, $CH_2Cl(NO_2)$. To prepare this compound, sodium nitromethane is brought in small quantities into saturated chlorine water, and when no further action takes place the mixture is distilled. It is a colourless oily liquid, having a penetrating smell, boiling at 122°-123°, and possessing a specific gravity at 16° of 1·466. It easily dissolves in alkalis, and gives the nitrolic acid reaction like other primary nitro-compounds (see p. 171).[2]

177 *Trichlornitromethane*, *Nitrochloroform*, or *Chloropicrin*, $CCl_3(NO_2)$, was discovered by Stenhouse,[3] who obtained it by distilling an aqueous solution of picric acid (trinitrophenol), $C_6H_2(NO_2)_3.OH$, with bleaching powder. Its correct composition was first recognised by Gerhardt.[4] Chloropicrin is also formed by a similar reaction from many other aromatic nitro-compounds, and may also be prepared as Geisse[5] has shown, by the following reactions :

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[1] *Compt. Rend.* lxxviii. 882.

[2] Tscherniak, *Ber. Deutsch. Chem. Ges.* viii. 608.

[3] *Phil. Mag.* [3], xxxiii. 53.

[4] *Compt. Rend. Trav. Chim.* 1859, 34.

[5] *Ann. Chem. Pharm.* cix. 282.

(1) Chloral (trichloracetaldehyde) is distilled with fuming nitric acid:

$$CCl_3.COH + 3HO.NO_2 = CCl_3(NO_2) + 2H_2O + CO_2 + N_2O_3.$$

(2) Methyl alcohol is heated with nitre, common salt, and sulphuric acid:

$$CH_3OH + NO_2.OH + 2Cl_2 = CCl_3(NO_2) + 2H_2O + HCl.$$

(3) Alcohol and common salt are distilled with nitric acid.

It is likewise obtained, though with greater difficulty, by heating chloroform with concentrated nitric acid:[1]

$$CHCl_3 + NO_2.OH = C(NO_2)Cl_3 + H_2O.$$

According to Hofmann[2] the following is a useful method of preparation: 50 kilos of freshly-prepared bleaching-powder are mixed to a thick paste with cold water and placed in a still surrounded by cold water. To this, a saturated solution of 4·5 kilos of picric acid heated to 30° is added. After a few minutes a violent reaction takes place, and the greater part of the chloropicrin distils over. The remainder is driven off by heating the still

Chloropicrin is a mobile liquid, boiling at 113°, having a specific gravity of 1·6657, and possessing a very penetrating smell resembling that of chloride of cyanogen. Its vapour acts powerfully on the eyes and mucous membranes, but the irritation does not last long. Heated in the form of vapour it decomposes with explosion. It is insoluble in alkalis, and is not attacked by sulphuric or nitric acid even when boiled. When treated with iron filings and acetic acid it is converted into methylamine:

$$CCl_3(NO_2) + 6H_2 = CH_3(NH_2) + 3\,HCl + 2H_2O.$$

Heated with ammonia under pressure it yields guanidine[3] (Vol. I. p. 680):

$$C(NO_2)Cl_3 + 7\,NH_3 = C(NH)(NH_2)_2 + 3\,NH_4Cl + 2\,H_2O + N_2.$$

Dichlordinitromethane, $CCl_2(NO_2)_2$, was discovered by Marignac,[4] who obtained it by distilling naphthalene tetrachloride,

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[1] Mills, *Journ. Chem. Soc.* xxiv. 641; Cossa, *Gaz. Chim. Ital.* 1872, 181.
[2] *Chem. Soc. Journ.* xix. 249.
[3] Hofmann, *Ber. Deutsch. Chem. Ges* i. 145.
[4] *Ann. Chem. Pharm.* xxxviii. 14.

$C_{10}H_8Cl_4$, with concentrated nitric acid, and hence it was formerly known as "Marignac's oil." It is a colourless liquid, smelling like chloropicrin, and having a specific gravity at 16° of 1·685. It is easily volatilized in a current of steam.

Monobromnitromethane, $CH_2Br(NO_2)$, is formed by the action of bromine on sodium-nitromethane. It is a colourless, very strongly-smelling liquid, boiling at 146°-147°, and is soluble in alkalis.

Dibromnitromethane, $CHBr_2(NO_2)$, is obtained by the action of bromine upon a freshly-prepared solution of the foregoing compound. It is an oily, strongly-smelling liquid, which decomposes on distillation, and possesses acid properties.[1]

Tribromnitromethane or Bromopicrin, $CBr_3(NO_2)$, was obtained by Stenhouse[2] by distilling a solution of picric acid with bromide of lime. It is also formed when nitro-methane is treated alternately with bromine and caustic potash.[3] It is a liquid closely resembling chloropicrin, and when strongly cooled forms prismatic crystals, melting at 10°·25. Its specific gravity at 12°·5 is 2·811. It may be distilled in a vacuum without decomposition, but decomposes even when carefully warmed under the ordinary circumstances with formation of tetrabrommethane, carbon dioxide, the oxides of nitrogen, and other bodies.[4]

Chlordibromnitromethane, $CClBr_2(NO_2)$, is obtained when chlornitromethane is dissolved in caustic potash and bromine added. It is a liquid possessing a similar smell to chloropicrin, having at 15° a specific gravity of 2·421, and being volatile in a current of steam.[5]

178 *Trinitromethane or Nitroform*, $CH(NO_3)_2$, was discovered by Schischkoff[6] in 1857, who prepared it by heating trinitroacetonitril with water. This substance dissolves with violent evolution of carbon dioxide, and the yellow solution contains the ammonium salt of trinitromethane:

$$\left\{\begin{matrix} C(NO_2)_3 \\ CN \end{matrix}\right. + 2\,H_2O = C(NO_2)_3NH_4 + CO_2.$$

Under certain conditions, which are not well understood, this action of water on trinitroacetonitril may be accompanied by

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[1] Tscherniak, *Ber. Deutsch. Chem. Ges.* vii. 916.

[2] *Phil. Mag.* [4], viii. 36.

[3] V. Meyer, *Ber. Deutsch. Chem. Ges.* viii. 816.

[4] Bolas and Groves, *Journ. Chem. Soc.* xxiii. 153 ; xxiv. 773.

[5] Tscherniak, *Ber. Deutsch. Chem. Ges.* viii. 608.

[6] *Ann. Chem. Pharm.* ci. 213 ; ciii. 364 ; cxix. 247.

serious explosions.[1] On evaporation the salt separates out in yellow monoclinic prisms. If dilute caustic potash be used instead of water, the yellow crystalline potassium salt is obtained; and if sulphuric acid be added to any of these salts, nitroform separates out in a liquid layer, which on cooling solidifies to a mass of large oblique crystals. It has a bitter taste and disagreeable smell, is very inflammable, and when warmed begins to decompose under 100° with rapid evolution of gas, exploding violently when quickly heated. Its yellow salts are also explosive, and frequently decompose spontaneously with evolution of gas.

When a mixture of nitroform and bromine is exposed to sunlight, *bromnitroform*, $C(NO_2)_3Br$, is formed as a colourless liquid, which crystallizes at 12° and is decomposed at 140°, but may be volatilized in a current of steam.

Tetranitromethane, $C(NO_2)_4$, is formed when a continuous current of air is passed through a mixture of nitroform, concentrated sulphuric acid, and nitric acid heated to 100°. On addition of water to the distillate, this compound separates out as a colourless mobile liquid, which crystallizes at 13°, boils at 126°, and is neither explosive nor inflammable. If, however, it be dropped on to glowing charcoal it burns with a bright flash.

179 *Methene Disulphonic Acid*, $CH_2(SO_3H)_2$. This compound, which was formerly called methionic acid, was first prepared by Liebig,[2] together with other products, by the action of sulphur trioxide on ether. Buckton and Hofmann[3] obtained it by treating acetonitril (methyl cyanide) with concentrated sulphuric acid, acetic acid, carbon dioxide and ammonia being formed at the same time. It may also be obtained from sulphoacetic acid, acetamide, and lactic acid, and also by heating chloroform with a solution of potassium sulphite.[4] In this case, methene dichloride is first formed, which is then converted into potassium methene disulphonate:

$$(a)\quad 2\,CHCl_3 + 3\,K_2SO_3 + H_2O = 2\,CH_2Cl_2 + 2\,K_2SO_4 + 2KCl + SO_2.$$

$$(b)\quad CH_2Cl_2 + 2\,K_2SO_3 = CH_2(SO_3K)_2 + 2\,KCl.$$

The free acid is best prepared by the action of sulphuretted hydrogen on an aqueous solution of the lead salt. On evaporation

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[1] V. Meyer, *Ber. Deutsch. Chem. Ges.* vii. 1744.

[2] *Ann. Pharm.* xiii. 35.

[3] *Chem. Soc. Journ.* ix. 241.

[4] Strecker, *Ann. Chem. Pharm.* cxlviii. 90.

in a vacuum it may be obtained in the form of a deliquescent striated crystalline mass. It is a very strong acid, and forms a series of well crystallizable salts.

Methine Trisulphonic Acid, $CH(SO_3H)_3$, is formed when dry calcium methyl sulphate is heated to 100° with a large excess of fuming sulphuric acid. The free acid is obtained by decomposing the lead salt with sulphuretted hydrogen; it forms long deliquescent colourless needles, and is a tribasic acid. It decomposes chlorides and nitrates, and forms well crystallizable salts.

Potassium Methine Trisulphonate, $CH(SO_3K)_3$, crystallizes in small hard glistening prisms, and is formed when chloropicrin is heated with a concentrated solution of potassium sulphite. As an intermediate product *potassium nitro-methene disulphonate*, $CH(NO_2)(SO_3K)_2$ is formed as a crystalline slightly soluble powder which deflagrates on heating.[1]

Barium Methine Trisulphonate, $[CH(SO_3)_3]_2Ba_3$, crystallizes from boiling water in glistening tablets. Its solution throws down the insoluble lead salt from a solution of acetate of lead.[2]

Methyl-mercaptan Trisulphonic Acid, $C(SO_3H)_3SH$. If bisulphide of carbon be treated with manganese dioxide and hydrochloric acid, a reaction takes place which becomes more rapid on the addition of a small quantity of iodine; and besides thiocarbonyl chloride, $CSCl_2$, and trichlor-methyl sulphonic chloride, $CCl_3.SO_2Cl$, the compound, *perchlor-methyl mercaptan*, $CCl_3.SCl$, is formed. This latter compound is a golden yellow, very powerfully-smelling liquid, boiling at from 146° to 147°.[3] It acts on an aqueous solution of potassium sulphite giving rise to the salt $C(SO_3K)_3SH$, which forms large, hard, colourless triclinic crystals. The same salt is formed by the action of potassium sulphite on thiocarbonyl chloride:

$$CSCl_2 + 3\,K_2SO_3 + H_2O = C(SO_3K)_3SH + 2\,KCl + KOH.$$

It gives a white precipitate with basic lead acetate, from which the free acid can be obtained by treatment with sulphuretted hydrogen. In a concentrated state this forms a thick very deliquescent syrup. Its dilute solution gives a deep blue coloration with ferric chloride. The free acid and its salts are readily decomposed in presence of water, with formation of sulphuric acid and *methyl-mercaptan-disulphonic acid*,

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[1] Rathke, *Ann. Chem. Pharm.* clxi. 149; clxvii. 219.

[2] Theilkuhl, *Ann. Chem. Pharm.* cxlvii. 134.

[3] Rathke, *Ber. Deutsch. Chem. Ges.* iii. 858.

$CH(SO_3H)_2SH$. This forms crystallizable salts, and is a dibasic acid. The hydrogen which is combined with the sulphur can, however, be replaced by metals possessing a strong affinity for sulphur, such as lead. This is not the case with the trisulphonic acid. By the action of nitric acid on the potassium salt of the latter compound potassium methyl oxytrisulphonate, $C(SO_3K)_3OH$, is formed, crystallizing in strongly refracting monoclinic prisms. The free acid is a deliquescent mass, and the salts crystallize well.[1]

THE FORMYL GROUP.

Formic Aldehyde, COH_2.

180 This interesting body may be regarded as the aldehyde and ketone of formic acid, or as the oxide of the dyad radical methene. Many attempts to prepare this substance have been unsuccessfully made, inasmuch as the oxidizing agents usually employed for the preparation of aldehydes yield at once formic acid. Hofmann was the first, in 1867, to succeed in preparing the substance by passing the vapour of methyl alcohol together with air over ignited platinum. For this purpose he employed the following apparatus. A three-necked flask of about two liters capacity is filled about five c.m. high with warm methyl alcohol. One of the necks of the flask is furnished with a cork, and a tube which passes to the surface of the liquid. The other necks are furnished with open glass tubes; the middle one carries a spiral of platinum wire fastened to a loosely-fitting cork, the spiral being brought nearly to the surface of the methyl alcohol. The third opening is connected with the upper end of the condenser, the lower end of which is fastened into a two-necked receiver; this receiver is in its turn connected with a series of wash-bottles, and the last of these communicates with a water-jet aspirator, by which a rapid current of air can be drawn through the whole system. The platinum spiral is next heated and lowered into the bottle, when the flameless combustion of the methyl alcohol begins to manifest itself by the evolution of vapour powerfully affecting the nose and eyes. Gradually the temperature of the apparatus rises and drops of a colourless liquid are soon condensed in the

[1] Albrecht, *Ann. Chem. Pharm.* clxi. 129.

[2] *Proc. Roy. Soc.* xvi. 156.

receiver, and if the apparatus be properly constructed a solution of aldehyde in dilute methyl alcohol is obtained whilst the portion which is not collected here passes into the wash-bottles. At the begninnig of the experiment a sharp explosion sometimes takes place, which drives the cork with the spiral out of the bottle. In order to prevent this, an improved apparatus has been suggested by Volhard.[1] This consists of a Davy's glow-lamp shown in Fig. 67, filled with methyl alcohol, over which a funnel is placed connected with a condenser as before. A stream of air can now be regulated so that the ignition of the platinum spiral is not visible in the daylight.

FIG. 67.

The solution of aldehyde, prepared by one or other of these means, only contains about 1 per cent. of formic aldehyde. In order to prepare a more concentrated solution, a regulated mixture of air and methyl alcohol vapour is passed through a tolerably wide platinum tube containing a bundle of fine platinum wires. By gently heating this, a current of formic aldehyde is obtained. This can be condensed to a liquid, which however does not contain more than 5 per cent. of aldehyde; but this apparatus when in proper action may be kept going for several months without intermission. If the methyl alcohol be driven out of the solution by distillation a certain amount of aldehyde passes over with it. A better plan is to expose the residual liquid repeatedly to a freezing mixture, the ice formed being each time removed; the residual liquid contains 10 per cent of formic aldehyde.[2]

A solution of formic aldehyde possesses a very penetrating smell, and when warmed with ammoniacal silver solution, a mirror-like deposit of metallic silver is formed. Ammonium formate is in this case produced. Up to the present time the separation of the aldehyde from its solution has not proved possible. If it be evaporated in a vacuum over sulphuric acid, part of the aldehyde passes into the state of vapour with the water, whilst another portion assumes a polymeric modification.[3]

181 *Paraformaldehyde*, $C_3H_6O_3$, has been known for some time, and was first obtained by Butlerow,[4] by acting on silver

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[1] *Ann. Chem. Pharm.* clxxvi. 128.

[2] Hofmann, *Ber. Deutsch. Chem. Ges.* xi. 1685.

[3] *Ibid.* ii. 152

[4] *Ann. Chem. Pharm.* cxi. 242.

oxalate with methene di-iodide, and was described as *dioxymethylene:*

$$3\,CH_2I_2 + 3\,Ag_2C_2O_4 = C_3H_6O_3 + 6\,AgI + 3\,CO_2 + 3\,CO.$$

This substance is, however, best prepared by heating glycollic acid with sulphuric acid to 150°, when it sublimes:

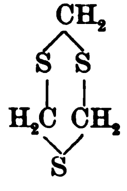
$$3\,CH_2(OH)CO.OH = 3\,C_3H_6O_3 + 3\,CO + 3\,H_2O.$$

Paraformaldehyde is a white indistinctly crystalline body, which is insoluble in water, alcohol, and ether. It possesses no smell and sublimes at 100°, melting, however, at 152°. Heated more strongly it dissociates into three molecules of formic aldehyde, the irritating smell of the gas being at once perceived. If this gas be collected over mercury and allowed to cool, it gradually disappears with formation of the trimolecular form.

When paraformaldehyde is heated with much water in a closed tube to 130°-150° it enters into solution again, splitting up into the simpler molecule. This solution does not undergo change in absence of air, probably because the aldehyde is combined with water, methylene alcohol, $CH_2(OH)_2$, being formed.

Parathioformaldehyde, $C_3H_6S_3$, was first described by Girard,[1] who obtained it by the action of nascent hydrogen on carbon disulphide. It has likewise been prepared by heating methene di-iodide with sodium sulphide,[2] as well as by treating the solution of formaldehyde or the para-compound with sulphuretted hydrogen, and then heating with hydrochloric acid. It is also formed by treating thiocyanic acid with nascent hydrogen:[3]

$$3\,SCNH + 6\,H_2 =$$



$$+\ 3\,NH_3.$$

This compound crystallizes in a shining white crystalline mass which melts at 216°. It combines with silver nitrate to form the crystalline compounds $C_3H_6S_3 + AgNO_3$ and $C_3H_6S_3 + 3AgNO_3$, whilst with platinic chloride it forms yellow needles of $2\,C_3H_6S_3 + PtCl_4$.

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[1] *Comptes Rendus*, xliii. 396.

[2] Husemann, *Ann. Chem. Pharm.* cxxvi. 291.

[3] Hofmann, *Zeitsch. Chem.* [2], iv. 689.

FORMIC ACID,

CH_2O_2.

182 In the sixteenth century Brunfels, and at the beginning of the seventeenth Baukin, noticed that red ants have the power of emitting an acid liquid which turns vegetable blue colours red. Formic acid was first obtained by John Ray in 1670, by distilling red ants, and he observed that this substance has the power of forming with white lead a kind of sugar of lead, which, like ordinary sugar of lead, possesses an astringent taste. Hence he concluded that the acid in question is similar to acetic acid.[1] About the same time a German chemist, Samuel Fischer, is said to have prepared formic acid. These observations were confirmed by Hiärne, Homberg, and Marggraf, the latter of whom found that this acid does not precipitate the salts of silver, lead and mercury, or nitrate of lime, and he adds that this shows that it is neither hydrochloric acid nor vitriolic acid. Calx of silver however dissolves in it, and calx of mercury on being warmed with it yields metallic mercury.[2] From this time forward, the acid compound obtained from ants was looked upon as a peculiar acid. Arvedson and Oehrn described the acid and its salts more exactly in a *Dissertatio de acido formicarum* in 1777, but even in 1802 it was stated by Fourcroy and Vauquelin that it was simply a mixture of acetic acid and malic acid. This statement was however contradicted by Suersen in 1805 and by Gehlen in 1810.

In addition to its occurrence in ants, this acid is also found in bodies of a caterpillar (*Bombyx processionea*), in common stinging nettles, in the fruit of the soapnut-tree (*Sapindus saponaria*), in tamarinds, and in shoots of various pines. It also occurs in small quantity in various animal liquids, as sweat, urine, the juice of muscle, &c. It is remarkable that this substance occurs together with other fatty acids in the putrefaction of diabetic urine, and that it occurs together with acetic acid and other homologues in small quantities in various natural mineral waters. It is likewise produced in the dry distillation of various organic substances, as well as by the oxidation of a large number of such bodies.

In his investigation on manganese in 1774 Scheele remarks

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[1] *Phil. Trans.* 1670, Jan. 13.

[2] *Berlin Akad.* 1749.

that when a mixture of this substance and sulphuric acid is heated with sugar or gum an acid vapour is evolved which when collected in a receiver turns out to be vinegar. Westrumb then mentions in 1785 that acetic acid is produced by the dephlogistication of tartaric acid by means of oxide of manganese, upon which Döbereiner in 1822 showed that the acid produced in this reaction is really formic acid. This observation gave rise to the process for its artificial production.

Starch was found to be the best material for the preparation of this acid, and, according to Liebig's receipt, 100 parts of starch, 370 parts of finely-divided oxide of manganese, and 300 parts of water are mixed together, and 300 parts of concentrated sulphuric acid added to the mixture whilst it is being stirred. By careful distillation the strongly frothing mixture yields about 33·5 parts of dilute formic acid, of which 100 parts saturate 15 parts of dry carbonate of sodium. This method, however, as well as other similar processes are now no longer used, formic acid being always prepared from oxalic acid, which, when heated, splits up directly into carbon dioxide and formic acid:

$$C_2H_2O_4 = CO_2 + CH_2O_2.$$

Gerhardt found that, when oxalic acid is mixed with fine quartz sand, a better yield of formic acid is obtained, but even in this case, and especially when the oxalic acid is heated alone, a large quantity of oxalic acid passes over undecomposed, whilst a part of the formic acid decomposes with formation of carbon monoxide and water. On the other hand, the above reaction takes place much more completely if the oxalic acid be carefully heated with glycerin. On this observation Berthelot has founded a method which now has come into general use for the preparation of formic acid, the details of the process having been carefully worked out by Lorin. According to this method, anhydrous glycerin is gradually heated with crystallized oxalic acid to a temperature of 75°-90° until the whole of the carbon dioxide has been evolved. Oxalic acid is again added and the mixture heated as before, this process being capable of repetition for any number of times. At the beginning of the reaction very dilute formic acid passes over, and this becomes stronger on each addition of oxalic acid until at last a liquid containing 56 per cent. of the acid distils over. Crystallized oxalic acid, $C_2H_2O_4 + 2H_2O$, first decomposes into water, carbon dioxide, and formic acid, which in the nascent state acts upon the glycerin, $C_3H_5(OH)_3$, with formation of monoformyl ether or monoformin:

$$C_3H_5\left\{\begin{matrix}OH\\OH\\OH\end{matrix}\right. + COH.OH = C_3H_5\left\{\begin{matrix}OH\\OH\\O.COH\end{matrix}\right. + H_2O.$$

If oxalic acid be again added, the water of crystallization decomposes a part of this ether with formation of formic acid and glycerin, but, at the same time, a fresh quantity of the ether is produced, and this continues until the liquid is saturated with monoformin, at which point both reactions take place simultaneously, and the acid of the above strength distils over. If anhydrous oxalic acid be employed, the reaction begins at 50°, and is accompanied by violent frothing; a dilute acid first distils over, triformin, $C_3H_5(CHO_2)_3$, is formed which soon saturates the liquid, and an aqueous formic acid, containing from 87 to 88 per cent. of the pure acid, distils over. When, however, a certain quantity of oxalic acid has been employed, the normal reaction does not hold good.

In place of glycerin many other polyatomic alcohols may be employed for the preparation of formic acid from oxalic acid.[1]

183 *Synthesis of Formic Acid.* The various methods for the synthetical formation of formic acid are of great theoretical interest.

(1) Berthelot has shown that it is formed when carbon monoxide is treated with caustic potash or other alkalis:

$$CO + \left.\begin{matrix}H\\K\end{matrix}\right\}O = \left.\begin{matrix}COH\\K\end{matrix}\right\}O.$$

This reaction requires about seventy hours to complete it at a temperature of 100°, whilst it is completed in ten hours at a temperature of 220°.[2] According to Merz and Tibiricá,[3] the action proceeds more quickly when moist carbon dioxide is passed over porous soda-lime loosely arranged in large U-tubes, and heated to about 200° in an oil-bath. Above 220° decomposition commences, with evolution of hydrogen and formation of carbonate.

(2) When moist carbon dioxide (which may be regarded as carbonic acid) acts upon potassium at the ordinary temperature,

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[1] Lorin, *Bull. Soc. Chim.* [2], v. 7, 12; xx. 241; xxiv. 22 and 436.

[2] *Ann. Chem. Pharm.* xcvii. 125; *Compt. Rend.* xli. 955.

[3] *Ber. Deutsch. Chem. Ges.* x. 2117, *Ibid.* xiii. 23.

a mixture of potassium carbonate and potassium formate is produced:[1]

$$2CO\left\{\begin{matrix}OH\\OH\end{matrix}\right. + K_2 = CO\left\{\begin{matrix}OK\\OH\end{matrix}\right. + CO\left\{\begin{matrix}H\\OK\end{matrix}\right. + H_2O.$$

(3) In a similar way, sodium formate is produced when a solution of carbonate of ammonia is treated with sodium amalgam.[2]

(4) If carbon disulphide be heated with water and iron borings at 100°, ferrous formate is produced, together with sulphide of iron, carbon dioxide, and other bodies.[3]

(5) A small quantity of the acid is likewise formed by the direct union of carbon dioxide and hydrogen under the influence of the silent electric discharge. Thus, if the electric discharge be passed through the mixed gases by a Siemens induction-tube, small drops of an acid liquid are formed, together with carbon monoxide and a small quantity of marsh gas, this liquid exhibiting the characteristic reactions of formic acid.[4]

(6) Hydrocyanic acid, HCN (Vol. I. p. 659), is the nitril of formic acid, and therefore, in the presence of alkalis or acids, it easily passes into the latter compound by absorption of water:

$$HCN + 2\,H_2O + HCl = HCO.OH + NH_4Cl.$$

(7) Formic acid is likewise produced when chloroform is heated with caustic potash:

$$CHCl_3 + 4\,KOH = 3\,KCl + CHKO_2 + 2\,H_2O.$$

184 *Preparation of Anhydrous Formic Acid.* In order to obtain pure anhydrous formic acid, the lead salt is prepared from the dilute acid, and this, when completely dried, is brought into a wide glass tube or retort and dry sulphuretted hydrogen passed over it. The lead salt is then gently heated just to the point at which the acid distils over, inasmuch as at higher temperatures disagreeably smelling sulphur products are formed.[5] Amongst these a body crystallizing in colourless needles is obtained, the exact nature of which has not yet been properly ascertained.[6] The distillate thus prepared usually contains some

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[1] Kolbe and Schmidt, *Ann. Chem. Pharm.* cxix. 251.

[2] Maly, *Phil. Mag.* [4], xxx. 360.

[3] Loew., *Ber. Deutsch Chem. Ges.* xiii. 324.

[4] Brodie, *Proc. Roy. Soc.* xxi. 245.

[5] Liebig, *Ann. Pharm.* xvii. 69.

[6] Wöhler, *Ann. Chem. Pharm.* xci. 125; Limprecht, *Ibid.* xcvii. 361; Hurst, *Journ. Chem. Soc.* xv. 278.

sulphuretted hydrogen, and this can be best got rid of by rectification over powdered lead formate (Landolt). Concentrated formic acid may also be obtained by distilling the anhydrous sodium salt with anhydrous oxalic acid.[1]

A strong acid, containing 77·5 per cent., may be obtained by simply distilling the dilute acid obtained from crystallized oxalic acid, a weaker acid passing over first. If anhydrous oxalic acid be dissolved in this warmed acid, it takes up the water, and then, when the cold liquid poured off from the crystals which are separated out is distilled, an almost anhydrous acid is obtained, from which, as well as from the distillate obtained by the other methods, pure formic acid can be obtained by cooling, the aqueous liquid being poured off from the crystals of formic acid which are deposited (Lorin).

185 *Properties.*—Formic acid is a colourless, slightly fuming liquid, possessing a penetrating acid smell, and acting so powerfully on the skin that one or two drops produce extreme pain and swelling, leaving a white blister, which afterwards forms a painful wound. The dilute acid has a peculiar acrid smell, and a purely acid taste (Liebig). The anhydrous acid boils at 99°·9, and at 20° has a specific gravity of 1·2211.[2] The vapour density at 111°·5 is 2·38; at 160°, 1·81; and at 214°, 1·62.[3] At a low temperature formic acid solidifies to a mass of crystals which melt at 8°·6.[4]

Mere traces of water lower the melting-point considerably, whilst, on the other hand, the boiling-point is raised by the presence of water. According to Liebig, the hydrate $CH_2O_2 + H_2O$ boils constantly at 106°. This compound has been termed orthoformic acid, $CH(OH)_3$, inasmuch as corresponding ethers such as ethyl orthoformate, $CH(OC_2H_5)_3$, are known, this latter body being obtained by the action of sodium ethylate, C_2H_5ONa, on chloroform. Roscoe[5] has, however, shown that this hydrate does not exist, and that a mixture of formic acid and water behaves like the various other aqueous acids. On repeated distillation under the ordinary pressure, a final product is always obtained, containing 77 per cent. of formic acid, and boiling constantly at 107°·1, whether a dilute or concentrated acid be employed. That

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[1] Lorin, *Bull. Soc. Chim.* [2], xxv. 519.
[2] Landolt, *Pogg. Ann.* cxvii. 362; and *Ann. Chem. Pharm. Suppl.* vi. 170.
[3] Petersen and Ekstrand, *Ber. Deutsch. Chem. Ges.* xiii. 1194.
[4] Berthelot, *Bull. Soc. Chim.* [2], xxii. 440.
[5] *Journ. Chem. Soc.* xv. 270.

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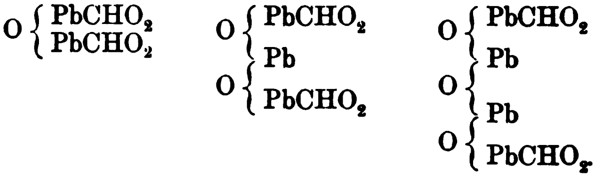
crystals, which dissolve in from eight to ten parts of cold and in not much less hot water, and are insoluble in alcohol.

Barium Formate, $(CHO_2)_2Ba$, forms transparent rhombic prisms, which are soluble in four parts of water, but do not dissolve in alcohol.

Lead Formate, $(CHO_2)_2Pb$, a very characteristic salt of formic acid, crystallizes in glistening white prisms, which are isomorphous with the barium salt. It possesses a sweet styptic taste, dissolves in sixty-three parts of cold and 5·5 parts of boiling water, but, like the foregoing salt, is insoluble in alcohol. When the solution is warmed with oxide of lead, the following basic salts are obtained:



$$O\left\{\begin{array}{l}PbCHO_2\\PbCHO_2\end{array}\right. \qquad \begin{array}{ll} & PbCHO_2\\ O\left\{\right. & \\ & Pb\\ O\left\{\right. & \\ & PbCHO_2\end{array} \qquad \begin{array}{ll} & PbCHO_2\\ O\left\{\right. & \\ & Pb\\ O\left\{\right. & \\ & Pb\\ O\left\{\right. & \\ & PbCHO_2.\end{array}$$

These are soluble in water, exhibit an alkaline reaction, and crystallize in needles.[1]

Copper Formate, $(CHO_2)_2Cu + 4H_2O$, crystallizes in light-blue monoclinic prisms, and yields with formic acid the compound $(CHO_2)_2Cu + 2CH_2O_2 + 3H_2O$, which also crystallizes in the monoclinic system.[2]

Silver Formate, CHO_2Ag. Silver oxide or silver carbonate dissolves in cold formic acid, although silver is reduced when the acid is hot. On evaporating in a vacuum, small six-sided rhombohedral tables are obtained, which are also deposited when a concentrated solution of silver nitrate is mixed with one of sodium formate. From concentrated solutions it separates out as a curdy precipitate. It blackens easily even in the dark, and especially when moist, and decomposes on heating according to the equation:

$$2\,CHO_2Ag = 2\,Ag + CH_2O_2 + CO_2.$$

Mercuric Formate, $(CHO_2)_2Hg$, is obtained by dissolving mercuric oxide in cold dilute formic acid, and remains, when the solution is evaporated in a vacuum at 0°, in the form of a white granular crystalline mass easily soluble in water.

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[1] Barfoed, *Journ. Pr. Chem.* cviii. 1.
[2] v. Hauer, *Wien. Akad. Ber.* xliii. 548.

Mercurous Formate, $(CHO_2)_2Hg_2$, is formed when the solution of the foregoing salt is gently warmed :

$$2\,(CHO_2)_2Hg = (CHO_2)_2Hg_2 + CH_2O_2 + CO_2.$$

It crystallizes in microscopic four-sided or six-sided tables, and dissolves at 17° in 520 parts of water. Like the silver salt, it blackens even in the dark, and, when heated with water, decomposes into mercury, carbon dioxide, and formic acid. The dry salt deflagrates slightly when it is quickly heated, and decomposes on percussion.

187 *Methyl Formate*, $CHO_2(CH_3)$. This ethereal salt was first prepared by Dumas and Péligot by distilling methyl sulphate with sodium formate. Volhard[1] recommends the following method: 130 parts of hydrochloric acid recently saturated with wood spirit are added gradually to 100 parts of calcium formate. As soon as the somewhat violent reaction is over, the distillate found in the cooled receiver is poured back into the retort, the whole warmed for a short time and then distilled on a water-bath. The liquid which passes over is washed with a saturated solution of common salt containing a little carbonate of soda, and then dried over a large quantity of finely powdered anhydrous calcium chloride, with which substance the ethereal salt combines on slightly warming, forming an apparently dry mass. This is then again distilled from a water-bath, and the first portions, which contain chlorine, are collected apart. According to Bardy and Bordet,[2] it is better to use a mixture of methyl alcohol and aqueous hydrochloric acid, and to act with this upon dry sodium formate. Methyl formate is also readily obtained by digesting methyl alcohol with concentrated formic acid,[3] as well as by acting upon hydrocyanic acid with wood spirit saturated with hydrochloric acid (Volhard) :

$$HCN + HO.CH_3 + HCl + H_2O = NH_4Cl + HCO.OCH_3.$$

Methyl formate is a mobile liquid possessing a peculiar smell, boiling at 30°·4 under a pressure of 712 mm. and having a specific gravity at 0° of 0·9928 (Volhard), and a vapour density of 2·084 (Dumas and Péligot). If its vapour be passed through a red-hot tube, it decomposes almost completely into carbon monoxide and methyl alcohol :

$$HCO.OCH_3 = CO + HO.CH_3.$$

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[1] *Liebig's Ann.* clxxvi. 128.

[2] *Bull. Soc. Chim.* xxxi. 531.

[3] Kraemer and Grodzki, *Ber. Deutsch. Chem. Ges.* ix. 1928.

Acted upon by chlorine, it yields as the last product *perchlormethyl formate*, $ClCO.OCl_3$, a powerfully smelling liquid, boiling at 180°, which when heated to 320° splits up by intermolecular interchange into two molecules of carbonyl chloride, $COCl_2$.

Methylorthoformate, $CH(OCH_3)_3$, is prepared by the action of chloroform on a solution of sodium methylate, and is a colourless, mobile liquid, with a pleasant odour, and boiling at 101° to 102°.[1] Substitution-products of formic acid are unknown, as the acid is decomposed by chlorine:

$$CH_2O_2 + Cl_2 = 2HCl + CO_2$$

The chlorocarbonic ethers, however, obtained by the action of carbonyl chloride on the alcohols, may be regarded as ethers of monochlorformic acid. Of these the methyl compound, $CClO_2(CH_3)$, has been already described. It is also formed by the action of perchlormethylformate on wood spirit. The formyl chloride, corresponding to formic acid, is likewise unknown, for by the action of phosphorus pentachloride on formic acid only carbon monoxide and hydrochloric acid are obtained. The anhydride is consequently unknown, nor has thioformic acid been prepared.

Formamide, $N(COH)H_2$, was discovered by Hofmann[2] in 1863. He obtained it by heating ethyl formate, saturated with ammonia, for two days at 100° in sealed tubes:

$$\left.\begin{matrix} COH \\ C_2H_5 \end{matrix}\right\} O + \left.\begin{matrix} H \\ H \\ H \end{matrix}\right\} N = \left.\begin{matrix} C_2H_5 \\ H \end{matrix}\right\} O + \left.\begin{matrix} COH \\ H \\ H \end{matrix}\right\} N.$$

Behrend[3] prepared it by heating two parts of ammonium formate with one of urea to 140°, as long as ammonium carbonate escaped. The ammonium salt thus decomposes into formamide and water; the latter, which would retard the reaction, at once combines with the urea to form ammonium carbonate, and thus becomes inactive. Lorin[4] has found that it can be readily obtained through dry distillation of ammonium formate, and also occurs as one of the products of the distillation of ammonium oxalate. It is a colourless liquid, soluble in water and alcohol, but insoluble in pure ether, and boiling at 192° to 195°, with partial decomposition. This takes place in two directions,

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[1] *Ber. Deutsch Chem. Ges.* xii. 117.

[2] *Journ. Chem.* [illegible]

[3] *Ann. Chem. Pharm.* cxxviii. 335.

[4] *Compt. Rend.* [illegible]

one part decomposing into water and formionitril (hydrocyanic acid):

$$N\left\{\begin{matrix}COH\\H\\H\end{matrix}\right. = H_2O + NCH,$$

and another part splitting up into ammonia and carbonic oxide. Under diminished pressure it volatilizes without decomposition at 140° to 150°. Phosphorus pentoxide withdraws water from this compound, forming hydrocyanic acid, and concentrated caustic potash decomposes it in the cold with formation of potassium formate and ammonia.

Methyl Formamide, $N\left\{\begin{matrix}COH\\CH_3\\H.\end{matrix}\right.$ This body, metameric with acetamide, is obtained by evaporating an aqueous solution of methyl ammonium formate to a syrupy consistency and distilling the residue. On the addition of potash to the distillate the amide separates out, and it is purified by rectification. It is a thick inodorous liquid, having a specific gravity of 1·011, and boils under a pressure of 740 mm. at 190°. It is soluble in water and alcohol, but insoluble in ether. It is inflammable, burning with a purple-bordered flame. Phosphorus pentoxide acts violently upon it, decomposing it into carbon monoxide and methylamine, and at the same time some hydrocyanic acid is formed.[1]

Reactions of Formic Acid and the Formates. Some of the more important reactions by which formic acid and its salts can be recognised have already been given.

On heating with concentrated sulphuric acid, pure carbon monoxide is evolved without any blackening, this gas burning, when ignited, with its characteristic pale blue flame. Ferric chloride colours neutral solutions of a formate a red brown with production of ferric formate. This reaction is, however, exhibited by acetic acid and the sulphites, but formic acid can readily be distinguished from these, inasmuch as its solution, when warmed with silver solution, evolves carbon dioxide, finely divided silver being at the same time precipitated and deposited in a mirror on the tube.

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[1] Linnemann, *Ber. Wien Akad.* lx. 44.

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[3] *Ibid.* ii. 157.

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Sadtler, *Amer.* [illegible] *Soc.* 1767;

glass cylinder (*b*), Fig. 68, open at both ends, is firmly fastened by a piece of sheet caoutchouc to the top of a small porous cell (*a*) of the same diameter. The cylinder is closed at the top with a well-fitting cork, to which two thin glass tubes are fixed; down one of these a stout platinum wire passes, to the lower end of which is attached a piece of platinum foil, bent as shown by the dotted lines, and serving as the electrode. The second tube (*e*) is connected with a gas-delivery tube. The whole apparatus stands in a wide glass cylinder open at the top (*c c*, Fig. 69), and is surrounded by a cylindrical piece of sheet copper placed outside the porous cell, and serving as the other electrode. Both vessels are filled to the same height with a solution of acetate of potash; the liquid is poured into the inner one by means of the tube until the columns of liquid inside and outside stand about two inches above the top of the band of caoutchouc. The solution of potassium acetate must be tolerably concentrated and free from chlorine. If the negative pole of a battery of four Bunsen's elements be connected with the copper electrode, and the positive with the platinum

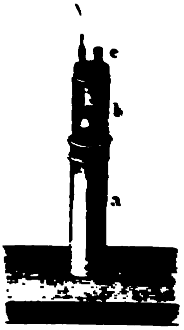

FIG. 68.

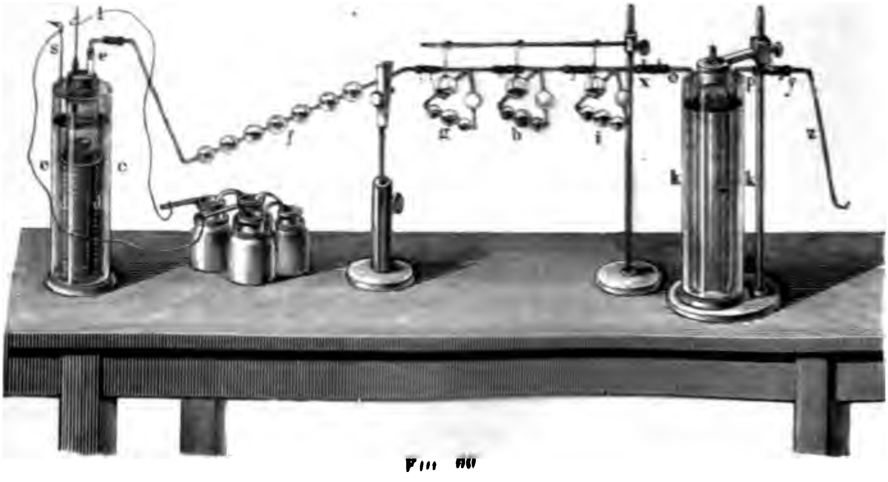

FIG. 69.

cylinder, pure hydrogen is first evolved, and afterwards a mixture of carbon dioxide and ethane, and this gaseous mixture passes through the bulb-tubes (*f*) filled with potash solution. The ethane is still mixed with another gas possessing a peculiar smell, whose nature has not yet been properly ascertained. To separate this gas, the ethane is next passed through the bulb-tube (G) containing fuming sulphuric acid. The gas is afterwards washed by passing through the bulbs (*h*) containing caustic potash, and again dried by passing through the bulb (*i*) containing strong sulphuric acid. The gas thus purified and consisting of a mixture of 66 volumes of hydrogen with 28·8 volumes of ethane is next passed into the small mercury gasholder (*k*), which is so arranged that by gradually raising the inner bell-jar any excess of pressure in the apparatus may be avoided.

Pure ethane can also be obtained by allowing zinc ethyl to pass drop by drop into water. The reaction is very violent, and the liquid must be well cooled to begin with (Frankland).

It is likewise easily formed by the action of sulphuric acid on mercuric ethyl, according to the following reaction:

$$2\,Hg(C_2H_5)_2 + H_2SO_4 = 2\,C_2H_6 + (C_2H_5Hg)_2SO_4.$$

In order to purify the gas thus obtained from traces of mercuric ethyl which evaporates with it, it is led through fuming sulphuric acid and then through water (Schorlemmer).

According to Schützenberger[1] it is also obtained by the action of barium dioxide on acetic anhydride, according to the following equation:

$$2\left.\begin{array}{l}CH_3.CO\\CH_3.CO\end{array}\right\}O + BaO_2 = \left.\begin{array}{l}CH_3\\CH_3\end{array}\right\} + \left.\begin{array}{l}CH_3CO.O\\CH_3CO.O\end{array}\right\}Ba + 2\,CO_2.$$

Darling,[2] who endeavoured to prepare it in this way, only succeded in obtaining a gaseous mixture containing less than one-fifth its volume of ethane, the remainder consisting of marsh gas and a small quantity of carbon monoxide.

189 *Properties.*—Ethane is a colourless odourless gas condensing to a liquid under a pressure of 46 atmospheres. It is a singular fact that the vapour-tensions of ethane, C_2H_6, ethylene, C_2H_4, acetylene, C_2H_2, stand in the same relation to one another as the quantities of hydrogen contained in their molecules do, that is as 3 : 2 : 1.[3]

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[1] *Compt. Rend.* lxi. 487.

[2] *Loc. cit.*

[3] Cailletet, *Compt. Rend.* lxxxv. 851.

Ethane is easily inflammable, burning with a faintly luminous flame. It is slightly soluble in water, according to Schickendantz, its absorption-coefficient is represented by the following expression :

$$C = 0{\cdot}094556 - 0{\cdot}0035324\,t + 0{\cdot}00006278\,t^2.$$

At the ordinary temperature alcohol dissolves about its own volume of this gas.

ETHYL ALCOHOL.

C_2H_6O.

190 Fermented drinks were known in very early times. Wine is mentioned in Homer and in the Old Testament, and the Egyptians, Gauls, and Germans, and other ancient nations, understood the art of brewing beer from malted grain, whilst the northern peoples prepared mead from honey. The existence of alcohol in all such substances was first recognised after the Alexandrians had perfected the extremely rough methods of distillation which had up to their times been employed.

Distillation.—This appears to be a fitting place to give some account of the history of distillation,[1] a process constantly employed by chemists. Aristotle refers to the fact that sea-water can be rendered fit for drinking by evaporation, but he does not explain by what means the vapour is condensed. Still there can be little doubt that this was effected by means of the cover of the vessel, for Alexander of Aphrodisias writing in the third century describes an apparatus of this kind.

Both Dioscorides and Pliny mention that an oil can be obtained from rosin by heating it in a vessel in the upper part of which some wool is placed for the condensation of the oil. The first-named author also mentions that quicksilver is obtained by heating cinnabar in an earthenware pot together with iron, a cover termed *ἄμβιξ* being placed over the pot. An important improvement in distillation was made by the Alexandrians, as they employed two vessels, one for evaporating the liquid and the other for condensing the vapour. The forms of apparatus which they employed are shown in Figs. 70 and 71. In principle they are similar to those used at the present day.

The two parts of the distilling apparatus were, first the

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[1] Kopp, *Gesch. der Chemie*, ii. 26, iv. 273 ; *Beiträge*, i. 217.

body, or still, and secondly the head, from which either one or several tubes passed to the receiver. The Arabians termed the head or cover *alambic* or alembic, and this word was subsequently employed to designate the whole apparatus.[1] The invention of the retort, a long-necked flask in which the neck was bent back (*Retorta, ampulla*), we also owe to the Arabians.

Basil Valentine was the first to mention a tubulated retort, and he illustrates its form by a figure. The cooling-vessel and condensing-worm were also first described by Valentine. Fig. 72 represents a form of distilling apparatus from a German edition of Geber's works dated 1710.

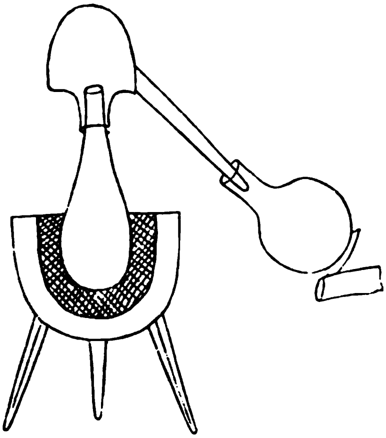

FIG. 70.

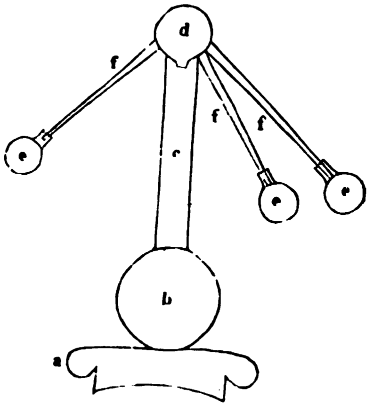

FIG. 71.

Other improvements in the arrangements for distillation will be described under the manufacture of alcohol.

191 The discovery of a combustible spirit of wine soon led to attempts to obtain it of a greater strength than was found possible by repeated distillation. Raymond Lully described this method, and also noticed that a still stronger spirit can be obtained by rectification over dry carbonate of potash, whilst Basil Valentine states, more precisely than Lully, the method to be adopted for obtaining strong spirit by means of calcined tartar and subsequent distillation. Thus in the *Offenbarung der Handgriffe*, &c., p. 487, he says: "Having now prepared

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[1] See E. Wiedemann, *Zur Chemie der Araber, Deutsch. Morgenländ. Ges.* 1878.

this *aqua vitæ* by distillation and rectification (take care that thou comest not near with a light during the process, and doest thyself damage), place in a still to every quart of this prepared *aqua vitæ* a quarter of a pound of well calcined sal tartari. Adapt to this a good sized alembic (head), and distil in a B.M. (water-bath)."

Robert Boyle likewise specially describes the means necessary for obtaining "dephlegmed spirit of wine" from ordinary spirit. He recommends[1] for this purpose not only the use of "white calx of tartar," but also of quick-lime. He states that on careful distillation "the phlegmatic part of the spirit of wine is soaked up by the alcalizate salt, and the inflammable part is freed from it;" adding, "therefore, this alcohol of wine we peculiarly call the alcalizate spirit of wine." Basil Valentine also mentions the use of freshly-burnt lime, but this process was used by him rather with the view of making the lime stronger than of preparing a more active spirit.

FIG. 72.

Rectification at a low temperature was, however, a much more common mode of dehydration than the use of potashes or lime. In order to condense the vapours completely they were passed through long cooling tubes, often curved and bent in an extraordinary fashion. Not unfrequently the head was

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[1] Boyle, *Opera*, i. 333.

raised high above the body of the still in order to retard the passing over of aqueous vapours. Indeed Michael Savonarola, in his treatise, *De Arte Conficiendi aquam Vitæ Simplicem et compositam* (1532), relates that a friend of his had built a still having its body in the cellar and its head under the roof of the house.

192 Alcohol was formerly designated by very different and often by most fanciful names. Thus, for instance, Marcus Græcus, who is said to have lived in the eighth century, calls it *aqua ardens*, and the Latin translators of Geber's writings term it *aqua vitæ*; and in addition to these names, of which the latter has come into general use, we also find *aqua vitis* (beetroot water), *spiritus vivus*, *mercurius vegetabilis*, and a number of other pharmaceutical names. Moreover, as it is used as one of the most important medicines, Raymond Lully terms it *consolatio ultima corporis humani*. The name of spirit of wine (*spiritus vini*) first occurs in Basil Valentine, and the name alcohol was first used in the sixteenth century. It has already been stated in the second volume (Part II., p. 301) that the word was first employed for designating the native sulphide of antimony (speissglass), and was afterwards made use of to denote any finely divided, but especially metallic, powder.

It is difficult to say how it came to be applied to spirits of wine. Libavius, in his *Alchymia*, published in 1594, says: "Quando vini spiritus rectificatur per suum salem (that is, carbonate of potash prepared with cream of tartar), seu potius exasperatur, nominant vini alcool, vel vinum alcalisatum." In Johnson's *Lexicon Chymicum*, published in 1657, pages 12 and 13, we find the following explanation: "Alcohol, est antimonium sive stibium." And again, "Alcohol, vini, quando ominis superfluistas vini à vino separatur, ita ut accensum ardeat, donec totum consumatur, nihilque fæcum aut phlegmatis in fundo remaneat."

The extract from Libavius, and that already cited from Boyle, appear to point to the fact that strong alcohol was formerly termed *vinum alcalisatum* (that is, wine strengthened by means of alkali), and that, perhaps by some misunderstanding, this came to be written *vinum alcoholisatum*, from which afterwards it became *alcohol vini*.

Another derivation which appears to be about as probable as the one just stated, is that the word alcohol, after its general employment to signify a very finely divided body, was made use of to designate spirits of wine, because this was wine freed from all grosser particles.

193 *Manufacture of Alcohol.*—The manufacture of alcohol on a large scale is carried on by distillers, and forms an important branch of industry, the gradual development of which has exerted no inconsiderable influence upon the history of civilization. Of all chemical compounds, alcohol is the one which has most materially affected human progress. Alcohol was originally obtained, as has been remarked, by the distillation of wine, and the fact that it was contained in beer naturally led to its preparation by the action of yeast upon malted grain. Up to the end of the fifteenth century, alcohol was used as a medicine, its taste being rendered agreeable by admixture of sugar, herbs, aromatic berries and essential oils, and so it gradually came into general demand, inasmuch as it was believed that, if daily taken in small doses, it had the effect of preserving youth and health, and thus it was that brandy soon became a recognised drink throughout Europe.

As soon as alcohol began to be used in the arts and manufactures, means were taken to find a cheaper method of preparing it than from malted grain, and for this purpose not only were potatoes and beet-root employed, but also cane-sugar, beet-root sugar, and molasses. The *marcs*, or residues of the wine presses, and sweet fruits, such as cherries, plums, all of which contain both sugar and starch, are also used for the preparation of spirit of wine, whilst, in the East, rice and sorghum are the chief sources, and in America, spirit is obtained from potatoes and Indian corn. The materials which are thus used in the preparation of spirit of wine may, therefore, be arranged in three groups. In the first of these are classed the grape and other sweet fruits which contain fermentable sugar, or glucose, $C_6H_{12}O_6$. The juice of such fruit enters into fermentation spontaneously on exposure to air, under the action of a ferment contained in the nitrogenous constituents of the juice, the sugar thus being converted into alcohol. Further remarks on this subject will be found in the chapter on Fermentation.

The second group includes substances which contain common or cane-sugar, $C_{12}H_{22}O_{11}$. In order to bring this into a state of fermentation, the ferment, yeast, must be added to a dilute solution, the first step in the process being the formation of fermentable sugar by assumption of the elements of water.

To the third class belong the various kinds of grain, potatoes, and other substances containing starch, $(C_6H_{10}O_5)_n$. This substance is insoluble in cold water, but forms a gelatinous mass when boiled with water, and can then be converted into fermentable sugar by the addition of malt or malt extract. This contains a peculiar ferment termed diastase, which is also formed in the process of malting the grain. Dilute sulphuric acid also possesses the power of effecting this same change, converting the starch meal into sugar on boiling with water.

Grain Spirit is usually prepared from barley, rye, wheat, or oats, but maize and rice and other grain are likewise employed for the purpose. In general, a mixture of several sorts of grain is made use of, inasmuch as it has been shown that when two kinds, such as barley and oats or wheat, are used, the yield of spirit is larger than when one kind is treated by itself. To 1 part of malted barley 2 to 3 parts of unmalted grain (termed the *grist*) are usually added, but in some cases the proportion of the latter is still larger. The grain is broken up tolerably finely, either between ordinary grindstones, or, in the case of the softer malted grain, between rollers of a suitable form.

Mashing.—The crushed grain and malt is next run into the mash-tun, where it is mixed, in the proportion of 1 litre to 1 kilo of malt, with water having a temperature of about 60° and carefully stirred so as to avoid the formation of lumps. After the first mash has stood for about half an hour, the liquid is drawn off, a second supply of water added, and the mash warmed by passing in steam until the whole is raised to a temperature of about 65°. The tun is then covered for some hours and allowed to stand, in order to permit the complete conversion of the starch of the grain into sugar by means of the soluble diastase of the malt. The cold wort is then brought into a fermenting vat and yeast added, in the proportion of 2½ to 3 kilos of dry brewer's yeast for every 100 kilos of grain. The fermentation begins after a few hours, and should last four or five days. The attenuated wort, the specific gravity of which ought to be nearly equal to that of pure water, is then submitted to distillation with as little delay as possible; and at the conclusion of the operations 100 kilos of grain should yield about 28 litres of pure alcohol.

Spirit of wine is largely obtained from potatoes, especially in Germany. The roots are first softened with steam, then rasped on a machine with warm water. Malt is then added to convert the potato-starch into sugar, and the processes of mashing, infusion, and fermentation carried on as in the manufacture of grain spirit.

Beet-root is worked up in different ways. The root is rubbed down and the juice pressed out; or the root is cut into slices and the sugar washed out by hot water, or by the residue of a distillation of a former operation. To the liquid, yeast is added, and the liquor allowed to ferment. Alcohol is also manufactured from the molasses obtained in the cane and beet-root sugar industries. The syrup, after sufficient dilution with water, is allowed to ferment, and on distillation a spirit, known as rum, is obtained.

194 Lavoisier, and at a later date Gay-Lussac, showed that the alcoholic fermentation of sugar proceeds according to the following equation:

$$C_6H_{12}O_6 = 2\,C_2H_6O + 2\,CO_2.$$

Pasteur afterwards found that the whole of the sugar does not undergo the above change, but that from 5 to 6 per cent. is converted partly into glycerin, $C_3H_8O_3$, and succinic acid, $C_4H_4O_4$, and partly used up for developing the growth of the ferment. In addition to this, and under conditions which are not yet properly understood, the alcoholic fermentation gives rise to higher homologues of common alcohol, fatty acids, and ethereal salts, which impart to the various spirituous liquors, as well as to plain spirit, its peculiar smell. These bodies, all of which boil higher than common alcohol, are classed together under the name of *fusel-oil*, though sometimes the name is applied simply to those which impart to the spirit a disagreeable odour.

195 The first crude forms of distillating apparatus have already been described. As soon as spirit was required in larger quantity these stills were increased in size, and made of copper and other metals instead of pottery. A simple apparatus which was formerly in general use and is still employed on the small scale for the manufacture of the more valuable kinds of brandy (from the old German *Brandewein*), is shown in Fig. 73. The wort is heated on the body of the still, and the vapour is condensed in the worm.

The distillate consists of a dilute alcohol termed "low wines" or "singlings," and from this, by a second distillation or "doubling," a stronger alcoholic distillate is obtained. This process is carried on until the spirit begins to acquire a disagreeable taste and smell, and to this the name of "faints" is given. By repetition of this operation, strong or rectified spirit is made, and at last a highly rectified spirit, containing 80 per cent. or more of alcohol, is obtained. The older operations for separating the spirit from the water are tedious and costly, and hence a simpler and cheaper method for effecting this object became a desideratum. The first apparatus of this kind was invented by Adam, in France, and introduced into industry by Bernard.[1] This original apparatus was soon improved, and has now been brought to a high degree of perfection. The stills employed at the present day consist essentially of two parts, (1) the *analyzer*, and (2) the *rectifier*. The action of the first depends upon the fact that when mixtures of the vapours of alcohol and water are cooled down by suitable arrangements, the condensed liquid is separated into two parts, one containing a large quantity, and the other a small quantity, of alcohol. This principle is made use of on the small scale in laboratories in the process of fractional distillation, when Wurtz's distillation-bulbs are employed (see p. 150). In the second part of the apparatus, the vapours are condensed in a rectifier, but none of the liquid is allowed to run back, as in the first part, the whole being heated by a current of steam to the boiling-point of the liquid, when vapour richer in alcohol is given off. This is condensed in a second vessel, again brought to the

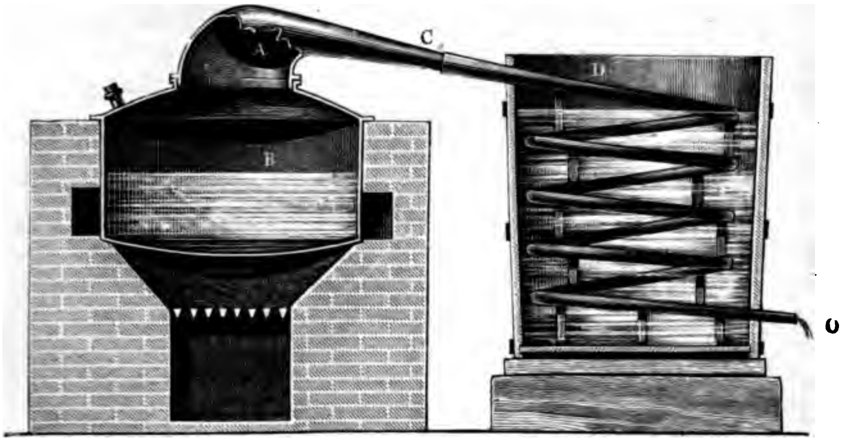

Fig. 73.

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[1] *Gilb. Ann.* xxxii. 129.

boiling-point by action of steam, and condensed in a third vessel in the form of strong alcohol, and this process repeated. This principle is likewise applied on the small scale for fractional distillation in the laboratory.

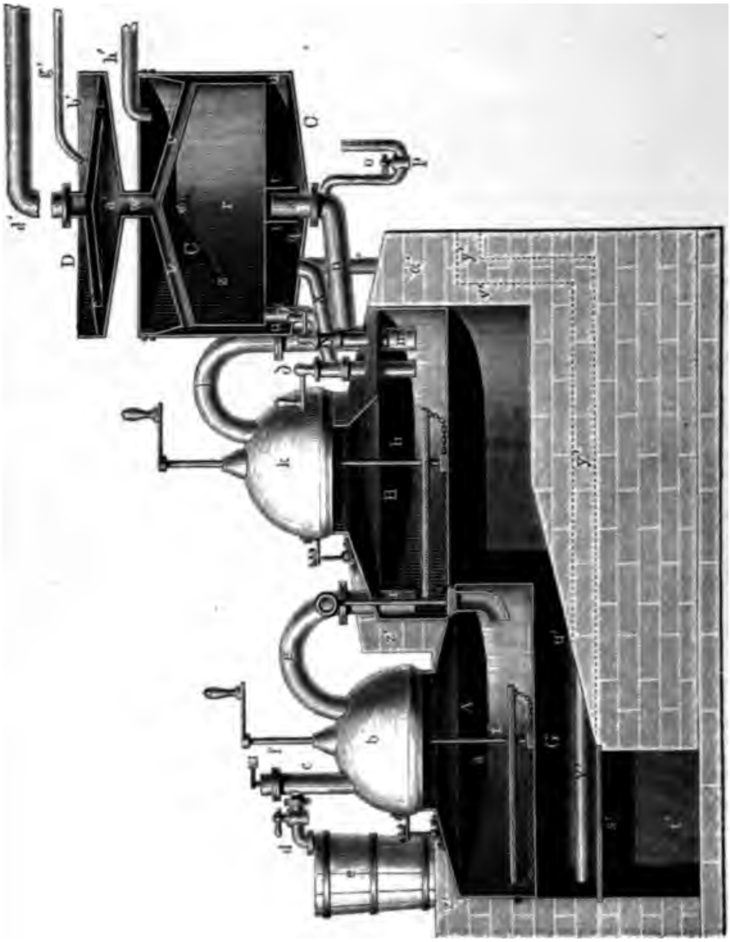

Fig. 74

196 The apparatus used for rectifying is constructed in very different ways. Of these various forms we shall first describe the large apparatus of Pistorius with direct heating, formerly much used in Germany, as it serves as the point of departure for almost all the other forms of stills and rectifiers now in use. At the commencement of the operation the first

charge of wort is allowed to enter by the pipe (*h'*) (Fig. 74), passing first into the heater (C), thence by the pipe (*y*) into the first boiler (B), and from this into the second boiler (A). The second charge is then brought into (B), the third remaining in the heater (C). The wort in boiler (A) is now heated to the boiling-point, the liquid being constantly stirred with the chain (*f*) to prevent it boiling over. The vapours from this pass through the tube (*g*) into boiler (B), which is warmed by the waste heat from the fire (G), and the contents are soon raised to the boiling-point. The vapours here given off pass by the tube (*l*) in the head of the still into the rectifying vessel (C). In this vessel a considerable portion of the water or weak spirit is condensed, flowing down to the lower portion, where it collects, and is from time to time allowed to enter the boiler (B). The vapour of the strong spirit passes through the tubes (*v v'*) into the condenser (D), where again weaker spirit runs back, and the uncondensed vapour passes into a second and third condenser (not shown in the drawing), until at last it comes to the tube (*d'*), whence it passes into a large condensing worm, placed in a tub of cold water, from the end of which it runs into the receiver.

Fig. 75 represents a Pistorius still, worked, as is now usual, by steam instead of an open fire. The boilers (A) and (B) are placed vertically above one another. (C) is the rectifier and (D) the condenser. The direction taken by the vapour is indicated by arrows.

197 When very large quantities of spirit have to be distilled, and especially in this country, where, owing to Excise regulations, large distilleries are the rule and grain-spirit is alone manufactured, an arrangement known as " Coffey's still " is employed. It consists of two columns (A) and (B) (Fig. 76) placed side by side. These are made of wood 5 or 6 inches thick, and are lined with copper. The " analyzer " (A) is divided into 12 small compartments by 11 horizontal plates of copper (*a*) perforated with numerous holes and furnished with valves opening upwards. Dropping pipes (*b b*) are also attached to each plate, the upper end of the pipe being an inch or two above the plate, and the lower end dipping into a shallow pan (*c*) placed on the lower plate.

The second column or " rectifier " (B) receives the spirituous vapours passing from the column (A) through the pipe (*g*). This column is also divided into compartments like (A), but there are 15 instead of 12. The 10 lower diaphragms (*l*) are

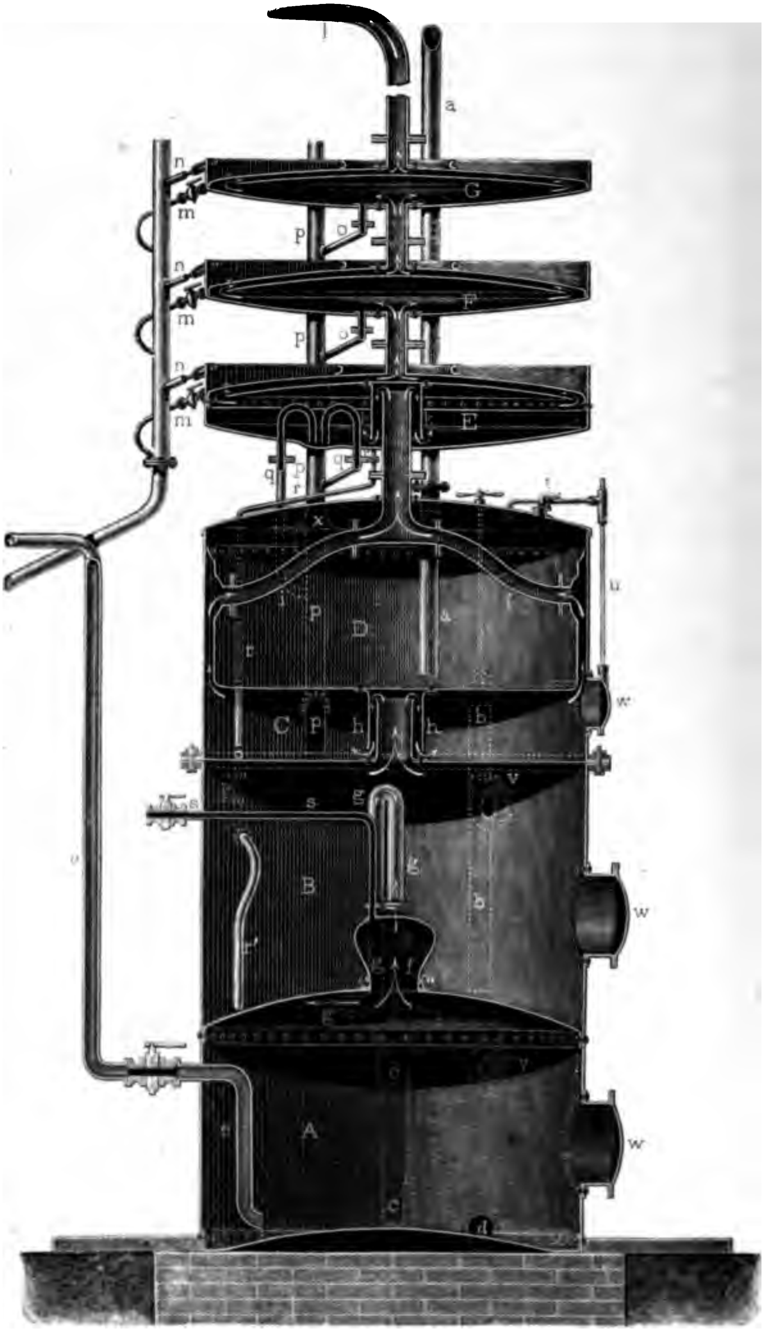
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Fig. 75.

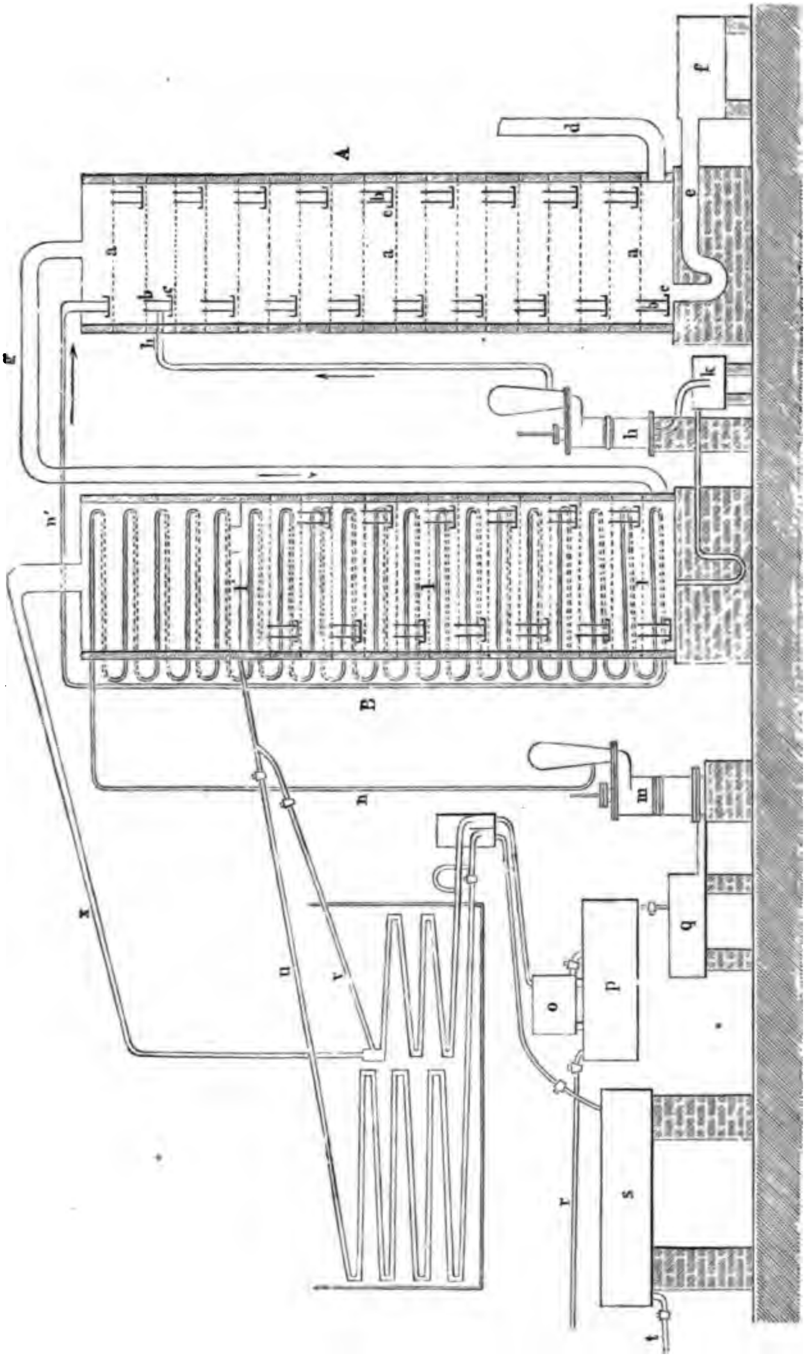

FIG 76

pierced with small holes and furnished with drop-pipes, whilst the upper 5 have only one large opening surrounded by a ring to prevent the finished spirit from returning.

Between each of these compartments passes a bend of a long zigzag pipe (*n n n'*), one end of which is attached to the pump (*m*), whilst the other end discharges the contents of the pipe into the top of the column (A), as indicated by the arrow. The following is the working of the apparatus. In the first place, the fermented liquor or wash is pumped up by the pump (*m*) until the zigzag pipe is filled and the wort flows over the compartments (*a a a*). Steam is then admitted into the analyzer by the pipe (*d*) and heats the wash, which is deprived of all its alcohol by the time it reaches the bottom of the cylinder and flows off by (*e f*) as spent wash. The strong spirituous vapour passes through (*g*) to the rectifier, and at last through the worm (*c*) of the refrigerator into the receiver.

198 In order to separate completely the spirit of wine from the strongly scented fusel-oil, the crude spirit may be filtered through freshly ignited and finely divided wood-charcoal, or, its vapour may be passed through a cylindrical vessel provided with a head, containing a large number of perforated plates upon which coarsely divided charcoal is placed.

Experience has however shown that the spirit may be freed from fusel-oil by bringing it up to a concentration of 90 per cent. of alcohol by rectification, as the fusel-oil boils higher than alcohol. Hence the simplest means of removing the fusel-oil is to concentrate the spirit. Coffey's still answers these requirements, producing a pure neutral spirit up to 68° over proof, and free from fusel-oils. In France and Germany, where Coffey's still is not used, a second distillation is carried on in a rectifying still. Fig. 77 shows the construction of such a still, much used on the continent and known as the French column apparatus. It consists of a boiler (A) heated by a steam-pipe; the vapours pass through the rectifier (B), then pass to the condenser (C), and the highly concentrated spirit condenses in the refrigerator (D), whilst the "phlegma" (or aqueous portion) flows by the tube (*e*) back into the rectifier.

Various products are obtained in the foregoing process. The first portion of the distillate serves to wash out the apparatus; it contains bodies which are much more volatile than alcohol, such as aldehyde.[1] Next comes the fine spirit, containing from

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[1] Krämer and Pinner, *Ber. Deutsch. Chem. Ges.* iii. 75.

90 to 95 per cent. of alcohol according to the more or less complete manner in which the apparatus works; and after this common spirit, containing 85 to 86 per cent., comes over, and lastly the "faints" containing the strong-scented fusel-oil. The first and last runnings are generally mixed together, and either sold as common spirit or worked up again by the distiller.

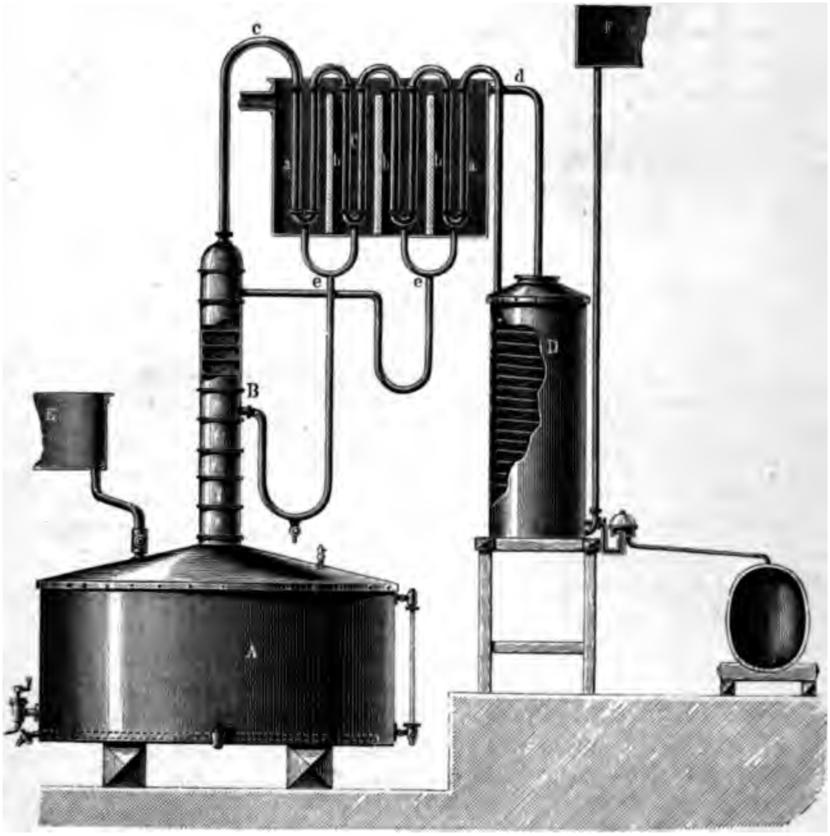

Fig. 77.

199 The preparation of rice-spirit, or shochu, is conducted in Japan according to the following primitive plan. Rice is allowed to undergo a peculiar kind of fermentation: this yields the beverage called saké (from ki, spirit), containing from 11 to 15 per cent. of alcohol. The residue, after pressing out the saké moistened with some poor qualities of saké, is then

subjected to distillation in the arrangement shown in Fig. [illegible]. The mash (A) is placed in a tub provided with a perforated bottom, which rests on the iron pot (B) containing water, which can be heated by a fire. The steam from the boiling water passes through the mash and carries off the spirit, which then condenses on the lower surface of the pan (C), kept cool with cold water, and runs into the bottle (D). The spirit thus obtained contains from 30 to 40 per cent of alcohol.

FIG. [illegible].

200 A singular proposal may here be mentioned, viz. that of obtaining spirit from the ethylene contained in common coal-gas. Faraday found that this latter gas is absorbed by concentrated sulphuric acid,[1] and Hennell, to whom Faraday gave the solution he had prepared, found that it contained sulphovinic acid (ethyl sulphuric acid), a body formed by the action of sulphuric acid on alcohol, and which when heated with water yields alcohol and sulphuric acid.[2] This important observation attracted but little notice until confirmed by Berthelot in 1855.[3] This indeed was the first step in the synthesis of alcohol, which Berthelot afterwards accomplished by showing that acetylene can be obtained by direct combination of its elements, and that this compound combines with nascent hydrogen to form ethylene. The same chemist also prepared alcohol by this method from coal-gas, and since that time many proposals have been made to carry out this reaction on a large scale. They have however hitherto proved unfruitful, and will probably remain so.

Other syntheses of alcohol have already been described (p. 179).

201 Alcohol occurs in nature, although in small quantities, in the vegetable kingdom. Thus it is found both in the free state and combined to form ethyl butyrate and other ethereal salts, in

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[1] "On New Compounds of Carbon and Hydrogen," *Phil. Trans.* 1825, 448.

[2] "On the Mutual Action of Sulphuric Acid and Alcohol," *Phil. Trans.* 1826, 240; 18[illegible]

[3] *Ann. Chim. Phys.* [3], xliii 385.

the unripe fruit of *Heracleum giganteum*;[1] also in those of *Anthriscus cerefolium* and *Pastinaca sativa*, which also contains a volatile ethyl compound, probably the butyrate.[2] Ethyl alcohol is also formed in small quantity in the dry distillation of organic substances. Thus, for instance, it occurs in coal-tar[3] and in bone-oil,[4] as well as in wood-spirit.[5] It also occurs in bread, being formed by the fermentation of dough, and not being completely removed in the process of baking. According to the experiments of Bolas,[6] new bread, made with yeast, contains on an average 0·314 per. cent., whilst in slices of bread a week old 0·12 to 0·13 per cent. of alcohol was found. Ethyl alcohol is also said to occur together with acetone, in the urine of diabetic patients,[7] and, according to Béchamp, it is found in small quantities in several of the animal fluids, and in larger quantities in their products of decomposition.

202 *Preparation of Absolute Alcohol.*—Although ethyl alcohol is a more volatile liquid than water, it cannot be obtained in the anhydrous state from an aqueous spirit by fractional distillation. In order to prepare anhydrous or absolute alcohol, substances must be added which possess a more powerful attraction for water than alcohol itself. It has already been stated that Raymond Lully employed potashes in order to strengthen alcohol, and the later chemists used the same means. As, for this purpose, they employed the air-dried salt which still contains water, they were unable thus to obtain anhydrous alcohol, which was first prepared by Lowitz in 1796, by the use of freshly ignited potashes. In the same year Richter showed that fused hydrochlorate of lime (calcium chloride) may be used for the same purpose. Caustic lime is however much more effective than either of these salts, and this substance too, it seems, was used in early times for strengthening spirit.

In order to prepare absolute alcohol a retort or flask is two-thirds filled with freshly burnt lime broken into small lumps, and so much spirit is poured on as not quite to cover the solid lime. The whole is allowed to stand overnight, and is then distilled from a water-bath. The distillate is usually not

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[1] Gutzeit, *Ber. Deutsch. Chem. Ges.* xii. 2016.

[2] Gutzeit, *Liebigs Ann.* clxxvii. 344.

[3] O. Witt, *Ber. Deutsch. Chem. Ges.* x. 2227; Vincent and Delachanal, *Comptes Rendus*, lxxxvi. 349.

[4] Richard, *Bull. Soc. Chim.* xxxii. 486.

[5] Hemilian, *Ber. Deutsch. Chem. Ges.* viii. 661.

[6] *Chem. News*, xxvii. 271.

[7] Markownikoff, *Liebigs Annalen*, clxxxii. 362.

anhydrous, and for this reason the treatment must be repeated, or, the whole may be boiled for an hour with a reversed condenser and then the alcohol distilled off. In this last process, however, a spirit should be used which does not contain more than 5 per cent. of water. If a weaker alcohol be employed, the distillation over lime must be repeated several times, and indeed, if too much water be present, less than half the retort must be filled with lime, as otherwise the vessel may burst from the expansion and heat caused by the slaking of this substance.

Anhydrous caustic baryta acts like lime. It is however much more costly, but a small quantity added to lime is useful, inasmuch as it possesses the property of dissolving completely in anhydrous alcohol, giving a yellow-coloured solution, and in this way the point when the last traces of water disappear may be easily recognised.[1]

The absolute alcohol of commerce, obtained from over-proof spirit by use of lime, usually contains half a per cent. of water, which can be got rid of by treating the alcohol with sodium.[2] This metal is also employed for separating the last traces of water from alcohol prepared by other methods, but in this case care must be taken not to add as much sodium as is needed to convert the whole of the water into caustic soda, otherwise a distillate is obtained which is weaker than the original alcohol. This singular result has been explained by Lieben.[3] It depends upon the fact that caustic soda partially decomposes in contact with anhydrous alcohol with formation of sodium ethylate and water. If only a small quantity of sodium be dissolved in anhydrous alcohol a decomposition takes place between the caustic soda and sodium ethylate, and at first a strong, but still not absolutely anhydrous, alcohol passes over; and if this treatment be repeated, the production of absolute anhydrous alcohol may be approached as near as is desired.

In order to ascertain whether alcohol contains water, it was formerly customary to add to the liquid white anhydrous copper sulphate, a substance which has also been employed for the preparation of absolute alcohol. This however is not suitable for the latter purpose, although it may be used as a test, as it quickly absorbs water from aqueous alcohol, thereby acquiring a blue colour.[4]

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[1] Mendelejeff, *Pogg. Ann.* cxxxviii. 246.

[2] *Ber. Chem. Industrie,* ii. 278.

[3] *Ann. Chem. Pharm.* clviii. 151.

[4] Cassoria, *Journ. Chem. Med.* 1846.

Pure anhydrous alcohol does not give any turbidity when shaken up with benzene;[1] it mixes in every proportion with carbon disulphide, and the more water it contains, the less carbon disulphide does it take up, the point of saturation in this case being rendered evident by a distinct turbidity occurring.[2] Another very delicate reaction for the presence of water in alcohol is a solution of caustic baryta in absolute alcohol, which instantly throws down a precipitate of barium hydroxide when brought in contact with alcohol containing water.[3]

203 *Properties.*—Pure ethyl alcohol has a peculiar pleasant smell, and when dehydrated by means of lime, it possesses according to Mendelejeff a somewhat ethereal smell, which however after several distillations is said to disappear. When anhydrous alcohol is cooled with a mixture of solid carbon dioxide and ether, it assumes a thick viscous condition, but even when exposed to the still lower temperature obtained by use of liquid nitrous oxide, alcohol does not freeze. Alcohol is easily inflammable, burning with a blue non-luminous flame, and depositing soot only when burnt with an insufficient supply of oxygen. That its vapour mixed with air forms an explosive mixture is a fact which was known to Basil Valentine.

The physical constants of pure and aqueous alcohol have been determined with the greatest care by many investigators. According to Mendelejeff, absolute alcohol boils under the normal pressure at 78°·3, and has the following specific gravity compared with water at 3°·9:

0°	5°	10°	15°	20°	25°	30°
0·80625	0·80207	0·79788	0·79367	0·78945	0·78522	0·78096.

For the purpose of calculating the specific gravity at other temperatures, Kopp's[4] formula may be employed, in which v at 0° = 1:

$$v = 1 + 0{\cdot}00104139\,t + 0{\cdot}0000007836\,t^2 + 0{\cdot}000000001768\,t^3.$$

The specific heat, latent heat, and vapour-tension have been determined by Regnault.[5] The vapour density of alcohol has been found by Gay Lussac[6] to be 1·6133.

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[1] Gorgen, *Compt. Rend* xxx 691.

[2] Tuchschmidt and Follenius, *Ber. Deutsch. Chem. Ges.* iv. 583.

[3] Berthelot, *Ann. Chim. Phys.* [3], xlvi. 180.

[4] *Pogg. Ann.* lxxii. 1 and 223.

[5] *Mém. Acad.* xxvi .701.

[6] *Ann. Chim.* [1], xcv. 311.

Absolute alcohol is a very hygroscopic substance, quickly absorbing water from the air, and hence care must be taken in its preparation that only dry air can find its way into the distilling apparatus. A peculiar observation was made by Sömmering,[1] namely, that aqueous alcohol contained in a bladder and hung up in a warm room loses water by evaporation, nearly absolute alcohol remaining behind. This observation has been confirmed by other persons.[2]

Boyle mentions in his *Experimental History of Cold* that when strong spirit of wine "drawn off from quick-lime, the better to dephlegm it," is mixed with snow, a freezing-mixture is formed;[3] whilst Boerhave in 1732 observed that when spirit is mixed with water a rise of temperature occurs; and Réaumur showed, in the following year, that a diminution of volume likewise takes place. This contraction is greatest when one molecule of alcohol is mixed with three molecules of water (Mendelejeff). In order to exhibit this contraction a long glass tube is half filled with coloured water, and then strong spirit poured carefully on to the surface until the tube is nearly filled and the volume of the two layers indicated. The liquids are then mixed by shaking and reversing the tube, and the diminution of volume noticed.

It has already been stated that alcohol and water, in spite of the difference in their boiling-points, cannot be completely separated by distillation. By means of a suitable fractionating apparatus, spirit containing 96·5 per cent. of alcohol may, however, be obtained. On the other hand, a residue of almost absolute alcohol can be procured, as Sömmering observed long ago, by distilling weaker alcohol off first. Thus by using fractionating tubes containing 33 cups of wire-gauze a spirit containing 98 per cent. of alcohol yields a distillate containing 97·4 per cent. and a residue containing 99·5 per cent. of alcohol. Hence it is clear that a mixture of ninety-seven parts of alcohol and three parts of water boils without any alteration in composition.[4]

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[1] *Denkschr. Akad. München*, 1811, 1814, 1820, 1821

[2] *Gmelin's Handbook*, viii. 260.

[3] *Boyle's Works*, ii. 511.

[4] Le Bel, *Compt. Rend.* lxxxviii. 912.

ALCOHOLOMETRY.

204 The commercial value of alcoholic liquids, except those which are used as beverages, depends as a rule on the percentage of alcohol which they contain. Hence a means by which the strength of spirit could be readily ascertained became a matter of importance at an early date. Raymond Lully considered alcohol to be pure when a cloth moistened with it took fire after the alcohol had burnt off, "id est aqua vitæ rectificata ut ardeat pannus madefactus in ea."

This method was employed until the introduction of gunpowder into Europe, which then was used instead of the cloth. This *powder-test* was in common use during the last century, and from this is derived the name of *proof-spirit,* to which we shall have to refer hereafter. Basil Valentine supposed that alcohol was pure when it left no water behind after it was burnt. This test was long used, and C. J. Geoffroy in 1718 suggested that the alcohol should be burnt in a graduated cylinder in order to compare the volume of the spirit with that of the residual phlegm. Bergmann, in 1775, also recommended this process.

The so-called *oil-test* was likewise in common use. Michael Savonarola (p. 285) explains this test by stating that the alcohol is poured on to the surface of oil, and notice is taken as to whether it remains on the surface or not. In a work published by Michael Schrick in 1483 we find, "Oil poured on to the surface of brandy falls to the bottom." Even at the beginning of the eighteenth century this method was in vogue, being believed to be a fairly accurate one.

Tables representing the contraction which ensues when alcohol is mixed with water, as well as the specific gravities of these mixtures, were given by Réaumur in 1733-5, and also by Brisson in the *Memoirs of the Paris Academy* for 1768. The first complete investigation which had for its object the determination of the composition of aqueous spirit from the specific gravity was, however, made at the suggestion of the English government in the year 1790 for Revenue purposes, and Sir Charles Blagden was employed to draw up these tables from the results of experiments made by Gilpin and published in the *Philosophical*

Transactions for 1794. Gilpin's experiments were so numerous and so remarkably accurate that they form, even at the present day, the foundation of the processes of alcoholometry, notwithstanding the fact that absolute alcohol was at that time unknown. On the discovery of anhydrous alcohol by Lowitz and Richter (p. 297), it was shown by Tralles,[1] in 1811, that Gilpin's normal alcohol contained 10·8 per cent. of water. He re-calculated Gilpin's numbers, and the tables thus obtained are those which are now in use. Tralles likewise made a series of experiments himself for the purpose of controlling Gilpin's results.

In France the standard alcoholometric tables are founded on experiments made by Gay-Lussac, the results of which have only been recently published.[2] These agree closely with Gilpin's, as Gay-Lussac's normal alcohol contained 10·86 per cent. of water. Several other investigations on this subject have since been made. Of these we may mention those of Drinkwater,[3] Fownes,[4] and Baumhauer,[5] and these very careful researches entirely confirm the experiments of Gilpin. More recently Mendelejeff[6] has investigated the matter again, discussing the errors of the various experimenters, and he finds that in the case of the most accurate of these older measurements the specific gravity is determined to within a mean error of 0 002, and the percentage of alcohol to within an error of 0·025. In his experiments Gilpin employed the Fahrenheit thermometer, which then was, as it now is, chiefly used in this country, whilst in Germany the measurements of temperature for alcoholometric purposes were made on Réaumur's scale.

205 The proportion between spirit and water contained in the aqueous spirit may be stated either by weight or by volume. For scientific purposes the former expression is always used, as this is independent of change of temperature. In commerce, however, it is usual to employ the proportion by volume, inasmuch as spirituous liquors are generally sold by measure.

Hence it is important to be able to calculate the composition by volume from that by weight. For this purpose some normal temperature must be chosen, and 60° Fahr. or 15°·5 C. is the one adopted in Gilpin and Tralles' determinations, whilst Gay-Lussac's experiments were made at 15° C.

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[1] *Gilberts Annalen*, xxxviii. 349.

[2] Pouillet, *Mém. Acad.* xxx. 1859.

[3] *Phil. Mag.* [3], xxxii. 123.

[4] *Pharm. Journ. Trans.* vii. 375.

[5] *Pogg. Ann.* cx 659.

[6] *Pogg Ann.* cxxxviii. 103 and 230.

Let S = spec. grav. of the aqueous spirit; a the weight in grains of alcohol in 100 parts of the same; V = the volume of the alcohol expressed in cbc., then $100 - a$ = the weight of the water, and

$$100 = V.S.$$

If further s = spec. grav. of alcohol (compared with water at the same temperature) then the volumes of alcohol and water contained in the spirit are $\frac{a}{s}$ and $100 - a$ respectively, and hence the percentage volumes of alcohol and water in the spirit are

$$\frac{a}{s} \cdot \frac{100}{V} \text{ or } a . \frac{S}{s} \text{ volumes of alcohol,}$$

and

$$(100 - a) . \frac{100}{V} \text{ or } (100 - a)\ S \text{ volumes of water.}$$

For the purpose of accurately determining the percentage of alcohol in aqueous spirit, its specific gravity must be determined by means of a specific gravity bottle. For excise, and general purposes, on the other hand, *hydrometers* are employed, special instruments being manufactured in which the percentages of alcohol by volume are marked on a scale. Thus for example 80 per cent. Tralles means that 100 volumes of such a spirit measured at 60° F. contain 80 volumes of absolute alcohol at the same temperature, but not that, when the latter quantity is mixed with 20 volumes of water, an alcohol of the above strength is obtained, as a contraction ensues when these liquids are mixed.

In England the normal temperature adopted at the present time is 51° F., and the spirit is not valued according to its percentage of absolute alcohol, but according to the amount of proof spirit it contains. This term is defined by the Act 58 George III. as "being such as shall at a temperature of 51° F. weigh exactly $\frac{12}{13}$ths part of an equal measure of distilled water." Proof spirit, therefore, contains 49·3 per cent. by weight or 57·09 per cent. by volume according to Tralles. Weaker spirits are termed underproof, and stronger spirits overproof. Thus 25° over proof means that 100 volumes of this spirit diluted with water yield 125 volumes of proof spirit, whilst 25° under proof means that it contains in 100 volumes seventy-five volumes of proof spirit.

The hydrometer chiefly used in England and sanctioned by the

Specific Weight (S.) *and Capacity* (C.) *of Alcohol, at* 60° F., *relative to Water of* 60° F. *as unity* (*more exactly* 12⅘° R. *or* 15⅝° C.), *at* 12·5° R. = 15·5° C.

I. *a*, Contents of Alcohol by Percentage of Volume. °/₀						I. *b*, Contents of Alcohol by Percentage of Weight. ·/.					
°/₀	S.	C.	°/₀	S.	C	·/.	S.	C.	·/.	S.	C
0	1·0000	1·0000	50	0·9343	1·0703	0	1·0000	1·0000	50	0·9183	1·0890
1	0·9985	1·0015	51	0·9323	1·0726	1	0·9981	1·0019	51	0·9160	1·0917
2	0·9970	1·0030	52	0·9303	1·0749	2	0·9963	1·0037	52	0·9138	1·0943
3	0·9956	1·0044	53	0·9283	1·0772	3	0·9944	1·0056	53	0·9116	1·0970
4	0·9942	1·0058	54	0·9263	1·0795	4	0·9928	1·0073	54	0·9094	1·0996
5	0·9928	1·0073	55	0·9242	1·0820	5	0·9912	1·0089	55	0·9072	1·1023
6	0·9915	1·0086	56	0·9221	1·0845	6	0·9896	1·0105	56	0·9049	1·1051
7	0·9902	1·0099	57	0·9200	1·0870	7	0·9880	1·0121	57	0·9027	1·1078
8	0·9890	1·0111	58	0·9178	1·0896	8	0·9866	1·0136	58	0·9004	1·1106
9	0·9878	1·0124	59	0·9156	1·0922	9	0·9852	1·0150	59	0·8981	1·1135
10	0·9866	1·0136	60	0·9134	1·0948	10	0·9839	1·0164	60	0·8958	1·1163
11	0·9854	1·0148	61	0·9112	1·0975	11	0·9826	1·0177	61	0·8935	1·1192
12	0·9843	1·0160	62	0·9090	1·1001	12	0·9813	1·0191	62	0·8911	1·1222
13	0·9832	1·0171	63	0·9067	1·1029	13	0·9800	1·0204	63	0·8888	1·1251
14	0·9821	1·0182	64	0·9044	1·1057	14	0·9788	1·0217	64	0·8865	1·1280
15	0·9811	1·0193	65	0·9021	1·1085	15	0·9775	1·0230	65	0·8842	1·1310
16	0·9800	1·0204	66	0·8997	1·1115	16	0·9763	1·0243	66	0·8818	1·1340
17	0·9790	1·0215	67	0·8973	1·1145	17	0·9751	1·0255	67	0·8795	1·1370
18	0·9780	1·0225	68	0·8949	1·1175	18	0·9739	1·0268	68	0·8772	1·1400
19	0·9770	1·0235	69	0·8925	1·1204	19	0·9727	1·0281	69	0·8748	1·1431
20	0·9760	1·0246	70	0·8900	1·1236	20	0·9714	1·0294	70	0·8724	1·1463
21	0·9750	1·0256	71	0·8875	1·1268	21	0·9702	1·0307	71	0·8700	1·1494
22	0·9740	1·0267	72	0·8850	1·1299	22	0·9690	1·0320	72	0·8676	1·1526
23	0·9729	1·0279	73	0·8825	1·1332	23	0·9677	1·0334	73	0·8652	1·1558
24	0·9719	1·0289	74	0·8799	1·1365	24	0·9664	1·0348	74	0·8629	1·1589
25	0·9709	1·0300	75	0·8773	1·1399	25	0·9651	1·0362	75	0·8605	1·1621
26	0·9698	1·0311	76	0·8747	1·1433	26	0·9637	1·0377	76	0·8581	1·1654
27	0·9688	1·0322	77	0·8720	1·1468	27	0·9622	1·0393	77	0·8557	1·1686
28	0·9677	1·0334	78	0·8693	1·1504	28	0·9607	1·0409	78	0·8533	1·1719
29	0·9666	1·0345	79	0·8666	1·1541	29	0·9592	1·0425	79	0·8509	1·1753
30	0·9655	1·0357	80	0·8639	1·1577	30	0·9577	1·0442	80	0·8484	1·1787
31	0·9643	1·0370	81	0·8611	1·1613	31	0·9560	1·0460	81	0·8459	1·1822
32	0·9631	1·0383	82	0·8583	1·1651	32	0·9544	1·0479	82	0·8435	1·1855
33	0·9618	1·0397	83	0·8555	1·1689	33	0·9526	1·0498	83	0·8409	1·1892
34	0·9605	1·0411	84	0·8526	1·1729	34	0·9508	1·0518	84	0·8385	1·1926
35	0·9592	1·0425	85	0·8496	1·1770	35	0·9490	1·0537	85	0·8359	1·1963
36	0·9579	1·0440	86	0·8466	1·1812	36	0·9472	1·0557	86	0·8333	1·2000
37	0·9565	1·0455	87	0·8436	1·1854	37	0·9453	1·0579	87	0·8307	1·2038
38	0·9550	1·0471	88	0·8405	1·1898	38	0·9433	1·0601	88	0·8282	1·2074
39	0·9535	1·0488	89	0·8373	1·1943	39	0·9413	1·0623	89	0·8256	1·2112
40	0 9519	1·0505	90	0·8339	1·1992	40	0·9394	1·0645	90	0·8229	1·2152
41	0·9503	1·0523	91	0·8306	1·2040	41	0·9374	1·0668	91	0·8203	1·2191
42	0·9487	1·0541	92	0·8272	1·2089	42	0·9353	1·0692	92	0·8176	1·2231
43	0·9470	1·0560	93	0·8237	1·2140	43	0·9332	1·0716	93	0·8149	1·2272
44	0·9452	1·0580	94	0·8201	1·2194	44	0·9311	1·0740	94	0·8122	1·2312
45	0·9435	1·0599	95	0·8164	1·2249	45	0·9291	1·0763	95	0·8094	1·2555
46	0·9417	1·0619	96	0·8125	1·2308	46	0·9269	1·0789	96	0·8065	1·2399
47	0·9399	1·0639	97	0·8084	1·2370	47	0·9249	1·0813	97	0·8036	1·2444
48	0·9381	1·0660	98	0·8047	1·2436	48	0·9227	1 0838	98	0·8006	1·2491
49	0·9362	1·0683	99	0·7995	1·2508	49	0·9204	1·0864	99	0·7976	1·2537
50	0·9343	1·0703	100	0·7946	1·2585	50	0·9183	1·0890	100	0·7946	1·2585

Excise is known as Sykes's hydrometer, Fig. 79. It is made of metal, and has a four-sided stem divided into ten equal parts, fitting into a brass ball, carrying a small conical stem, terminating in a pear-shaped loaded bulb. The instrument is also provided with nine circular weights numbered 10, 20, 30, 40, 50, 60, 70, 80, 90, each having a slit by which it can be fixed on to the stem. The instrument is so adjusted as to float with the zero of the scale coincident with the surface of the liquid when it is immersed in spirit having a specific gravity of 0·825 at 60°, this being the standard alcohol of the Excise. If the alcoholometer be placed in weaker spirit than this, it will need to be weighted, in order to bring the zero point to the level of the liquid; and the sum of weights, together with the number on the scale at the level of the spirit, give by reference to a table the quantity of proof spirit contained in the sample.

FIG. 79.

As the alteration of volume effected in spirit by the variation of a few degrees of temperature is considerable, the reading on the hydrometer will only be correct at the normal temperature. As, however, this point is difficult to attain, Gilpin determined the specific gravity of aqueous spirit of different strengths at different temperatures. All these tables were recalculated by Tralles, and have since his time been corrected by the investigations of Brix,[1] von Kupffer,[2] and others.[3]

By the help of these results, a table of corrections is obtained, by means of which the true percentage of alcohol contained in any spirit at any given temperature may be ascertained from its apparent percentage as read off on the hydrometer (*see* Tables pp. 306-7).

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[1] *Das Alkoholometer*, &c., Berlin, 1864.

[2] *Handb. Alkoholometrie*, Berlin, 1865.

[3] See also Watts's Dictionary, vol. i. article "Alcoholometry."

Tables for Calculating the Real Strength of Alcohol by the Apparent Strength observed with a glass Alcoholometer.

Percentage of Volume (c/o).

Add the number in the upper horizontal line, which represents the observed apparent strength, to the number in the vertical column, which corresponds to the observed temperature, to the latter. N.B. At temperatures above 12$\frac{4}{9}$° R. (or 60° Fahr.) the numbers to be added are negative; their absolute value is therefore to be subtracted.

Percentage of Volume of Apparent Strength.

Temp R	18	20	22	24	26	28	30	32	34	36	38	40	42	44	46	48	50	52	54	56	58	60
—20	—	—	—	—	—	—		17,2	16,8	16,2	15,9	15,7	15,2	14,8	14,4	14,1	13,8	13,6	13,4	13,2	13,0	12,8
18	—	—	—	—	—	—	16,3	15,9	15,7	15,1	14,8	14,6	14,3	13,9	13,5	13,3	13,0	12,8	12,6	12,4	12,2	12,0
16	—	—	—	—	—	14,7	15,1	14,7	14,5	14,1	13,9	13,7	13,4	13,0	12,7	12,4	2,2	11,9	11,8	11,6	11,4	11,3
14	—	—	—	—	13,3	13,7	14,1	13,7	13,5	13,1	12,9	12,7	12,4	12,1	11,8	11,6	1,3	11,1	11,0	10,9	10,7	10,6
12	—	—	—	11,7	12,3	12,6	13,0	12,7	12,5	12,2	12,0	11,7	11,5	11,2	11,0	10,7	0,5	10,3	10,2	10,1	9,9	9,8
10	—	—	9,9	10,8	11,3	11,6	11,9	11,7	11,5	11,2	11,0	10,8	10,6	10,3	10,1	9,9	9,7	9,5	9,4	9,3	9,1	9,0
8	—	—	9,0	9,8	10,3	10,6	10,8	10,7	10,5	10,3	10,1	9,9	9,7	9,5	9,3	9,1	8,9	8,7	8,6	8,5	8,4	8,3
6	—	—	8,1	8,8	9,2	9,5	9,7	9,7	9,5	9,3	9,2	9,0	8,8	8,6	8,5	8,3	8,1	7,9	7,8	7,7	7,6	7,5
4	—	—	7,2	7,8	8,2	8,5	8,6	8,7	8,5	8,4	8,2	8,1	7,9	7,8	7,6	7,4	7,3	7,1	7,0	6,9	6,8	6,7
2	—	—	6,2	6,8	7,2	7,5	7,5	7,6	7,5	7,4	7,3	7,1	7,0	6,9	6,7	6,6	6,5	6,4	6,2	6,1	6,1	6,0
0	3,9	4,6	5,4	6,1	6,3	6,5	6,5	6,5	6,5	6,3	6,2	6,1	6,0	5,9	5,8	5,7	5,6	5,5	5,4	5,4	5,3	5,2
+ 2	3,3	3,9	4,4	4,9	5,2	5,3	5,4	5,4	5,4	5,3	5,2	5,1	5,0	5,0	4,9	4,8	4,7	4,6	4,6	4,5	4,5	4,4
4	2,7	3,1	3,5	3,8	4,1	4,2	4,3	4,4	4,3	4,3	4,2	4,1	4,1	4,0	4,0	3,9	3,8	3,8	3,7	3,6	3,6	3,6
6	2,1	2,4	2,7	2,9	3,2	3,3	3,3	3,3	3,2	3,2	3,2	3,1	3,1	3,1	3,0	3,0	2,9	2,9	2,9	2,8	2,8	2,8
8	1,5	1,7	1,9	2,1	2,2	2,3	2,3	2,3	2,3	2,2	2,2	2,2	2,1	2,1	2,1	2,1	2,1	2,0	2,0	1,9	1,9	1,9
10	0,9	0,9	1,0	1,0	1,1	1,3	1,3	1,3	1,3	1,2	1,2	1,1	1,2	1,2	1,2	1,1	1,1	1,1	1,1	1,1	1,1	1,1
12	0,1	0,1	0,2	0,2	0,2	0,2	0,2	0,2	0,2	0,2	0,2	0,2	0,2	0,2	0,2	0,2	0,2	0,2	0,2	0,2	0,2	0,2
13	—0,2	—0,2	—0,2	—0,2	—0,2	—0,3	—0,3	—0,3	—0,3	—0,3	—0,3	—0,3	—0,3	—0,3	—0,3	—0,3	—0,3	—0,2	—0,2	—0,2	—0,2	—0,2
15	0,8	0,9	1,0	1,0	1,1	1,1	1,2	1,3	1,3	1,4	1,3	1,2	1,3	1,3	1,3	1,2	1,2	1,1	1,1	1,1	1,1	1,1
17	1,6	1,7	1,9	1,9	2,0	2,1	2,2	2,3	2,3	2,3	2,3	2,3	2,3	2,2	2,2	2,1	2,1	2,1	2,0	2,0	2,0	2,0
19	2,2	2,5	2,7	2,8	3,0	3,1	3,2	3,3	3,3	3,3	3,3	3,3	3,3	3,2	3,2	3,1	3,1	3,0	2,9	2,9	2,9	2,9
21	—	—	3,4	3,7	3,9	4,1	4,2	4,3	4,3	4,3	4,3	4,3	4,2	4,2	4,1	4,1	4,0	3,9	3,8	3,8	3,8	3,7
23	—	—	4,2	4,5	4,8	5,0	5,2	5,3	5,4	5,4	5,4	5,3	5,3	5,2	5,1	5,1	5,0	4,9	4,9	4,8	4,7	4,6
25	—	—	5,0	5,4	5,7	5,9	6,1	6,3	6,3	6,4	6,4	6,3	6,3	6,2	6,1	6,0	6,0	5,9	5,8	5,8	5,7	5,6

Percentage of Volume of Apparent Strength.

Temp. R.	62	64	66	68	70	72	74	76	78	80	82	84	86	88	90	92	94	96	98	100
—20°	12,6	12,4	12,2	12,1	11,8	11,6	11,0	11,3	10,9	10,6	10,3	10,0	—	—	—	—	—	—	—	—
18	11,9	11,7	11,5	11,4	11,1	10,9	10,6	10,4	10,3	10,0	9,7	9,4	8,8	—	—	—	—	—	—	—
16	11,1	10,9	10,8	10,7	10,4	10,2	10,0	9,7	9,6	9,4	9,1	8,8	8,3	—	—	—	—	—	—	—
14	10,4	10,2	10,0	9,9	9,7	9,6	9,3	9,1	9,0	8,7	8,5	8,2	7,7	—	—	—	—	—	—	—
12	9,6	9,4	9,3	9,2	9,0	8,9	8,7	8,4	8,3	8,1	7,9	7,6	7,2	6,8	—	—	—	—	—	—
10	8,9	8,7	8,6	8,5	8,3	8,2	8,0	7,8	7,7	7,5	7,3	7,0	6,7	6,3	6,0	5,7	5,3	—	—	—
8	8,1	8,0	7,9	7,8	7,7	7,5	7,4	7,2	7,0	6,9	6,7	6,5	6,2	5,9	5,5	5,2	4,9	—	—	—
6	7,4	7,3	7,2	7,1	7,0	6,8	6,7	6,6	6,4	6,3	6,1	6,0	5,7	5,4	5,1	4,8	4,4	—	—	—
4	6,6	6,5	6,5	6,4	6,3	6,2	6,1	5,9	5,8	5,7	5,6	5,4	5,2	4,9	4,6	4,3	4,0	3,7	—	—
2	5,9	5,8	5,7	5,6	5,6	5,5	5,4	5,3	5,1	5,0	4,9	4,7	4,6	4,4	4,2	3,9	3,6	3,3	—	—
0	5,2	5,1	5,0	4,9	4,8	4,8	4,7	4,6	4,5	4,4	4,3	4,2	4,1	3,9	3,7	3,5	3,2	3,0	—	—
+ 2	4,4	4,3	4,2	4,2	4,1	4,0	4,0	4,0	3,9	3,8	3,7	3,5	3,4	3,3	3,1	3,0	2,8	2,5	—	—
4	3,6	3,5	3,4	3,4	3,4	3,3	3,3	3,2	3,2	3,1	3,0	2,9	2,8	2,7	2,6	2,4	2,3	2,1	1,9	—
6	2,7	2,7	2,6	2,6	2,6	2,5	2,5	2,4	2,4	2,4	2,3	2,2	2,1	2,0	2,0	1,9	1,8	1,6	1,5	—
8	1,9	1,9	1,8	1,8	1,8	1,7	1,7	1,6	1,6	1,6	1,5	1,5	1,5	1,4	1,4	1,3	1,3	1,1	1,0	-
10	1,1	1,1	1,0	1,0	1,0	0,9	0,9	0,9	0,9	0,9	0,8	0,8	0,8	0,8	0,8	0,7	0,7	0,6	0,6	—
12	0,2	0,2	0,2	0,2	0,2	0,2	0,2	0,2	0,2	0,2	0,2	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	—
13	—0,2	—0,2	—0,2	—0,2	—0,2	—0,2	—0,2	—0,2	—0,2	—0,2	—0,2	—0,2	—0,2	—0,2	—0,2	—0,2	—0,2	—0,2	—0,1	—0,1
15	1,0	1,0	1,0	1,0	1,0	0,9	0,9	0,9	0,9	0,9	0,9	0,9	0,8	0,8	0,8	0,8	0,8	0,8	0,6	0,5
17	1,9	1,9	1,9	1,8	1,8	1,7	1,7	1,7	1,7	1,7	1,7	1,6	1,6	1,5	1,5	1,4	1,4	1,3	1,2	1,0
19	2,9	2,8	2,7	2,6	2,6	2,6	2,6	2,6	2,5	2,5	2,4	2,3	2,3	2,2	2,1	2,0	1,9	1,9	1,7	1,4
21	3,7	3,7	3,6	3,5	3,4	3,4	3,4	3,3	3,3	3,2	3,1	3,0	3,0	2,9	2,8	2,6	2,5	2,4	2,2	1,9
23	4,6	4,6	4,5	4,4	4,3	4,3	4,3	4,2	4,1	4,0	4,0	3,9	3,8	3,6	3,5	3,3	3,2	3,0	2,8	2,4
25	5,6	5,5	5,5	5,4	5,3	5,2	5,1	5,0	5,0	4,9	4,8	4,7	4,5	4,4	4,2	4,1	3,9	3,6	3,4	2,9

206 *Determination of Alcohol in Beers and Wines.*—The percentage of alcohol contained in liquids such as beer, wine, &c., in which other materials besides water and alcohol are present in solution, cannot be directly ascertained by the use of the hydrometer. In such cases the simplest plan is to take a measured volume of the liquid and to prepare pure aqueous alcohol from this by distillation, and then to determine its volume and specific gravity. For the purpose of making such estimations, which often require to be quickly and accurately carried out, an apparatus has been devised by Descroizelles, which was afterwards improved by Gay-Lussac, and others. Savalle uses an apparatus, the construction of which depends upon the same principle as the rectification of spirit and is shown in Fig. 80. The liquid to be examined, several liters of which should be used, is brought into the still, *a*, and heated with gas to the boiling point. The vapour passes through the tube *b*, to the worm *c*, cooled by the water *d*. When the water in *c* becomes warm, the vapours condense in the cooler, and the distillate is collected in the cylinder *e*. For liquids which do not contain more than 16 per cent. of alcohol it is only necessary to distil off one-third; if they contain more, a larger amount must be driven off. In this way 5 liters of wine give 751 cbc. of a distillate containing 56·99 per cent. and hence the wine contains $\frac{56 \cdot 99 \times 751}{5,000} = 8 \cdot 56$ per cent. By means of this apparatus the amount of spirit in weak alcohols can be ascertained even when they contain as little as 0·01 per cent.

If only a small quantity of liquid be at disposal, Gay-Lussac's wine-tester as modified by Mohr may be employed, and by means of this instrument the quantity of alcohol in so small a volume of liquid as ten cbc. may be determined with tolerable accuracy. For this purpose 10 cbc. or a larger volume, is measured out in a pipette, and brought into the flask, Fig. 81, an equal volume of water added, and the whole distilled over into a small wide flask upon the neck of which a mark is made, indicating exactly the same volume of distillate as that of the original wine or beer. In order to prevent the liquid from bumping it is advisable to add a small quantity of tannic acid, and to distil the liquid until the distillate comes nearly up to the mark. The distillate is then cooled to the normal temperature, and water added to fill up to the mark, and the whole again weighed. The weight in grams divided by the number of cubic centimeters gives the specific gravity. Another arrangement for distilling wines is shown in Fig. 82.

207 The ebullioscope is an instrument by means of which the amount of alcohol in a liquid can be determined by ascertaining its boiling point, as this is higher the less alcohol is contained in it. Various kinds of instruments of this sort have been made. Fig. 83 shows the construction of Pohl's ebullioscope.

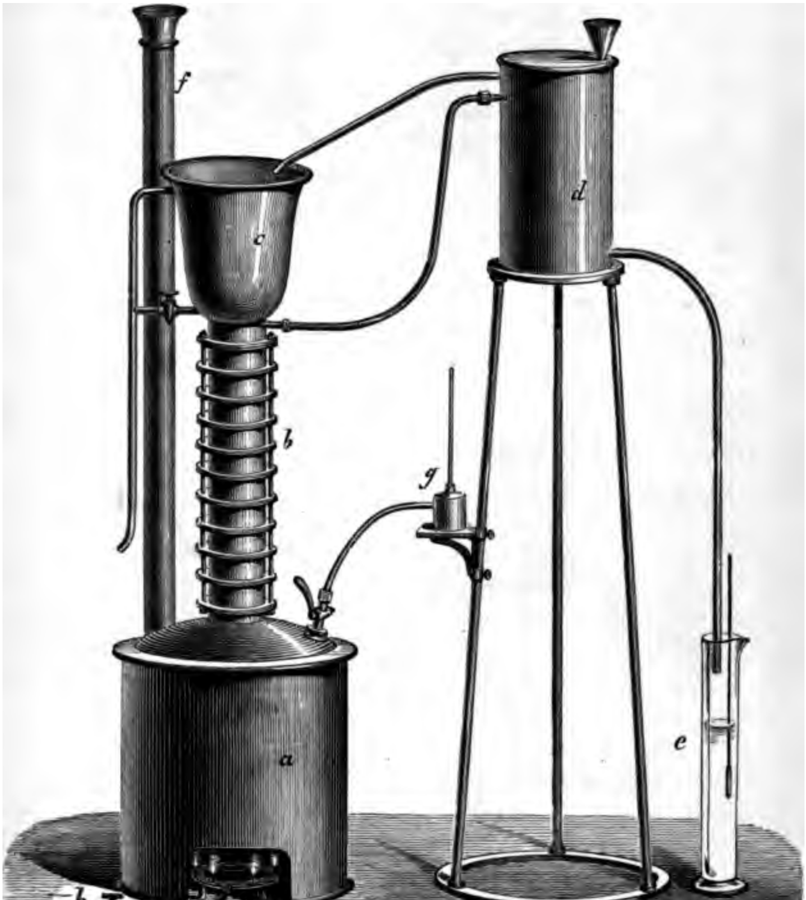

Fig. 80.

Usually the thermometer has an empirical division from which the percentage amount can be directly read off. According to Griessmayer[1] the ebullioscope of Malligand[2] is the best for the

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[1] Dingler, *Polyt. Journ.* ccxviii. 262.

[2] *Compt. Rend.* lxxx..1114.

FIG. 81.

FIG. 82.

determination of the amount of alcohol contained in beer and wine, inasmuch as the process is much simpler and quicker than by the method of distillation. For over-proof spirit this method is, however, perfectly useless, because the difference in boiling-point becomes very slight for a considerable difference in the percentage of alcohol.

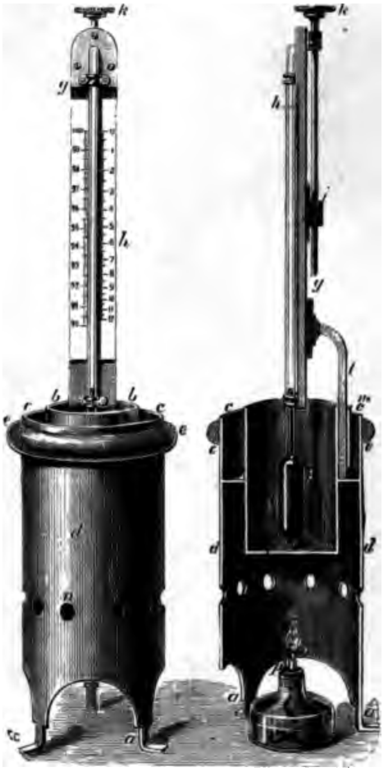

FIG. 83.

Fig. 84 shows Crockford's patent spirit indicator, as described in Thudicum and Dupré's treatise on wines. A small condenser is fixed on the top of the boiler to prevent loss of alcohol during boiling.

208 Another instrument designed with the same object depends upon the determination of the tension of aqueous alcohol at 100° as determined by Plücker.[1] The instrument, shown in

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[1] *Pogg. Ann.* xcii. 193.

Fig. 85, has been made by the well-known glass-blower Geissler,[1] and termed by him the *vaporimeter*. The tube (o) Fig. 85 first contains mercury up to the mark, and then is filled completely with the beer or wine to be examined. It is then

FIG. 84.

fastened into the ground neck of a syphon barometer tube (B), this being placed in a vertical position, and then exposed to the action of steam coming from boiling water, when the liquid evolves a large quantity of vapour and the mercury in the tube is driven up to a certain height

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[1] *Polyt. Centralb.* 1834, 1438.

according to the amount of alcohol contained in the liquid. An empirical scale is placed on the barometer tube by

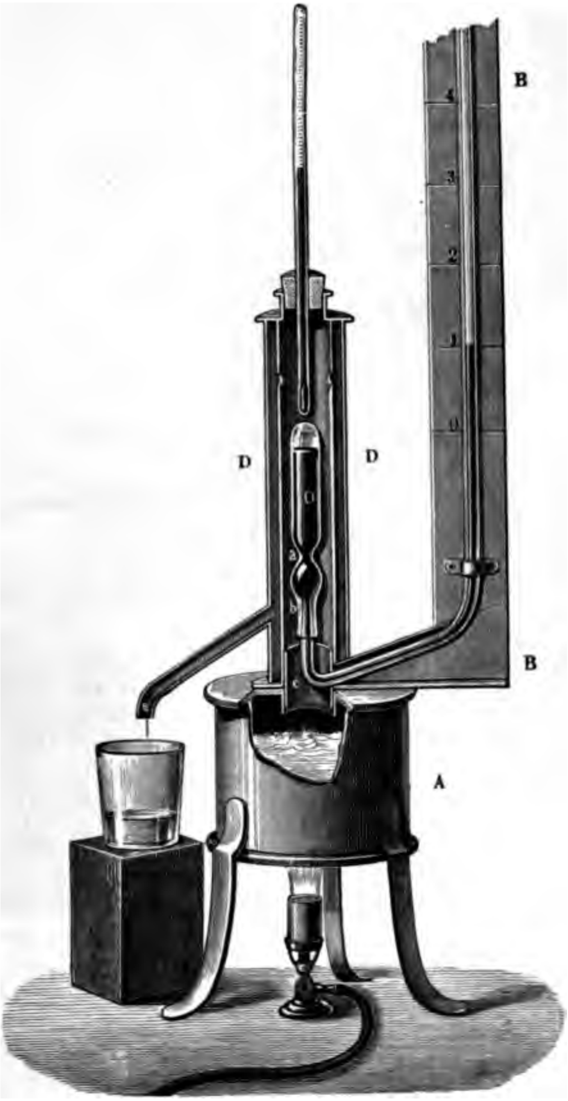

FIG. 85.

means of which the percentage of alcohol can be read off. Should the liquid under examination contain carbon dioxide, this gas must, of course, be removed before the operation, and this is best effected by shaking it with freshly burnt lime. If the solution contain a large quantity of dissolved matter, the results are usually inexact, and, in this case, a given volume of the liquid is distilled off and this treated as above described.

Alcohol expands on warming much more rapidly than water; and founded upon this property Silbermann[1] has described an instrument termed a *dilatometer* (Fig. 86). This consists of a thermometer tube having a scale etched upon it, into which a certain volume of the liquid is brought at 25°, and the expansion observed which this undergoes in heating to 50°.

Many other methods are employed for determining the strength of alcoholic liquids. For a description of these we must refer to the undermentioned works.[2]

FIG. 86.

209 The following table gives the percentage of alcohol contained in various wines and other fermented liquors:

Port (old bottled)	20·2
,, (newly bottled)	17·4
Montilla sherry (1854	16·3
Fine Marsala	17·0
Madeira	16·1
Beaune	13·5
Oberingelheimer	9·4
Assmannshäuser	9·1
Château-Lafitte	8·7
Ordinary Bordeaux	6·4 to 8·7
Johannisberger (1842)	8·1
Rüdesheimer	9·2
Auerbacher	8·4
Burton Ale	5·9
Edinburgh Ale	5·7 to 6·1
London Porter	5·4 to 6·9
Munich Lagerbier	5·1
Schenkbier	3·8
Berlin Weissbier	1·8 to 2·0.

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[1] *Compt. Rend.* xxvii. 418.

[2] *Neu. Handwörterb. Chem.* i. 267; Stammer, *Branntweinbrennerei*, 9.

The value of a wine does not, as is well known, depend upon its percentage of alcohol. Thus, the price of Château Lafitte containing only 8·7 per cent. is much higher than any ordinary port containing about 20 per cent. So, too, the percentage of sugar and of acids contained in the wine may be almost identical in the case of different wines of the same class, as for instance, in clarets, but the value of these various clarets may be very different. On the other hand, it appears that the total amount of solid constituents contained in a pure wine bears a very distinct relation to its value, which is also of course greatly determined by its bouquet.

In order to show the presence of alcohol in beer or wine the liquid may be boiled in a flask having a tube 1½ m. long and 1 cm. wide fastened to it, and which serves as a rectifying column so that the alcohol vapour becomes so concentrated that it may be lighted at the end of the tube.[1]

When pure alcohol is taken in small quantities in the form of good beer or pure wine it appears to improve the digestion by an increase of the secretion of the gastric juice. Especially for old persons and those having weak digestions it is useful, and indeed wine and spirits are frequently termed the milk of old age. In large doses however it acts as a powerful poison.

After the imbibition of alcohol small quantities of this substance are found in the urine.[2]

The feeling of warmth experienced after indulgence in alcohol is a subjective phenomenon, as the temperature of the body sinks under such circumstances from 0°·5 to 2°·0, according to the quantity of alcohol taken.[3] If alcohol be taken during a meal no such diminution of temperature is observed.[4]

The higher homologues of ethyl alcohol exert a still more distinct physiological action than common alcohol does, and to these is especially to be ascribed the evil effects which ensue from an indulgence in common brandy.[5] Manufactured wine also produces, even when taken in small quantity, headache and unpleasant symptoms, whilst pure wine does not produce these effects unless it is taken in excess. Wine is manufactured

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[1] Tollens, *Ber. Deutsch. Chem. Ges.* ix. 1540.

[2] Lieben, *Ann. Chem. Pharm.* Suppl. vii. 236; Dupré, *Proc. Roy. Soc.* xx. 268.

[3] Binz. *Ber. Deutsch. Chem. Ges.* v. 1082.

[4] Parkes, *Proc. Roy. Soc.* xxii. 172.

[5] Dujardin-Beaumetz and Audigé, *Compt. Rend.* lxxxi. 152.

by Gall's process by the addition of starch sugar before fermentation to a grape-must poor in sugar. The starch sugar is obtained from potato-starch, and is. however, not pure, but leaves behind a quantity of unfermentable residue, which, as experiments with dogs have shown, acts in a similarly poisonous manner to potato fusel oil.[1]

210 *Uses of Alcohol in the Arts.*—Pure as well as impure spirit of wine is used for a great variety of purposes. In the first place, strong alcohol is largely employed as a fuel, as it readily burns with a non-luminous and smokeless flame. Before Bunsen invented his well-known gas-lamp, spirit-lamps were in general use in almost all laboratories.

In the second place, it is largely employed both in the arts and in scientific investigations as a solvent, and as a means of separating one substance from another. This depends on the fact that many bodies which are insoluble or difficultly soluble in water, dissolve in alcohol, and, on the other hand, that many substances readily soluble in water do not dissolve in this menstruum. Thus, for example, the carbonates and sulphates of the metals are insoluble in alcohol; whilst some chlorides, bromides, and iodides readily dissolve, others again not possessing this property. Raymond Lully observed long ago that this substance creates a turbidity in a solution of ammonium carbonate: "Hic etiam spiritus (animalis) habet proprietatem congelandi spiritus vegetabilis vel aquam vitæ perfecte rectificatum. Nam eam in salem convertit, qui plurimas proprietates et virtutes excellentissimas habet." Boyle showed in 1675 that strong alcohol precipitates a saturated solution of common salt, and Boulduc in 1726 employed alcohol for the separation of salts in mineral-water analysis. In 1762 Macquer determined more exactly the solubility of many salts in alcohol, and Lavoisier, as well as Bergmann, used this solvent in their analytical researches. At the present day its employment in analysis is somewhat restricted. It is, however, used in qualitative analysis for the separation of strontium chloride from barium chloride, and in quantitative analysis for washing precipitates which are slightly soluble in water, such as lead sulphate, lead chloride, potassium platinichloride, ammonium platinum chloride, &c.

Spirit of wine is likewise employed in the laboratory for the purification of commercial caustic potash which dissolves in it,

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[1] Schmidt, *Biederm. Centralbl.* 1879, 712.

leaving a residue of carbonate, sulphate, alumina, &c. Amongst the solid and liquid elements, phosphorus and sulphur dissolve slightly in alcohol, and iodine and bromine to a much larger extent.

Some gases are absorbed by alcohol even in larger quantity than by water. In this respect the hydrocarbons are especially distinguished. The coefficients of absorption of the different gases in alcohol have been determined by Carius.[1]

Alcohol is used as a solvent especially for ethereal oils, resins, alkaloids, and many other carbon compounds which are insoluble or difficultly soluble in water. For this reason it is employed in the preparation and purification of such compounds, and it is also used for the manufacture of tinctures, essences, liqueurs, perfumes, colours of various kinds, varnishes, lacs, polishes, &c.

Methylated Spirit.—For most of the above purposes methylated spirit is employed instead of pure alcohol. In this country a heavy excise duty on spirit of wine has always existed, and the manufacture and sale of this article is placed under strict supervision. Hence many branches of manufacturing industry, as well as the investigations of the scientific chemist, were, in this country, much impeded, until in 1856 the late Mr. John Wood, Chairman of the Board of Inland Revenue, obtained Government permission for the manufacture of *methylated spirit* which is sold by licensed dealers free of duty. This substance is a mixture of 90 per cent. of spirit of wine of density not less than 0·830 sp. gr., and 10 per cent. of purified wood-spirit. Such a mixture is unfit for human consumption, and the wood-spirit cannot again be separated from the spirit of wine by any commercial process.

Methylated spirit is largely used instead of pure spirit in the manufacture of the aniline colours as well as of ether, chloroform, fulminating mercury, iodide of ethyl, olefiant gas, and a number of other substances. The same mixture is used for the preservation of anatomical preparations, and of small animals and other zoological specimens.

The possibility of thus obtaining cheap alcohol has moreover beneficially influenced the recent progress of organic chemistry in this country.[2]

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[1] *Ann. Chem. Pharm.* xciv. 129.

[2] "Report to the Chairman of Inland Revenue on the Supply of Sprit free from Duty," by Professors Graham, Hofmann, and Redwood, *Quart. Journ. Chem. Soc.* viii. 120 (1856).

211 *Detection of Alcohol.*—In order to detect small quantities of alcohol in an aqueous liquid, it is gently warmed, a few crystals of iodine added, and then so much caustic potash that the solution just becomes colourless, when, either at once or after a short time, a bright yellow precipitate of iodoform is thrown down. In this way one part of alcohol may be detected in 2,000 parts of water, but in the case of such dilutions the liquid must be allowed to stand for a night in order to allow the precipitate to subside. The deposit consists of microscopic six-sided tablets or six-sided stellar groups.[1]

Alcohol may be detected in presence of ether, chloroform, &c., by withdrawing it from such liquids by shaking with water, and then acting on the aqueous extract as above described. It must, however, not be forgotten that several other substances yield iodoform by the same reaction.

Another good reagent for alcohol is benzoyl chloride. If a few drops of this be added to dilute alcohol and the mixture gently warmed, ethyl benzoate is formed. As, however, the chloride is only slightly decomposed by water, it is better to add caustic potash when the characteristic smell of the ether is rendered evident. By means of this reaction 0·1 per cent. of alcohol may be detected.[2] It must, however, be remembered that other alcohols treated in the same way yield ethers possessing a similar smell.

If large quantities of an aqueous liquid have to be examined for alcohol, it is, of course, best to fractionate the liquid, the first portions coming over being collected and concentrated, until, on addition of potassium carbonate, a layer of light liquid separates out, which then can be further examined (Lieben).

In order to detect the presence of fusel oil in spirits of wine, the simplest plan is to pour a few drops on to the hand and rub the palms together, when evaporation takes place, and the more difficultly volatile fusel oil remains on the skin and can readily be detected by its unpleasant smell. A more reliable process, however, is to allow the liquid gradually to evaporate in an open glass dish, and then to notice the smell of the residue. As fusel oil consists chiefly of higher homologues, the spirit under examination may be oxidized by the action of a solution of potassium dichromate in dilute sulphuric acid, when acetic acid is mainly produced, together, however, with its

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[1] Lieben, *Ann. Chem. Pharm. Suppl.* vii. 218, 377.

[2] Berthelot, *Compt. Rend.* lxxiii. 496.

homologues, if fusel oil be present. These latter, in contradistinction to acetic acid, distil over first with the aqueous vapour, and from the smell of the first portions of the distillate it is often possible to detect the presence of the higher homologues of acetic acid. A more certain plan is to saturate the acid distillate with baryta-water, and to determine the quantity of baryta contained in the salts produced.[1]

It sometimes happens in this country that the unpleasant smell of the methylated spirit is partially removed by means of acids or oxidizing agents, and that the spirit thus obtained, though still containing methyl-alcohol, is sufficiently tasteless to be used for adulterating the commoner kinds of whisky and other alcoholic liquors. According to Dupré such an adulteration may be detected by Geissler's vaporimeter, as the tension of methyl alcohol is much higher than that of spirits of wine. Its presence may also be ascertained by oxidizing the spirit as above described; in presence of methyl alcohol an evolution of carbon dioxide is, under these circumstances, observed.

Methyl alcohol, as well as its various derivatives, are largely used (as has been already stated) for the preparation of aniline colours. The wood-spirit used for this purpose must, however, not contain any ethyl alcohol, as the presence of this substance greatly influences the shades of the colours produced. In order to detect its presence the alcohol is treated with permanganic acid, which oxidizes the methyl alcohol to carbonic acid and the ethyl alcohol to aldehyde. The mixture is then distilled, and a solution of rosaniline, rendered acid by sulphuric acid, added to the distillate. If the methyl alcohol be pure this will remain yellow, but in the presence of aldehyde it becomes violet or blue coloured.[2] The alcohol to be tested may also be heated with double its volume of concentrated sulphuric acid, whereby the methyl alcohol is converted into methyl ether, and this is readily soluble in water and concentrated sulphuric acid, whilst ethyl alcohol is almost entirely resolved into olefiant gas, which is only slightly soluble in water and dissolves but slowly in sulphuric acid, and is easily recognised, and its quantity ascertained by its reaction with bromine. The other bodies usually present in common wood-spirit do not yield any ethylene, and in this way 1 per cent. of alcohol may be readily detected.[3]

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[1] Dupré, *Pharm. Journ. Trans.* (3) vi. 867.

[2] Riche and Bardy, *Compt. Rend.* lxxxii. 768.

[3] Berthelot, *Compt. Rend.* lxxx. 1039.

212 *Decompositions of Alcohol.*—Alcohol serves as a point of departure for all other ethyl compounds. These can be obtained from it by various reactions, and hence the action of chemical agents on alcohol has been most carefully examined. In some of these, the radical ethyl remains unchanged, whilst in other reactions, however, the radical undergoes alteration. Thus, for example, by a moderate oxidation, aldehyde, C_2H_4O, and acetic acid, $C_2H_4O_2$, are formed. This change can also be brought about by the oxygen of the air, but not immediately, for concentrated as well as dilute spirit of wine are not attacked at the ordinary temperature by oxygen. If, however, platinum-black be mixed with alcohol, or if this powder be placed on paper and moistened with alcohol, oxidation takes place, accompanied by an evolution of heat and followed by ignition of the alcohol. Addition of water diminishes the intensity of this action. Upon this observation of Edmund Davy's, Döbereiner founded his vinegar-lamp. This consists of a flask filled with alcohol, in the neck of which is placed a glass funnel, upon which slightly moistened platinum-black is spread, whilst a piece of cotton wick brings the alcohol into contact with this powder. The flask or bottle stands on a dish, over which a glass bell-jar is so placed that a small amount of air is allowed to enter. In this way the alcohol undergoes oxidation, the vapour of acetic acid being formed, and this gradually collects on the inside of the bell-jar. According to Döbereiner, platinum-black used in this way is an excellent means of detecting small traces of alcohol. If a drop of alcohol be allowed to evaporate in 50 or 60 cbc. of air and a small quantity of platinum-black put into this, the formation of acetic acid can be readily noticed.[1]

When strongly heated platinum wire or platinum foil is brought into a mixture of air and alcohol vapour, the metal gradually becomes heated to redness (Vol. II. Part II. p. 397).

Whilst pure alcohol does not undergo spontaneous oxidation on exposure to air, beer or wine soon becomes sour with formation of acetic acid. This depends on the presence of nitrogenous bodies, which act as carriers of oxygen from the air to the alcohol.

Oxidizing bodies, according to their nature and the mode in which they act, convert alcohol into other products in addition to alcohol and acetic acid. Thus, for example, if strong nitric

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[1] Gmelin's *Handbook*, viii. 207.

acid be added to alcohol, an explosive action takes place, and, in addition to the oxides of nitrogen and the above-named compounds, we find amongst the products ethyl nitrate, formic acid, oxalic acid, hydrocyanic acid, &c. A more moderate action yields chiefly glycollic acid, and aldehydes of oxalic acid.

A mixture of dilute sulphuric acid and manganese dioxide, as well as a solution of chromium trioxide, yield acetal, $C_2H_4(OC_2H_5)_2$, together with aldehyde and acetic acid. If, however, strong alcohol be dropped on to dry chromium trioxide, ignition and complete combustion take place.

Alcohol is also readily acted upon by chlorine and bromine, oxidation-products being first formed and then substitution-products being produced, the description of which will be found later on.

Alcohol vapour may be heated to 300° without decomposition occurring. At a red-heat, however, dry distillation commences, hydrogen, marsh gas, ethylene, acetylene, benzene, naphthalene, carbon monoxide, aldehyde, acetic acid, phenol, &c., being produced (Berthelot).

THE ALCOHOLATES.

213 This name was given by Graham to compounds discovered by him in 1828,[1] and formed by the combination of anhydrous salts with alcohol, the latter substance playing the part of water of crystallization. Other chemists have increased our knowledge of these compounds,[2] and from these investigations it appears that only those salts form alcoholates which are easily soluble in water, and which usually contain water of crystallization. The following are some of the more important of these :

$LiCl + 4C_2H_6O$, is formed with evolution of heat when lithium chloride is brought into contact with absolute alcohol. It crystallizes on cooling in nacreous glistening prisms.

$CaCl_2+4C_2H_6O$, is produced in the same way as the foregoing compound, and forms a white crystalline mass.

$MgCl_2+6C_2H_6O$ corresponds closely to the lithium compound and is very deliquescent.

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[1] *Phil. Mag* iv. 265, 331.

[2] Chodnew, *Ann. Chem. Pharm.* lxxi. 241 ; Levy, *Ann. Chim. Phys.* [3], xvi. 309 ; Robiquet, *Journ. de Pharm.* [3], xxvi. 161 ; de Luynes, *Journ. Pr. Chem.* lxxx. 503 ; Bauer, *ib.* lxxx. 361 ; Simon, *ib.* [2]. xx. 371.

$Mg(NO_3)_2 + 6C_2H_6O$ forms a pearly crystalline mass.

In addition to these, many other chlorides and nitrates, as well as certain bromides, form alcoholates.

ETHYLATES.

214 These compounds are formed from alcohol by the replacement of the hydrogen of the hydroxyl by metals, and this may be accomplished in a variety of ways. The ethylates are readily decomposed by water with formation of alcohol and the corresponding hydroxide.

Potassium Ethylate, C_2H_5OK. Potassium dissolves in absolute alcohol with evolution of heat and liberation of hydrogen. Transparent colourless crystals separate out on cooling the concentrated solution, and these contain alcohol of crystallization.

Sodium Ethylate, C_2H_5ONa, is obtained in a similar way,[1] and forms a mass consisting of transparent needles, which have the composition $C_2H_5ONa + 2C_2H_6O$. The alcohol of crystallization is easily lost in a vacuum over sulphuric acid. Wanklyn obtained crystals of the formula $C_2H_5ONa + 3C_2H_6O$, melting at 100° without losing their alcohol of crystallization, which, however, escapes at a higher temperature, and is completely driven off on heating to 200°. The compound, free from alcohol, is a light amorphous powder, which, when prepared in absence of air, is perfectly white, and may be heated to 290° without any decomposition taking place.[2]

Thallium Ethylate, C_2H_5OTl, is formed by the action of alcohol vapour on finely divided thallium. It is a colourless liquid having a specific gravity of 3·55, and possessing a refracting power as strong as that of carbon disulphide. It solidifies at -3°, and is easily inflammable, burning with a bright green flame.[3]

Barium Ethylate, $(C_2H_5O)_2Ba$, is formed by dissolving anhydrous baryta in absolute alcohol and boiling, when a precipitate is thrown down. This must be dried at 100° in a current of hydrogen, and is difficult to obtain in the pure state.[4]

Zinc Ethylate, $(C_2H_5O)_2Zn$, is a white amorphous mass formed by the slow oxidation of zinc ethide.

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[1] Guerin Varry, *Journ. Science Phys.* iii. 273.

[2] Wanklyn, *Phil. Mag.* [4], xxxvii. 117.

[3] Lamy, *Compt. Rend.* lxv. 836; lix. 780.

[4] Berthelot, *Bull. Soc. Chim.* [2], viii. 389.

Aluminium Ethylate, $(C_2H_5O)_6Al_2$. This is formed by the action of iodine and fine aluminium foil on alcohol, hydrogen being given off, whilst the compound $(C_2H_5O)_3Al_2I_3$ is also formed in small quantities; when the whole is heated to 270°, the latter compound decomposes into ethyl iodide and alumina. If the residue be distilled in a vacuum, or under diminished pressure, aluminium ethylate passes over, solidifying to a yellowish white mass, melting at 115°, and boiling at the same temperature as mercury.[1] It is somewhat soluble in absolute alcohol, and is quickly decomposed by water.

ETHYL ETHER OR ETHYL OXIDE.

$(C_2H_5)_2O$.

215 Raymond Lully, as well as Basil Valentine, examined the action of sulphuric acid upon spirit of wine, and hence it is generally assumed that they were acquainted with ethyl oxide, or ether, as it is still generally termed. This is possible, for Basil Valentine speaks of a spirit obtained in this way which has a "subtle, penetrating, pleasant taste, and an agreeable smell."

We owe our special knowledge of the existence of ether to Valerius Cordus, a German physician, who died in Italy in 1544. His process for the preparation of this body was published by Conrad Gessner in 1552, and occurs in the later editions of the first German Pharmacopœia, this work, which was first published in 1535, having been re-edited by Cordus at the request of the Council of Nuremberg. According to this receipt, equal parts of thrice rectified spirit of wine and oil of vitriol are allowed to remain in contact for two months, and then the mixture is distilled from a water- or sand-bath. The distillate consists of two layers of liquid, of which the upper one is the *oleum vitrioli dulce verum.*

Various chemists mention this body, but at the beginning of the eighteenth century the details of its preparation appear to have been almost entirely lost, although, at this period, a mixture of spirit of wine and ether was used in medicine; indeed it seems not improbable that Paracelsus employed such a mixture. It was, however, first brought into commerce by an

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[1] Gladstone, *Journ. Chem. Soc.* 1876, i. 158.

apothecary in Halle, under the name of *Panacea Vitrioli*, and afterwards having been recommended by Hoffmann, it received the name of *Liquor anodynus Hoffmanni*, or Hoffmann's drops. Under this name it soon became generally known, and even to the present time is thus designated in Germany. The preparation of this medicine was long kept secret, and the positive existence of ether was not proved until it was first prepared free from spirit of wine, and then it was found that it swims on the surface of water, and is not miscible with this liquid.

In 1730 Sigismund Augustus Frobenius published a memoir in the *Philosophical Transactions*,[1] entitled, "Of a *spiritus vini æthereus*," in which he describes, in general terms, the preparation of this compound, though without giving any details. He manufactured the ether in Godfrey Hanckewitz's laboratory, and as he sold it at a high price, he endeavoured to keep the process a secret one, and in forwarding some of the new substance to St. F. Geoffroy, he writes, after extolling its virtues, as follows: "Paratur ex sale volatili urinoso, plantarum phlogisto, aceto valde subtili, per summam fermentationem cunctis subtillissime resolutis et unitis." On the 18th November, 1731, he made experiments with ether and phosphorus before a meeting of the Royal Society, which are thus described by Dr. Mortimer, the secretary:[2] "He took a solution of phosphorus in the ethereal spirit of wine, which he called *Liquor luminosus*, and poured it into a tub of warm water, whereupon it gave a blue flame and smoke, attended with so small a degree of heat as not to burn the hand if put into it. He poured some of his ethereal spirit of wine upon a tub of cold water and set it on fire with the point of his dagger (which being first heated a little, he touched with it a piece of phosphorus lodged beforehand on the side of the tub). After the deflagration the water was cold."

In his second communication to the Society he described more fully his method for the preparation of ether; this description was, however, at his request not made public until after his death in 1741, when the following receipt was published by the secretary:[3]

"Take 4 lbs. in weight of the best oil of vitriol, and as much in weight (not measure) of the best alcohol, or the highest rectified spirit of wine.

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[1] xxxvi. 283, Feb. 19, 1729-30.

[2] *Phil. Trans.* Abstr. ix. 372.

[3] *Phil. Trans.* Abridg. ix. 380.

" 1. First, pour the alcohol into a chosen glass retort, then pour in, by little and little, ℥j of oil of vitriol; then shake the retort till the two liquors are thoroughly mixed, when the retort will begin to grow warm; then pour in more of the spirit of vitriol, and shake it again; then the retort will become very hot. Do not pour in the spirit of vitriol too fast, or too much at a time, lest the glass retort, by being heated too suddenly, should burst; you must allow about an hour's time for pouring in the spirit of vitriol, not pouring in above an ounce at a time, and always shaking the retort, till the whole quantity of the ponderous mineral spirit is intimately united with the light inflammable vinous spirit.

" 2. In the next place, examine with your hand the heat of the glass retort, and have a furnace ready, with the sand in the iron pot heated exactly to the same degree as acquired by the mixture of the two liquors; take out some of the sand, and, having placed your retort in the middle of the iron pot, put in the hot sand again round the retort, and apply a capacious receiver to it; set it into cold water, and wrap it over with double flannel dipped in cold water.

" Raise your fire gradually, that the drops may fall so fast that you may count five or six between each, and that, beside this quick discharge of the drops, the upper hemisphere of your receiver appear always filled with a white mist or fumes; continue this heat as long as they emit the scent of true marjoram. As soon as the smell changes to an acid, suffocating one, like that of brimstone, take out the fire and lift the retort out of the sand, and change the receiver, for all that arises afterwards is only a mere gas of brimstone, and of no use.

" If you do not use the greatest precaution, the liquor in the retort will run over; the fire must cease as soon as the ethereal spirits are gone over, for there remains behind an *oleum vini*, which is extracted by the force of the acid out of the spirit, which will arise, run over, and often cause explosions.

" The second day, when your glass is cold, infuse the remainder with half as much alcohol, and distil again as before, and you will have the same; the third day again with as much, and proceed as at first, it gives it again. Go on as long as you can obtain any (of the ethereal spirit) till all turns to a *carbo;* then separate it, and alcalize it with spirits of *salt armoniac* made without spirits of wine, till all effervescence ceases, and distil it once more *è Balneo Mariæ;* so is it ready for experiments."

This mode of making ether was soon pretty generally adopted; various German and French chemists having occupied themselves with the preparation of this body. Amongst the more complete descriptions of the substance may be mentioned Baumé's *Dissertation sur l'ether* (1757).

By reason of its easy inflammability it was also called at this time "naphtha," a name originally given to rock-oil, whilst at the same time it was termed vitriolic ether, sulphuric ether, or *ether sulphuricus*, and vitriol-naphtha, or *naphtha vitrioli*, inasmuch as it was obtained by the action of sulphuric acid on alcohol in much the same way as other similar volatile ethereal liquids are prepared by the action of other acids on alcohol.

In 1800 Valentin Rose[1] showed that the name sulphuric-ether is a misleading one, inasmuch as this substance does not contain any sulphur or sulphuric acid. Fourcroy[2] was the first to propound the idea that ether is formed from alcohol by the withdrawal of the elements of water; and he and Vauquelin[3] endeavoured to enforce this view by experiments, the results of which were confirmed in 1807 by Saussure's analysis of ether, and subsequently by Gay Lussac's analysis in 1815. It was then believed that the action of sulphuric acid upon alcohol could be simply explained by the fact that this acid removed from the alcohol either the elements of water, or water already present in the compound. Many facts, however, contradicted this view. Thus, as we have seen, Frobenius had observed that the residue in the manufacture of ether may again be employed for a further conversion of alcohol into ether, a fact which was confirmed by many other chemists, and especially by Cadet in 1774.

By the introduction of a simple process of manufacture the price of ether was considerably diminished, as is seen from a discussion between Beaumé and Cadet, in which the former criticised the new method of Cadet, and the latter stated that whilst Beaumé sold the compound at twelve livres per ounce, he charged only forty sous for the same quantity.

It is to Boullay[4] that we owe the discovery of the continuous process now universally employed for the manufacture of ether, depending on the fact that a small quantity of sulphuric acid

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[1] *Scherer, Journ.* iv. 253.

[2] *Elements d'Histoire Naturelle et de Chimie.*

[3] *Scherer, Journ.* vi. 432.

[4] *Journ. Pharm.* i. 97.

is sufficient to convert a large quantity of spirit of wine into ether. From this observation it appears very improbable that sulphuric acid acts in this case simply as a hygroscopic substance; indeed, it soon became evident that this explanation was insufficient, because it was found that the whole of the water produced in the reaction distils over together with the ether, and it can scarcely be imagined that the sulphuric acid first exerts its power of removing water from the alcohol and then immediately parts with the water again which distils over with the ether.

216 *Theories of Etherification.*—As in many other reactions where a sufficient explanation is wanting, chemists (as well as other men) have long been in the habit of taking refuge in a name, and this peculiar action of the sulphuric acid was termed a catalytic or contact action,

> "Denn eben wo Begriffe fehlen,
> Da stellt ein Wort zur rechten Zeit sich ein."

This catalytic hypothesis was first proposed by Mitscherlich,[1] and Berzelius gave his adhesion to the view. These observers omitted, however, to notice that the first action of sulphuric acid on alcohol, in the manufacture of ether, is the production of sulphovinic acid (hydrogen ethyl sulphate). This fact did not, however, escape the observation of Hennell, who found that a concentrated solution of this acid yielded ether on distillation; whilst a dilute solution, on similar treatment, yielded only alcohol. This subject was more carefully investigated by Liebig,[2] who came to the conclusion that ethyl sulphuric acid which is first formed, decomposes at a temperature of 126° to 140° into ether, sulphuric acid, and anhydrous sulphuric acid (sulphur trioxide), this latter combining instantly with the water formed in the reaction with production of sulphuric acid; this again forming ethyl sulphuric acid with the alcohol, which is being constantly added. This, according to Liebig, accounted for the continuous nature of the reaction. The simultaneous evolution of water and of strong sulphuric acid was explained by assuming that this latter only combined with the water in its immediate neighbourhood, whilst, in the other parts of the liquid, the passage of the ether vapour carried away some aqueous vapour with it. The singular fact

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[1] *Pogg. Ann.* xxxi. 273 ; liii. 95 ; lv. 209 ; Taylor, *Sc. Mem.* iv. 1.

[2] *Ann. Pharm.* lx. 31 ; xxiii. 39 , xxx. 129

that ethyl sulphuric acid should be both formed and decomposed at the same time and in the same liquid was explained by Heinrich Rose, by the suggestion that a diminution of temperature sufficient to permit of the formation of ethyl sulphuric acid took place at the point where the alcohol flowed in, but that the other portions of the liquid were sufficiently hot to cause the decomposition of this acid. Mitscherlich soon rendered this hypothesis untenable by showing that the continuous formation of ether may be carried on under circumstances in which no such local diminution of temperature can occur, as it is produced equally well when a current of the vapour of alcohol is passed in, in place of the liquid.[1] Upon this, Leopold Gmelin remarked that at the point where the vapour enters the liquid we have an excess of alcohol present, and there the formation of ethyl sulphuric acid may take place more easily in consequence of the presence of this excess of alcohol. Graham next proved that ethyl sulphuric acid when heated by itself to 140° does not yield any ether, and that on addition of water only alcohol is formed, whereas ether is produced when the ethyl sulphuric acid is heated with alcohol to 140°. It has already been stated that Hennell also found that when the acid is heated with water it yields alcohol, whilst a concentrated solution gives rise to ether; and the same fact was also observed by Sertürner. In the latter case we must assume that alcohol is also formed, but that it contains a small quantity of water only, and forms ether with the excess of ethyl sulphuric acid present, which when dilute it cannot do. Still no completely satisfactory theory of the formation of ether could be established upon the facts which were then known. In order to understand this it must be remembered that the equivalent weights were then in general use, and that the following formulæ were adopted:

Alcohol.	Ethyl Sulphuric Acid.	Ether.
C_4H_5O,HO	$HO,SO_3 + C_4H_5O,SO_3$	C_4H_5O.

217 *Williamson's Theory of Etherification.*—Graham, like Mitscherlich and Berzelius, assumed the existence of contact action, but shortly afterwards the classical researches of Williamson[2] placed the true theory of the continuous etherification process on the firm basis of experiment. This theory of the formation

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[1] *Journ. Chem. Soc.* iii. 24.

[2] *Brit. Assoc. Reports*, 1850, p. 65; *Phil. Mag.* [3] xxxvii. 350.

of ether has played a most important part in the development of our theoretical views; the recognition of its truth has rendered it possible to explain a large number of similar reactions, and it has moreover led to the discovery of many new groups of compounds.

Williamson, adopting the views of Laurent and Gerhardt, gave to ether the molecular formula $C_4H_{10}O$, according to which this substance contains the radical ethyl twice. But according to the theory of types, alcohol is derived from water by the replacement in it of one atom of hydrogen by ethyl, and hence ether, according to Williamson's view, must be regarded as alcohol in which the second atom of hydrogen is replaced by ethyl. To prove the truth of this he made the following experiment. By dissolving sodium in alcohol he first prepared sodium ethylate, or, as he termed it, ethylate of soda; and upon this he acted with ethyl iodide, by which reaction he obtained pure ether:

$$\left.\begin{matrix} C_2H_5 \\ Na \end{matrix}\right\} O + \left.\begin{matrix} I \\ C_2H_5 \end{matrix}\right\} = \left.\begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix}\right\} O + \left.\begin{matrix} I \\ Na \end{matrix}\right\}.$$

This proof, however, did not satisfy him, for, according to the old theory, it might happen that in this reaction two molecules (or atoms as they then were termed) of ether, each containing half the number of carbon atoms, had been formed. Williamson, therefore, acted with ethyl iodide on sodium methylate, and with methyl iodide on sodium ethylate, and in both cases he obtained a single compound, viz. methyl-ethyl-ether, and not a mixture of two compounds, viz. methyl-ether and ethyl-ether. In a similar way he obtained amyl-ethyl-ether or the seven-carbon ether, $\left.\begin{matrix} C_2H_5 \\ C_5H_{11} \end{matrix}\right\} O$.

The formation of ether from alcohol and sulphuric acid could now be readily explained. Ethyl sulphuric acid is, in the first place, formed, and alcohol acts again upon this substance:

$$(1)\ \left.\begin{matrix} C_2H_5 \\ H \end{matrix}\right\} O + \left.\begin{matrix} H \\ H \end{matrix}\right\} SO_4 = \left.\begin{matrix} C_2H_5 \\ H \end{matrix}\right\} SO_4 + \left.\begin{matrix} H \\ H \end{matrix}\right\} O.$$

$$(2)\ \left.\begin{matrix} H \\ C_2H_5 \end{matrix}\right\} O + \left.\begin{matrix} C_2H_5 \\ H \end{matrix}\right\} SO_4 = \left.\begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix}\right\} O + \left.\begin{matrix} H \\ H \end{matrix}\right\} SO_4.$$

Water and ether distil over, whilst the sulphuric acid which is reproduced yields ethyl sulphuric acid again on contact with more alcohol, and hence the formation of ether becomes continuous. That this is the true explanation of the process was clearly proved by Williamson by first preparing amyl-sulphuric acid and then treating this with common alcohol as in the ordinary continuous process. At first amyl-ethyl-ether distils over, then common ether, and the residue no longer contains amyl-sulphuric acid, but consists entirely of ethyl-sulphuric acid. As a further proof of the truth of his theory, Williamson used a mixture of ethyl and amyl alcohols and allowed this to act on sulphuric acid exactly in the same way as common alcohol is used in the ordinary preparation of ether, when, as he predicted, he obtained a mixture of amyl-ethyl-ether and amyl-ether.

Further confirmation of the correctness of Williamson's views was afterwards given by Berthelot.[1] By heating 222 grams of ethyl bromide with alcoholic potash, this chemist obtained 12 grams of ether; whilst if according to the old view the ether had been obtained by a simple replacement of bromine by oxygen, only 7·5 grams could have been produced. Hence it is clear that alcohol must take a part in the reaction:

$$\left.\begin{matrix} C_2H_5 \\ Br \end{matrix}\right\} + \left.\begin{matrix} C_2H_5 \\ H \end{matrix}\right\} O + \left.\begin{matrix} K \\ H \end{matrix}\right\} O = \left.\begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix}\right\} O + \left.\begin{matrix} H \\ H \end{matrix}\right\} O + \left.\begin{matrix} K \\ Br \end{matrix}\right\} .$$

According to this equation 15 grams of ether should have been formed, but owing to the nature of the experiment it was impossible to avoid a certain amount of loss.[2]

218 Ether can be prepared by a great number of other processes. Thus, for example, it is formed with evolution of heat by the action of ethyl iodide on dry silver oxide:

$$2\,C_2H_5I + Ag_2O = (C_2H_5)_2O + 2\,AgI.$$

In place of silver oxide, sodium oxide, Na_2O, may be used. The reaction then does not occur until a temperature of 180° is reached.[3]

Ether is also formed when a haloid ethereal salt is heated with alcohol, or with a small quantity of water under pressure. If, however, the water be present in excess, alcohol is produced.

The action of the hydracids of the chlorine group on alcohol

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[1] *Journal de Pharmacie*, [3], xxvi. 25.
[2] Wurtz, *Ann. Chim. Phys.* [3], xlvi. 222.
[3] Greene, *Bull. Soc. Chim.* [2], xxix. 458.

also gives rise to ether, but this only when the latter is present in excess, as in the opposite case the haloid ethereal salts are formed. This reaction serves as an excellent example of the action of mass, to which Bertholet, in his classical *Essai de Statique Chimique*,[1] first drew attention. When two bodies act chemically upon one another they may give rise to various products according to the quantitative relations in which they stand to one another. And hence reactions which take place under certain circumstances may under other conditions be even reversed. Thus, for example, alcohol when heated with an excess of hydriodic acid yields water and ethyl iodide, but if a large excess of water be allowed to act on ethyl iodide, alcohol and hydriodic acid are formed:

$$C_2H_5\overrightarrow{OH + HI} = \underleftarrow{C_2H_5I + H_2O}.$$

If, in the first case, the quantity of alcohol be large, the ethyl iodide acts upon it to form ether:

$$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O + \left.\begin{matrix}I\\C_2H_5\end{matrix}\right\} = \left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O + \left.\begin{matrix}I\\H\end{matrix}\right\}.$$

When ethyl iodide is heated with a small quantity of water, alcohol is first formed, and this is then converted into ether.

From the foregoing it is distinctly seen that a small quantity of a haloid ethereal salt or its corresponding acid is able to convert a large quantity of alcohol into ether, and moreover that the water which is constantly formed will gradually retard and ultimately stop the reaction, inasmuch as the various products will then be held in a condition of equilibrium.

Many chlorides, bromides, and sulphates convert alcohol into ether,[2] but usually only at a high temperature. In this case the free acids doubtless are also formed, together with basic salts; and it is these acids which then act in the manner already described in the process of etherification, this reaction being brought to an end by the presence of the water which is formed, and the acid again uniting with the basic salt.

The change of alcohol into ether can also be brought about by phosphoric and arsenic acids. The reaction is in this case

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[1] *Paris An.* xi. (1803).

[2] Masson, *Ann. Chem. Pharm.* xxxi. 63; Kuhlmann, *ib.* xxxiii. 97 and 192; Reynoso, *Ann. Chim. Phys.* [3], xlviii. 385.

exactly the same as that of sulphuric acid. In consequence of this method of preparation ether was at one time also termed arsenic and phosphoric ether.

219 *Manufacture of Ether by the Continuous Process.*—For the preparation of ether on the large or small scale the method employed by Boullay is always adopted. A mixture of sulphuric acid and alcohol is made in such proportions that the liquid boils at about 140°, the relation varying according to

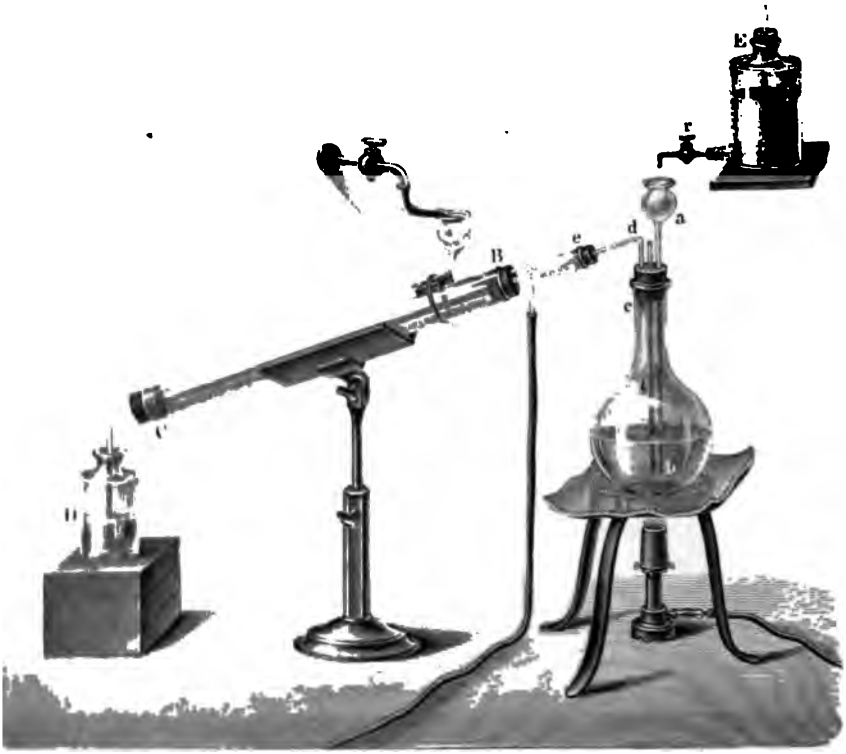

FIG. 87.

the strength of the two constituents. A mixture of 5 parts of 90 per cent. spirit with 9 parts of concentrated sulphuric acid is a very usual one. This is heated in a flask or cast-iron boiler. The neck of the flask (Fig. 87) or the opening of the boiler is furnished with three tubes. Into one of these a tube-funnel is fitted, another is connected with a condensing apparatus, whilst in the third opening a thermometer is placed, which must dip into the liquid. The mixture is then heated to the boiling-point, and alcohol allowed to flow from the bottle (E) through the tube-funnel (which must also dip into the liquid) in such quantity that the temperature remains nearly constant.

According to theory an unlimited quantity of alcohol can be thus converted into ether. Practice has, however, shown that the operation must be interrupted when a quantity of alcohol about six times the volume of that originally contained in the vessel has been added. This depends chiefly on the fact that the materials used are never anhydrous, and therefore, that the mixture in the retort becomes after a while so diluted with water that the reaction comes to an end. Besides, the liquid does not wholly consist of sulphovinic acid, but always contains free sulphuric acid, and this gives rise to secondary reactions, blackening occurs, sulphur dioxide and water are formed, and the presence of this latter exercises a further retarding influence on the reaction.

The distillate, which, together with ether and water, contains alcohol and sulphur dioxide, is then treated with milk of lime or caustic soda, and rectified from a water-bath, when the ether first passes over, still, however, containing some alcohol and water. To remove these, the distillate is allowed to stand over fused chloride of calcium, a method described by Lowitz in the year 1796. The ether is then poured off from the chloride of calcium and again rectified, when it is found to be pure enough for all technical purposes and for general laboratory use, although it still contains small traces of water and alcohol. This latter is extremely difficult to remove, and can only be completely got rid of by repeatedly shaking the ether with a small quantity of water, and continuing this operation until the wash-water no longer gives the iodoform reaction. It is then dried over calcium chloride, and the liquid poured off from this treated with sodium until no further evolution of hydrogen takes place, and again distilled from a water-bath. In this purification of ether a considerable quantity dissolves in the wash-water. This may, however, be regained by rectification.

220 *Properties.*—Ether is a very mobile liquid having a peculiar odour which affects the head, and a burning taste. It boils at 34°·9 (Kopp, Andrews); at 0° it possesses a specific gravity of 0·73568, and at 15° of 0·70240. It volatilizes quickly not only at the ordinary temperature, but at a much lower point. The tension of ether vapour is as follows:—

Temperature.	Mm.
−20°	67·49
[illegible]	182·34
10°	286·4
20°	433·2
30°	636·3
40°	909·6
60°	1725·5
80°	3022·[illegible]
120°	77[illegible]2·2

Ether is extremely inflammable, burning with a white luminous flame. The vapour, which from its high specific gravity may be poured from one vessel to another like carbon dioxide, forms with air a highly explosive mixture, and care is needed in working with large quantities of ether, no flame being permitted in its neighbourhood. If a large quantity of ether be allowed to evaporate in a closed space a mixture is obtained which explodes with the force of gunpowder. The high specific gravity of ether vapour may be strikingly shown as follows. A small quantity of ether is brought into a flask and the short end of a glass syphon is brought one centimeter above the surface of the liquid. If the opposite and long end of the syphon be now sucked out, ether vapour will flow down in a continuous stream, and a small cylinder may be filled up with it and the contained vapour then ignited.

Fourcroy and Vauquelin state that ether when cooled to −31° crystallizes in long white glistening tablets, which, at −44° form a continuous solid crystalline mass. Thénard and Mitchell were unable to confirm this statement, and the latter found that pure ether remains liquid at −90°.[1] This question has lately been investigated by Franchimont,[2] and his conclusions agree with those of the two latter chemists. He found that moist ether, when cooled, deposits crystals, probably consisting of ice, but he did not obtain a solid mass at −44°. This may be explained by the fact that not enough water was present, as, according to Guthrie, ether unites with ice to form a cryohydrate. Such a compound, having the formula $C_4H_{10}O + 2H_2O$, was obtained by Tanret by quickly evaporating ether on filter paper. It melts at −3°·5, which is the minimum temperature obtained by mixing ether and ice.[3]

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[1] [illegible] xxii. 289.

[2] *Ber. Deutsch. Chem. Ges.* x. 830.

[3] *Comptes Rendus*, lxxxvi. 765.

It was formerly believed that ether, like oil, is insoluble in water, until Lauragnais showed, in 1758, that ten parts of water was sufficient to dissolve the ether completely. According to Boullay, on the other hand, one part dissolves in fourteen parts, whilst Draper states that ten volumes of ether dissolve, in 100 parts of water, at 11°. Concentrated hydrochloric acid dissolves it in much larger quantities than water.[1] On the other hand, one part of water dissolves in about thirty-four parts of ether. Ether is miscible with alcohol and with almost all other hydrocarbon derivative compounds as well as with carbon dioxide. Many solid bodies, such as resins, fats, alkaloids, &c., dissolve easily in ether. Some of these are soluble in aqueous ether but not in absolute ether. This is the case with gallic acid, and this reaction is so characteristic that it may be employed to ascertain the presence of water in ether. If the latter liquid contains only a little moisture the dry powder balls itself up; if more be present it deliquesces to a thick syrup, which does not mix with the layer of ether above, and consists of a solution of tannic acid in aqueous ether.[2] Many inorganic substances are soluble in ether; thus sulphur dissolves slightly, and phosphorus dissolves in rather larger quantity. This latter solution, which becomes yellow on exposure to light, was formerly known as *Ætheran phosphoratus*. Ether dissolves iodine and bromine in larger quantity, as well as chromium trioxide, ferric chloride, mercuric chloride, auric chloride, platinum chloride, several other chlorides and iodides, and some few salts. Various gases are also absorbed by ether, such as ammonia, which is taken up in considerable quantity, other gases being less soluble. According to Regnault, ether undergoes a change when preserved even in well-closed vessels, assuming a different vapour-tension. If ether be contained in a flask with air, acetic acid is formed after some time; this change taking place more quickly in presence of an alkali. On the other hand, Lieben states that pure ether, either alone or in contact with potash, lime, or sodium, does not undergo any alteration on standing, but that if water or fused sodium chloride, or calcium chloride, or anhydrous sulphate of copper, be present, a slow change takes place, the liquid exhibiting the iodoform reaction.[3]

221 *Decompositions of Ether.*—When ether is heated with water and a trace of sulphuric acid to a temperature of 150°

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[1] Draper, *Chem. News*, xxxv. 87. [2] Bolley, *Ann. Chem. Pharm.* cxv. 63.
[3] *Ber. Deutsch. Chem.* iv. 758.

to 180° it is converted into alcohol.[1] If ether be treated with hydriodic acid gas at a temperature of 0° to 4°, alcohol and ethyl iodide are formed:

$$\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O + \left.\begin{matrix}H\\I\end{matrix}\right\} = \left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O + \left.\begin{matrix}C_2H_5\\I\end{matrix}\right\}.$$

Mixed ethers are decomposed in a similar way, the radical containing the most carbon being converted into an alcohol.[2] Ethyl iodide is also formed in a violent reaction, probably together with oxyethyl aluminium iodide, which has already been referred to, when ether is brought in contact with iodine and aluminium foil.

The ordinary oxidizing agents give with ether the same products as with alcohol. If some ether be dropped on to platinum-black, ignition takes place, and when a few drops are allowed to evaporate in a beaker-glass and a hot spiral of platinum wire placed above it, the spiral continues to glow, a phosphorescent light being noticed over the wire in the dark as soon as the glow ceases (H. Davy). When ozonized oxygen is led into ether, each bubble produces a violent reaction and a solution is thus obtained containing oxalic acid, acetic acid, hydrogen dioxide, and a small quantity of formic acid (A. W. Wright).

If ether vapour be passed over heated potash, lime, or carbonate of potassium, marsh gas and hydrogen are formed, but neither acetic acid nor formic acid (Dumas and Stas). This reaction is probably due to the previous formation of potassium acetate according to the equation:

$$(C_2H_5)_2O + 2KOH + H_2O = 2C_2H_3KO_2 + 4H_2,$$

and this acetate is then decomposed into carbonate and marsh gas in the presence of alkali.

222 *Uses.*—Ether is largely used in the laboratory as well as in the arts and manufactures as a solvent, for the preparation of collodion, the extraction of tannic acid, &c. From its great volatility it has also been used in the manufacture of ice. If brought in the form of a fine spray upon the skin it produces such a degree of cold as to induce complete insensibility, and hence the employment of the ether-spray has been proposed for effecting local anaesthesia.

Ether vapour when inhaled produces similar effects to nitrous

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[1] Erlenmeyer and Tscheppe, *Zeitsch. Chem.* 1868, 343.

[2] Silva, *Compt. Rend.* lxxxi. 323.

oxide. This appears to have been first observed in 1818 by Faraday who was investigating the subject. The introduction of ether as a general anæsthetic agent is due to Dr. C. Long of the United States in 1842. He did not however publish anything until three years later, when two dentists, Messrs. Morton and Jackson, made independent observations on the subject, and suggested the employment of ether for this purpose. The inhalation of ether was soon widely adopted in medicine. In Europe Sir James Simpson of Edinburgh was especially active in its introduction, and he showed that this body under certain conditions might be employed without any danger, especially in obstetric cases. The employment of this and other anæsthetics met with much opposition from a certain class of persons, but all such objections were successfully overcome by Simpson's energy and determination.

223 Ether unites with bromine to form the compound $2C_4H_{10}O + 6\,Br$, when the two liquids are brought together in the cold. This compound is a crystalline mass somewhat resembling chromium trioxide, possessing a strong smell, and being decomposed by water into its constituents. It is a very unstable compound, and on standing decomposes spontaneously with formation of water, hydrobromic acid, ethyl bromide, tribromaldehyde, C_2HBr_3O, &c.[1] Various metallic chlorides and bromides also form compounds with ether. One of the first of these was obtained by Kuhlmann by bringing together anhydrous ether and stannic chloride. It forms a feathery crystalline mass of the composition $2\,C_4H_{10}O + SnCl_4$, which distils at 80°, yielding glistening rhombic tables which are decomposed by water.[2] Various other compounds of ether with metallic chlorides and bromides have been obtained by Nicklès.[3] These are mostly crystalline, and some are volatile without decomposition, as for instance $Al_2Br_6 + 2\,C_4H_{10}O$, which sublimes in yellow needles. The trichloride and tribromide of antimony and of arsenic form similar compounds. Ether combines with antimony pentachloride to form a greyish white crystalline mass, $SbCl_5 + C_4H_{10}O$, a very unstable compound.[4] With titanium chloride it also forms the body $TiCl_4 + C_4H_{10}O$, crystallizing in small yellow tables melting at 42° to 45°, and boiling at 118° to 120.° Ether

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[1] Schutzenberger, *Compt. Rend.* lxxv. 1511.

[2] Lewy, *Compt. Rend.* xxi. 371.

[3] *Ann. Chim. Phys.* [3], lxii. 230; *Compt. Rend.* lii. 396; lviii. 537; lx. 300.

[4] Williams, *Journ. Chem. Soc.* 1876, ii. 463.

also combines with vanadium oxychloride. By distilling the product under diminished pressure large stellated crystals having the formula $C_4H_{10}O + VOCl_3$ are obtained, appearing reddish-brown by transmitted but green by reflected light. They melt below 100° and are decomposed by water into ether, hydrochloric acid, and vanadium pentoxide.[1]

CHLORINE SUBSTITUTION-PRODUCTS OF ETHER.

224 Chlorine acts violently upon ether. If a few grams of ether be poured into a flask filled with chlorine gas white fumes are after some time given off, and then an explosion takes place, accompanied by flame and considerable deposition of charcoal (Cruikshank). If chlorine gas be led into ether, every bubble sets fire to the ether, which becomes heated throughout, and is ultimately converted into a black tarry mass. If, however, chlorine be passed, especially in the dark, into ether, very well cooled, substitution products are formed. These have been investigated by [illegible] Regnault,[3] Malaguti,[4] Lieben,[5] Abeljanz,[6] and Jacobsen.

[illegible] *Oxide* or *Monochlorether*, C_4H_9ClO. This, according to Jacobsen, is the first product of the reaction, and [illegible] with the compounds which Frapolli and Wurtz[8] [illegible] by the action of hydrochloric acid on a [illegible] alcohol and aldehyde, and which they believed [illegible] the latter substance with ethyl chloride. It [illegible] which is decomposed by sulphuric [illegible] aldehyde, hydrochloric acid, and ethyl [illegible] with sodium ethylate it yields acetal, [illegible] described under the ethidene compounds. [illegible] of monochlorethyl oxide as well as [illegible] aldehyde, which is ethidene oxide, is [illegible]

$$[illegible] - \begin{matrix} CH_3.CHCl \\ C_2H_5 \end{matrix} O - H_2O.$$

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[1] [illegible] 341

[2] [illegible]

[3] [illegible]

[4] [illegible]

[5] [illegible] Pharm. [illegible]

[6] [illegible] xvi. 5.

[7] [illegible]

[8] Ann. Chem. Pharm. cviii. 226.

Dichlor-Ethyl Oxide, $C_4H_8Cl_2O$. For the preparation of this compound Lieben recommends that chlorine should be passed into ether cooled to 0° and the temperature gradually allowed to rise to 20°. It is then distilled off on the water-bath and the distillate again treated with chlorine. By repeating these operations, the above compound is at last obtained as a strongly smelling liquid which boils with decomposition at 140° to 145° and has a specific gravity of 1·174 at 23° and burns on ignition with a luminous green-mantled flame. By the moderate action of zinc ethyl on dichlorinated ether, ethyl chlorinated ether, $C_4H_8Cl(C_2H_5)O$, is obtained. This possesses a pleasant ethereal smell, boils at 141°, and has a specific gravity of 0·9735 at 0°. Heated with an excess of concentrated hydriodic acid in closed tubes to 100° it forms ethyl iodide and secondary butyl iodide. The formation of this compound shows that substitution has not taken place in both of the ethyl groups, as was originally supposed; and Lieben explains this by the following equations:

$$\left.\begin{array}{r}C_2H_3Cl(C_2H_5)\\C_2H_5\end{array}\right\}O + 2\,HI = C_2H_3Cl(C_2H_5)I + C_2H_5I + H_2O.$$

$$C_2H_3Cl(C_2H_5)I + HI = C_2H_3Cl(C_2H_5)H + I_2.$$

$$C_2H_3Cl(C_2H_5)H + HI = C_2H_4(C_2H_5)I + HCl.$$

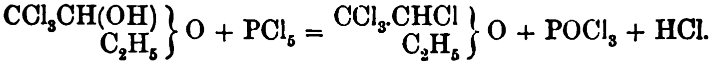
By the further action of zinc ethyl on ethyl chlorinated ether, or more simply if iodide of ethyl and zinc be heated with it, the so-called *di-ethyl ether*, $C_2H_3(C_2H_5)_2O.C_2H_5$, is obtained, a body which boils at 131° and is a compound ethyl hexyl ether, yielding, on heating with hydriodic acid, ethyl iodide and secondary hexyl iodide. By the action of sodium ethylate on dichlorinated ether, *ethyl-oxide-chlorinated-ether* is formed. This is identical in composition with monochloracetal, $CH_2Cl.CH(OC_2H_5)_2$, and for this reason dichlorinated ether must possess the composition $\left.\begin{array}{r}CH_2Cl{\cdot}CHCl\\C_2H_5\end{array}\right\}O.$

Trichlor-Ethyl Oxide, $C_4H_7Cl_3O$, is not known in the pure state. If the residue boiling above 153° obtained in the preparation of dichlorinated ether be heated with sodium ethylate it dissolves, and from the product of the reaction dichloracetal, $CHCl_2.CH(OC_2H_5)_2$, separates out, and hence it would appear that a trichlorinated ether exists having the composition $\left.\begin{array}{r}CHCl_2.CHCl\\C_2H_5\end{array}\right\}O.$

Tetrachlor-Ethyl Oxide, $C_4H_6Cl_4O$. This body was discovered by Malaguti, and first termed chlorinated ether and afterwards bichlorinated ether. It is formed by the continued action of chlorine upon ether, when the liquid is gradually heated to 100°. The chlorine is absorbed quickly to begin with, then, however, a stormy evolution of hydrochloric acid takes place, so that the liquid requires to be cooled. After this chlorine is again led in, and then the whole heated to 140° until the mass begins to blacken. It is then mixed with water, dried in a vacuum over lime and sulphuric acid, and thus a thick liquid is obtained which has a pungent smell and a specific gravity of 1·5. It has no constant boiling point, but decomposes when heated. Alcoholic potash yields acetic acid together with other products, and on heating with sulphuric acid, trichloraldehyde or chloral, $CCl_3.CHO$, is formed, and from this it appears that Malaguti's chlorinated ether is a mixture which contains the compound

$$\left.\begin{array}{r}CCl_3.CHCl\\ C_2H_5\end{array}\right\}O.$$

This latter body was first prepared in the pure state by L. Henry,[1] by the action of phosphorus pentachloride on the so-called chloral alcoholate (see Ethidene Compounds):



$$\left.\begin{array}{r}CCl_3CH(OH)\\ C_2H_5\end{array}\right\}O + PCl_5 = \left.\begin{array}{r}CCl_3.CHCl\\ C_2H_5\end{array}\right\}O + POCl_3 + HCl.$$

The same compound is likewise formed when chlorine is allowed to act on the monochlorinated ether obtained from aldehyde.[2] It boils at 188° to 190°, possesses a specific gravity at 15° of 1·4211, and has a sweetish-bitter taste and a pungent camphor-like smell.

Pentachlor-Ethyl Oxide, $C_4H_5Cl_5O$, is obtained, according to Jacobsen, by the further action of chlorine on Malaguti's compound. It is a thick liquid having a specific gravity of 1·645, which is probably, however, a mixture. It gives ethyl compounds by various reactions, and probably, therefore, contains the compound $C_2Cl_5(C_2H_5)O$. This latter compound is also obtained from the last described tetrachlorinated ether; by the action of alcoholic potash the compound $CCl_2 = CCl.OC_2H_5$ is produced, and this unites with chlorine directly to form pentachlorinated ether, a liquid boiling at 190°—210° with partial decomposition being obtained.

[1] *Ber. Deutsch. Chem. Ges.* iv. 101, 435; vii. 762; *Comptes Rendus*, xlvii. 418.
[2] Vogt and Wurtz, *Comp. Rend.* lxxiv. 777.

The bromine compound, $CCl_2Br.,CClBr.O.C_2H_5$, is obtained as a colourless, heavy liquid having a pleasant smell, by the action of bromine on the latter body, and this on cooling crystallizes in large clear crystals, which melt at 17°.[1] An isomeric pentachlorinated ether was obtained by Henry[2] by acting with phosphorus pentachloride on a compound also belonging to the ethidene series obtained by the union of chloral and ethylene chlorhydrate (monochlorethyl alcohol).

This latter compound corresponds to the above-mentioned chloral alcoholate.

This pentachlorinated ether is a colourless, thick liquid, possessing a sweetish taste and a strong camphor-like smell. It possesses the constitution $\left.\begin{array}{l}CCl_3.CHCl\\CH_2Cl.CH_2\end{array}\right\}O$.

Perchlorinated Ether, $C_4Cl_{10}O$, is the last product of the action of chlorine on ethyl oxide, and is formed only in the sunlight. It is a solid body, possessing a penetrating camphor-like smell, and crystallizes from alcohol in orthorhombic crystals which melt at 69°, and have a specific gravity of 1·9. In its preparation, hexchlorethane, C_2Cl_6, and trichloracetyl chloride, $CCl_3.COCl$, are usually formed, and the perchlorinated ether decomposes completely into these compounds on heating to 300°. By the action of an alcoholic solution of potassium sulphide, a compound is formed termed by Malaguti *chloroxethose*:

$$\left.\begin{array}{l}C_2Cl_5\\C_2Cl_5\end{array}\right\}O + 2K_2S = \left.\begin{array}{l}C_2Cl_3\\C_2Cl_3\end{array}\right\}O + 4KCl + S_2.$$

This is a liquid boiling at 210°, which unites with chlorine in the sunlight to form perchlorinated ether, and with bromine to yield the compound $C_4Cl_6Br_4O$. If chlorine be allowed to act in presence of water on chloroxethose, trichloracetic acid is formed as follows:

$$\left.\begin{array}{l}CCl_2{=}CCl\\CCl_2{=}CCl\end{array}\right\}O + 2Cl_2 + 3HOH = 2CCl_3.CO.OH + 4HCl.$$

Methyl-Ethyl-Ether, $\left.\begin{array}{l}CH_3\\C_2H_5\end{array}\right\}O$, is a liquid possessing a smell resembling that of ethyl oxide, and boiling at 11°. It is best obtained by the action of ethyl iodide on sodium methylate. This compound is also produced by treating sodium ethylate with methyl iodide (Williamson), and it was originally termed

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[1] Busch, *Ber. Deutsch. Chem. Ges.* xi. 445.

[2] *Ib.* vii. 762.

by him the three-carbon ether. It may also be obtained by distilling together potassium ethyl sulphate and potassium methylate,[1] and by the action of dry silver oxide on a mixture of the iodides of ethyl and methyl (Wurtz).

THE ETHEREAL SALTS OF ETHYL, OR ETHYL COMPOUND ETHERS.

ETHYL CHLORIDE, C_2H_5Cl.

225 This compound was first obtained in alcoholic solution by Basil Valentine, who thus describes its preparation:[2] "This I also say that, when the spirit of common salt unites with spirit of wine, and is distilled three times, it becomes sweet, and loses its sharpness." In his Last Testament he also says:[3] "Take of good spirit of salt which has been well dephlegmated and contains no watery particles one part; pour to this, half a part of the best and most concentrated *spiritus vini* which also contains no phlegma or vegetable mercury." He goes on to state that this mixture must be repeatedly distilled, and then "placed in a well-closed bottle, and allowed to stand for a month or until it has all become quite sweet, and has lost its acid taste. Thus is the *spiritus salis et vini* prepared, and may be readily extracted."

The mixture thus obtained of alcohol and ethyl chloride, or sweet spirit of salt, was well known to the later chemists. Thus Glauber speaks of it in 1648 in describing strong hydrochloric acid: "When dephlegmated spirit of wine is poured into such strong spirit of salt and digested for a long time, the spirit of wine makes a separation and kills its *sal volatile*, so that a fine clear *oleum vini* swims on the top, which is not the least potent of the cordials."

Pott then showed in 1739 that this sweet spirit of salt could be obtained by the action of butter of arsenic or butter of antimony on spirit of wine, and other chemists found that other metallic chlorides may be employed for the like purpose. Ludolf, in his work on *Medical Chemistry*, states in 1749, that on heating spirit of wine with sulphuric acid and common salt a distillate is obtained which when treated with lime yields an ether,

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[1] Chancel, *Compt. Rend.* xxxi. 521.

[2] *Wiederholung des grossen Steins der uralten Weisen*, ed. Petraeus, p. 72.

[3] *Basilius Valentinus*, ed. Petraeus, p. 785.

but he vainly endeavoured to obtain a similar compound by the action of muriatic gas on spirit of wine. Beaumé's experiments in this direction also did not succeed, but Woulfe[1] obtained hydrochloric ether in this way, and it was afterwards prepared and sold by an apothecary in Germany and known as Basse's hydrochloric ether. This same compound was afterwards termed light hydrochloric ether, in order to distinguish it from the so-called heavy hydrochloric ether obtained by heating alcohol with common salt, manganese dioxide, and oil of vitriol. This latter body, which was prepared in 1782 by Westrumb, and afterwards observed by Scheele, is however a mixture of various oxidation-products.

Colin and Robiquet[2] were the first to point out the true composition of ethyl chloride. The above-mentioned method of distillation has been used until recently in order to obtain this compound, although it is not in every respect satisfactory. Boullay found that, when obtained by means of common salt and sulphuric acid, the product usually contains a small quantity of ethyl oxide.

Pure ethyl chloride is prepared by passing hydrochloric acid gas into strong spirit of wine. The saturated solution is allowed to stand for some time, and then distilled off on a water-bath. The yield is, however, not more under the most favourable circumstances than corresponds to 15 per cent. of the alcohol employed. The alcohol may, as Groves[3] has shown, be completely converted into the chloride, if zinc chloride be added and hydrochloric acid gas passed into the boiling solution; this gas is then completely absorbed, and when the liquid has become saturated, pure ethyl chloride is evolved, the reaction going on until the whole of the alcohol has been converted.

According to the experiments of Krüger,[4] ether is likewise formed in this process when the mixture is heated to begin with. This can be avoided by saturating the solution of one part of zinc chloride, and 82 parts of spirit with hydrochloric acid in the cold, and then heating to the boiling-point, the gas being passed in so long as ethyl chloride is formed. The evolution-flask must, of course, be connected with an inverted condenser in order to retain the alcohol vapour, whilst the more volatile chloride of ethyl passes into a vessel surrounded either with ice or a freezing mixture, where it is condensed. In this

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[1] *Phil. Trans.* 1767, p. 520.

[2] *Ann. Chim. Phys.* i. 348.

[3] *Journ. Chem. Soc.* 1874, 636.

[4] *Journ. Prakt. Chem.* [2], xiv. 193.

way it is easy to obtain a kilogram of the compound in a few hours, and this method serves admirably as a lecture illustration. The action of hydrochloric acid on alcohol is explained by the following equation:

$$C_2H_5.OH + HCl = C_2H_5Cl + H_2O.$$

Hence the conclusion that zinc chloride simply acts as a strong hygroscopic agent would not appear improbable, but this is not the case, inasmuch as it cannot be replaced by other equally efficacious hygroscopic agents such as chloride of calcium or sulphuric acid. Its peculiar action depends upon the fact that the alcohols very easily decompose, with elimination of water, into the olefines, that is the hydrocarbons of the series C_nH_{2n}, which unite with hydrochloric acid to form the monochlorides. Accordingly, in the preparation of ethyl chloride according to Groves's method two reactions take place; one part is produced by the direct action of hydrochloric acid on alcohol, and the other part by the union of ethylene in the nascent condition with hydrochloric acid. The truth of this explanation is proved by the fact that when amyl alcohol is thus treated, a considerable quantity of the secondary chloride is found, together with the primary chloride, and this, as we know, can only be obtained from the olefine amylene C_5H_{10}.[1]

Ethyl chloride is also formed by the action of phosphorus pentachloride on alcohol (Wurtz), and, together with other products, when alcohol is treated with chlorine, and this accounts for the production of this substance in considerable quantity in the manufacture of chloral.

226 *Properties.*—Ethyl chloride is a colourless mobile liquid having a peculiar and pleasant odour, and a sweetish, burning taste. It does not solidify at −29°, boils at 12°·5 (Regnault), at 0° possesses a specific gravity of 0·9214 (Pierre) and its vapour density is 2·219 (Thénard).[2] It is but slightly soluble in water, though dissolving readily in alcohol, strong spirit taking up half its weight. This solution may easily be kept in well-stoppered bottles, and chloride of ethyl may readily be separated out from such a solution by gently warming it and freeing the gas from alcohol vapour by passing it through sulphuric acid (Groves).

Ethyl chloride is easily combustible, burning with a luminous green-mantled flame. When its vapour is passed over heated

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[1] Schorlemmer, *Journ. Chem. Soc.* 1875, 308.

[2] *Ann. Chim.* lxiii. 49.

soda-lime, olefiant gas is formed, according to Stas, whilst L. Meyer[1] finds that in this reaction a mixture of hydrogen and marsh gas is obtained together with sodium acetate and carbonate:

$$(a)\quad C_2H_5Cl + 2\,KOH = C_2H_3KO_2 + KCl + 2\,H_2.$$

$$(b)\quad C_2H_3KO_2 + KOH = K_2CO_3 + CH_4.$$

FIG. 88.

Substitution-products are formed by the action of chlorine on ethyl chloride. These will be described hereafter.

The apparatus shown in Fig. 88 serves to exhibit, in the case

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[1] *Ann. Chem. Pharm.* cxxxix. 289.

of ethyl chloride, the passage from the liquid to the gaseous state, and *vice versâ*.[1] In order to liquefy the gas contained in the shorter and stoppered limb of the syphon tube, mercury must be poured into the longer limb and the compressed gas cooled by pouring some ether over the shorter limb. On allowing the temperature to rise, and on permitting the mercury to run out by the lower stop-cock, the liquid will be seen to boil, and the whole again assume the gaseous condition.

227 *Ethyl Bromide*, C_2H_5Br, was first prepared by Serullas[2] in 1827 by gradually adding bromine to a mixture of alcohol and phosphorus. It is also formed, together with other products, by the action of bromine on absolute alcohol (Löwig), as well as by heating spirit of wine with strong hydrobromic acid and by various other reactions. In order to prepare it, Personne's[3] method is probably the best. For this purpose 40 parts of amorphous phosphorus and 160 parts of absolute alcohol are brought into a flask connected with a reversed condenser, and gradually 100 parts of bromine allowed to flow in, the flask being first well cooled in order to moderate the violence of the reaction. As soon as this has been added, the mixture is distilled on a water-bath, the distillate being shaken up with water and the bromide which separates out being then dried over chloride of calcium or potassium carbonate and afterwards purified by distillation.

Ethyl bromide is a liquid resembling the chloride in its smell and taste, boiling at 38°·37 (Regnault), and having at 0° a specific gravity of 1·4733 (Pierre), whilst at 15° it is 1·4189 (Mendelejeff). Its vapour density was ascertained by Marchand[4] to be 3·754. It burns, when ignited, with a fine green smokeless flame, evolving vapours of bromine.

228 *Ethyl Iodide*, C_2H_5I, was discovered by Gay-Lussac[5] in 1815, and is formed by heating together spirit of wine and hydriodic acid, as well as by the simultaneous action of iodine and phosphorus on alcohol[6] (Serullas):

$$5\,C_2H_5OH + 5\,I + P = 5\,C_2H_5I + H_3PO_4 + H_2O.$$

This last reaction is now always employed for the preparation of this important substance. It is largely used in the arts and

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[1] Hofmann, *Ber. Deutsch. Chem. Ges.* xii. 1123.

[2] *Ann. Chim. Phys.* xxxiv. 99.

[3] *Compt. Rend.* lii. 468.

[4] *Journ. Prakt. Chem.* xxxiii. 186.

[5] *Ann. Chim. Phys.* xci. 89.

[6] *Ib.* xxv. 323; xlii. 110.

manufactures, and for the preparation of other ethyl compounds. Formerly, of course, common phosphorus was employed, and a number of receipts were given for this purpose. In all of these, precautions had to be taken to avoid explosions due to the violence of the reaction, and to prevent loss of substance.

Personne[1] was the first to suggest the employment of amorphous phosphorus, and Beilstein and Rieth,[2] who especially worked out this method, found the following proportions to be the best. Ten parts of red phosphorus and 50 parts of spirit are brought into a tubulated retort connected with a Liebig's condenser, and to these 100 parts of iodine are gradually added. After standing for 24 hours, the ethyl iodide is distilled off. Of course the iodine and spirit may be mixed to begin with, and the phosphorus then added from time to time, and in this case 67 parts of this latter body are sufficient. The distillate is washed with dilute caustic soda and water, and the iodide of ethyl which separates dried over calcium chloride. The residue in the retort consists chiefly of ethyl phosphoric acid, and, for this reason, an excess of alcohol, as is shown in the above proportions, must be used.

Ethyl iodide is also formed when potassium iodide is distilled with a saturated solution of hydrochloric acid in spirit of wine,[3] or when concentrated hydriodic acid is heated under pressure together with ethyl chloride.[4] Another remarkable reaction is its formation on heating ethyl nitrate with potassium iodide.[5]

Ethyl iodide is a colourless, strongly refracting liquid, possessing a peculiar ethereal and somewhat pleasant smell, boiling at 71°·3 (Andrews), or at 71°·6 (Frankland). Its specific gravity at 0° is 1·9755 (Pierre), and at 15°, 1·9309 (Mendelejeff); whilst its vapour density was found by Marchand to be 5·417. Ethyl iodide is almost insoluble in water, but is miscible with alcohol and ether. It is only difficultly inflammable, burning with evolution of iodine vapours. When heated with fifteen times its weight of water to 100°, it gradually dissolves with formation of alcohol. Chlorine decomposes it with formation of ethyl chloride and separation of iodine, and, like many other organic iodides, it is also decomposed when exposed to the action of light, iodine being set free and the liquid becoming gradually red and afterwards brown. This decomposition takes place especially quickly

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[1] *Compt. Rend.* lii. 468.

[2] *Ann. Chem. Pharm.* cxxvi. 250.

[3] De Vrij, *Journ. Pharm.* xxxi. 169.

[4] Lieben, *Zeitsch. Chem.* 1868, 712.

[5] Juncadella, *Compt. Rend.* xlviii. 315.

231 *Ethyl Sulphite*, $(C_2H_5)_2SO_3$, was first prepared by Ebelmen and Bouquet[1] in 1845 by acting on absolute alcohol with sulphur monochloride. It is also formed when thionyl chloride is brought in contact with alcohol.[2] For the purpose of preparing this substance, an excess of absolute alcohol is added to well-cooled chloride of sulphur or thionyl chloride, the product being purified by fractional distillation. Its formation from thionyl chloride is explained by the equation:

$$SO\left\{\begin{matrix} Cl \\ Cl \end{matrix}\right. + 2\,HO.C_2H_5 = SO\left\{\begin{matrix} OC_2H_5 \\ OC_2H_5 \end{matrix}\right. + 2\,HCl.$$

When alcohol is treated with chloride of sulphur, thionyl chloride appears to be first produced, and this acts again on the ethyl hydrosulphide formed at the same time:

$$(1)\quad S_2Cl_2 + HO.C_2H_5 = SOCl_2 + HS.C_2H_5.$$

$$(2)\quad 3\,SOCl_2 + 4\,HS.C_2H_5 = SO(OC_2H_5)_2 + 2\,C_2H_5Cl + 4\,HCl + 2\,S_2.$$

According to this reaction the sulphur monochloride may be regarded as a sulpho-thionyl chloride (Carius).

Ethyl sulphite is a mobile liquid which smells of peppermint, and has at first a cooling but afterwards a burning sulphurous taste. It has a vapour density of 4·78 (Ebelmen and Bouquet) and a specific gravity of 1·1063 at 0°, and boils at 161°·3.[3] It is combustible with difficulty, and can be inflamed only when it has been previously warmed.

Ethyl Sulphurous Acid, $H(C_2H_5)SO_3$, is not known in the free state, and of its salts, *potassium ethyl sulphite* is the only one which has been prepared. This is formed when a solution of caustic potash in five parts of water is gradually added to well-cooled ethyl sulphite, so that the liquid always remains colourless. The mixture is then allowed to stand until the whole of the ethyl sulphite is dissolved, and the solution next saturated with carbon dioxide and the whole allowed to evaporate in a vacuum. The residue is dissolved in 90 per cent. spirit, this evaporated, and the residual salt crystallized from boiling absolute alcohol. It forms delicate silky glistening crystals easily soluble in water. The yield is only small, as the body is very readily decomposed,

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[1] *Ann. Chim. Phys.* [3], xvii. 66.

[2] Carius, *Ann. Chem. Pharm.* cxi. 93.

[3] Carius, *Journ. Prakt. Chem.* [2], ii. 285.

and much potassium sulphate is formed during its preparation. Freshly prepared, it is odourless, but after some time it acquires the smell of ethyl sulphite, and the aqueous solution contains potassium sulphate.[1]

HYDROGEN ETHYL SULPHATE OR ETHYL SULPHURIC ACID.

$$H(C_2H_5)SO_4.$$

232 The calcium and barium salts of this acid were obtained in 1802 by Dabit from the residues of the preparation of ether. These were, however, regarded as salts of an acid having a composition intermediate between sulphurous and sulphuric acids. These observations remained unnoticed until 1819, when Sertürner remarked, from experiments made in 1806, that spirit of wine unites with sulphuric acid, forming a compound to which he gave the name of sulphovinic acid. He showed moreover that other acids were also able to form similar vinic acids. Vogel,[2] in 1819, then investigated sulphovinic acid and its salts more accurately, and came to the conclusion that the acid prepared by Sertürner's method may be considered as a compound of hyposulphuric acid with a heavy ethereal oil, and is identical with Dabit's acid. Gay-Lussac, in 1820, came to the same conclusion, and so indeed did Boullay and Dumas, whilst Hennell looked upon it as a compound of sulphuric acid with a hydrocarbon, having the composition of olefiant gas.

In 1828 Serullas proved that the compound might be regarded as an acid sulphuric ether, and its salts as compounds of sulphates with the then unknown normal ethyl sulphate. This view was adopted by the supporters of the radical theory, by whom ethyl sulphuric acid was considered as a compound analogous to bisulphate of potash containing as its constituents sulphuric acid and neutral sulphate of ethyl oxide:

$$KO.SO_3 + HO.SO_3.$$
$$KO.SO_3 + C_4H_5O.SO_3.$$

Preparation.—In order to prepare ethyl sulphuric acid, concentrated oil of vitriol is quickly but carefully mixed with strong alcohol, and the mixture heated for some time on a water-bath:

$$SO_4\left\{\begin{matrix}H\\H\end{matrix}\right. + C_2H_5.OH = SO_4\left\{\begin{matrix}H\\C_2H_5\end{matrix}\right. + H_2O.$$

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[1] Warlitz, *Ann. Chem. Pharm.* cxliii. 72.

[2] *Gilb. Ann.* lxiii. 81.

The product always contains free sulphuric acid and unaltered alcohol, both when equal molecules are employed or when an excess of either compound is used, and even if the heating be carried on for any length of time. Hennell,[1] who used equal parts by weight of alcohol of specific gravity of 0·82 and oil of vitriol, found that 56 per cent. of the latter is converted into ethyl sulphuric acid. Berthelot,[2] in mixing equal molecules of acid and alcohol of 94 per cent. strength, obtained the following yields:

After 40 hours	56 per cent.
„ 90 „	57·4 „
„ 20 days	59 „
„ 147 „	58·8 „

When alcohol containing 20·7 per cent. of water was employed, the production of the acid went on much more slowly, and after a lapse of 147 days the liquid contained only 54·8 per cent. of ethyl sulphuric acid. On the other hand, by using absolute alcohol, the yield can, according to Claesson,[3] be raised to 77·4 per cent. This last-named chemist heated a mixture of alcohol and pure sulphuric acid on the water-bath, and employing, to one molecule of acid, varying quantities of alcohol, expressed in molecules, obtained to 100 parts of sulphuric acid the yields as noted below:

0·5	1	1·5	2	2·5	3	4
73·1	57·1	59·6	65	72	77·4	77·4.

From this it appears that, when equal molecules of acid and alcohol are employed, 57·1 per cent. of ethyl sulphuric acid is formed. This yield increases, however, with an increase in the quantity either of acid or of alcohol.

Ethyl sulphuric acid is also formed when sulphuric acid, warmed on a water-bath, is saturated with ether vapour:

$$2\,SO_4\left\{\begin{matrix}H\\H\end{matrix}\right. + (C_2H_5)_2O = 2\,SO_4\left\{\begin{matrix}H\\C_2H_5\end{matrix}\right. + H_2O.$$

In order to prepare ethyl sulphuric acid from the product obtained by one or other of these reactions, the mixture is allowed to cool completely, then several times its volume of water is added, and the whole is neutralized with barium

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[1] *Phil. Trans.* 1828, ii. 365.

[2] *Bull. Soc. Chim.* xix. 227.

[3] *Journ. Prakt. Chem.* [2], xix. 246.

carbonate or white-lead. In all these operations a rise of temperature must, as much as possible, be avoided. The solution of the barium salt is then carefully acted upon with the requisite quantity of sulphuric acid, or the lead salt is decomposed with sulphuretted hydrogen, and the filtered liquid evaporated in a vacuum over sulphuric acid. A colourless, oily, very acid liquid is thus obtained which has a specific gravity of 1·035 to 1·037. This is insoluble in ether, and is decomposed on long continued exposure to sulphuric acid in a vacuum. On heating a little ether is given off (Hennell, Sertürner). This is explained by the fact that the acid cannot be obtained quite anhydrous, inasmuch as some alcohol is formed, and this acts in the usual way on the ethyl sulphuric acid.

Its dilute aqueous solution decomposes slowly on standing, and quickly when warmed or boiled, into sulphuric acid and alcohol.

Anhydrous ethyl sulphuric acid is obtained, according to Claesson, by slowly dropping chlorsulphonic acid into well-cooled alcohol. Like the corresponding methyl compound, it is an oily liquid which does not adhere to the surface of glass.

THE ETHYL SULPHATES.

233 Ethyl sulphuric acid is a monobasic acid forming a series of salts, all of which are soluble in water, and usually crystallize well. Some are very stable compounds, whilst others decompose on standing. Their dilute solutions can be boiled without decomposition, but in concentrated solution they decompose with formation of alcohol, sulphuric acid, and a sulphate. This decomposition does not take place in the cases of the salts of the alkalis or alkaline earths, provided an excess of alkali be present.

Potassium Ethyl Sulphate, $K(C_2H_5)SO_4$, is obtained from the barium or calcium salt by double decomposition with potassium carbonate. It is usually obtained in tablets closely resembling those of boric acid, but when slowly crystallized, it yields large transparent monoclinic tables. At 17° it dissolves in 0·8 part of water. It is also soluble in spirit, but not in absolute alcohol, and deliquesces on exposure to moist air When fused with caustic potash, alcohol is formed, and, on heating with dilute sulphuric acid, ether is produced. This salt is frequently employed for the preparation of other ethyl compounds, because this, as well as other ethyl sulphates, when heated with salts of other acids, yields a new ethereal salt by replacement of the metal by ethyl.

Sodium Ethyl Sulphate, $Na(C_2H_5)SO_4 + H_2O$, is formed as a cauliflower-like deliquescent mass, which is soluble in alcohol.

Ammonium Ethyl Sulphate is easily soluble in water, alcohol, and ether, depositing from solution in large, colourless, deliquescent crystals, which fuse without decomposition at 62°.

Calcium Ethyl Sulphate, $Ca(C_2H_5SO_4)_2 + 2H_2O$, is obtained by saturating crude ethyl sulphuric acid with chalk. The solution thus obtained, which contains gypsum, may be conveniently used for the preparation of the foregoing salts. It crystallizes in tablets, and also in transparent monoclinic crystals, which are unalterable in the air and easily soluble in water.

Barium Ethyl Sulphate, $Ba(C_2H_5SO_4)_2 + 2H_2O$, is isomorphous with the calcium salt, and crystallizes in colourless glistening tables or prisms, which dissolve at 17° in 0·92 part of water, and is also soluble in spirit, but not in absolute alcohol, which on boiling removes from the salt one molecule of water.

Lead Ethyl Sulphate, $Pb(C_2H_5SO_4)_2 + 2H_2O$, crystallizes in large colourless tables, soluble in water and spirit. These lose water easily, and decompose slowly on keeping, with formation of lead sulphate, sulphuric acid, ether, and ethyl sulphate, for which reason the salt attains a pleasant smell. When its solution is saturated with lead hydroxide, a liquid having a neutral reaction is obtained, and this on evaporation in a vacuum leaves a residue of a basic salt, $(PbC_2H_5SO_4)_2O$, as an amorphous mass. This is much more permanent than the normal compound, although very hygroscopic and easily soluble in water.

Silver Ethyl Sulphate, $Ag(C_2H_5)SO_4 + H_2O$, forms small glistening tablets, readily soluble in spirit.

Besides the compounds above described, various other ethyl sulphates are known.

NORMAL ETHYL SULPHATE, $(C_2H_5)_2SO_4$.

234 This compound was examined by chemists in the last century, but its nature has only quite recently been ascertained. Formerly this ether was prepared by distilling spirit of wine with oil of vitriol. This operation was conducted in a retort heated in a sand-bath, and as soon as the ordinary

ether had come over, the receiver was changed and normal ethyl sulphate, or, as it was termed, wine-oil or *oleum vitrolii dulce*, collected. Concerning the formation and composition of this body, very different views were held. Towards the end of the last century it was generally assumed that wine-oil is ether rendered impure by the presence of a large quantity of sulphuric acid, for Wiegleb stated that common ether is obtained in large quantities when this substance is distilled with caustic potash. In the year 1797 the difference between wine-oil and common ether was distinctly pointed out by Fourcroy and Vauquelin, who assumed that the first compound stood in the same relation to ether as ether does to alcohol. This view was generally adopted until Hennell, in 1826, proved that the compound contains sulphuric acid, and that it is to be considered as a compound of this acid with carbon and hydrogen, in which the latter elements are present in the same relative quantities as in ether itself. He also showed that, when wine-oil is heated with water or with alkalis, sulphovinic acid is formed, whilst a liquid hydrocarbon is liberated. This in some cases crystallizes, and possesses the composition of olefiant gas. These facts were fully confirmed by the subsequent investigation of Serullas,[1] Marchand,[2] and Liebig.[3] Serullas found that, when wine-oil undergoes distillation, it yields the salts of ethyl sulphuric acid, and Liebig gave to it the formula $(C_2H_5)_2SO_4 + C_4H_8SO_3$, and termed it sulphovinate of wine-oil.

According to the recent experiments of Claesson,[4] wine-oil consists chiefly of ethyl sulphate, generally mixed with a larger or smaller quantity of the polymers of ethylene, a fact already observed by Hennell; this latter chemist distinguishing between wine-oil, a liquid boiling at 280°, and etherin, a solid crystalline mass obtained when the wine-oil is allowed to stand for some days.

The first attempt to obtain pure normal ethyl sulphate was made by Wetherill,[5] who passed the vapour of sulphur trioxide into ether or alcohol. He thus obtained a colourless liquid smelling like peppermint which decomposes on heating, and which, as Erlenmeyer afterwards showed, is a mixture of normal ethyl sulphate and ethyl isothionate, $C_2H_4\left\{\begin{matrix}OH\\SO_3C_2H_5\end{matrix}\right.$.

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[1] *Ann. Chim. Phys.* xxxix. 153.
[2] *Journ. Prakt. Chem.* xv. 8.
[3] *Pogg. Ann.* xxi. 40.
[4] *Journ. Prakt. Chem.* [2], xix. 255.
[5] *Ann. Chem. Pharm.* lxvi. 117.

Ethyl sulphate was first obtained in the pure state by Claesson in acting on alcohol with ethyl chlorsulphonate, a body which will be described immediately. He also prepared it by the action of sulphuric acid on absolute alcohol. If ice and then water be added to the cold mixture and the liquid shaken up with chloroform, the sulphate is dissolved and left behind on evaporation. Ethyl sulphate is also formed when silver sulphate is heated with ethyl iodide to 150°,[1] Claesson obtaining a satisfactory yield in this way.

Ethyl sulphate is a colourless liquid, insoluble in water, possessing a pleasant peppermint-like smell; it boils at 208° with slight decomposition, but may be distilled unaltered under diminished pressure. At 19° it possesses a specific gravity of 1·1837. It is only very slowly decomposed by cold water, but boiling water decomposes it more or less quickly according to the amount present, alcohol and ethyl sulphuric acid being first formed. If ethyl sulphate be heated with alcohol, the following reaction takes place:[2]

$$SO_4\left\{\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right. + \left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O = SO_4\left\{\begin{matrix}H\\C_2H_5\end{matrix}\right. + \left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O.$$

Ethyl Chlorsulphonate, $Cl.SO_2.OC_2H_5$, was first prepared by Kuhlmann,[3] and afterwards more carefully examined by Williamson[4] and Purgold.[5] According to the latter chemist, the compound is an oily, strongly smelling liquid, which can be distilled in a vacuum. The same compound is obtained purer and more readily, as was found by Müller,[6] by leading ethylene gas into chlorsulphonic acid. In order to purify the crude product, it is either distilled in a vacuum or mixed with ice-cold water and dried over anhydrous copper sulphate. The pure compound boils under ordinary pressure with slight decomposition at from 151° to 154° (Claesson). It has a penetrating pungent smell, and acts very violently upon the eyes. When absolute alcohol is allowed slowly to run into this compound, a violent reaction occurs, which, according to Claesson, may be represented as taking place in two directions:

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[1] Stempnewsky, *Ber. Deutsch. Chem. Ges.* xi. 514.

[2] Erlenmeyer, *Ann. Chem. Pharm.* clxii. 373.

[3] *Ann. Chem. Pharm.* xxxiii. 108.

[4] *Quart. Journ. Chem. Soc.* x. 97.

[5] *Ber. Deutsch. Chem. Ges.* vi. 502.

[6] *Ibid.* vi. 227.

$$(1)\ SO_2\left\{\begin{matrix}Cl\\ OC_2H_5\end{matrix}\right. + C_2H_5OH = SO_2\left\{\begin{matrix}OH\\ OC_2H_5\end{matrix}\right. + C_2H_5Cl.$$

$$(2)\ SO_2\left\{\begin{matrix}Cl\\ OC_2H_5\end{matrix}\right. + 2C_2H_5.OH = SO_2\left\{\begin{matrix}OH\\ OC_2H_5\end{matrix}\right. + \left.\begin{matrix}C_2H_5\\ C_2H_5\end{matrix}\right\}O + HCl.$$

If alcohol be added to ethyl chlorsulphonate, ethyl chloride, hydrochloric acid, and a small quantity of ethyl ether is formed, and a considerable quantity of ethyl sulphate:

$$SO_2\left\{\begin{matrix}Cl\\ OC_2H_5\end{matrix}\right. + HOC_2H_5 = SO_2\left\{\begin{matrix}OC_2H_5\\ OC_2H_5\end{matrix}\right. + HCl.$$

235 *Hydrogen Ethyl Selenate*, $H(C_2H_5)SeO_4$, is formed when equal parts of spirit of wine and concentrated selenic acid are heated together for some time to 100°. In order to purify the product, it is diluted with an equal volume of water, neutralized with lead carbonate, and allowed to evaporate to one-half in a vacuum. The greater portion of the lead is then thrown down in combination with selenic acid, and the rest precipitated as sulphide with sulphuretted hydrogen, and thus an aqueous, strongly acid liquid, containing ethyl selenic acid, is obtained. It very readily decomposes, and forms a series of salts which are also very prone to decomposition.[1]

Potassium Ethyl Selenate, $K(C_2H_5)SeO_4$, forms small talc-like tablets which possess a sweetish saline taste.

Lead Ethyl Selenate also crystallizes in tablets, and is so unstable that it has not been analyzed. If a solution of lead ethylsulphate be added to its solution and the mixture evaporated in a vacuum, tablets having the composition

$$3\,[Pb(C_2H_5SO_4)_2 + 2\,H_2O] + 2\,[Pb(C_2H_5SeO_4)_2 + 2\,H_2O]$$

are deposited. The normal ethyl selenate is not known.

ETHYL NITRITE, $C_2H_5NO_2$.

236 Raymond Lully is generally said to have been the discoverer of this compound, which was formerly known as nitric ether, and it is certainly true that he was acquainted with the violent action which nitric acid produces on alcohol, but in his process he allowed the ether to escape. Later chemists who speak of the *spiritus nitri dulcis s. dulcificatus*, understood by this term the residue which remains behind after the reaction. Hugens

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[1] Fabian, *Ann. Chem. Pharm.* Suppl. i. 241.

and Papin[1] showed that when alcohol and nitric acid are mixed together under the receiver of an air-pump, an elastic fluid is formed. Kunkel,[2] however, was the first to observe that a liquid which swims on the surface of water may be obtained from such a mixture. This observation remained unnoticed, because the so-called nitric ether, largely used as a medicine, was obtained by distilling a considerable quantity of alcohol with a small quantity of nitric acid, and was, therefore, only obtained in dilute alcoholic solution. Navier, a physician at Chalons sur Marne, observed in 1742 the fact already noticed by Kunkel, namely, that an ethereal smell is perceived when nitric acid and spirit of wine are mixed together, and that when a mixture of equal volumes of these liquids is placed in a vessel and allowed to stand for ten days, an ethereal liquid swims on the top. This fact was communicated to the French Academy by Duhamel in the above year, and the liquid thus produced was believed to be closely allied with Frobenius's ether.

Another method of preparing nitric ether which was afterwards largely employed, especially by Berzelius, was suggested by Black in 1769. It consists in pouring nitric acid, water, and spirit of wine into a tall vessel, in alternate layers one above the other, when nitric ether is formed by the gradual mixture of the liquids. Tielebein, in 1782, stated that the best yield was obtained when the process of Navier was adhered to, and strong nitric acid and spirit of wine mixed in the cold, the vessel being quickly closed. This proposal gave rise to the publication of a great number of receipts on the best means of preparing nitric ether, all of which, however, depended on the alcohol being gradually added to nitric acid, and the separation of the nitric ether, which is formed, from the rest of the liquid either by pouring off or by distillation.

The compound formed by this action of nitric acid on alcohol is, however, not ethyl nitrate as was formerly supposed, but ethyl nitrite, one part of the alcohol being oxidized, and the nitrogen trioxide, thus formed, combining with another part of the alcohol in the following way:

$$2\,C_2H_5OH + N_2O_3 = 2\,C_2H_5NO_2 + H_2O.$$

Ethyl nitrite thus obtained always contains oxidation-products of alcohol, especially aldehyde, and this turns alcoholic potash brown when shaken up with the liquid.

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[1] *Phil. Trans.* 1675

[2] *Epistola contra spiritum vini sine acido*, 1681.

penetrating ethereal smell, resembling apples or Hungarian wine, and a peculiar pungent taste. It boils at 18°, and has a specific gravity of 0·900 at 15°5 and a vapour density of 2·627 (Dumas and Boullay). When ignited in contact with air it burns with a bright white flame. The pure ether can be kept for many years without undergoing any change, but if impure, and especially if it contains water, it soon becomes acid and gradually evolves oxides of nitrogen in such quantities that the bottle containing it frequently bursts. Alkalis, especially in alcoholic solution, decompose it quickly with formation of alcohol. Ammonium sulphide acts violently upon it according to the following equation:

$$C_2H_5.O.NO + 3\,(NH_4)_2S = C_2H_5.OH + 7NH_3 + H_2O + 3S.$$

No trace of an ethyl-base is formed in this reaction (E. Kopp; Carey Lea).

The alcoholic solution of ethyl nitrite is known under the name of *spiritus aetheris nitrosi* and is used as a medicine. According to the British Pharmacopœia it is prepared as follows: To 1 pint of rectified spirit of wine add 2 fluid ounces of sulphuric acid, stirring them together: then add in the same way 2½ fluid ounces of nitric acid. Put the mixture into a retort into which 2 ounces of fine copper-wire (No. 25) has been introduced and into which a thermometer is fitted. Attach a condenser and apply gentle heat; let the spirit distil at a temperature from 170° to 175° (Fah.) until 12 fluid ounces have passed over. Then add half an ounce more nitric acid to the residue in the retort and distil as before until the whole product makes up fifteen ounces. Mix this with two pints of rectified spirit, or enough to bring the specific gravity to 0·845.

In former days this sweet spirit of nitre stood in high repute amongst physicians, and is now used as a pleasant and mild irritant.

Ethyl Nitrate, $C_2H_5NO_3$.

237 It has already been stated that common nitric acid acts as an oxidizing agent on alcohol, and the more violently the more nitrous acid it contains. Millon[1] showed in the year 1843 that this oxidizing action does not take place, and that nitric ether is formed, provided that the lower oxides of nitrogen

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[1] *Ann. Chim. Phys.* [3], viii. 233.

present in the nitric acid be destroyed by the addition of a small quantity of urea, the decomposition effected by the urea being:

$$CO(NH_2)_2 + 2\,HNO_2 = 3\,H_2O + CO_2 + 2\,N_2$$

In order to prepare ethyl nitrate according to Millon's process a mixture of 60 to 75 grams of spirit of specific gravity 0·854, and a like quantity of nitric acid of specific gravity 1·4, is distilled with 1 to 2 grams of nitrate of urea at a gentle heat. The receiver is changed as soon as ethyl nitrate begins to distil over instead of aqueous alcohol, and this point may be recognised by the peculiar odour of the distillate. When seven-eighths of this have come over, the operation is stopped, the distillate mixed with dilute caustic potash and water, and the ether dried over calcium chloride and rectified.

Carey Lea[1] has improved this method inasmuch as he dissolves from four to five times the quantity of urea recommended by Millon in warm alcohol, adding an equal quantity of nitric acid of specific gravity 1·401 and distils the mixture until one-fifth of the whole has passed over. To the residue, alcohol and nitric acid are again added, and these operations are repeated several times until the whole of the urea is decomposed.

According to Heintz[2] the best proportion is as follows: 80 grams of nitric acid of specific gravity 1·4 are warmed with some nitrate of urea, and to this, when it is cold, 60 grams of spirit of specific gravity 0·81 and 15 grams of nitrate of urea are added, and the mixture distilled to one-eighth. A similar method has been described by Bertoni[3] for the preparation of large quantities of the nitrate.

Ethyl nitrate is also formed, as Persoz[4] has shown, when to 20 grams of perfectly pure highly concentrated nitric acid cooled in a mixture of ice and salt, 10 grams of absolute alcohol are added drop by drop, the mixture being continually stirred. In order to separate the ether, ice is then added.

Chapman and Smith[5] have not found this method advantageous and have suggested the following. Two volumes of concentrated sulphuric acid and one volume of fuming nitric acid, of specific gravity 1·36, which has previously been heated

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[1] *Sillim. Amer. Journ.* [2], xxxii. 178; xxxiii. 86.

[2] *Ann. Chem. Pharm.* cxxvii. 43.

[3] *Ber. Deutsch. Chem. Ges.* ix. 1692.

[4] *Compt. Rend.* lv. 572.

[5] *Journ. Chem. Soc.* xx. 584.

with a small quantity of urea, are mixed together. To the cold mixture a few grams of urea are added, and then gradually one part of alcohol for every three parts of the mixture, the whole being then well stirred. The nitrate then separates out as a light layer. Champion[1] states that ethyl nitrate can be more simply obtained by bringing a cold mixture of one part of strong nitric acid and two parts of sulphuric acid into a well-cooled mixture of sulphuric acid and strong spirit.

Ethyl nitrate is also formed by the action of ethyl iodide on silver nitrate.[2]

Ethyl nitrate prepared according to one or other of these various processes, is well washed with water and dried over chloride of calcium or ignited carbonate of potash. It is a mobile liquid possessing a pleasant smell which however is quite different from that of the nitrite. It has a sweet taste, but a bitter after-taste. It boils at 86°·3, and has a specific gravity at 0° of 1·1322 (H. Kopp). When ignited it burns with a bright white flame. Whilst Millon was ascertaining the vapour density of nitric ether according to Dumas's method and attempted to seal the neck of the bulb containing the vapour, heated above its boiling point, with a blowpipe flame, a violent explosion took place which broke the bulb. The vapour, when heated to a lower temperature may, however, be inflamed without explosion. Concentrated caustic potash does not act at ordinary temperatures on ethyl nitrate, but an alcoholic solution quickly decomposes it with separation of crystals of nitre.

Phosphites and Phosphates of Ethyl.

238 *Hydrogen Ethyl Phosphite* or *Ethyl Phosphorous Acid*, $H_2(C_2H_5)PO_3$, is formed when phosphorus trichloride is allowed to fall drop by drop into well-cooled spirit of wine of specific gravity 0·850.[3]

$$PCl_3 + 2\,C_2H_5OH + H_2O = H_2(C_2H_5)PO_3 + C_2H_5Cl + 2\,HCl.$$

The solution is then gently heated in order to drive off the hydrochloric acid and chloride of ethyl, and the residue is allowed to evaporate to a syrupy consistency in a vacuum. The

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[1] *Compt. Rend.* lxxviii. 1150.

[2] Warster, *Ber Deutsch. Chem. Ges.* v. 406.

[3] Wurtz, *Ann. Chim. Phys.* [3], xvi. 218.

acid thus obtained very readily decomposes into alcohol and phosphorous acid. The salts, which however do not crystallize well, are more permanent than the acid. In order to obtain the barium salt, the acid solution is saturated with barium carbonate, and filtered from the barium phosphite. The other salts can be obtained from the barium salt by double decomposition.

Potassium Ethyl Phosphite forms a thick syrup.

Barium Ethyl Phosphite, Ba $\begin{cases} H(C_2H_5)PO_3 \\ H(C_2H_5)PO_3 \end{cases}$, is an amorphous deliquescent friable mass.

Lead Ethyl Phosphite, Pb $\begin{cases} H(C_2H_5)PO_3 \\ H(C_2H_5)PO_3 \end{cases}$, crystallizes in unctuous, shining scales, unalterable in the air. Its aqueous solution gradually deposits lead phosphite.

Normal Ethyl Phosphite, $(C_2H_5)_3PO_3$, is obtained by acting on absolute alcohol with phosphorus trichloride, or better by dissolving sodium in alcohol, evaporating to dryness, and gradually adding the calculated quantity of phosphorus trichloride. In order to diminish the violence of the reaction, which otherwise takes place with evolution of light, the mixture is diluted with five volumes of pure ether. The mixture is heated during the operation to the boiling point of ether, until no further acid vapours are evolved. The ether is then distilled off on a water-bath, and the ethyl phosphite is obtained by subsequent distillation from an oil-bath. It is purified by rectification in a current of hydrogen as it undergoes oxidation in the air.[1]

Ethyl phosphite is a colourless disagreeably smelling liquid which boils in an atmosphere of hydrogen at 188° and in the air at 191°. It has a specific gravity of 1·075 at 15°·5, is easily inflammable and burns with a bluish-white flame. It is not only soluble in spirit of wine, but also in water. Heated with the exactly requisite quantity of baryta it forms alcohol and *barium diethyl phosphite* $[PO_3(C_2H_5)_2]_2Ba$, which remains as a deliquescent crystalline mass. Other diethyl phosphites may be obtained from this by double decomposition; these are all soluble and difficultly or non-crystallizable. When diethyl phosphite is heated with an excess of baryta solution the soluble barium salt of dibasic ethyl phosphoric acid, $PO_3(C_2H_5)Ba$, crystallizes out. The other salts of this acid do not crystallize. The existence of two ethyl phosphoric acids, the one monobasic

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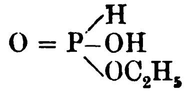
[1] Railton, *Chem. Soc. Journ.* vii. 216.

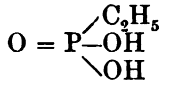
(Wurtz) and the other dibasic (Railton), can be explained by the following formulæ:

Wurtz's Acid.



$$O = P\begin{cases} H \\ OH \\ OC_2H_5 \end{cases}$$

Railton's Acid.



$$O = P\begin{cases} C_2H_5 \\ OH \\ OH \end{cases}$$

According to this, the latter acid should be identical with ethyl phosphinic acid obtained by oxidizing ethyl phosphine, but this is not the case. Whilst the latter is a very stable compound, the dibasic ethyl phosphoric acid cannot be isolated, and if the barium salt be boiled with water, barium phosphite and alcohol are formed. These compounds require re-investigation.

Chloride of Ethyl Phosphorous Acid, $P(OC_2H_5)Cl_2$, is formed when absolute alcohol is allowed to run into the calculated quantity of phosphorus trichloride.[1] It is a strongly refracting fuming liquid, boiling at 117° and having a specific gravity at 0° of 1·316. Water acts violently upon it with formation of phosphorous acid, hydrochloric acid and alcohol. By the further action of alcohol it is transformed into the compound $P(OC_2H_5)_2Cl$.

The three compounds obtained by the action of phosphorus trichloride on alcohol, yield with chlorine or bromine, the ethyl group in the form of haloid salt:

$$P(OC_2H_5)_3 + Cl_2 = PO(OC_2H_5)_2Cl + C_2H_5Cl.$$

In this case the chloride of diethylphosphoric acid is obtained, whilst the chloride of diethylphosphorous acid yields dichloride of ethylphosphoric acid, $PO(C_2H_5O)Cl_2$, and the chloride of ethyl phosphorous acid is converted into phosphorus oxychloride.[2]

Acid Ethyl Pyrophosphite, $O\left\{\begin{array}{l} P(OC_2H_5)OH \\ P(OC_2H_5)OH \end{array}\right.$, is not known in the free state, but its zinc salt is produced together with other products when zinc ethyl is heated to 140° with phosphorus pentoxide. The barium salt has the composition $P_2O_5(C_2H_5)_2Ba$.[3]

239 *Phosphates of Ethyl.* Tribasic orthophosphoric acid forms three ethyl compounds, two acid and one normal.

$$PO\left\{\begin{array}{l} OH \\ OH \\ OC_2H_5 \end{array}\right. \qquad PO\left\{\begin{array}{l} OH \\ OC_2H_5 \\ OC_2H_5 \end{array}\right. \qquad PO\left\{\begin{array}{l} OC_2H_5 \\ OC_2H_5 \\ OC_2H_5. \end{array}\right.$$

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[1] Mentschutkin, *Ann. Chem. Pharm.* cxxxix. 343.

[2] Wichelhaus, *Ann. Chem. Pharm.* Suppl. vi. 257.

[3] Dilling, *Zeitsch. Chem.* [2], iii. 266.

Ethyl Phosphoric Acid, $PO_2C_2H_5(OH)_2$, was discovered in 1820 by Lassaigne[1] and afterwards investigated by Pelouze[2] and Liebig.[3] In order to prepare it, equal parts of vitreous phosphoric acid and strong spirit are heated for some minutes to from 60° to 80°. After standing for twenty-four hours the liquid is diluted with eight volumes of water, neutralized with barium carbonate, and boiled in order to drive off the excess of alcohol. When the liquid has cooled down to 70°, it is filtered and allowed to stand in order that the barium salt may crystallize out. The aqueous solution is then decomposed with the requisite quantity of sulphuric acid. The lead salt may also be prepared, and this decomposed by sulphuretted hydrogen. The filtrate is first evaporated over a lamp, and is then concentrated by standing over sulphuric acid. An oily odourless liquid is thus obtained which possesses a biting acid taste. When heated, it evolves the vapours of alcohol and ether, and afterwards ethylene gas. Its aqueous solution may be concentrated by boiling up to a certain point without decomposition ensuing.

Ethyl phosphoric acid is also formed when ether is treated with concentrated phosphoric acid.[4] It may also be prepared by acting with phosphorus oxychloride on aqueous spirit (Schiff), as well as by the action of iodine and phosphorus in the preparation of ethyl chloride (Reynoso).

The *ethyl phosphates* of the alkaline metals are deliquescent, and crystallize imperfectly.

Barium Ethyl Phosphate, $BaC_2H_5PO_4$, crystallizes in short quadratic prisms or six-sided tables, and possesses an unpleasant bitter saline taste. It loses its water of crystallization at 120°. Its solution saturated at 40° deposits crystals both on cooling and on heating.

Lead Ethyl Phosphate, $PbC_2H_5PO_4 + H_2O$, is the least soluble of all the ethyl phosphates, and is therefore easily obtained by precipitating the foregoing salts with sugar of lead. It can be obtained in the crystalline state from solution in boiling water.

Arsenic Ethyl Phosphate, $As_2(C_2H_5PO_4)_3$, is formed by dissolving arsenic trioxide in a boiling solution of the acid, and forms fine feathery needles.

Chloride of Ethyl Phosphoric Acid, $PO_2(C_2H_5)Cl_2$, is not only formed by the methods above described, but also when equal

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[1] *Ann. Chim. Phys.* [2], xiii. 294.

[2] *Ib.* lii. 37.

[3] *Ann. Pharm.* vi. 149.

[4] Vögeli, *Ann. Chem. Pharm.* lxix. 180.

molecules of alcohol and phosphorus trichloride are allowed to act upon one another. It is an oily, readily decomposable substance, which, when distilled in a current of hydrogen, boils pretty constantly at 167°.

Diethyl Phosphoric Acid, $H(C_2H_5)_2PO_4$. In order to prepare this acid, phosphorus pentoxide is allowed to deliquesce under a bell-jar in the vapours of anhydrous alcohol or ether. After one or two weeks a syrupy liquid is formed which contains the above compound, together with phosphoric acid, ethyl phosphoric acid, and frequently traces of triethyl phosphine. The easily soluble lead diethyl phosphate is then prepared, and this decomposed by sulphuretted hydrogen, the filtrate being allowed to evaporate in a vacuum over sulphuric acid, when the acid is obtained as a non-crystallizable syrup. The *diethylphosphates* are soluble in water and easily crystallizable.

Lead Diethyl Phosphate, $Pb(C_2H_5)_4(PO_4)_2$. If the impure acid obtained as above described be saturated with white-lead, and the filtrate evaporated, tablets of a difficultly soluble lead salt first separate out, and the solution becomes acid. If this be again neutralized with white-lead, an insoluble lead precipitate is thrown down, and the filtrate yields on evaporation crystals of lead diethylphosphate, which may be purified by recrystallization. The salt is deposited in needles easily soluble in water and in hot spirit. They melt at 180°, and the fused salt cools to a stellar crystalline mass.

Chloride of Diethylphosphoric Acid, $PO_3(C_2H_5)_2Cl$, has been already mentioned (see p. 363). It is formed by the action of phosphorus oxychloride on the calculated quantity of alcohol, and is a liquid decomposing on distillation.

Normal Ethyl Phosphate, $(C_2H_5)_3PO_4$, was first obtained by Vögeli by heating lead diethyl phosphate to 190°:

$$Pb(C_2H_5)_4(PO_4)_2 = (C_2H_5)_3(PO_4) + PbC_2H_5PO_4.$$

It is also formed when silver phosphate is heated to 100°[1] with ethyl iodide, as well as when phosphorus oxychloride,[2] or pentachloride[3] acts on sodium ethylate or absolute alcohol:[4]

$$POCl_3 + 3\,HO.C_2H_5 = PO(OC_2H_5)_3 + 3\,HCl.$$

It has already been stated that small quantities of these

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[1] Clermont, *Ann. Chim. Phys.* [3], xliv. 330.

[2] Limpricht, *Ann. Chem. Pharm.* cxxxiv. 347.

[3] Geuther and Bischoff, *Journ. Prakt. Chem.* [2], vii. 101.

[4] Schiff, *Ann. Chem. Pharm.* ci. 299.

compounds are also formed when alcohol vapour acts upon phosphorus pentoxide. If the reaction be allowed to take place quickly, a considerable quantity is formed. According to Carius[1] the pentoxide should be mixed with three or four times its volume of anhydrous ether, and then half the theoretical quantity of alcohol added, and the ethyl phosphate separated from the diethylphosphoric acid by distillation.

Ethyl phosphate is a colourless liquid possessing a peculiar pleasant smell and a burning taste, having at 12° a specific gravity of 1·072 and boiling at 215°, though towards the end of the distillation the boiling-point reaches as high as 240°, and a black acid residue remains. In a current of hydrogen, on the other hand, it boils constantly at 203° (Wichelhaus). It is miscible with water, and the solution soon becomes acid with formation of diethylphosphoric acid (Carius); this decomposition takes place, however, very slowly (Limpricht).

Ethyl Pyrophosphate, $(C_2H_5)_4P_2O_7$, is obtained by heating silver pyrophosphate with ethyl iodide to 100°, as an oily liquid possessing a peculiar smell and a burning taste. It is soluble in water, alcohol, and ether, and its aqueous solution soon becomes acid.[2]

THE ARSENITES, ARSENATES, AND BORATES OF ETHYL.

240 *Ethyl Arsenite*, $(C_2H_5)_3AsO_3$, is formed by the action of ethyl iodide on silver arsenite, as well as by heating together ethyl silicate and arsenic trioxide to 200°, when silica or an ethyl polysilicate separates out. It is, however, best obtained by treating arsenic tribromide with sodium ethylate, an excess of the latter substance being carefully avoided, as it acts at once upon the ethereal salt with formation of common ether. In order to decompose the excess of arsenic tribromide, the resulting material is treated with dry ammonia, which unites with the bromide to form a compound insoluble in spirit and in ether. It is then filtered off, and the arsenite purified by distillation. It is a colourless liquid boiling at 165° to 166°, and having a specific gravity of 1·224 at 0°. It is quickly decomposed by water, with separation of arsenic trioxide.[3]

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[1] Carius, *Ann. Chem. Pharm.* cxxxvii. 121.

[2] Clermont, *Ann. Chem. Pharm.* xci. 375.

[3] Clermont, *Bull. Soc. Chim.* [2], viii. 206; xiv. 99.

Ethyl Arsenate, $(C_2H_5)_3AsO_4$, is obtained by heating silver arsenate to 100° with the calculated quantity of iodide of ethyl diluted with ether. It is a colourless liquid, which boils under the ordinary atmospheric pressure, with slight decomposition at 235° to 238°, but may be distilled in a vacuum without decomposition. It dissolves in water with decomposition, the solution yielding all the reactions of arsenic acid.[1]

Ethyl Orthoborate, $(C_2H_5)_3BO_3$, was discovered by Ebelmen in 1845, and investigated by this chemist and Bouquet. They obtained it by saturating alcohol with gaseous boron trifluoride.[2] These experiments were afterwards corroborated by Bowman,[3] and H. Rose noticed that ethyl borate could also be easily prepared by distilling a mixture of two parts of anhydrous borax and three parts of potassium ethyl sulphate.[4] Frankland employed this reaction in his investigation on the organic compounds containing boron,[5] and found that from the distillate, which contains a large quantity of alcohol, ethyl borate could be best separated by the addition of one-fourth part its weight of fused calcium chloride; after this has dissolved, two layers of liquid make their appearance, of which the upper one contains the whole of the ethereal salt, and this can be purified by fractional distillation. It also is formed by heating boron trioxide with alcohol for some time to 120°, and may be readily obtained from the portion of the distillate coming over above 100°, by addition of a small quantity of sulphuric acid.

Ethyl borate is a thin colourless liquid boiling at 120°, having a specific gravity of 0·861 at 26°·5, a vapour density of 5·14, and burning with a green flame. It has a peculiar pleasant smell and a hot bitter taste. It is easily decomposed by water, with separation of boric acid. When heated with boric trioxide, *ethyl metaborate*, $(C_2H_5)_2B_2O_4$, is formed as a thick colourless liquid, converted at 200° into orthoborate and *ethyl triborate*, $C_2H_5B_3O_5$. This latter is a gummy mass, which, like the other borates is decomposed by water, with separation of boric acid.[6]

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[1] Clermont, *Bull. Soc. Chim.* [2], viii. 206; xiv. 99.

[2] *Ann. Chim. Phys.* [3], xvii. 55.

[3] *Phil. Mag.* [3], xxix. 546.

[4] *Pogg. Ann.* xcviii. 245.

[5] *Ann. Chem. Pharm.* cxxiv. 129; *Phil. Trans.* 1862, 167.

[6] Schiff, *Ann. Chem. Pharm.* Suppl. v. 154.

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[1] Carius, *Ann. Chem. Pharm.* cxxxvii. 121.

[2] Clermont, *Ann. Chem. Pharm.* xci. 375.

[3] Clermont, *Bull. Soc. Chim.* [2], viii. 206; xiv. 99.

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[1] Clermont, *Bull. Soc. Chim.* [2], viii. 206; xiv. 99.

[2] *Ann. Chim. Phys.* [3], xvii. 55.

[3] *Phil. Mag.* [3], xxix. 546.

[4] *Pogg. Ann.* xcviii. 245.

[5] *Ann. Chem. Pharm.* cxxiv. 129; *Phil. Trans.* 1862, 167.

[6] Schiff, *Ann. Chem. Pharm.* Suppl. v. 154.

ETHYL SILICATES.

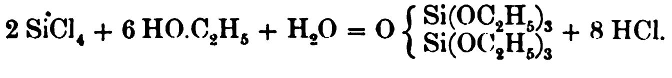
241 *Ethyl Orthosilicate*, $(C_2H_5)_4SiO_4$, is formed, as Ebelmen[1] has shown, by the action of silicon chloride on absolute alcohol. It is a mobile pleasantly smelling liquid, having a strong taste of peppermint, boiling at 165°·5, and having at 0° a specific gravity of 0·9676. This ethereal salt is easily inflammable, burning with a brilliant white flame, depositing clouds of very finely divided silica, which is insoluble in alkali. It is slightly attacked by water, in which it is insoluble. On exposure to moist air, it gradually decomposes, and a small quantity which Friedel and Crafts[2] had kept for three years in a badly stoppered bottle was completely converted into a mass of silicic acid, which was so hard that it scratched glass. Absolute alcohol dissolves this ethereal salt without alteration, and aqueous spirit decomposes it quickly, with formation of ethyl polysilicates. When ethyl silicate is heated with silicon chloride in a closed tube to 150°, one or other of the following chlorhydrins are formed, according to the quantities of the constituents present:

	Boiling-point.
$Si(OC_2H_5)_3Cl$	155°·7 to 157°
$Si(OC_2H_5)_2Cl_2$. . . .	136° to 138°
$Si(OC_2H_5)Cl_3$	103° to 105°

These compounds are colourless liquids, easily decomposed by water, and converted by the action of ethyl alcohol into ethyl silicate, whilst the other alcohols give mixed ethers, as, for example, the following:

	Boiling-point.
$Si(OC_2H_5)_3OCH_3$. . . .	155° to 157°
$Si(OC_2H_5)_2(OCH_3)_2$ . .	143° to 147°
$Si(OC_2H_5)(OCH_3)_2$. . .	133° to 135°

Ethyl Disilicate, $(C_2H_5)_6Si_2O_7$, is formed by the action of silicon chloride on alcohol containing a small quantity of water, and is hence usually formed in the preparation of the orthosilicate:



$$2\,SiCl_4 + 6\,HO.C_2H_5 + H_2O = O\left\{\begin{matrix} Si(OC_2H_5)_3 \\ Si(OC_2H_5)_3 \end{matrix}\right. + 8\,HCl.$$

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[1] *Ann. Chim. Phys.* [3], xvi. 144.

[2] *Bull. Soc. Chim.* v. 174, 238.

It is an oily liquid, resembling the orthosilicate in its smell; is easily inflammable, boils between 233° and 234°, and possesses at 0° a specific gravity of 1·0196 (Friedel and Crafts).

Ethyl Metasilicate, $(C_2H_5)_2SiO_3$. This is formed, according to Ebelmen, by the action of silicon chloride on aqueous alcohol. It is a slightly smelling liquid, which boils at 350°, and is decomposed by water. Heated with a small quantity of water, a gummy mass is obtained, which on cooling forms a glassy solid, and is said to have the composition $(C_2H_5)_2Si_2O_5$. Friedel and Crafts were unable to obtain this compound.

ETHYL CARBONATES.

242 *Hydrogen Ethyl Carbonate* or *Ethylcarbonic Acid,* $H(C_2H_5)CO_3$. This compound is not known in the free state, but its corresponding potassium salt has been obtained by Dumas and Peligot[1] by passing dry carbon dioxide into a solution of caustic potash in absolute alcohol, the solution being well cooled:

$$CO_2 + C_2H_5.OH + KOH = CO\left\{\begin{array}{l}OK\\OC_2H_5\end{array}\right. + H_2O.$$

At the same time both normal and acid potassium carbonate are formed. In order to separate these, the liquid, as soon as a considerable quantity of precipitate has been formed, is shaken with an equal volume of ether and the solid mass collected on a filter. From this mass absolute alcohol dissolves only the ethyl potassium carbonate, and this may be obtained, on addition of ether, in the form of a pearly crystalline precipitate, which is decomposed slowly by aqueous alcohol, but quickly by water:

$$CO\left\{\begin{array}{l}OK\\OC_2H_5\end{array}\right. + H_2O = CO\left\{\begin{array}{l}OK\\OH\end{array}\right. + HO.C_2H_5.$$

The corresponding sodium compound is formed, according to Beilstein, as a white precipitate, when carbon dioxide acts, on an alcoholic solution of sodium ethylate,[2] and when normal ethyl carbonate is heated with sodium ethylate to 120° (Geuther):

$$CO\left\{\begin{array}{l}OC_2H_5\\OC_2H_5\end{array}\right. + O\left\{\begin{array}{l}C_2H_5\\Na\end{array}\right. = CO\left\{\begin{array}{l}ONa\\OC_2H_5\end{array}\right. + O\left\{\begin{array}{l}C_2H_5\\C_2H_5.\end{array}\right.$$

Normal Ethyl Carbonate, $(C_2H_5)_2CO_3$. This body was discovered by Ettling[3] in 1836, and obtained by him, tog

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[1] *Ann. Chim. Phys.* lxxiv. 9.

[2] *Ann. Chem. Pharm.* cxli

[3] *Ann. Pharm.* xix. 17.

with carbon monoxide and other products, by heating pure ethyl oxalate, $(C_2H_5)_2C_2O_4$, with sodium. Cahours[1] then showed that it was also formed when the metal potassium was employed.

This peculiar reaction has not as yet found any satisfactory explanation. Ethyl oxalate is indeed distinguished from ethyl carbonate by an increment of CO, but as in the formation of this latter compound the alkali metal disappears, the decomposition cannot, as Gmelin[2] remarks, be explained by the supposition of a catalytic action. Hence it is probable that the following reaction takes place:

$$2\,(C_2H_5)_2C_2O_4 + Na_2 = (C_2H_5)_2CO_3 + 2\,C_2H_5ONa + 3\,CO.$$

The other products which have been observed are formed by the action of sodium ethylate on ethyl oxalate. Geuther,[3] who has investigated this subject carefully, states that oxalic ether can also be converted into ethyl carbonate when it is treated with sodium ethylate, and Dittmar and Cranston[4] came to the same conclusion, finding that, when one molecule of sodium ethylate was used with four molecules of ethyl oxalate, three molecules of ethyl carbonate, and three molecules of carbon dioxide, together with about 0·4 molecule of alcohol, as well as other products not exactly examined, were formed. According to Geuther, ethyl formate is also produced, as well as a small quantity of a crystalline acid and two different brown amorphous bodies having an acid character.

Ethyl carbonate is prepared by distilling a mixture of ethyl potassium carbonate and ethyl potassium sulphate,[5] as well as by acting on ethyl iodide with silver carbonate.[6] It is a colourless, pleasantly smelling liquid, boiling at 126°, and having a specific gravity of 0·9998 at 0° (Kopp) and a vapour density of 4·09 (Cahours). It is easily inflammable, burning with a blue flame. Treated with chlorine, it yields substitution-products, of which the last is perchlorethyl carbonate, $(C_2Cl_5)_2CO_3$.[7] This crystallizes in small white needles, which have a faint smell, melt at 85°—86°, and may be partially distilled without decomposition, though yielding at the same time carbon dioxide, hexchlorethane, and trichloracetyl chloride.[8]

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[1] *Ann. Pharm.* xlvii. 291.

[2] *Handbook*, ix. 182.

[3] *Zeitsch. Chem.* 1868, 652.

[4] *Journ. Chem. Soc.* [2], vii. 441.

[5] Chancel, *Compt. Rend.* xxxii. 587.

[6] Clermont, *ib.* xxxix. 338.

[7] Cahours, *Ann. Chem. Pharm.* xlvii. 294.

[8] Malaguti, *Ann. Chim. Phys.* [3], xvi. 30.

$$CO\left\{\begin{matrix}OC_2Cl_5\\OC_2Cl_5\end{matrix}\right. = C_2Cl_6 + CO_2 + CCl_3.COCl.$$

Ethyl Orthocarbonate, $C(OC_2H_5)_4$, was discovered by Basset,[1] who prepared it by the action of sodium on a solution of chloropicrin in absolute alcohol:

$$4NaOC_2H_5 + CCl_3.NO_2 = C(OC_2H_5)_4 + 3NaCl + NaNO_2.$$

It is an aromatic-smelling liquid, boiling at 158°—159°, and easily decomposed by alcoholic potash, with formation of potassium carbonate. When heated for six hours with boron trioxide to 100°, the following reaction takes place:[2]

$$(C_2H_5)_4CO_4 + 2\,B_2O_3 = (C_2H_5)_2CO_3 + (C_2H_5)_2B_4O_7.$$

Ethyl Chlorocarbonate, $CO\left\{\begin{matrix}Cl\\OC_2H_5\end{matrix}\right.$. This compound was first obtained in 1833, by Dumas,[3] by the action of carbonyl chloride on absolute alcohol:

$$CO\left\{\begin{matrix}Cl\\Cl\end{matrix}\right. + HO.C_2H_5 = CO\left\{\begin{matrix}Cl\\OC_2H_5\end{matrix}\right. = HCl.$$

It is a colourless mobile liquid, boiling at 94°, and having a specific gravity of 1·133 at 15°. It possesses a suffocating and irritating odour, but if the vapour be mixed with a large quantity of air, it possesses a pleasant smell. In contact with warm water, partial decomposition occurs, with formation of hydrochloric acid, and with alcohol it decomposes slowly, with formation of ethyl carbonate.[4] This last ether is also formed when ethyl chlorocarbonate is treated with sodium:

$$2\,CO\left\{\begin{matrix}Cl\\OC_2H_5\end{matrix}\right. + Na_2 = CO\left\{\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix}\right. + CO + 2\,NaCl.$$

A similar reaction also occurs when this chloro-ether is acted upon with sodium ethyl carbonate:[5]

$$CO\left\{\begin{matrix}Cl\\OC_2H_5\end{matrix}\right. + CO\left\{\begin{matrix}OC_2H_5\\ONa\end{matrix}\right. = CO\left\{\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix}\right. + CO_2 + NaCl.$$

243 *Ethyl Carbamate*, $CO\left\{\begin{matrix}NH_2\\OC_2H_5\end{matrix}\right.$ was obtained by Dumas,[6] in

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[1] *Journ. Chem. Soc.* [2], ii. 198; *Ann. Chem. Pharm.* cxxxii. 54.

[2] *Ann. Chim. Phys.* [2], liv. 226; *Ann. Pharm.* x. 277.

[3] Butlerow, *Zeitsch. Chem.* 1863, 484.

[4] Wilm and Wischin, *Ann. Chem. Pharm.* cxlvii. 150.

[5] Wyss, *Ber. Deutsch. Chem. Ges.* ix. 847.

[6] *Ann. Chim. Phys.* liv. 225.

1833, by acting with ethyl chlorocarbonate on ammonia, and he termed it urethane, because it may be considered as a compound of urea with ethyl carbonate. This name was afterwards changed in accordance with the usually adopted nomenclature for the carbamine salts. Ethyl carbamate is also formed when the carbonate is allowed to remain in contact with cold ammonia, whilst when heated, urea is formed.[1] It is also produced by the action of cyanogen chloride on alcohol.[2]

$$ClCN + 2\,C_2H_5OH = C_2H_5Cl + \left.\begin{matrix} NH_2 \\ C_2H_5O \end{matrix}\right\} CO.$$

Ether may be also employed instead of alcohol, the reaction then taking place slowly.[3] It is also formed together with ethyl allophanate, when the vapour of cyanic acid is passed into alcohol or ether:[4]

$$HO.CN + C_2H_5.OH = \left.\begin{matrix} NH_2 \\ C_2H_5O \end{matrix}\right\} CO.$$

In order to prepare this compound, ethyl carbonate is allowed to remain in contact with an equal volume of aqueous ammonia until the ether has all dissolved, and then the liquid is allowed to evaporate in a vacuum. In this way fine transparent crystals are obtained, easily soluble in water and alcohol. Ethyl carbamate melts below 100°, and on cooling, again solidifies to a spermaceti-like mass. When perfectly dry, it boils without decomposition at 180°, subliming, however, at a lower temperature. In the moist state it partially decomposes on heating, with formation of ammonium carbonate.

Ethylamidomethyl Carbonate, $CO\left\{\begin{matrix} N(CH_3)H \\ OC_2H_5 \end{matrix}\right.$, is formed by acting on ethyl chlorocarbonate with a strong aqueous solution of methylamine. It is a colourless not unpleasantly smelling ethereal liquid, lighter than water, and boiling at 170°. The ether produced in a corresponding way from ethylamine is a very similar body, boiling between 175-6°.[5]

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[1] Cahours, *Compt. Rend.* xxi. 129.
[2] Wurtz, *Compt. Rend.* xxii. 503.
[3] Cloëz, *Inst.* 1857, 207
[4] Liebig and Wohler, *Ann. Chem. Pharm.* liv. 370; lviii. 260.
[5] Schreiner, *Journ. Prakt. Chem.* [2], xxi 121.

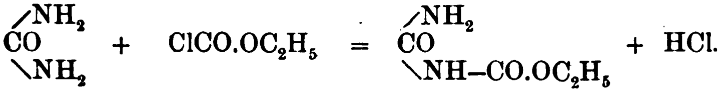
ETHYL ALLOPHANATE, $C_2N_2H_3O_3.C_2H_5$.

244 This ether was first obtained by Liebig and Wöhler, in 1830, by passing the vapour of cyanic acid into alcohol, and described by them under the name of cyanic ether.[1] Fifteen years later they found that this compound contains neither cyanic acid nor cyanuric acid, but a new acid, for which they proposed the name of allophanic acid, because it is a substance different from that which from its mode of formation might have been expected.[2] Absolute alcohol absorbs the vapour of cyanic acid with such avidity that the liquid begins to boil. Hence it is best to dilute the alcohol with an equal volume of ether, and to allow the saturated liquid to stand for twenty-four hours, when the compound crystallizes out in fine prisms, having a pearly lustre. These are best obtained by saturating ether with cyanic acid, evaporating, and then adding 95 per cent. spirit, and allowing the solution to stand.

Ethyl allophanate is also formed when a solution of potassium cyanate in aqueous alcohol is acidified,[3] as likewise, together with ethyl carbonate, when ethyl chlorocarbonate is brought into contact with potassium cyanate and absolute alcohol:[4]

$$\begin{aligned}2\,ClCO_2C_2H_5 + 2\,KOCN + 3\,HOC_2H_5 &= 2\,KCl\\ &+ 2\,(C_2H_5O)_2CO + C_2H_3N_3O_3C_2H_5.\end{aligned}$$

Ethyl allophanate is tasteless and odourless, only slightly soluble in cold water, alcohol, and ether, but more soluble in the warm liquids. It also dissolves without alteration in hot nitric acid and dilute sulphuric acid. It melts at 190-1°, and decomposes when it is allowed to stand at this temperature for some time, with formation of alcohol and cyanuric acid (Amato). Its constitution is recognised by the fact that it is also formed when ethyl chlorocarbonate acts upon urea:[5]



$$CO\begin{cases}NH_2\\ NH_2\end{cases} + ClCO.OC_2H_5 = CO\begin{cases}NH_2\\ NH{-}CO.OC_2H_5\end{cases} + HCl.$$

It is also formed by the direct union of cyanic acid and ethyl

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[1] *Pogg. Ann.* xx. 396.

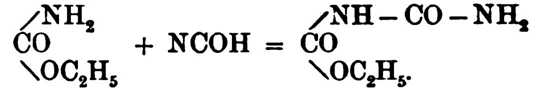
[2] *Ann. Chem. Pharm.* lix. 291.

[3] Amato, *Gazz. Chim. Ital.* iii. 469.

[4] Wilm, *Liebig's Ann.* cxcii. 24[illegible]

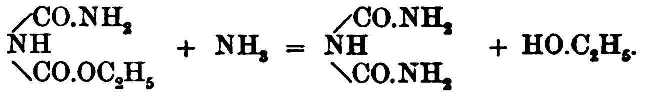
[5] Wilm and Wischin, *Ann. Chem. Pharm.* cxlvii. 150.

carbamate, which is the first product of the action of cyanic acid on alcohol (par. 243).[1]



$$\begin{array}{l}\diagup NH_2\\ CO\\ \diagdown OC_2H_5\end{array} + NCOH = \begin{array}{l}\diagup NH-CO-NH_2\\ CO\\ \diagdown OC_2H_5.\end{array}$$

On the other hand, the allophanate is decomposed into two molecules of ethyl carbamate by heating it with spirits of wine to 160°. If ethyl allophanate be heated with ammonia to 100° biuret is formed:

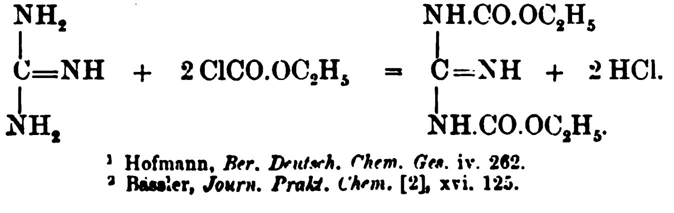


$$\begin{array}{l}\diagup CO.NH_2\\ NH\\ \diagdown CO.OC_2H_5\end{array} + NH_3 = \begin{array}{l}\diagup CO.NH_2\\ NH\\ \diagdown CO.NH_2\end{array} + HO.C_2H_5.$$

Hence biuret (Vol. I. p. 652) is the amide of allophanic acid, a substance which does not exist in the free state, although a series of ethers and a few unstable salts are known. These latter are obtained by the action of alkalis and alkaline earths upon the ethers, and their aqueous solutions decompose very easily on heating with formation of urea.

Diethyl Cyanamidocarbonate, $N(CN)(CO.OC_2H_5)_2$, is formed by the action of ethyl chlorocarbonate on sodium cyanamide (Vol. I. p. 676). It is easily soluble in alcohol, separating from the solution in large glistening crystals. When heated with sodium ethylate the sodium salt, $N(CN)(CO.OC_2H_5)Na$, is formed, crystallizing in glistening crystals which melt at 241°. Concentrated sulphuric acid acting upon this latter compound, yields the *monethyl ether*, $N(CN)(CO.OC_2H_5)H$, a yellowish syrupy liquid having an acid reaction and a burning taste. This is decomposed by boiling water into carbon dioxide and alcohol. If the sodium salt be heated with ethyl iodide, an ether is formed, having the composition $N(CN)(CO.OC_2H_5)C_2H_5$; this is an oily liquid boiling at about 213°.[2]

Diethyl Guanidine Carbonate, $CNH(NH.CO.O.C_2H_5)_2$, is formed by the action of ethyl chlorocarbonate on guanidine (Vol. I. p. 680):



$$\begin{array}{l}NH_2\\ |\\ C{=}NH\\ |\\ NH_2\end{array} + 2\,ClCO.OC_2H_5 = \begin{array}{l}NH.CO.OC_2H_5\\ |\\ C{=}NH\\ |\\ NH.CO.OC_2H_5.\end{array} + 2\,HCl.$$

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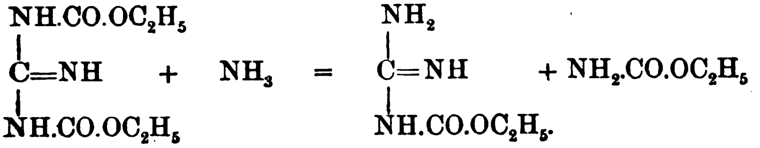
[1] Hofmann, *Ber. Deutsch. Chem. Ges.* iv. 262.

[2] Bässler, *Journ. Prakt. Chem.* [2], xvi. 125.

This compound is insoluble in water, but dissolves readily in alcohol, crystallizing in colourless crystals melting at 162°. When heated with alcoholic ammonia to 100°, the monethyl compound of urethane is produced:



$$\begin{array}{l} NH.CO.OC_2H_5 \\ | \\ C{=}NH \\ | \\ NH.CO.OC_2H_5 \end{array} + NH_3 = \begin{array}{l} NH_2 \\ | \\ C{=}NH \\ | \\ NH.CO.OC_2H_5. \end{array} + NH_2.CO.OC_2H_5$$

This monethyl ether is a powerful base, crystallizing from aqueous solution in rhombic tablets and forming a series of well-crystallizable salts.[1]

ETHYL FORMATE, $C_2H_5CHO_2$.

245 In the communication already referred to under formic acid, Arfvedson, in 1777, states that when formic acid is distilled with spirit of wine, oily drops of a liquid appear, the properties of which he did not further investigate. Five years later Bucholz obtained this ether in the same way, separating it from the alcoholic distillate by means of water.

According to Kopp[2] ethyl formate is best prepared by bringing 8 parts of anhydrous sodium formate into a retort and pouring on it a mixture of 7 parts of 88 per cent. spirit and 11 parts of sulphuric acid, so much heat being evolved that the ether distils and may be collected in a well-cooled receiver. This ether is also formed as a by-product in the preparation of ethyl oxalate (Löwig), and also by heating hydrogen ethyl oxalate, $(C_2H_5)HC_2O_4$, with glycerin to 100°, the reaction which here takes place being exactly analogous to that of the formation of formic acid from oxalic acid. It is not necessary for this purpose to prepare pure ethyl oxalic acid, but the crude product obtained by heating oxalic acid for a long time with alcohol may be employed.[3] A still more simple method is to heat anhydrous glycerin with equal molecules of alcohol and oxalic acid, connecting the flask with a reversed condenser until complete decomposition has occurred; the oxalic acid then requires to be warmed and the ether distils over.[4]

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[1] Nencki, *Ber. Deutsch. Chem. Ges.* vii. 1588; *Journ. Prakt. Chem.* [2], xvii. 237.

[2] *Ann. Chem. Pharm.* lv. 180.

[3] Church, *Phil. Mag.* [4], xi. 527.

[4] Lorin, *Bull. Soc. Chim* [2], v. 12.

compounds are also formed when alcohol vapour acts upon phosphorus pentoxide. If the reaction be allowed to take place quickly, a considerable quantity is formed. According to Carius[1] the pentoxide should be mixed with three or four times its volume of anhydrous ether, and then half the theoretical quantity of alcohol added, and the ethyl phosphate separated from the diethylphosphoric acid by distillation.

Ethyl phosphate is a colourless liquid possessing a peculiar pleasant smell and a burning taste, having at 12° a specific gravity of 1·072 and boiling at 215°, though towards the end of the distillation the boiling-point reaches as high as 240°, and a black acid residue remains. In a current of hydrogen, on the other hand, it boils constantly at 203° (Wichelhaus). It is miscible with water, and the solution soon becomes acid with formation of diethylphosphoric acid (Carius); this decomposition takes place, however, very slowly (Limpricht).

Ethyl Pyrophosphate, $(C_2H_5)_4P_2O_7$, is obtained by heating silver pyrophosphate with ethyl iodide to 100°, as an oily liquid possessing a peculiar smell and a burning taste. It is soluble in water, alcohol, and ether, and its aqueous solution soon becomes acid.[2]

THE ARSENITES, ARSENATES, AND BORATES OF ETHYL.

240 *Ethyl Arsenite,* $(C_2H_5)_3AsO_3$, is formed by the action of ethyl iodide on silver arsenite, as well as by heating together ethyl silicate and arsenic trioxide to 200°, when silica or an ethyl polysilicate separates out. It is, however, best obtained by treating arsenic tribromide with sodium ethylate, an excess of the latter substance being carefully avoided, as it acts at once upon the ethereal salt with formation of common ether. In order to decompose the excess of arsenic tribromide, the resulting material is treated with dry ammonia, which unites with the bromide to form a compound insoluble in spirit and in ether. It is then filtered off, and the arsenite purified by distillation. It is a colourless liquid boiling at 165° to 166°, and having a specific gravity of 1·224 at 0°. It is quickly decomposed by water, with separation of arsenic trioxide.[3]

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[1] Carius, *Ann. Chem. Pharm.* cxxxvii. 121.

[2] Clermont, *Ann. Chem. Pharm.* xci. 375.

[3] Clermont, *Bull. Soc. Chim.* [2], viii. 206; xiv. 89.

Ethyl Arsenate, $(C_2H_5)_3AsO_4$, is obtained by heating silver arsenate to 100° with the calculated quantity of iodide of ethyl diluted with ether. It is a colourless liquid, which boils under the ordinary atmospheric pressure, with slight decomposition at 235° to 238°, but may be distilled in a vacuum without decomposition. It dissolves in water with decomposition, the solution yielding all the reactions of arsenic acid.[1]

Ethyl Orthoborate, $(C_2H_5)_3BO_3$, was discovered by Ebelmen in 1845, and investigated by this chemist and Bouquet. They obtained it by saturating alcohol with gaseous boron trifluoride.[2] These experiments were afterwards corroborated by Bowman,[3] and H. Rose noticed that ethyl borate could also be easily prepared by distilling a mixture of two parts of anhydrous borax and three parts of potassium ethyl sulphate.[4] Frankland employed this reaction in his investigation on the organic compounds containing boron,[5] and found that from the distillate, which contains a large quantity of alcohol, ethyl borate could be best separated by the addition of one-fourth part its weight of fused calcium chloride; after this has dissolved, two layers of liquid make their appearance, of which the upper one contains the whole of the ethereal salt, and this can be purified by fractional distillation. It also is formed by heating boron trioxide with alcohol for some time to 120°, and may be readily obtained from the portion of the distillate coming over above 100°, by addition of a small quantity of sulphuric acid.

Ethyl borate is a thin colourless liquid boiling at 120°, having a specific gravity of 0·861 at 26°·5, a vapour density of 5·14, and burning with a green flame. It has a peculiar pleasant smell and a hot bitter taste. It is easily decomposed by water, with separation of boric acid. When heated with boric trioxide, *ethyl metaborate*, $(C_2H_5)_2B_2O_4$, is formed as a thick colourless liquid, converted at 200° into orthoborate and *ethyl triborate*, $C_2H_5B_3O_5$. This latter is a gummy mass, which, like the other borates is decomposed by water, with separation of boric acid.[6]

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[1] Clermont, *Bull. Soc. Chim.* [2], viii. 206; xiv. 99.

[2] *Ann. Chim. Phys.* [3], xvii. 55.

[3] *Phil. Mag.* [3], xxix. 546.

[4] *Pogg. Ann.* xcviii. 245.

[5] *Ann. Chem. Pharm.* cxxiv. 129; *Phil. Trans.* 1862, 167.

[6] Schiff, *Ann. Chem. Pharm.* Suppl. v. 154.

SULPHUR COMPOUNDS OF ETHYL.

246 *Ethyl Hydrosulphide or Ethyl Mercaptan,* $C_2H_5.SH$. This compound was obtained by Zeise in 1833 by distilling calcium ethyl sulphate with a solution of barium hydrosulphide:

$$Ca(SO_4C_2H_5)_2 + Ba(SH)_2 = 2\,C_2H_5.SH + CaSO_4 + BaSO_4.$$

Mercaptan, as Zeise named this substance, is also formed when an alcoholic solution of potassium hydrosulphide is saturated with ethyl chloride and then the product distilled, the current of ethyl chloride being continued.[1] According to Liebig,[2] it is best obtained by saturating caustic potash of specific gravity 1·3 with sulphuretted hydrogen, adding an equal volume of a solution of calcium ethyl sulphate of the same specific gravity and distilling. It is likewise easily obtained by acting with phosphorus pentasulphide on alcohol.[3] For other methods of preparing mercaptan the original memoirs may be consulted.[4]

In order to purify the crude product it is first separated from water, dried over chloride of calcium, and distilled. The first portions passing over consist of almost pure mercaptan, whilst a quantity of ethyl disulphide formed at the same time remains behind. This latter substance is not formed when the mercaptan is prepared according to Regnault's method.

In order to free it from sulphuretted hydrogen, which is difficult to remove, it is best to rectify it over mercury mercaptide. It may also be obtained in the pure state by the decomposition of this same compound, a description of which will be found in the sequel (Zeise).

Ethyl hydrosulphide is a colourless liquid having a penetrating garlic-like smell, and unpleasant taste. It boils at 36°·2, has at 21° a specific gravity of 0·835, and possesses a vapour density of 2·188 (Regnault). A drop solidifies on a glass rod exposed to a current of air, yielding a white mass which soon melts and evaporates (Liebig). When mixed with water, and the mixture cooled to + 2°, crystals are formed which melt again at 12°, decomposing into mercaptan and water.[5] These possess the composition $C_2H_6S + 18H_2O$ (Claesson). Mercaptan forms

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[1] Regnault, *Ann. Chim. Phys.* [2], lxxi. 390.

[2] *Ann. Pharm.* xi. 14.

[3] Kekulé, *Ann. Chem. Pharm.* xc. 310.

[4] Sace, *Ann. Chem. Pharm.* li. 348; E. Kopp, *ib.* lxiv. 320; Debus, *ib.* lxxii. 18; lxxv. 121; Carius, *ib.* cxii. 190; Schiff, *ib.* cxviii. 90.

[5] H. Müller, *Arch. Pharm.* [2], cl. 147.

two compounds with titanium chloride, of which the first, $TiCl_4 + C_2H_6S$, is deposited in blackish-red crystals, whilst the other, $TiCl_4 + 2C_2H_6S$, has a bright scarlet-red colour, and crystallizes well.[1] Mercaptan is easily inflammable, burning with a blue sulphur-like flame. Nitric oxide is quickly absorbed by this substance giving rise to a dark blood-red solution. Ethyl mercaptan, both in the pure state and in solution in water, possesses a neutral reaction. The hydrogen which is combined with the sulphur may readily be replaced by metals with formation of compounds termed mercaptides.

Potassium Mercaptide, C_2H_5SK, is formed with evolution of hydrogen, when potassium is dissolved in mercaptan; and it remains behind, when the excess of the volatile liquid is evaporated, in the form of a granular mass, which, when heated, undergoes decomposition.

The sodium compound, prepared in a similar way, forms a snow-like mass.[2]

Lead Mercaptide, $(C_2H_5S)_2Pb$, is thrown down on mixing alcoholic solutions of mercaptan and lead acetate as a yellow crystalline precipitate, which dissolves in an excess of lead acetate and crystallizes from solution in needles. It is unaltered by caustic potash.

Copper Mercaptide, $(C_2H_5S)_2Cu$, is a pale yellow precipitate obtained when a solution of potassium mercaptide is brought in contact with one of copper sulphate.

Silver Mercaptide, C_2H_5SAg. Mercaptan acts upon silver oxide so violently, even when it is diluted with alcohol, that ignition may take place. Mercaptan produces a snow-white precipitate in solution of silver nitrate, but this precipitate appears always to contain nitric acid.

Mercuric Mercaptide, $(C_2H_5S)_2Hg$. Mercaptan acts violently, with evolution of heat, on solutions of mercuric salts yielding a precipitate of the above compound. In order to prepare it, mercury oxide is added in small quantities to ethyl hydrosulphide well cooled with ice, and the mass thus obtained recrystallized from boiling alcohol. Glistening, colourless, transparent tablets are obtained, which melt at 80°, and then solidify to a solid mass. This compound is decomposed above 130° with formation of vapours which attack the eyes powerfully. It dissolves in concentrated hydrochloric acid without

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[1] Demarçay, *Bull. Soc. Chim.* [2], xx. 127.

[2] Claesson, *Bull. Soc. Chim.* [2], xxv. 184; *Journ. Prakt. Chem.* [2], xv. 193.

decomposition, and on cooling the dilute boiling acid, it separates out in glistening crystals. It is also unattacked by caustic potash. It forms a difficultly soluble compound with mercuric chloride $(C_2H_5S)_2Hg + HgCl_2$, obtained in the form of glistening tablets from boiling alcoholic solution.

Bismuth Mercaptide, $(C_2H_5S)_3Bi$, is obtained by the action of bismuth nitrate, and crystallizes in elastic yellow needles easily soluble in acids and alcohol, and precipitated when the acid solution is neutralized (Claesson).

Gold Mercaptide, C_2H_5SAu. Mercaptan does not act upon gold oxide so violently as upon silver oxide. If dilute aqueous solutions of auric chloride and mercaptan are mixed, a semi-solid mass of aurous mercaptide is formed, the chlorine which is evolved decomposing a portion of the mercaptan. This compound, when dried, forms a light amorphous mass resembling aluminium hydroxide.

Platinum Mercaptide, $(C_2H_5S)_2Pt$, is a pale yellow precipitate, which on exposure to air becomes heated nearly to incandescence, leaving a black residue of sulphide of platinum.

ETHYL SULPHIDE, $(C_2H_5)_2S$.

247 This was first obtained in 1833 by Döbereiner,[1] and afterwards more fully examined by Regnault.[2] In order to obtain it, gaseous ethyl chloride is passed into an alcoholic solution of potassium hydrosulphide, and the operation conducted exactly as described under methyl sulphide. It may also be easily prepared by distilling an alcoholic solution of potassium monosulphide with potassium ethyl sulphate.[3] It is further obtained by the action of phosphorus pentasulphide on ether,[4] and, together with mercaptan, when the pentasulphide is allowed to act upon alcohol. The metallic sulphides, which are decomposed by hydrochloric acid, also yield this compound when they are heated with the haloid ethyl ethers,[5] and some ethyl sulphide is likewise formed when these sulphides are brought together with a mixture of hydrochloric acid and alcohol.[6]

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[1] *Schweigg. Journ.* lxi. 377.

[2] *Ann. Chim. Phys.* [2], lxxi. 387.

[3] Hobson, *Quart. Journ. Chem. Soc.* x. 56.

[4] Beckmann, *Journ. Prakt. Chem.* [2], xvii. 451.

[5] Regnault, *loc. cit.*

[6] Loir, *Ann. Chim. Phys.* [3], xxxix 441; liv. 42.

To prepare pure ethyl sulphide the crude liquid is washed with water, dried over chloride of calcium, or, better, over phosphorus pentoxide, and then carefully distilled. It is a colourless liquid, having a strong garlic-like smell, but somewhat less unpleasant than mercaptan. At 0° its specific gravity is 0·8367; it boils at 92°,[1] and its vapour has a density of 3·10. (Regnault.)

If chlorine be passed into cold ethyl sulphide in the dark, substitution-products are formed, which have been investigated by Regnault[2] and Riche.[3] Ethyl sulphide also combines with many metallic chlorides and iodides.[4]

Ethyl Sulphide Mercuric Chloride, $(C_2H_5)_2S,HgCl_2$, is obtained as a white crystalline mass, when an aqueous solution of corrosive sublimate is shaken up with ethyl sulphide. It is soluble in alcohol and ether, and crystallizes from solution in the latter solvent in fine monoclinic prisms melting at 90°, and possessing an aromatic smell. These lose ethyl sulphide on exposure to air, and become opaque.

Ethyl Sulphide Mercuric Iodide, $(C_2H_5)_2S.HgI_2$, is formed by heating the foregoing compound, or mercuric sulphide, with alcohol and ethyl iodide to 100° for several hours. It is deposited in yellow needles soluble in alcohol and ether, melting at 110° and decomposing at 180°.

Ethyl Sulphide Titanium Chloride, $2(C_2H_5)_2S.TiCl_4$, forms fine dark-red crystals. Another compound of a similar constitution is known, which does not crystallize well, and has a rose-red colour, $(C_2H_5)_2S + TiCl_4$ (Demarçay).

Ethyl Sulphide Platinum Chloride, $2(C_2H_5)_2S.PtCl_4$, is obtained in a similar way to the mercury compound, and crystallizes in yellow needles.

Ethyl Methyl Sulphide, $C_2H_5(CH_3)S$, was first obtained by Carius[5] by heating ethyl dithiophosphate with methyl alcohol to 150°. It is also formed when the alcoholic solution of sodium ethyl mercaptide is heated with methyl iodide.[6] This compound is a disagreeably smelling liquid boiling at 68°, and forming a crystalline compound with mercuric chloride.

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[1] Beckmann, *loc. cit.*

[2] *Ann. Chim. Phys* [2], lxxi. 387.

[3] *Ib.* [3], xliii 283

[4] Loir, *loc. cit.*

[5] *Ann. Chem. Pharm.* cxix 313.

[6] Kruger. *Journ Prakt. Chem.* [2], xiv. 206

ETHYLSULPHINE COMPOUNDS.

248 *Diethylsulphine Compounds.* When ethyl sulphide is added drop by drop to well-cooled nitric acid of specific gravity 1·2 it dissolves, and forms a nitrate corresponding to the methyl compound. This is a thick liquid. The compound has not been obtained in the pure state. By the action of barium carbonate on its aqueous solution, *diethylsulphine oxide*, $(C_2H_5)_2SO$, is obtained.

This is a thick colourless liquid soluble in water, alcohol and ether, which on cooling yields a crystalline mass, and decomposes on heating.[1] When treated with hydriodic acid, or with zinc and sulphuric acid, it is reduced to ethyl sulphide, and when warmed with fuming nitric acid it is partially converted into *diethylsulphone*, $(C_2H_5)_2SO_2$. This latter compound may be obtained in the pure state by shaking ethyl sulphide with a solution of potassium permanganate.[2] It forms rhombic tables soluble in water and alcohol, melting at 72°, and subliming at 100°, though not boiling till 248°.[3] On treatment with zinc and sulphuric acid it remains unaltered, and is likewise unacted upon by hydriodic acid and phosphorus pentachloride (Beckmann).

Triethylsulphine Compounds. These bodies were discovered by Oefele,[4] and afterwards investigated more carefully by Dehn[5] and Cahours.[6] The iodide is easily formed by heating ethyl sulphide with ethyl iodide.

Triethylsulphine Hydroxide, $(C_2H_5)_3SOH$, is obtained by the action of freshly precipitated silver oxide on an aqueous solution of the iodide. The solution when dried in an exsiccator leaves a crystalline extremely deliquescent mass. This possesses a strongly alkaline reaction, attacks the skin like caustic potash, decomposes ammoniacal salts, precipitates the solutions of metals, and dissolves aluminium hydroxide.

Triethylsulphine Chloride, $(C_2H_5)_3SCl$, is obtained from the hydroxide by saturation with hydrochloric acid. It crystallizes in deliquescent needles difficultly soluble in alcohol, and combines with a number of metallic chlorides to form double salts such as $2(C_2H_5)_3SCl + PtCl_4$. This latter is deposited from solution in hot water in yellowish-red monoclinic prisms.

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[1] Beckmann, *Journ. Prakt. Chem.* [2], xvii. 452.

[2] Oefele, *Ann. Chem. Pharm.* cxxvii. 370; cxxxii. 82.

[3] *Ib.* cxxxii. 88.

[4] *Loc. cit.*

[5] *Ann. Chem. Pharm.* Suppl. iv. 83.

[6] *Ann. Chim. Phys.* [5], x. 18.

Triethylsulphine Bromide, $(C_2H_5)_3SBr$, is obtained on heating ethyl bromide with ethyl sulphide to a temperature of 130°—140°. It forms colourless rhombic crystals, easily soluble in water and difficultly soluble in alcohol.

Triethylsulphine Iodide, $(C_2H_5)_3SI$, is easily formed by heating ethyl sulphide with ethyl iodide in a flask connected with an inverted condenser. It is easily soluble in water and boiling alcohol, and crystallizes in colourless and odourless rhombic crystals which have a disagreeable taste.

Triethylsulphine Nitrate, $(C_2H_5)_3SNO_3$, is obtained by decomposing the iodide with silver nitrate. It crystallizes in extremely deliquescent needles, and forms with silver nitrate the double salt $(C_2H_5)_3SNO_3 + AgNO_3$. This latter compound crystallizes in tablets difficultly soluble in alcohol.

Triethylsulphine Sulphate, $[(C_2H_5)_3S]_2SO_4$, crystallizes imperfectly and is easily soluble in water, but dissolves with difficulty in alcohol.

Triethylsulphine Cyanide, $(C_2H_5)_3SCN$, is obtained by heating a solution of the iodide with silver cyanide, and forms, on concentration, a thick syrup, which on long standing in the exsiccator yields deliquescent needles. Caustic potash decomposes it into ethyl sulphide, propionic acid, and ammonia.[1]

Several triethylsulphine salts of organic acids are known.

Diethylmethylsulphine Compounds. When ethyl sulphide is heated with methyl iodide, diethylmethylsulphine iodide is formed. This is not crystallizable, and decomposes easily with evolution of ethyl sulphide. When its solution is heated with moist silver chloride the corresponding chloride is obtained, and this is also a very unstable compound. Its solution evaporated in a vacuum yields a thick syrup. The hydroxide obtained from the iodide by means of silver oxide does not crystallize, and the salts obtained by the action of acids are also mostly non-crystallizable. On the other hand, the chloride yields well-defined double salts.

Diethylmethylsulphine Platinic Chloride, $2(C_2H_5)_2CH_3SCl + PtCl_4$, crystallizes from water in bright yellow cubes, octohedrons, tetrahedrons, and other forms of the regular system. These on drying fall to a yellow powder, and they melt at 214° with evolution of unpleasantly smelling vapours.

Diethylmethylsulphine Mercuric Chloride, $(C_2H_5)_2CH_3SCl + 6HgCl_2$, forms colourless apparently hexagonal crystals which melt at 198°.

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[1] Gautre, *Zeitsch. Chem.* 1868, 622.

Ethylmethylethylsulphine Compounds. The iodide, $C_2H_5(CH_3)C_2H_5SI$, is obtained by the union of ethyl iodide and methyl ethyl sulphide, and crystallizes in long, very deliquescent needles, and yields a non-crystalline chloride.

Ethylmethylethylsulphine Platinic Chloride, $2C_2H_5(CH_3)C_2H_5SCl + PtCl_4$, is a dark-red precipitate insoluble in alcohol. It crystallizes from aqueous solution in long, apparently monoclinic prisms which on drying fall to a rose-red powder, melting with decomposition at 186°. If crystallized frequently from water, or warmed for a long time on the water-bath, this compound is converted into the isomeric diethylmethyl compound, which, however, cannot be reconverted into the compound under discussion.

Ethylmethylethylsulphine Mercuric Chloride, $C_2H_5(CH_3)C_2H_5SCl + 2HgCl_2$, is a difficultly soluble white precipitate crystallizing from hot water in rhombic tables melting at 112°.

Besides these, other double salts belonging to both series are known.[1]

Ethyl-thiocarbamide Iodide, $CS(NH_2)_2C_2H_5I$, may be considered in connection with the triethylsulphine compounds. It is obtained by heating ethyl iodide with sulphur-urea (Vol. I. p. 654), and yields with water and silver oxide a strongly alkaline solution from which rhombic crystals separate on addition of hydrochloric acid and platinic chloride.[2]

Constitution of the Sulphine Compounds.—Two explanations have been given respecting the constitution of the sulphine compounds. According to one of them, these compounds are to be regarded as built up of two molecules, and the isomerism of the two groups above mentioned can in this way be readily explained. Moreover this explanation is in accordance with the fact that triethylsulphine cyanide on heating with alkalis acts as if it were a compound of ethyl sulphide and ethyl cyanide.

According to the second hypothesis, these bodies are not molecular compounds, but contain tetrad sulphur. Much may be said for this view. If the iodides are heated, they do not decompose into the constituents from which they were obtained. One part volatilizes without decomposition, but the larger portion decomposes with formation of free iodine, hydriodic acid, and other products.

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[1] Krüger, *Journ. Prakt. Chem.* [2], xiv. 193.

[2] Bernthsen and Klinger, *Ber. Deutsch. Chem. Ges.* xi. 492.

If the first view of their constitution be accepted, the hydr- ides must be regarded as compounds of a sulphide with an lcohol, and they, therefore, ought easily to decompose into these hen heated. This, however, is not the case; they yield, on the ontrary, various other products of decomposition, which as yet ave not been properly investigated. If the sulphines are regarded as atomic compounds, we must assume that the four combining units of sulphur are unsymmetrical. On this point the subsequent chapters on theoretical chemistry must be consulted.

ETHYL DISULPHIDE, $(C_2H_5)_2S_2$.

249 This compound was obtained first by Zeise[1] by distilling calcium polysulphide with potassium sulphovinate, and was termed by him thialöl. It is also formed by various other reactions, of which the most important theoretically is the action of iodine on sodium mercaptide.[2]

$$\begin{array}{c} NaSC_2H_5 \\ NaSC_2H_5 \end{array} + I_2 = \begin{array}{c} SC_2H_5 \\ | \\ SC_2H_5 \end{array} + 2\,NaI.$$

Ethyl disulphide is also formed when mercaptan is heated for six hours at 150° with the requisite quantity of sulphur:[3]

$$2\,C_2H_5SH + S_2 = (C_2H_5)_2S_2 + SH_2.$$

In order to prepare it a mixture of 2 parts of potassium disulphide, 3 parts of potassium ethyl sulphate, and 5 parts of water are distilled, water being added from time to time so long as any oily drops are carried over. It is a colourless liquid having a strong garlic-like smell, boiling at 151°, and possessing a vapour density of 4·270 (Cahours). When heated with dilute nitric acid it forms *diethyl-disulpho-dioxide*, $(C_2H_5)_2S_2O_2$, a body which is the first oxidation-product of mercaptan, and is a colourless oily liquid possessing a penetrating smell and volatilizing in presence of aqueous vapour. Caustic potash decomposes it into ethyl disulphide, ethyl sulphonic acid, and ethyl sulphinic acid[4] (pars. 254-5), and if it be treated with zinc-dust and water

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[1] *Ann. Pharm.* xi. 1.

[2] Kekulé and Linnemann, *Ann. Chem. Pharm.* cxxiii. 273.

[3] M. Müller, *Journ. Prakt. Chem.* [2], iv. 39.

[4] Pauly and Otto, *Ber. Deutsch. Chem. Ges.* xi. 2073.

the zinc compound of mercaptan and ethyl sulphinic acid are obtained:

$$2\left.\begin{matrix}C_2H_5\\C_2H_5SO_2\end{matrix}\right\}S + 2Zn = (C_2H_5S)_2Zn + (C_2H_5SO_2)_2Zn.$$

Ethyl Thiosulphuric Acid, $SO_2\left\{\begin{matrix}OH\\SC_2H_5\end{matrix}\right.$, is not known in the free state, but salts of this acid are known. The sodium compound, $S_2O_3NaC_2H_5$, is obtained by heating ethyl bromide with an aqueous solution of sodium thiosulphate. It crystallizes in thin six-sided tablets, and when the aqueous solution is warmed with hydrochloric acid, sodium sulphate and mercaptan are formed:

$$SO_2\left\{\begin{matrix}ONa\\SC_2H_5\end{matrix}\right. + H_2O = SO_2\left\{\begin{matrix}ONa\\OH\end{matrix}\right. + HS.C_2H_5.$$

The silver and mercury salts are difficultly soluble precipitates,[1] which quickly blacken. If the sodium salt be added to barium chloride decomposition takes place in a few hours, common salt, barium dithionate, and ethyl disulphide being formed.[2]

Ethyl Trisulphide, $(C_2H_5)_2S_3$, was obtained by Cahours[3] in the impure state by distilling potassium trisulphide with potassium ethyl sulphate. It is also formed when the disulphide is heated with sulphur (M. Müller). It is an unpleasantly smelling liquid which decomposes on heating, but may be distilled in presence of water.

Ethyl Tetrasulphide, $(C_2H_5)_2S_4$, is obtained by the action of sulphur chloride on mercaptan:

$$2\,C_2H_5.SH + S_2Cl_2 = (C_2H_5)_2S_4 + 2\,HCl.$$

It is a heavy colourless oil having a most unpleasant smell and decomposing on heating into sulphur and the disulphide.

Ethyl Pentasulphide, $(C_2H_5)_2S_5$, is formed when the foregoing compound is heated with sulphur to 150°. It is said to be an elastic mass, but it has not been obtained in the pure state.[4]

Ethyl Thiophosphite, $(C_2H_5S)_3P$, is obtained by the action of phosphorus trichloride on mercaptan. It is a heavy oily liquid possessing a penetrating and unpleasant smell, and on heating splitting up into phosphorus and ethyl disulphide.[5]

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[1] Bunte, *Ber. Deutsch. Chem. Ges.* vii. 646.

[2] Ramsay, *Journ. Chem. Soc.* xxviii. 687.

[3] *Bull. Soc. Chim.* [2], xxv. 184.

[4] Claesson, *Bull. Soc. Chim.* [2], xxv. 185.

[5] *Ibid.*

Ethyl Tetrathiophosphate, $(C_2H_5S)_3PS$, is formed by the action of phosphorus pentasulphide on mercaptan:

$$6\,HS.C_2H_5 + P_2S_5 = 2\,PS(SC_2H_5)_3 + 3\,H_2S.$$

It is an oily liquid having a very disagreeable smell. In small quantities it may be distilled undecomposed at 200°. Water decomposes it with formation of sulphuretted hydrogen, mercaptan, and ethyl thiophosphoric acid. In the preparation of this thio-ether, diethyltetrathiophosphoric acid, $H(C_2H_5)_2PS_4$, is formed, a body which is very unstable in the free state, but which forms a series of crystallizable salts.[1]

Intermediate between these thio-compounds and the phosphoric ethers several compounds exist containing both oxygen and sulphur. These, as well as the foregoing compounds, have been investigated by Carius, and amongst them we shall here only mention the normal ethers.

Ethyl Trithiophosphate, $(C_2H_5)_3PS_3O$, is formed by heating mercaptan with phosphorus pentoxide:

$$5\,HS.C_2H_5 + P_2O_5 = PO(SC_2H_5)_3 + PO\left\{\begin{array}{l}OH\\SC_2H_5\\SC_2H_5\end{array}\right. + 2\,H_2O.$$

This compound may be separated from phosphoric acid and from ethyl dithiophosphoric acid, which are formed at the same time, by means of water. Ethyl trithiophosphate is an oily liquid, which has a peculiar alliaceous smell, and decomposes with violence on heating to 150°, ether, ethyl sulphide, and ethyl disulphide being evolved, and an unpleasantly smelling mass containing phosphoric acid remaining behind. Water decomposes this compound with formation of ethyl thiophosphoric acid.

Ethyl Dithiophosphate, $(C_2H_5)_3PS_2O_2$, is formed by the action of phosphorus pentasulphide on alcohol:

$$5\,HO.C_2H_5 + P_2S_5 = PO\left\{\begin{array}{l}SC_2H_5\\OC_2H_5\\SC_2H_5\end{array}\right. + PO\left\{\begin{array}{l}SC_2H_5\\OH\\SC_2H_5.\end{array}\right. + H_2O + SH_2$$

Ethyl dithiophosphoric acid, formed at the same time, is also obtained (as has been stated) when mercaptan is brought in contact with phosphorus pentoxide. It might have been expected that in these two distinct reactions isomeric compounds would have been produced, of which the one would contain the

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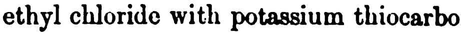
[1] Carius, *Ann. Chem. Pharm.* cxix. 289.

radical phosphoryl, PO, and the other the radical thiophosphoryl, PS; this, however, is not the case, either in this or other similar reactions.

Ethyl dithiophosphate is a colourless oily liquid possessing a faint garlic-like smell. When heated or placed in contact with water it acts like the foregoing compound. When heated with sulphuric acid *ethyl pentathiophosphate*, $(C_2H_5S)_2PO.S.PO(SC_2H_5)_2$ is formed. This compound yields large monoclinic crystals having a fatty lustre melts at 71°·2, and possesses on warming an unpleasant smell.

Ethyl Monothiophosphate, $(C_2H_5)_3PSO_3$, is obtained by heating thiophosphoryl chloride with absolute alcohol. It is a colourless not unpleasantly-smelling oil, which can be distilled without alteration in a current of carbon dioxide. This same compound was obtained by Chevrier[1] by acting on phosphorus thiochloride by sodium ethylate. It also has an unpleasant smell like decomposing turnips. On boiling this with water, ethyl monothiophosphoric acid, $H(C_2H_5)_2PSO_3$, is formed, and this body may be obtained in the same way with evolution of sulphuretted hydrogen from dithiophosphoric acid. If a salt of ethyl monothiophosphoric acid be warmed with phosphorus oxychloride, an oily, slightly smelling liquid, *ethyl dithiopyrophosphate*



$\left.\begin{matrix} C_2H_5S \\ C_2H_5O \end{matrix}\right\} PO.O.PO \left\{\begin{matrix} SC_2H_5 \\ OC_2H_5 \end{matrix}\right.$, is formed.

Ethyl Thioarsenite, $(C_2H_5S)_3As$, is formed by the action of sodium mercaptide on arsenic trichloride diluted with ether. It is a heavy, oily, very unpleasantly smelling liquid, which on heating decomposes into arsenic and ethyl sulphide.[2]

Ethyl Trithiocarbonate, $(C_2H_5S)_2CS$. This compound was discovered by Schweizer[3] in 1844, and obtained by acting upon ethyl chloride with potassium thiocarbonate. It was more carefully investigated by Debus.[4] According to Husemann,[5] it is best prepared by shaking up sodium thiocarbonate with two to three times its weight of alcohol, and rather less than the equivalent quantity of ethyl iodide. A reaction then occurs with considerable evolution of heat. In place of the iodide, bromide of ethyl may also be employed.[6]

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[1] *Bull. Soc. Chim.* [2], xii. 372.

[2] Claesson, *Bull. Soc. Chim.* [2], xxv. 185.

[3] *Journ. Prakt. Chem.* xxxii. 54.

[4] *Ann. Chem. Pharm.* lxxv. 147.

[5] *Ann. Chem. Pharm.* cxxiii. 66

[6] Salomon, *Journ. Prakt. Chem.* [2], vi 433.

Sulphocarbonate of ethyl, as this compound was formerly called, is a yellow liquid possessing an alliaceous smell and a pleasant sweetish taste, resembling anise. It is scarcely soluble in water, and boils at 240°. Ammonia decomposes it with formation of ethyl mercaptan and ammonium thiocyanate.

Ethyl Orthotetrathiocarbonate, $C(SC_2H_5)_4$, is formed by the action of sodium mercaptide, C_2H_5SNa (page 379), on tetrachlormethane, CCl_4. It is a light-yellow, peculiarly smelling oil, which decomposes on heating.[1]

Intermediate between these ethers and the ethyl carbonates a series of compounds exist, which may be divided into two classes according as they contain the radical carboxyl, CO, or thiocarbonyl, CS.[2]

Xanthic Acid, or Ethyl-Oxydithiocarbonic Acid,

$$CS\begin{cases} OC_2H_5 \\ SH \end{cases}.$$

250 The potassium salt of this acid is easily obtained by the action of carbon disulphide on an alcoholic solution of potash.[3] In order to prepare this salt a solution of caustic potash in absolute alcohol is mixed with an excess of carbon disulphide, and the crystalline mass which is soon deposited brought on to a filter, quickly washed with ether, and dried over sulphuric acid.[4]

Potassium Xanthate, $K(C_2H_5)CS_2O$, forms colourless silky needles, which become yellow on exposure to moist air. It possesses a peculiar faint smell and a strongly sulphurous taste. It is easily soluble in water, more difficultly in alcohol, and colours the skin yellow. When heated with water this compound decomposes in the following way:

$$2\,K(C_2H_5)CS_2O + 2\,H_2O = K_2CS_3 + 2\,HO.C_2H_5 + H_2S + CO_2.$$

The potassium salt when treated at 0° with dilute sulphuric or hydrochloric acid yields xanthic acid as a heavy, colourless oil, which must be quickly washed with water and dried over chloride of calcium, and then may be kept in a cold place without decomposition. It has a penetrating smell somewhat resembling sulphur dioxide, and a sharp penetrating astringent taste. On warming it decomposes into carbon disulphide and

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[1] Claesson, *Journ. Prakt. Chem.* [2], xv. 193.

[2] Salomon, *ib.* [2], vi. 433.

[3] Zeise, *Schweig. Journ.* xxxvi. 1 ; xliii. 160 ; *Pogg. Ann.* xxxv. 487.

[4] Sace, *Ann. Chem. Pharm.* li. 345.

alcohol; this decomposition begins at 24°, the liquid becoming turbid, and at last beginning to boil with evolution of disulphide of carbon. Xanthic acid decomposes the carbonates and forms a series of salts, some of which possess a very characteristic colour, such, for instance, as the fine yellow and very stable cuprous salt, $(C_2H_5COS_2)_2Cu_2$, from which, indeed, the name of the acid is derived (ξανθός, yellow). This is obtained by precipitating the potassium salt, best in alcoholic solution, by means of cupric chloride, when a blackish-brown precipitate falls, consisting probably of the cupric salt, and this soon changes into fine yellow flocks and other products.

Amongst other salts the following may be described:

Ammonium Xanthate, $C_2H_5(NH_4)COS_2$, can be obtained by double decomposition with other salts, or by saturating the free acid with ammonia. The solution yields, on evaporation in a vacuum, glistening crystals, resembling those of urea, which easily decompose and volatilize in a current of steam (Debus).

Lead Xanthate, $(C_2H_5.COS_2)_2Pb$, is a crystalline precipitate insoluble in cold water.

Ferric Xanthate, $(C_2H_5.COS_2)_6Fe_2$, is obtained by boiling ferric chloride with a potassium salt and carbon disulphide. It forms large regular glistening black monoclinic crystals, of which the smallest quantity imparts to carbon disulphide a very deep colour.

The *chromic salt* which can be prepared in a similar way from the violet chromic chloride, forms dark-blue glistening crystals which dissolve in carbon disulphide, imparting to the liquid a violet-blue colour.

Arsenic Xanthate, $(C_2H_5COS_2)_3As$, is formed by the action of arsenic trichloride on the potassium salt. It forms large thick monoclinic tables without colour and odour, which melt easily, and on cooling yield a crystalline mass.

The antimony salt may be prepared in a similar way. It is deposited in large glistening, bright-yellow crystals, whilst the bismuth salt crystallizes in bright golden-yellow tables.[1]

Ethyl Xanthate, or *Ethyl Oxysulphocarbonate*, $CS\left\{\begin{matrix}OC_2H_5\\SC_2H_5\end{matrix}\right.$, is obtained by the action of ethyl chloride, or better of ethyl bromide, on the potassium salt. It is a colourless liquid boiling at 200°, and possesses a strong unpleasant smell and a sweetish taste.

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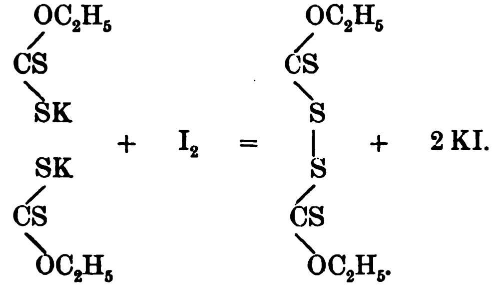
[1] Hlasiwetz, *Ann. Chem. Pharm.* cxxii. 87.

By the action of ammonia it is transformed into *xanthamide* or *ethyl monothiocarbamide*, $CS\left\{\begin{matrix}NH_2\\OC_2H_5\end{matrix}\right.$, a body crystallizing in modified monoclinic pyramids, which melt at 36°, and are easily soluble in alcohol, but dissolve with greater difficulty in water, and on heating are converted into mercaptan and hydrocyanic acid. By the action of nitrogen trioxide in presence of water this body is converted into the compound $(C_2H_5)_2C_2N_2O_2S$, to which Debus has given the name of *oxy-sulphocyanic-ethyl-oxide*.[1] It crystallizes in thin white prisms, which melt at 100°, and on boiling with baryta-water form barium carbonate, ammonia, sulphur, and alcohol.

Xanthic Disulphide, $C_2O_2S_4(C_2H_5)_2$. This compound was discovered by Desains[2] and examined by Debus,[3] who termed it ethyl bioxysulphocarbonate. It is formed by the action of chlorine or iodine on the xanthates according to the following equation:[4]



Xanthic disulphide is insoluble in water, crystallizing from alcohol in glistening white prisms, which do not smell unpleasantly, possess a biting taste, and melt at 28°. When heated to 210° they decompose into sulphur, carbon monoxide, carbon disulphide, ethyl xanthate, and the following compound.

Ethyl Dioxythiocarbonate, $CS(OC_2H_5)_2$, is a pleasantly smelling, strongly refracting liquid, boiling at 160°, and converted by ammonia into alcohol and ammonium thiocyanate:

$$CS\left\{\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix}\right. + 2\,NH_3 = 2\,HOC_2H_5 + NCS(NH_4).$$

251 *Ethyl Monothiocarbonic Acid*, $CO(OC_2H_5)SH$. This compound is not known in the free state, but its potassium salt is

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[1] *Ann. Chem. Pharm.* lxxxii. 279; *Chem. Soc. Journ.* iii. 84.
[2] *Ib.* lxiv. 325. [3] *Ib.* lxxii. 1; lxxv. 121; lxxxii. 255.
[4] Kekulé and Linnemann, *Ann. Chem. Pharm.* cxxiii. 273.

formed by the action of alcoholic potash on ethyl xanthate (Debus), when the following peculiar action occurs:

$$CS\begin{cases}OC_2H_5\\SC_2H_5\end{cases} + 2\,KOH = CO\begin{cases}OC_2H_5\\SK\end{cases} + HO.C_2H_5 + KSH.$$

It is soluble in water and alcohol, and appears to be isomorphous with potassium xanthate. Acids decompose it into alcohol, carbon dioxide, and sulphuretted hydrogen, and when its solution is boiled, alcohol, carbonyl sulphide, potassium sulphide, and potassium carbonate are formed.[1]

When a solution of lead acetate is added to its solution, a white precipitate of lead ethyl monothiocarbonate, $(CO_2.C_2H_5)_2S_2Pb$, is formed, and this crystallizes from hot alcohol in needles. Iodine acts upon these salts as it does on the xanthates with the formation of the ethyl ether of *dithiocarbonic acid* or *diethylcarboxydisulphide*, $\begin{cases}S.CO.OC_2H_5\\S.CO.OC_2H_5.\end{cases}$ This is a colourless, strongly refracting oil, heavier than water.[2]

The monosulphide, $S(CO_2.C_2H_5)_2$, corresponding to the former compound, was obtained by Victor Meyer by acting on ethyl chlorocarbonate with sodium sulphide. It was termed by him ethyl dicarbothionate. It is a colourless liquid, boiling about 180°, and possessing a peculiar, but faint smell.[3]

Ethyl Thioxycarbonate, $CO(OC_2H_5)SC_2H_5$, is obtained by acting with ethyl bromide or potassium ethyl monothiocarbonate, and also when sodium mercaptide is treated with ethyl chlorcarbonate:

$$CO\begin{cases}OC_2H_5\\Cl\end{cases} + NaSC_2H_5 = CO\begin{cases}OC_2H_5\\SC_2H_5\end{cases} + NaCl.$$

It is a colourless, strongly refracting liquid, boiling at 156°. It possesses a smell like that of decaying fruit, and has an aromatic taste. Cold ammonia decomposes this compound, which is isomeric with ethyl dioxythiocarbonate into mercaptan and urethane:

$$CO\begin{cases}OC_2H_5\\SC_2H_5\end{cases} + NH_3 = CO\begin{cases}OC_2H_5\\NH_2\end{cases} + HS.C_2H_5.$$

On heating with water to 100°, alcohol, carbon dioxide, and mercaptan are formed.[4]

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[1] Bender, *Ann. Chem. Pharm.* cxlviii. 137.

[2] Debus, *Ann. Chem. Pharm.*

[3] *Ber. Deutsch. Chem. Ges.* ii. 297.

[4] Salomon, *Journ. Prakt. Chem.* [2], vi. 433.

Ethyl Dithioxycarbonate, $CO(SC_2H_5)_2$. This compound, isomeric with ethyl xanthate, was discovered by Schmitt and Glutz,[1] and obtained by the action of sulphuric acid on ethyl thiocyanate, and termed by the discoverers carbonyl disulphodiethyl. It is also formed by the action of sodium mercaptide on carbonyl chloride:[2]

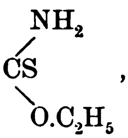
$$CO\left\{\begin{matrix}Cl\\Cl\end{matrix}\right. + 2\,NaS.C_2H_5 = CO\left\{\begin{matrix}SC_2H_5\\SC_2H_5\end{matrix}\right. + 2\,NaCl.$$

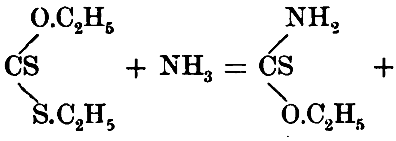
In this reaction the chloride, $COCl(SC_2H_5)$, a liquid boiling at 136°, is first formed. Ethyl dithioxycarbonate is a strongly refracting liquid possessing a garlic-like smell, and boiling at 196°. Ammonia decomposes this ether into mercaptan and urea.

252 The following table exhibits the composition of the thiocarbonates compared with ethyl carbonate:

		B.P.
Ethyl Carbonate.	$CO\left\{\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix}\right.$	126°
Ethyl Thioxycarbonate.	$CO\left\{\begin{matrix}OC_2H_5\\SC_2H_5\end{matrix}\right.$	156°
Ethyl Dioxythiocarbonate.	$CS\left\{\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix}\right.$	162°
Ethyl Dithioxycarbonate.	$CO\left\{\begin{matrix}SC_2H_5\\SC_2H_5\end{matrix}\right.$	196°
Ethyl Xanthate, or Ethyl Oxydithiocarbonate.	$CS\left\{\begin{matrix}SC_2H_5\\OC_2H_5\end{matrix}\right.$	200°
Ethyl Trithiocarbonate.	$CS\left\{\begin{matrix}SC_2H_5\\SC_2H_5\end{matrix}\right.$	240°

Some similar compounds of the methyl series are also known, as well as others which contain both methyl and ethyl.[3]

253 *Ethyl Thiocarbamate*, , is formed by the action of xanthic ether on ammonia:



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[1] *Ber. Deutsch. Chem. Ges.* i. 166.

[2] Salomon, *Journ. Prakt. Chem.* [2], vii. 252.

[3] Salomon and Manitz, *Journ. Prakt. Chem.* [2], viii. 114.

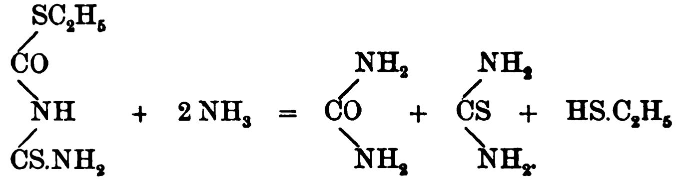
It is a crystalline compound, and combines with many salts of the heavy metals. On warming it splits up into mercaptan and cyanic acid, and, on boiling with alkalis, into alcohol and thiocyanates.

Ethyl Thioallophanate, $C_2H_3N_2S_2O.C_2H_5$, is formed by the action of hydrochloric acid on a hot concentrated alcoholic solution of potassium thiocyanate, thus:

$$2\,CNSK + 2\,HCl + CH_5.OH = \underset{\text{Ethyl Thioallophanate.}}{CO.SC_2H_5(NH)CS.NH_2.}$$

Recrystallized from hot water and ether, this compound forms white needle-shaped crystals, which are odourless, possess a bitter taste, and melt with decomposition between 170° and 175°.[1]

By the action of ammonia, in the cold, on ethyl thioallophanate the following decomposition takes place, furnishing the clue to the constitution of this ether:



ETHYL SULPHONIC ACID, $(C_2H_5)SO_3H$.

254 This was discovered by Löwig and Weidmann[2] in 1839, and prepared by the oxidation of ethyl mercaptan with nitric acid. It was afterwards more fully investigated by H. Kopp.[3] It is also formed by the oxidation of ethyl disulphide, as well as of the higher sulphides of ethyl, and also of ethyl thiocyanate.[4]

In order to prepare it, liver of sulphur, obtained by fusing potashes with sulphur, is distilled with solution of potassium ethyl sulphate, and the impure disulphide thus obtained oxidized with an equal volume of nitric acid.[5] This reaction is best carried out in a retort of which the neck is placed in an upward position and connected with the lower part of an inverted condenser. The reaction is, to begin with, extremely

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[1] Blankenhorn, *Journ. Prakt. Chem.* [2], xvi. 358.

[2] *Pogg. Ann.* xlvii. 153; xlix. 329; Löwig, *Ann. Chem. Pharm.* lxxv. 349.

[3] *Ann. Chem. Pharm.* xxxv. 343.

[4] Muspratt, *Chem. Soc. Journ.* i. 45.

[5] M. Müller, *Journ. Prakt. Chem.* [2], iv. 39.

violent, but afterwards it must be aided by warmth, and lastly, the mass must be gently boiled until it is all dissolved. The product is heated on a water-bath, to drive off nitric acid, until it possesses a syrupy consistency. The residue is dissolved in water, and neutralized with lead carbonate in order to separate the excess of sulphuric acid formed. The amount of this, however, if the sulphuric acid be not too strong, is not large. The filtered solution is then evaporated, and the ethyl sulphonic acid is thus obtained as an oily liquid of specific gravity 1·3, and crystallizing in the cold. It rapidly absorbs water from the air, is odourless, has a strong acid taste, and on heating to a high temperature decomposes with evolution of vapours of sulphuric acid and sulphur dioxide.

Ethyl Sulphonic Chloride, $C_2H_5SO_2Cl$, was discovered by Gerhardt and Chancel,[1] and is formed by the action of phosphorus oxychloride or phosphorus pentachloride on ethyl sulphonate:

$$2\,SO_2\left\{\begin{matrix}C_2H_5\\ONa\end{matrix}\right. + 2\,PCl_5 = 2\,SO_2\left\{\begin{matrix}C_2H_5\\Cl\end{matrix}\right. + 2\,NaCl + 2\,POCl_3.$$

It is a colourless liquid, smelling like mustard-oil, boiling at 177°·5,[2] and having a specific gravity of 1·357 at 22°·5. It fumes slightly in the air, and is slowly decomposed by water with formation of ethyl sulphonic acid and hydrochloric acid. Nascent hydrogen converts it into mercaptan.[3] When heated with phosphorus pentachloride to 120°, phosphorus oxychloride, ethyl chloride, and thionyl chloride are formed:

$$SO_2\left\{\begin{matrix}C_2H_5\\Cl\end{matrix}\right. + PCl_5 = POCl_3 + C_2H_5Cl + SOCl_2.$$

When kept for any length of time it decomposes into sulphur dioxide and ethyl chloride.[4]

Ethyl sulphonic acid forms a series of stable salts, obtained by neutralizing the free acid with an oxide, as well as by other methods.

Potassium Ethyl Sulphonate, $C_2H_5SO_3K + H_2O$, crystallizes in hygroscopic tablets, which lose water on heating, melt at 120°, and on cooling yield the anhydrous salt in the form of a crystalline mass. If it be more strongly heated it becomes

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[1] *Compt. Rend.* xxxv. 690.

[2] Carius, *Journ. Prakt. Chem.* [2], ii. 262.

[3] Vogt, *Ann. Chem. Pharm.* cxix, 152; Endemann, *ib.* cxl. 333.

[4] Carius, *Ann. Chem. Pharm.* cxi. 93; cxiv. 140.

brown, evolves unpleasantly smelling vapours, and leaves a residue of potassium sulphide.

Sodium Ethyl Sulphonate, $C_2H_5SO_3Na$, resembles the potassium salt, and is very deliquescent. It contains water of crystallization which it loses at 100°, and when a concentrated solution of sodium sulphite is heated with ethyl iodide to from 130° to 150°, the double salt $4C_2H_5SO_3Na + NaI$ is formed. This crystallizes from alcohol in silky needles.[1]

Ammonium Ethyl Sulphonate, $C_2H_5SO_3NH_4$, is a crystalline deliquescent mass, obtained by boiling ethyl iodide with a solution of ammonium sulphite. This reaction is well suited for the preparation of ethyl sulphonic acid. The product of this reaction is boiled with lead oxide as long as ammonia is evolved, and the solution filtered and decomposed with sulphuretted hydrogen.[2]

Barium Ethyl Sulphonate, $(C_2H_5SO_3)_2Ba + H_2O$, crystallizes in oblique rhombic tables which effloresce readily, and have an unpleasant taste.

Lead Ethyl Sulphonate, $(C_2H_5SO_3)_2Pb+H_2O$, is soluble in water and alcohol, crystallizing from hot aqueous solution in tablets.

Silver Ethyl Sulphonate, $C_2H_5SO_3Ag$, crystallizes from hot water in scales. It is also soluble in alcohol, melts when warmed, and may be heated to a tolerably high temperature without undergoing change.

Besides these, various other ethyl sulphonates have been prepared.

Methyl-Ethyl Sulphonate, $C_2H_5SO_3CH_3$, is obtained by acting on ethyl sulphonic chloride with sodium methylate. It is a colourless, slightly smelling liquid boiling between 197°·5 to 200°·5.

Diethyl Sulphonate, or *Ethyl Sulphonic Ethyl Ether*, $C_2H_5SO_3.C_2H_5$, is prepared in an analogous way to the foregoing compound, and has a smell not unlike its isomeride, ethyl sulphite.[3] It is also formed when ethyl iodide is allowed to act on silver sulphite.[4] It boils at 213°.

255 *Ethyl Sulphinic Acid*, $C_2H_5SO_2H$. By the action of sulphur dioxide on zinc ethyl Hobson[5] obtained the zinc compound of an acid to which he gave the name of ethyl trithionic acid,

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[1] Bender, *Ann. Chem. Pharm.* cxlviii. 96.

[2] Hemilian, *ib.* clxviii. 145.

[3] Carius, *Journ. Prakt. Chem.* [2], ii. 262.

[4] Kurbatow, *Ber. Deutsch. Chem. Ges.* vi. 197.

[5] *Chem. Soc. Journ.* x. 58.

and, according to his analyses, it possessed the formula, $C_2H_5S_3O_6$. Neither Wischin[1] nor Zuckschwerdt[2] could obtain this compound, but when the experimental conditions were somewhat altered, *zinc ethyl sulphinate,* $(C_2H_5SO_2)_2Zn$, was obtained.

This is difficultly soluble in water, and may be obtained in soft pearly scales from alcoholic solution. The same salt is also formed when ethyl sulphonic chloride is brought in contact with zinc-dust and water.[3] By decomposing with baryta-water barium ethyl sulphinate, $(C_2H_5SO_2)_2Ba$, may be obtained. This is easily soluble in water, and on evaporation in a vacuum is deposited in crystals. Besides these, other crystalline compounds have been prepared. When a solution of the barium salt is treated with sulphuric acid *ethyl sulphinic acid* is obtained. This has a pleasant sweet taste, and remains, on evaporation in a vacuum, as a syrupy liquid. If the acid or the zinc salt be oxidized with nitric acid a crystalline compound is obtained, together with ethyl sulphonic acid, and this crystallizes from hot alcohol in large glistening tablets melting at 81°·5 and which when carefully heated may be sublimed without decomposition. This body possesses the formula $C_6H_{15}S_3O_7N$, and when boiled with alkalis, or heated with hydrochloric acid, it is converted into ethyl sulphonic acid and ammonia, some sulphuric acid being always formed. Hence this body is *triethyl sulphonic nitric oxide,* $(C_2H_5SO_2)_3NO$, which probably decomposes in contact with water into sulphonic acid and hydroxylamine, NOH_3, and this latter compound acts as an oxidizing agent and ammonia is reduced.

COMPOUNDS OF ETHYL AND SELENIUM.

256 *Ethyl Hydroselenide,* C_2H_5SeH, was discovered by Siemens,[4] who prepared it by distilling a solution of potassium hydroselenide with potassium ethyl sulphate. It is a colourless liquid boiling below 100°, and possessing a most unpleasant smell resembling that of cacodyl, which is doubtless caused by the presence of a small quantity of ethyl diselenide. It forms with mercuric oxide a yellow amorphous selenium mercaptide.

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[1] *Ann. Chem. Pharm.* cxxxix. 364.

[2] *Ber. Deutsch. Chem. Ges.* vii. 292.

[3] Pauly, *Ber. Deutsch. Chem. Ges.* x. 941.

[4] *Ann. Chem. Pharm.* lxi. 360.

Ethyl Selenide, $(C_2H_5)_2Se$, was first prepared by Löwig[1] in 1836 by distilling ethyl oxalate with potassium selenide, and afterwards more accurately examined by Joy[2] who obtained it by distilling potassium ethyl sulphate with potassium selenide. He was, however, unable to complete his experiments owing to the intolerable odour which the body possesses. This, as was afterwards shown by Rathke,[3] is due to the presence of a small quantity of ethyl diselenide. In order to prepare the monoselenide, the best plan, according to this latter chemist, is to take a pure solution of caustic potash and distil it with potassium ethyl sulphate, to which a small quantity of selenium phosphate is added, which, however, must contain no free selenium. In this way potassium phosphate and potassium selenide are formed, and on distillation a mixture of monoselenide and diselenide is formed, the latter being formed by the action of oxygen on the former compound. They may be then separated by fractional distillation. It is, however, simpler to treat the distillate again with half the quantities of potassium ethyl sulphate, caustic potash, and water, which were originally employed, and to add to this a small piece of ordinary sulphur. On distillation for several hours with a reversed condenser this compound is obtained in the pure state.[4]

Ethyl selenide is a colourless, easily mobile, strongly refracting liquid, boiling at 108°, and having a peculiar but not unpleasant smell. It dissolves easily in dilute nitric acid with formation of the nitrate $(C_2H_5)_2Se(OH)NO_3$, which is decomposed on concentration. Hydrochloric acid precipitates ethyl selenium dichloride, $(C_2H_5)_2SeCl_2$, as a yellowish oil, slightly soluble in water, but rather more soluble in hydrochloric acid. Aqueous ammonia converts it into ethyl selenium oxychloride, $(C_2H_5)_4Se_2OCl_2$, which crystallizes from alcohol in glistening colourless cubes, and is converted, in presence of hydrochloric acid, into the original compound. Hydrobromic acid precipitates ethyl selenium bromide, $(C_2H_5)_2SeBr_2$, from solutions of the nitrate, in the form of a light yellow coloured soluble oil; the iodide prepared in a similar way is a yellow lustrous liquid somewhat resembling bromine.

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[1] *Pogg. Ann.* xxxvii. 552.

[2] *Ann. Chem. Pharm.* lxxxvi. 35.

[3] *Ann. Chem. Pharm.* clii. 210.

[4] Pieverling, *Lieb. Ann.* clxxxv. 331; *Ber. Deutsch. Chem. Ges.* ix. 1469.

Triethyl Seleniodide, $(C_2H_5)_3SeI$, is formed by the combination of the foregoing compound with ethyl iodide.[1] It forms glistening white crystalline needles closely resembling Epsom salts, and very soluble in water. They decompose, on heating, into their constituents which on cooling gradually again unite with one another. Moist silver oxide acts on the solution of this body as it does on the corresponding sulphine iodides. The hydroxide thus formed is left on evaporation in a vacuum as a syrupy liquid, which is as alkaline and caustic as potash. Its salts are, most of them, deliquescent, possessing an alliaceous smell, and having a bitter and burning taste. The platinichloride, $(C_2H_5)_6Se_2PtCl_6$, crystallizes on evaporating the hot saturated solution in glistening red acute rhombohedrons with basic terminal faces (Pieverling).

Ethyl Diselenide, $(C_2H_5)_2Se_2$, which is formed as a by-product in the preparation of the above-mentioned selenium compounds, was first obtained by Wöhler and Dean,[2] mixed with some monoselenide, by heating potassium selenide (obtained by heating potassium selenite and carbon together) with potassium ethyl sulphate. Rathke has however shown that when a selenite is heated with carbon, polyselenides are formed, scarcely any monoselenide being produced, the reaction beginning before the moisture in the carbon is driven off and this then acting as an oxidizing agent.

Ethyl diselenide is a heavy brownish-red oil, boiling at 180°, and having a frightful smell, and acting as a poison (Pieverling). When it is dissolved in nitric acid, and hydrochloric acid is added, the compound $C_2H_5SeSO_2H + HCl$ is formed, crystallizing in fine monoclinic prisms (Rathke).

COMPOUNDS OF ETHYL AND TELLURIUM.

257 *Ethyl Telluride,* $(C_2H_5)_2Te$, was first obtained in 1840 by Wöhler[3] by distilling potassium telluride with barium ethyl sulphate. It was then prepared by Mallet,[4] and afterwards more exactly investigated by Wöhler.[5] In order to prepare it, one part of tellurium is treated with 10 parts of ignited cream of tartar in a porcelain retort to the neck of which a bent glass tube is attached. When no further evolution of carbon dioxide takes place, the glass tube is placed in a large flask filled with

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[1] Cahours, *Comptes Rendus,* lx. 620.

[2] *Ann. Chem. Pharm.* xcvii. 1.

[3] *Ann. Chem. Pharm.* xxxv. 111.

[4] *Chem. Soc. Journ.* v. 71.

[5] *Ann. Chem. Pharm.* lxxxiv. 69.

carbon dioxide, in order to prevent the entrance of air into the apparatus, and then, after the vessel has cooled, the requisite quantity of concentrated solution of potassium ethyl sulphate dissolved in water free from air is added, and the whole warmed, the contents of the retort being brought into a flask filled with carbon dioxide and the whole distilled in a current of this gas. These precautions are necessary in order to prevent the oxidation of the potassium telluride, but in spite of this a quantity of ethyl ditelluride is usually formed, and this comes over towards the end of the distillation.

Ethyl telluride is a thick red liquid boiling at 98°,[1] and yielding a deep yellow-coloured vapour. It is heavier than water, possesses a strong, very unpleasant smell, reminding one at the same time of ethyl selenide and telluretted hydrogen. Its vapour attacks the lungs and appears to be poisonous. During the whole time that Wöhler was occupied in this investigation his breath was tainted with the unpleasant smell of this compound. When a small dose of potassium telluride, namely, from 0·04 to 0·05 gram, is taken, the breath after a few minutes becomes for a length of time tainted with this unpleasant odour.[2] Ethyl telluride is easily inflammable, and burns with a bright blue flame evolving clouds of tellurium dioxide. Exposed to the air it soon becomes covered with a white crust, and the whole mass gradually changes to a white earthy solid. This oxidation occurs so quickly in sunlight that the liquid begins to fume, without however taking fire.

Ethyl Tellurium Oxide, $(C_2H_5)_2TeO$, has not yet been obtained in the pure state. Its solution, prepared by treating the chloride or oxychloride with silver oxide, turns turmeric paper brown, and absorbs carbon dioxide from the air. On evaporation, decomposition occurs. When saturated with an acid, ethyl tellurium salts are obtained, the point of departure for which is the nitrate.

Ethyl Tellurium Nitrate, $Te(C_2H_5)_2(OH)NO_3$, is formed by dissolving ethyl telluride in nitric acid. It forms monoclinic crystals, which on heating deflagrate like gunpowder.

Ethyl Tellurium Chloride, $Te(C_2H_5)_2Cl_2$, is obtained from the solution of the nitrate by the addition of concentrated hydrochloric acid, when an oily liquid is formed, possessing an unpleasant smell, and volatilizing at a high temperature without

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[1] Heeren, *Chem. Centr.* 1861, 916.

[2] Hansen, *Ann. Chem. Pharm.* lxxxvi. 208.

decomposition. When it is dissolved in warm ammonia and the liquid allowed to evaporate, the oxychloride, $Te_2(C_2H_5)_4OCl_2$, is formed in glistening six-sided prisms, which are difficultly soluble in water but readily so in ammonia and alcohol.

The *bromide* is a light yellow oil, and the *iodide* an orange-yellow precipitate. Treated with ammonia they both yield crystallizable oxy-compounds.

Ethyl Tellurium Sulphate, $Te_2(C_2H_5)_4(OH)_2SO_4$, is obtained by decomposing the oxychloride with silver sulphate, or by acting with lead dioxide and dilute sulphuric acid on ethyl telluride. It crystallizes in colourless prisms.

Ethyl Tellurium Carbonate, $Te_2(C_2H_5)_4(OH)_2CO_3$, is obtained by saturating the solution of the oxide with carbon dioxide, or by decomposing the oxychloride with silver carbonate. It forms small well-defined crystals.

Various ethyl tellurium salts of organic acids are also known.

Ethyl Ditelluride, $(C_2H_5)_2Te_2$, is always formed in the preparation of the monotelluride; it is a dark-red liquid having a high boiling point.

Triethyl Tellurium Iodide, $(C_2H_5)_3TeI$, is a crystallizable body obtained by the combination of ethyl iodide with ethyl telluride.[1] It crystallizes from aqueous solution in a vacuum in bright yellow monoclinic prisms, which melt at 90°—92°. On distillation it decomposes into its constituents which after some hours unite together on standing (Pieverling). By treating the aqueous solution of this body with silver oxide, a liquid having an alkaline reaction is obtained, and this, when saturated with hydrochloric acid and treated with platinum chloride, yields an orange-yellow crystalline precipitate of $[(C_2H_5)_3Te]_2PtCl_6$.[2]

NITROGEN BASES OF ETHYL.

THE ETHYLAMINE COMPOUNDS.

258 *Ethylamine*, $NH_2C_2H_5$, was first prepared by Wurtz[3] in 1848, by distilling ethyl isocyanurate with caustic potash, and Hofmann[4] soon afterwards obtained the other ethyl bases. These discoveries not only exerted a great influence on the

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[1] Cahours, *Bull. Soc. Chim.* [2], iv. 40.

[2] Becker, *Liebig's Ann.* clxxx. 262.

[3] *Comptes Rendus*, xxviii. 223; *Ann. Chim. Phys* [3], xxx. 443.

[4] *Phil. Trans.* 1850 [1], 93; *Ann. Chem. Pharm.* lxxiii. 91.

progress of theoretical chemistry but also on the industrial application of the science, inasmuch as by their means an important branch of the manufacture of aniline colours was called into being. In order to prepare the ethyl bases, a haloid salt of ethyl is heated with ammonia. The ethyl ethers of other inorganic acids, such for instance as the nitrate (Juncadella), the sulphite (Carius), the sulphate (Strecker), and the phosphate (Clermont), are attacked in a similar way by ammonia, but in all these cases the three other bases are formed together with the primary base.[1]

In order to prepare large quantities of these compounds, the method proposed by Hofmann[2] is the best. For this purpose the crude ethyl chloride obtained as a by-product in the preparation of chloral is employed. This contains higher substitution-products, but these may afterwards be readily separated. One part of this crude ethyl chloride is digested with three times its volume of spirit, containing 95 per cent. of alcohol, previously saturated with ammonia at 0°. For this purpose a wrought iron digester is usually employed, the whole being heated for an hour in boiling water. On cooling, the liquid deposits sal-ammoniac, this is filtered off, and the liquid distilled on a water-bath. The higher chlorinated chlorides of ethyl pass over first, and then alcohol containing ammonia, which after a further saturation with ammonia may be used in a second preparation. As soon as the distillation is complete, the residue left in the retort is evaporated in a basin until all the alcohol is removed. On cooling, the liquid solidifies to a feathery crystalline mass of the ethylamine hydrochlorates, with which a small quantity of sal-ammoniac is mixed. Concentrated caustic soda is now added, and the liquid layer which separates out, consisting of a mixture of the three bases, is drawn off and dried over solid caustic soda. Although the boiling points of the three bases differ very considerably, they cannot be separated by fractional distillation, and in order to obtain them in the pure state a plan similar to that adopted in the case of the methyl compounds must be employed. The product is, therefore, treated with ethyl oxalate, when the triethylamine remains unaltered, and may be distilled off from the water-bath. The residue consists of a mixture of solid diethyloxamide, $C_2O_2(NH.C_2H_5)_2$, and liquid diethyl oxamic ethyl ether, $C_2O_2N(C_2H_5)_2OC_2H_5$, which is then

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[1] Hofmann, *Proc. Roy. Soc.* xi. 66, Carey-Lea, *Sillim. Am. Journ.* [2], xxxii. 25 ; xxxiv.

[2] *Ber. Deutsch. Chem. Ges.* iii. 109.

washed and mechanically separated, and then purified as hereafter described.[1] Duvillier and Buisine have described a modification of this method of separation.[2]

Ethylamine, $C_2H_5.NH_2$.

259 In order to obtain this compound pure, diethyloxamide is recrystallized from hot water and then distilled with caustic potash:

$$C_2O_2(NH.C_2H_5)_2 + 2\,HOK = 2\,NH_2.C_2H_5 + C_2O_2(OK)_2.$$

Pure ethylamine is also obtained by reducing nitroethane.

It is a mobile liquid boiling at 18°·7, and having a specific gravity of 0·6964 at 8°. It possesses a strong ammoniacal smell and a powerful caustic taste. It is miscible in all proportions with water with evolution of heat, and when ignited it burns with a yellow flame.

Ethylamine is also formed when sal-ammoniac and ammonium iodide are heated with alcohol to 400°,[4] as well as when sal-ammoniac is fused with crystallized sodium ethylate.[5]

Ethylamine is so powerful a base that it decomposes ammoniacal salts, and, like ammonia, throws down many metallic hydroxides. It is, however, distinguished from ammonia by the fact that precipitated aluminium hydroxide redissolves in excess of ethylamine. This base may, therefore, be employed for the separation of ferric oxide and alumina.[6] Other points of difference are that cupric hydroxide dissolves only with difficulty in excess of ethylamine, whilst the salts of cadmium, nickel, and cobalt yield precipitates which are insoluble in excess.

Ethylamine Hydrochloride, or *Ethylammonium Chloride*, $N(C_2H_5)H_3Cl$, crystallizes from water in fine very deliquescent prisms, and from hot alcohol in tablets. Stas obtained it in large crystals by allowing a mixture of ethyl chloride and an ethereal solution of ammonia to stand for some time exposed to the action of the sun's rays.[7] According to Groves this salt is best obtained by heating a mixture of one volume of ethyl

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[1] Hofmann, *Proc. Roy. Soc.* xi. 66; *Ber. Deutsch. Chem. Ges.* iii. 776; *Ber. Berlin. Acad.* 1871, 26.

[2] *Compt. Rend.* lxxxviii. 31.

[3] V. Meyer, *Liebigs Ann.* clxxv. 88.

[4] Berthelot, *Ann. Chim. Phys.* [3], xxxviii. 64.

[5] Köhler, *Ber. Deutsch. Chem. Ges.* xi. 2093.

[6] E. Meyer, *Journ. Prakt. Chem.* lxvii. 147.

[7] Kekulé, *Lehrbuch*, i.

chloride and three volumes of strong alcoholic ammonia for seven hours to 100°.[1] It melts at 76°—80° and on cooling solidifies to a crystalline mass. Heated from 315° to 320°, it evolves vapours, and on cooling forms a milk-white amorphous mass melting at 260°. It forms double salts with metallic chlorides.

The *bromide* and *iodide* closely resemble the chloride but have not been more exactly described. According to Wöhler and Dünhaupt pure ethylamine hydriodide is obtained when a boiling mixture of equal volumes of ethyl iodide and absolute alcohol is saturated with dry ammonia and then allowed to stand until water produces no further turbidity.[2]

Ethylammonium Sulphate, $(NC_2H_5)_2H_6SO_4$, is an uncrystallizable deliquescent mass, easily soluble in alcohol. It forms double salts with the sulphates of magnesium, copper and aluminium. Aluminium ethylammonium alum, $Al_2(SO_4)_3 + (NC_2H_5)_2H_6SO_4 + 24H_2O$, crystallizes in octohedrons.

Ethylammonium Nitrate crystallizes only with difficulty in very deliquescent scales.

Ethylammonium Carbonate is obtained by distilling the anhydrous chloride with dry carbonate of soda. It is obtained as a liquid which solidifies to a crystalline mass. It has a strong smell of ammonia and is deliquescent. Its composition closely corresponds to that of the normal salt.

Ethylammonium Carbamate, $CO\left\{\begin{matrix}N(C_2H_5)H\\ ON(C_2H_5)H_3\end{matrix}\right.$, is a white powdery mass obtained by passing dry carbon dioxide into ethlyamine. It is soluble in water and its solution precipitates calcium chloride on standing.

Ethylammonium Chloraurate, $N(C_2H_5)H_3AuCl_4$, is obtained by evaporating a solution of the hydrochloride with gold chloride, and crystallizes in fine golden-yellow prisms, soluble in water, alcohol, and ether.

Ethylammonium Platinichloride, $N_2(C_2H_5)_2H_6PtCl_6$, is formed as a yellow precipitate when concentrated solutions of its two constituents are mixed and alcohol added. It crystallizes from hot water in obtuse rhombohedrons, which were long supposed to be cubes (Schabus).

Platodiethylammonium Platinochloride, $Pt(NC_2H_5H_2)_4PtCl_4$. This compound, which corresponds to *Magnus's green salt*, is a reddish insoluble powder, obtained by Würtz by acting on ethylamine with platinous chloride. When it is heated with a

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[1] *Quart. Journ. Chem. Soc.* xiii. 331.

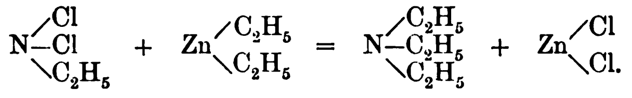
[2] *Ann. Chem. Pharm.* lxxxvi. 371.

solution of ethylamine it dissolves, frequently leaving a residue of an insoluble black powder, and on evaporating the solution, fine colourless prisms of platodiethylammonium chloride, $Pt(NC_2H_5H_2)_4Cl_2$ (see Vol. II. Part II. p. 412), are obtained.

Corresponding palladium compounds are also known,[1] and in addition to those already described, several other ethylamine salts have been investigated by E. Meyer.[2]

Ethylammonium Hydrosulphide is obtained by acting with sulphuretted hydrogen on ethylamine cooled with ice. It forms fine colourless crystals which become yellow-coloured on exposure and deliquesce. Its solution dissolves antimony sulphide.

Dichlorethylamine, or *Ethylated Chloride of Nitrogen*, $NC_2H_5Cl_2$. This singular compound was first obtained by Wurtz,[3] by acting with chlorine on an aqueous solution of ethylamine. In order to prepare it, 250 grams of bleaching powder are rubbed up with water to a thick paste and placed in a two-liter flask, 100 grams of ethylamine hydrochloride being added in four portions, a strong evolution of heat occurring. The mixture is then distilled so long as oily drops pass over, and the product is subjected to a second treatment with bleaching powder. The distillate is then washed with water, shaken up with 50 per cent. sulphuric acid, washed with dilute caustic soda, dried over chloride of calcium, and fractionated.[4] Dichlorethylamine is a strongly refracting golden-yellow liquid, having a highly penetrating smell resembling chlorpicrin and hypochlorous acid. It boils at 88°—89°, and at 5° has a specific gravity of 1·2397. By the action of zinc-ethyl it is converted into triethylamine:



$$\mathrm{N}\begin{array}{l}\diagup \mathrm{Cl}\\ -\mathrm{Cl}\\ \diagdown \mathrm{C_2H_5}\end{array} + \mathrm{Zn}\begin{array}{l}\diagup \mathrm{C_2H_5}\\ \diagdown \mathrm{C_2H_5}\end{array} = \mathrm{N}\begin{array}{l}\diagup \mathrm{C_2H_5}\\ -\mathrm{C_2H_5}\\ \diagdown \mathrm{C_2H_5}\end{array} + \mathrm{Zn}\begin{array}{l}\diagup \mathrm{Cl}\\ \diagdown \mathrm{Cl}.\end{array}$$

When kept, it frequently decomposes with formation of hydrochloric acid, sal-ammoniac, ethylamine hydrochloride, chloroform, acetonitril, and acetyl chloride.[5] This decomposition, however, only takes place when the body is not perfectly pure.[6]

Di-iodoethylamine, $C_2H_5NI_2$. This ethylated iodide of nitrogen was obtained by Wurtz, together with ethylamine hydriodide,

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[1] H. Müller, *Ann. Chem. Pharm.* lxxxvi. 367.

[2] *Journ. Prakt. Chem.* lxvii. 147 ; lxviii. 279.

[3] *Compt. Rend.* xi. 810.

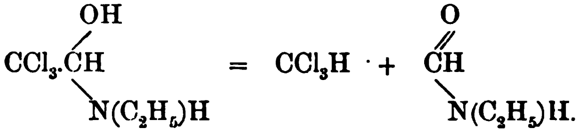
[4] Tscherniak, *Ber. Deutsch. Chem. Ges.* ix. 146.

[5] Köhler, *ib.* xii. 1869.

[6] Tscherniak, *Ber. Deutsch. Chem. Ges.* xii 2120.

by treating an aqueous solution of ethylamine with iodine. It is a dark blue liquid which decomposes on heating with carbonization and evolution of iodine vapours.

Ethyl Formamide, $N\left\{\begin{matrix}C_2H_5\\COH\\H\end{matrix}\right.$, is obtained by distilling an aqueous solution of ethylamine formate, and separates from the distillate on addition of potash.[1] If ethylamine be brought in contact with chloral, a crystalline compound is formed, which on distillation decomposes into chloroform and ethyl formamide:[2]



$$CCl_3.CH(OH)N(C_2H_5)H = CCl_3H + CH(O)N(C_2H_5)H.$$

Ethyl formamide is a thick, almost odourless liquid, boiling at 199° and having a specific gravity of 0·952 at 21°

DIETHYLAMINE, $N(C_2H_5)_2H$.

260 Diethylamine is obtained by distilling the before-mentioned ether of diethyloxamic acid with potash:

$$C_2O_2\left\{\begin{matrix}N(C_2H_5)_2\\OC_2H_5\end{matrix}\right. + 2\,KOH = C_2O_2\left\{\begin{matrix}OK\\OK\end{matrix}\right. + N(C_2H_5)_2H + HO.C_2H_5.$$

In order to obtain this ether in the pure state, the crude oil is cooled to 0°, poured off from the diethyl oxamide which separates out, and distilled, when the pure ether comes over at 260°.

Diethylamine is a colourless liquid boiling at 57°·5, possessing a strongly ammoniacal smell, and being easily soluble in water. It is distinguished from ethylamine by the fact that copper hydroxide dissolves only very slightly in excess, whilst zinc hydroxide is altogether insoluble (Carey Lea). Its salts have been but slightly investigated. The platinichloride, $[N(C_2H_5)_2H_2]_2PtCl_6$, forms large orange-red monoclinic crystals resembling octohedrons (Müller, Schabus).

Nitrosodiethylamine, $N(C_2H_5)_2NO$, was obtained by Geuther

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[1] Linnemann, *Wien. Akad. Ber.* 2te Abth. lx. 44.

[2] Hofmann, *Ber. Deutsch. Chem. Ges.* v. 247.

by acting on a concentrated solution of potassium nitrite with a perfectly neutral solution of diethylamine hydrochloride:

$$N\left\{\begin{array}{l}C_2H_5\\C_2H_5\\H\end{array}\right. + HO.NO = N\left\{\begin{array}{l}C_2H_5\\C_2H_5\\NO\end{array}\right. + H_2O.$$

This compound, to which he gave the name of nitro-diethylin, and which has likewise been termed diethyl-nitrosamine, is a yellowish oil having an aromatic smell and a burning taste, boiling at 177°, and having at 17°·5 a specific gravity of 0·951. When acted upon by hydrochloric acid in presence of water it dissolves, and on heating forms diethylamine hydrochloride, whilst nitric oxide is evolved, produced from the decomposition of the nitrous acid formed. Dry hydrochloric acid gas also converts it with evolution of nitrosyl chloride into diethylamine hydrochloride, and when it is treated with water and sodium amalgam the following reaction takes place:[1]

$$2\,N(C_2H_5)_2NO + 3\,H_2 = 2\,N(C_2H_5)_2H_2 + N_2O + H_2O.$$

Diethyl Formamide, $N(C_2H_5)_2COH$, is formed by distilling diethylamine formate, as a thick odourless liquid boiling at 175°—178°, and having at 19° a specific gravity of 0·908 (Linnemann).

TRIETHYLAMINE, $N(C_2H_5)_3$.

261 This is a colourless, oily, pleasantly smelling, strongly alkaline liquid, boiling at 91°, lighter than water, and slightly soluble in this liquid. It precipitates many metallic salts. The precipitates are, however, not soluble in an excess of the reagent, with the exception of silver oxide, which dissolves sparingly, and of the aluminium and stannic hydroxides, which are readily soluble, in excess.

Triethylamine Hydrochloride, $N(C_2H_5)_3HCl$, is an inflammable substance crystallizing in feathery non-deliquescent scales which may be sublimed without decomposition. It forms with platinic chloride the compound $[N(C_2H_5)_3H]_2PtCl_6$, easily soluble in water, and yielding, on evaporation, large red rhombic crystals.

Triethylamine Hydrobromide, $N(C_2H_5)_3HBr$, forms large feathery crystals resembling sublimed sal-ammoniac.

The *sulphate* is a very soluble salt crystallizing with difficulty.

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[1] *Journ. Prakt. Chem.* [2], iv. 435.

Triethylamine Nitrate, $N(C_2H_5)_3HNO_3$, is, according to Lea, uncrystallizable, whereas V. v Lang mentions that it forms rhombic crystals which are isomorphous with those of nitre.[1]

The Tetraethylammonium Compounds.

262 *Tetraethylammonium Hydroxide*, $N(C_2H_5)_4OH$, is obtained by gradually adding freshly precipitated silver oxide to a weak warm solution of the corresponding iodide. If the filtrate be evaporated first on a water-bath and then in a vacuum, long very deliquescent needles are frequently obtained. These disappear on further evaporation, the compound drying up to a semi-solid deliquescent mass which in its reactions closely resembles caustic potash, with the exception that chromium hydroxide is insoluble in an excess of this reagent.

When heated with ethyl iodide, alcohol is formed:

$$N(C_2H_5)_4OH + C_2H_5I = N(C_2H_5)_4I + C_2H_5.OH.$$

The hydroxide when heated alone decomposes into triethylamine, ethylene, and water.

Tetraethylammonium Chloride, $N(C_2H_5)_4Cl$, is obtained by saturating the hydroxide with hydrochloric acid. It is crystalline but very deliquescent, and forms with various metallic chlorides crystallizable double salts.

The *bromide* is a very similiar body, uniting with bromine to form the tribromide, $N(C_2H_5)_4Br_3$, crystallizing from alcoholic solution in bright yellow needles which melt at 78° without decomposition.[2]

Tetraethylammonium Iodide, $N(C_2H_5)_4I$. This forms the starting-point for the preparation of the tetraethylammonium compounds, and is formed, as has already been stated, by the action of ethyl iodide on ammonia or on the ethylamines. If iodide of ethyl be mixed with triethylamine the mixture soon becomes hot, and, after some days, solidifies to a white crystalline mass. The combination takes place more rapidly when the mixture is heated in sealed tubes to 100°. The iodide is easily soluble in water, and separates on evaporation in fine well-formed crystals. When heated it decomposes into ethyl iodide and triethylamine which distil over separately, but, on cooling, again unite. It is insoluble in caustic potash, and

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[1] *Zeitsch. Chem.* 1867, 405.

[2] Marquart, *Ber. Deutsch. Chem. Ges.* iii. 284.

hence separates out when caustic potash is added to its solution, without undergoing the slightest decomposition. Exposed to the air, the salt changes to the *tri-iodide*, $N(C_2H_5)_4I_3$, a fact first observed by Hofmann, but afterwards more exactly examined by Weltzien.[1] This compound is also obtained by treating the product of the reaction of iodide of ethyl on ammonia with iodine. It crystallizes from hot alcohol in feathery needles, but is deposited from a solution in potassium iodide in quadratic prisms which exhibit a fine blue lustre by reflected light, and a reddish-brown colour by transmitted light. On addition of water to the mother-liquor, a brownish oil separates out, probably the pentaiodide. By the action of iodine monochloride on tetraethylammonium chloride, the compound $N(C_2H_5)_4Cl_2I$ is formed in fern-shaped crystals like sal-ammoniac.[2]

Tetraethylammonium Chloraurate, $N(C_2H_5)_4AuCl_4$, is a lemon-yellow crystalline precipitate deposited from solution in hot water.

Tetraethylammonium Platinichloride, $N_2(C_2H_5)_8PtCl_6$, is exactly analogous to the corresponding potassium compound, and crystallizes from hot water in octohedrons.

Besides these bodies, a large number of other tetraethylammonium salts exist. These have been examined by Hofmann and by Classen.[3]

Methyltriethylammonium Iodide, $NCH_3(C_2H_5)_3I$, is easily formed by the combination of methyl iodide with triethylamine. It is obtained in crystals which are exceedingly soluble in water, and which, in chemical reaction, exhibit great analogy with tetraethylammonium iodide.[4]

Dimethyldiethylammonium Iodide, $N(CH_3)_2(C_2H_5)_2I$, is formed by the prolonged action of ethyl iodide on dimethylamine, as also by acting on diethylamine with methyl iodide. In its properties it closely resembles the other ammonium iodides. If the corresponding chloride be heated it decomposes into methyl chloride and methyldiethylamine, $N(CH_3)(C_2H_5)_2$.[5] Hence we see that the salts, $N\left\{\begin{array}{l}CH_3\\CH_3\\C_2H_5\end{array}\right. + C_2H_5Cl$ and $N\left\{\begin{array}{l}C_2H_5\\C_2H_5\\CH_3\end{array}\right. + CH_3Cl$

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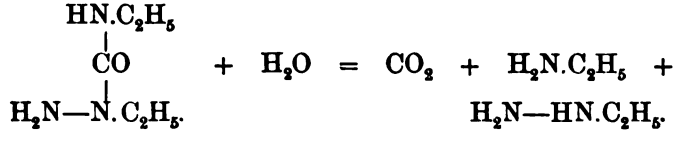
[1] *Ann. Chem. Pharm.* lxxxvi. 292; xci. 33.
[2] Tilden, *Journ. Chem. Soc.* [2], xix. 145.
[3] *Journ. Prakt. Chem.* xciii. 446.
[4] Hofmann, *Phil. Trans.* 1851 (ii.) 357.
[5] Meyer and Lecco, *Ann. Chem. Pharm.* clxxx. 173.

are identical and cannot be considered as molecular compounds, one of which contains ethyl chloride and the other methyl chloride. Hence it also follows *that in all the ammonium compounds nitrogen acts as a pentad.*[1]

ETHYL HYDRAZINES.

263 These compounds (see *ante*, p. 161) were discovered by E. Fischer[2] and carefully investigated by him.

Ethyl Hydrazine, $C_2H_5.N_2H_3$. Diethyl urea, $CO(NH.C_2H_5)_2$, is the starting point for this compound, being first converted by means of nitrogen trioxide into the nitroso-compound $CON_2(NO)(C_2H_5)_2H$. This is next treated with acetic acid and zinc dust, diethyl semicarbazide being formed, and this, on boiling with hydrochloric acid, is converted into ethyl hydrazine, carbon dioxide, and ethylamine:



$$\begin{matrix} HN.C_2H_5 \\ | \\ CO \\ | \\ H_2N{-}N.C_2H_5 \end{matrix} + H_2O = CO_2 + H_2N.C_2H_5 + H_2N{-}HN.C_2H_5.$$

As soon as the decomposition is complete, the solution is cooled by ice and saturated with hydrochloric acid, when hydrazine hydrochloride separates out as a crystalline mass. When concentrated caustic potash is added to the dry salt, a solution of the base is obtained, which separates out as an oily liquid on the addition of powdered caustic potash. It may be completely dehydrated by the addition of anhydrous baryta.

Ethyl hydrazine is a mobile colourless liquid possessing an ethereal slightly ammoniacal smell, and boiling at 99°·5 when the barometer stands at 709 mm. It is very hygroscopic, and at the ordinary temperature possesses a high vapour-tension, and, for this reason, it emits thick white fumes on exposure to moist air. It dissolves in water and alcohol with evolution of heat; it is very caustic, in a short time destroying cork and caoutchouc. With acids two series of salts are formed, of which the hydrochloride is the only one hitherto carefully examined. The acid

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[1] In pars. 34 and 35 of Vol. I. it is stated that the elements of the nitrogen group are trivalent, but that they possess the peculiarity of acting as pentads in certain compounds. The facts above stated, as well as others, such as the existence of a stable phosphorus pentafluoride, prove that these elements do not possess a constant valency. The compounds in which they are pentads decompose more or less readily into two molecules.

[2] *Liebig's Annalen*, cxcix, 281.

salt, $C_2H_5.N_2H_3(ClH)_2$, forms white needles, and its aqueous, as well as its alcoholic solution, has an acid reaction. When this solution is evaporated, or when the dry salt is heated to 110°, the neutral compound is obtained as a horny deliquescent mass. The neutral sulphate is very soluble in water, and crystallizes from hot alcohol in fine glistening tablets or scales.

Ethyl hydrazine is only slowly attacked by oxidizing agents in acid solution, but it is quickly destroyed in alkaline liquids. It reduces Fehling's solution in the cold with evolution of nitrogen mixed with a combustible gas. The oxides of silver and mercury act in a similar way, the latter with formation of a small quantity of mercuric ethide. Ethyl hydrazine behaves like ammonia with respect to the salts of lead, nickel, cobalt and iron. The cobalt precipitate, however, is prevented from oxidation by the reducing action of the base, and hence it preserves its blue colour for a long time, whilst the precipitated ferric hydroxide is rapidly converted into the black hydroxide on warming. Heated with alcoholic potash and chloroform hydrazine gives the carbamine reaction (see p. 413), whilst with ethyl iodide it forms diethyl hydrazine and other ethylated bases.

Potassium Ethyl Hydrazine Sulphonate, $C_2H_5.NH.NH.SO_3K$, is formed by warming the base with potassium disulphate. It is very soluble in water, and separates out on addition of alcohol in fine glistening scales. When boiled with hydrochloric acid it decomposes into the base, and acid potassium sulphate, and when its concentrated solution is treated with mercuric oxide *potassium diazoethane sulphonate*, $C_2H_5N{=}N.SO_3K$, is formed. This crystallizes in scales or needles which deflagrate strongly on heating when dry, and on treatment with zinc-dust and acetic acid is again converted into the original compound.

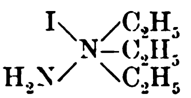
264 *Diethyl Hydrazine*, $(C_2H_5)_2N_2H_2$, is obtained by the action of zinc-dust and acetic acid on an aqueous solution of nitrosodiethylamine, when at the same time ammonia and diethylamine are produced:

$$(C_2H_5)_2N{-}NO + 2\,H_2 = (C_2H_5)_2N{-}NH_2 + H_2O.$$

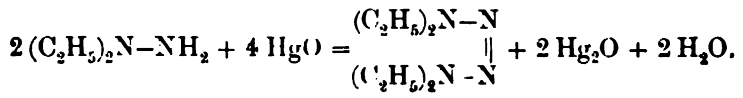
$$(C_2H_5)_2N{-}NO + 3\,H_2 = (C_2H_5)_2NH + NH_3 + H_2O.$$

In order to separate it from the diethylamine formed at the same time, it is converted into the difficultly soluble urea, which will be afterwards described, and which is decomposed by hydrochloric acid into diethyl hydrazine, carbon dioxide, and ammonia. The base dried over caustic baryta is an easily mobile colourless liquid which possesses an ethereal and faint ammoniacal odour. It boils at 96° to 99° and is easily soluble in water and alcohol. It is a monacid base, and forms soluble salts which as a rule crystallize with difficulty. The platinichloride, $(C_2H_5)_4N_4H_6PtCl_6$, separates out in yellow needles on addition of platinic chloride to the alcoholic solution of the hydrochloride. Fehling's solution is reduced by the free base only on warming, with evolution of nitrogen and formation of diethylamine. This reaction may be employed to detect the presence of a nitrosamine in aqueous solution. It is heated slowly with zinc-dust and acetic acid to the boiling point, filtered and warmed with Fehling's solution after saturation with an alkali. The smallest quantity of the hydrazine which is formed may be detected by the precipitation of cuprous oxide. This reaction is only of course available when no other substances are present which either alone or by the action of nascent hydrogen act as reducing agents, such for example as the hydrazine bases, hydroxylamine, and the nitrogen acids, which latter yield bases. In such cases these bodies must be removed by distillation, either with an alkali or with an acid.

265 *Triethylazonium Iodide*, $(C_2H_5)_3N_2H_2I$. This is formed by the union of diethyl hydrazine with ethyl iodide. It is easily soluble in water, and crystallizes from hot alcohol in white needles, which yield with silver oxide a strong alkaline hydroxide analogous to tetraethylammonium hydroxide, and this when heated with water yields diethyl hydrazine and ethylene. If its aqueous solution be treated with zinc-dust and dilute sulphuric acid on a water-bath, triethylamine, hydriodidic acid and ammonia are formed. This decomposition is a further proof that ammonium compounds contain pentad nitrogen, for this reaction can only be explained under the supposition that the iodide possesses the following composition:



Tetraethyl-Tetrazone, $(C_2H_5)_4N_4$, is formed by the action of yellow mercuric oxide on a cold aqueous solution of diethyl hydrazine:



$$2\,(C_2H_5)_2N{-}NH_2 + 4\,HgO = \begin{array}{c}(C_2H_5)_2N{-}N\\ \Vert\\ (C_2H_5)_2N{-}N\end{array} + 2\,Hg_2O + 2\,H_2O.$$

This compound is an almost colourless oil insoluble in water but soluble in alcohol, possessing a peculiar alliaceous smell. It does not solidify at – 20°. It volatilizes in aqueous vapour but cannot be distilled by itself, and when quickly heated partially decomposes with deflagration into diethylamine and nitrogen. It is easily soluble in acids, but its salts are very unstable. Thus the hydrochloric acid solution when heated to 70°—80° decomposes with a rapid evolution of nitrogen:

$$(C_2H_5)_4N_4 + H_2O = C_2H_5.NH_2 + (C_2H_5)_2NH + C_2H_4O + N_2.$$

This reaction is remarkable for the ease with which the ethyl group separates from the nitrogen and is converted into aldehyde, in order to yield the hydrogen necessary for the formation of the amine.

The platinichloride, $(C_2H_5)_8N_8H_2PtCl_6$, separates out from alcoholic solution in small golden yellow prisms. It dissolves in cold water without alteration, but like the chloride, decomposes on boiling.

Tetraethyl-tetrazone acts as a strong base, decomposing many salts of the heavy metals. If a solution of this substance be brought in contact with silver nitrate, an almost instantaneous evolution of nitrogen takes place with formation of a silver mirror. Warmed with water and silver oxide the same phenomenon takes place, silver acetate being at the same time formed. When shaken with a solution of iodine in potassium iodide a dark oil separates out which deflagrates when slightly warmed under water.

CYANOGEN COMPOUNDS OF ETHYL.

266 *Ethyl Carbamine*, $CN.C_2H_5$. If a mixture of ethylamine, chloroform, and alcohol be poured into a retort containing powdered caustic potash the liquid soon begins to boil violently and ethyl carbamine distils over together with ethylamine, chloroform, alcohol, and water, the first-mentioned substance being separated by repeated fractional distillation.[1] It is, however, obtained in the pure state more readily by acting with one molecule of ethyl iodide upon two molecules of silver cyanide in presence of some ether, the mixture being heated in sealed tubes for several hours to 130°—140°.[2] The crystallized

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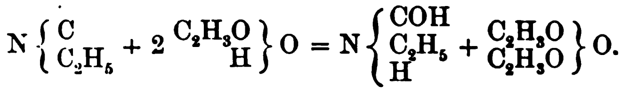
[1] Hofmann, *Ann. Chem. Pharm.* cxlvi. 107.

[2] Gautier, *Bull. Soc. Chim.* [2], viii. 216, 395, 400.

compound $CNAg + CNC_2H_5$ is then formed, and this is distilled, after the evaporation of the ether, with half its weight of potassium cyanide and some water, the product being subsequently dried over calcium chloride and rectified.[1]

Ethyl carbamine is a colourless liquid having a repulsive penetrating odour. The inhalation of its vapour produces headache and giddiness. It possesses a slightly alkaline reaction, boils at 78°—80°, and is converted into ethylamine formate when heated with water for twelve hours to 180°. Anhydrous hydrochloric or hydrobromic acid is absorbed with such avidity that a tarry mass is formed. In presence of ether the salts of ethyl carbamine are obtained, of which the hydrochloride possesses the composition $(CN.C_2H_5)_2(ClH)_3$.[2] It forms white scales having a bitter taste. It is deliquescent and its solution quickly decomposes with formation of ethylamine and formic acid. If, however, it be treated with concentrated caustic potash in the cold, ethyl formamide is obtained as the chief product. This is also formed together with acetic anhydride when the carbamine is mixed with anhydrous acetic acid, considerable heat being evolved:



$$N\left\{\begin{matrix} C \\ C_2H_5 \end{matrix}\right. + 2\left.\begin{matrix} C_2H_3O \\ H \end{matrix}\right\}O = N\left\{\begin{matrix} COH \\ C_2H_5 \\ H \end{matrix}\right. + \left.\begin{matrix} C_2H_3O \\ C_2H_3O \end{matrix}\right\}O.$$

Ethyl carbamine is also formed in small quantity by distilling the isomeric propionitril, a body to be afterwards described, and it is converted into this substance when heated in closed glass tubes to 180°.

267 *Ethyl Cyanate*, $NC.OC_2H_5$, the normal cyanic ether, was obtained by Cloëz[3] by acting with cyanogen chloride on a solution of sodium ethylate in a mixture of ether and alcohol. It was called by him *cyanetholin* in order to distinguish it from the isocyanate which was then supposed to be the true cyanic ether.

It is a colourless oily liquid, possessing an ethereal smell and a sharp bitter taste, having a specific gravity of 1·1271 at 15°. Caustic potash decomposes it with formation of alcohol and potassium cyanurate. If hydrochloric or hydrobromic acid be passed into the solution, a thick mass is obtained which becomes solid within twenty-four hours, and on slightly warming yields

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[1] Gautier, *Bull. Soc. Chim.* [2], ix. 211.

[2] *Bull. Soc. Chim.* [2], ii. 212.

[3] *Compt. Rend.* xliv. 428.

a distillate of ethyl chloride or bromide, cyanuric acid remaining behind.[1] Ethyl cyanate decomposes easily into a crystalline mass which is a mixture of the two following compounds:[2]

Diethyl amidocyanurate, $C_3N_3(OC_2H_5)_2NH_2$, crystallizing in slender white prisms, melting at 97°.

Ethyl diamidocyanurate, $C_3N_3(OC_2H_5)(NH_2)_2$, a white crystalline mass fusing above 190°.

268 *Ethyl Isocyanate*, or *Ethyl Carbimide*, $CO.NC_2H_5$, was obtained by Wurtz[3] by distilling a mixture of one part of freshly prepared and well-dried potassium cyanate with two parts of potassium ethyl sulphate. The reaction begins at 180°, and is completed at 250°. The distillate is a mixture of ethyl isocyanate and isocyanurate, and these can be readily separated by distillation. Ethyl carbimide is a mobile liquid, boiling at 60°, and having a specific gravity of 0.898. It possesses a suffocating, very irritating smell. It is converted by the action of water, ammonia, and the amines into the ethylated ureas.

The following reaction takes place when it is heated with caustic potash:

$$N\left\{\begin{matrix} C_2H_5 \\ CO \end{matrix}\right. + 2\,HOK = CO(OK)_2 + N\left\{\begin{matrix} C_2H_5 \\ H \\ H \end{matrix}\right.$$

It has already been stated that this was the reaction by which the amines were first obtained by Würtz (see p. 401).

Ethyl carbimide combines with anhydrous hydrochloric acid to form *ethyl carbonyl ammonium chloride*, $N(CO)(C_2H_5)HCl$, a liquid possessing a penetrating odour, boiling at 98°, and decomposed by water into ethylamine hydrochloride and carbon dioxide.[4] It forms similar compounds with hydrobromic acid.[5]

Ethyl Isocyanurate, $C_3O_3(NC_2H_5)_3$, is easily formed from the foregoing compound, as also when potassium cyanurate and potassium ethyl sulphate are heated together to 200°. It crystallizes from boiling alcohol in rhombic prisms, which melt at 85° and boil at 276° (Limpricht and Habich). When heated with ammonia it does not undergo change, whereas on treatment with potash, it decomposes with formation of

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[1] Gal, *Compt. Rend.* lxi. 527.

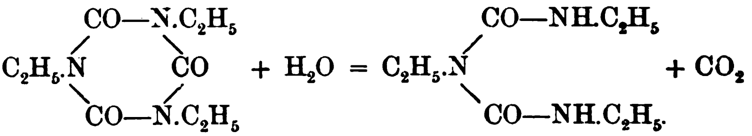
[2] Hofmann and Olshausen, *Ber. Deutsch. Chem. Ges.* iii. 269.

[3] *Ann. Chim. Phys.* [3], xlii. 43.

[4] Limpricht and Habich, *Ann. Chem. Pharm.* cix. 107.

[5] Gal, *Bull. Soc. Chim.* vi. 439.

ethylamine and potassium carbonate. On the other hand, boiling baryta-water decomposes it into *triethyl-biuret:*



Ethyl isocyanurate is a thick oily liquid, which when heated yields diethyl-urea and ethyl carbimide.[1]

Diethyl-isocyanuric Acid, $C_3O_3N_3(C_2H_5)_2H$, is contained in combination with ethylamine in the crude product obtained by distilling potassium cyanurate with potassium ethyl sulphate, and is prepared from the mother-liquors of ethyl isocyanurate by boiling with baryta-water until ethylamine is evolved. Carbon dioxide is then passed through the liquid, and the filtrate evaporated, when triethyl-biuret first separates out and then the barium salt of diethyl-cyanuric acid; this latter is then decomposed by sulphuric acid. The free acid crystallizes in hexagonal prisms or obtuse rhombohedrons. It melts at 173°, and volatilizes without decomposition. If silver nitrate be added to a hot ammoniacal solution, the salt, $C_3O_3N_3(C_2H_5)_2Ag$, separates out in needles (Limpricht and Habich).

Ethyl Ferrocyanide, $(C_2H_5)_8(C_3N_3)_4Fe_2 + 12H_2O$. When an alcoholic solution of ferrocyanic acid is saturated with hydrochloric acid, the compound $(C_2H_5)_8(C_3N_3)_4Fe_2 + 4C_2H_5Cl + 12H_2O$ is formed. This is deposited in colourless crystals which rapidly become blue on exposure to air. If these be dissolved in alcohol, and ether added, ethyl ferrocyanide separates out in pearly crystals which readily turn blue on exposure to air.[2]

Ethyl Platinocyanide, $(C_2H_5)_2Pt(CN)_4 + 2H_2O$, is obtained by passing hydrochloric acid into a concentrated alcoholic solution of platinocyanic acid (Vol. I., p. 417). It crystallizes in quadratic pink needles which easily decompose in the air with formation of alcohol. When heated on a water-bath they become lemon-yellow with formation of the anhydrous platinocyanic acid:[3]

$$(C_2H_5)_2Pt(CN)_4 + 2\,H_2O = H_2Pt(CN)_4 + 2\,C_2H_5.OH.$$

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[1] Limpricht and Habich, *loc. cit.*

[2] H. L. Buff, *Ann. Chem. Pharm.* xci. 253.

[3] v. Thann, *Ann. Chem. Pharm.* cvii. 315.

Ethyl Cyanamide, $N(C_2H_5)CNH$, is formed by passing cyanogen chloride into an ethereal solution of ethylamine when a neutral syrupy liquid is obtained which, when dissolved in water and evaporated, and these operations frequently repeated, is converted into the polymeride, triethyl cyanuramide, $N_3H_3(C_2H_5)_3(CN)_3$. This has an alkaline reaction and crystallizes in needles. When heated with hydrochloric acid it is converted into triethyl isocyanurate. Both these amides decompose when heated, solid *ethyl dicyanamide*, $(NC)_2N_2(C_2H_5)H_3$, being left behind, and *diethylcyanamide*, $(NC)N(C_2H_5)_2$, distilling over.[1] This latter is also formed when ethyl iodide is heated with silver cyanamide (Vol. I., p. 676). It is a liquid, boiling at 186°, and decomposing when heated with strong hydrochloric acid as follows:[2]

$$N\left\{\begin{array}{l}CN\\ C_2H_5\\ C_2H_5\end{array}\right. + 2\,H_2O = N\left\{\begin{array}{l}H\\ C_2H_5\\ C_2H_5\end{array}\right. + NH_3 + CO_2.$$

269 *Ethyl Thiocyanate*, $NC.SC_2H_5$. Cahours[3] first obtained this compound by distilling a concentrated solution of potassium thiocyanate with potassium ethyl sulphate, and Löwig[4] prepared it by the action of ethyl chloride on potassium thiocyanate. It is also easily formed by heating ethyl iodide together with many metallic thiocyanates, of which the mercury salt is however not one.[5] In order to prepare it, an alcoholic solution of potassium thiocyanate is heated with ethyl iodide. The compound is separated out by the addition of water, and washed with a concentrated solution of common salt, as its specific gravity is very nearly equal to that of water. It is then dried over chloride of calcium.[6]

It is a mobile liquid possessing a penetrating alliaceous smell and sweet taste, boiling at 141°—2° when the barometer is at 733°,[7] and having at 0° a specific gravity of 1·033, and a vapour-density of 3·018 (Cahours). Ethyl thiocyanate is oxidized by nitric acid with formation of ethyl sulphonic acid, and on boiling with an alcoholic solution of potassium

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[1] Cahours and Cloëz, *Compt. Rend.* xxxviii. 354; Hofmann, *Ber. Deutsch. Chem. Ges.* ii. 600; iii. 264.

[2] Fileti and Schiff, *Ber. Deutsch. Chem. Ges.* x. 427.

[3] *Ann. Chim. Phys.* [3], xviii. 264.

[4] *Pogg. Ann.* lxvii. 101.

[5] Schlagdenhauffen, *Ann. Chim. Phys.* [3], lvi. 297.

[6] Baudrimont, *Bull. Soc. Chim.*

[7] V. Meyer, *Liebig's Ann* clxxi. 47.

sulphide it is converted into potassium thiocyanate and mercaptan. Caustic potash converts it into potassium cyanide, potassium cyanate and ethyl disulphide.[1]

The latter reaction is represented as follows:

$$2\,NC.SC_2H_5 + 2\,KOH = \left\{\begin{matrix} SC_2H_5 \\ SC_2H_5 \end{matrix}\right. + NCK + NCOK + H_2O.$$

270 *Ethyl Thiocarbimide,* or *Ethyl Mustard Oil,* $CS.NC_2H_5$. An alcoholic solution of ethylamine becomes warm on addition of sulphide of carbon, and fine six-sided tables separate out from the neutral solution consisting of *ethylammonium ethylthiocarbamate,* $CS\left\{\begin{matrix} NH.C_2H_5 \\ SN(C_2H_5)H. \end{matrix}\right.$ When acted upon by caustic soda it yields, with evolution of ethylamine, the sodium salt of ethyl thiocarbamic acid. This latter, on addition of hydrochloric acid, separates out as a clear light oil, solidifying after some time to a saponaceous crystalline mass, whilst if a larger quantity of hydrochloric acid be added it dissolves, carbon disulphide and ethylamine hydrochloride being formed. If the ethyl-ammonium salt above mentioned be heated under pressure to 110°—120°, sulphuretted hydrogen is evolved, and diethylthio-urea is formed (see p. 422), which, when heated with phosphorus pentoxide yields ethyl thiocarbimide:[2]

$$S = C\begin{matrix}\diagup N(C_2H_5)H \\ \diagdown N(C_2H_5)H\end{matrix} \quad = \quad S{=}C{=}N.C_2H_5 + N(C_2H_5)H_2.$$

This compound is more easily obtained by boiling the ethylammonium salt of ethyl thiocarbamic acid and water with silver nitrate, mercuric chloride, or cupric chloride. The corresponding metallic salts of the thiocarbamic acid are first formed, and these decompose with production of a metallic sulphide, suphuretted hydrogen, and ethyl mustard oil.[3] Instead of the metallic salts an alcoholic iodine solution may be employed:

$$CS\left\{\begin{matrix} N(C_2H_5)H \\ SN(C_2H_5)H_3 \end{matrix}\right. + I_2 = CS.NC_2H_5 + HI + S + N(C_2H_5)H_3I.$$

As soon as the colour of the iodine has disappeared, the liquid is distilled and the thiocarbimide precipitated from the distillate by water.[4]

[1] Brüning, *Ann. Chem. Pharm.* civ. 198.
[2] Hofmann, *Ber. Deutsch. Chem. Ges.* i. 25.
[3] *Ber. Deutsch. Chem. Ges.* i. 169.
[4] *Ib.* ii. 452.

Ethyl mustard-oil is also formed when ethylamine is heated with thiocarbonyl chloride, $CSCl_2$.[1]

Ethyl thiocarbimide is a mobile liquid boiling at 134° and possessing a very irritating smell, and when dropped on the skin producing a burning sensation. The specific gravity of its vapour is 2·98.

Heated with absolute alcohol to 110° *monothioethylurethane* is formed:

$$CS.NC_2H_5 \ + \ HO.C_2H_5 \ = \ CS\left\{\begin{matrix} N(C_2H_5)H \\ OC_2H_5. \end{matrix}\right.$$

This is a liquid possessing an alliaceous smell, boiling at 204°—208°, and decomposed by dilute acids with formation of alcohol, ethylamine, carbon dioxide, and sulphuretted hydrogen.

A compound isomeric with this is obtained when mercaptan is heated with ethyl isocyanate. It smells like the foregoing compound, boils at the same temperature, but is decomposed by dilute acids, as might be expected from its mode of formation, into mercaptan, carbon dioxide, and ethylamine. Its constitution is, therefore, $CO\left\{\begin{matrix} N(C_2H_5)H \\ SC_2H_5. \end{matrix}\right.$

When mercaptan is heated together with ethyl mustard oil a combination takes place, and a body is obtained resembling the foregoing. This cannot, however, be obtained in the pure state, as on distillation it decomposes into its constituents. This body is doubtless *dithioethylurethane*, $CS\left\{\begin{matrix} N(C_2H_5)H.^2 \\ SC_2H_5. \end{matrix}\right.$

ETHYLATED UREAS.

271 *Ethyl Carbamide*, $CO.N_2H_3(C_2H_5)$, is formed by the action of cyanic acid on ethylamine, and also by acting upon ammonia with ethyl carbimide:

$$CO.NC_2H_5 + NH_3 = CO\left\{\begin{matrix} N(C_2H_5)H \\ NH_2. \end{matrix}\right.$$

In order to prepare this body a solution of ethylamine sulphate is boiled down to dryness with potassium cyanide, and the residue treated with alcohol. Ethyl urea crystallizes in striated monoclinic prisms, easily soluble in water and alcohol,

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[1] Rathke, *Ann. Chem. Pharm.* clxvii. 211.

[2] Hofmann, *Ber. Deutsch. Chem. Ges.* ii. 116.

melting at 92°, and decomposing at a higher temperature with formation of diethyl cyanuric acid (p. 416). When heated with caustic potash, potassium carbonate, ammonia, and ethylamine are formed.[1] It absorbs hydrochloric acid gas with formation of the salt $CO.N_2H_4(C_2H_5)Cl$. The corresponding nitrate crystallizes in short thick prisms and, like the oxalate, it is slightly soluble in water. The hot aqueous solution of the urea dissolves freshly precipitated mercuric oxide, and on heating this solution, small needles separate out of the compound

$$\begin{matrix} CO \left\{ \begin{matrix} N(C_2H_5)H \\ NH \end{matrix} \right. \\ CO \left\{ \begin{matrix} NH \\ N(C_2H_5)H. \end{matrix} \right. \end{matrix} \!\!\left.\begin{matrix} \\ \\ \end{matrix}\right\} Hg$$

, which is almost insoluble in cold water.[2]

a-Diethyl Carbamide, $CO(NH.C_2H_5)_2$, is formed by the decomposition of ethyl isocyanate by water, as well as by the union of this substance with ethylamine. It crystallizes from water in flat prisms, and from alcohol in silky needles. It melts at 112°·5 and boils at 263°. Heated with caustic potash it decomposes with formation of ethylamine, and combines with nitric acid to form a deliquescent nitrate (Wurtz).

β-Diethyl Carbamide, $CO\left\{\begin{matrix} NH_2 \\ N(C_2H_5)_2 \end{matrix}\right.$, is formed by the combination of diethylamine and cyanic acid. The only reaction of this substance with which we are acquainted is that when heated with caustic potash it yields potassium carbonate, diethylamine, and ammonia.

Triethyl Carbamide, $CO\left\{\begin{matrix} N(C_2H_5)H \\ N(C_2H_5)_2 \end{matrix}\right.$, is obtained by dropping ethyl isocyanate into diethylamine. It forms white crystals, is soluble in water, alcohol, and ether, melts at 63°, and boils at 223°. It decomposes with alkalis with formation of ethylamine and diethylamine.[3]

Tetraethyl Carbamide, $CO\left\{\begin{matrix} N(C_2H_5)_2 \\ N(C_2H_5)_2 \end{matrix}\right.$, is not produced by the action of ethyl isocyanate upon triethylamine (Hofmann),[4] but is formed by passing carbonyl chloride mixed with double or treble its volume of petroleum-spirit into dilute diethylamine. It is a pleasantly-smelling liquid, boiling at 205°, dissolving in acids, and again separating out on the addition of alkalis.[5]

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[1] Wurtz, *Compt. Rend.* xxxii. 414; *Rép. Chim. Pure.* iv. 199.

[2] Leuckart, *Journ. Prakt. Chem.* [2], xxi. 1. [3] Wurtz, *Rép. Chim. Pure.* iv. 199.

[4] Hofmann, *Phil. Trans.* 1851, ii. 370.

[5] Michler, *Ber. Deutsch. Chem. Ges.* viii. 1664.

ETHYL SEMICARBAZIDES.

272 The name azide has been given by Fischer to compounds formed by the replacement of the hydrogen in the hydrazine group by acid radicals. The corresponding ureas must, therefore, be termed carbazides, and if these contain only one amido-group they are called semicarbazides.[1]

Ethyl Semicarbazide, or *Ethylhydrazine Urea*, $C_2H_5.NH - NH.CO.NH_2$. In order to prepare this compound, an equivalent quantity of pure potassium cyanate is heated to boiling with ethyl hydrazine hydrochloride in concentrated aqueous solution. On cooling, the urea, which is easily soluble in water, separates out on careful addition of solid caustic potash. The crystallized mass is dissolved in chloroform, the solution concentrated and ether added, when the compound is deposited in thin glistening tablets melting at 105°—106°.[2]

a-Diethyl Semicarbazide, $C_2H_5.N(NH)_2.CO.N(C_2H_5)H$. For the preparation of this compound, nitrosodiethyl-urea is employed. This latter body was discovered by v. Zotta,[3] but its constitution was first recognised by E. Fischer.[4] It is obtained by passing an excess of nitrogen trioxide into an ethereal solution of diethyl-urea. It is a yellow oil insoluble in water, from which solution transparent tablets separate at a low temperature. It possesses a burning taste and decomposes suddenly on heating. When brought in contact with phenol and sulphuric acid it colours the liquid first brown, then green, and finally a bright blue.[5] By the action of acetic acid and zinc-dust it is converted into diethyl-hydrazine urea, an oily liquid which is easily soluble in water and alcohol, and can with difficulty be obtained crystallized. Its hydrochloride crystallizes in needles, and forms a difficultly soluble platinichloride. When this urea is boiled with concentrated hydrochloric acid it at once decomposes into carbon dioxide, ethylamine, and ethylhydrazine (p. 410).

β-Diethyl Semicarbazide, $(C_2H_5)_2N - NH. - CO.NH_2$. This urea forms the point of departure, as has already been stated, for

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[1] *Ber. Deutsch. Chem. Ges.* ix. 883.

[2] Fischer and Troschke, *Liebig's Ann.* cxcix. 294.

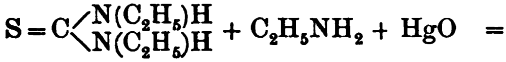
[3] *Ann. Chem. Pharm.* clxxix. 101.

[4] *Ib.* cxcix. 283.

[5] This reaction depends upon the liberation of nitrous acid. It was discovered by Liebermann (*Ber. Deutsch. Chem. Ges.* vii. 247, 1098), and occurs in the case of almost all nitroso-compounds.

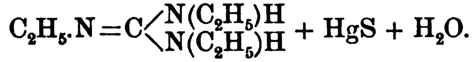
diethyl carbamide (p. 420) is formed. If, however, ethylamine be present at the same time *triethyl guanidine* is formed:

Diethylthiocarbamide. Ethylamine.



$$S=C\left\langle\begin{matrix}N(C_2H_5)H\\N(C_2H_5)H\end{matrix}\right. + C_2H_5NH_2 + HgO \;=$$

Triethylguanidine.



$$C_2H_5.N=C\left\langle\begin{matrix}N(C_2H_5)H\\N(C_2H_5)H\end{matrix}\right. + HgS + H_2O.$$

This latter compound is also formed by the action of sodium ethylate on ethyl isocyanurate,[1] and by heating chlorpicrin with ethylamine. It is very soluble in water. Its solution is caustic and alkaline, and it solidifies gradually on exposure to air by absorption of carbon dioxide. At a high temperature it distils, and partially decomposes with formation of ethylamine and α-diethyl carbamide. Hence it contains one molecule of water in very persistent combination, and, therefore, as it is a monacid base it is probably an ammonium hydroxide.

NITRO-COMPOUNDS OF ETHYL.

274 *Nitroethane*, $C_2H_5NO_2$, was discovered by V. Meyer, and Stüber,[2] who obtained it by the action of ethyl iodide on silver nitrite, when together with this nitro-compound about the same quantity of isomeric ethyl nitrite is produced. In order to prepare it on the large scale the following process may be adopted: 2090 grams of dry silver nitrite are brought into a large flask connected with a reversed condenser, and to this 1700 grams of ethyl iodide are gradually added by means of a stoppered funnel, so that the liquid boils quickly but not too violently. As soon as all the ethyl iodide is added, the liquid is heated for some time on the water-bath, and then the condenser is turned round and the liquid distilled in the water-bath as long as any liquid comes over. It is next heated in an oil-bath, and the distillate collected separately. The residue in the flask, which consists of silver iodide and silver nitrite, is then finely powdered, and, on to this residue, the distillate which came over at 100° is poured, and the whole again digested in the manner described, when a further quantity of nitroethane is obtained. This is now added to the first portion,

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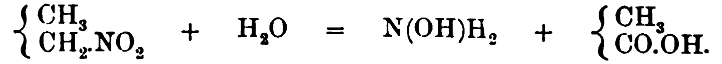
[1] Hofmann, *Proc. Roy. Soc.* xi. 281.

[2] *Ber. Deutsch. Chem. Ges.* v. 399; *Ann. Chem. Pharm.* clxxi. 1.

and, in order to remove any ethyl iodide which may be present it is digested with an inverted condenser with 10 grams of silver nitrite, the whole being heated to boiling. The product is then purified by fractional distillation, when about 340 grams of nitroethane are obtained.

Nitroethane is a colourless strongly-refracting liquid having a pleasant peculiar ethereal smell. It boils at 113°—114° under a pressure of 737 mm. and has a specific gravity at 13° of 1·0582, that of its vapour being 2·557. When ignited it burns with a pale flame. Its vapour cannot be heated above the boiling point without exploding.

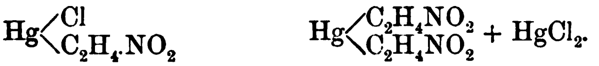
In contact with nascent hydrogen it is converted into ethylamine. This latter compound can be obtained in a perfectly pure state by digesting nitroethane in a flask with an excess of iron filings, and then adding acetic acid and a few drops of water, the whole being warmed until a reaction takes place, after which the flask is placed in cold water and the reaction is so regulated that the liquid does not boil. The liquid is then distilled with caustic potash, and a large yield of the base is thus obtained. If nitroethane be employed which contains a small quantity of ethyl nitrite, some ammonia is formed at the same time, and this can readily be removed by collecting the distillate in hydrochloric acid, evaporating over sulphuric acid, crystallizing, and treating with alcohol, when the insoluble sal-ammoniac remains behind. If nitroethane be heated with hydrochloric acid of specific gravity 1·14 it is converted into hydroxylamine and acetic acid:



$$\left\{\begin{matrix}CH_3\\CH_2.NO_2\end{matrix}\right. + H_2O = N(OH)H_2 + \left\{\begin{matrix}CH_3\\CO.OH.\end{matrix}\right.$$

That nitroethane acts as a weak acid might be expected from the fact that it contains the nitro-group (see p. 188).

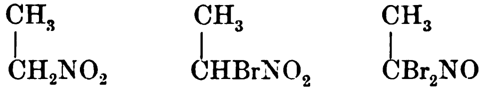
Sodium-nitroethane, $C_2H_4NaNO_2$, is obtained by acting on sodium with nitroethane diluted with benzene, or on nitroethane alone with alcoholic soda, when a white solid mass is obtained. This may be washed with absolute alcohol and dried on a water-bath. This compound is so slightly soluble in alcohol that very small quantities of nitroethane produce a precipitate with alcoholic solution of soda, whereby it may be readily detected. Alcoholic potash or ammonia however do not give any precipitate. Sodium nitroethane is a white light amorphous powder, which on heating in the open air burns off like gun-cotton, but when heated in a narrow test-tube detonates loudly. If kept for a length of time it becomes brown, and it deliquesces quickly on exposure to air. The aqueous solution gives a blood-red colour with ferric chloride, and a deep green colour with sulphate of copper. Silver nitrate gives a white precipitate which soon becomes brown and afterwards black from separation of metallic silver. Mercurous nitrate gives a dirty green precipitate, whilst mercuric chloride added to the concentrated solution of the sodium compound yields, after standing for a few moments, a crystalline mass consisting of a very stable compound having the composition $ClHgC_2H_4NO_2$, the constitution of which is represented by one of the following formulæ:



$$Hg\begin{cases} Cl \\ C_2H_4.NO_2 \end{cases} \qquad Hg\begin{cases} C_2H_4NO_2 \\ C_2H_4NO_2 \end{cases} + HgCl_2.$$

It is soluble in water with difficulty, and acids separate nitroethane from its solution.

275 *Monobromnitroethane*, $C_2H_4BrNO_2$. When nitroethane is dissolved in an equivalent quantity of caustic soda or potash, and bromine added drop by drop, the colour of this substance disappears, and, on cooling with water, the addition of bromine may be continued until the liquid appears yellow, when a heavy oil separates out. This is a mixture of nitroethane, monobromnitroethane and dibromnitroethane, and from this the pure monobromnitroethane can be obtained only with difficulty. It is, however, easily prepared by adding little by little to the calculated quantity of bromine a solution of nitroethane in caustic potash.[1] The explanation of the fact that when bromine is added in excess at the commencement of the operation only the monobrom compound is formed, but that when it is added little by little the dibromnitroethane is produced, may be readily explained. The constitution of nitroethane and its bromine substitution-products is given by the following formulæ:



$$\begin{array}{c} CH_3 \\ | \\ CH_2NO_2 \end{array} \qquad \begin{array}{c} CH_3 \\ | \\ CHBrNO_2 \end{array} \qquad \begin{array}{c} CH_3 \\ | \\ CBr_2NO_2, \end{array}$$

and from these it is easy to understand why bromnitroethane is a stronger acid than nitroethane, whilst dibromnitroethane possesses no acid properties (p. 426). The following equation represents the change which occurs when bromine is added to potassium nitroethane:

$$C_2H_4KNO_2 + Br_2 = C_2H_4BrNO_2 + KBr.$$

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[1] Tscherniak, *Liebig's Ann.* clxxx. 126.

The bromnitroethane, however, at once decomposes a corresponding quantity of the potassium salt, and nitroethane is liberated, upon which the bromine does not act, whilst the potassium compound of the bromnitroethane produced is acted upon by bromine.[1] According to this explanation only nitroethane and dibromnitroethane should be formed. The occurrence of the monobrom-compound is accounted for by the fact that the potassium nitroethane is more slowly attacked by the brom-compound than the potassium salt is by bromine itself. The decomposition takes place more slowly, and a certain excess of the monobrom-compound must be present, so that the quantity of the dibrom-compound obtained depends entirely upon the length of time during which the reaction proceeds. If this time be reduced to a minimum, a product is obtained which boils at 140°—149°, from which the pure compound boiling at 146°—147° may be easily obtained by fractional distillation. It is a very heavy oily liquid having an extremely penetrating smell, is easily soluble in alkalis, and yields a crystalline compound with caustic soda, whilst with alcoholic ammonia it unites to form a mass of glistening crystalline scales. These salts cannot, however, be obtained in the pure state, as they decompose easily with formation of a bromide.

Dibromnitroethane, $C_2H_3Br_2NO_2$. In order to obtain this compound the requisite quantity of bromine is added to nitroethane, and a small quantity of water poured on to the top of the liquid, and to this mixture (which must be cooled down and shaken) dilute caustic potash is added until decolorization ensues. The dibromnitroethane which then separates out is removed, and bromine again added to the aqueous solution until it becomes yellow-coloured, when a further quantity of the dibrom-compound is obtained. The raw product is decolorized by shaking with caustic potash and adding it to that obtained, mixed with water, dried over chloride of calcium and distilled.[2]

This substance is a colourless mobile liquid, having a very penetrating odour, and boiling at 165°.

276 *Dinitroethane*, $C_2H_4(NO_2)_2$. To prepare this compound, bromnitroethane is dissolved in twice its volume of alcohol, and the liquid shaken up with a solution of potassium nitrite dissolved in its own weight of water. Alcoholic caustic

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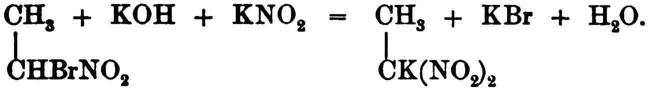
[1] Meyer and Tscherniak, *Liebig's Ann.* clxxx. 114.

[2] V. Meyer, *Liebig's Ann.* clxxv. 128.

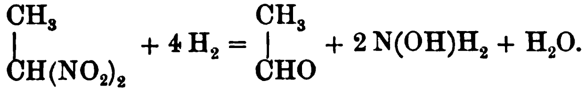
potash is then added, the liquid being cooled, and a mixture of potassium bromide and the potassium salt of dinitroethane separates out, as is seen by the following equation:



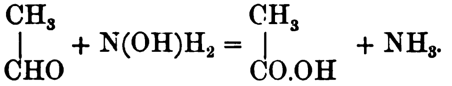
$$\begin{array}{l}CH_3\\|\\CHBrNO_2\end{array} + KOH + KNO_2 = \begin{array}{l}CH_3\\|\\CK(NO_2)_2\end{array} + KBr + H_2O.$$

The crystalline mass is washed out with ether, and then the dinitroethane separated by means of dilute sulphuric acid.

It is a colourless strongly-refracting liquid, having a faint alcohol-like smell, and a peculiar sweetish taste, boiling at 185°—186°, and having a specific gravity of 1·3503 at 23°·5. It is somewhat soluble in water, and is a tolerably strong acid which decomposes carbonates, although not very easily. It is converted into hydroxylamine, ammonia and acetic acid, by the addition of tin and hydrochloric acid, and the product also contains some aldehyde. This decomposition is represented by the following equations:



$$\begin{array}{l}CH_3\\|\\CH(NO_2)_2\end{array} + 4H_2 = \begin{array}{l}CH_3\\|\\CHO\end{array} + 2N(OH)H_2 + H_2O.$$



$$\begin{array}{l}CH_3\\|\\CHO\end{array} + N(OH)H_2 = \begin{array}{l}CH_3\\|\\CO.OH\end{array} + NH_3.$$

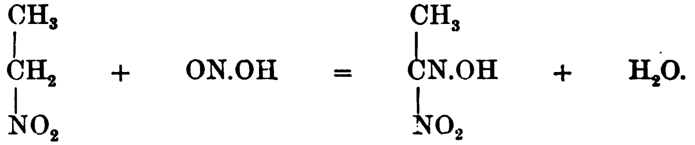
Dinitroethane forms well crystallized salts. The potassium compound, $C_2H_3K(NO_2)_2$, is obtained by adding alcoholic potash to a solution of dinitroethane in alcohol. It forms pure yellow, brightly glistening crystals, which become opaque and red on exposure to air, but regain their colourless appearance when again placed in the dark. On quickly cooling the hot aqueous solution, the compound separates out in the form of tables or long needles, and by evaporation, or by slow cooling, it is obtained in fine monoclinic prisms. It explodes very violently by a slight blow, or even at the touch of a warm object, with formation of red vapours.

The yellow salts which dinitroethane forms with sodium, ammonium, barium and calcium, are also soluble in water and crystallize well. The silver salt, $C_2H_3Ag(NO_2)_2$, is a fine yellow crystalline precipitate, which is deposited from warm solution in bright metallic-glistening scales, and is as explosive as the potassium compound.[1]

Bromdinitroethane, $C_2H_3Br(NO_2)_2$, is formed when an aqueous solution of potassium dinitroethane is shaken with the calculated quantity of bromine water. It is a colourless heavy oil having an extremely pungent smell. It is volatile in presence of aqueous vapour, but when it is heated alone it decomposes suddenly with formation of bromine vapours. It is decomposed by caustic potash as follows (ter Meer):

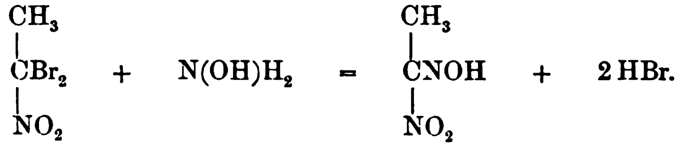
$$C_2H_3Br(NO_2)_2 + 2\,KOH = C_2H_3K(NO_2)_2 + KBr + H_2O + O.$$

277 *Ethyl Nitrolic Acid*, $C_2H_3(NO_2)NOH$. This compound, discovered by Victor Meyer,[2] is easily formed when an alkaline solution of nitroethane is mixed with potassium nitrite and then acidified with dilute sulphuric acid:



$$\begin{array}{l} CH_3 \\ | \\ CH_2 \\ | \\ NO_2 \end{array} \quad + \quad ON.OH \quad = \quad \begin{array}{l} CH_3 \\ | \\ CN.OH \\ | \\ NO_2 \end{array} \quad + \quad H_2O.$$

It also occurs when an aqueous solution of hydroxylamine is well shaken with dibromnitroethane dissolved in alcohol for the purpose of fine division:



$$\begin{array}{l} CH_3 \\ | \\ CBr_2 \\ | \\ NO_2 \end{array} \quad + \quad N(OH)H_2 \quad = \quad \begin{array}{l} CH_3 \\ | \\ CNOH \\ | \\ NO_2 \end{array} \quad + \quad 2\,HBr.$$

In order to prepare it, nitroethane is dissolved in the requisite quantity of weak caustic soda, an excess of potassium nitrite added, and the whole acidified, so that nitrous fumes are evolved. Alkali is then added in excess, the reddish-brown solution again acidified, and this process repeated three or four times.[3] The liquid is then shaken up several times with ether, which dissolves the nitrolic acid, and this separates out in crystals on evaporating the ethereal solution. A single crystallization from water suffices to yield it chemically pure. It crystallizes in splendid pale-yellow transparent rhombic prisms

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[1] ter Meer, *Liebig's Ann.* clxxxi. 1.

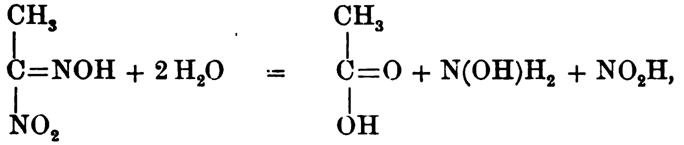
[2] *Liebig's Ann.* clxxv. 88.

[3] ter Meer, *Liebig's Ann.* clxxxi. 1.

having a bright lustre and a slight bluish fluorescence and resembling in general appearance crystals of saltpetre. This body has an intensely sweet taste. It is so much more soluble in hot than in cold water that if a solution be saturated by the warmth of the hand, crystals at once form when the hand is removed. Nitrolic acid dissolves in solutions of the alkalis and alkaline earths with an intense red colour. The salts which are thus formed are, however, extremely readily decomposed, and have not been obtained in the pure state. Their solutions yield, with various metallic salts, coloured precipitates, which are also very unstable. Nitrolic acid gradually decomposes on keeping, leaving acetic acid containing the oxides of nitrogen, and when heated it begins to melt at 81° and decomposes quickly, often with explosive violence, according to the equation:

$$2\,C_2H_4N_2O_3 = 2\,C_2H_4O_2 + NO_2 + N$$

If it be heated with water, or better with dilute sulphuric acid, nitrogen monoxide is obtained, together with acetic acid, and the same reaction takes place with concentrated sulphuric acid in the cold. In this way two successive reactions take place. At first acetic acid, hydroxylamine, and nitrous acid are formed:

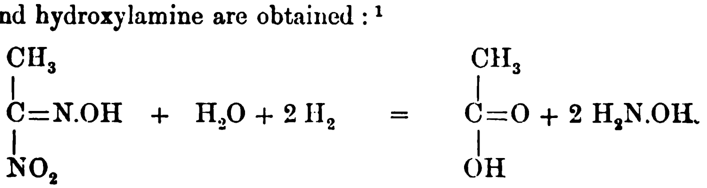


$$\begin{array}{l}CH_3\\ |\\ C{=}NOH\\ |\\ NO_2\end{array} + 2\,H_2O = \begin{array}{l}CH_3\\ |\\ C{=}O\\ |\\ OH\end{array} + N(OH)H_2 + NO_2H,$$

and the latter two compounds mutually decompose as follows:

$$NOH_3 + NO_2H = 2H_2O + N_2O.$$

Sodium amalgam and water also give rise to acetic acid and nitrous acid, together with ammonia formed by the reduction of the hydroxylamine. It is clear that hydroxylamine is produced in this decomposition, because if zinc and dilute hydrochloric acid be employed for the reduction, only acetic acid and hydroxylamine are obtained:[1]



$$\begin{array}{l}CH_3\\ |\\ C{=}N.OH\\ |\\ NO_2\end{array} + H_2O + 2\,H_2 = \begin{array}{l}CH_3\\ |\\ C{=}O\\ |\\ OH\end{array} + 2\,H_2N.OH.$$

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[1] Meyer and Locher, *Liebig's Ann.* clxxx. 170.

The separation and purification of the phosphines is accomplished without any difficulty, these bodies thus exhibiting a marked difference from the amine bases, the separation of which is difficult and tedious. In the first place it must be borne in mind that under the above conditions a tertiary base is not formed. In order to separate the ethyl phosphine, the contents of the tube are brought into an apparatus filled with hydrogen (Fig. 62), into which a slow current of water, free from air, is allowed to enter. This decomposes the salt of the primary base, corresponding to the iodide of phosphonium, into ethyl phosphine and hydriodic acid. The first of these is condensed by passing through a spiral tube surrounded by ice and dried over caustic potash. As the current of hydrogen carries away a considerable quantity of the very volatile ethyl phosphine, the gas is passed through a concentrated solution of hydriodic acid. At last the whole is warmed, and when no further evolution of ethyl phosphine takes place, a strong solution of caustic soda is allowed to run into the retort, when so much heat is evolved that diethyl phosphine volatilizes; and this is then condensed by an ordinary cooling apparatus in an atmosphere of hydrogen, and also dried over caustic potash.

Ethyl phosphine is a very mobile colourless liquid, insoluble in water, and possessing a strong refractive power. It boils at 25°, and does not act on vegetable colouring matters. Its smell is most overpowering, closely resembling that of the carbamines, and its vapour, like that of the latter bodies, produces an intense bitter taste on the tongue and in the throat. The vapours bleach cork like chlorine, and caoutchouc brought in contact with them is rendered translucent and loses its elasticity. Ethyl phosphine ignites in contact with chlorine, bromine, and fuming nitric acid, and yields with sulphur and carbon disulphide volatile compounds.

Ethyl phosphine is a weak base, which unites with concentrated hydracids and the elements of the chlorine group to form salts which are quickly decomposed by water. The hydrochloride forms a platinichloride which crystallizes in fine crimson-red needles. Ethyl phosphonium iodide is a splendid salt, crystallizing in shining white four-sided tables slightly soluble in concentrated hydriodic acid. On the addition of ether it separates out in large well-formed tables, which are so thin that they exhibit iridescence. Heated in an atmosphere of hydrogen they sublime at 100°, forming a mass resembling sal-ammoniac.

280 *Ethyl Phosphinic Acid*, $P(C_2H_5)O_3H_2$. This substance is obtained by the action of fuming nitric acid on ethyl phosphine, and may be regarded as orthophosphoric acid in which hydroxyl is replaced by ethyl. It is separated from the phosphoric acid, which is formed at the same time, by boiling the solution with oxide of lead, and treating the mixture of the lead salts with acetic acid, which leaves the lead phosphate insoluble. Sulphuretted hydrogen is then passed through the solution, and the filtrate evaporated on a water-bath. The residual oily liquid solidifies on cooling to a spermaceti-like mass, which melts at 41° and can easily be distilled. Although it is very soluble in water, it is only with difficulty moistened by this substance. It is dibasic; the silver salt, $P(C_2H_5)O_3Ag_2$, is an insoluble yellow powder.[1]

DIETHYL PHOSPHINE, $P(C_2H_5)_2H$,

is a colourless liquid, lighter than water and having a high refractive power. It boils at 85°, and possesses an extremely penetrating smell, but one quite different from ethyl phosphine. It absorbs oxygen with great avidity, becoming thereby so hot that inflammation may ensue. It dissolves very easily in acids. Its salts, which are not decomposed by water, crystallize only with difficulty, with the exception of the hydriodide and the platinichloride, the latter forming fine large orange-yellow prisms, which however are very unstable.

Diethyl phosphine combines with sulphur and carbon disulphide to form liquid compounds. Nitric acid oxidizes the base to *diethyl phosphinic acid*, $P(C_2H_5)_2O_2H$, a liquid which does not solidify at − 25°, and yields a silver salt, $P(C_2H_5)_2O_2Ag$, which is precipitated from its aqueous solution in fine silky needles.

TRIETHYL PHOSPHINE, $P(C_2H_5)_3$.

281 This was first prepared by Cahours and Hofmann,[2] by the action of zinc ethyl on phosphorus trichloride, in a similar way as the corresponding methyl compound (see p. 232). Hofmann afterwards found that it is better to decompose the double compound of triethyl phosphine and zinc chloride, formed by the continued action of concentrated caustic potash, and to distil the base from this mixture.[3] This compound is also

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[1] Hofmann, *Ber. Deutsch. Chem. Ges.* v. 110; *Chem. Soc. Journ.* xxv. 422.

[2] *Chem. Soc. Journ.* xi. 61.

[3] *Phil. Trans.* 1860, 410.

278 *Dinitroethylic Acid,*[1] $(C_2H_5)N_2O_2H$. Nitric oxide is very slowly absorbed by zinc ethyl. The reaction may, however, be accelerated by working under pressure. The first product of this reaction is ethyl zinc dinitroethylate, $N_2O_2\left\{\begin{matrix}C_2H_5\\ ZnC_2H_5,\end{matrix}\right.$ which may be obtained when an ethereal solution is employed, in large colourless transparent rhombohedral crystals which oxidize in the air, and are decomposed by water with evolution of gas, as follows:

$$2N_2O_2\left\{\begin{matrix}C_2H_5\\ ZnC_2H_5\end{matrix}\right. + 2H_2O = 2C_2H_6 + N_2O_2(C_2H_5)_2\,Zn + Zn(OH)_2.$$

Zinc hydroxide is, however, not precipitated, but a basic salt is formed which yields an opalescent solution having a strong alkaline reaction and a peculiar bitter taste. When carbon dioxide is passed into the liquid the normal zinc salt, $2N_4O_4(C_2H_5)_2Zn + H_2O$, is formed, crystallizing in thick rhombic prisms (Zuckschwerdt). If this be decomposed with dilute sulphuric acid, and the liquid distilled under diminished pressure, a solution of the free acid is obtained, possessing an acid reaction and a pungent taste. It is an extremely unstable compound, decomposing even at the ordinary temperature with evolution of nitrogen, of the monoxide and dioxide of nitrogen, and of ethylene.

The sodium salt is easily prepared by passing nitric oxide into sodium zinc ethyl, $Na\,Zn\,(C_2H_5)_3$.[2]

A series of other salts have been prepared from the zinc salt, of which those of the alkalis and alkaline earths deflagrate like gunpowder when heated below a red-heat, and the zinc salt when quickly warmed to 300° burns with a fine bluish-green flame. The copper salt, $2N_4O_4(C_2H_5)_2Cu + H_2O$, crystallizes from a fine purple-coloured solution in long needle-shaped four-sided prisms of the same colour. Nascent hydrogen converts dinitroethylic acid into ammonia and ethylamine:[3]

$$N_2O_2(C_2H_5)H + 4\,H_2 = NH_3 + C_2H_5.NH_2 + 2\,H_2O.$$

From this it appears that the acid contains one atom of

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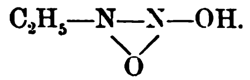
[1] Frankland, *Phil. Trans.* 1857, p. 63.
[2] Frankland and C. C. Graham, *Journ. Chem. Soc.* 1880, I. 578.
[3] Zuckschwerdt, *Ann. Chem. Pharm.* clxxiv. 302.

nitrogen in direct combination with ethyl, and that the following formula represents its constitution:



$$C_2H_5—\overset{}{N}—N—OH. \quad (N\text{—}O\text{—}N)$$

Diazoethoxane, $(C_2H_5)_2N_2O_2$, is produced by the action of ethyl iodide on silver hyponitrite (Vol. I. par. 237); it is a light, colourless liquid, possessing a peculiar ethereal odour. Although it is almost as explosive as nitrogen chloride, it was found possible to determine its vapour density, which is 4·1. Hydrogen in the nascent state converts it into alcohol and nitrogen gas. Hence its constitution is most probably expressed by the formula:

$$C_2H_5 - O - N = N - O - C_2H_5.$$[1]

PHOSPHORUS BASES OF ETHYL.

279 *Ethyl Phosphine*, $P(C_2H_5)H_2$. This compound, discovered by Hofmann,[2] is obtained by a method analogous to that employed for the preparation of the corresponding methyl compounds (p. 229). A mixture of five grams of zinc oxide, twenty grams of phosphonium iodide, and twenty grams of ethyl iodide, is heated in a closed glass tube of about 50 cbc. capacity for from six to eight hours to 150°. It is best first to bring the phosphonium iodide into the tube, then the oxide of zinc, and lastly the iodide of ethyl. Mixed in this way the bodies do not attack one another in the cold; and the tube may be easily sealed up. On opening the tube, after the operation is over, a disengagement of gas takes place, as various gaseous bodies are formed in the reaction, amongst which ethane is probably contained, and also frequently phosphuretted hydrogen. The chief product of this reaction is ethyl phosphonium hydriodide, which forms a double salt with the zinc iodide also formed:

$$2\,C_2H_5I + 2\,PH_4I + ZnO = 2\,P(C_2H_5)H_3I + ZnI_2 + H_2O.$$

This reaction is accompanied by another one, in which diethyl phosphine is produced, this body combining directly with zinc iodide:

$$2\,C_2H_5I + PH_4I + ZnO = P(C_2H_5)_2H_2I, ZnI_2 + H_2O.$$

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[1] Zorn, *Ber. Deutsch. Chem. Ges.* xi. 1630.

[2] *Ber. Deutsch. Chem. Ges.* iv. 430; *Chem. Soc. Journ.* xxiv. 713.

insoluble in ether. If an aqueous solution of the hydrochloride be mixed with a slight excess of platinic chloride, and heated to boiling, the red precipitate which at first forms disappears, and light yellow crystals separate out from the concentrated solution, having the composition $Pt[P(C_2H_5)_3]_4PtCl_4$, and therefore analogous to *Magnus's green salt* (Vol. II. part ii. p. 411). This compound is readily soluble in ether, and crystallizes from ethereal solution in large amber-yellow transparent monoclinic prisms, which melt at 150°, and may be heated to 250° without decomposition. Together with this compound an isomeric body is formed, crystallizing in small white prisms. If the yellow compound be heated with triethylphosphine and water, colourless crystals having the composition $[P(C_2H_5)_3]_4PtCl_2$ are formed, which are easily converted with separation of triethylphosphine into the white compound already mentioned, and give with silver oxide and water a strongly alkaline solution, from which other salts corresponding to the plato-diammonium compounds can be prepared.[1]

283 *Triethylphosphine Sulphide*, $P(C_2H_5)_3S$. If a piece of sulphur be thrown into a test-tube containing triethylphosphine it melts with evolution of heat, running about on the top of the liquid until at last it disappears. On cooling, the liquid solidifies to a splendidly crystalline mass. This experiment requires care, inasmuch as the vapour of the base when brought in contact with air forms an explosive mixture. In order to prepare the sulphide in larger quantity, flowers of sulphur are heated in a dilute ethereal solution of the base as long as they dissolve. The ether is then evaporated off and the residue crystallized from boiling water. On cooling, it separates out in long glistening needles or hexagonal prisms, which melt at 94°, and are volatile in a current of steam. When heated with sodium, triethylphosphine is produced, whilst nitric acid converts this compound into the oxide.

Triethylphosphine Selenide, $P(C_2H_5)_3Se$. Selenium combines directly with this base, but with less energy than sulphur. The compound crystallizes from aqueous solution with the same ease with which the sulphide does, and is decomposed in contact with the air.

Triethylphosphine Carbonyl Sulphide, $P(C_2H_5)_3CS_2$. This magnificent and characteristic compound is formed by the direct union of the base with carbon disulphide, the combination

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[1] Cahours and Gal. *Bull Soc. Chim.* [2]. xiv. 386.

taking place so energetically that an explosion may occur. It is, therefore, better to prepare the compound in an alcoholic or ethereal solution. It is insoluble in water, difficultly soluble in ether, but easily dissolves in hot alcohol, from which, on cooling, it is deposited in red needles resembling chromium trioxide, whilst by the spontaneous evaporation of the ethereal solution large deep-red monoclinic crystals are obtained exhibiting dichroism, melting at 95° and evaporating at 100°. The compound is soluble in strong hydrochloric acid, and this solution yields, with platinic chloride, a yellow amorphous compound, $[P(C_2H_5)_3H]_2PtCl_6$, which is insoluble in alcohol, and very easily decomposed. When an alcoholic solution is boiled with silver oxide or silver nitrate the following reaction takes place:

$$P(C_2H_5)_3CS_2 + 2\,Ag_2O = Ag_2S + Ag_2 + CO_2 + P(C_2H_5)_3S.$$

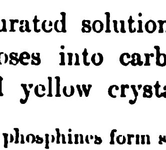
Moist air gradually produces a similar change. If, however, it is heated with water to 100° the following reaction occurs:

$$4\,P(C_2H_5)_3CS_2 + 2\,H_2O = 2\,P(C_2H_5)_3S + P(C_2H_5)_3O + P(C_2H_5)_3(CH_3)OH + 3\,CS_2.$$

The methyl triethyl phosphonium hydroxide thus formed yields a platinichloride crystallizing in splendid octohedrons.

The formation of the red compound takes place so easily and so quickly that it may be used as a means of detecting the smallest trace either of carbon disulphide or of triethyl phosphine.[1] If it is desired to test for the latter body, the liquid is poured on to a watch-glass, and the vapour of carbon disulphide allowed to flow on to it from a bottle containing this liquid, when the glass becomes covered with a network of red crystals. By help of the triethylphosphine the presence of exceedingly small traces of sulphide of carbon may be detected, as, for example, in the most carefully purified coal-gas.[2]

The constitution of this peculiar compound is probably as follows:



When heated with a saturated solution of sulphuretted hydrogen to 100° it decomposes into carbon disulphide, triethylphosphine sulphide, and yellow crystals having the formula

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[1] The other tertiary phosphines form similar compounds.

[2] Hofmann, *Phil. Trans.* 1860, p. 431.

$C_8H_{19}PS_3$, insoluble in ether, and probably having the constitution $CS\left\{\begin{array}{l}SCH_3\\ SP(C_2H_5)_3H.\end{array}\right.$ If these be heated with water, carbon disulphide is separated, and an alkaline solution is formed which yields with acids well-defined salts. The difficultly soluble iodide crystallizes in long needles, having the composition $P(SCH_3)(C_2H_5)_3I$.[1]

TETRAETHYLPHOSPHONIUM COMPOUNDS.

284 When triethylphosphine is mixed with ethyl iodide a violent reaction takes place in a few moments. The liquid froths up, and solidifies on cooling to a white crystalline mass of tetraethylphosphonium iodide. This compound is also formed together with triethylphosphine, when absolute alcohol acts on phosphonium iodide (Vol. I. p. 477):

$$4C_2H_5.OH + PH_4I = P(C_2H_5)_4I + 4H_2O.$$

It is exceedingly soluble in water, less so in alcohol, and insoluble in ether. If ether be added to an alcoholic solution until the white crystalline powder which begins to separate dissolves on boiling, finely formed crystals are deposited on cooling. If silver oxide be added to its solution, silver iodide is quickly formed, and a strongly alkaline liquid which retains some silver oxide in solution. If this be allowed to dry over sulphuric acid, metallic silver separates out in the form of a black powder or in that of a mirror, and a crystalline mass of the hydroxide is obtained, which is odourless, and possesses a bitter taste somewhat resembling that of phosphorus itself. Its solution exhibits most of the reactions of caustic potash, except that it does not easily dissolve the oxides of zinc and aluminium. On dry distillation it is decomposed into triethylphosphine oxide and ethane. The chloride, sulphate, and nitrate prepared from this are crystalline, but extremely deliquescent bodies. The platinichloride is an orange-yellow precipitate, which is difficultly soluble in boiling water. The aurichloride crystallizes from hot water in glistening golden needles.

Triethylmethylphosphonium Iodide, $P(C_2H_5)_3(CH_3)I$. If methyl iodide be brought together with triethylphosphine, it unites with it with such force that an explosion may occur, and hence it is necessary to dilute with ether. The compound resembles

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[1] Hofmann, *Proc. Roy. Soc.* xi. 283.

that of tetraethylphosphonium, and, like this, yields a strongly alkaline hydroxide and a platinichloride which has already been mentioned.

ARSENIC COMPOUNDS OF ETHYL.

285 These bodies exhibit close analogy with the corresponding methyl compounds. But, with the exception of the triethylarsine, they have not been so carefully examined as the latter series.

Triethylarsine, $As(C_2H_5)_3$, occurs together with arsendimethyl, $As_2(C_2H_5)_4$, as the principal product of the action of ethyl iodide on sodium arsenide :

$$AsNa_3 + 3\,C_2H_5I = As(C_2H_5)_3 + 3\,NaI.$$

The product is subjected to distillation, and the distillate rectified in an atmosphere of carbon dioxide.[1] Triethylarsine is also formed by the action of zinc ethyl on arsenic trichloride.[2] It is a highly refracting mobile liquid possessing a disagreeable smell, boiling at 140° and having a specific gravity of 1·151 at 16°·7, whilst that of its vapour is 5°·278 (Landolt). It fumes in the air and takes fire when slightly warmed. When the air is allowed to act slowly upon it, tabular crystals having an acid reaction are formed. The composition of these has however not been determined. Triethylarsine is decomposed by concentrated nitric acid with evolution of light and heat, but an acid of specific gravity 1·42 converts it into triethylarsine nitrate, which forms deliquescent crystals.

Triethylarsine Oxide, $As(C_2H_5)_3O$, is formed, together with other bodies, when an ethereal solution of triethylarsine is allowed to evaporate in the air, as well as when the corresponding iodide is heated with caustic potash. It is a liquid insoluble in water, which may be distilled without decomposition, and possesses an irritating smell. When warmed with concentrated hydrochloric acid it evolves a most unbearable odour, probably due to the formation of a chloride which however has not yet been isolated.

Triethylarsine Bromide, $As(C_2H_5)_3Br_2$, is produced when an alcoholic solution of its constituents is allowed to evaporate.

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[1] Landolt, *Ann. Chem. Pharm.* lxxxix. 301 ; xcii. 361.
[2] Cahours and Hofmann, *Compt. Rend.* xli. 831.

It forms yellow crystals which have a bitter taste and excite sneezing.

Triethylarsine Iodide, $As(C_2H_5)_3I_2$, is obtained as a yellow precipitate by adding iodine to an ethereal solution of triethylarsine. By the action of platinic chloride on triethylarsine the salt $Pt[As(C_2H_5)_3]_4PtCl_4$ is produced which is isomorphous with the corresponding phosphine compound (p. 437). An isomeride is also formed at the same time in long light yellow prisms. Both bodies are converted into the salt $[As(C_2H_5)_3]_4PtCl_2$ by the further action of the arsenic base (Cahours and Gal.)

Triethylarsine Sulphide, $As(C_2H_5)_3S$, is produced when an ethereal solution of triethylarsine is warmed with flowers of sulphur. It crystallizes in fine prisms soluble in hot water and melting a little above 100°. It has a bitter taste. Hydrochloric acid decomposes it with evolution of sulphuretted hydrogen, and its solution precipitates black sulphide of silver from silver salts, but it has no action on those of copper and lead.

TETRAETHYLARSONIUM COMPOUNDS.

286 The iodide, $As(C_2H_5)_4I$, is readily produced by gently heating ethyl iodide with triethyl arsine. It is easily soluble in water and alcohol, and crystallizes in long colourless needles which turn brown on exposure to air. When distilled with caustic potash it decomposes into the bodies from which it is formed. It unites with iodine to form the periodide, $As(C_2H_5)_4I_3$, a body which in appearance resembles potassium permanganate. A compound with arsenic tri-iodide, $As(C_2H_5)_4I + AsI_3$, may be obtained by heating arsenic with ethyl iodide to 180°; it forms red tables and crystallizes from alcohol in needles, and is decomposed by caustic potash with formation of tetraethylarsonium iodide, and distilled with this body it yields pure triethylarsine.

If an alloy of arsenic and zinc be heated with ethyl iodide to 175°—180°, the compound $2As(C_2H_5)_4I + ZnI_2$ is obtained crystallizing from alcohol in fine prisms. A corresponding cadmium compound has also been prepared. Both bodies are decomposed by caustic potash in a similar way to the arsenic iodide compound.[1]

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[1] Cahours, *Compt. Rend.* xlix. 87; l. 1022. *Ann. Chem. Pharm.* cxii. 228; cxvi. 364.

Tetraethylarsonium Hydroxide, $As(C_2H_5)_4OH$, is obtained by acting with silver oxide on an aqueous solution of the iodide. A strongly alkaline caustic liquid is left behind, which on evaporation in a vacuum yields the hydroxide as a deliquescent crystalline mass, and this when saturated with hydrochloric acid gives the chloride, $As(C_2H_5)_4Cl + 4H_2O$, a crystalline substance soluble in water and alcohol and uniting with mercuric chloride and platinic chloride to form crystalline compounds.

Various other tetraethylarsonium salts are known. Moreover *dimethylethylarsine, diethylmethylarsine*, and their compounds and derivatives have been prepared.[1]

Diethylarsine or *Ethyl Cacodyl*, $As_2(C_2H_5)_4$. In order to prepare this body, a mixture of one part of sodium arsenide and five parts of quartz sand is placed in a number of small flasks and each moistened with ethyl iodide. As soon as the energetic reaction is over, the mass is heated in connection with a reversed condenser and ethyl iodide again added until all the triethylarsine is converted into the arsonium iodide. The product is then extracted with ether in an atmosphere of carbon dioxide, the solution mixed with absolute alcohol and the ether distilled off. On addition of water free from air to the residue, diethylarsine separates out, and this is dried and rectified in a current of carbon dioxide. The same compound is also formed when diethylarsine iodide, $As(C_2H_5)_2I$, is distilled with zinc amalgam.[2]

Diethylarsine is a heavy highly refracting liquid having an unbearable alliaceous odour and boiling at 185°—190°, and oxidizing quickly in the air without however taking fire. In this case diethylarsine oxide, a substance which has not yet been fully examined, is produced. It unites also with the elements of the chlorine group and with sulphur, forming compounds which closely resemble the corresponding methyl compounds but have not been further examined.

Ethyl Cacodylic Acid, $AsO(C_2H_5)_2OH$, is formed by the action of air on the foregoing compound in the presence of water, or, more rapidly when diethylarsine is shaken up with water and mercuric oxide, when a readily soluble and crystalline mercuric salt is formed. This is decomposed by baryta-water,

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[1] Cahours, *Ann. Chem. Pharm.* cxxii. 192, 329; *Ann. Chim. Phys.* [3], lxii. 291.

[2] Cahours and Riche, *Compt. Rend.* xxxvi. 1001; xxxix. 541.

the liquid treated with carbon dioxide, and afterwards the barium exactly precipitated with sulphuric acid. On evaporating this solution, the free acid is obtained in glittering scales or tables which have an acid reaction and a bitter taste. They melt at 190° and are not attacked by concentrated nitric acid or even by aqua-regia (Landolt). The same compound is also formed when diethylarsine iodide is treated with silver oxide and water:

$$2\,As(C_2H_5)_2I + 3\,Ag_2O + H_2O = 2\,AsO(C_2H_5)_2OH + 2\,AgI + 4\,Ag.$$

Monethylarsine Compounds are but little known. The iodide is formed by the action of iodine on diethylarsine iodide:

$$As(C_2H_5)_2I + I_2 = As(C_2H_5)I_2 + C_2H_5I.$$

It may also be prepared in a similar way from diethylarsine. Its properties have not been fully examined. When treated with silver oxide and water it forms a crystallizable *arsenmonoethylic acid*, $AsO(C_2H_5)(OH)_2$ (Cahours).

Some compounds are also known which contain both methyl and ethyl, but they have not been more definitely examined (Cahours).

ANTIMONY COMPOUNDS OF ETHYL.

287 *Triethylstibine* or *Stibethyl*, $Sb(C_2H_5)_3$. In order to prepare this compound, ethyl iodide is allowed to act on potassium antimonide,[1] mixed with three times its weight of sand, in an atmosphere of carbon dioxide. The violent reaction which takes place must, to begin with, be moderated by cooling down the flask, which is afterwards gently warmed and the products of the reaction distilled off. In this case not only stibethyl but also tetraethylstibonium iodide is formed, and hence the crude product is rectified over potassium antimonide. It is perhaps better to prepare triethylstibine iodide, which will be hereafter described, from the crude product and to decompose this with zinc. Triethylstibine is also easily formed by the action of zinc ethyl on antimony trichloride.[2]

Triethylstibine is a highly refracting thin liquid possessing

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[1] Potassium antimonide is obtained by igniting five parts of cream of tartar with four parts of antimony, when a crystalline regulus is obtained, having a bright metallic lustre, and containing twelve per cent. of potassium (C. Löwig and E. Schweizer, *Ann. Chem. Pharm.* lxxv. 315).

[2] A. W. Hofmann, *Phil. Mag.* [4], xv. 147.

an unpleasant alliaceous odour, boiling at 158°·5 under a pressure of 730 mm. and having a specific gravity at 16° of 1·3244, that of its vapour being 7·438. It fumes strongly on exposure, and takes fire in the presence of excess of air as well as in oxygen, burning with a luminous flame. By the action of alcoholic solution of platinic chloride on triethylstibine a fine crystalline compound, $Pt[Sb(C_2H_5)_3]_4PtCl_4$, is obtained (Hofmann).

Triethylstibine Oxide, $Sb(C_2H_5)_3O$, is formed by the slow oxidation of triethylstibine in the air or under water, as well as by evaporating its alcoholic solution. It is best obtained by acting on silver oxide with an aqueous solution of the iodide or oxyiodide.[1] It can also be prepared by decomposing the sulphate with baryta water. The aqueous solution gives, on evaporation in a vacuum, a syrup which gradually solidifies to an amorphous mass. Its solution has a bitter taste and, like the alkalis, precipitates many metallic salts. With acids it forms salts which have a bitter taste, but do not act as emetics.

Triethylstibine Chloride, $Sb(C_2H_5)_3Cl_2$. Triethylstibine takes fire in chlorine gas. In order to prepare the chloride, the oxide or one of its salts is treated with concentrated hydrochloric acid, when the above compound is precipitated as an oily liquid which smells like turpentine and has a specific gravity of 1·540 at 17°.

Triethylstibine Bromide, $Sb(C_2H_5)_3Br_2$, is obtained by adding an alcoholic solution of bromine to a well-cooled alcoholic solution of triethylstibine, and precipitating the product with water. It is a colourless, highly refracting liquid, having a specific gravity of 1·953 at 17°, and possessing an unpleasant, turpentine-like smell, and on warming giving off a vapour which excites tears and sneezing. Like the chloride, it decomposes when strongly heated. Its alcoholic solution acts on metallic salts like potassium bromide.

Triethylstibine Iodide, $Sb(C_2H_5)_3I_2$. In order to prepare this compound, iodine is added to an alcoholic solution of triethylstibine so long as the colour disappears. The solution is allowed to evaporate, and crystals separate out, which may be purified by recrystallization from alcohol and ether. This body forms colourless transparent needles, which melt at 70°·5, and begin to volatilize at 100°, though they decompose at a temperature slightly above this. Triethylstibine iodide dissolves in water, and is easily soluble in alcohol and ether. It acts

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[1] Merk, *Ann. Chem. Pharm.* xcvii. 322.

towards chlorine, concentrated sulphuric acid, and metallic salts like potassium iodide. By the action of zinc ethyl on the iodide a pasty mass is obtained which, on distillation, yields a heavy liquid, probably pentaethyl-stibine.

Triethylstibine Oxyiodide, $Sb_2(C_2H_5)_6OI_2$, is formed by allowing an alcoholic solution of triethylstibine iodide, to which ammonia has been added, to evaporate spontaneously. It is also produced by the union of the iodide and oxide in alcoholic solution, or by adding hydriodic acid to a solution of the oxide in ether until a turbidity occurs.[1] The oxyiodide deposits in hard, colourless, glassy, odourless octohedrons or tetrahedrons. When treated with an aqueous solution of mercuric chloride, the corresponding chlorine compound is formed, consisting of a striated crystalline, very deliquescent mass.[2]

Triethylstibine Sulphate, $Sb(C_2H_5)_3SO_4$, is best obtained by acting with copper sulphate on triethylstibine sulphide. It is very easily soluble in water, and separates out from the syrupy solution in small white crystals. When decomposed by baryta water, and the filtrate evaporated, a soluble compound of triethylstibine and baryta remains behind, which is soluble in alcohol; this solution is decomposed by carbon dioxide with .formation of triethylstibine oxide.[3] The basic salt, $[Sb(C_2H_5)_3]_2(OH)_2SO_4$, is formed by decomposing the oxyiodide with silver sulphate. On drying the solution in a vacuum over sulphuric acid, a gummy mass remains.

Triethylstibine Nitrate, $Sb(C_2H_5)_3(NO_3)_2$, is obtained by dissolving triethylstibine or its oxide in nitric acid. It is easily soluble in water, and crystallizes in large rhombic prisms melting at 62°·5, having an acid reaction, and deflagrating on heating. The basic salt, $Sb(C_2H_5)_3(OH)NO_3$, is formed by the decomposition of the oxyiodide with silver nitrate, and forms a striated crystalline mass which is not deliquescent, though readily soluble in water.

Triethylstibine Antimonite, $Sb(C_2H_5)_3(SbO_2)_2$, is obtained, together with the oxide, when triethylstibine is slowly oxidized. In order to prepare it, an ethereal solution of the latter compound is allowed to evaporate by exposure to air. The residue is then extracted with a mixture of alcohol and ether, and the

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[1] Buckton, *Quart. Journ. Chem. Soc.* xiii. 115.

[2] Strecker, *Ann. Chem. Pharm.* cv. 308.

[3] *Ibid.*

antimonite obtained as an amorphous powder, easily soluble in water and alcohol.[1]

Triethylstibine Sulphide, $Sb(C_2H_5)_3S$, is formed by dissolving flowers of sulphur in an ethereal solution of triethylstibine and evaporating the filtrate. It is also produced by the action of sulphuretted hydrogen on the oxide, and forms a light crystalline mass, having a silver-white colour, and smelling like mercaptan. It has a bitter taste, is easily soluble in water, and is decomposed by dilute acids with evolution of sulphuretted hydrogen. When boiled with a solution of potassium cyanide, triethylstibine and potassium thiocyanate are produced, and its aqueous solution behaves towards metallic salts like potassium sulphide (Buckton).

Triethylstibine Thioantimonite, $Sb(C_2H_5)_3(SbS_2)_2$, is obtained as a pale yellow amorphous precipitate when sulphuretted hydrogen is passed into a solution of the antimonite, and it is also formed when freshly precipitated sulphide of antimony containing free sulphur is added to an alcoholic solution of triethylstibine. Dilute sulphuric acid decomposes it with separation of antimony trisulphide and evolution of sulphuretted hydrogen.

Triethylstibine Selenide, $Sb(C_2H_5)_3Se$, is formed in an analogous way to the sulphide, which it closely resembles.

TETRAETHYLSTIBONIUM COMPOUNDS.

288 These were discovered by R. Löwig,[2] and termed by him stibethylium compounds. The point of departure for these is the iodide obtained by the combination of ethyl iodide with triethylstibine.

Tetraethylstibonium Hydroxide, $Sb(C_2H_5)_4OH$, is obtained by the action of silver oxide on an aqueous solution of the iodide. The filtrate is first evaporated on a water-bath and then in a vacuum, and it leaves the compound as an oily liquid which does not solidify, is easily soluble in water, has a strong alkaline reaction, and behaves like caustic potash towards the metallic salts, &c.

Tetraethylstibonium Chloride, $Sb(C_2H_5)_4Cl$, is obtained by neutralizing the hydroxide with hydrochloric acid. It crys-

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[1] C. Löwig, *Ann. Chem. Pharm.* lxxxviii. 323.

[2] *Ann. Chem. Pharm.* xcvii. 322.

tallizes in deliquescent needles, and unites with platinic chloride and other metallic chlorides.

The *bromide* is a similar substance, but is not deliquescent.

Tetraethylstibonium Iodide, $Sb(C_2H_5)_4I + 3H_2O$, is obtained by heating ethyl iodide, triethylstibine, and water together to 100°. On slowly evaporating the solution, the compound crystallizes in hexagonal prisms, but separates out in needles, when a hot solution is quickly cooled. This compound is always formed as a by-product in the preparation of triethylstibine.

Other salts of this group have been prepared. They are crystallizable, but have not been accurately investigated.

Tetraethylstibonium Hydrosulphide, $Sb(C_2H_5)_4SH$, is obtained by the action of sulphuretted hydrogen on the hydroxide. It is an oily liquid, miscible with water, which behaves towards the metallic salts like potassium hydrosulphide.

In addition to the above, certain *Methyltriethyl stibonium compounds* have been prepared and examined by Friedländer.[1]

BISMUTH COMPOUNDS OF ETHYL.

289 *Triethylbismuthine*, $Bi(C_2H_5)_3$, was obtained by Breed[2] by the action of ethyl iodide on an alloy of bismuth and potassium, and afterwards examined more particularly by Dünhaupt.[3] It is a mobile liquid having a specific gravity of 1·82, possessing a very unpleasant smell, and producing, when inhaled, a burning taste on the tip of the tongue. Exposed to the air, it evolves thick yellow fumes, which ignite with a slight explosion. It is not volatile, but if it is heated by itself it begins to decompose at 50° to 60°, with separation of bismuth and evolution of a combustible gas, and when the temperature reaches 150°—160° a sharp explosion takes place.

Ethyl-Bismuth Oxide, $Bi(C_2H_5)O$, is obtained from the corresponding iodine compound by precipitation with caustic potash as an amorphous yellow powder, which takes fire on exposure to air.

Ethyl-Bismuth Chloride, $Bi(C_2H_5)Cl_2$, is formed by the action of a warm alcoholic solution of corrosive sublimate on a dilute solution of triethyl bismuthine in alcohol:

$$Bi(C_2H_5)_3 + 2\,HgCl_2 = Bi(C_2H_5)Cl_2 + 2\,Hg(C_2H_5)Cl.$$

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[1] *Journ. Prakt. Chem.* lxx. 449.

[2] *Sill. Journ.* [2], xiii. 404.

[3] *Journ. Prakt. Chem.* lxi. 399.

On cooling, ethylmercury chloride first separates out, and then the mother-liquor yields on evaporation small white crystals of ethylbismuth chloride.

Ethyl-Bismuth Iodide, $Bi(C_2H_5)I_2$, is formed by the double decomposition of the chloride with potassium iodide. It is scarcely soluble in water, and crystallizes from alcohol in yellow six-sided scales.

Ethyl-Bismuth Nitrate, $Bi\ C_2H_5\ (NO_3)_2$, is obtained by the action of an alcoholic solution of silver nitrate on the iodide. When evaporated on the water-bath, the solution deposits basic bismuth nitrate, but on evaporating the liquid in a vacuum, a striated crystalline mass, having an unpleasant metallic taste, is obtained. This has a smell of rancid butter, and decomposes with deflagration when heated to 40°.

BORON COMPOUNDS OF ETHYL.

290 These compounds, discovered and investigated by Frankland,[1] have a special interest, inasmuch as they have not only led to the recognition of the quantivalence of boron, but have also pointed the way to a new method for determining this element quantitatively.

Triethylborine or *Borethyl*, $B(C_2H_5)_3$, is formed by the action of zinc ethyl on ethyl borate (see p. 367):

$$3\,Zn(C_2H_5)_2 + 2\,B(OC_2H_5)_3 = 2\,B(C_2H_5)_3 + 3\,Zn(OC_2H_5)_2.$$

Triethylborine is also formed when the vapour of boron trichloride is passed into zinc-ethyl.

It is a colourless, easily mobile liquid, having a penetrating smell. Its vapour acts violently upon the mucous membrane, and provokes a copious flow of tears. It boils at 95°, and at 23° has a specific gravity of 0·6961, that of its vapour being 3·400. When the vapour comes in contact with air, it forms a slight bluish-white smoke, which when in the dark is seen to be caused by a lambent blue flame. The liquid is spontaneously inflammable in air, burning with a beautiful green and somewhat fuliginous flame. In contact with oxygen it explodes.

Boron Diethylethoxide, $B(C_2H_5)_2OC_2H_5$, is formed when one molecule of ethyl borate is acted upon by two molecules of zinc-ethyl. It is a colourless, mobile liquid, possessing an ethereal

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[1] *Phil. Trans.* 1862, part i. p. 167; *Proc. Roy. Soc.* xxv. 165 (1876).

smell, and a sharp taste. It boils at 102°, and takes fire on exposure to the air, burning with a green, slightly luminous flame. The specific gravity of its vapour is 3·914. In contact with water it is converted into *Boron Diethylhydroxide*, $B(C_2H_5)_2OH$, a liquid which also takes fire spontaneously, and decomposes on heating; it has an ethereal smell, and a sharp, pungent taste.

This latter body slowly absorbs oxygen on exposure to air, with formation of *Boron Ethyl-hydroxethoxide*, $B(C_2H_5)(OC_2H_5)OH$, a colourless and mobile liquid, which crystallizes about 8°, and smells like borethyl, and has a sharp taste. On treatment with water, it decomposes with formation of alcohol and ethyl boric acid, $B(C_2H_5)(OH)_2$, a crystalline and volatile body, possessing an intensely sweet taste and a pleasant ethereal smell. When heated in a current of carbon dioxide to 100°, it sublimes in splendid crystals closely resembling those of napthalene. Although the compound has an acid reaction no salts have been obtained from it.

Boron Etho-diethoxide $B(C_2H_5)(OC_2H_5)_2$, is formed by the slow action of the air on borethyl. It is a colourless liquid, which may be distilled under diminished pressure with only partial decomposition. It is decomposed at once by water with formation of alcohol and ethylboric acid, which was first obtained in this way.

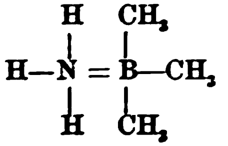
Diboron Ethopentethoxide, $B_2(C_2H_5)(OC_2H_5)_5$, is formed by heating two molecules of ethyl borate with one of zinc ethyl. It is a colourless mobile liquid, having a sweet taste, and a faint ethereal odour. It boils at 112°, and distils without decomposition, but its vapour-density, which was found to be 2·78, indicates that its vapour is a mixture of ethyl borate, and boron ethodiethoxide :

$$B_2(C_2H_5)(OC_2H_5)_5 = (C_2H_5)B(OC_2H_5)_2 + B(OC_2H_5)_3.$$

Water decomposes it into boric acid, ethylboric acid, and alcohol.

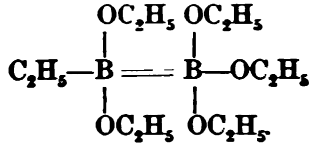
Ammonio-boric Ethide, $B(C_2H_5)_3NH_3$. Borethyl absorbs ammonia with avidity with formation of the above compound, which is an oily liquid, having an aromatic smell and an alkaline reaction. Carbon dioxide does not act upon it even in the presence of water, but it is decomposed by acids. Its vapour-density has not been determined, although that of ammonio-boric methide has been ascertained, and in this case the vapour-density corresponds to that of a mixture of equal molecules of its components. From this, as well as from the vapour-density of the pentaethylate, it would appear that triad boron may, like the elements of the nitrogen group, occur in the pentatomic condition. Hence the above compounds in the liquid state have the following constitution:

Ammonio-boron Methide.



$$\begin{array}{ccccc} & & \mathrm{H} & & \mathrm{CH_3} \\ & & | & & | \\ \mathrm{H} & - & \mathrm{N} & = & \mathrm{B}-\mathrm{CH_3} \\ & & | & & | \\ & & \mathrm{H} & & \mathrm{CH_3} \end{array}$$

Boron-ethopentethoxide.



$$\begin{array}{ccccc} & & \mathrm{OC_2H_5} & & \mathrm{OC_2H_5} \\ & & | & & | \\ \mathrm{C_2H_5} & - & \mathrm{B} & = & \mathrm{B}-\mathrm{OC_2H_5} \\ & & | & & | \\ & & \mathrm{OC_2H_5} & & \mathrm{OC_2H_5}. \end{array}$$

SILICON COMPOUNDS OF ETHYL.

291 *Silicon Tetraethide*, $Si(C_2H_5)_4$, was discovered by Friedel and Crafts,[1] and is obtained by heating zinc-ethyl with silicon chloride to 160°:

$$2\,Zn(C_2H_5)_2 + SiCl_4 = 2\,ZnCl_2 + Si(C_2H_5)_4.$$

The reaction is complete in three hours, and on opening the tube a considerable quantity of a gaseous hydrocarbon issues, which burns with an almost non-luminous flame. The residue, on distillation, yields silicon-ethyl, whilst zinc chloride and metallic zinc remain behind. The distillate, which also contains silicon tetrachloride and a hydrocarbon, is treated with water, dried, and the liquid subjected to fractional distillation.

Silicon-ethyl is a colourless liquid, lighter than water, boiling at 152°—154°, and possessing a specific gravity of 0·8341 (Ladenburg), whilst the specific gravity of its vapour is 5·13. It is easily inflammable, and burns with a luminous flame, emitting a white cloud of silica. It is not attacked either by potash or nitric acid, and with chlorine it forms substitution products. In these properties it closely resembles the paraffins. It may, indeed, be regarded as nonane, C_9H_{20}, in which one atom of carbon is replaced by silicon, and may therefore be termed silico-nonane, or tetraethyl-silicomethane.

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[1] *Bull. Soc. Chim.* v. 174, 238; *Ann. Chim. Phys.* [4], xix. 334.

Silicon Hexethyl or *Hexethyl-silicoethane,* $(C_2H_5)_3Si—Si(C_2H_5)_3$, is formed by the action of zinc-ethyl on silicon tri-iodide (vol. i. 563). It is an oily liquid, in smell somewhat resembling silicon tetraethyl, and boiling at 250°—253°.[1]

Silico-nonyl Compounds.—The chloride, $SiC_8H_{19}Cl$, is the first product of the action of chlorine on silicon-ethyl. At the same time other isomeric compounds are formed, from which the monochloride boiling at 185° can only be separated with difficulty. It is, however, easy to prepare the corresponding alcohol, inasmuch as if the portion of the crude product, boiling between 180° and 200°, be heated with potassium acetate and alcohol, the dichlorsilico-nonane present is alone attacked. An oily liquid separates out from the contents of the tube on addition of water, and this is treated with strong sulphuric acid, which leaves silico-nonyl chloride unattacked. The liquid, which then is still not pure, and boils between 180°—190°, is heated to 180° for some hours with an alcoholic solution of potassium acetate, when the acetate is formed. This compound boils at 208°—214°, and has a faint smell like acetic acid; and when it is heated with a solution of potash in dilute alcohol to 120°—130°, silico-nonyl alcohol, $SiC_8H_{19}.OH$, is obtained. This is a liquid insoluble in water, having a smell like camphor, and boiling at 190.° Sodium dissolves in this alcohol with evolution of hydrogen, and the formation of gelatinous sodium silico-nonylate, which is decomposed by water into the alcohol and caustic soda.[2]

Silico-heptyl Compounds.—When zinc-ethyl is allowed to act on ethyl silicate, a reaction takes place which, however, soon ceases. If sodium be added, a violent action begins even at the ordinary temperature, zinc separating out and a considerable evolution of gas occurring. The following products are thus obtained:

		B.P.
Ethyl orthosilicopropionate,	$SiC_2H_5(OC_2H_5)_3$	166°·5
Diethyl silicon-diethyl-oxide,	$Si(C_2H_5)_2(OC_2H_5)_2$	159°
Ethyl silocoheptyl-oxide,	$Si(C_2H_5)_3OC_2H_5$	155°·5
Silicon ethyl,	$Si(C_2H_5)_4$	153°
Silicoheptane,	$Si(C_2H_5)_3H$	107°

Silicoheptane or *Triethylsilico-methane,* $Si(C_2H_5)_3H$, is the last product of the above reaction, and is formed, together with

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[1] Friedel and Ladenburg, *Ann. Chim. Phys.* [5] xix. 390.

[2] Friedel and Crafts, *Compt. Rend.* lxi. 792; *Ann. Chem. Pharm.* cxxxviii. 19.

silicon ethyl, from the ethyl silicoheptyl-oxide, this giving off oxygen and ethylene. It is a colourless liquid boiling at 107°, having a specific gravity of 0·7510 at 0°, and possessing a smell resembling the petroleum hydrocarbons. It is insoluble in water and in concentrated sulphuric acid, does not undergo alteration in the air, and is easily inflammable, burning with a luminous flame. The specific gravity of its vapour is 4·1.

This compound contains one atom of hydrogen in direct combination with silicon, and hence this should possess the properties of the hydrogen in silicon hydride; and this is, indeed, the case, for whilst silicon ethyl or silicononame is not attacked by fuming nitric acid, silicoheptane is oxidized at once with explosive violence by this acid.

292 *Silicoheptyl Alcohol* or *Triethylsilicol,* $Si(C_2H_5)_3OH$. This singular compound is of great theoretical interest, as it is the first example of a silicon alcohol. It is a tertiary alcohol which not only in its constitution, but also in most of its properties, may be considered to be triethyl-carbinol, in which one atom of carbon has been replaced by silicon. It is obtained by the action of the corresponding chloride on dilute ammonia:

$$Si(C_2H_5)_3Cl + NH_3 + H_2O = Si(C_2H_5)_3OH + NH_4Cl.$$

Triethylsilicol is a colourless thick liquid, insoluble in water, having a strong smell resembling camphor, boiling at 154°, and having a specific gravity of 0·8709 at 0°, and a vapour density of 4·67. It is easily combustible, burning with a luminous flame, and leaving a residue of silica. When treated with fuming sulphuric acid the following decomposition occurs:

$$(C_2H_5)_3SiOH + SO_3 = C_2H_5SiO_2H + 2\,C_2H_4 + H_2 + SO_2.$$

This oxidation is very similar to that which the tertiary alcohols undergo. The silicopropionic acid, which is formed at the same time, will be described hereafter.

Silicol forms with sodium the very deliquescent compound $(C_2H_5)_3Si.ONa$. If carbon dioxide be passed into an ethereal solution of silicol, another amorphous deliquescent compound, $(C_2H_5)_3Si.O.CO.ONa$, is deposited. This sodium silicoheptyl carbonate leaves, on ignition, a residue of pure sodium carbonate:

$$2\,(C_2H_5)_3SiCO_3Na = \left.\begin{matrix}(C_2H_5)_3Si\\(C_2H_5)_3Si\end{matrix}\right\}O + CO_2 + Na_2CO_3.$$

Ethyl Silicoheptyl Oxide or *Triethylsilicon Ethylate,* $\left.\begin{matrix}(C_2H_5)_3Si\\ C_2H_5\end{matrix}\right\}O$, is the third product of reduction of ethyl silicate. It is a pleasantly smelling liquid, boiling at 153°, insoluble in water, and undergoing no change on exposure to air. When heated with acetyl oxide (acetic anhydride) for some time in closed tubes to 250°, the following reaction takes place :

$$\left.\begin{matrix}(C_2H_5)_3Si\\ C_2H_5\end{matrix}\right\}O + \left.\begin{matrix}C_2H_3O\\ C_2H_3O\end{matrix}\right\}O = \left.\begin{matrix}(C_2H_5)_3Si\\ C_2H_3O\end{matrix}\right\}O + \left.\begin{matrix}C_2H_5\\ C_2H_3O\end{matrix}\right\}O.$$

The silicoheptyl acetate thus formed is a liquid boiling at 168°, and having a pleasant ethereal smell, resembling at the same time camphor and acetic acid. By heating it with a solution of sodium carbonate it is converted into triethyl-silicol.

Silicoheptyl Oxide, $\left.\begin{matrix}(C_2H_5)_3Si\\ (C_2H_5)_3Si\end{matrix}\right\}O$. This ether was discovered by Friedel and Crafts, and obtained as a by-product in the preparation of silicon-ethyl.[1] It was afterwards obtained by Friedel and Ladenburg, by acting with zinc-ethyl on silicon oxychloride, Si_2Cl_6O.[2] It is also obtained from triethyl-silicol by removing from this body the elements of water, either by means of sulphuric acid or phosphorus pentoxide. It is likewise formed by the action of caustic potash on silicoheptyl chloride, and, lastly, by heating ethyl-silcoheptyl oxide with hydriodic acid:

$$2\left.\begin{matrix}Si(C_2H_5)_3\\ C_2H_5\end{matrix}\right\}O + 2HI = \left.\begin{matrix}Si(C_2H_5)_3\\ Si(C_2H_5)_3\end{matrix}\right\}O + 2C_2H_5I + H_2O.$$

It is a thick, colourless, almost odourless liquid, boiling at 231°, and having at 0° a specific gravity of 0·8590.

Silicoheptyl Chloride, $(C_2H_5)_3SiCl$, is formed by heating ethyl silicoheptyl oxide with acetyl chloride for some hours to 180°:

$$\left.\begin{matrix}(C_2H_5)_3Si\\ C_2H_5\end{matrix}\right\}O + C_2H_3OCl = (C_2H_5)_3SiCl + \left.\begin{matrix}C_2H_3O\\ C_2H_5\end{matrix}\right\}O.$$

It is a colourless liquid, fuming on exposure to air, and possessing a penetrating camphor-like smell, and burning with a luminous green-mantled flame. It boils at 143°·5, has a specific gravity at 0° of 0·9249, and is slowly decomposed by water.

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[1] *Ann. Chem. Pharm.* cxxxviii. 19.

[2] *Ibid.* cxlvii. 355.

Silicoheptyl Bromide, $(C_2H_5)_3SiBr$. Bromine acts violently on silicoheptane, and hence it must only be added drop by drop, and the mixture well cooled. The bromide is a liquid boiling at 161°, and possessing properties analogous to the chloride.

Silicon-diethyl Compounds. When equal molecules of ethyl silicate and zinc-ethyl are heated in a closed tube with sodium the chief product consists of *silicon diethyl-ether* or *diethylsilicon-diethylate*, $Si(C_2H_5)_2(OC_2H_5)_2$. This is a pleasantly smelling liquid, boiling at 155°·8, and having at 0° a specific gravity of 0·8752, and a vapour-density of 6·02.

When heated with an acid chloride under pressure, the oxy-ethyl groups are replaced one after another by chlorine. The compound which is first formed, $(C_2H_5)_2Si(OC_2H_5)Cl$, is a liquid fuming strongly in the air, boiling between 146° and 148°, and being slowly decomposed by water. *Diethylsilicon dichloride*, $(C_2H_5)_2SiCl_2$, boils at 128°—130°, possesses a smell resembling silicon chloride, and, like this compound, fumes in the air, and is decomposed by water with formation of *diethylsilico-ketone*, $(C_2H_5)_2SiO$. This latter compound, previously obtained by Friedel and Crafts by the oxidation of silicon-ethyl, is also formed when silicon-diethyl ether is heated with hydriodic acid:

$$Si(C_2H_5)_2(OC_2H_5)_2 + 2\,HI = Si(C_2H_5)_2O + 2\,C_2H_5I + H_2O.$$

It is a deliquescent syrup, insoluble in water, which can be distilled at a high temperature without decomposition. At −15° it does not solidify, and it is a substance possessing few characteristic properties.

Silicon-monethyl Compounds. The first product of the action of zinc-ethyl and sodium on ethyl silicate is *monethyl silicic ether*, or *orthosilico propionic ether*, $C_2H_5Si(OC_2H_5)_3$. This body was discovered by Friedel and Ladenburg,[1] and prepared in a similar way by the action of zinc-ethyl and sodium upon *triethylsilico-chloroformate*, $SiCl(OC_2H_5)_3$. It is a pleasantly smelling liquid, boiling at 159°, and having a vapour-density of 6·92. When heated with acetyl chloride under pressure it forms *ethylsilicon trichloride*, $C_2H_5SiCl_3$, a strongly refracting liquid, boiling at about 100°, which is decomposed by water with violence into silicopropionic and hydrochloric acids.

$$C_2H_5SiCl_3 + 2\,H_2O = C_2H_5SiO_2H + 3\,HCl.$$

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[1] *Ann. Chem. Pharm.* cxlix. 259.

Silicopropionic acid, which is thus formed, is also produced by warming ethyl orthosilicopropionate or diethyl silico-ketone with concentrated potash. A better plan, however, is to warm the ortho-ether with concentrated hydriodic acid:

$$C_2H_5Si(OC_2H_5)_3 + 3\,HI = C_2H_5SiO.OH + 3\,C_2H_5I + H_2O.$$

It is a white amorphous powder, which on heating becomes incandescent, leaving behind silica containing finely divided carbon. The acid is soluble in caustic potash, and is precipitated from the solution either by hydrochloric acid or by sal-ammoniac.

Ethyl silicate is not attacked at the ordinary atmospheric pressure when heated with zinc-methyl and sodium. If, however, ethyl silicate be heated with zinc-methyl gradually to 300° in closed tubes, *ethyl orthosilico-acetate*, $CH_3Si(OC_2H_5)_3$, is formed. This is a liquid boiling between 145° and 151°, and which, when heated with hydriodic acid, is converted into *orthosilico-acetic acid*, $CH_3SiO.OH$, a body which closely resembles orthosilico-propionic acid.[1]

COMPOUNDS OF ETHYL WITH THE METALS.

BERYLLIUM ETHIDE, $Be(C_2H_5)_2$,

293 Is formed by heating crystallized beryllium with mercury-ethyl to 130°. It is a colourless liquid, which fumes in the air, and takes fire when slightly warmed. It boils at 185°—188°, and is decomposed by water with violence, beryllium hydroxide being produced.[2]

MAGNESIUM ETHIDE, $Mg(C_2H_5)_2$,

Is formed by heating ethyl iodide with magnesium filings to 120°—130°. It is a colourless, very mobile liquid, possessing a strong alliaceous odour. It takes fire when exposed to air, and is violently decomposed by water with formation of magnesium hydroxide.[3]

[1] Ladenburg, *Ann. Chem. Pharm.* clxxiii. 143.

[2] Cahours, *Compt. Rend.* lxxvi.

[3] Cahours, *Ann. Chim. Phys.* [3], lviii. 5.

ZINC ETHIDE, OR ZINC-ETHYL, $Zn(C_2H_5)_2$.

294 This important compound, which has already frequently been mentioned, was discovered on the 12th June, 1849, by Frankland,[1] in Bunsen's laboratory in Marburg, at the same time as zinc-methyl. He obtained it by heating ethyl iodide with an excess of finely granulated zinc in a strong tube drawn out to a capillary point, as in Fig. 89. As soon as the zinc is introduced, the tube is drawn out, as shown in the figure, and then it is warmed, and the point *a* dipped into ethyl iodide, which, when the air cools, rises into the tube. This is then boiled so as to drive out the air, and again inserted into the iodide, the requisite quantity of which can then be introduced. The tube is melted off at the point *b*, and as soon as the reaction is complete, the point is softened in the flame of the blowpipe, and the gases allowed to escape as gradually as possible.

FIG. 89.

This method is, however, not adapted for preparing zinc-ethyl on a large scale, as the employment of glass tubes of sufficient dimensions under so high a pressure is accompanied by considerable danger. Frankland, who was then Professor in Owens College, obtained from James Nasmyth an apparatus of such strength that the preparation of the substance could be conducted on a large scale without fear of explosions occurring.

This apparatus although not now used in the manufacture of zinc-ethyl merits description as having done good service, and being of historical interest. It consists of a tube of wrought copper (*a*, Figs. 90, 91) 45 c.m. in length and 3 c.m. internal diameter, the sides being 1·25 c.m. in thickness. This tube is closed at bottom by a screw-plug, and is furnished at top with a brass flange (*b b*), which can be closed by the brass cap (*d d*), which screws on to a lead collar. A stopcock placed in the position of the screw-plug (*c*) serves as an outlet for the generated gases or for distilling off the liquid formed. This digester is heated by means of a cylindrical oil-bath (Figs. 92 and 93) heated by a suitable gas-lamp.

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[1] *Chem. Soc. Journ.* ii. 297; *Phil. Trans.* clxv. 259.

An equal volume of anhydrous ether was added by Frankland to the ethyl iodide, as this accelerates the reaction, prevents the formation of large quantities of gaseous products, and largely increases the yield of zinc-ethyl (Brodie).[1]

Pebal[2] afterwards found that zinc which had been once acted upon by ethyl iodide, or which had been washed with sulphuric acid, attacked the iodide under the ordinary atmospheric pressure. Rieth and Beilstein[3] employed in place of zinc an alloy of this metal with sodium, obtained by heating 4 parts of zinc to the boiling-point and then adding 1 part of sodium, the whole being well mixed, poured out, and when cold the outer layer cut off, and the last traces of free sodium being got rid of by washing with water. It is not necessary in this case to add ether. Beilstein and Alexejeff[4] afterwards noticed that the reaction takes place easily when a mixture of one part of this alloy is heated with 8 parts of zinc turnings and 10 parts of

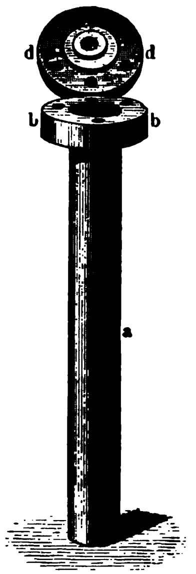

FIG. 90.

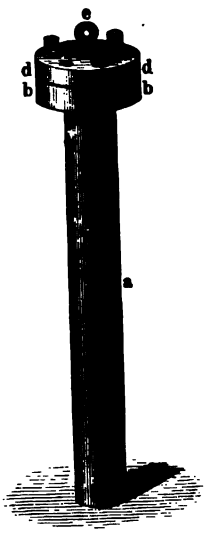

FIG. 91.

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[1] *Journ. Chem. Soc.* iii. 409.

[2] *Ann. Chem. Pharm.* cxviii. 22; cxx. 194; cxxi. 105.

[3] *Ann. Chem. Pharm.* cxxiii. 245; cxxiv. 248.

[4] *Zeitsch. Chem.* 1864, 101; *Bull. Soc. Chim.* [2], ii. 51.

ethyl iodide. Wichelhaus[1] found that the addition of the alloy is not necessary, and recommends zinc to be used in the form of coarse filings. Chapman[2] has shown that the reaction takes place more quickly if to the mixture a small quantity of zinc-ethyl be added.

FIG. 92.

FIG. 93.

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[1] *Ber. Deutsch. Chem. Ges.* i. 140.
[2] *Laboratory*, i. 195; *Zeitsch. Chem.* 1867, 74.

In order to prepare zinc-ethyl according to one of the latter-mentioned methods the apparatus Fig. 94 is used, already described under Zinc-methyl (see p. 248). This is filled with carbon dioxide, and shut off at C with a small quantity of mercury. It is heated in a water-bath so long as the iodide of ethyl is condensed in the receiver, and continues to run back into the flask, this process generally lasting from two to three hours. The gases which are continually evolved escape through the short column of mercury. They consist, according to Beilstein and Rieth, of a mixture of ethane, ethylene, and butane, formed by the action of iodide of ethyl on the zinc-ethyl, and their quantity is considerably increased if the zinc is not present in excess. In order to carry out the operation successfully it is absolutely necessary that no trace of moisture shall be present either in the materials employed or in the apparatus, as otherwise the reaction is much retarded. Extraordinary care, therefore, in freeing the materials perfectly from moisture

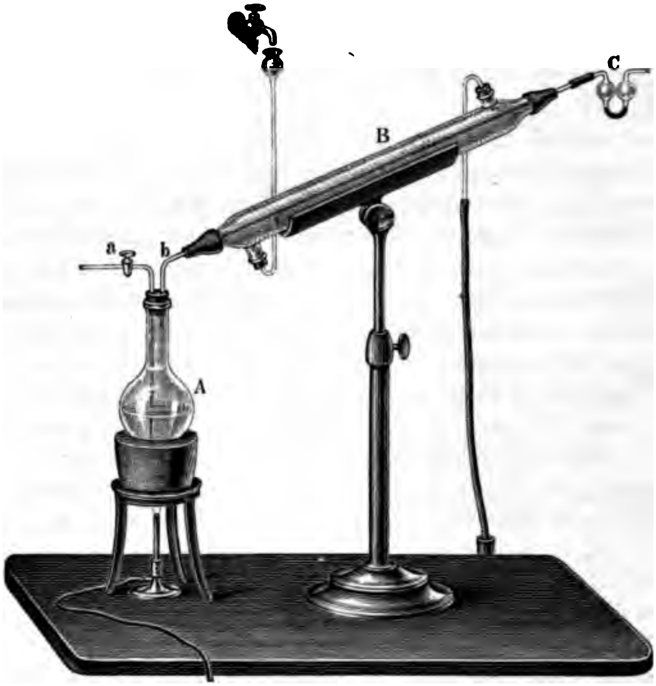

Fig. 94.

is amply repaid in the increased quantity of the product (Frankland). When the reaction is complete, the flask contains a solid mass consisting of excess of zinc together with a compound of zinc-ethyl and zinc iodide, having the composition $Zn(C_2H_5)I$. The flask is then connected with the upper part of the condenser, and placed in a paraffin- or oil-bath, a current of carbon dioxide being led in through the stopcock A, and the zinc-ethyl which distils over being collected in a vessel provided with a mercury valve. The whole must be at last heated to 180° in order to decompose the above-mentioned compound:

$$2\left.\begin{matrix}C_2H_5\\I\end{matrix}\right\}Zn = \left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}Zn + \left.\begin{matrix}I\\I\end{matrix}\right\}Zn.$$

The method proposed by Gladstone and Tribe[1] for the preparation of zinc-methyl (p. 246) is also recommended for that of zinc-ethyl, as the following experiment shows. Ninety grams of zinc filings and 10 grams of reduced copper are placed in a flask of 300 cc. capacity, and heated over the flame of a Bunsen's burner for about five minutes until the whole consists of dark-grey small granular masses, care being taken not to heat the metals so as to form an alloy. The mass is then allowed to cool, and 87 grams of ethyl iodide added, and the whole warmed in connection with a reversed condenser to 90°, when in a few seconds the reaction begins, and is completed in fifteen minutes. On heating in the oil-bath, in an atmosphere of hydrogen, the distillation of zinc-ethyl began at 160°, and after an hour the whole had passed over. In this way 31 grams was obtained instead of the calculated quantity, 34·3, or 90·4 per cent., whilst in the older operations not more than 80 per cent. of the quantity is obtained.

An improved method of preparation now employed in Professor Frankland's laboratory is first to heat the zinc filings, after they have been washed with acid, strongly in a glass flask, so as to decompose all the hydroxide. Next, to add an equal weight of ethyl iodide and a single crystal of iodine, and heat gradually to about 90° with a reversed condenser. As soon as no ethyl iodide is seen to run back, the whole is allowed to cool, and a bent tube is attached to the flask, the zinc-ethyl being distilled from an oil-bath. In this way zinc-ethyl can be easily prepared in any quantity.

Properties. Zinc-ethyl is a colourless, mobile, highly re-

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[1] *Journ. Chem. Soc.* 1879, i. 571.

fracting liquid, possessing a peculiar but not unpleasant smell, boiling at 118°, and having a specific gravity of 1·182 at 18°. It takes fire at once on exposure to air, burning with a luminous green-mantled flame and evolving dense white fumes of zinc oxide. If a porcelain capsule be held in the flame, a black spot of metallic zinc is formed, surrounded by a deposit of the white oxide. Zinc-ethyl takes fire instantly in chlorine, burning with a pale smoky flame. When brought in contact with bromine, a violent explosion occurs; but when the action is moderated, ethyl bromide and zinc bromide are formed. Iodine acts in a similar way, and if ether be not employed as a diluent a violent decomposition takes place with evolution of light and heat.

ZINC-ETHYL COMPOUNDS.

295 *Zinc-Ethyl-Ethoxide*, $C_2H_5Zn(OC_2H_5)$. When dry oxygen is passed into an ethereal solution of zinc-ethyl it is absorbed, and the vessel becomes filled with thick white vapours, which disappear as soon as one atom of oxygen has been employed for every molecule of zinc-ethyl. The compound, which is insoluble in ether, has not been accurately studied. It appears also to be formed by the action of zinc-ethyl on absolute alcohol.[1] Water decomposes it according to the following equation:

$$Zn\left\{\begin{matrix}C_2H_5\\OC_2H_5\end{matrix}\right. + 2\,H_2O = Zn\left\{\begin{matrix}OH\\OH\end{matrix}\right. + HO.C_2H_5 + C_2H_6.$$

By the further action of oxygen on the ethereal solution of zinc-ethyl, *zinc-ethoxide* or *zinc diethylate*, $Zn(OC_2H_5)_2$,[2] a compound already mentioned, is formed as a white powder, which is decomposed by water with evolution of gas.

Zinc-amine. If dry ammonia be passed into an ethereal solution of zinc-ethyl, ethane is evolved, and zinc-amine, $Zn(NH_2)_2$, is produced in the form of a white amorphous precipitate:

$$Zn\left\{\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right. + 2\,NH_3 = Zn\left\{\begin{matrix}NH_2\\NH_2\end{matrix}\right. + 2\,C_2H_6.$$

Water and alcohol decompose this compound instantly, with formation of ammonia. When heated with ethyl iodide to 150° diethylammoniumiodide is produced. At a red-heat zincamide decomposes into ammonia and *zinc-nitride*, N_2Zn_3, a grey non-volatile infusible powder, which decomposes water with formation of ammonia with such energy that it becomes red-hot on being moistened.

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[1] Lissenko, *Zeitsch. Chem.* 1864, 578.

[2] Frankland, *Phil. Trans.* 1855, 267.

If zinc-ethyl and diethylamine be heated together, *zinc-di ylamine*,[1] $Zn\left\{\begin{matrix}N(C_2H_5)_2,\\ N(C_2H_5)_2,\end{matrix}\right.$ is produced, and is a body resembling zincamine in properties.

SODIUM ETHIDE.

296 If one part of sodium and 10 parts of zinc-ethyl be brought together at the ordinary temperature, the sodium dissolves after some days completely, and an equivalent quantity of zinc is precipitated. On distilling off the excess of zinc-ethyl from the clear thick liquid in a current of hydrogen, the compound, $NaC_2H_5 + Zn(C_2H_5)_2$, is obtained in crystals melting at 27°. All attempts to prepare pure sodium-ethyl from this have as yet proved unsuccessful. When gently warmed, decomposition takes place, zinc and sodium remaining behind and hydrocarbons being evolved. If the compound be heated with sodium in the water-bath it also decomposes easily. On exposure to air it at once takes fire, burning with almost explosive violence.[2] If ethyl iodide be added to its solution in zinc-ethyl, the following reaction takes place:

$$NaC_2H_5 + C_2H_5I = NaI + C_2H_4 + C_2H_6.$$

This explains why sodium-ethyl is not produced when sodium is heated with ethyl iodide, as this substance, when formed, is at once decomposed by the excess of ethyl iodide according to the above equation.[3]

Sodium ethide absorbs dry carbon-dioxide with formation of sodium propionate (Wanklyn). Potassium acts on zinc-ethyl even more powerfully than sodium does, a double compound analogous to the preceding being obtained.

CADMIUM ETHIDE, $Cd(C_2H_5)_2$,

Is formed by heating cadmium with ethyl-iodide, when the compound of the metallic iodide with cadmium-ethyl is obtained, and this is decomposed at a temperature between 180° and 220°, at which temperature, however, the cadmium-ethyl undergoes partial decomposition. It is a colourless liquid, resembling zinc-ethyl, is spontaneously inflammable, and burns with the evolution of brown fumes.[4]

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[1] Frankland, *Proc. Roy. Soc.* viii. 502.

[2] Wanklyn, *Phil. Mag.* [4], xvii. 225.

[3] Frankland, *Proc. Roy Soc.* ix. 345.

[4] Wanklyn, *Quart. Journ. Chem. Soc.* ix. 193.

MERCURY ETHIDE, $Hg(C_2H_5)_2$,

297 Was first prepared by Buckton,[1] by the action of mercuric chloride on zinc-ethyl. It is now obtained by a much more simple reaction, according to the method of Frankland and Duppa.[2] For this purpose a mixture of one part of ethyl acetate and ten parts of ethyl iodide is shaken up with sodium amalgam containing 0·2 per cent. of the former metal:

$$Hg + Na_2 + 2\,C_2H_5I = Hg(C_2H_5)_2 + 2\,NaI.$$

In this case the flask must be dipped frequently into cold water, in order that the temperature may not rise too high. When a sufficient quantity of sodium iodide has been formed to render the mass thick, the acetic ether is distilled off from a water-bath, together with the excess of ethyl iodide, and this mixture used for a second operation. Water is then added to the residue. The mercury ethide which separates out is separated from the liquid and treated with alcoholic potash, washed with water, dried over chloride of calcium and rectified. The part which the acetic ether plays in this reaction is not understood. No reaction takes place, however, unless it be present, even when ethyl-ether is used. On the other hand, the ethyl acetate may be replaced by ethyl formate or methyl acetate. None of these ethers appear to suffer any alteration, and it is, moreover, remarkable that this reaction takes place the more readily the smaller the quantity of sodium present in the amalgam. Mercury ethide is a colourless liquid, having a peculiar but not unpleasant smell, boiling at 159°, and having a specific gravity of 2·444, that of its vapour being 9·97. It is easily inflammable, burning with a luminous flame, and giving off vapours of mercury. It is poisonous, but acts much less violently than mercury methide, inasmuch as it is less volatile.

At the ordinary temperature sodium acts slowly on mercury ethide, giving rise to a grey spongy mass which takes fire on exposure to air, and explodes under the most trifling change of condition. When gently warmed, it yields a mixture of ethane and ethylene, from which it would appear that this body contains sodium-ethyl (Buckton; see p. 462).

When mercury ethide is heated in a closed vessel with granulated zinc to 100°, it is completely converted into zinc-ethyl. Cadmium acts only slowly and incompletely on it. Bismuth, on the other hand, acts on it somewhat easily with formation of triethyl-bismuthine.

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[1] *Journ. Chem. Soc.* xvi. 17.

[2] *Journ. Chem. Soc.* xvi. 415.

it yields butane, or its products of decomposition, and mercury iodide.

Mercury-Ethyl Sulphate, $(C_2H_5Hg)_2SO_4$, is formed, together with pure ethane, by the action of concentrated sulphuric acid on mercury-ethyl. It crystallizes from alcohol in silvery-white scales (Buckton).

Mercury-Ethyl Nitrate, $C_2H_5HgNO_3$, is obtained by acting upon the base with nitric acid, as also by the decomposition of the iodide with silver nitrate. It is easily soluble in water, less so in alcohol, and crystallizes in transparent prisms, which on heating decompose with slight deflagration.

Mercury-Ethyl Cyanide, C_2H_5HgCN, is obtained by saturating the hydroxide with alcoholic hydrocyanic acid. It deposits in large crystals which are very volatile and when heated emit an intolerable odour. The vapour violently attacks the mucous membrane, and the compound appears to be very poisonous.

Mercury-Ethyl Sulphide, $(C_2H_5Hg)_2S$, is precipitated in the form of a yellowish-white powder by the action of ammonium sulphide on an alcoholic solution of the chloride. It is soluble in an excess of the precipitant as well as in ether, and, when the ether is allowed to evaporate, separates out in the crystalline form.

In addition to the above, many other mercury-ethyl compounds have been prepared.

ALUMINIUM-ETHYL, $Al(C_2H_5)_3$.

299 The first observations on this compound were made almost simultaneously by Cahours [1] and by Hallwachs and Schafarik.[2] It is, however, to the investigations of Buckton and Odling [3] that we owe our more exact knowledge of this body. It is obtained by heating mercury-ethyl with aluminium foil to 100°. A colourless liquid is thus obtained, which fumes in the air, and even takes fire when exposed to the air in thin layers, burning with a bluish-red-mantled flame. The compound boils at 194°, and the specific gravity of its vapour at 234° is 4·5, whereas that corresponding to the above formula is 3·9. Hence it would appear this body does not possess a constitution similar to that of aluminium chloride. Water decomposes it with great

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[1] *Ann. Chim. Phys.* [3], lviii. 5.

[2] *Ann. Chem. Pharm.* cix. 206.

[3] *Proc. Roy Soc.* xiv. 19.

violence; iodine converts it into *aluminium-ethyl iodide*, $Al_2(C_2H_5)_3I_3$. This compound can also be obtained by heating aluminium with ethyl iodide. It is a colourless, unpleasantly-smelling liquid, fuming in the air, and boiling at 340°—350°, and being likewise decomposed by water.

When dropped into a vessel filled with oxygen or chlorine it takes fire, burning with a violet light.

Compounds of Lead with Ethyl.

300 Of these two are known:

Lead Tetraethyl.	Lead Triethyl.
$Pb(C_2H_5)_4$.	$Pb_2(C_2H_5)_6$.

The formula of the first of these compounds points out that lead acts as a tetrad element towards the positive elements or radicals. In its compounds with the negative elements, however, it acts as a diad, as is shown by the fact ascertained by Roscoe,[1] that the vapour-density of lead chloride corresponds to the formula $PbCl_2$. In lead-triethyl, on the other hand, two atoms of metal are connected together by one combining unit.

Lead-Tetraethyl, $Pb(C_2H_5)_4$, is formed, together with lead triethyl, by the action of ethyl iodide on an alloy of lead and sodium. It may be more readily obtained in the pure state by treating zinc-ethyl with lead chloride.[2] Frankland and Lawrance[3] recommend the following plan. Dry lead chloride is added to zinc-ethyl, contained in a thick glass vessel, until no further action takes place, the whole being stirred with a glass rod. Metallic lead then separates out in a spongy form:

$$2\,PbCl_2 + 2\,Zn(C_2H_5)_2 = Pb(C_2H_5)_4 + Pb + 2\,ZnCl_2.$$

The product is carefully mixed with water, and subjected to distillation.

Lead-tetraethyl is a colourless, slightly smelling liquid, having a specific gravity of 1·62°, and boiling at about 200° with partial decomposition and separation of lead. Under a pressure of 190 mm. it may be distilled without decomposition at 152°, and it may also be volatilized in a current of steam without

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[1] *Proc. Roy. Soc.* xxvii. 426.

[2] Buckton, *Chem. Gaz.* 1858, 415; *Proc. Roy. Soc.* ix. 685; Cahours, *Ann. Chim. Phys.* [3], lxii. 257.

[3] *Journ. Chem Soc.* 1879, i. 244.

the slightest decomposition occurring. It is easily inflammable, burning with an orange-coloured, blue-mantled flame, emitting clouds of lead oxide. It is not attacked by ammonia, carbon dioxide, carbon monoxide, cyanogen, oxygen, nitric acid, or sulphuretted hydrogen; but it absorbs sulphur dioxide quickly, with formation of diethyl-sulphone and lead-diethyl sulphonate (Frankland and Lawrance):

$$Pb(C_2H_5)_4 + 3SO_2 = (C_2H_5)_2SO_2 + (C_2H_5.SO_2)_2Pb.$$

Weak acids do not act upon it. Concentrated acids, on the other hand, decompose it with formation of lead-triethyl compounds and ethane.

Lead-Triethyl, $Pb_2(C_2H_5)_6$, is easily formed by the action of ethyl iodide on an alloy of lead and sodium.[1] For its preparation the best mode is that suggested by Klippel.[2] Three parts of lead are fused in a crucible, which is then withdrawn from the fire, and one part of sodium added, the whole being stirred. The crucible is then filled with sand, and allowed to cool slowly. In this way a fine crystalline alloy is obtained, and this, having been finely powdered, is placed in a flask connected with an inverted condenser, the mass having been previously moistened with ethyl iodide. A violent reaction takes place, and lead-triethyl is formed, which is then extracted with ether.

Lead-triethyl is a mobile liquid insoluble in water, only slightly soluble in alcohol, but readily so in ether, having a specific gravity at 10° of 1·471. Heated alone it undergoes decomposition, but it volatilizes slightly in an atmosphere of ether. The vapours of this body attack the mucous membranes with great violence, exciting a flow of tears (Klippel). On exposure to light, as well as on heating with .water, it decomposes with separation of lead.

Lead-Ethyl Compounds. If iodine be slowly added to a solution of lead-triethyl in alcohol and ether, the unstable iodide, $(C_2H_5)_3PbI$, is formed, and this, when treated with freshly precipitated oxide of silver, yields *lead-ethyl hydroxide*, $(C_2H_5)_3PbOH$. This hydroxide is also obtained, according to Cahours, by the distillation of the chloride with solid caustic potash. The oily distillate solidifies after some time to a crystalline mass, possessing a slight but peculiar odour provocative of sneezing. It is slightly soluble in water, and easily so in

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[1] Löwig, *Journ. Prakt. Chem.* lx. 304.
[2] *Journ. Prakt. Chem.* lxxxi. 287.

alcohol and ether. Its solution has a strong alkaline reaction and a sharp caustic taste, giving rise to an unpleasant sensation in the throat. Like caustic potash, it saponifies fats, and, even at the ordinary temperature, it is slightly volatile, and for this reason it produces white fumes when brought into contact with hydrochloric acid. It decomposes ammoniacal salts, and precipitates the salts of many metals.

Lead-Ethyl Chloride, $(C_2H_5)_3PbCl$, is obtained by heating lead-tetraethyl with hydrochloric acid:

$$(C_2H_5)_4Pb + HCl = (C_2H_5)_3PbCl + C_2H_6.$$

If the action be continued too long a further decomposition occurs, and lead chloride is formed (Cahours). Lead-ethyl chloride is easily soluble in alcohol and ether, crystallizing in long bright needles, which when warmed emit a mustard-like smell, and when more strongly heated decompose with detonation.

Lead-Ethyl Sulphate, $[(C_2H_5)_3Pb]_2SO_4$, is obtained by the action of dilute sulphuric acid on the solution of the base. It is a white precipitate, which is only slightly soluble in water, but dissolves in alcohol if free sulphuric acid be present, and crystallizes from this solution in hard glistening octohedrons.

Lead-Ethyl Nitrate is formed when an ethereal solution of lead-triethyl is brought in contact with an alcoholic solution of silver nitrate:

$$(C_2H_5)_6Pb_2 + 2\,AgNO_3 = 2\,(C_2H_5)_3PbNO_3 + 2\,Ag.$$

The nitrate remains on evaporation as a thick liquid, having a butter-like smell. This on standing solidifies to a saponaceous mass, which detonates on heating.

Lead-Ethyl Carbonate, $[(C_2H_5)_3Pb]_2CO_3$, is obtained in small hard glistening crystals by allowing the alcoholic solution of the base to evaporate spontaneously. It is scarcely soluble in water, has a strong burning taste, and can be recrystallized from ether.

Lead-Ethyl Cyanide, $(C_2H_5)_3PbCN$, is formed by heating the chloride with alcohol and potassium cyanide in closed tubes to 100°. It forms a blood-red liquid, which on the addition of water yields a white precipitate, and this can be obtained crystallized in fine prisms from an ethereal solution.

Lead-Ethyl Thiocyanate, $(C_2H_5)_3PbSCN$, is prepared by heating the chloride with silver thiocyanate. It is soluble in water, alcohol, and ether, and crystallizes from the last solvent in prisms resembling those of potassium thiocyanate.

In addition to the salts of lead-ethyl above described, other compounds with both inorganic and organic acids have been prepared.

Compounds of Tin with Ethyl.

301 The following compounds of tin and ethyl are known:

(1)	(2)	(3)
Tin-Tetraethyl or Stannic Ethide.	Tin-Triethyl or Stannoso-Stannic Ethide.	Tin-Diethyl or Stannous Ethide.
$Sn(C_2H_5)_4$	$Sn_2(C_2H_5)_6$	$Sn_2(C_2H_5)_4$

Of these the first corresponds to tin tetrachloride, and the last to tin dichloride. As the molecular formula of the last-named substance has been shown by Victor Meyer[1] to be Sn_2Cl_4 from its vapour-density determination, we must assume that in the stannous compounds the two atoms of tin are connected by double linkage, whilst in the triethyl compounds a single linking only exists.

Tin-Tetraethyl or *Stannic Ethide*, $Sn(C_2H_5)_4$, is obtained by the action of zinc ethyl on tin tetrachloride,[2] tin-triethyl iodide, or tin-diethyl di-iodide.[3] It is, however, best obtained by gradually adding fused anhydrous stannous chloride to zinc-ethyl, until the latter has been almost completely decomposed. The mass is then distilled in an oil-bath, the liquid distillate treated with water and dilute sulphuric acid, washed with water, dried, and rectified over chloride of calcium.[4] In this process tin-diethyl is first formed, but this easily decomposes, as Cahours has shown, into tin and tin-tetraethyl.[5]

Stannic ethide is a colourless liquid, having a slightly ethereal odour, boiling at 181°, possessing a specific gravity of 1·187, while that of its vapour is 8·021 (Frankland). It is very inflammable, burning with a luminous blue-mantled flame, and emitting clouds of stannic oxide. In oxygen it burns with a very bright white flame. Neither sodium, magnesium, nor aluminium acts upon it at its boiling point; nor is it attacked in the cold either by ammonia, carbon dioxide, carbon monoxide, cyanogen, nitric oxide, oxygen, or sulphuretted hydrogen.

Tin-Triethyl or *Stannoso-Stannic Ethide*, $Sn_2(C_2H_5)_6$, is

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[1] *Ber. Deutsch. Chem. Ges.* xii. 1195.

[2] Buckton, *Phil. Trans.* 1859, 426.

[3] Buckton, *ib.* 424.

[4] Frankland and Lawrance, *Journ. Chem. Soc.* 1879, i 130.

[5] *Ann. Chem. Pharm.* cxiv. 227 and 354.

small quantity of alcohol. The residue is then purified by distillation.

Tin-triethyl iodide is a colourless liquid having a very pungent smell. It boils at 235°—238°, and at 22° has a specific gravity of 1·833. It forms a crystalline mass when cooled in a mixture of ether and carbon dioxide. It combines with ammonia to form *tin-triethyl-ammonium-iodide*, $(C_2H_5)_3SnNH_3I$, a compound soluble in water and alcohol, and crystallizing in long prisms. On heating this melts, and may be sublimed in fine crystals. It has a strong pungent and ammoniacal smell, and is decomposed by boiling water. The iodide also forms similar compounds with the monamines.

Tin-triethyl Sulphate, $(C_2H_5)_6Sn_2SO_4$, is obtained by neutralizing the oxide with sulphuric acid or decomposing the iodide with silver sulphate. It is slightly soluble in water, and crystallizes from alcohol in glistening colourless prisms. This compound is also formed by the action of sulphur dioxide on tin-tetraethyl in presence of air. At the same time *Tin-triethyl ethyl sulphonate*, $(C_2H_5)_3SnSO_3C_2H_5$, is produced, and forms an oily liquid (Frankland and Lawrance).

The *nitrate* is obtained as a syrup by evaporating its aqueous solution. Indistinct crystals may also be obtained.

Tin-triethyl Cyanide, $(C_2H_5)_3SnCN$, is obtained by warming the iodide with silver cyanide. It sublimes as a snow-white mass, or crystallizes in thin needles. It crystallizes from alcohol in silky elastic prisms.

Tin-triethyl Cyanate, $(C_2H_5)_3SnOCN$, is obtained by warming the iodide with silver cyanate in presence of alcohol. It crystallizes in thin prisms, and produces compound-ureas, with ammonia and the amines. That obtained by the action of ammonia, which yields a well crystallizable oxalate, has the composition, $CO\begin{cases} NH_2 \\ NH.Sn(C_2H_5)_3. \end{cases}$

Tin-triethyl Thiocyanate, $(C_2H_5)_3SnSCN$, is formed by the decomposition of the iodide with silver thiocyanate, and crystallizes in colourless prisms from alcohol.

Tin-triethyl Hydrosulphide, $(C_2H_5)_3SnSH$, is produced by the action of sulphuretted hydrogen on an alcoholic solution of the oxide, and it crystallizes on evaporation. If an equivalent quantity of the hydrate be added to its solution, the sulphide is formed, which is left behind as an oily liquid on evapor[illegible]ff the alcohol.

n addition to these, various other salts have been prepared. *iethyl Sulphide*, $(C_2H_5)_2SnS$, is a white powder precipi- y sulphuretted hydrogen from a solution of one of its is insoluble in dilute acids and ammonia, but dissolves ng hydrochloric acid, caustic potash, and the sulphides the alkali metals. In the dry state this body has a most disagreeable smell, resembling that of decomposing horse-radish.

A peculiar compound having the composition $(C_2H_5)_4Sn_2I_2$ is formed amongst the products of the action of tin on ethyl iodide, and is obtained, according to Frankland, by treating tin-diethyl-dimethyl with iodine. It is a heavy oily liquid, having a strong smell resembling mustard-oil, and acting very injuriously on the lungs. This compound requires further investigation.

THALLIUM-DIETHYL COMPOUNDS.

304 When an ethereal solution of thallium trichloride acts on zinc-ethyl, thallium-diethyl chloride, $(C_2H_5)_2TlCl$, is produced, and this crystallizes from hot water in glistening scales. A series of crystalline thallium-diethyl salts are obtained from this by double decomposition with silver salts. If the easily soluble sulphate be decomposed by caustic baryta, *thallium-diethyl hydroxide* is obtained, crystallizing from hot water in fine silky glistening needles, having an alkaline reaction, and decomposing at 211° with explosive violence.[1]

ACETYL COMPOUNDS.

305 *Aldehyde* or *Acetaldehyde*, C_2H_4O. In his memoir on oxide of manganese, published in 1774, Scheele mentions that if this oxide be placed in a closed flask, together with strong rectified spirit of wine and vitriolic or muriatic acid, and the mixture distilled at a moderate temperature, the alcohol which passes over possesses the smell of nitric ether. On the other hand, in his treatise on ether, published in 1782, Scheele states that if alcohol be distilled with sulphuric acid and black oxide of manganese, ether is first obtained, whilst towards the end of the

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[1] Hansen, *Ber. Deutsch. Chem. Ges.* iii. 9; [illegible] *Chem. Pharm.* clxxvi. 257.

operation acetic acid passes over. Other chemists made observations of a similar character. Thus, Dabit, in the year 1800, recommended, for the preparation of ether, the addition of black oxide of manganese to a mixture of sulphuric acid and alcohol. He explained the formation of ether from alcohol by the removal of a part of the hydrogen and its oxidation to water, and not, as Fourcroy and Vauquelin had shortly before suggested, by the removal of the elements of water. In the same year the last-named chemists repeated Dabit's experiments,[1] and found that the ethereal liquid thus produced is distinctly different from common ether, possessing a smell resembling that of ordinary nitric ether. Their views with regard to the relation of this body to alcohol are remarkable. "In this operation," they say, "the alcohol does not lose any carbon but only a portion of its hydrogen, which combines with the oxygen of the black oxide of manganese." Hence they conclude that the liquid obtained in this way contains more carbon and oxygen and less hydrogen than alcohol. From their statements it is clear that the body which they examined was a mixture of several compounds. This product was, at the time, not further investigated, and it was not until 1828 that Döbereiner, studying the action of oxidizing agents upon alcohol, observed the occurrence of a peculiar liquid to which he gave the name of oxygen-ether. This he prepared by the action of a mixture of alcohol and sulphuric acid upon either potassium chromate, potassium manganate, or manganese dioxide. At the same time Gay-Lussac stated that the body possessing the peculiar suffocating odour which had before been noticed was a mixture of alcohol, ether, and oil of wine. In the following year Döbereiner expressed the opinion that in the oxidation of alcohol two substances are formed, a heavy and a light oxygen-ether, the latter differing from common ether, as he had found in 1823, not only by its peculiar smell, but also inasmuch as it is converted into a resin when heated with potash. He also showed that a liquid possessing similar properties may be obtained by the action of platinum black on alcohol. Various chemists now investigated this subject without coming to a satisfactory conclusion. They, however, proved that the heavy oxygen-ether, obtained by the action of sulphuric acid and manganese dioxide, mainly consists of oil of wine. The body obtained by the action of platinum black was found to contain a compound to

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[1] Sur l'éther préparé à la manière du Citoyen Dabit, *Ann. de Chimie*, xxxiv. 318.

which Liebig gave the name of *acetal* (to be hereafter described). In addition, however, to acetal, the product contains a still more volatile liquid possessing a pungent smell, and this is the cause of the production of the brown resinous mass formed by the action of caustic potash. Liebig then pointed out the peculiar power of reducing silver salts which this substance possesses, and Döbereiner observed that this same body is produced by the action of nitric acid upon alcohol, thus accounting for the fact that it always occurs in crude so-called nitric ether (ethyl nitrite). He next showed that the body thus obtained possesses the power of forming a crystalline compound with ammonia, and three grains of this compound were sent by its discoverer to Liebig, and it was the examination of this preparation which led to the true explanation of this somewhat complicated subject. Liebig proved that in the first act of oxidation alcohol loses two atoms of hydrogen, as Döbereiner had supposed, giving rise to the above-mentioned volatile liquid, for which he proposed the name of *alcohol-dehydrogenatum* or *aldehyde*.[1]

Aldehyde is not only formed by the action of various oxidizing agents, such as chlorine, upon alcohol, ether, and other ethyl compounds, but is also produced when the vapours of these bodies are passed through a red-hot tube, a variety of other compounds being formed at the same time.

306 *Preparation.*—Liebig gives the following directions for the preparation of aldehyde: A mixture of 4 parts of 80 per cent. spirit, 6 of manganese dioxide, 6 of sulphuric acid, and 4 of water is distilled. When gently warmed the mixture begins to froth slightly, and the aldehyde, together with alcohol and a few other products, passes over. The process is interrupted as soon as the distillate begins to redden litmus, which is usually the case when 6 parts of liquid are contained in the receiver. The distillate, consisting of aldehyde, alcohol, &c., is mixed with an equal weight of calcium chloride and again distilled, the receiver being kept very cold. After 3 parts have passed over the distillate is again rectified with an equal weight of calcium chloride until 1½ parts have passed over. This last portion is anhydrous, but the aldehyde contains alcohol and certain compound ethers. For the purpose of purification one volume of this liquid is mixed with two volumes of ether, the mixture surrounded by cold water, and dry ammonia gas passed in to

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[1] *Ann. Pharm.* xiv. 133; xxii. 273.

saturation. The gas is rapidly absorbed with great evolution of heat, and crystals of aldehyde-ammonia separate out. These crystals are washed three times with absolute ether and dried.

The preparation of the aldehyde from this compound is very easy. The aldehyde-ammonia is dissolved in its own weight of water, the solution brought into a retort, and 3 parts of sulphuric acid previously mixed with 4 parts of water added. On gently warming this in the water-bath the aldehyde is evolved with frothing. The distillation is stopped as soon as the water in the water-bath begins to boil. The hydrated aldehyde which passes over is then dried by rectification over an equal bulk of calcium chloride in coarse lumps. Heat enough is evolved by the combination of the calcium chloride with the water to raise the liquid to the boiling-point, so that good condensation is required from the very beginning. The distillate thus obtained is mixed with pounded chloride of calcium and again distilled from a lukewarm water-bath at a heat not exceeding 30°.

Städeler[1] recommends the use of potassium dichromate in place of manganese for the oxidation. Fifteen parts of this salt are brought into a large retort standing in a freezing mixture and connected with a spiral condensing-tube surrounded with water having a temperature of 50°. A cold mixture of 10 parts of alcohol and 20 parts of sulphuric acid, previously diluted with three times its volume of water, is then poured on to the broken pieces of dichromate, the freezing mixture removed, and the vapours of aldehyde which come off condensed in the cylinders c, c, Fig. 95, partly filled with ether and surrounded by a freezing mixture. At the end of the operation the retort requires to be slightly warmed. The ethereal solution is then treated with ammonia in the way already described, and the aldehyde regained from the aldehyde-ammonia, which has the empirical formula $C_2H_4O.NH_3$, by the above-mentioned method.[1]

Aldehyde is obtained on the large scale as a by-product in the manufacture of spirit, where it comes over with the first runnings (see p. 294), and may be obtained perfectly pure by the use of a rectifying column.[2]

It may also be cheaply obtained and in quantity by the action of ozonized air upon alcohol, and is likewise formed by the dry distillation of a mixture of the calcium salts of acetic and formic acids:

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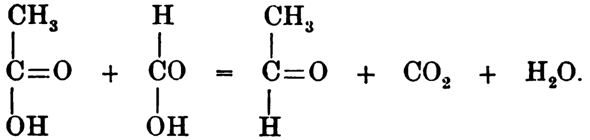
[1] *Journ. Prakt. Chem.* lxxvi. 54.

[2] Bannow, *Entw. Chem. Ind.* ii. 275.



$$\begin{array}{c}CH_3\\|\\C{=}O\\|\\OH\end{array} + \begin{array}{c}H\\|\\CO\\|\\OH\end{array} = \begin{array}{c}CH_3\\|\\C{=}O\\|\\H\end{array} + CO_2 + H_2O.$$

307 *Properties.*—Acetaldehyde is a colourless, easily mobile liquid, boiling at 20°·8, and having at 0° a specific gravity of 0·8009 (Kopp). Its vapour density was found by Liebig to be 1·532. It has a peculiar ethereal suffocating odour, and its vapour, when inhaled in large quantity, produces a cramp, which for a few seconds takes away the power of respiration (Liebig). It is miscible with water in all proportions, heat being evolved, and it is likewise soluble in both alcohol and ether. The addition of water raises the boiling-point of aldehyde. Thus, a mixture of one part of aldehyde and three parts of water boils at 37°. It is, however, separated from its aqueous solution by the addition of calcium chloride. Aldehyde likewise dissolves sulphur, phosphorus, and iodine, the last with a brown colour, and it is easily inflammable, burning with a luminous flame.

FIG. 95.

Like all aldehydes (see page 172), acetaldehyde readily undergoes change. It absorbs atmospheric oxygen, and is slowly converted into acetic acid. Oxidizing substances bring about this change more quickly. When warmed with an ammoniacal solution of silver nitrate, silver separates out as a mirror-like deposit which adheres firmly to the glass:

$$C_2H_4O + Ag_2O = 2\,Ag + C_2H_4O_2.$$

This serves for the detection of the smallest trace either of aldehyde or of silver. When the solution contains one part of silver nitrate to 1,000 of water a brilliant mirror is formed, with 2,000 of water, the mirror-like deposit is only partial, and the solution becomes violet coloured, owing to the presence of finely-divided silver. When the solution is still more dilute, no deposit of silver is obtained, the violet tint alone being observed. This can be noticed when one part of nitrate solution is diluted with 4,000 of water, such a liquid producing only the slightest opalescence[1] on admixture with a chloride.

It was formerly supposed that when aldehyde acts upon silver oxide, or when alcohol is oxidized by platinum black, a compound was formed intermediate between aldehyde and acetic acid. To this the name of acetous, aldehydic, or lampic acid was given. Heintz and Wislicenus proved that this body is a mixture of acetic acid and aldehyde.[2]

Under certain circumstances aldehyde combines with nascent hydrogen to form ethyl alcohol. This reduction is not brought about by zinc and hydrochloric acid, whereas sodium amalgam, in presence of water, as well as in presence of dilute acids, does effect this change.[3] Alcohol is also produced when aldehyde is heated with zinc and ammonia at 30° to 40° under a slight increase of pressure.[4]

When chlorine acts upon aldehyde, acetyl chloride, as well as various other products which will be afterwards described, are formed, according to the duration and other conditions of the experiment.[5]

According to the theory of types, aldehyde is considered as acetyl hydride, $\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}$. This view is in accordance with

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[1] W. and H. Rogers, *Journ. Prakt. Chem.* xl. 240.

[2] *Pogg. Ann.* cviii. 101.

[3] Wurtz, *Compt. Rend.* liv. 915; *Ann. Chem. Pharm.* cxxiii. 140.

[4] Lorin, *Compt. Rend.* lvi. 845; *Ann. Chem. Pharm.* cxxviii. 355, 384.

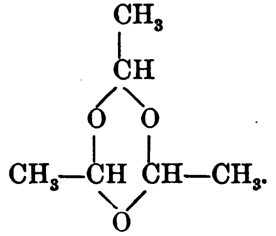
[5] Wurtz, *Ann. Chim. Phys.* [3], xlix. 58; *Bull. Soc. Chim.* [2], xiv. 98; *Ber. Deutsch. Chem. Ges.* iii. 790.

its formation from acetic acid, as well as with the action of chlorine upon it. In many other reactions, however, it behaves as the oxide of the dyad radical ethidene. Thus, phosphorus pentachloride converts it into ethidene dichloride or dichlorethane, $CH_3.CHCl_2$. These compounds, as well as others which it forms with ammonia and with the acid sulphites of the alkali metals and other bodies, will be described under the ethidene compounds.

Aldehyde is used in the arts for the manufacture of aldehyde green, one of the so-called aniline colours.

308 *Polymerization of Aldehyde.*—Small quantities of weak reagents convert aldehyde into polymeric modifications. Of these a large number were formerly supposed to exist. A more accurate examination has reduced this number to two.

Paraldehyde, $C_6H_{12}O_3$, was first obtained by Fehling, and described as elaldehyde.[1] It is easily formed by the action of small quantities of mineral acids, zinc chloride, or carbonyl chloride on aldehyde. It is best obtained by adding a few drops of concentrated sulphuric acid to aldehyde, evolution of heat and contraction taking place. On cooling the liquid to 0°, paraldehyde crystallizes in large prisms which melt at 10°·5. The liquid boils at 124°, and at 15° has a specific gravity of 0·998. A determination of its vapour density gives the number 4·583,[2] which agrees with the above molecular formula; the constitution of paraldehyde is, therefore, probably represented by the following formula:



It is slightly soluble in water, dissolving more readily in cold than in hot water. Phosphorus trichloride converts it into dichlorethane, being first split up into three molecules of acetaldehyde. This decomposition also takes place when its vapour is heated, or when it is distilled in contact with a body

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[1] *Ann. Chem. Pharm.* xxvii. 319.

[2] Weidenbusch, *Ann. Chem. Pharm.* lxvi. 152.

in presence of which it has been formed, as, for instance, with sulphuric acid.

The behaviour of paraldehyde towards carbonyl chloride is remarkable. A mixture of these two bodies is extremely difficult to separate, boiling pretty constantly about 45°. Harnitz-Harnitzky, who first examined the substance, believed it to be a definite compound and termed it *chloracetene*, giving to it the formula C_2H_3Cl, and remarking that it decomposes into aldehyde and hydrochloric acid. This fact was afterwards confirmed by Friedel, who showed that on standing it decomposes gradually.

The existence of a compound isomeric with chlorethylene, possessing such singular properties, could not be theoretically accounted for, and this gave rise to many hypotheses, until Kekulé and Zincke proved that "the most remarkable property of this body is its non-existence."[1] They noticed that carbonyl chloride acts as a kind of ferment on aldehyde, small traces being able to convert a large quantity into paraldehyde, heat being evolved. If, however, this latter substance remain for any length of time in contact with carbonyl chloride it is partly re-converted into aldehyde without evolution of heat. The substance obtained by the action of aldehyde or paraldehyde on carbonyl chloride is, therefore, a mixture of the two modifications of aldehyde, the proportion between these being dependent on the temperature and the quantity of the ferment. If this mixture be gently warmed, aldehyde and carbonyl chloride pass over first; the distillate becomes warm by the renewed formation of paraldehyde, but on quickly shaking the compound with lead oxide, pure aldehyde is first obtained, and afterwards pure paraldehyde. Hydrochloric acid acts similarly to carbonyl chloride, but, as it appears, still more energetically.[2]

309 *Metaldehyde.* The formation of this substance was first observed by Liebig, who found that needle-shaped crystals are occasionally deposited from aldehyde, and that these possess a composition identical with the original substance.[3] This compound was then further investigated by Fehling,[4] Weidenbusch,[5] and Kekulé and Zincke.[6] It is formed together with paraldehyde by the action of acids, carbonyl chloride, &c., on aldehyde,

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[1] *Ber. Deutsch. Chem. Ges.* iii. 136; *Chem. Soc. Journ.* xxv. 491.

[2] *Ann. Chem. Pharm.* clxii. 125.

[3] *Ann. Pharm.* xiv. 141; xxv. 17.

[4] *Ib.* xxvii. 319.

[5] *Ib.* lxvi. 152.

[6] *Ib.* clxii. 145.

cooled in a freezing mixture. It is likewise produced when aldehyde is allowed to remain in contact with calcium chloride or zinc chloride at ordinary temperatures. Moreover, it is sometimes formed, under unknown conditions, when aldehyde is allowed to stand by itself.

Metaldehyde separates out in needles, or in clear colourless quadratic prisms, which sublime at 100°, without previous fusion. When heated to 112° to 115°, in a closed tube, metaldehyde passes into ordinary aldehyde, and for this reason it has not been possible to determine its vapour-density, or its molecular weight. On heating with carbonyl chloride, sulphuric acid, &c., it yields aldehyde, and it behaves like the mono-molecular compound towards phosphorus pentachloride.

Aldehyde-Resin is formed by the action of aqueous or alcoholic potash on aldehyde, when the liquid first becomes yellow, next brown, and then solidifies to a reddish-brown resinous mass, the composition of which has not been ascertained. At the same time formic acid and acetic acid are formed, together with a very volatile, strongly-smelling compound, which, when well-cooled, condenses to an oily liquid. This quickly absorbs oxygen, and is converted into a golden-yellow, thick liquid, smelling of cinnamon, which quickly becomes resinous (Weidenbusch). This same resin is also formed when alcoholic solution of potash is allowed to remain in contact with the air. The colour as well as the smell which alkalis produce with aldehyde are so characteristic that the latter compound may be easily detected by this means when mixed with other bodies.

When the vapour of aldehyde is passed over heated caustic potash or soda-lime the following reaction takes place:[1]

$$C_2H_4O + KOH = C_2H_3KO_2 + H_2.$$

310 *Parathialdehyde,* $C_6H_{12}S_3$. By passing sulphuretted hydrogen into an aqueous solution of aldehyde, Weidenbusch obtained a colourless oily liquid, which, when treated with small quantities of sulphuric or hydrochloric acid, is converted into a white crystalline mass, to which he gave the name of acetyl mercaptan.[2] This liquid was afterwards termed sulphaldehyde. Hofmann then showed that it possesses the above molecular formula, as its vapour density is 6°·29,[3] and Klinger proved that

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[1] Dumas and Stas, *Ann. Chim. Phys.* [2], lxxiii. 115; *Ann. Chem. Pharm.* xxxv. 161.

[2] *Ann. Chem. Pharm.* lxvi. 158.

[3] *Ber. Deutsch. Chem. Ges.* iii. 588.

the compound obtained in the above manner is a mixture of two isomeric modifications.[1]

a-Parathialdehyde is obtained by repeated crystallization of the above compound from alcohol, or by passing sulphuretted hydrogen into a dilute acidified solution of aldehyde in alcohol, when other bodies are formed at the same time. These can be separated by repeated crystallization. To the above-mentioned liquid thialdehyde, Klinger gave the probable formula, $C_4H_8S_2$. This, when suspended in water and treated for some time with sulphuretted hydrogen, passes into another oily body, which apparently has the composition $4C_4H_8S_2 + H_2S$, and does not undergo change in presence of hydrochloric acid. If, however, some aldehyde be added to this, it quickly solidifies, and the solid mass consists mainly of a-parathialdehyde. This crystallizes from alcohol in long white prisms, or from concentrated solution in thin tables. These melt at 101°, and the liquid boils at 246°—247°. It forms with silver nitrate two compounds; one, $C_6H_{12}S_3 + AgNO_3$, forms white opaque needles concentrically grouped, the other, $C_6H_{12}S_3 + 3AgNO_3$, crystallizes in microscopic prisms. A warm solution of common salt separates the thialdehyde from both of these.

β-Parathialdehyde is formed from the foregoing compound by warming it with acetyl chloride, and also by dissolving it in cold sulphuric acid and adding water. It crystallizes from solution in glacial acetic acid in long glistening needles which melt at 124°—125°, the liquid boiling with slight decomposition at 245°—248°. The determination of its vapour density gave the number 6·0, which is rather lower than that required by theory. With silver nitrate this body also yields two compounds, viz., $C_6H_{12}S_3 + AgNO_3$, crystallizing in compact colourless needles, and $C_6H_{12}S_3 + 3AgNO_3$, in fine scales possessing a pearly lustre.

The cause of the isomerism of the above thialdehydes has not yet been established. It is possible that they have a different chemical constitution, but it is more probable that their difference is due to physical isomerism.

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[1] *Ber. Deutsch. Chem. Ges.* x. 1893; xi. 1023.

ACETIC ACID, $C_2H_4O_2$.

311 It has already been mentioned that the only acid with which the ancients were acquainted was vinegar, and that the idea of acidity was expressed by a closely related word. The effervescence produced by vinegar when poured on certain substances was also noticed in very early times, and is mentioned in the Proverbs of Solomon,[1] whilst the solvent action of vinegar on many bodies had also attracted attention. Thus Pliny says, concerning the properties of vinegar, "Aceto summa vis est in refrigerando, non tamen minor in discutiendo; ita fit ut infusum terrae spumet."

The ancients held exaggerated views respecting the solvent power possessed by vinegar. This is shown by the well-known story, related by both Livy and Plutarch, of Hannibal dissolving the Alps by means of vinegar, whilst Vitruvius states that silicious rocks, which can be neither attacked by the chisel nor by fire, are dissolved when heated and then moistened with vinegar.

The vinegar of the ancients was of course an impure wine-vinegar, and it is to the alchemists that we owe the first production of pure acetic acid by distillation. Geber, in his treatise *De Investigatione Magisterii*, writes: "Aceti acerrimi, cujuscunque genera, subtiliantur et depurantur, et illorum virtus sive effectus per destillationem melioratur." Basil Valentine appears to have been acquainted with the preparation of strong but impure acetic acid, obtained by the distillation of verdigris (which he termed a vitriol), for he says: "Take the proper *oleum vitrioli* made out of the vitriol of verdigris." But on the other hand, the alchemists often used the name of philosophical vinegar for oil of vitriol.

Acetic acid obtained from verdigris was afterwards termed *spiritus veneris* or *acetum radicale.* Stahl in 1697 described better methods for obtaining strong acetic acid. Thus, he allowed weak vinegar to freeze, and poured off the acid, which remained liquid, from the solid mass which separated out. In his *Specimen Becherianum*, published in 1702, Stahl describes the neutralization of the vinegar with alkali, the evaporation

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[1] See vol. ii. part. i. p. 32.

of the solution, and the distillation of the solid salt with sulphuric acid. He states in another work, published in 1723, that acetic acid may be obtained in a similar way from sugar of lead by the action of oil of vitriol. He also mentions that the strong acid is inflammable, a fact which had not been recognised up to that time, as it had been supposed that acetic acid differed from alcohol, especially in not being inflammable. Von Lauraguais made the same observation in 1759, and he also noticed that concentrated *acidum radicale* could be obtained in the crystalline state, a fact soon afterwards confirmed by other observers. So that Durande, in editing Morveau's *Handbook of Chemistry* in 1777, terms the solid acid *vinaigre glacial*, a name still used. In 1772 Westendorf suggested the use of acetate of soda instead of the potash salt for the preparation of the acid, and Lowitz in 1789 discovered that aqueous acetic acid may be so far concentrated by frequent rectification over powdered charcoal as to crystallize when cooled, and to this substance he gave the name of ice-like acetic acid.

312 The production of acetic acid by the dry distillation of wood or other vegetable fibre must have been known in early times; thus Glauber speaks of it in his *Furni Novi Philosophici*, published in 1648, in a way which shows that wood-vinegar was a well-known substance at that time. He says that its properties do not differ greatly from those of common vinegar, for which reason he termed it *acetum lignorum*, and states that by rectification it may be made as good as *acetum vini*.[1] Boyle is even more precise in his identification of pyroligneous with ordinary acetic acid, for he says, "Also guiacum and divers other woods, that do not at all taste sour, will, being distilled in retorts, afford spirits, that are furnished with store of acid particles, which as I have tried will hiss upon alkalies, and will dissolve coral, and even lead itself calcined to minium and make *saccharum saturni* of it."

In his *Elementa Chemiae*, published in 1732, Boerhaave states that *acida acetosa* is formed by the action of heat on vegetable substances. This expression points to the conclusion that in former days the existence of a variety of different kinds of acetic acid was assumed. Indeed every organic acid was looked upon as a modification of acetic acid. Thus, the plants now known to contain oxalic acid are still termed *acetosa*, *acetosella*,

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[1] Glauber, *Op.* (ed. 1659) p. 31.

&c. Even when formic acid was discovered, it also was believed to be a modification of acetic acid. It therefore appears not unnatural that a distinction should have been drawn between acetic acid and pyroligneous acid, and it was not until the year 1800 that Fourcroy and Vauquelin proved that the acid obtained by the dry distillation of wood, as well as of sugar, gum, &c., is simply acetic acid mixed with a small quantity of an empyreumatic oil.

When animal substances undergo dry distillation acetic acid is also formed. The substance thus obtained was, however, considered by Berthollet in 1798 to be a peculiar substance to which he gave the name of *acide zoonique.* But Thénard showed in 1802 that this substance is identical with ordinary acetic acid, as well as with the acid obtained by the destructive distillation of wood.

313 The early views concerning the formation of acetic acid from alcohol are but vague. They agree in considering that no addition is made to the alcoholic liquid in its conversion into acetic acid, the change consisting essentially of a decomposition of the constituents of the alcohol, but not of a combination of them with another body. Thus, Basil Valentine says that the materials placed in the fermenting vat have assumed another property, being no longer wine, having been transmuted into vinegar by putrefaction.[1] It was later assumed that vinegar was formed by the combination of alcohol with saline particles, such, for instance, as those of cream of tartar. For example, Lemery says: "The spirit of vinegar consists in an acid; essential or tartareous salt is very different from spirit of wine;"[2] and Macquer in 1778, in his *Dictionary of Chemistry,* says that it is not possible to form any definite idea of the changes which take place in the acetic fermentation, though it appears as if an intimate combination of the acid constituents with the combustible constituents of the wine takes place.

Priestley having proved that common muriatic acid is an aqueous solution of "a marine acid air," and hydrofluoric acid a solution of "fluor acid air," he, for a short time, looked upon acetic acid as containing "a vegetable acid air," but soon found that no such thing could be obtained from it.[3]

We owe to Lavoisier the first proof that acetic acid is a product of the oxidation of alcohol. He observed that when

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[1] *Ed. Petraeus,* p. 51.

[2] Keill's transl. p. 577.

[3] Observations on different kinds of Air, iii. 403.

wine exposed to the action of the air is converted into vinegar its volume becomes smaller. He showed, moreover, that wine is converted into vinegar by other oxidizing agents.

The composition of acetic acid was accurately determined by Berzelius in 1814, and Saussure having at the same time ascertained the composition of alcohol, it now became possible to explain the mode in which the latter was converted into the former substance. It was, however, at this time supposed that a large quantity of carbonic acid escapes during the process, and it was not until 1822 that Döbereiner showed that in the oxidation of alcohol only acetic acid and water are formed. And it is to him that we owe the true explanation, for he determined the quantity of oxygen which is needed to produce the change.[1]

314 Acetic acid occurs widely distributed in nature, partly in the free state and partly in the form of salts and ethers. According to Vauquelin, Hermstädt, and others, it is contained in the juices of many plants, and especially of trees, either free or combined as potassium or calcium acetate. It also occurs, together with other volatile acids, in water which has been distilled from odoriferous flowers or from aromatic acids and other vegetable substances. As triacetin, $C_3H_5(C_2H_3O_2)_3$, it is found as an oil in the fruit of the spindle-tree, *Eronymus europaeus*, and in the oil of the seeds of *Croton tiglium*, whilst the liquid oil from the seeds of *Heracleum giganteum* and *H. spondyleum* contain octyl acetate, $C_8H_{17}.C_2H_3O_2$, whilst sycoceryl acetate, $C_{18}H_{29}.C_2H_3O_2$, is found in the resin of the *Ficus rubiginosa*. Various animal liquids also contain small quantities of acetic acid, and it is likewise found in other products of fermentation and putrefaction of organic bodies, as well as formed by their dry distillation. It is, moreover, a product of a large number of oxidizing processes, and, as it does not undergo change, even in the presence of powerful oxidizing agents, it is often the final product of the complete oxidation of compounds which contain one or more methyl groups. Many carbon compounds which do not contain the methyl group, also yield this acid when heated with alkalis, for the alkali not only acts as an oxidizing but also as a hydrogenating agent.

315 *Synthesis of Acetic Acid.*—It has already been stated that acetic acid can be built up from its elements (see page 179). Of the different synthetic methods, that by means of trichlor-

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[1] *Schweig. Journ.* liv. 416.

acetic acid claims our attention, as having been discovered the first.

Trichloracetic acid was first prepared by Dumas in 1830, by acting on acetic acid with chlorine. In 1843 Kolbe found that when carbon disulphide is treated with chlorine at a red-heat, carbon tetrachloride, CCl_4, is formed. And two years later he discovered that the vapour of this compound, when passed through a red-hot tube, is converted into chlorine and tetrachlorethylene, C_2Cl_4. Chlorine in the sunlight acts upon this latter body in presence of water, giving rise to trichloracetic acid, inasmuch as hexchlorethane is formed, and this in the nascent condition is decomposed as follows:

$$CCl_3.CCl_3 + 2\,H_2O = CCl_3.CO.OH + 3\,HCl.$$

Now shortly before this, Melsens had observed that trichloracetic acid in aqueous solution is converted into acetic acid in presence of potassium amalgam, and thus the problem of the synthetic production of acetic acid was satisfactorily solved.

316 *Manufacture of Vinegar.*—All oxidizing agents convert alcohol first into aldehyde and then into acetic acid. Ozone readily effects this change, as does pure oxygen or air in presence of platinum black. In absence of this latter substance neither strong nor dilute alcohol can be thus oxidized. On the other hand, fermented liquors, when exposed to air, soon become sour. This depends upon the fact that they contain nitrogenous compounds which are able to act as carriers of atmospheric oxygen. This, however, they can only do when the percentage of alcohol present does not rise above a certain limit. It is for this reason that strong wine, such as port or sherry, does not become sour on exposure to air.

Various processes are adopted for the manufacture of vinegar, and the product, according to its mode of preparation, goes by various names.

Wine Vinegar is prepared in large quantities in wine-growing countries, and especially near Orleans, from the poorer qualities of wine. The manufacture is carried on in the open air, or in buildings termed *vinaigreries*, which always have a southern aspect. The vinegar casks, called *mothers*, hold from 50 to 100 gallons, and a number of these casks are placed in rows. The process is often carried on in the open air, and then from 8 to 20 such rows form what is termed a *vineg*[illegible]*ld.* Two holes are bored on the top of the front end of e[illegible] for the purpose of charging, and also for allowing free access of air.

In commencing the operation, these casks are one-third filled with the strongest vinegar, boiling hot, and to this, the charges of wine, 2½ gallons to each cask, are added at intervals of eight days. When the casks are more than half filled, one-third of the contents of each "mother" is syphoned off, and this operation repeated as long as desired. The temperature of the whole should be kept from 24° to 27° C. Wine vinegar always contains acetic ether, as well as the other ethereal salts contained in wine, and these give to it the fragrant smell and taste for which it is valued. The wine prepared from other fruit as well as grapes is sometimes also used for the manufacture of vinegar. For the explanation of the changes which here take place the chapter on fermentation must be consulted.

Malt Vinegar is largely manufactured in England. In this process the wort is allowed to ferment and the fermented liquor brought into casks placed on their sides with the bung-holes open, an additional circulation of air being kept up by means of an orifice bored at each end of the cask near its upper edge.

317 *Quick Vinegar Process.*—After it had been proved that acetic acid is an oxidation product of alcohol, the manufacture of vinegar by a quick process was introduced in 1823 by Schützenbach. The vinegar generator, technically called a graduator, is a large tun of oak (Fig. 96), frequently 13 feet high, 15 feet wide at the bottom and 14 feet wide at the top. A horizontal perforated shelf is fastened in the tub, 18 inches from the bottom, and two inches above this eight or ten holes are bored in the side of the tub and inclining downward from the outside. A similar disc is placed one foot from the top of the tub, with the holes 1 inch apart and ¼ inch in diameter. These holes are loosely filled with cotton-wick or pack-thread, a knot being made at the top to prevent them falling through. Between these shelves the interior of the tun is filled with deal shavings, which have been well washed and afterwards stove-dried. Charcoal is sometimes used. The whole being arranged, strong vinegar heated to 20°—25° is poured into the graduator and allowed to stand for one or two days, and after this weak spirit containing 5—7 per cent. of alcohol is introduced, some fermented malt-liquor being also added. This then runs through the shavings and comes in contact with a large quantity

of air, when oxidation occurs, and consequently evolution of heat takes place and the circulation of air becomes rapid. The fresh air comes in through the lower holes, and having lost some of its oxygen passes out through the upper ones. The graduator, to begin with, acts but slowly, and it is only after some time that a quick action commences. This depends upon the fact that the acetification is due to the shavings becoming gradually covered with a microscopic organism (*Mycoderma aceti*), or, as it is sometimes called, "mother-of-vinegar." It has been shown by Pasteur that the formation of vinegar is due to the growth of this organism, which plays the part of a carrier of atmospheric oxygen, and according to the observations of this distinguished chemist the rapidity of the process may be greatly increased by the addition of a small quantity of the mycoderm at the beginning of the operation. The constant presence of alcohol is, however, necessary, as in its absence the acetic acid is burnt by the ferment into carbon dioxide and water. Weak alcohol is oxidized more

FIG. 96.

quickly than strong. When very strong acetic acid is needed, the mixture has to be passed through three tubs and a fresh quantity of alcohol added, and sometimes submitted to a fourth tub in order to obtain an acid of the requisite strength.

As the successful working of the graduator is greatly dependent on the temperature, which must range between 36° and 40°, a thermometer is always employed, and it is moreover necessary to ascertain that the flow of the liquor is regular, and that it is properly diffused over the chips. The amount of air which is allowed to have access must also be regulated. If this is insufficient a loss takes place, inasmuch as a considerable quantity of volatile aldehyde is formed, the smell of this compound being almost always recognisable in the vinegar-house. If, on the other hand, too much air be allowed to pass through the graduator a loss takes place through the volatilization of alcohol vapours. To regulate the supply of air it is not uncommon to join the top of the graduator with a flue and damper connected with a chimney.

According to theory, each percentage-volume of alcohol should yield a vinegar containing one per cent. by weight of acetic acid, but, owing to unavoidable loss, these proportions are not attained in practice. In addition to this, a portion of the alcohol does not undergo oxidation, and this is larger as the strength of the vinegar increases; and thus the strongest vinegar which can be prepared in this way, rising up to 10 to 15 per cent. of acetic acid, usually contains several tenths per cent. of alcohol. In good working, 100 liters of any given percentage of alcohol by volume will yield 84 kilos. of vinegar containing the given percentage of acetic acid by weight; but the process is often attended with a loss of 20 per cent., as it is difficult to keep the summer temperature exactly at the requisite point, and when the ferment becomes hot the oxidation takes place at an extremely rapid rate.[1] In many vinegar-works the vinegar fly (*Drosophila cellaris*) occurs in enormous numbers. The larvæ of this fly live in fermenting liquors, especially in those undergoing the acetous fermentation, and are also found in decaying fungi and rotten fruit. The vinegar eel (*Anguillula aceti*) is also frequently found in the vats, and is often from 1 to 2 mm. in length. It was formerly supposed to be an infusoria, but is now recognised as belonging to the *Nematoidea*.

Spirit vinegar is colourless. The vinegar for table use is

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[1] Kramer, *Ber. Entw. Chem. Ind.* ii. 399.

often coloured yellow by burnt-sugar, and not unfrequently cream of tartar and acetic ether are added to give it the flavour of wine-vinegar. The adulteration of vinegar with sulphuric acid is not infrequent, the law permitting an addition of 0·1 per cent. of this latter acid, as it was believed that by this means the vinegar was rendered more stable, although this is an error. In order to detect the presence of free sulphuric acid in vinegar, a piece of filter-paper is wetted with the vinegar under examination and dried, or the acid is evaporated with a small quantity of sugar. In either case carbonization occurs if free sulphuric acid be present. Free mineral acids may also be detected by boiling 100 grams of the vinegar with about 50 milligrams of starch for about thirty minutes. If mineral acids are present the starch is converted into dextrin and starch-sugar, neither of which are turned blue by iodine.

318 *Preparation of Concentrated Acetic Acid.*—In addition to its uses for the table, vinegar is employed for the preparation of various acetates, and these again for the preparation of strong acetic acid. This is, however, obtained in larger quantity from pyroligneous acid, which is neutralized with lime and thus separated from wood-spirit and acetone, and the residue evaporated to dryness. In this way a crude calcium acetate is obtained which has a brown or black colour and yields, on distillation with hydrochloric acid, acetic acid, possessing a strong empyreumatic odour, largely used for many purposes in the arts. In order to obtain a pure acid from this source the crude brown or black calcium salt is heated in a drying furnace to a temperature of about 232° to carbonize the resins and other impurities. The mass thus obtained is termed white or grey acetate. Another process, proposed by Völckel,[1] accomplishes this end more completely. The solution of the crude salt when about half evaporated is treated with hydrochloric acid until a weak acid reaction is observed, when a large quantity of tar as well as of carbolic acid, creosote, and other bodies, separates out. The clear solution yields, on evaporation, a brownish coloured residue, which can then be ignited for further purification. By distillation with the requisite quantity of hydrochloric acid, acetic acid containing from 40 to 50 per cent. of the pure acid can be obtained. When this has a tarry smell or contains any free hydrochloric acid, it may be purified by distillation over a small quantity of potassium dichromate or potassium permanganate.

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[1] *Ann. Chem. Pharm.* lxxxii. 49.

When chloride of calcium is added to a solution of calcium acetate and the whole concentrated, crystals of calcium chloracetate, $Ca(C_2H_3O_2)Cl$, are obtained. This salt can easily be prepared from the pure pyrolignite of lime, and it has been suggested by Condy to employ this salt as a means of preparing pure acetic acid.[1] Acetic acid is now manufactured in Newcastle-on-Tyne according to this process, although it does not appear to have been generally adopted. There seems to be a prejudice, although quite an unfounded one, against the use of the acid thus prepared.

The sodium salt is now always employed for the preparation of concentrated acetic acid, as this salt can be easily obtained. The water of crystallization which it contains must be first removed by heating, and at last the temperature is raised up to the fusing point of the anhydrous salt. This operation was formerly conducted in iron boilers, in which very serious explosions took place, owing to the top layers of hydrated salt falling into the fused mass at the bottom. Sheet-iron pans are now employed, 6 feet long, 4 feet wide, and 2 feet deep. Care has to be taken that no sparks fall into the fused mass, as if this is the case the whole takes fire and burns away like tinder. After cooling, the solidified crystalline mass is broken up into small pieces and distilled with the requisite quantity of strong sulphuric acid. The distillate is not anhydrous acetic acid, but contains a few per cents. of water, owing to the fact that the sulphuric acid used for the decomposition is never anhydrous, and that in the operation of fusing a certain quantity of sodium carbonate is formed. It is, however, easy to obtain pure acetic acid from this product, for, on distillation, an aqueous acid passes over first, and afterwards the anhydrous acid. This latter separates out in crystals when it is cooled, and the liquid portion being poured off, the crystals are melted again, so that by a repetition of this operation pure glacial acetic acid is obtained.

319 *Properties.*—Pure acetic acid is a colourless liquid having a strongly acid and pungent smell and taste. It crystallizes on cooling in large transparent glistening tables which melt at 16°·7.[2] If melted in a closed vessel and allowed to cool down, acetic acid retains its liquidity, even at a temperature below 0°, but on opening or shaking the vessel, or on dropping in a

[1] Spon's *Encycl. Industr. Arts.* 25.

[2] Rudorff, *Ber. Deutsch. Chem. Ges.* iii. 390.

small piece of solid acid, the whole solidifies, and the temperature rises to 16°·7. A small addition of water lowers the melting point considerably, so that an acid containing 13 per cent. of water melts below 0°, and one containing 38 per cent. of water and corresponding to the formula $C_2H_4O_2 + 2H_2O$ has a melting-point of −24°. If more water be added the melting-point rises again.[1] The specific gravity of acetic acid at 0° is 1·0800 (Kopp), whilst at 15° it possesses the specific gravity of 1·0553 (Oudemanns).[2] If water be added, the specific gravity rises at first until an acid containing 70 per cent. is obtained. On a further addition of water the specific gravity remains unaltered, so that aqueous acetic acid containing 76·5 to 80 per cent. possesses the same specific gravity, namely, according to van Toorn[3] and Roscoe,[4] 1·0754 at 15°·5. The specific gravity then diminishes, so that an acid containing 43 per cent. has at 15° the same specific gravity as the anhydrous acid (Oudemanns). Hence it follows that the concentration of the aqueous acid cannot be determined, as that of alcohol can be, by the specific gravity, but trituration with an alkali must be employed. Rüdorff has shown that the melting-point of the pure acid is considerably lowered by the presence of a slight trace of water, and upon this fact he has founded a method for determining the strength of high percentage acetic acid.[5] This was formerly ascertained by shaking up the acid, together with oil of lemon, and observing how much of this dissolved. The German Pharmacopœia still states that 10 parts of pure concentrated acetic acid dissolve 1 part of this oil. A dilute acid takes up less, and in proportion to the quantity of water which it contains.

Basil Valentine was aware that vinegar when distilled yielded, to begin with, a weaker, and later on a stronger acid; and in his treatise, "Vom grossen Stein der uralten Weisen," he distinguishes in this respect between the behaviour of acetic acid and that of alcohol, and he says that "in the distillation of spirit of wine the spirit comes over first and the phlegma last; when, however, this by a long-continued warmth has been converted into vinegar, its spirit is not so volatile as before, and on distilling the vinegar the aquosity passes over first and the spirit last."[6] It has already been stated that Lowitz found that a low

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[1] Grimaux, *Compt. Rend.* lxxvi. 486.

[2] *Journ. Prakt. Chem.* v. 452.

[3] *Journ. Prakt. Chem.* vi. 171.

[4] *Journ. Chem. Soc.* xv. 270.

[5] *Loc cit.*

[6] *Ed. Petraeus*, p. 51.

[illegible]

323. A [illegible]

[illegible] H [illegible] on

[illegible] A [illegible]

[illegible] for the

[illegible] In presence of potassium [illegible]

[illegible] and water, but if free [illegible]

A [illegible] with

[illegible]

evolution of heat. If bromine be added to the solution containing hydrobromic acid, red needle-shaped crystals separate out, and these on drying over caustic lime possess the composition $4(C_2H_4O_2.Br_2)+HBr$. The hydrochloric acid solution yields a similar compound with bromine.[1]

As acetic acid is very hygroscopic, it absorbs water from various saline solutions and precipitates the salts, this being especially the case with many sulphates. It withdraws the water of crystallization from Glauber-salt, whilst on the other hand Glauber-salt crystallizes from a warm solution of anhydrous sodium sulphate in dilute acetic acid.

Acetic acid is employed for a variety of purposes. In the concentrated state it acts as a valuable solvent for many carbon compounds, as the hydrocarbons, &c., and it is, therefore, employed in the laboratory in organic researches, and it is largely used in those industries which are dependent on organic chemistry. When warm it dissolves phosphorus and considerable quantities of sulphur. It acts as a strong caustic on tender parts of the skin, producing blisters and wounds which heal only with difficulty.

Aromatic vinegar is also used largely in cases of fainting, whilst acetic acid serves as the best antidote for poisoning with alkalis or their carbonates. A more or less dilute acetic acid is largely employed in calico-printing in the preparation of the acetates of iron and alumina, respectively termed iron- and red-liquors. It is also used in the manufacture of colouring matters, and in other branches of industry. In pharmacy, photography, and chemical analysis it is also extensively employed.

Acetic acid, which is used for analytical, pharmaceutical, and certain other purposes, must be free from mineral acids and metals, nor should it contain any empyreumatic admixtures. It ought not to decolourize a solution of potassium permanganate. Pure dilute acetic acid does not do this, although the strong acid does so if it be allowed to remain for any length of time in contact with the air, inasmuch as it acts as a solvent for the small organic particles which occur in the atmosphere. In order to purify such an acid it requires to be distilled over potassium dichromate or potassium permanganate; on the large scale this is effected in copper retorts having a silver condenser, and in order to prevent the metal being attacked the distillation is generally carried on in an atmosphere of carbon dioxide.

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[1] Hell and Mühlhauser, *Ber. Deutsch. Ch*[illegible]x. 2102 ; xi. 241 ; xii. 727.

THE ACETATES, OR THE SALTS AND ETHERS OF ACETIC ACID.

321 It has already been stated that the first organic compounds obtained were those prepared by the action of acetic acid on the alkalis. The property possessed by acetic acid of attacking metals was also early observed, and a test employed to detect the presence of gold depended upon the fact that it is unattacked by this solvent, whilst copper is converted into verdigris. In the following pages only such of the acetates will be described as have either a special practical value or a theoretical interest.

Potassium Acetate, $C_2H_3KO_2$. In the impure state this salt was known to the ancients. It is stated by Pliny that a solution of wood-ashes in vinegar was used as a medicine. By evaporating such a solution, Raymond Lully obtained this salt in the solid state, without however noticing its peculiar properties; for, on heating the residue, he obtained carbonate of potash, which he considered to be a body differing from that obtained by lixiviating the ashes with water. The first description of the true salt was given by Philip Müller, a surgeon in Freiberg, who described it under the name of *terra foliata* in his *Miracula et Mysteria Chymico-Medica*, published in 1610. At that time, and for many years later, acetic acid and tartaric acid were not distinguished as different bodies; and, as acetate of potash was chiefly prepared with ignited cream of tartar, it received the name of *tartarus vini, tartarus regeneratus, arcanum tartari*, &c.

In order to prepare this salt, acetic acid is neutralized with purified potashes, and the solution evaporated. A white finely-divided powder is then obtained, or a foliated white crystalline mass, from which appearance its name of *terra foliata* was derived. It is extremely deliquescent, dissolving at 2° in 0·531, and at the boiling-point in 0·125 part of water, the saturated solution boiling at 169°. The salt crystallizes from this solution, on cooling, in transparent prisms, but only with difficulty. It is also easily soluble in dilute, as well as in absolute alcohol, and is precipitated in the crystalline form from this solvent by the addition of ether. It possesses a strong saline taste. On heating it melts, forming an oily liquid, which solidifies at 292° to an opaque crystalline mass. In this act of solidification, especially if the salt be not completely fused, large crystals are thrown up out of the mass. It decomposes at a red-heat with evolution of acetone and other products. A current of carbon dioxide passed through the alcoholic solution precipitates potassium carbonate.

Acid Potassium Acetate or *Potassium Diacetate* $C_2H_3KO_2 + C_2H_4O_2$, is formed by dissolving the normal acetate in acetic acid. If the solution be allowed to evaporate over sulphuric acid, crystals containing six molecules of water are obtained, but on evaporation at a high temperature the anhydrous salt is formed in long colourless needles, which are less deliquescent than the normal salt. It melts at 112°, and decomposes at 200°, with evolution of pure anhydrous acetic acid, which however is not completely driven off till 300°. Hence Melsens[1] suggested the preparation, by this means, of pure glacial acetic acid from dilute acid by distilling the latter with potassium acetate, the receiver being changed as soon as the temperature reaches 300°. This method has not, however, come into use.

Potassium Triacetate, $C_2H_3KO_2 + 2\,C_2H_4O_2$, is obtained by dissolving five parts of anhydrous potassium acetate in eight parts of glacial acetic acid, when it is deposited in fine deliquescent tablets, melting at 112°, and decomposing with evolution of acetic acid at 170°.

322 *Sodium Acetate*, $C_2H_3NaO_2$, was first described in 1736 by Duhamel, who showed that it is a different compound from the potassium salt. J. F. Meyer mentions this compound in his Alchemical Letters as *terra foliata tartari crystallisabilis*. In order to prepare it, dilute acetic acid is saturated with sodium carbonate and the solution concentrated by evaporation. It is also prepared by neutralizing distilled pyroligneous acid with soda, evaporating and fusing the residue to destroy empyreumatic tarry matters. It is likewise obtained by decomposing calcium acetate with Glauber-salt, the compound obtained in this latter manner being purified by recrystallization. It crystallizes with three molecules of water in monoclinic prisms. It dissolves at the ordinary temperature in about 2·8, and at 124°, the boiling-point of the saturated solution, in 0·5 parts of water. In spirit of wine it is less soluble, and in absolute alcohol almost insoluble. The crystals possess a mild bitter saline taste. At 58° the salt begins to fuse, and is perfectly liquid at 75°, again solidifying to a mass of prismatic

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[1] *Ann. Chem. Pharm.* lii. 274.

needles on cooling, the mass remaining for some length of time at 58°. If the hot liquid be poured into a closed flask, or one the neck of which is stopped with cotton-wool and allowed to cool, it remains liquid for a length of time even at 0°, but solidifies with evolution of heat when a small crystal of the salt is dropped in. It loses its water of crystallization when placed over sulphuric acid, as well as when heated to 100°. The anhydrous salt fuses without decomposition at 319° and solidifies, frequently forming large pearly crystals which take up seven molecules of water on exposure to air, and deliquesce to a supersaturated solution. The salt dried over sulphuric acid, on the other hand, only re-absorbs its water of crystallization, and does not deliquesce. According to Berthelot, this depends upon the fact that the anhydrous salt obtained by the latter process still contains traces of the aqueous solution, which prevent the formation of a supersaturated solution. It has already been stated that sodium acetate is employed for the manufacture of pure acetic acid, and it is also largely used in the preparation of other acetyl compounds and likewise in medicine.

Sodium Diacetate, $C_2H_3NaO_2 + C_2H_4O_2 + H_2O$, is prepared by quickly evaporating a solution of the normal salt in concentrated acetic acid (Fehling).

Sodium Triacetate, $C_2H_3NaO_2 + 2C_2H_4O_2$, is formed by dissolving one part of fused sodium acetate in six parts of boiling glacial acetic acid (Lescœur).

Other molecular compounds of sodium acetate and acetic acid have been prepared by Villiers.[1]

323 *Ammonium Acetate*, $C_2H_3(NH_4)O_2$.—At the beginning of the seventeenth century this substance was recommended as a medicine by Raymund Minderer, an Augsburg physician. Hence it was termed *liquor ophthalmicus Minderii*. Tachenius, in his *Hippocrates Chymicus*, published in 1666, states that this medicine is prepared from acetic acid and the volatile alkali. As it was for a long time known only in solution, it was frequently termed *sal-ammoniacum liquidum*. In order to prepare it in the solid state, either its solution is evaporated in a current of ammonia, or glacial acetic acid is saturated with ammonia gas. The salt is then obtained as an odourless, saline mass. When hot glacial acetic acid is saturated with carbonate of ammonia, ammonium acetate separates out on cooling in large needles easily soluble in water, and which readily lose ammonia.

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[1] *Compt. Rend.* lxxxiv. 774; lxxxv. 755, 1284.

t is used in medicine in cases of alcoholic poisoning. The *liquor mmoniæ acetatis* or *spiritus Mindererii* of the Pharmacopœia ontains 15 per cent. of ammonium acetate, and is obtained by neutralizing dilute acetic acid with ammonia. According to Berthelot, the ammonium acetate of the shops is an imperfectly crystalline mass, having the composition $2\ C_2H_3(NH_4)O_2 + C_2H_4O_2 + 3\ H_2O$.

Ammonium Diacetate, $C_2H_3(NH_4)O_2 + C_2H_4O_2$, is formed by evaporating a solution of the normal salt, and also by distilling the dry salt. It is obtained as an oily liquid, which gradually solidifies, but often still remains fluid, and this when touched with a crystal of the solid salt solidifies. It fuses when warmed, and distils without decomposition at 120°, and hence it may also be obtained by distilling a mixture of sal-ammoniac and potassium acetate. It crystallizes on cooling from aqueous solution in long needles, which deliquesce on exposure to moist air.

Ammonium Sesquiacetate, $2\ C_2H_3(NH_4)O_2 + 3C_2H_4O_2 + H_2O$, is obtained by dissolving the commercial salt in its own weight of glacial acetic acid. It crystallises in flat needles.

324 *Calcium Acetate*, $(C_2H_3O_2)_2\,Ca + 2H_2O$, crystallizes in needles or prisms, which effloresce partially on exposure at the ordinary temperature and completely at 100°, forming a white powder. It possesses a saline taste, is easily soluble in water, less so in spirit of wine, and dissolves lead sulphate easily. It has already been stated that this salt is used in the preparation of acetic acid and pyroligneous acid, and is employed in calico-printing. With calcium chloride it forms the compound $CaCl(C_2H_3O_2) + 5H_2O$, crystallizing in large monoclinic crystals, which do not undergo change on exposure to air, but at 100° lose their water of crystallization without alteration of form.

Zinc Acetate, $(C_2H_3O_2)_2Zn$, is formed by dissolving zinc, its oxide, or carbonate, in acetic acid. It seems to have been known to Geber, who says: "Tutia calcinatur, et resolvitur in aceto distillato, et sic est præparata." On evaporating its solution at a high temperature, it separates out as a white crystalline crust, and this contains one molecule of water. This salt is employed as an astringent in medicine, both for inward and outward use.

325 *Lead Acetate*, $(C_2H_3O_2)_2Pb$.—This salt is first mentioned by Basil Valentine, who says:[1] "Mark that pure distilled acetic acid poured on powdered saturnum (lead oxide)

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[1] *Opera, Ed. Petr.* 98.

and warmed in the water-bath entirely loses its acid and becomes sweet like sugar. If then two or three parts of the vinegar be distilled off, and the rest placed in a cellar, thou wilt find a white transparent stone like a crystal." In another place[1] he describes the preparation from white lead, and says the crystals "look like well-refined sugar or saltpetre." This salt was soon afterwards known under the name of *sugar of lead*, and Libavius, in his Alchymia, calls it *saccharum plumbi quintessentiale.*[2]

Sugar of lead is prepared on the large scale by dissolving the calculated quantity of litharge in acetic acid. For this purpose it is best to employ a 45 per cent. acid, and to every 100 parts of such an acid to add 86·5 parts of finely ground litharge, the mixture being heated to the boiling-point. The liquid is first allowed to clarify, and then brought into a crystallizing vat, where it remains for from one to two days. It is usual, however, to employ a more dilute acid, this being heated in a copper pan, at the bottom of which a piece of metallic lead is soldered to prevent the copper being acted on; to this the requisite quantity of litharge is added. The clarified liquid is then boiled down in a second pan to a specific gravity of 1·5, and the crystals allowed to deposit in wooden vessels lined with lead or copper. In this way sugar of lead is obtained as a coarsely crystalline mass, which is broken up into lumps, dried, and in this form sent into the market. An excellent quality of sugar of lead is obtained by exposing sheet lead in a closed chamber to the united action of air and the vapour of acetic acid. A mixture of normal and basic acetates is obtained, which is then dissolved in acetic acid and allowed to crystallize. The mother-liquors from the various portions are again worked up till they become too impure to yield a fine commercial article. They are then evaporated, and thus the so-called grey sugar of lead is obtained.

For certain commercial purposes a brown sugar of lead is manufactured, cheap pyroligneous acid being substituted for the more expensive colourless acid.

Lead acetate dissolves at the ordinary temperature in 1·5, at 40° in 1·0, and above 100° in 0·5 parts of water. From the hot solution it separates out on cooling, in monoclinic prisms or tables, which contain 3 molecules of water of crystallization, and it is less soluble in alcohol. Exposed to warm air it effloresces slightly, and loses the whole of its water when dried over

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[1] *Opera*, 808.

[2] Lib. II. Tract. II. Cap. IV.

sulphuric acid. At 100° it also loses water, and at the same time a small quantity of acetic acid. The anhydrous salt crystallizes from hot alcohol in six-sided tables. It melts at 280°, the liquid solidifying again at 200° to a crystalline mass. When heated more strongly, the fused salt loses acetic acid, and the liquid suddenly solidifies, with formation of a basic salt. Lead acetate has a weak acid reaction and a sweetish and an astringent metallic after-taste. If paper be dipped in a solution of lead acetate and then dried, it burns like tinder when ignited. Lead acetate is largely used in the arts, as, for example, in the preparation of the alum mordants, chrome-yellow, and other lead pigments, as well as in the laboratory for the preparation of the various acetyl compounds. In medicine it is used as a sedative and astringent, and in cases of diarrhœa, &c. Taken in large quantities it acts as a powerful poison.

Basic Lead Acetates are formed from the normal salt by removal of acetic acid, or by the assumption of lead oxide. Only two such salts are with certainty known. Others have been described, but they are probably mixtures.[1]

Dibasic Lead Acetate, $\left.\begin{matrix} C_2H_3O_2Pb \\ C_2H_3O_2Pb \end{matrix}\right\} O + H_2O$ is obtained by dissolving the calculated quantity of litharge in a solution containing the calculated quantity of the normal acetate. It is also formed when the latter salt is incompletely decomposed by ammonia. It is very soluble in water, but dissolves less readily in alcohol and separates out in crystals on addition of the latter solvent to its aqueous solution. At 100° it loses its water and is converted into a white mass.

Tribasic Lead Acetate, $\left.\begin{matrix} C_2H_3O_2Pb \\ Pb \\ C_2H_3O_2Pb \end{matrix}\right\} \begin{matrix} O \\ \\ O \end{matrix}$. — This salt is formed when a solution of sugar of lead is treated for a length of time with an excess of lead oxide. It is obtained in pearly crystalline needles when 100 volumes of a solution of the normal acetate saturated at 30° are mixed with 100 volumes of boiling water, and 20 volumes of pure strong ammonia added to the mixture and the whole allowed to cool. Ammonia precipitates from this solution either other basic salts or lead hydroxide according to the amount added.

Solutions of basic lead acetates rapidly absorb carbon dioxide from the air, and then become turbid. This also occurs

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[1] Löwe, *Journ. Prakt. Chem.* xcviii. 385.

when spring-water is added. Such solutions were known in very early times, as the fact is mentioned by Geber; they become milky on exposure to air, and hence were afterwards called *lac virginale*. The French chemist, Goulard, employed this solution in 1760 as a medicine, which, mixed with alcohol, was known as *Goulard's lotion, lead-vinegar*, or *acetum saturni*. According to the Pharmacopœia, *Liquor plumbi subacetatis* is prepared by boiling 5 oz. lead acetate, 3½ ozs. of lead oxide, with a pint of water, and then adding as much water to the filtered solution as will bring the whole up to 20 fluid ounces.

Lead Acetochloride, $C_2H_3O_2PbCl$, is obtained by heating lead chloride with lead acetate and acetic acid, or by using the chloride of an alcohol-radical instead of the first of these substances. It crystallizes in needles, which are decomposed by water with separation of lead chloride.

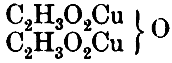
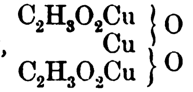
Corresponding compounds with bromine and iodine are also known.

326 *Copper Acetate*, $(C_2H_3O_2)_2Cu$.—Theophrastus, who wrote 300 B.C., describes in his treatise "περὶ λίθων," a basic acetate of copper, to which we give the name of verdigris (*vert de gris*). He terms it ἰός and describes the method of preparation which is still adopted, namely, that of exposing plates of copper to the air in contact with the marc or refuse of grapes, that is, the grapes after the juice has been expressed. Dioscorides also mentions that verdigris is formed when copper plates are hung above a strong vinegar, or when the residues from working up the copper are moistened with vinegar. Pliny describes the manufacture of the same body, termed by him *aerugo*, in much the same way. Geber appears, however, to have been the first to observe that verdigris can be obtained from vinegar in the form of crystals. This preparation, which is the normal salt, was called distilled verdigris; but in 1789, when the anti-phlogistic nomenclature came into use, it was termed *acétite de cuivre crystallisé*, as distinguished from *acétite de cuivre avec excès d'oxide de cuivre*.

Normal Copper Acetate, $(C_2H_3O_2)_2Cu + H_2O$, is obtained by dissolving verdigris, copper hydroxide or the carbonate in acetic acid. It dissolves in 13 parts of cold and 5 parts of boiling water, and crystallizes in dark blue transparent prisms which effloresce on the surface when exposed to the air, and at 100° or over sulphuric acid lose their water and become white. If a solution saturated at 60° be acidified with acetic acid and allowed to stand in the cold, large blue rhombic prisms are obtained, and these on warming to 30° become green and moist, being converted into the ordinary salt and water.

Basic Copper Acetate, commonly termed verdigris, is formed by the action of acetic acid on copper in the presence of air. Verdigris was formerly entirely manufactured in France and Belgium, and especially at Montpellier ; and hence the French name for this is *vert de Montpellier.*

Large quantities of verdigris are now made in England and Germany by steeping cloths in pyroligneous acid, or the refuse grapes from the wine factories, and bringing these in contact with sheets of copper.

After some weeks these plates are taken out and exposed to the air for some time, and then dipped into water, or, preferably, into damaged wine, again set up to dry and the verdigris scraped off; and this process of dipping, drying, and removing the verdigris occupies about eight days, and is repeated until the whole of the copper is converted into verdigris. The blue verdigris thus obtained chiefly consists of the dibasic copper acetate,  $\left.\begin{matrix}C_2H_3O_2Cu\\ C_2H_3O_2Cu\end{matrix}\right\}O + 6H_2O$. The same salt is prepared, according to Berzelius, in blue needle-shaped crystals by covering a copper plate with a mixture of the normal salt and water, and allowing this to remain in contact with the air for several months. When blue verdigris is brought in contact with water it decomposes, a light-bluish crystalline powder of *tribasic copper acetate* remaining behind. This substance also occurs when a solution of the normal salt is treated with copper hydroxide. In this case a green powder is obtained which, however, possesses the same composition as the blue, namely,  $\begin{matrix}C_2H_3O_2Cu\\ Cu\\ C_2H_3O_2Cu\end{matrix}\begin{matrix}\}O\\ \}O\end{matrix} + 2H_2O$. By decomposing the blue verdigris by means of water the normal salt is formed, and the *sesquibasic copper acetate,* $(C_2H_3O_2)_2OCu_2 + (C_2H_3O_2)_2Cu + 6H_2O$; and this latter salt is also produced when ammonia is added to a hot solution of the normal salt until the precipitate which is formed dissolves ; on cooling, this salt separates out, and more is formed on the addition of alcohol to the mother liquor. The so-called green verdigris is, according to Berzelius, a mixture of this salt with two other basic acetates. It is prepared by throwing vinegar frequently on to copper-scale.

The various acetates of copper are used as pigment colours, and also in dyeing and calico-printing as resists, preventing the indigo imparting a permanent blue colour to the cloth. They are also used in medicine, and are extremely poisonous.

Copper Acetoarsenite, $3CuAs_2O_4 + Cu(C_2H_3O_2)_2$. —This substance, according, to Ehrmann,[1] is the chief constituent of emerald-green and imperial- or mitis-green. It is obtained by boiling together verdigris, arsenic trioxide, and water; also by dissolving arsenic trioxide in a boiling solution of potash, and adding copper sulphate, when a dirty-green precipitate is formed which, on addition of sufficient acetic acid to impart to the liquid a distinct smell, and on continued boiling and on slow cooling, separates out as a fine bright-green powder. According to the proportions between the copper salt and the arsenic trioxide, a lighter or darker green precipitate is obtained.[2] These differences are probably due to variations in the composition of the precipitates.

327 *Silver Acetate*, $C_2H_3AgO_2$, is a very characteristic salt of acetic acid. It is obtained as a white precipitate by adding silver nitrate to a moderately concentrated solution of an acetate; or by dissolving silver carbonate in hot acetic acid. In each case it crystallizes out on cooling in glistening flat elastic needles, which dissolve in about 100 parts of cold water and blacken on exposure to daylight. When the acetic acid which is used for its preparation contains small traces of homologous acids, instead of forming fine bright broad needles the salt is deposited in small indistinct crystals or is thrown down in the form of a crystalline powder (Schorlemmer).

Mercurous Acetate, $(C_2H_3O_2)_2Hg_2$, is obtained by precipitating the nitrate with a soluble acetate in the form of delicate micaceous laminæ, which at the ordinary temperature dissolve in 133 parts of water, and readily blacken on exposure to air.

Mercuric Acetate, $(C_2H_3O_2)_2Hg$, crystallizes in transparent four-sided tables which dissolve in 4 parts of water at 10° and in one part of water at 100.°

328 *Aluminium Acetates*.—We owe to Walter Crum[4] the complete investigation of these salts. The normal salt is not known. When a solution of aluminium sulphate is mixed with one of sugar of lead or calcium acetate, the liquid obtained, which

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[1] *Ann. Pharm.* xii. 92.

[2] Braconnot, *Ann. Chim. Phys.* [2], xvi. 53.

[3] Liebig, *Repert. Pharm.* xiii 446.

[4] *Chem. Soc. Journ.* vi. 216

smells of acetic acid, acts as a mixture of the normal with a basic salt. This, known under the name of red-liquor,[1] is used in calico-printing, and is obtained for certain purposes by dissolving freshly precipitated aluminium hydroxide in strong acetic acid. If the solution obtained by decomposing sulphate of alumina with sugar of lead is afterwards freed from lead by sulphuretted hydrogen, and from sulphuric acid by baryta water, and allowed to evaporate in a flat dish at a temperature below 38°, a residue having the composition $(C_2H_3O_2)_4\ Al_2O + 4H_2O$ is obtained, which is a gummy mass perfectly soluble in water. If the above solution be diluted until it contains from 4 to 5 per cent. of alumina, an insoluble sesquibasic salt containing five molecules of water separates out in white crusts after standing for some days. If, however, the solution be heated to boiling the basic salt separates out as a granular powder insoluble in acetic acid.

329 *Ferrous Acetate*, $(C_2H_3O_2)_2\ Fe + 4H_2O$, is obtained by dissolving iron in acetic acid and evaporating the solution in absence of air, when it is deposited in greenish-white monoclinic crystals, very soluble in water, and absorbing oxygen rapidly, especially in solution. This salt is also used largely in calico-printing, and known under the name of black-liquor or iron-liquor. Iron mordants appear to have been used in early times in the East. They were first obtained by placing fermentable organic bodies, such as malt, in contact with iron and water. In 1782 Boothman patented the steeping of iron-filings, &c., in water mixed with some such fermentable vegetable matter; whilst in 1780 the first English patent on the subject was taken out by Flight, who proposed to "steep iron in water drawn from tar or tarry oil, and to mix the liquor with starch or gum." In order to prepare iron-liquor, iron-filings or any refuse scrap-iron is digested with crude pyroligneous acid of specific gravity 1·035, usually at a temperature of 66°, but occasionally in the cold. It is also obtained by decomposing green vitriol with calcium acetate, or by the action of a solution of sugar of lead on ferrous carbonate.

Ferric Acetate, $(C_2H_3O_2)_6Fe_2$.—Geber mentions the solubility of ferric oxide in acetic acid,—"Crocus ferri dissolvendus est in aceto distillato, et est clarificandus et hæc aqua rubicunda, crocea congelata, dat tibi crocum aptum, et est factum." It is obtained by dissolving the calculated quantity of ferric hydroxide in

[1] So called because it yields madder reds and pinks.

acetic acid, or by the decomposition of lead acetate with ferric sulphate. According to E. Meyer, this solution deposits transparent dark red glistening crystals which contain four molecules of water. When this reddish-brown solution is boiled it becomes of a darker colour, the basic salt being formed which, on slight dilution, separates out, but, on cooling, either partially or wholly re-dissolves. Ferric acetate is used in medicine as *Tinctura ferri acetatis.* According to the Pharmacopœia, it is formed by mixing solutions of persulphate of iron and acetate of potash, shaking well, filtering to separate the precipitated sulphate of potash, and then adding to the filtrate as much rectified spirit as will make the filtered product measure one pint. This is sometimes called *Klaproth's iron tincture.*

Ferric acetate is also used in dyeing as a mordant, and is usually prepared by decomposing calcium acetate with ferric sulphate or iron alum.

With ferric chloride and ferric nitrate, acetic acid forms a series of double salts studied by Scheurer-Kester.[1] These are all soluble in water and possess the following composition and appearance:

$Fe_2Cl_2(C_2H_3O_2)_4 + 3H_2O$, yellowish-red prisms.
$Fe_2Cl_2(C_2H_3O_2)_3OH + 3H_2O$, hard black crystals.
$Fe_2Cl_2(NO_3)_2(C_2H_3O_2)_2 + H_2O$, yellowish-red crystals.
$Fe_2(NO_3)_2(C_2H_3O_2)_4 + 6H_2O$, blood-red deliquescent needles.
$Fe_2(NO_3)_4(C_2H_3O_2)_2 + 8H_2O$, small monoclinic prisms.
$Fe_2(NO_3)(C_2H_3O_2)_4OH + 2H_2O$, hard red-brown rhombic prisms.
$Fe_2(NO_3)_2(C_2H_3O_2)_3OH + 2H_2O$, dark red crystals, resembling potassium ferrocyanide.

Ferric hydroxide dissolves easily in ferric acetate, with formation of easily decomposable basic salts.

330 *Reactions of Acetic Acid and its salts.*—The acetates, with the exception of a few basic salts, are all soluble in water, the most difficultly soluble being mercurous acetate and silver acetate; for this reason the nitrates of these metals produce a white precipitate in a not too dilute solution of an acetate. This dissolves in hot water, separating out on cooling in characteristic crystals. When an acetate is heated with concentrated sulphuric acid, a strong smell of acetic acid is evolved, and on the addition of alcohol the pleasant and characteristic odour of acetic ether is noticed. A still more characteristic test is the

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[1] *Ann. Chim. Phys.* [3], lv. 330; lxiii. 422; lxviii. 472.

conversion of acetic acid into cacodyl oxide (see p. 238). For this purpose the acid is saturated with caustic potash, evaporated with a small quantity of powdered arsenic trioxide and the mixture heated in a test-tube, when the characteristic smell is perceived (Bunsen). The acetates, like the formates, give with ferric chloride a dark red coloration, which disappears on the addition of a mineral acid. They are distinguished from the formates inasmuch as they do not reduce silver and mercury salts, and likewise by their reaction with concentrated sulphuric acid.

ETHERS OF ACETIC ACID.

331 *Methyl Acetate*, $C_2H_3O_2CH_3$.—This was first prepared in 1835 by Dumas and Péligot[1] by distilling a mixture of wood-spirit, glacial acetic acid and oil of vitriol. It is contained in crude wood-tar and in crude wood-spirit. In order to prepare this ether, the method adopted is similar to that used for the preparation of ethyl acetate. Methyl oxalate may also be heated with its own weight of glacial acetic acid and some fuming hydrochloric acid added.[2]

It is a mobile liquid, possessing a pleasant refreshing smell, boiling at 59°·5, and having a specific gravity at 0° of 0·86684 (Pierre) and a vapour-density of 2·595 (Cahours).

Ethyl Acetate or *Acetic Ether*, $C_2H_3O_2.C_2H_5$.—This substance was discovered by Lauraguais, who published a mode of preparation in the *Memoirs of the Paris Academy* in 1759. It consisted in heating strong acetic acid, obtained by distilling verdigris, with alcohol. The fact that the ether could be thus produced was contradicted by some, but corroborated by other chemists. Thus, for instance, Scheele in 1782 denied that acetic acid when distilled alone with alcohol produced the ether, but he added that it was easily formed when a mineral acid was present in the mixture of alcohol and acetic acid, or when an acetate was treated with a mixture of alcohol and a mineral acid. Pelletier in 1786 proved that by frequent cohobation acetic acid and alcohol alone are able to form acetic ether.

For the preparation of acetic ether an excellent plan, proposed by Frankland and Duppa, is usually adopted. 9 kg. of concentrated sulphuric acid is brought into a deep earthenware vessel and 3·6 kg. of alcohol of 93 per cent. is mixed with this, being brought to the bottom of the vessel by means of a

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[1] *Ann. Chim. Phys.* lviii. 46.

[2] Dittmar, *Journ. Chem. Soc.* xxi. 480.

narrow glass tube connected by a caoutchouc tube with a convenient reservoir standing at a considerable elevation. The glass tube is used as an agitator during the continuance of the flow of the alcohol. In this way the liquid attains a high temperature without loss of alcohol, and this greatly favours the formation of sulphovinic acid. This mixture is allowed to stand protected from moisture for twenty-four hours before use. It is then poured gradually, so as to prevent heating, on to 6 kg. of previously dried and fused sodium acetate broken into small pieces and placed in a copper still immersed in cold water. The mixture is then allowed to stand for twelve hours before distillation is commenced. This can then be carried on over a naked fire or gas-flame, and continued until water alone passes over. In this way about 6 kg. of acetic ether absolutely free from alcohol can be obtained, and this requires only one rectification over fused and powdered calcium chloride.[1]

Ethyl acetate is also formed easily when a mixture of alcohol and acetic acid, in the proportion of equal molecules, is allowed to run into sulphuric acid heated to 130°. In this way ethylsulphuric acid is first formed, and this decomposes with the acetic acid, forming acetic ether, which distils over whilst the sulphuric acid is again acted upon. By means of 10 grms. of sulphuric acid 232 grms. of crude ethyl acetate are obtained.[2]

Acetic ether is a mobile liquid possessing a penetrating, refreshing smell and a pleasant burning taste. It boils at 74°·3 under the normal pressure, and has a specific gravity at 0° of 0·91046 (H. Kopp). Its vapour-density was found by Boullay and Dumas to be 3·016. It easily dissolves in about 12 parts of water, of which, on shaking, it takes up about 3·3 per cent. It mixes with alcohol, ether, acetic acid, &c., in all proportions, and dissolves a large number of resins, oils, and other organic bodies. When in the pure state it does not undergo alteration on exposure to the air, but if it contains water it gradually becomes acid. Its purity cannot be tested by a determination of specific gravity, inasmuch as mixtures of water and alcohol or ether in certain proportions do not affect this. In order to detect these impurities it is heated in a closed vessel with an excess of titrated solution of caustic soda and the amount of alkali used for the decomposition determined volumetrically. If acetic

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[1] *Phil. Trans.* (1865), clvi. 37.

[2] Eghis, *Ber. Deutsch. Chem. Ges.* vi. 1177. A similar method has also been described by Pebal (*Bull. Soc. Chim.* xxxiii. 350).

ether be brought in contact with iodine and aluminium foil, a violent reaction takes place represented by the following equation:[1]

$$2\,Al + 6\,C_2H_5.C_2H_3O_2 + 3\,I_2 = 6\,C_2H_5I + Al_2(C_2H_3O_2)_6.$$

Acetic ether is used in medicine. Its action in many cases resembles that of common ether, but it possesses a more agreeable taste and smell. It is also used for addition to the poorer classes of wine, liqueurs, &c. It is also sometimes employed as a solvent, and is used in the laboratory for the synthetic preparation of fatty acids, ketones and other compounds, as will be hereafter described.

Chlorine and bromine form substitution-products with ethyl acetate. By the action of chlorine *perchloracetic ether*, $CCl_3.CO_2.C_2Cl_5$, is obtained as the last product. This is an oily liquid, smelling like chloral, possessing a burning taste, and boiling under partial decomposition at 245°.[2] It is polymeric with trichloracetyl chloride, and easily splits up into two molecules of this substance, which it resembles in its reactions with water and alkalis.

Ethyl Orthoacetate, $CH_3C(OC_2H_5)_3$, is obtained by heating sodium ethylate free from alcohol with trichlorethane, $CCl_3.CH_3$, to from 100° to 120°. It is a colourless, peculiarly unpleasant-smelling liquid which has not yet been obtained in the pure state. When heated with water to 100°—120° it is converted into alcohol and common acetic ether.[3]

OXIDES OF ACETYL.

332 *Acetyl Oxide*, or *Acetic Anhydride*, $(C_2H_3O)_2O$, was discovered by Gerhardt,[4] and formerly termed anhydrous acetic acid. He obtained it by the action of acetyl chloride on anhydrous sodium acetate:

$$\left.\begin{matrix} C_2H_3O \\ Cl \end{matrix}\right\} + \left.\begin{matrix} Na \\ C_2H_3O \end{matrix}\right\} O = \left.\begin{matrix} C_2H_3O \\ C_2H_3O \end{matrix}\right\} O + \left.\begin{matrix} Na \\ Cl \end{matrix}\right\}$$

In order to prepare it by this process, one part of acetyl

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[1] Gladstone and Tribe, *Journ. Chem. Soc.* 1876 (2), 357.

[2] Leblanc, *Ann. Chim. Phys.* [3], x. 197.

[3] Geuther, *Zeitsch. Chem.* 1871, 128.

[4] *Comptes Rendus*, xxxiv. 755; *Ann. Chim. Phys.* [3], xxxvii. 311.

chloride is allowed slowly to flow on to one part of finely powdered sodium acetate or 1·25 parts of potassium acetate, the whole being distilled as soon as the reaction is complete. As, however, acetyl chloride is formed by the action of the chlorides of phosphorus on acetates, it is not necessary to employ acetyl chloride already prepared, and the reaction may be modified in a variety of ways. Thus, for example, one part of phosphorus oxychloride may be allowed to act on two parts of potassium acetate, when sufficient heat is evolved to cause the mixture of acetyl chloride and acetyl oxide to distil over, and this can be rectified over potassium acetate until a drop of the distillate shaken up with water does not give any reaction for hydrochloric acid. For this method of preparation the apparatus used in Fig. 97 is used. The arrangements are simple. The double-necked bottle contains quicklime or caustic soda, in order to retain the vapours of the chloride, which would otherwise escape into the air, and are very irritating.

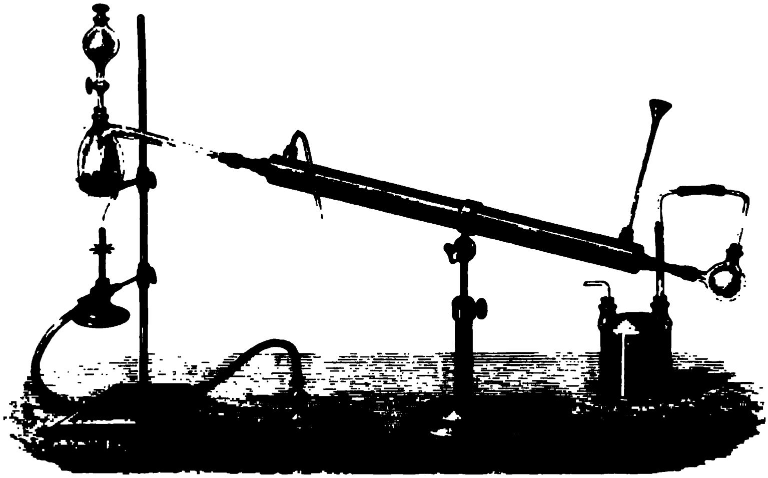

FIG. 97.

Another method of preparation consists in adding, by degrees, 7 parts of phosphorus pentachloride to 2 parts of glacial acetic acid. The mixture of acetyl chloride and phosphorus oxychloride thus obtained is then distilled with 20 parts of sodium acetate or an equivalent quantity of potassium acetate. Acetic anhydride is also easily prepared by acting on acetyl chloride with an equal number of molecules of glacial acetic acid, in connection with an inverted condenser, until no further fumes of hydrochloric acid escape.[1]

The anhydride prepared by one or other of these processes is then purified by fractional distillation.

The following methods of preparation are of special theoretical interest:

(1) By heating lead acetate with carbon disulphide:[2]

$$2\,(C_2H_3O_2)_2Pb + CS_2 = 2\,(C_2H_3O)_2O + CO_2 + 2\,PbS.$$

(2) By heating acetyl chloride with caustic baryta;[3] and

(3) By distilling glacial acetic acid with phosphorus pentoxide, when acetic anhydride is produced in small quantity.[4]

Properties.—Acetyl oxide is a colourless, mobile, highly refracting liquid, having a smell resembling acetic acid, but being less acid and much more irritating. It has a specific gravity at 0° of 1·0969, and at 15° of 1·0799, and boils at 137°·8 (Kopp). Its vapour-density at 152° is 3·673, whilst at 255° it is 3·489, theory requiring 3·533. It is insoluble in water, but when allowed to remain for some time in contact with the liquid it is converted into acetic acid, and hence it becomes acid on exposure to moist air. It is also quickly decomposed in presence of alkalis. When heated with caustic lime, anhydrous baryta, oxide of lead, or mercuric oxide, the corresponding acetates are formed.[5] When warmed with anhydrous potassium acetate, it forms a solution which on cooling deposits colourless needles, having the composition $2C_2H_3KO_2 + (C_2H_3O)_2O$. These deliquesce slowly in the air, and when heated decompose into their constituents. This occurs, however, at a temperature above the boiling-point of acetyl oxide; and for this reason, in the preparation of the anhydride, the temperature at the end of the operation must be considerably raised.

When acetyl oxide is heated with the alcohols, it forms the corresponding acetates, and hence it may be used for the preparation of such bodies, and is especially useful in enabling us to determine the number of alcoholic hydroxyls contained

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[1] Kanonikoff and Saytzeff, *Ann. Chem. Pharm.* clxxxv. 192.

[2] Broughton, *Chem. Soc. Journ.* xviii. 21.

[3] Gal, *Ann. Chem. Pharm.* cxxviii. 126.

[4] Gal and Etard, *Compt. Rend.* lxxxii. 457.

[5] Béchamp, *Ann. Chim. Phys.* [5], xii. 504.

in the compounds of the polyvalent radicals.[1] It is decomposed by chlorine into acetyl chloride and monochloracetic acid:[2]

$$\left.\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\right\}O+\left.\begin{matrix}Cl\\Cl\end{matrix}\right\}=\left.\begin{matrix}C_2H_3O\\Cl\end{matrix}\right\}+\left.\begin{matrix}C_2H_2ClO\\H\end{matrix}\right\}O.$$

Bromine acts in a similar way upon it. Aluminium chloride acts in the cold on the anhydride with formation of acetyl chloride and aluminium acetate.[3] According to Schützenberger it also combines with chlorine monoxide to form a colourless liquid, which decomposes very easily, and is explosive. This he terms chlorine acetate, and he gives to it the formula $C_2H_3O_2Cl$.[4] Aronheim,[5] in investigating this subject, came to the conclusion that this body is only a mixture, which, however, Schützenberger does not admit.[6] By acting with iodine upon it, colourless, shining, short prisms are obtained, having the composition $(C_2H_3O_2)_3I$, which explode when heated above 100°. Aronheim did not succeed in preparing this substance.

Silico-acetic Anhydride, or *Silicon Acetate*, $SiO_4(C_2H_3O)_4$, was obtained by Friedel and Ladenburg[7] by acting with silicon chloride upon glacial acetic acid or the anhydride. It forms white, apparently quadratic, crystals, which rapidly absorb moisture from the air, and are violently decomposed by water with formation of acetic and silicic acids. The compound decomposes when heated under ordinary pressure, but under a pressure of 5 to 6 mm. it melts at 110° and distils at 148°. It can be recrystallized from anhydrous ether.

When ethyl silicate is heated with acetic anhydride to 180° the compound $SiO_4(C_2H_5)_3C_2H_3O$ is formed as an oily liquid, boiling between 192° and 197°.[8]

Acetyl Dioxide, or *Acetyl Peroxide*, $(C_2H_3O_2)O_2$, was discovered by Brodie,[9] and obtained by gradually adding barium dioxide to an ethereal solution of acetyl oxide:

$$2\left.\begin{matrix}CH_3.CO\\CH_3.CO\end{matrix}\right\}O+BaO_2=\left.\begin{matrix}CH_3.CO.O\\CH_3.CO.O\end{matrix}\right\}+\left.\begin{matrix}CH_3.CO.O\\CH_3.CO.O\end{matrix}\right\}Ba.$$

It is a thick and very strongly smelling liquid, which may be

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[1] Schützenberger, *Compt. Rend.* lxi. 485.

[2] Gal, *Ann. Chim. Phys.* [3], lxvi. 187.

[3] Andrianowsky, *Bull. Soc. Chim.* [2], xxxi. 199.

[4] *Ann. Chem. Pharm.* cxx. 113.

[5] *Ber. Deutsch. Chem. Ges.* xii. 26.

[6] *Bull. Soc. Chim.* xxxi. 194.

[7] *Ann. Chem. Pharm.* cxlv. 174.

[8] Friedel and Crafts, *Ann. Chim. Phys.* [4]. ix. 5.

[9] *Proc. Roy. Soc.* ix. 361; *Phil. Trans.* 1863, 407.

kept for some time in the dark without decomposition, but, on heating, explodes as violently as chloride of nitrogen does. It resembles hydrogen dioxide, inasmuch as it bleaches indigo-solution, and oxidizes potassium iodide, potassium ferrocyanide, &c., but it does not reduce solutions of either chromic or permanganic acid.

Baryta-water decomposes it, with formation of barium acetate and hydrated dioxide of barium.

HALOID COMPOUNDS OF ACETYL.

333 *Acetyl Chloride*, C_2H_3OCl, was discovered by Gerhardt, and obtained by acting with phosphorus oxychloride on fused potassium acetate :[1]

$$POCl_3 + 2\,C_2H_3O_2Na = 2\,C_2H_3OCl + NaCl + NaPO_3.$$

To prepare it in this way it is advisable to add the phosphorus oxychloride, which must be well cooled, to the calculated quantity of potassium or sodium acetate in order to avoid the formation of acetyl oxide. The apparatus, Fig. 98, may be used for this purpose. The powdered acetate is contained in the glass flask connected with the tubulus of the retort by means of a piece of caoutchouc tubing. By raising the flask the substance falls into the retort, whilst by lowering it an air-tight caoutchouc joint is formed.

It may also be obtained by adding phosphorus pentachloride to acetic anhydride,[2] when the same apparatus may be used. A better yield is obtained by using phosphorus oxychloride.[3] The apparatus described under acetic anhydride may be employed. Another very convenient method of preparation is by the action of phosphorus trichloride on glacial acetic acid :

$$PCl_3 + 3\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O = 3\left.\begin{matrix}C_2H_3O\\Cl\end{matrix}\right\} + P(OH)_3.$$

The trichloride is mixed in the cold with an excess of glacial acetic acid, and the mixture heated on the water-bath. At

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[1] *Ann. Chim. Phys.* [3], xxxvii. 285.

[2] Ritter, *Ann. Chem. Pharm.* xcv. 208.

[3] Kanonnikow, *ib.* clxxv. 378.

about 40° the reaction begins, and as the temperature rises it is quickly completed.[1] The product is purified by fractional distillation; and if the distillate contains any chlorine compounds of phosphorus, it may be conveniently distilled over some anhydrous sodium acetate.

Acetyl chloride is a highly refracting mobile liquid, which at 0° has a specific gravity of 1·1305 and boils at 55°. Its vapour-density is 2·87. On exposure to moist air it fumes strongly, and it possesses a suffocating smell, resembling both hydrochloric and acetic acids. Its vapour rapidly attacks the eyes and the mucous membrane, and when inhaled produces coughing and even spitting of blood. If a few drops are brought into water, they soon dissolve, acquiring a rotatory motion, and forming acetic acid and hydrochloric acid. If a small quantity of water is poured into the chloride, a violent reaction takes place, which may even become explosive. When a mixture of acetyl chloride and acetyl oxide is treated with sodium-amalgam, and the product distilled with water, acetic ether is obtained.[2]

FIG. 98.

When acetyl chloride is treated with sodium-amalgam until the reaction is complete, and then snow added, and afterwards some

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[1] Béchamp, *Compt. Rend.* xl. 944, xlii. 224

[2] A. Saytzeff, *Zeitsch Chem.* 1870, 105.

more amalgam, a liquid is obtained containing ethyl alcohol, which can be readily isolated.[1]

Acetyl Bromide, C_2H_3OBr, was obtained by Ritter in 1855 by acting with phosphorus pentabromide on acetic acid.[2] In order to prepare it, 240 grams of bromine are gradually added to a mixture of 90 grams of glacial acetic acid and 33 grams of amorphous phosphorus, and the whole distilled, when the reaction is complete.[3] It is a colourless liquid, which fumes in the air, becomes yellow on exposure, and boils at 81°. In its general properties it closely resembles the chloride.

Acetyl Iodide, C_2H_3OI, is formed by acting with iodide of phosphorus on acetyl oxide:

$$3(C_2H_3O)_2O + 3I_2 + P_2 = 6C_2H_3OI + P_2O_3.$$

The mixture is heated until no further reaction takes place; then the whole is distilled, and the distillate shaken up with some mercury and rectified.

Acetyl iodide is a brown transparent liquid, which, when freshly prepared, does not contain any free iodine, and does not become decolorized on shaking with mercury. It boils, with decomposition, at about 108°. It has a very suffocating smell, and is at once decomposed in contact with water.[4]

SULPHUR COMPOUNDS OF ACETYL.

334 *Thiacetic Acid*, C_2H_3OSH.—Kekulé first prepared this compound by acting on glacial acetic acid with phosphorus pentasulphide.[5] It is also obtained by treating potassium mercaptide with acetyl chloride.[6] For the purpose of preparing thiacetic acid 300 parts of phosphorus pentasulphide are warmed with 108 parts of acetic acid, the retort being half filled with the mixture and heated until the reaction begins: the flame is then withdrawn, when the thiacetic acid comes over without

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[1] Linnemann, *Ann. Chem. Pharm.* cxlviii. 249.

[2] *Loc. cit.*

[3] Gal, *Ann. Chem. Pharm.* cxxix. 53.

[4] Guthrie, *Ann. Chem. Pharm.* ciii. 335.

[5] *Proc. Roy. Soc.* vii. 38.

[6] Jaquemin and Vosselmann, *Compt. Rend.* xlix. 371.

Acetamide forms colourless needles, which have a strong smell resembling that of the excrement of mice. They melt at 78°, forming a liquid which solidifies to a crystalline mass. This boils at 222°, is easily soluble in water and alcohol, but insoluble in pure ether. When heated with water it decomposes into acetic acid and ammonia. In the presence of alkalis or acids this decomposition takes place more quickly. It may be heated almost to 360° without suffering decomposition. Distilled with phosphorus pentoxide or zinc chloride it is converted into acetonitril with loss of water, and at the same time some quantity of acetic and hydrocyanic acids are formed. When brought into the animal body it passes out in the urine unaltered (Bödecker).

Acetamide acts as a weak base and combines with a few of the strong acids.[1] The hydrochloride, $(C_2H_3O.NH_2)_2HCl$, is obtained by passing gaseous hydrochloric acid into an alcohol-ether solution of the amide. It forms long sharp needles with a strong acid taste, and is soluble in water and alcohol, but not in ether. The alcoholic solution, on standing for some time, deposits crystals of sal-ammoniac. In the preparation the compound, $C_2H_3ONH_2,HCl$, is first formed, and this readily passes into the foregoing body by loss of hydrochloric acid.[2]

If acetamide be dissolved in cold strong nitric acid, and the solution allowed to evaporate, colourless crystals of the composition $C_2H_3O.NH_2,HNO_3$, are formed, and these, on heating, first fuse and then deflagrate.

Like the other acid-amides the hydrogen in acetamide can be replaced by certain metals (Strecker). Of the products thus formed, *silver acetamide*, $C_2H_3O.NHAg$, and *mercury acetamide*, $(C_2H_3O.NH)_2Hg$, are the most important.

Ethyl Acetamide, $C_2H_3O.NH(C_2H_5)$, was obtained by Wurtz,[3] by evaporating a solution of ethylamine and ethyl acetate, as well as by acting on ethyl isocyanate with glacial acetic acid:

$$N\left\{\begin{matrix} C_2H_5 \\ CO \end{matrix}\right. + C_2H_3O.OH = N\left\{\begin{matrix} C_2H_5 \\ C_2H_3O \\ H \end{matrix}\right. + CO_2.$$

It is also formed by heating ethylamine acetate.[4]

It is a thick colourless liquid, soluble in water, boiling at 205°. Dry chlorine gas converts it into *chlorethyl acetamide*,

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[1] Strecker, *Ann. Chem. Pharm.* ciii. 321.

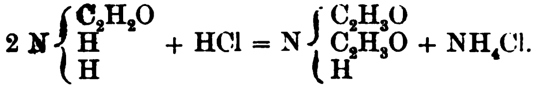
[2] Pinner and Klein, *Ber. Deutsch. Chem. Ges.* x. 1889.

[3] *Ann. Chem. Pharm.* lxxvii. 334.

[4] Linnemann, *Wien. Akad. Ber.* lx. 44.

$C_2H_3O.NCl(C_2H_5)$, a neutral mobile liquid, which has a faint camphor-like smell, and easily undergoes decomposition.[1]

336 *Diacetamide*, $(C_2H_3O)_2NH$, was first obtained by Strecker by heating acetamide hydrochloride in closed tubes to 200°, as well as by acting on heated acetamide with hydrochloric acid. It is then formed by the following equation:



$$2\,N\begin{cases}C_2H_2O\\H\\H\end{cases} + HCl = N\begin{cases}C_2H_3O\\C_2H_3O\\H\end{cases} + NH_4Cl.$$

The distillate, which contains some acetyl chloride, acetonitril, and much free acetic acid, as will be explained hereafter, solidifies to a mixture of acetamide and diacetamide. This is dissolved in ether and hydrochloric acid passed in, when acetamide hydrochloride separates out, whilst diacetamide remains in solution.[2] It is also formed in small quantity by the action of acetyl chloride on acetamide (Kekulé), as well as when acetonitril is heated with glacial acetic acid to 200°—250°.[3] Its formation is perfectly analogous to that of acetamide from acetonitril and water.

Diacetamide is easily soluble in water, alcohol, and ether, and crystallizes in long needles which melt at 74°—75° (Wichelhaus), the liquid boiling at 215° (Linnemann). It is distinguished from acetamide by not possessing basic properties, but acting as a weak acid, turning litmus red, and forming a silver salt which has not been specially examined.

Ethyl Diacetamide, $N(C_2H_3O)_2C_2H_5$, is a colourless liquid boiling at 185°—192°, obtained by Wurtz by acting on glacial acetic acid with ethyl isocyanate at a temperature of 180°—200°.

337 *Triacetamide*, $N(C_2H_3O)_3$, is formed with difficulty by heating acetonitril with acetic anhydride to 200°. It crystallizes from anhydrous ether in small elastic needles, which melt at 78°—79°, are odourless, possess a perfectly neutral reaction, and do not exhibit any basicity. This is easily explained, inasmuch as the basic character of the ammonia is altogether destroyed by the replacement of the three hydrogen atoms by three acid radicals. It however does not possess the character of an acid, because it does not contain any hydrogen replaceable by a metal, whilst diacetamide is a stronger acid than acetamide.

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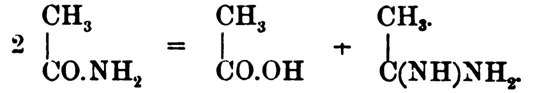
[1] Tscherniak and Norton, *Compt. Rend.* lxxxvi. 1409.

[2] *Ann. Chem. Pharm.* ciii. 321.

[3] Kekulé, *Lehrb.* i. 574; Gautier, *Compt. Rend.* lxvii. 1255; Linnemann, *Wien. Akad. Ber.* lx. 44.

Acetdiamine, $C_2H_6N_2$.—The hydrochloride of this base remains, mixed with sal-ammoniac, in the residue obtained in the preparation of diacetamide from acetamide and hydrochloric acid. It may be separated from sal-ammoniac by dissolving it in a mixture of ether and alcohol. It crystallizes in colourless prisms, and with platinum chloride forms the compound $(C_2H_6N_2,HCl)_2PtCl_4$. It is easily soluble in water, and on evaporation is deposited in reddish-yellow crystals. If the hydrochloride be treated with silver sulphate, the sulphate of acetdiamine, $(C_2H_6N_2)_2SO_4H_2$, is obtained, and this separates from alcoholic solution in pearly scales. The free base cannot be prepared, inasmuch as in presence of water it decomposes into ammonia and acetic acid. Its formation and constitution are seen from the following equation:



$$2\begin{array}{l}CH_3\\ |\\ CO.NH_2\end{array} = \begin{array}{l}CH_3\\ |\\ CO.OH\end{array} + \begin{array}{l}CH_3.\\ |\\ C(NH)NH_2.\end{array}$$

Tawildarow, who repeated Strecker's experiments on heating acetamide and hydrochloric acid, obtained only a mixture of sal-ammoniac and acetamide.[1]

338 *Acetyl Carbamide* or *Acetyl Urea*, $CO(NH_2)(NH.C_2H_3O)$, is produced by heating urea with acetyl chloride to 120°. It crystallizes from water, in which it is easily soluble, in stellar prisms. It is difficultly soluble in alcohol, and separates from alcoholic solution in four-sided silky needles. It melts at 200°, and solidifies to a crystalline mass, which, when dissolved in alcohol, deposits thick rhombic prisms.[2]

Diacetyl Carbamide, $CO(NH.C_2H_3O)_2$, is produced by heating urea with carbonyl chloride to 50°, whilst at the same time acetyl chloride, sal-ammoniac, carbon dioxide, and acetonitril are formed. Diacetyl urea crystallizes from hot alcohol in rhombic needles, which on heating first melt and then sublime.[3]

Acetyl Cyanide, $C_2H_3O.CN$, is obtained by heating silver cyanide with acetyl chloride to 100°. It is a colourless liquid, boiling at 93°, and its vapour possesses a density of 2·4. It has a smell analogous to that of hydrocyanic and acetic acids,

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[1] *Ber. Deutsch. Chem. Ges.* v. 477.
[2] Zinin, *Ann. Chem. Pharm* xcii. 403.
[3] E. Schmidt, *Journ. Prakt. Chem.* [2], v. 35.

and is insoluble in water, swimming on the surface of this liquid like oil, and being gradually converted into these two compounds.[1] Owing to its easy decomposability, it must be assumed that this compound is related to the carbamines, and that the cyanogen in this is connected with the acetyl group by means of nitrogen. If, however, it be heated with hydrochloric acid it is transformed into pyro-racemic acid, $CH_3.CO.CO.OH$, and hence it behaves as the nitril of this acid.[2] It is, therefore, probable, that this latter is formed only under the action of heat, or in the presence of hydrochloric acid.

Acetyl cyanide is easily converted into the polymeric compound $(C_2H_3O)_2(CN)_2$; this forms large tabular crystals, melting at 69°, and remaining liquid for some time. This boils at 208°-209°, and yields a vapour which has a density of 4·9 to 5·0. It decomposes with water into hydrocyanic and acetic acids. (Hübner).

Acetyl Thiocyanate, $C_2H_3O.SCN$, is formed by the action of acetyl chloride on lead thiocyanate. It is a colourless liquid, which becomes red on exposure to air, attacks the eyes violently, and boils at 131°—132°.[3] This compound may perhaps be acetyl mustard-oil, $N\left\{\begin{matrix}C_2H_3O\\CS.\end{matrix}\right.$

ACETONITRIL AND ITS DERIVATIVES.

339 *Acetonitril* or *Methyl Cyanide*, CH_3CN, was discovered by Dumas[4] in 1847, who obtained it by distilling ammonium acetate with phosphorus pentoxide. In conjunction with Leblanc and Malaguti, Dumas afterwards prepared it by distilling potassium cyanide with potassium ethyl sulphate. The authors state that the compound thus prepared is mixed with hydrocyanic acid and ammonium formate, which impart to it a most unpleasant smell and taste, and render it poisonous. These impurities may, however, be got rid of by heating it

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[1] Hübner, *Ann. Chem. Pharm.* cxx. 334.

[2] Claisen and Shadwell, *Ber. Deutsch. Chem. Ges.* xi. 1563.

[3] Miquel, *Compt. Rend.* lxxxi. 1209.

[4] *Compt. Rend.* xxv. 383.

with mercuric oxide, and then distilling with phosphorus pentoxide. The poisonous properties then, to a great extent, disappear.[1] We now know that the unbearable odour arises from an admixture of the isomeric methyl carbamine (see p. 224), and this may easily be got rid of by treatment with dilute sulphuric acid.[2]

Pure acetonitril is likewise obtained, according to Hofmann and Buckton, by mixing equal volumes of acetamide and phosphorus pentoxide, when a rapid evolution of heat takes place and the compound distils over:

$$CH_3.CO.NH_2 = CH_3.CN + H_2O.$$

The product is then washed with dilute caustic potash in order to remove hydrocyanic and acetic acids, and dried over phosphorus pentoxide.[3]

It may likewise be prepared by boiling acetamide with some glacial acetic acid, and passing the vapour through a distillation-tube, suggested by Bel-Henninger, which is so long that the undecomposed amide flows back again, whilst water and the nitril distil over. This decomposition, however, only takes place very slowly.[4]

Acetonitril is also found in the products of distillation of the beet-root vinasse,[5] and likewise occurs in coal-tar naphtha. It is a colourless liquid, which at 0° has a specific gravity of 0·8052, possesses an ethereal and aromatic smell, and boils at 82° (Gautier). It is singular that on addition of alcohol the boiling point of this substance is considerably reduced. The mixture which boils at the lowest point is one containing 44 per cent. of the nitril, and the boiling point is lowered to 72°·6, whilst on further addition of alcohol it again rises. In order to separate the acetonitril from admixture with alcohol, the whole is frequently distilled over calcium chloride from a water-bath, and the last traces of alcohol removed by distillation over phosphorus pentoxide. Methyl alcohol acts similarly to the ethyl alcohol.[6]

The vapour-density of acetonitril is 1·45 (Dumas). When

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[1] *Compt. Rend.* xxv. 442 and 474.

[2] Gautier, *Bull. Soc. Chim.* [2], ix. 2.

[3] *Ann. Chem. Pharm.* c. 130.

[4] Demarçay, *Bull. Soc. Chim.* xxxiii. 456.

[5] Vincent, *Bull. Soc. Chim.* xxxi. 156.

[6] Vincent and Delachanal, *Bull. Soc. Chim.* xxxiii. 405.

ignited, the nitril burns with a bright red-mantled flame. It is miscible with water, and when heated with caustic potash acetic acid is formed (Dumas). When its solution in absolute alcohol is treated with hydrochloric acid or sulphuric acid it forms ethyl nitrate.[1] When mixed with an equal number of molecules of dry hydrobromic or hydriodic acids, it forms crystalline compounds which have not been fully investigated.[2] Heated with bromine to 100°, it forms the compound $C_2H_3NBr_2$, a slightly yellow crystalline mass, which fumes on exposure to air, melts when gently heated at 65°, and sublimes in apparently rhombic prisms. When silver nitrate is added to its alcoholic solution, only half of the bromine is precipitated, and hence it is probably bromacetonitril hydrobromide, $CH_2BrCN.HBr$.[3]

Phosphorus pentoxide dissolves readily in acetonitril; and if this liquid be distilled at first, a portion of the acetonitril passes over, and afterwards a gelatinous residue remains behind, resembling silicic acid. This is a compound of phosphorus pentoxide with acetonitril, and decomposes into its constituents when more strongly heated (Vincent and Delachanal).

When acetamide is distilled with phosphorus pentachloride, and the distillate rectified, that portion being collected by itself which boils at 72°, a colourless thin liquid is obtained, having the composition $C_2H_3NPCl_3$. This has a strong smell, and attacks the eyes and mucous membrane. It sinks, when poured into water, and decomposes after a short time into phosphorous acid, hydrochloric acid, and acetamide.

When heated with an equal number of molecules of titanium tetrachloride, tin tetrachloride, or antimony pentachloride, acetonitril combines directly to form white crystalline compounds capable of being sublimed, and of being decomposed by water.[4]

Cyanmethine, $C_6H_9N_3$, is formed by the action of sodium on acetonitril, when at first a violent action takes place, but the action must be stimulated afterwards by warming on a water-bath. In this reaction marsh gas is evolved, together with other products (see Cyanethine).

The cyanmethine or trimethyl cyanuride thus obtained is

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[1] Backuntz and Otto, *Ber. Deutsch. Chem. Ges.* ix. 1590.
[2] Gautier, *Ann. Chem. Pharm.* cxlii. 289.
[3] Engler, *Ann. Chem. Pharm.* cxxix. 124 ; cxxxiii. 137 ; cxlii. 65.
[4] Henke, *Ann. Chem. Pharm.* cvi. 272.

soluble in water, difficultly soluble in alcohol, and crystallizes in monoclinic prisms which melt at 180°—181°, and sublime in white needles. It has a bitter taste, like quinine, and its vapour has an irritating smell. Cyanmethine is a monacid base. Its salts, as a rule, crystallize well, and, like many organic bases, it combines with iodine in alcoholic solution, when crystals are formed of the composition $C_6H_9N_3I_2$. These appear red by reflected and yellow by transmitted light. When exposed to the air, or on heating with water, they give up iodine. The hydriodide also unites with iodine to form the compound $C_6H_9N_3.HI.I_2$, forming crystals which are violet by reflected and orange-yellow by transmitted light. This compound can take up another molecule of iodine, when dark-blue prisms are formed; but this body owing to its extreme unstability has not yet been obtained in the pure state.[1]

340 *Fulminic Acid* or *Nitro-acetonitril*, $CH_2(NO_2)CN$.—In the Philosophical Transactions for the year 1800,[2] Howard states that he had found that when mercury is heated with nitric acid and alcohol an explosive compound is formed. This compound was afterwards known as Howard's fulminating mercury. The same chemist then proved that a similar compound was formed in the case of silver, as indeed Brugnaletti[3] had also shown. Howard[4] believed that fulminating mercury was a compound of nitrous ether (or, as he termed it, "nitrous etherized gas") and oxalate of mercury, with an excess of oxygen. Brugnaletti, on the other hand, considered the explosive body to be oxalate of silver. Again, at a later date, it was believed to be a double salt of oxalate of ammonia and the oxalate of mercury or silver. This view of the composition of these explosive bodies was held until 1822, when Liebig, in his first research, showed that they are the salts of a peculiar acid to which he gave the name of *fulminic acid*, and the composition of which he sought to determine.[5] This was definitely ascertained in a research which he made in 1824 in association with Gay-Lussac,[6] in which it was shown that fulminic acid possesses the same composition as cyanic acid. As, however, at this period, the existence of isomeric bodies had not been proved, it was not deemed possible that bodies possessing properties so totally different could have an

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[1] Bayer, *Ber. Deutsch. Chem. Ges.* ii. 319; iv. 176

[2] Part i. p. 204.

[3] *Ann. de Chim.* xxvii. (1798), p. 331.

[4] *Phil. Trans.* 1800, p. 222.

[5] *Ann. de Chim.* xxiv. 294 (1823).

[6] *Ib.* xxv. 285 (1824). Compare also Liebig, *Ann. Chem. Pharm.* l. 429.

identical composition. Liebig, therefore, in 1825 suggested that perhaps cyanic acid contains somewhat less oxygen than fulminic; but this was disproved by Wöhler in the same year. Shortly afterwards Liebig ascertained beyond doubt that fulminate and cyanate of silver have the same composition.

Respecting the constitution of the first of these acids, a variety of views were put forward. That it contained cyanogen was shown by the fact that, in a variety of decompositions, its salts yield hydrocyanic acid. Laurent and Gerhardt were the first to propose the view that it is a nitro-compound, and they considered it as a secondary nucleus derived from the primary nucleus, C_2H_4, namely, $C_2N(NO_2)H_2$. The investigations of Schischkoff[1] and Kekulé[2] then proved that fulminic acid, which is not known in the pure state, must be regarded as nitro-acetonitril. Being a nitro-compound, it possesses acid properties, and forms salts, all of which are highly explosive. Of these fulminate of mercury is prepared on the large scale.

Silver Fulminate, $C_2(NO_2)NAg_2$.—In order to prepare fulminating silver the following process is recommended by Liebig and Gay-Lussac. One part of silver is dissolved in 20 parts of nitric acid of specific gravity 1·36, and 27 parts of 86 per cent. spirit of wine added, and the whole gently heated until it froths up. The liquid is then removed, and 27 parts or more of spirit of the same strength added, in order to reduce the violence of the reaction. Fulminating silver separates out on cooling, the weight of which is equal to that of the metal employed. The reaction is represented by the following equation :

$$CH_3.CH_2.OH + 2\,AgNO_3 + N_2O_3 = CN.CAg_2(NO_2) + 2\,HNO_3 + 2\,H_2O.$$

The nitrogen trioxide required for this reaction is obtained by the action of the nitric acid on the alcohol. That the above correctly represents the reaction was proved by Liebig, inasmuch as he showed that it is also obtained when nitrogen trioxide is passed into an alcoholic solution of silver nitrate.[3] Silver fulminate crystallizes in white opaque glistening needles, having a bitter metallic taste, and being scarcely soluble in water. It has been shown that, given in certain doses, it produces violent convulsions (Pagot-la-Forêt), while in doses of 0·3 gram it acts as a narcotic (Ittner).

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[1] *Ann. Chem. Pharm.* ci. 213 ; Suppl. i. 104.
[2] *Ib.* ci. 200 ; cv. 279.
[3] *Ann. Pharm.* v. 287.

Fulminating silver is an extremely dangerous body, as it explodes most violently on percussion or on heating, emitting a blue-reddish-white flame (Liebig). It is therefore necessary that the greatest care be taken in its preparation. Large vessels must be employed, in order that none of the liquid may froth over and afterwards dry up and the dry mass explode. The vapours which are evolved must not come in contact with any flame; and when the liquid is stirred, a wooden stirrer, and not a glass one, must be made use of. It even explodes in the moist state, but not so readily as when dry. Hence it must be taken up only with paper, and kept in vessels of paper or cardboard, and not placed in a glass bottle, where the friction of the stopper might cause explosion. If fulminate of silver be thrown into a bottle containing chlorine, it deflagrates before it touches the bottom, and does not crack the vessel (E. Davy). When ignited under a diminished pressure amounting to 2 to 3 mm. by means of a platinum wire heated by an electric current, it burns slowly with a visible flame. It dissolves in hot aqueous ammonia, and on cooling white crystalline grains separate out of *ammonium silver fulminate*, $C_2(NO_2)NAg(NH_4)$. This explodes more violently than silver fulminate, and deflagrates even under a liquid when it is touched with a glass rod. If fulminate of silver be heated with water to the boiling point, and potassium chloride added as long as an opalescence is produced, *potassium silver fulminate*, $C_2(NO_2)NAgK$, is formed, and this, on evaporating the solution, is deposited in long, white, glistening tablets, which are also very explosive. Similar double salts are also formed with the chlorides of the other metals of the alkalis and alkaline earths. When nitric acid, not in excess, is added to a solution of the potassium salt, *hydrogen silver fulminate*, $C_2(NO_2)NAgH$, is thrown down as a white powder, which can be obtained in crystals from hot aqueous solution and has an acid reaction. If this be boiled with mercuric oxide and water, a double salt of the fulminates of mercury and silver is obtained (Liebig).

341 *Mercury Fulminate*, $C_2(NO_2)NHg$.—Various methods have been published for the preparation of this compound. According to Liebig it is best prepared on the small scale as follows. Three parts of mercury are dissolved in 36 parts of nitric acid of specific gravity 1·34, without warming. After complete solution the liquid is poured into a glass flask which is capable of containing 18 times the quantity, and containing 17 parts

of alcohol of from 90 to 92 volumes per cent. The liquids are then well mixed and again poured into the first vessel, which is of the same size, shaken in order that the nitrous fumes shall be absorbed, and the whole then allowed to stand. After a few minutes, bubbles are seen to be evolved, and a highly refracting liquid is seen to separate out on the bottom of the flask, and the whole is then well shaken up so as to mix this with the rest. The liquid then becomes black, with separation of metallic mercury, and a very violent reaction takes place, which is moderated by the gradual addition of 17 parts of alcohol. Thin crystals of mercuric fulminate separate out on cooling.

On the large scale it is best prepared by dissolving 1 part of mercury in 10 parts of nitric acid of specific gravity 1·33, and to every kilogram of the acid 1 liter of alcohol of specific gravity 0·833 is added. The reaction generally begins spontaneously, but sometimes it has to be induced by slight warming. The operation is carried on either in a tubulated retort, in which case the gases evolved, consisting of nitrous fumes, hydrocyanic acid, &c., are led into a flue, or large glass balloons are employed, and the decomposition carried on in these in an open wooden shed. The reaction is left to itself as soon as the alcohol has been added, and the operator does not again approach the shed until the operation is complete.

Fulminating mercury forms white or often grey-coloured prisms, which are anhydrous and have a specific gravity of 4·42. It is insoluble in cold water, and crystallizes from hot water in silky needles which have the composition $2C_2(NO_2)NHg + H_2O$ (Schischkoff) and have a sweet metallic taste. Warm aqueous ammonia at 30°—35° dissolves about four times its weight of mercuric fulminate, and on cooling large finely developed prisms separate out (Steiner).

Mercuric fulminate explodes violently on percussion, but when ignited with a flame it only burns quickly like gunpowder, and with a reddish flame, the following decomposition taking place:

$$CHg(NO_2)CN = 2\,CO + N_2 + Hg.$$

In the moist state it can be handled without danger, and when heated to 100° it does not explode if the crystals do not contain any inclosed mother-liquor. If this be the case, however, they decrepitate on heating, and the flame thus produced may cause violent explosions to take place below 100°. Hennell, whose name has formerly been mentioned, and who was chemical operator to the Apothecaries' Company in London, was killed in 1842 when conducting experiments on filling hand-grenades with fulminating mercury to be used in the first Afghan war. The effects of the explosion of this compound are, however, only felt at a short distance from the point of explosion. Thus, the substance may be detonated by heat in a glass tube from 2 to 3 cm. in width without the tube being broken, the metallic mercury which is formed condensing on the cold parts of the tube.[1] The pressure exerted by the gases which are evolved by the decomposition of fulminating mercury is less than that caused by the explosion of an equal weight of gun-cotton, the much greater action of the former detonating agent being accounted for by the density of the compound, and by the fact that the decomposition occurs in an infinitely short space of time. For this reason, the gases evolved, at the first moment are actually compressed into the volume of the solid compound, and a pressure of no less than 48,000 atmospheres is exerted on a solid surface exposed to the detonating agent. Berthelot and Vieille have recently exploded fulminating mercury in a steel bombshell of such dimensions that the final pressure did not rise above fifty atmospheres, and yet a distinct impression of the solid salt was made in the steel where the detonator was placed. Fulminating mercury was formerly solely used for the preparation of percussion caps, and it is still used for this purpose; but it is now employed on a much more extensive scale for the manufacture of the detonators used for exploding gun-cotton, dynamite and other nitro-glycerin preparations.

Mercuric fulminate readily forms soluble double salts with potassium cyanide, potassium thiocyanate, and ammonium thiocyanate (Steiner).

Other metallic fulminates can easily be obtained from mercuric fulminate.

Zinc Fulminate, $C_2(NO_2)NZn$.—A solution of this salt is obtained by leaving zinc and water in contact with mercuric fulminate. On allowing the solution to evaporate spontaneously clear rhombic tables of the above salt are obtained, and these are very explosive. If baryta water be added to the freshly-prepared solution until no further precipitation takes place, and the baryta contained in solution be precipitated by means of carbon dioxide

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[1] Silliman, *Amer. Journ.* (1819), i. 169.

and the solution evaporated, bright four-sided prisms separate out from the syrupy residue, consisting of a double salt of barium fulminate and zinc fulminate. If this be decomposed with the exactly necessary quantity of sulphuric acid, a liquid is obtained which has a smell resembling hydrocyanic acid, and a taste which is at first sweet and afterwards pungent and astringent. This dissolves various bases, giving rise to double salts containing zinc, which were investigated by E. Davy,[1] and looked upon by him as pure fulminates. This, however, was shown by Fehling[2] to be erroneous. These are chiefly soluble in water, possess a sweetish taste, precipitate a silver solution, and are explosive.

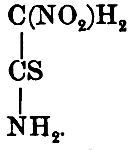
Copper Fulminate, $C_2(NO_2)NCu$, is obtained by boiling copper with water and mercuric fulminate. It forms green crystals, difficultly soluble in water, which when heated explode violently.

342 *Decompositions of the Fulminates.* If a fulminate be distilled with bleaching powder and water, chloropicrin is formed, and this is also produced, together with cyanogen chloride, by the action of chlorine:

$$CHg_2(NO_2)CN + 3\,Cl_2 = CCl_3NO_2 + CNCl + Hg_2Cl_2.$$

Bromine acts in a similar way, but at the same time *dibrom-nitro-acetonitril*, $C_2(NO_2)NBr_2$, is formed. This is insoluble in water, and separates out from ether and alcohol in large well-formed crystals, which smell like chloropicrin, melt at 50°, and begin to decompose above 130°, but may be distilled in a current of steam. If iodine be added to mercuric fulminate in the presence of ether, *di-iodo-nitro-acetonitril*, $C_2(NO_2)NI_2$, is formed. This separates out in large monoclinic prisms on evaporating the solution, which melt at 86° with decomposition.[3]

By the action of sulphuretted hydrogen on the fulminates, ammonium thiocyanate and carbon dioxide are produced, together with a metallic sulphide. According to Steiner,[4] a very unstable intermediate product is obtained, having the composition $C_2H_4N_2O_2S$, produced by the combination of sulphuretted hydrogen with nitro-acetonitril, and possessing the following constitution:



$$\begin{array}{c} C(NO_2)H_2 \\ | \\ CS \\ | \\ NH_2. \end{array}$$

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[1] *Trans. Dubl. Soc.* 1829; *Berzelius, Jahresb.* xii. 95 and 120.

[2] *Ann. Pharm.* xxvii. 130.

[3] Sell and Biedermann, *Ber. Deutsch. Chem. Ges.* v. 89.

[4] *Ber. Deutsch. Chem. Ges.* viii. 1177; ix. 779.

In order to obtain this in the pure state, ether is poured on to mercuric fulminate, and sulphuretted hydrogen led into the mixture, which is kept well cooled. On allowing the ether slowly to evaporate spontaneously, the above compound separates out in microscopic crystals. If it is gently warmed with water it is decomposed into the above products, and when quickly warmed sulphur separates out. The body undergoes the same decomposition at the temperature of summer in a few hours. By the further action of sulphuretted hydrogen on the ethereal solution, ammonium thiocyanate, oxalic acid, and free sulphur are obtained.

If mercuric fulminate be heated with aqueous ammonia, urea and guanidine are formed, together with other substances (Steiner). Gladstone also obtained urea, together with ammonium thiocyanate, by acting with sulphuretted hydrogen on a solution of copper fulminate in an excess of ammonia.[1]

FULMINURIC ACID, OR ISOCYANURIC ACID, $C_3H_3N_3O_3$.

343 This compound was obtained almost simultaneously by Liebig[2] and by Schischkoff.[3] It is formed by boiling a soluble metallic chloride or iodide with water and mercuric fulminate:

$$2\,C_2(NO_2)NH_2 + H_2O = C_3(NO_2)H_3N_2O + CO_2 + NH_3.$$

It is also produced, together with ammonium thiocyanate, by acting on an aqueous solution of barium sulphide with mercuric fulminate (Kekulé), as well as when the same is warmed with alcoholic solution of ammonia, when the basic mercuric salt is formed (Steiner). In order to prepare the acid, from 60 to 75 grams of well-washed mercuric fulminate are boiled with 700 to 800 cc. of water and 60 cc. of a saturated solution of sal-ammoniac until the yellow crystalline precipitate of oxy-di-mercuric ammonium chloride, NH_2Hg_2OCl, separates out. The flame is then removed, and ammonia added to the solution in order to precipitate the mercury as mercury ammonium chloride. On evaporating the filtrate impure ammonium fulminurate is obtained, which can be purified by recrystallization.

On precipitating with acetate of lead the insoluble basic lead fulminurate is obtained, and this is then decomposed by sulphuretted hydrogen. Instead of the lead salt, the difficultly soluble silver fulminurate may also be employed, and this may be obtained from the potassium salt, whose preparation is described below.

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[1] *Journ. Chem. Soc.* i. 228 (1849).

[2] *Ann. Chem. Pharm.* xcv. 282.

[3] *Ann. Chem. Pharm.* xcvii. 53; ci. 213; Suppl. i. 101.

On evaporating the aqueous solution of fulminuric acid, a syrupy liquid is obtained, which, when placed in a warm situation, solidifies to an indistinctly crystalline mass, crystallizing from alcohol in small colourless prisms. It has an acid taste and reaction, and decomposes on heating with slight deflagration.

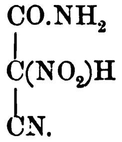
Potassium Fulminurate, $C_3H_2KN_3O_3$. In order to prepare this salt two parts of mercuric fulminate are gradually added to a saturated solution of one part of potassium chloride, and the mixture boiled gently until the whole is dissolved. It is then filtered through a warmed filter, and on cooling deposits a curdy precipitate consisting of a compound of the potassium salt with mercuric oxide, and this may be decomposed by sulphuretted hydrogen. Potassium fulminurate crystallizes from solution in hot water in colourless, long, glistening, highly refracting prisms, which decompose with incandescence when heated to 225°.

Ammonium Fulminurate, $C_3H_2(NH_4)N_3O_3$, forms fine, shining, white, highly refracting needles, melting and blackening at 150°, and evolving hydrocyanic acid, cyanic acid, and ammonia, which latter partially unite to form urea.

Cuprammonium Fulminurate, $C_6H_4Cu(NH_3)_4N_6O_6$. When an ammoniacal solution of copper sulphate is heated with fulminuric acid to the boiling-point, and the solution allowed to cool, the above salt separates out in splendid, glistening, dark-blue, very characteristic prisms. It is scarcely soluble in water, and slightly soluble in ammonia, permanent in the air, and decomposes at 150° with detonation.

Silver Fulminurate, $C_3H_2AgN_3O_3$, separates out in long, thin, silky needles when hot solutions of the ammonium salt and silver nitrate are mixed and allowed to cool.

The constitution of fulminuric acid is not known with certainty. From the reactions which follow it appears probably to be



$$\begin{array}{l} CO.NH_2 \\ | \\ C(NO_2)H \\ | \\ CN. \end{array}$$

Trinitroacetonitril, $C(NO_2)_3CN$, is formed when a fulminurate is gradually added in small quantities to a well-cooled mixture of concentrated sulphuric acid and nitric acid:

$$CN.C(NO_2)H.CO.NH_2 + 2\,NO_3H = CN.C(NO_2)_3 + CO_2 + NH_3 + H_2O.$$

It is a white crystalline substance, closely resembling camphor, melting at 41°·5, and decomposing with explosion when heated to 220°, but may be volatilized in a current of air at 60°. It is decomposed by water, especially quickly on warming, into carbon dioxide, ammonia, and nitroform (see p. 263).

Dinitroacetonitril, $C(NO_2)_2H.CN$. The ammonium compound of this body is formed when sulphuretted hydrogen is passed into an ethereal solution of the foregoing compound:

$$CN.C(NO_2)_3 + 4\,H_2S = CN.C(NO_2)_2NH_4 + 2\,H_2O + 2\,S_2.$$

It crystallizes from water in colourless glistening needles, which, when gently heated, have a strong smell, and on quick heating decompose. If sulphuric acid be added to the aqueous solution and the whole shaken up with ether, a syrupy liquid is left on evaporation, from which dinitroacetonitril separates out in transparent tables. This forms several crystalline salts, of which the silver compound, $CN.C(NO_2)_2Ag$, is as explosive as fulminating silver.

Concentrated sulphuric acid acts upon ammonium fulminurate violently; carbon dioxide is evolved, and with it a powerfully smelling body which attacks the eyes and mucous membrane, and may be condensed to an oily liquid and solidified to crystals. This compound is easily inflammable, and burns with a light almost equal to that of magnesium wire. Steiner[1] considers that this is nitro-acetonitril, but he could not fix its composition in consequence of not obtaining a sufficient amount of substance.

If the action of sulphuric acid be moderated by cooling and mixing, a compound isomeric or polymeric with fulminic acid is obtained according to the equation:

$$C_3H_3N_3O_3 + H_2O = C_2H_2N_2O_2 + NH_3 + CO_2.$$

This is insoluble in cold water, and separates out from boiling water in crystals. It has an acid reaction, deflagrates on heating, and is not altered even by concentrated nitric acid. From its aqueous solution, mercuric nitrate throws down a white amorphous precipitate of $(C_2HN_2O_2)_2Hg$, which also decomposes with deflagration when heated.

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[1] *Ber. Deutsch. Chem. Ges.* ix. 782.

SUBSTITUTION PRODUCTS OF ACETIC ACID.

344 The three atoms of hydrogen of the methyl in acetic acid can be replaced one by one by different elements or radicals. The mono-substitution products contain the dyad radical *glycolyl*, $-CH_2-CO-$, and these compounds will therefore be described at a later period, only those being now mentioned which contain the halogens, as these latter are closely connected with the di- and tri-substitution products, and these cannot so readily be genetically connected with any other groups.

CHLORINE SUBSTITUTION PRODUCTS.

Monochloracetaldehyde, C_2H_3ClO, is obtained by the action of sulphuric acid on chlor-acetal, $C_2H_3Cl(OC_2H_5)_2$, and also by treating chlor-ethylene, C_2H_3Cl, with hypochlorous acid in the presence of mercuric oxide.[1] The same compound is contained in the products of the reaction of phosphorus trichloride on dichlor-ether.[2] It is a powerfully smelling liquid, which has not yet been obtained in the pure state, and easily oxidizes on exposure to air with formation of chloracetic acid.

MONOCHLORACETIC ACID, $C_2H_3ClO_2$,

Was first prepared in 1844 by Leblanc,[3] by acting with chlorine on acetic acid, but not in the pure state, whereas, by passing chlorine on to the surface of heated glacial acetic acid which was exposed to the action of sunlight, R. Hoffmann[4] succeeded in preparing it in the pure condition. For the preparation of this substance on the large scale, the process suggested by Hugo Müller[5] is the best. For this purpose 500 cc. of acetic acid of 95 per cent. are mixed with about 50 grams of iodine in a large flask having a long wide tube attached to its neck, and then the whole heated to the boiling point, whilst a steady current of dry chlorine is passed into the liquid. The hydrochloric acid which is evolved, passes away through a side-tube

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[1] Saytzeff and Glinsky, *Zeitsch. Chem.* 1867, 675; 1868, 617.

[2] Abeljanz, *Ber. Deutsch. Chem. Ges.*

[3] *Ann. Chim. Phys.* [3], x. 212.

[4] *Ann. Chem. Pharm.* cii 1.

[5] *Journ. Chem. Soc.* xvii. 398.

whilst the vapours condense and flow back through the long neck of the retort. A violent reaction begins as soon as iodine trichloride is formed. The mixture is well heated for some time to the boiling-point, even after the chlorine has been passed in for some days, until vapours of free iodine make their appearance, due to the decomposition of some iodacetic acid which is formed. Then the product is submitted to fractional distillation, and the portion which passes over below 180° is again treated with chlorine, whilst the portion between 180° and 188° solidifies on cooling, and can be purified by recrystallization and rectification.

Pure monochloracetic acid is also easily obtained by acting upon acetic anhydride, placed in a water-bath, with chlorine:

$$\left.\begin{matrix} C_2H_3O \\ C_2H_3O \end{matrix}\right\} O + Cl_2 = C_2H_3ClO_2 + C_2H_3ClO.$$

Acetyl chloride then distils off, and the residue consists of chloracetic acid, which may be purified in the way already described.[1]

Monochloracetic acid solidifies, on slow cooling, in long needles, and crystallizes from glacial acetic acid in large transparent rhombic tables. When carefully heated it sublimes in pointed needles, which melt at 62°, and boil between 185° and 187°, yielding a vapour which at 203° has a specific gravity of 3·81, and this density diminishes as the temperature rises; at 270° it is 3·283, whilst according to theory the number is 3·263 (Cahours). The specific gravity of the fused acid is 1·3947 at 73° compared with water at the same temperature. It deliquesces in the air, has a slight smell when cold, which on heating becomes stronger and more pungent. When brought on to the skin it produces blisters and destroys the epidermis. Hence it is frequently used for the cure of warts and corns. When a tolerably concentrated aqueous solution is boiled, hydrochloric acid and oxyacetic acid or glycollic acid, $C_2H_3(OH)O_2$, are formed. Its salts decompose in a similar way on heating with water. Most of them are easily soluble and crystallizable.

Potassium Monochloracetate, $2C_2H_2ClO_2K + 3H_2O$, crystallizes on evaporation in a vacuum over sulphuric acid in non-deliquescent tablets, which decompose easily on heating. It combines with chloracetic acid to form a difficultly soluble salt, having

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[1] Gal, *Ann. Chim. Phys.* [3], lxvi. 187.

the composition $C_2H_2ClO_2K + C_2H_3ClO_2$, which crystallizes in pearly scales.

Barium Monochloracetate, $(C_2H_2ClO_2)_2Ba + 2H_2O$, crystallizes from hot saturated solution in small rhombic prisms.

Silver Monochloracetate, $C_2H_2ClO_2Ag$, is difficultly soluble in cold water, and forms pearly glistening scales which easily blacken on exposure to light, and deflagrate when heated from 110° to 120.°

Ethyl Monochloracetate, $C_2H_2ClO_2C_2H_5$, was first prepared by Willm[1] by the action of chloracetyl chloride on alcohol. It is also formed by passing hydrochloric acid into a mixture of chloracetic acid and alcohol.[2] In order to prepare this ether, the solution thus saturated is distilled until the residue divides into two layers. The upper one is poured off, washed with water, and then dried over calcium chloride, and the pure ether is separated by fractional distillation.[3] It is also obtained easily by distilling a mixture of sulphuric acid, chloracetic acid, and alcohol.

Ethyl monochloracetate is a colourless liquid, heavier than water, possessing a burning taste and an ethereal smell. It boils at 143°·5, and its vapour, which has a density of 4·46 (Willm), attacks the eyes.

Monochloracetyl Chloride, $\left.\begin{matrix}C_2H_2ClO\\ Cl\end{matrix}\right\}$, was first prepared by Wurtz[4] by the action of chlorine on acetyl chloride. It is easily formed when iodine is also added,[5] and is likewise produced by the action of phosphorus trichloride on ammoniacal acetic acid.[6] It is a liquid which boils at 110°, possesses a strong smell, fumes in the air, and acts in a similar way upon water and alcohol as acetyl chloride does.

Monochloracetyl Bromide, $\left.\begin{matrix}C_2H_2ClO\\ Br\end{matrix}\right\}$, is formed by the action of bromine on a mixture of chloracetic acid and amorphous phosphorus. It is a liquid boiling at 127°, the vapour of which acts powerfully upon the eyes (Gal, De Wilde).

Monochloracetamide, $C_2H_2ClONH_2$, is obtained by the action of ammonia on the corresponding chloride or on the ethyl

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[1] *Ann. Chim. Phys.* [3], xlix. 97.

[2] Heintz, *Pogg. Ann.* cxiv. 440.

[3] Menschutkin and Jermokajew, *Zeitsch. Chem.* 1871, 5.

[4] *Ann. Chim. Phys.* [3], xlix. 58.

[5] Jazukowitsch, *Zeitsch. Chem.* 1868, 234.

[6] De Wilde, *Ann. Chem. Pharm.* cxxx. 372; Gal, *ib.* cxxxii. 177; *Bull. Soc. Chem.* [2], i. 428.

compound ether (Willm). It crystallizes from aqueous solution in prisms, and from alcohol in glistening tablets. It melts at 119°·5, and sublimes at a higher temperature. When distilled with phosphorus pentoxide, *chloracetonitril*, C_2H_2ClN, is formed, a liquid which boils at 115°—120°.[1]

Monochloracetyl Phosphamide, $C_2H_2ClOPH_2$, is formed by the action of phosphuretted hydrogen on the chloride as a yellowish powder, which on exposure to moist air decomposes into chloracetic acid and phosphuretted hydrogen.[2]

Dichloracetic Acid, $C_2H_2Cl_2O_2$,

345 Was obtained by Müller as a by-product in the preparation of monochloracetic acid, and by Maumené[3] by exposing the latter substance in a large balloon to the action of dry chlorine in the light. The formation of this compound from chloral or trichloracetic acid, first observed by Maumené, is of much interest. He obtained it from this body by the action of silver oxide.[4] Wallach[5] then showed that the compound ethyl-ether is obtained by the action of chloral upon an alcoholic solution of potassium cyanide whilst the aqueous solution of the latter salt, as also of potassium ferrocyanide, gives rise to the free acid or to potassium dichloracetate.[6] This peculiar reaction is represented by the following equation:

$$CCl_3.COH + KCN + H_2O = CHCl_2.CO.OH + HCN + KCl.$$

It is thus seen that an atom of chlorine is removed by the potassium, the cyanogen combining with one atom of the hydrogen of the water, whilst the second replaces the atom of chlorine, and the oxygen converts the aldehyde into the acid.

In order to prepare dichloracetic acid it is best to start from dichloracetic ether,[7] for the preparation of which pure potassium cyanide must be employed if a good yield be desired,[8] and care must be taken to work in a good draught owing to the rapid evolution of torrents of hydrocyanic acid. The ether is diluted with its equal volume of alcohol, and to this the calculated quantity of alcoholic potash is added, when the

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[1] Engler, *Ann. Chem. Pharm.* cxlix. 297.

[2] Steiner, *Ber. Deutsch. Chem. Ges.* viii. 1178.

[3] *Compt. Rend.* lix. 84.

[4] *Compt. Rend.* lxi. 953.

[5] *Ber. Deutsch. Chem. Ges.* vi. 114; *Ann. Chem. Pharm.* clxxiii. 293.

[6] *Ber. Deutsch. Chem. Ges.* x. 1525.

[7] *Ber. Deutsch. Chem. Ges.* ix. 1212.

[8] *Ib.* x. 477.

liquid is converted, with evolution of heat, into a thick pasty mass, consisting of glistening scales of potassium dichloracetate. These are then washed with alcohol and dried. The salt is next brought into a tube lying in a slanting position in a combustion furnace, and dry hydrochloric acid led over it until the gas escapes at the other end, when the dichloracetic acid is distilled off in a current of hydrochloric acid. It is a liquid which boils at 189°—191°, crystallizes at 0°, and at 15° has a specific gravity of 1·5216. It is very caustic, and on heating evolves suffocating vapours. The salts are chiefly easily soluble.

Ethyl Dichloracetate, $C_2HCl_2O_2C_2H_5$, is a liquid boiling at 156°—157°, and having a specific gravity at 22° of 1·29. By the action of ammonia it yields *dichloracetamide*, $C_2HCl_2O_2NH$, crystallizing in large rhombic prisms melting at 94°·5, and beginning to sublime at 100°, and being volatile in a current of steam.

TRICHLORACETALDEHYDE, OR CHLORAL, C_2HCl_3O,

346 Was discovered in 1832 by Liebig, who obtained it by the action of chlorine upon alcohol,[1] its true composition being first recognized by Dumas in 1834.[2] It is formed when nascent chlorine is brought in contact with sugar or starch.[3] Although it is a trichlorinated aldehyde, it is not formed when chlorine is passed into aldehyde, as condensation-products are then formed, as, for instance, trichlorbutyl aldehyde. If, however, water and calcium carbonate be added, the hydrochloric acid is neutralized, and the trichlorinated product is then formed.[4] The view entertained by Liebig and by Regnault,[5] that aldehyde is first formed by the action of chlorine upon alcohol, and this afterwards converted into chloral by substitution, would thus appear to be untenable, and a more satisfactory explanation of its formation had to be found. This was at last given by Lieben,[6] as follows:

Aldehyde is first formed:

$$CH_3.CH_2OH + Cl_2 = CH_3.COH + 2\,HCl.$$

The nascent aldehyde acts upon the alcohol with formation of ethidene diethyl ether or acetal:

$$CH_3COH + 2\,HO.C_2H_5 = CH_3.CH(OC_2H_5)_2 + H_2O.$$

[1] *Ann. Pharm.* i. 189.

[2] *Ann. Chim. Phys.* lvi. 123.

[3] Städler, *Ann. Pharm.* lxi. 101.

[4] Pinner, *Ber. Deutsch. Chem. Ges.* iv. 256.

[5] *Ann. Chim. Phys.* [2], lxxi. 420.

[6] *Ber. Deutsch. Chem. Ges.* iii. 76, 390.

The acetal is converted into trichloracetal, and this is converted by the hydrochloric acid into ethyl chloride and the so-called chloral alcoholate:

$$CCl_3.CH\left\{\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix}\right. + HCl = CCl_3.CH\left\{\begin{matrix}OH\\OC_2H_5\end{matrix}\right. + C_2H_5Cl.$$

From the solid mass thus obtained the chloral is liberated by the action of sulphuric acid:

$$CCl_3.CH\left\{\begin{matrix}OH\\OC_2H_5\end{matrix}\right. + H_2SO_4 = CCl_3.CHO + C_2H_5HSO_4 + H_2O.$$

The chloral is then purified by distillation over quicklime. It is a colourless mobile liquid, which boils at 99°·6, and has, at 0°, a specific gravity of 1·5183 (Kopp), and a vapour density of 5·13 (Dumas). When cooled in a mixture of solid carbonic acid and ether, it solidifies to a mass which melts at — 75°.[1] It has a peculiar sweet and pungent smell, and a bitter, biting taste, and acts, especially in the form of vapour, destructively on the skin. Nascent hydrogen reduces it to aldehyde. Like this latter compound, it combines with the acid sulphites of the alkali-metals to form crystalline compounds, and it also unites with ammonia to form a body which reduces silver from its solution in the form of a mirror. When heated with alkalis it decomposes into chloroform and formic acid:

$$CCl_3.CHO + H_2O = CCl_3H + CH_2O_2.$$

Chemically pure chloral may be kept for any length of time without undergoing change; but if it contains impurities, it undergoes polymerization, and this takes place especially quickly in presence of sulphuric acid. It is thus converted into *metachloral* or *insoluble chloral*, a white amorphous body, insoluble in water, alcohol, or ether. If heated to 180°—250°, or with sulphuric acid, this yields ordinary chloral. Small quantities of anhydrous trimethylamine convert chloral violently into a perfectly white mass, from which, however, the base can again be driven off in a current of air. This body appears to be a mixture partly of soluble and partly of insoluble polychlorals. If treated with alcoholic ether, chloral alcoholate is obtained.[2] Concentrated sulphuric acid converts chloral into *chloraldid*, $C_5HCl_6O_3$, a substance which will be hereafter described (see Trichlorlactic Acid).

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[1] Berthelot, *Bull. Soc. Chim.* xxix. 3.

[2] Meyer and Dulk, *Ann. Chem. Pharm.* clxxi. 77.

CHLORAL HYDRATE, $C_2Cl_3HO+HO_2$ OR $CCl_3.CH(OH)_2$.

347 This is the most important compound of the group. It is formed by the direct union of water with chloral, and is prepared on the large scale as it is a most valuable medicine. For this purpose 25 kg. of absolute alcohol are placed in each of several large glass balloons, and treated with chlorine continuously for six to eight weeks. The vessels are surrounded by cold water, and this is gently heated with steam, so soon as the chlorine ceases to be absorbed, and then the temperature gradually allowed to rise to 60°. When the action is complete the alcoholate is allowed to remain in contact with sulphuric acid for several hours, at a temperature of 60°, and the chloral which separates out is rectified over calcium carbonate. It is then brought in contact with the requisite quantity of water, and the product purified by recrystallization. As a solvent, either chloroform or a mixture of ethylene chloride and ethidene chloride, obtained as a product in the manufacture of the chloral, is made use of.[1]

Chloral hydrate crystallizes in monoclinic prisms, which easily dissolve in water, alcohol, carbon disulphide, and liquid hydrocarbons, &c. It has a peculiar and, on warming, a somewhat pungent smell, a sharp taste, and a specific gravity of 1·8. It melts at 50°—51°, and boils at 97°·5. The specific gravity of its vapour is 2·83 (Naumann), from which it appears to be a mixture of the vapours of water and chloral, and these, on cooling, again unite together. This is also proved by the fact that it is possible, by help of a fractionating apparatus, partially to separate these constituents.[2] Concentrated sulphuric acid decomposes it into chloral and water, and the alkalis act upon it as upon chloral.

In the year 1869 Liebreich[3] discovered that, when taken internally, chloral hydrate produces sleep, and acts as an anæsthetic agent; and he introduced it with great success into medicine, so much so, that one manufactory in Berlin, which in 1869 prepared about 150 kg., in 1873 manufactured 13,000 kg., and a like increase is noticed in several other manufactories. The sleep produced by chloral is quiet, and

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[1] *Neu. Handwörterb.* ii. 597.

[2] Naumann, *Ber. Deutsch. Chem. Ges.* xii. 738.

[3] *Ib.* ii. 269; *Das Chloral Hydrate, ein neues Hypnoticum und Anästheticum.* Berlin, 1871.

is without any unpleasant symptoms. Liebreich was led from his experiments to conclude, from the ready conversion of chloral into chloroform by alkalis, that its physiological action depended on the formation of chloroform produced by the weak alkaline reaction of the blood. Other physiologists are of opinion that, in the passage of chloral hydrate through the body, chloroform is not produced, and that its action is to be ascribed to its own specific properties. The doses prescribed for sleeplessness amount to from 1·5 to 5·0 grams.

According to Liebreich, chloral hydrate is an antidote for strychnine, whilst the latter substance serves as an antidote for the former.[1]

Chloral hydrate, which is to be used in medicine, should give a clear solution in water, and, on addition of sulphuric acid, the chloral should separate without any brown colour. The aqueous solution should have a neutral reaction, and, on the addition of nitric acid and nitrate of silver, no opalescence should occur. For the purpose of determining the quantity present in the commercial product, according to the method of V. Meyer and Haffter,[2] a weighed quantity is brought into contact with an excess of a normal soda-solution, and the amount of formic acid produced is determined by titration with normal acid. If, to begin with, the chloral hydrate had an acid reaction, the aqueous solution must be shaken up with calcium carbonate before addition of standard soda.

Chloral not only combines with water, but also with sulphuretted hydrogen, alcohols, and various other bodies. The compounds thus formed must be regarded as containing the dyad radical trichlorethidene, and a description of these will be given hereafter.

TRICHLORACETIC ACID, $CHCl_3O_2$,

348 Was discovered by Dumas in 1838, who obtained it by the action of chlorine on acetic acid in presence of sunlight.[3] Malaguti then found that the substance believed by him to be chloraldehyde, C_2Cl_4O, when decomposed by water yields this same acid, from which reaction it is seen that the substance supposed to be the aldehyde is indeed the

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[1] *Ber. Deutsch. Chem. Ges.* ii. 673.

[2] *Ber. Deutsch. Chem. Ges.* vi. 600.

[3] *Comptes Rendus*, viii. 609; *Ann. Chem. Pharm.* xxxii. 101.

chloride of this acid.[1] Cloëz[2] obtained it by the action of water upon perchlorformic ethyl ether:

$$ClCO.O.CCl_2.CCl_3 + 2\,H_2O = HO.CO.CCl_3 + 3\,HCl + CO_2.$$

It has already been stated that Kolbe obtained it by synthesis. He also found that it might be obtained by treating solid chloral with nitric acid or other oxidizing agents.[3] Judson[4] showed that it may also be obtained from liquid chloral; but as chloral hydrate is a commercial article it is now always prepared from this substance, and many oxidizing agents are used for this purpose.[5] The simplest plan of preparation is to treat chloral hydrate with three times its volume of fuming nitric acid, and to place the whole mixture in the sunlight until the red fumes have disappeared; the liquid is distilled until the temperature reaches 190°, and the residue is then heated for some time to the boiling point.

If chloral be saturated with nitrogen trioxide and heated in a closed tube in the water-bath, trichloracetic acid is also formed, and is obtained in the pure state on opening the tube and allowing the gases which are formed to escape.[6]

Trichloracetic acid crystallizes in rhombohedral scales or needles, melts at 52°·3 (Clermont), boils at 195° (Judson, Clermont), and its vapour has a specific gravity of 5·3 (Dumas). It deliquesces in moist air, and on heating has a very pungent and suffocating odour. It destroys the epidermis, and produces blisters on the skin. It is not attacked by concentrated sulphuric acid even when warmed, but alkalis decompose it easily with formation of chloroform:

$$CCl_3.CO.OK + HOK + CCl_3H + CO\left\{\begin{matrix}OK\\OK.\end{matrix}\right.$$

An alcoholic solution of sodium alcoholate, containing caustic soda, decomposes it as follows:[7]

$$CCl_3.CO.ONa{+}5HONa{=}3NaCl{+}CO(ONa)H{+}CO(ONa)_2{+}2H_2O$$

It is a very strong acid, forming a series of salts which are very similar to the acetates, and have been especially examined by Clermont.

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[1] *Ann. Chim. Phys.* [3], xvi. 4; xxx.

[2] *Ib.* xvii. 297.

[3] *Ann. Chem. Pharm.* liv. 182.

[4] *Chem. Soc. Journ.* xxiv. 232.

[5] Clermont, *Compt. Rend.* lxxiii. 112; lxxiv. 1492; lxxvi. 774.

[6] Wallach, *Ber. Deutsch. Chem. Ges.* v. 256.

[7] Klien, *Jahresb.* 1876, 521.

Ammonium Trichloracetate, $C_2Cl_3O_2(NH_4)$, is deposited in fine prisms on the spontaneous evaporation of its neutral solution. These melt at 80°, and begin to give off ammonia and chloroform at 110°—150°, until at 160° the liquid solidifies to nacreous scales consisting of the anhydrous salt. At a higher temperature it decomposes into ammonium chloride, carbon monoxide, and carbonyl chloride (Malaguti). When distilled with phosphorus pentoxide it yields trichloracetonitril, C_2Cl_3N, a liquid boiling at 81°. The normal salt combines with one molecule of trichloracetic acid to form the so-called acid salt, which crystallizes in octohedrons unalterable in the air.

Potassium Trichloracetate, $C_2Cl_3O_2K$, is obtained by the action of potassium permanganate on chloral hydrate. It forms thin silky needles which deliquesce in moist air, and it also unites with one molecule of the acid to form an acid salt, which is likewise formed by the action of the permanganate on an excess of chloral hydrate. It crystallizes in transparent octohedrons which are not altered on exposure.

Ethyl Trichloracetate, $C_2Cl_3O_2(C_2H_5)$, is obtained by distilling the acid with alcohol and sulphuric acid, as well as by the action of trichloracetyl chloride on alcohol. Perchlorformic ether and perchloracetic ether and similar perchlorinated compounds react in an analogous way. Ethyl trichloracetate is an oily liquid, possessing a peppermint-like smell and a specific gravity of 1·367. It boils at 164°, yielding a vapour whose density is 6·64 (Leblanc).

Trichloracetic Anhydride, $(C_2Cl_3O)_2O$, is obtained by the action of an excess of phosphorus trichloride on trichloracetic acid. It is a liquid possessing a faint not unpleasant smell, boiling at 222°—224°, and rapidly absorbing moisture from the air and thus passing into trichloracetic acid.[1]

Trichloracetyl Chloride, C_2Cl_3OCl, was prepared by Malaguti in 1844 by heating perchlorethyl ether:

$$\left.\begin{array}{l} CCl_3.CCl_2 \\ CCl_3.CCl_2 \end{array}\right\} O = CCl_3.COCl + C_2Cl_6.$$

It also occurs in the preparation of the perchlorinated ethers, and, as has been stated, was first termed chloraldehyde. It is evident that this compound may also be obtained by the action of phosphorus trichloride on trichloracetic acid. It is a caustic,

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[1] Buckney and Thomsen, *Ber. Deutsch. Chem. Ges.* x. 698.

strongly smelling liquid, which fumes in the air, has a specific gravity at 18° of 1·608, boils at 118°, and has a vapour density of 6·32.

Trichloracetamide, $CCl_3.CO.NH_2$, was first prepared by Cloëz in 1845 by the action of ammonia on perchlorethyl formate. It is formed in a similar way from the other perchlorinated ethers. It forms white scales, and crystallizes from ether in flat prisms or six-sided prisms. It possesses a sweetish taste and aromatic smell, melts at 138°, and boils at 238°—240°. When heated with phosphorus pentoxide, trichloracetonitril is formed.

Trichloracetophosphamide, $C_2Cl_3O.PH_2$, is obtained by acting on phosphuretted hydrogen with the chloride, and forms colourless scales which have a slight garlic-like smell and a bitter taste. It is insoluble in water.[1]

BROMINE SUBSTITUTION PRODUCTS.

349 *Monobromacetic Acid*, $C_2H_3BrO_2$, was first prepared by Duppa and Perkin[2] by heating acetic acid with bromine to 120°—125°, and is also formed, together with acetyl bromide, when acetyl oxide is treated with bromine.[3] In order to prepare it, three parts of acetic acid are heated with four parts of bromine in a sealed tube for several hours to 120°, and at last from 150° to 160°, this being done to avoid a rapid evolution of hydrobromic acid, which would burst the tube. Air is then led through the tube in order to remove the greater quantity of the hydrobromic acid, and the residue is slowly distilled. The portion passing over between 200° and 210° is almost pure bromacetic acid, which can then be purified by rectification and crystallization. It forms glistening tablets which melt at 100°. The liquid boils at 208° with slight evolution of bromine vapour, and the crystals deliquesce rapidly in the air. When brought upon the skin it produces deep wounds, and on heating with water it decomposes like trichloracetic acid. The salts are usually crystalline, and mostly deliquescent.

Ethyl Monobromacetate, $C_2H_3BrO_2(C_2H_5)$, is obtained by distillation of equal parts of acid, alcohol, and sulphuric acid. It is a liquid which possesses a powerful smell, and boils at 159°. Ammonia decomposes it easily, with formation of ammonium

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[1] Cloëz, *Ann. Chim. Phys.* [3], xvii. 309.

[2] *Chem. Soc. Journ.* xi. 22 ; xii. 1.

[3] Gal, *Ann. Chim. Phys.* [3], lxvi. 187.

bromide; but at 0° it forms monobromacetamide, which may be purified by recrystallization from alcohol. It melts at 165°.[1]

Monobromacetyl Chloride, $CH_2Br.COCl$, is a colourless, slightly fuming, strongly smelling liquid, boiling at 127°, or at the same temperature as its isomeride chloracetylbromide.

Monobromacetyl Bromide, $CH_2Br.COBr$, is obtained by the action of bromine on acetyl bromide. It is a very strongly smelling liquid, boiling at 150°.

Dibromacetyl Aldehyde, $C_2H_2Br_2O$, is produced by the regulated action of bromine upon aldehyde. It is an oily liquid, possessing a penetrating smell, boiling at 140°—142°, and forming with water the hydrate, $C_2H_2Br_2O + H_2O$, crystallizing in long needles.[2]

Dibromacetic Acid, $C_2H_2Br_2O_2$, was prepared by Duppa and Perkin at the same time as bromacetic acid. According to Carius,[3] it is best obtained by heating acetic ether with bromine to 120°—130°:

$$C_2H_3O_2(C_2H_5) + 2\,Br_2 = C_2H_2Br_2O_2 + C_2H_5Br + HBr.$$

It is a white crystalline mass, melting at 45°, and boiling with slight decomposition at 232°—234°.

Ethyl Dibromacetate, $C_2HBr_2O2(C_2H_5)$, is formed by the action of sulphuric acid on a mixture of alcohol and dibromacetic acid, as well as by boiling an alcoholic solution of tribromacetaldehyde with potassium cyanide.[4] It is an oily liquid, smelling like peppermint, which boils at 192°, and is converted by ammonia into dibromacetamide, $C_2HBr_2O.NH_2$, which crystallizes in long needles, melting at 156°.

Dibromacetyl Bromide, $CHBr_2.COBr$, is formed by heating acetyl bromide with the requisite quantity of bromine to 150°. It is a colourless liquid, fuming in the air, and boiling at 194°.

Tribromacetaldehyde, or *Bromal*, $CBr_3.COH$, was discovered in 1832 by Löwig,[5] and is contained amongst other products of the action of bromine upon alcohol and ether. In order to prepare it, it is best, according to Schäffer,[6] to pass bromine vapours slowly into alcohol, and to subject the product to distillation. The product passing over between 165° and 180° is treated with water, when bromal hydrate is formed; and this

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[1] Kessel, *Ber. Deutsch. Chem. Ges.* xi. 2115.

[2] Pinner, *Ber. Deutsch. Chem. Ges.* vii. 1499.

[3] *Ib.* iii. 336.

[4] Remi, *Ber. Deutsch. Chem. Ges.* viii. 695.

[5] *Ann. Pharm.* iii. 288.

[6] *Ber. Deutsch. Chem. Ges.* iv. 366.

can be purified by re-crystallization, and bromal obtained from this by the action of sulphuric acid. It is an oily liquid, possessing a peculiar pungent smell and a sharp burning taste. It boils at 172°—173°, and has a specific gravity of 3·34. It decomposes in contact with acids into formic acid and bromoform.

Bromal Hydrate, $C_2Br_3HO+2H_2O$, or $C_2Br_3H(OH)_2+H_2O$, crystallizes, according to Löwig, in large transparent prisms having the form of sulphate of copper.

Tribromacetic Acid, $C_2HBr_3O_2$, was prepared by Gal[1] by decomposing its bromide with water. It is also easily formed by exposing bromal[2] or bromal hydrate[3] to the action of fuming nitric acid. It crystallizes in transparent, glistening, permanent, monoclinic prisms, melting at 135°, and boiling with partial decomposition at 250°.

Its salts, which have been investigated by Schäffer, are, with the exception of the mercurous and silver salts, easily soluble in water, and, on warming the solution, are easily converted into bromoform and a carbonate.

Ethyl Tribromacetate, $C_2Br_3O_2(C_2H_5)$, is produced by the action of the bromide upon alcohol, and is an oily, pleasantly smelling liquid, boiling at 225°.

Tribromacetyl Bromide, $CBr_3.COBr$, is formed by heating the dibrom-compound with an excess of bromine to 200°. It is a fuming liquid, boiling at 220°—225°, and being slowly decomposed by water.

Tribromacetamide, $CBr_3.CO.NH_2$, has as yet only been obtained by the action of bromine on asparagine[4] and by that of ammonia on hexbromacetone:[5]

$$CBr_3.CO.CBr_3 + NH_3 = CBr_3.CO.NH_2 + CBr_3H.$$

It is slightly soluble in cold, and rather more so in hot water; but may be readily crystallized from benzene in large prisms, melting at 119°—121°, and possessing a sweet and burning taste. Sulphuric acid converts it into ammonia and tribromacetic acid.

Bromchloracetic Acid, $C_2H_2BrClO_2$, is formed by heating equal molecules of chloracetic acid and bromine to 160°. It is a caustic, strongly smelling liquid, boiling at 201°. It forms an

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[1] *Compt. Rend.* lvi. 1257.

[2] Schäffer, *loc. cit.*

[3] Gal, *Compt. Rend.* lxxvii. 786.

[4] Guareschi, *Ber. Deutsch. Chem. Ges.* ix. 1436.

[5] Weidel and Gruber, *ib.* x. 1148.

ether boiling at 160°—163°, smelling like peppermint, and by ammonia is converted into an amide which crystallizes in long needles melting at 126°.[1]

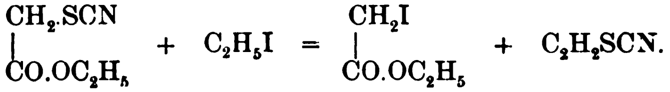
IODINE SUBSTITUTION-PRODUCTS.

350 *Moniodacetic Acid,* $C_2H_3IO_2$, was obtained by Perkin and Duppa [2] from its ethyl ether by decomposition with baryta water, barium being precipitated from solution by dilute sulphuric acid, and the liquid evaporated in a vacuum. It is also formed by heating acetic anhydride with iodine and iodic acid:

$$3\,(C_2H_3O)_2O + 3\,I_2 + IO_3H = 6\,C_2H_3IO_2 + HI.$$

The iodic acid must be present in excess in order to prevent the formation of free hydriodic acid. On cooling, the product solidifies, and this is treated with boiling benzol.[3] The compound crystallizes out from this in pearly scales, and from aqueous solution it can be obtained in rhombic tables which melt at 82°, and decompose when more strongly heated. Hydriodic acid reduces it in the cold with separation of iodine to acetic acid, and this reaction explains why iodine alone does not form substitution-products with acetic acid. Its salts are easily soluble, and readily decompose.

Ethyl Moniodacetate, $C_2H_2IO_2(C_2H_5)$, is formed by heating the chlor- or brom-acetic ether with alcohol and potassium iodide, as well as when ethyl thiocyanacetate, a body to be hereafter described under the glycolyl compounds, is heated with ethyl iodide to 120°:



$$\begin{array}{l}CH_2.SCN\\ |\\ CO.OC_2H_5\end{array} + C_2H_5I = \begin{array}{l}CH_2I\\ |\\ CO.OC_2H_5\end{array} + C_2H_2SCN.$$

If the resulting mixture of ethers be treated with baryta-water the iodine compound is decomposed, and the iodoacetic acid can then be easily obtained by the method above described.[4] Ethyl iodoacetate is a heavy oily liquid, which becomes brown and boils at 178°—180°.

Moniodacetamide, $C_2H_2IO_2.NH_2$, is formed by the action of potassium iodide on an alcoholic solution of the corresponding

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[1] Čech and Steiner, *Ber. Deutsch. Chem. Ges.* viii. 1174.

[2] *Phil. Mag.* [4], xviii. 54.

[3] Schützenberger, *Compt. Rend.* lxvi. 1340.

[4] *Journ. Chem. Soc.* xiii. 1.

chloro-compound. It crystallizes in transparent prisms, which, when heated, melt, become yellow, and decompose, with evolution of iodine vapours.

Di-iodacetic Acid, $C_2H_2I_2O_2$, was obtained by Perkin and Duppa[1] by the action of milk of lime on the ethyl ether, and decomposing the calcium salt with hydrochloric acid. The heavy oily liquid which then separates out gradually solidifies, forming large sulphur-yellow opaque rhombohedrons, which have a slightly acid reaction and a metallic taste, and smell somewhat like iodine. It does not act on the skin, and is only slightly soluble in water. It volatilizes slowly in the air, and melts on heating, decomposing at a higher temperature with partial sublimation. It forms slightly yellow-coloured crystalline salts which are readily decomposed.

Ethyl Di-iodacetate, $C_2HI_2O_2(C_2H_5)$, is formed by heating the corresponding brom-ether with potassium iodide and alcohol. It is a yellowish liquid which has a sharp burning taste, and attacks the eyes and nose strongly. Treated with aqueous ammonia, *di-iodacetamide*, $C_2HIO_2.NH_2$, separates out as a light-yellow crystalline mass.

Cyanacetic Acid, $CN.CH_2.CO_2H$, is easily formed from the mono-substituted acetic acids by replacing the halogen by cyanogen. It acts as a nitril of the dibasic malonic acid, $CH_2(CO_2H)_2$, under which it will be afterwards described.

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[1] *Loc. cit.*

COMPOUNDS CONTAINING THREE ATOMS OF CARBON, OR THE PROPYL GROUP.

351 *Propane*, C_3H_8. This gas, formerly called propyl hydride, was obtained by Berthelot by heating propylene dibromide, $C_3H_6Br_2$, or other compounds containing three atoms of carbon, with potassium iodide and water.[1] Another method adopted by the same chemist was to heat allyl iodide, C_3H_5I, acetone, C_3H_6O, glycerin, $C_3H_8O_3$, &c., with hydriodic acid of specific gravity 1·9 to 275°.[2] Ronalds[3] then showed that crude American petroleum contains propane in solution, and Schorlemmer[4] prepared it by the action of zinc and sulphuric acid on propyl iodide.

Propane is a colourless gas, slightly soluble in water, and somewhat more soluble in alcohol. When exposed to a temperature of from —25° to —30° it condenses to a colourless liquid.[5] Propane is easily attacked by chlorine in diffused daylight with formation of primary and secondary propyl chloride, as well as higher substitution-products (Schorlemmer).[6]

PRIMARY PROPYL ALCOHOL, C_3H_7OH.

352 Chancel[7] in 1853 showed that this compound was contained in fusel oil obtained in the manufacture of wine-brandy, but he did not investigate it fully. Mendelejeff,[8] who in 1867 examined a sample of this same fusel oil, did not succeed in separating

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[1] *Ann. Chim. Phys.* [3], li. 56 and 70.

[2] *Bull. Soc. Chim.* [2], vii. 56.

[3] *Journ. Chem. Soc.* xviii. 54.

[4] *Proc. Roy. Soc.* xvi. 34 ; xvii. 372.

[5] Lefebre, *Compt. Rend.* lvii. 1352.

[6] *Proc. Roy. Soc.* xviii. 29.

[7] *Compt. Rend.* xxxviii. 410 ; *Ann. Chem. Pharm.* lxxxvii. 127.

[8] *Zeitsch. Chem.* [2], iv. 25.

propyl alcohol from it, and Tromsdorff[1] was also unable to find it in fusel oil. From the above observations it might naturally be inferred that the existence of the primary alcohol is doubtful, the more so as all attempts to prepare it synthetically proved abortive. Thus Butlerow[2] endeavoured to obtain it by acting with zinc-methyl on ethylene iodhydrin, $IH_2C.CH_2.OH$, but only obtained the secondary alcohol; and Linnemann and Siersch[3] arrived at the same result in attempting its synthesis by acting on propylamine prepared from ethyl alcohol, with nitrous acid. Shortly afterwards, however, Fittig[4] succeeded in recognizing the presence of the primary alcohol in fusel oil. The explanation of the failure of other chemists to obtain this compound is the impossibility of separating it by fractional distillation when present in only small quantities. If, however, the mixed alcohols be converted into the bromides, a separation of these latter compounds may then easily be effected. At the same time Schorlemmer[5] prepared the alcohol from propane, and Linnemann[6] obtained it by the reduction of propionic anhydride, which he had prepared synthetically from ethyl alcohol. The existence of considerable quantities of propyl alcohol in a variety of different kinds of fusel oils was then recognized, and the properties of this alcohol were more exactly examined.[7] Krämer and Pinner[8] found that the "faints," or the latter portions of the distillate obtained on rectifying crude spirit of wine (p. 295), is rich in propyl alcohol. Indeed it is now prepared in quantity by fractionating this liquid, and sold by Kahlbaum of Berlin.[9] These "faints," as well as the still less volatile or ordinary fusel oil, are mixtures of several alcohols and of fatty acid ethers, and their relative quantities depend on the nature of the material from which the alcohol was obtained. The following gives the composition of the "faints" from potato-spirit according to Rabuteau:[10]

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[1] Tagblatt, *Frankf. Naturf.* 1867, 52.
[2] *Zeitsch. Chem.* [2], iii. 680.
[3] *Ann. Chem. Pharm.* cxliv. 137.
[4] *Zeitsch. Chem.* [2], iv. 44.
[5] *Proc. Roy. Soc. loc. cit.*
[6] *Ann. Chem. Pharm.* cxlviii. 251.
[7] Pierre and Puchot, *Compt. Rend.* lxvi. 302; lxx. 354; *Bull. Soc. Chim.* [2], xiv. 53; Chancel, *Ann. Chem. Pharm.* cli. 298; *Compt. Rend.* lxviii. 659; Chapman and Smith, *Journ. Chem. Soc.* xxii. 193.
[8] *Ber. Deutsch. Chem. Ges.* iii. 75.
[9] *Ber. Entw. Chem. Ind.* ii. 274-276.
[10] *Compt. Rend.* lxxxvii. 500.

	Cbc. per liter.	B.P.
Secondary propyl alcohol	150	85°
Primary propyl alcohol	30	97°
Isobutyl alcohol	50	109°
Normal butyl alcohol	65	116°·9
Methylpropyl carbinol	60	120°
Isomeric amyl alcohols	275	128°-132°
Mixture of higher homologues of the alcohols and ethers . . .	170	
Water	125	
Mixture of aldehyde, acetic acid, and alcohol	75	
	1,000	

Trimethyl carbinol, or tertiary butyl alcohol, also appears to be contained in this liquid.

Primary propyl alcohol is also found, together with ethyl alcohol and butyl alcohol, in the acid liquors of the starch manufacture, and also in the products of the lactic and butyric fermentations.[1] It is also formed in the peculiar fermentation of glycerin,[2] about which information will be hereafter given.

It has been already stated that Linnemann was the first to obtain propyl alcohol synthetically. Saytzeff[3] also prepared it by synthesis by acting with sodium amalgam on a mixture of propionic acid and propionyl chloride; whilst Rossi[4] obtained it, by a method already described, from ethyl alcohol.

Propyl alcohol resembles spirit of wine in its odour. It has a specific gravity at 0° of 0·8198, and boils, according to various observers, from 96° to 98°. The latter number is probably the correct one, as the boiling-points of the normal alcohols increase 19°·6 for every increment in composition of CH_2.[5] It is miscible in every proportion with water, but, on the addition of calcium chloride and other easily soluble salts, it separates out from aqueous solution. The specific gravity of the vapour is, according to Chancel, 2·02. If the alcohol be treated with aluminium and iodine, hydrogen is evolved and aluminium propylate, $Al_2(OC_3H_7)_6$, formed. On distillation under diminished

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[1] Bouchardat, *Compt. Rend.* lxxviii. 1145.

[2] Fitz, *Ber. Deutsch. Chem. Ges.* xiii. 36.

[3] *Zeitsch. Chem.* 1870, 105.

[4] *Compt. Rend.* lxx. 129.

[5] Grimshaw and Schorlemmer, *Journ. Chem. Soc.* xxvi. 1082.

pressure, this compound comes over as a heavy liquid, solidifying to an amorphous mass.[1]

Primary propyl alcohol is not used in the arts or manufactures, but frequently employed in scientific research. Its derivatives closely resemble those of ethyl alcohol, and are prepared in a like manner. A short description of these may therefore suffice.

Propyl Oxide or *Dipropyl Ether*, $(C_3H_7)_2O$, is a colourless liquid smelling like common ether and boiling at 85°—86°, obtained by Chancel by heating a solution of caustic potash in the alcohol with propyl iodide. *Methylpropyl Ether* may be obtained in a similar way, as a liquid boiling at 49° to 52° and possessing analogous properties to common ether. *Ethylpropyl Ether*, boiling at about 63°—64°, can likewise be prepared (Brühl).

Propyl Chloride, C_3H_7Cl, is obtained by acting with hydrochloric acid or phosphorus trichloride on the alcohol (Pierre and Puchot). It is also formed when the iodide is heated to 130° with mercuric chloride (Linnemann). It is an easily mobile liquid boiling at 46°·5 and having a specific gravity at 0° of 0·9156.

Propyl Bromide, C_3H_7Br. In order to prepare this compound it is not necessary to employ the pure alcohol, but fusel oil or the residual spirit rich in propyl alcohol may be at once treated with bromine and phosphorus. The products can be easily separated by fractional distillation, and the propyl bromide thus obtained boils at 71°, and has a specific gravity of 1·3497. The remarkable fact must here be noticed that primary propyl bromide when heated with aluminium bromide is transformed by intramolecular change into the secondary compound.[2]

Propyl Iodide, C_3H_7I, boils at 102°, and has a specific gravity at 0° of 1·7842. Heated with six times its volume of water for twenty-four hours at 100°, it is converted into the alcohol.

Propyl Nitrite, $C_3H_7O.NO$, was prepared by Cahours, by acting with nitrous acid upon the alcohol. It is a pleasantly smelling liquid, boiling at 46°—56°.

Propyl Borate, $(C_3H_7)_3BO_3$, is obtained by acting upon propyl alcohol with boron trichloride. It is a mobile, slightly ethereal smelling liquid, possessing a burning and bitter taste; it boils at 172° to 175°, and has a specific gravity at 16° of 0·867 (Cahours).

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[1] Gladstone and Tribe, *Chem. Soc. Journ.* 1880, i. 4.

[2] Kekulé and Schrötter, *Ber. Deutsch. Chem. Ges.* xii. 2279.

Propyl Silicate, $(C_3H_7)_4SiO_4$, is formed in a similar way to the foregoing compound, and is a liquid boiling at 225° to 227° and having a specific gravity at 18° of 0·915. It is easily decomposed by water with separation of silica (Cahours).

Propyl Carbonate, $(C_3H_7)_2CO_3$, is obtained, according to Cahours, by treating the oxalate with sodium. It is a liquid boiling at 156°—160° and possessing a pleasant smell.[1]

Propyl Chlorocarbonate, $C_3H_7O.COCl$, is obtained by acting with carbonyl chloride on the alcohol. It is a very pungent liquid which attacks the eyes, and boils at 115°·2. If this ether be allowed to act on sodium propionate, the carbonate is formed, boiling at 168°·2.[2] Ammonia converts the chlorocarbonate into propyl carbamate, $C_3H_7O.CO.NH_2$, which is also obtained by heating the alcohol with urea (Cahours). It forms large colourless prisms difficultly soluble in water, which melt at 50°, the liquid boiling at 194°—196°. If an excess of urea be employed, *propyl allophanate*, $H_2N.CO.NH.CO.O.C_3H_7$, is formed. This crystallizes from alcohol in pearly crystals which melt at 150° to 160°.

Propyl Formate, $(C_3H_7)CHO_2$, is a pleasantly smelling liquid boiling at 83°.

Propyl Orthoformate, $(C_3H_7O)_3CH$, boils at 196°—198°.

Propyl Acetate, $(C_3H_7)C_2H_3O_2$, resembles acetic ether, but smells like pears. It boils at 102°, and has a specific gravity at 0° of 0·913.

Propyl Hydrosulphide, $C_3H_7.SH$, was obtained by Römer by treating the bromide with potassium hydrosulphide. It is a disagreeably smelling liquid boiling at 67°—68°.[3]

Propyl Sulphide, $(C_3H_7)_2S$, is obtained by the action of the iodide on an alcoholic solution of potassium sulphide. It is a disagreeably smelling liquid, boiling at 130°—135°, which forms trisulphine compounds with the iodides of the alcohol radicals.[4]

Propylamine, $C_3H_7NH_2$, was first prepared by Mendius,[5] by acting with hydrochloric acid and zinc on an alcoholic solution of propionitril. Silva[6] then obtained it by acting on silver cyanate with propyl iodide, and treating the mixture of propyl isocyanate

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[1] *Compt. Rend.* lxxvii. 749.

[2] Roese, *Ann. Chem. Pharm.* ccv. 227.

[3] *Ber. Deutsch. Chem. Ges.* vi. 784.

[4] Cahours, *Compt. Rend.* lxxvi. 133.

[5] *Ann. Chem. Pharm.* cxxi. 129.

[6] *Ib.* lxix. 473; *Ber. Deutsch. Chem. Ges.* ii. 559.

and isocyanurate thus obtained, with potash and distilling. Linnemann also prepared it in the same way.[1]

It is a liquid possessing a strongly ammoniacal smell and boil- at 49°·7. It is miscible with water with evolution of heat, and the aqueous solution precipitates the salts of iron, copper, lead, aluminium, nickel, cobalt, silver, and mercury, and, of these, the aluminium and silver precipitates dissolve in an excess of the base. Propylamine forms crystallizable salts and easily combines with the iodides of the alcohol radicals.

Tetrapropylammonium Iodide, $N(C_3H_7)_4I$, was obtained by Römer by heating propyl iodide with alcoholic ammonia, separating the bases which are formed by treatment with soda, and mixing with propyl iodide, when the above compound is formed with considerable evolution of heat. It crystallizes from water in fine white prisms, and yields an alkaline very deliquescent hydroxide on treatment with silver oxide, and this, on heating with water, is converted into propylene and *tripropylamine,* $N(C_3H_7)_3$, the platinichloride of which crystallizes in splendid red tablets.[2]

Propyl Carbamine, $CN.C_3H_7$, is obtained by the action of the bromide on cyanide of silver. It is a strongly smelling liquid, boiling at 95°—100°.[3]

Propyl Thiocyanate, $NCS.C_3H_7$, is obtained by acting on silver thiocyanate with the bromide. It boils at 163°, and has a disagreeable smell (Schmitt).

NITRO-COMPOUNDS OF PROPYL.

353 *Primary Nitropropane,* $C_3H_7NO_2$, is formed together with propyl nitrite when silver nitrite acts upon propyl iodide. It is a liquid very similar to nitroethane, and boils at 125°—127°.[4] By the action of bromide on its solution in potash, substitution-products occur similar to those of nitroethane.

Monobromnitropropane, $C_3H_6BrNO_2$, is a heavy, oily, strongly smelling liquid, boiling at 160°—165°, and easily soluble in alkalis.

Dibromnitropropane, $C_3H_5Br_2NO_2$, is an oil closely resembling the foregoing compound, boiling at 184°—186°, but is not soluble in alkalis.[5]

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[1] *Ann. Chem. Pharm.* clxi. 45.

[2] *Ber. Deutsch. Chem. Ges.* vi. 784.

[3] Schmitt, *Zeitsch. Chem.* [2], vi. 576.

[4] V. Meyer, *Ann. Chem. Pharm.* clxxi. 36.

[5] Meyer and Tscherniak, *Ann. Chem. Pharm.* clxxx. 118.

Dinitropropane, $C_3H_6(NO_2)_2$. When a solution of monobromnitropropane and potassium nitrite in dilute spirit of wine is mixed with alcoholic potash, the potassium salt, $C_3H_5K(NO_2)_2$, separates out, mixed with potassium bromide. This latter is removed by washing with cold water. If the potassium compound be added to dilute sulphuric acid, dinitropropane separates out as an oily, colourless liquid, which possesses a faint alcoholic smell and a sweet taste. It boils at 189°, and has a specific gravity of 1·258 at 22°·5, and reddens litmus-paper. Its salts have a yellow colour, and are explosive. The potassium salt is difficultly soluble in cold water, and crystallizes from the hot solution in needles or striated prisms.[1]

Dinitropropane is also formed by the action of hot concentrated nitric acid on dipropylketone, $(C_3H_7)_2CO$. The body thus obtained was formerly considered to be nitropropionic acid, as no determination of the nitrogen had been made, and the analyses of the few salts which were examined pointed to this conclusion.[2]

Propyl Nitrolic Acid, $C_3H_5(NO_2)NOH$, is prepared in a similar way to ethyl nitrolic acid. It crystallizes from ether in large light yellow prisms, having a bluish fluorescence, possesses a sweet taste, and in its other properties closely resembles the ethyl compound.[3]

COMPOUNDS OF PROPYL AND THE METALS.

354 *Arsenic Compounds of Propyl.* When propyl iodide is heated with arsenic for about thirty hours to 180°, the compound $AsI_3 + As(C_3H_7)_4I$ is formed, and this, on cooling, solidifies to reddish-brown crystals. If zinc arsenide be employed in place of the latter element, prismatic crystals having the composition $ZnI_2 + 2As(CH_3)_4I$ are produced. Both these compounds yield, on distillation with potash, the very unpleasantly smelling *tripropylarsine*, $As(C_3H_7)_3$, which readily unites with the alcoholic iodides.[4]

Beryllium Propyl, $Be(C_3H_7)_2$, is obtained by heating beryllium with mercury propyl, and is a liquid boiling at 244°—246°, fuming in the air, and not being spontaneously inflammable.[5]

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[1] ter Meer, *Liebig's Ann.* clxxxi. 19.

[2] Chancel, *Ann. Chim. Phys.* [3], xii. 146; Kurz, *Ann. Chem. Pharm.* clxi. 209.

[3] Meyer, *Ib.* clxxv. 114.

[4] Cahours, *Compt. Rend.* lxxvi. 752.

[5] *Compt. Rend.* lxxvi. 1383.

Zinc Propyl, $Zn(C_3H_7)_2$, was prepared by Cahours by heating zinc, together with propyl iodide, to 120°—130°. It boils at 158°—160°, fumes in the air, and is easily inflammable.[1]

Mercury Propyl, $Hg(C_3H_7)_2$. This compound is obtained by acting upon the iodide with sodium amalgam in presence of acetic ether. It is a mobile liquid, having a faint smell when cold, and, on heating, this becomes stronger. It has a specific gravity at 16° of 2·124, and boils at 189°—191°. It is easily attacked by acids, with formation of propyl mercury salts. The iodide, C_3H_7HgI, is converted by moist silver oxide into the crystalline, strongly alkaline, hydroxide (Cahours).

Aluminium Propyl, $Al(C_3H_7)_3$, is prepared similarly to the zinc compound, and is a spontaneously inflammable liquid, which boils at 248—252°.

Tin Propyl Compounds. By heating propyl iodide with tinfoil, *dipropyl tin di-iodide*, $(C_3H_7)_2SnI_2$, is formed. This is a liquid boiling at 270°—273°, and is converted by alkalis into the corresponding amorphous oxide. Hydrochloric acid converts it into the dichloride, which forms fine crystals, melting at 80°—81°. If propyl iodide be brought in contact with an alloy of tin and sodium containing 10 per cent. of the latter metal, *tripropyl tin iodide*, $(C_3H_7)_3SnI$, is formed as a liquid possessing a pungent smell, and boiling at 260°—262°. This, when heated with caustic potash, yields the hydroxide, $(C_3H_7)_3SnOH$, which distils over as an oily liquid, and this on cooling solidifies to a crystalline mass. It has a powerful smell, an alkaline reaction, and on distillation with caustic baryta yields the oily oxide $(C_3H_7)_6Sn_2O$, which again easily combines with water. Hydrochloric acid converts the oxide into the volatile chloride, which has a smell stronger than that of the iodide.

Tin Tetrapropyl, $Sn(C_3H_7)_4$, is obtained by heating tripropyl tin iodide with zinc propyl. It is a liquid possessing a strongly ethereal smell, boiling at 222°—225°, and having a specific gravity at 14° of 1·179.[2]

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[1] *Compt. Rend.* lxxvi. 751.

[2] Cahours, *Compt. Rend.* lxxvi. 136 ; lxxxviii. 725 ; Cahours and Demarçay, *ib* lxxxviii. 1112.

PROPIONIC ALDEHYDE AND PROPIONIC ACID.

355 *Propionic Aldehyde*, C_3H_6O, is formed when propyl alcohol is acted upon by moderate oxidizing agents, and also when a mixture of calcium formate and calcium propionate is subjected to dry distillation. It is a thin liquid, possessing a suffocating smell, boiling at 49°·5, and having a specific gravity at 0° of 0·804 (Rossi).[1] It is not miscible in all proportions with water, requiring five times its volume for complete solution, and it is easily transformed into propionic acid by further oxidation.

PROPIONIC ACID, $C_3H_6O_2$.

356 This acid was obtained by Gottlieb,[2] in 1844, by oxidizing metacetone, $C_6H_{10}O$, and also by heating sugar, starch, gum, &c., with concentrated caustic potash; and to it he gave the name of metacetonic acid.[3] Redtenbacher then obtained it by fermenting an aqueous solution of glycerin by means of yeast.[4]

The synthetic production of propionic acid from ethyl cyanide (propionitril) was discovered by Dumas, Malaguti, and Leblanc,[5] as well as by Frankland and Kolbe.[6] Wanklyn[7] afterwards showed that it is formed by the direct combination of carbon dioxide and sodium ethylate. Lastly, Ulrich[8] obtained it by indirect reduction from lactic or oxypropionic acid.

Propionic acid is also formed in a variety of other ways, thus, Strecker[9] obtained it by the fermentation of calcium lactate. Nöllner,[10] in 1841, proved that a peculiar acid is found amongst the fermentation-products of calcium tartrate, and to this he gave the name of pseudo-acetic acid. Berzelius[11] considered this to be a mixture of butyric and acetic acid, whilst Nicklès[12] believed it to be a peculiar compound of these two acids, and therefore termed it butyro-acetic acid. On the other hand, Dumas and his friends came to the conclusion that it is

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[1] *Liebig's Ann.* clix. 79.

[2] *Ann. Chem. Pharm.* lii. 121.

[3] *Ann. Chem. Pharm.* lii. 11.

[4] *Ib.* lvii. 174.

[5] *Compt. Rend.* xxv. 676 and 781; *Ann. Chem. Pharm.* lxiv. 329, 334.

[6] *Chem. Soc. Journ.* i. 60.

[7] *Ib.* x. 103.

[8] *Ib.* cix. 271.

[9] *Ann. Chem. Pharm.* xcii. 80.

[10] *Ib.* xxxviii. 299

[11] *Berzelius Jahresb.* xxii. 233.

[12] *Ann. Chem. Pharm.* lxi. 343.

identical with propionic acid, because, like this last-named acid, it possesses a constant boiling-point.[1] Again, Limpricht and Uslar[2] found that though butyro-acetic acid forms salts which have the same composition as the corresponding propionates, the free acid may be converted by simple distillation into acetic and butyric acids.

These contradictory statements have recently been fully explained by the investigations of Fitz.[3] He finds that the fermentation of calcium lactate, calcium tartrate, calcium malate, and glycerin may give rise to any one of these free acids, or a mixture of them, the exact nature of the product depending upon the special ferment causing the change. This chemist has shown that various species of schizomycetes (*Bacillus*) exist, and that the particular fermentation which takes place depends upon the presence of a certain definite species of the ferment. This he has proved by preparing these several ferments in the pure state, and thus bringing about any special kind of fermentation desired. For further information on this point, the article on "Fermentation" must be referred to.

In order to prepare propionic acid, propionitril is heated in a flask connected with an inverted condenser with either aqueous or alcoholic potash until no further evolution of ammonia occurs, and until the smell of the nitril has disappeared. The liquid is then evaporated down, and the residue distilled with slightly diluted sulphuric acid. In this case it is not necessary to employ pure propionitril; it suffices to heat ethyl iodide with alcohol and powdered potassium cyanide until it is decomposed, and then to treat the distillate as described.[4]

Propionic acid, as Frankland and Kolbe have shown, is also formed when the nitril is heated with tolerably dilute sulphuric acid. In order to prepare it in this way, Linnemann[5] recommends treating the nitril with its own weight of strong sulphuric acid previously mixed with water in the proportion of seven to three. The mixture of nitril and diluted acid is then heated in connection with a reversed condenser, and the acid distilled off.

The aqueous acid obtained by one or other of these methods is then converted into the sodium salt, which may again be decomposed by concentrated sulphuric acid or heated in a stream of dry hydrochloric acid gas (Linnemann).

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[1] *Ann. Chem. Pharm.* lxiv. 329.

[2] *Ib.* xciv. 321.

[3] *Ber. Deutsch. Chem. Ges.* xii. 476.

[4] Williamson, *Phil. Mag.* [4], vi. 204.

[5] *Ann. Chem. Pharm.* cxlviii. 251.

According to Beckurts and Otto,[1] the acid is most readily prepared by heating to 100° one part by weight of the nitril with three parts by weight of a mixture of three volumes of water and two of sulphuric acid until the oily layer which is separated out does not increase in volume. This latter is then almost pure propionic acid, which may be easily freed from water by rectification.

Fitz[2] states that the fermentation of calcium lactate and calcium malate is much to be recommended as a source of propionic acid. Propionic acid is also formed, together with other acids of the fatty series, in the putrefaction of various organic bodies, and it is likewise found in the products of distillation of wood.[3]

Propionic acid is a colourless liquid, possessing a smell resembling acetic acid, but also like that of butyric acid. It boils at 140°, and has a specific gravity of 1·016 at 0°. It is miscible in all proportions with water, but on the addition of calcium chloride, or other easily soluble salts, it separates out and swims on the surface as an oily liquid. For this reason, as well as because its salts have a fatty feel, the name which it now bears was given to this acid by Dumas (*προτος*, the first, *πιον*, fat).

The Propionates.

357 The propionates are all soluble in water, and almost all crystallize readily. Those of the alkali-metals yield, when heated with arsenic trioxide, a smell resembling that of cacodyl.

The following are the most characteristic salts:

Silver Propionate, $C_3H_5O_2Ag$, is thrown down as a crystalline precipitate when silver nitrate is added to a solution of a propionate. It dissolves in 119 parts of water at 18°, and much more easily in boiling water. It crystallizes on cooling in glistening tablets, and sometimes in large broad needles.

Lead Propionate, $(C_3H_5O_2)_2Pb$, crystallizes with great difficulty, and on evaporating its solution, it usually remains in the form of a gummy mass. When its solution is evaporated with finely divided oxide of lead, a basic salt of the composition $3(C_3H_5O_2)_2Pb + 4PbO$ is formed. This may be dissolved from the residue by cold water. On boiling this solution it separates out in needles

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[1] *Ber. Deutsch. Chem. Ges.* x. 262.

[2] *Ib.* xi. 1899.

[3] Barré, *Compt. Rend.* lxviii. 1222; Anderson, *Chem. News*, xiv. 257; Krämer, and Grodski, *Ber. Deutsch. Chem. Ges.* xi. 1356.

or as a crystalline powder. It dissolves at the ordinary temperature in from 8 to 10 parts of water.

This characteristic salt is well adapted for the separation of propionic from formic and acetic acids. The mixture of acids is evaporated to dryness with oxide of lead, the residue treated with cold water, and the precipitate of the basic lead propionate thrown down on boiling the solution. The basic salts of the other two acids remain in solution, and may be separated by filtration of the boiling liquid.[1]

Methyl Propionate, $C_3H_5O_2.CH_3$, possesses a pleasant smell, boils at 79°·5, and has at 0° a specific gravity of 0·9578.

Ethyl Propionate, $C_3H_5O_2.C_2H_5$, boils at 100°, and has at 0° a specific gravity of 0·9138.

Propyl Propionate, $C_3H_5O_2.C_3H_7$, is a liquid boiling at 124°, and having a specific gravity of 0·9022 at 0°.

PROPIONYL COMPOUNDS.

358 *Propionic Anhydride* or *Propionyl Oxide*, $(C_3H_5O)_2O$, is obtained by the action of propionyl chloride on sodium propionate. It has a smell resembling acetyl oxide, and is a liquid boiling at 168°–169°, and having a specific gravity at 15° of 1·0169.

Propionyl Chloride, C_3H_5OCl, is formed by heating propionic acid with phosphorus trichloride, but has as yet not been obtained pure.

Propionyl Bromide, C_3H_5OBr, is prepared in a similar way, and is a pungent smelling liquid, fuming on exposure to the air, boiling at 96°–98°, and having at 14° a specific gravity of 1·465.[2]

Propionyl Iodide, C_3H_5OI, is obtained by the action of phosphorus and iodine upon the acid. It is a colourless heavy liquid, boiling at 127°—128° (Sestini).

Propionamide, $C_3H_5ONH_2$, is formed by acting with aqueous ammonia on ethyl propionate,[3] or by passing ammonia into heated propionic acid until the boiling-point rises to 200°. It forms readily soluble crystals which melt at 75°—76°.[4]

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[1] Linnemann, *Ann. Chem. Pharm.* clx. 195.

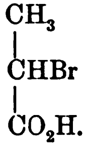
[2] Sestini, *Bull. Soc. Chim.* [2], xi. 468.

[3] *Bull. Soc. Chim.* [2], xv. 228.

[4] Engler, *Ann. Chem. Pharm.* cxxxiii. 143.

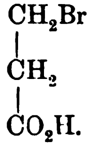
Substituted Propionic Acids. The mono-substitution products exist in two isomeric forms:

α-Brompropionic Acid.



$$\begin{array}{l} CH_3 \\ | \\ CHBr \\ | \\ CO_2H. \end{array}$$

β-Brompropionic Acid.



$$\begin{array}{l} CH_2Br \\ | \\ CH_2 \\ | \\ CO_2H. \end{array}$$

The first of these is formed by heating propionic acid with bromine; if the bromine be employed in excess *Dibrompropionic* acid, $CH_3CBr_2CO_2H$, is formed. Hence it is seen that the substitution here takes place in the carbon atom attached to the carboxyl group; this is also found to be the case with the other fatty acids. The β-compounds, as well as the remaining α-compounds, are not formed by the direct action of bromine on the acid; they will, therefore, be described further on (see Lactic and Glyceric Acids).

PROPIONITRIL AND ITS DERIVATIVES.

359 *Propionitril*, C_2H_5CN, was first prepared by Pelouze,[1] by distilling a mixture of barium ethylsulphate and potassium cyanide. He termed it *cyanure d'éthyle*, and described it as a very poisonous liquid possessing a strong alliaceous odour. Its chief reactions were then examined, as has been stated, by Dumas, Malaguti, and Leblanc, as well as by Frankland and Kolbe.

Pelouze's method does not give a good yield, and the product contains the isomeric ethylcarbamine, which imparts to it an unpleasant smell and poisonous properties. According to Gautier,[2] it may be purified by treating it with dilute sulphuric acid and then warming it for some time with mercuric oxide.

Linnemann[3] obtained it by distilling equal weights of potassium cyanide and potassium ethylsulphate. The portion boiling at 110° is heated with dilute hydrochloric acid until it has an acid reaction, and then distilled; the distillate is shaken first with caustic potash, and afterwards with a concentrated solution of calcium chloride. It is then dried over anhydrous potassium carbonate, and, lastly, washed for several times with small

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[1] *Journ. Pharm.* xx. 399; *Ann. Pharm.* x. 249.

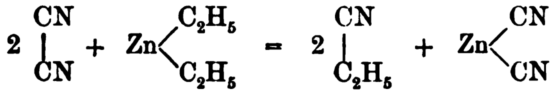
[2] *Ann. Chim. Phys.* [4], xvii. 180.

[3] *Ann. Chem. Pharm.* cxlviii. 252.

quantities of water. By this process he obtained 2·65 kilos. from 20 kilos. of potassium cyanide.

Hofmann and Buckton[1] prepared it by heating propionamide with phosphorus pentoxide. According to Gautier,[2] it is best obtained by Williamson's method.[3] For this purpose ethyl iodide is heated with potassium cyanide in closed tubes to 180° and the product distilled. The distillate is then washed with a weak solution of calcium chloride, when any undecomposed ethyl iodide sinks to the bottom, whilst the nitril swimming on the top may be washed several times.

Propionitril is also obtained by the action of cyanogen chloride on zinc-ethyl,[4] and also when the last-named substance is treated with cyanogen gas,[5] when the following reaction occurs:



$$2\begin{array}{c}CN\\|\\CN\end{array} + Zn\left\langle\begin{array}{l}C_2H_5\\C_2H_5\end{array}\right. = 2\begin{array}{c}CN\\|\\C_2H_5\end{array} + Zn\left\langle\begin{array}{l}CN\\CN\end{array}\right.$$

The substance obtained by one or other of these processes is dried over chloride of calcium and rectified.

Pure propionitril is a mobile, peculiar, ethereal smelling liquid, boiling at 97°, and solidifying at 68°, and possessing at 0° a specific gravity of 0·8010 (Thorpe), that of its vapour being 1·928. It is tolerably soluble in water, but may be separated by the addition of calcium chloride.

Propionitril combines with the hydracids.[6] The hydrochloride, C_3H_5NHCl, is gradually formed when propionitril saturated with hydrochloric acid is allowed to stand in a closed vessel. It forms apparently monoclinic prisms which are slightly soluble in water. It is decomposed into its constituents by dry ammonia. On exposure to air, propionitril absorbs water and is converted into sal-ammoniac and propionic acid. It melts at 121°, and on standing at this temperature for some time is converted into a yellow oil which does not again solidify. It also forms compounds with the metallic chlorides, with carbonyl chloride, and with cyanogen chloride.[7]

By distilling one part of potassium cyanide with three parts of potassium ethylsulphate, Gautier obtained a compound of the nitril with alcohol, $C_3H_5N_33C_2H_6O$, which boils at 79°, and is

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[1] *Proc. Roy. Soc.* viii. 158 (1856).

[2] *Loc. cit.*

[3] *Phil. Mag.* [4], ii. 205.

[4] Gal, *Ann. Chem. Pharm.* cxlvii. 126.

[5] Frankland and Graham, *Chem. Soc. Journ.* 1880, i. 740.

[6] Gautier, *loc. cit.*

[7] Henke, *Ann. Chem. Pharm.* cvi. 280.

miscible in all proportions with water. It forms a crystalline mass with cyanide of potassium, from which it may be again obtained in the pure state by distillation. The specific gravity of the vapour is 1·618, from which it is seen that the above compound cannot exist in the form of vapour.

Cyanethine, $(C_3H_5)_3N_3$, was first prepared by Frankland and Kolbe[1] by the action of potassium on moist propionitril. E. von Meyer[2] found that a better yield is obtained by employing dry propionitril and sodium. In this preparation ethane is evolved, and a yellow solid mass remains, which is decomposed by water, yielding caustic soda, sodium cyanide, propionitril, ammonia, and sodium propionate. Cyanethine is very slightly soluble in cold water, and crystallizes from hot water in pearly scales melting at 189°, and boils with partial decomposition at 280°. It is a monad base, possessing a weak alkaline reaction. The hydrochloride, $C_9H_{15}N_3HCl + H_2O$, is very soluble, crystallizes in large transparent striated prisms, and forms with platinic chloride a double salt crystallizing in ruby red octohedrons. The nitrate, $C_9H_{15}N_3NO_3H$, crystallizes in large prisms.

Cyanethine is a tertiary base, capable of uniting with one molecule of ethyl iodide. If the resulting compound be treated with oxide of silver and water, a strongly alkaline solution is obtained of *ethylcyanethonium hydroxide*, $C_2H_5(C_9H_{15})N_3OH$.

When cyanethine is heated with strong hydrochloric acid, sal-ammoniac is obtained, together with a monad tertiary base, $C_9H_{14}ON_2$. This crystallizes from hot aqueous solution in splendid groups of needles which melt at 156°—157°. By the action of phosphorus pentachloride the compound $C_9H_{13}ClN_2$ is obtained. This is an oily liquid, possessing an unpleasant persistent smell; it can be distilled in a vacuum without decomposition, and when heated with ammonia is reconverted into cyanethine, whilst nascent hydrogen converts it into the base, $C_9H_{14}N_2$, a colourless oily liquid boiling at 204°—205°. It dissolves readily in water with alkaline reaction, but, on heating, the solution becomes turbid, owing to the separation of the compound. This compound possesses an unpleasant stupifying smell, and acts as a powerful poison. When the vapour is inhaled even in small quantities it produces stupor, and its physiological action appears to be similar to that of conine, $C_8H_{15}N$, the poisonous principle of the hemlock; but its action

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[1] *Journ. Chem. Soc.* i. 60.

[2] *Journ. Prakt. Chem.* [2], xxii. 261.

is even more powerful than that of this alkaloid, from which it differs in composition by the replacement of one atom of hydrogen by the elements of cyanogen. Hence it is perhaps *conine cyanide*, $C_8H_{14}(CN)N$ (v. Meyer).

SECONDARY PROPYL ALCOHOL, $(CH_3)_2CHOH$.

360 This compound, also termed *isopropyl alcohol*, was obtained first by Berthelot,[1] in 1855, by combining propylene, C_3H_6, with sulphuric acid and distilling the propyl sulphuric acid thus obtained with water. At that time no isomeric alcohols were known, and it was therefore assumed that Berthelot's alcohol was identical with that first obtained from fusel oil.

Friedel[2] then obtained a substance having the composition of propyl alcohol by the action of sodium amalgam and water on acetone or dimethyl ketone $(CH_3)_2CO$; and Kolbe[3] gave it as his opinion that this must be the first member of the series of secondary alcohols, the possible existence of which he had already predicted (see p. 182), and stated that this body on oxidation would be found again to yield acetone, and this on being put to the test of experiment by Friedel[4] was actually the case.

A year before this, Erlenmeyer had obtained a compound having the composition of propyl iodide by heating glycerine with hydriodic acid. Further examination showed that this belongs to the series of secondary compounds,[5] and Berthelot proved that this is the case with the alcohol obtained from propylene.[6]

In order to prepare isopropyl alcohol, glycerine is distilled with an excess of fuming hydriodic acid with addition of amorphous phosphorus, when allyl iodide is first obtained, according to the following equation:

$$C_3H_5(OH)_3 + 3\,IH = C_3H_5I + 3\,H_2O + I_2.$$

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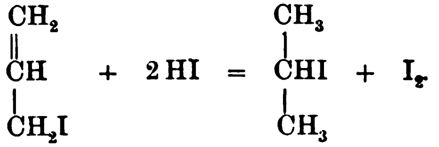
[1] *Ann. Chim. Phys.* [3], xliii. 399; *Ann. Chem. Pharm.* xciv. 78.
[2] *Rép. Chim. Pure*, iv. 351; *Ann. Chem. Pharm.* cxxiv. 324.
[3] *Zeitsch. Chem.* 1862, 627.
[4] *Rép. Chim. Pure*, v. 247.
[5] *Zeitsch. Chem.* 1861, 362; *ib.* 1862, 43; *Ann. Chem. Pharm.* cxxvi. 305; *Zeitsch.* 1863, 380; *ib.* 1864, 642.
[6] *Compt. Rend.* lvii. 797; *Ann. Chem. Pharm.* cxxix. 126.

This is then converted into secondary propyl iodide[1] by the excess of hydriodic acid.



$$\begin{matrix} CH_2 & & & & CH_3 & & \\ \| & & & & | & & \\ CH & + & 2HI & = & CHI & + & I_2 \\ | & & & & | & & \\ CH_2I & & & & CH_3 & & \end{matrix}$$

The addition of the phosphorus serves for the purpose of at once converting the iodine which is set free into hydriodic acid.

The iso-alcohol can be prepared from the iodide in a variety of ways. In the first place, propyl acetate can be obtained by heating the iodide with acetic acid and potassium or lead acetate, and this is easily converted by caustic potash into the alcohol. Secondly, the iodide may be heated with lead hydroxide and water in connection with a reversed condenser;[2] or, again, it may be simply heated with twenty times its weight of water for forty hours to 100°.[3] On distilling the product obtained by one or other of these processes, aqueous isopropyl alcohol is obtained, and this can be rendered anhydrous in the usual manner.

Isopropyl alcohol is a mobile liquid possessing a slightly spirituous smell, boiling at 83°—84°, and having a specific gravity at 15° of 0·791. It forms with water the hydrate $2C_3H_8O + H_2O$, boiling constantly at 80°, and having the same percentage composition as ethyl alcohol (Erlenmeyer). According to Linnemann, other hydrates exist, namely, $3C_3H_8O + 2H_2O$, boiling at 78°—80°, and $3C_3H_8O + H_2O$, boiling at 81°—82°.[4]

Isopropyl Oxide or *Di-isopropyl Ether*, $(C_3H_7)_2O$, is formed by the action of silver oxide on the iodide. It is a liquid boiling between 60° and 62°, and possessing a smell of peppermint (Erlenmeyer).

Isopropyl Chloride, C_3H_7Cl, is easily formed by heating the alcohol with hydrochloric acid, or the iodide with corrosive sublimate. It boils at 34°—36°, and has a specific gravity at 0° of 0·874 (Linneman).

Isopropyl Bromide, C_3H_7Br, is best obtained by acting upon

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[1] Maxwell Simpson, *Proc. Roy. Soc.* xii. 533.

[2] Flawitzky, *Liebig's Ann.* clxxv. 380.

[3] Niederist, *ib.* clxxxvii. 391.

[4] *Ann. Chem. Pharm.* cxxxvi. 40.

the iodide with bromine. It boils between 61° and 63°, and at 13° has a specific gravity of 1·320 (Linnemann).

The remarkable conversion of the primary into the secondary bromide by contact with aluminium bromide has already been mentioned.[1]

Isopropyl Iodide, C_3H_7I. The preparation of this compound has already been described. It boils at 89°, and has a specific gravity at 0° of 1·735 (Erlenmeyer). It has already been stated that this iodide can be readily converted into propane, which may in its turn be transformed, at any rate partially, into the primary chloride. It is thus seen that it is possible to pass from the secondary compounds to the primary series, and *vice versâ*.

Isopropyl Nitrite, $C_3H_7NO_2$, is formed, together with secondary nitro-propane, by the action of silver nitrite on the iodide. It is an easily inflammable liquid which boils at 45°.[2]

Isopropyl Nitrate, $C_3H_7NO_3$, was obtained by Silva by acting with isopropyl iodide upon silver nitrate. It is a liquid boiling at 101°—102°, and having at 0° a specific gravity of 1·054. It is easily inflammable, burning with a white luminous flame, and its superheated vapour explodes violently when ignited.

Isopropyl Borate, $B(OC_3H_7)_3$, is obtained by heating the alcohol with boron trioxide to 110°—120°. It is a mobile liquid, resembling ethyl borate, and boiling at 140°.[3]

Isopropyl Acetate, $C_3H_7.OC_2H_3O$, is a liquid possessing a smell resembling acetic ether, and boiling at 90°—93°.

COMPOUNDS OF ISOPROPYL WITH SULPHUR.

361 These are obtained by processes similar to those described under the corresponding ethyl compounds. The mercaptan, C_3H_7SH, boils at 45°, and the sulphide, $(C_3H_7)_2S$, at 105°. This latter forms with mercuric chloride the compound $(C_3H_7)_2S,HgCl_2$, crystallizing in white needles.[4]

COMPOUNDS OF ISOPROPYL WITH NITROGEN.

362 *Isopropylamine*, $C_3H_7NH_2$, is formed by the action of ammonia upon the iodide[5] or nitrate,[6] or by the action of hydrochloric

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[1] Kekulé and Schrötter, *Ber. Deutsch. Chem. Ges.* xii. 2279.

[2] Silva, *Bull. Soc. Chim.* xii. 227; V. Meyer, *Ann. Chem. Pharm.* clxxi. 39.

[3] Councler, *Ber. Deutsch. Chem. Ges.* xi. 1107.

[4] Henry, ib. ii. 496.

[5] Siersch, *Ann. Chem. Pharm.* cxlviii. 261.

[6] Silva, *Bull. Soc. Chim.* xii. 228.

acid on isopropyl carbamine. It is a mobile liquid, which has a sharp characteristic smell resembling herring-brine. It boils at 31°·5—32°·5, and at 18° has a specific gravity of 0·690.

Di-isopropylamine, $(C_3H_7)_2NH$, boils at 83°·5—84°, and has a specific gravity of 0·722 at 22°.

Tri-isopropylamine has not yet been obtained in the pure state.

Isopropyl Carbamine, $CN.C_3H_7$, is formed by heating the iodide with silver cyanide. It is a liquid boiling at 87°, and possessing an ethereal smell which afterwards becomes offensive and bitter.[1]

Isopropyl Cyanate, C_3H_7OCN, is a liquid boiling at 74°·5, and possessing at 0° a specific gravity of 0·8897, whilst that of the vapour is 2·944.[2]

Isopropyl Thiocyanate, C_3H_7SCN, is formed by heating the iodide with potassium thiocyanate, and is a liquid possessing an alliaceous smell and boiling at 149°—151° (Henry).

NITRO-COMPOUNDS OF ISOPROPYL.

363 *Secondary Nitropropane*, or *Pseudonitropropane*, $(CH_3)_2CHNO_2$, is formed, together with isopropyl nitrite, by acting with the iodide on silver nitrite. It is a liquid resembling primary nitropropane, but boiling at 115°—118°, and being a little heavier than water. Heated with alcoholic soda, the crystalline compound $(CH_3)_2CNaNO_2$ separates out, and this deflagrates on heating. It deliquesces on exposure to moist air, and its solution gives precipitates with the various metallic salts.[3]

If pseudonitropropane be dissolved in an equivalent quantity of strong caustic potash, and the requisite amount of bromine added, *brompseudonitropropane*, $(CH_3)_2CBrNO_2$, separates out. This is a heavy powerfully refracting oily liquid, which possesses a very strong smell and boils at 148°—150°, and does not possess acid properties.

Propylpseudonitrol, $(CH_3)_2C(NO)NO_2$. In order to prepare this compound, pseudonitropropane is dissolved in caustic potash, rather more than one molecule of potassium nitrite in aqueous solution added, and a slow stream of dilute sulphuric acid allowed slowly to flow into this mixture, the whole being cooled. The

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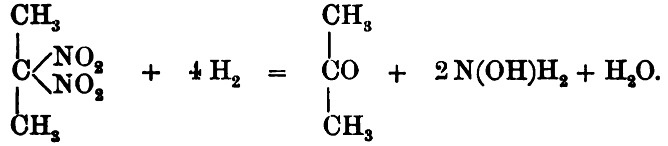
[1] *Compt. Rend.* lxvii. 723; *Ann. Chem. Pharm.* cxlix. 155.
[2] Silva, *Dict. Chim.* iii. 158 (*loc. cit.*).
[3] V. Meyer, *Ann. Chem. Pharm.* clxxi. 39.

liquid soon becomes of a fine blue colour, and the nitrol separates out as a solid mass insoluble in water, alkalis, and acids. It is slightly soluble in cold alcohol and chloroform, but readily so when warmed, giving rise to a pure blue-coloured solution, from which the compound separates out on evaporation in transparent crystals resembling those of calc-spar, but belonging to the monoclinic system.[1]

Propylpseudonitrol melts at 76°, forming a blue liquid which on rapid cooling again solidifies, but decomposes when heated for some time with evolution of red fumes, another product, *β-dinitropropane*, $(\mathrm{CH_3})_2\mathrm{C}(\mathrm{NO_2})_2$, being formed. This is also produced when the pseudonitrol is treated with a solution of chromium trioxide in glacial acetic acid. This body is slightly soluble in water and dissolves readily in alcohol, forming bright white translucent crystals which closely resemble camphor. They melt at 53°, and volatilize easily even at the ordinary temperature, as well as in presence of aqueous vapour, although the body does not boil until 185°·5. It does not possess acid properties, and when treated with tin and hydrochloric acid yields acetone and hydroxylamine:



$$\begin{matrix}\mathrm{CH_3}\\ | \\ \mathrm{C}\begin{matrix}\diagup\mathrm{NO_2}\\ \diagdown\mathrm{NO_2}\end{matrix}\\ | \\ \mathrm{CH_3}\end{matrix} + 4\,\mathrm{H_2} = \begin{matrix}\mathrm{CH_3}\\ | \\ \mathrm{CO}\\ | \\ \mathrm{CH_3}\end{matrix} + 2\,\mathrm{N(OH)H_2} + \mathrm{H_2O}.$$

Compounds of Isopropyl with Phosphorus.[2]

364 *Isopropyl Phosphine*, $(\mathrm{C_3H_7})\mathrm{PH_2}$, is a strongly refracting liquid, possessing a penetrating smell, boiling at 41°, and taking fire at the summer temperature on exposure to air. Its vapour has a specific gravity of 2·673. When oxidized with nitric acid *isopropyl phosphinic acid*, $\mathrm{C_3H_7PO(OH)_2}$, is formed. This is a solid paraffin-like mass, which melts at 60°—70°.

Di-isopropylphosphine, $(\mathrm{C_3H_7})_2\mathrm{PH}$, boils at 118°, possesses an intense phosphine smell, and is much more readily ignited than the foregoing compound. If a drop be brought on to filter-paper it inflames at once, and burns with evolution of a dense white luminous vapour without igniting the paper.

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[1] V. Meyer, *Liebig's Ann.* clxxv. 120; clxxx. 144.

[2] Hofmann, *Ber. Deutsch. Chem. Ges.* vi. 292 and 304.

Tri-isopropylphosphine, $(C_3H_7)_3P$, closely resembles the corresponding ethyl compound, and forms a crystalline hydriodide. It likewise yields with carbon disulphide fine red crystals, and also unites with sulphur, but the compound thus formed is not crystalline.

Tetra-isopropylphosphonium Iodide, $P(C_3H_7)_4I$, crystallizes from water in cubes or octohedrons.

ACETONE, OR DIMETHYL KETONE,

$(CH_3)_2CO$.

365 In early times it was noticed that when sugar of lead is subjected to dry distillation, a peculiar liquid is formed which Libavius termed the quintessence of this salt. Boyle supposed that it is formed from the vinegar, this giving up some of its constituents to the lead. He also noticed that when potassium acetate is distilled, a spirituous liquid possessing a strong smell and taste is formed. Becher, who first observed the inflammability of the substance obtained from sugar of lead, thought that the *spiritus ardens* was in fact spirit of wine which had been regenerated; and Lemery, as well as Stahl, believed that vinegar is a compound of spirit of wine and acid, the former being carried away with the acids into the pores of lead,[1] and the latter being held back by the metal during the process of distillation. The difference between this combustible spirit and alcohol was first pointed out by Boerhaave in 1732. After his time the body was but little investigated until 1805, when Trommsdorff stated that on distilling acetate of potash or soda a liquid was obtained which stands between alcohol and ether. Two years later the brothers Derosne, in Paris, examined the liquid which was obtained, mixed with acetic acid, in the distillation of acetate of copper, and as the liquid appeared to them closely to resemble the various compound ethers, they termed it *éther pyroacétique*.[2] Lastly Chenevix found, in 1809, that the same compound is obtained when any one of the acetates is distilled, and he gave to it the name of pyroacetic spirit, and believed

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[1] Lemery, *A Course of Chemistry*, translated by Keili, 1698, p. 140.

[2] *Ann. Chim.* lxiii. 267.

that it contained less oxygen than acetic acid.[1] Various other chemists also worked upon this subject.[2]

The correct composition of the compound we now term acetone was first given by Liebig[3] and Dumas.[4] Kane[5] investigated it carefully, and came to the conclusion that it was an alcohol, giving to it the name of mesityl alcohol. Chancel,[6] on the other hand, believed it to be a copulated compound, and having the formula C_2H_4O,CH_2.

After Williamson had ascertained the constitution of the ketones, acetone was looked upon as being methyl acetyl, or aldehyde (acetyl hydride) in which one atom of hydrogen had been replaced by methyl. This view was corroborated by the synthesis of acetone, accomplished by the action of zinc-methyl on acetyl chloride, a reaction suggested by Chiozza,[7] but carried out by Freund.[8] As, however, the radical acetyl itself may be considered to be composed of the groups carbonyl and methyl, the present view respecting the composition of acetone, as also of all ketones, is that these are compounds of two alcohol-radicals with carbonyl. A further corroboration of this view was given by Wanklyn,[9] who observed that propione, or diethyl ketone, is formed by the action of carbon monoxide on sodium-ethyl.

It has already been stated that acetone is formed by the dry distillation of the acetates. According to Liebig,[10] the barium salt is best suited for this purpose, as it decomposes at a comparatively low temperature, and hence the formation of tarry products which occurs when the calcium or the lead salt is used is avoided.

Acetone is also formed, together with other products, when the vapour of acetic acid is passed through a red-hot tube:

$$2\,CH_3.CO.OH = CH_3.\,CO.CH_3 + CO_2 + H_2O.$$

It is likewise formed by acting on aldehyde with heated caustic potash,[11] as well as by the dry distillation of the following substances together with lime, viz. citric, tartaric, and lactic acids, sugar, gum, starch, &c.

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[1] Nicholson's *Journ.* xxvi. 225, 340.

[2] Macaire and Marcet, *Bib. Univ.* xxiv. 126; *Quart. Journ. Science*, xvii. 171; Matteucci, *Ann. Chim. Phys.* [2], xlvi. 429.

[3] *Ann. Pharm.* i. 223.

[4] *Ann. Chim. Phys.* [2], xlvii. 203.

[5] *Pogg. Ann.* xliv. 473; *Trans. Irish Acad.* xviii. 134 (1838).

[6] *Compt. Rend.* xx. 1590.

[7] *Ann. Chem. Pharm.* lxxxv. 232.

[8] *Ib.* cxviii. 1.

[9] *Phil. Mag.* [4], xxxi. 505.

[10] *Loc. cit.*

[11] Schlömilch, *Zeitsch. Chem.* 1869, 336.

It is contained in large quantity in the products of the dry distillation of wood, and is obtained from this on the large scale (see p. 196). It was also formerly obtained as a by-product in the preparation of aniline,[1] by the action of acetic acid and iron on nitrobenzol and the distillation of the product with lime. At present, however, hydrochloric acid is used in place of acetic acid, and the crude aniline contains no acetone.

Acetone is found in the urine in cases of *diabetes mellitus.*[2] Geuther believes that in these cases it is derived from the decomposition of aceto-acetic acid,[3] but this has not been proved.

Properties.—Acetone is a colourless mobile liquid, possessing a penetrating, refreshing, ethereal smell and a burning taste. It boils at 56°·3 (Regnault), and has a specific gravity at 0° of 0·8144 (Kopp), that of its vapour being 2·002 (Dumas). It is soluble in water, and acts as a solvent for many other carbon compounds, such as fats, resins, camphors, &c.

When shaken with a concentrated solution of hydrogen sodium sulphite, acetone deposits the compound $C_3H_6O+NaHSO_3$, in pearly scales, easily soluble in water, and less so in alcohol. The sulphites of potassium and ammonium form similar compounds. This process may be employed for purifying acetone, the crystals being distilled with potash.

366 *Monochloracetone*, $CH_3.CO.CH_2Cl$, was first prepared by Riche,[4] by the electrolysis of a mixture of acetone and hydrochloric acid, and then more fully investigated by Linnemann,[5] who obtained it by acting with hypochlorous acid in presence of mercuric oxide on monobrompropylene, $CH_3.-CBr{=}CH_2$. It is also formed when pure acetone is treated with chlorine, but not to saturation,[6] as well as by the action of sulphuric acid on dichlorglycide, $CHCl_2-CCl{=}CH_2$[7] (see Glycerin). It is a strongly smelling, pungent, caustic liquid. It boils at 119°—120°, and at 16° has a specific gravity of 1·16, that of its vapour being 3·13. When brought in contact with potassium iodide, *monoiodoacetone*, $CH_3.CO.CH_2I$, is formed, a heavy oily liquid which cannot be distilled without decomposition.

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[1] G. Williams, *Chem. News*, ii. 231.

[2] Petters, Kaulich, and Betz, *Schmidt*, *Jahrb. Ges. Med.* cxii. 145; Markownikoff, *Liebig's Ann.* clxxxii. 362.

[3] *Zeitsch. Chem.* 1868, 5.

[4] *Compt. Rend.* xlix. 176.

[5] *Ann. Chem. Pharm.* cxxxiv. 170; cxxxviii. 122.

[6] Glutz and Fischer, *Journ. Prakt. Chem.* [2], iv. 52; Bischoff, *Ber. Deutsch. Chem. Ges.* v. 863, 963; Mulder, *ib.* 1007.

[7] Henry, *ib.* 965.

Dichloracetone, $C_3H_4Cl_2O$, exists in two isomeric conditions; the one obtained by Liebig and Kane, and termed by the latter chemist *mesilchloral*, was afterwards investigated by Fittig.[1] It is formed when acetone is saturated with chlorine or when potassium chlorate is added to a solution of acetone in hydrochloric acid.[2] The crude dichloracetone is a very caustic body, possessing a pungent smell, due, however, to an impurity. When purified by repeated fractional distillation it is obtained in the form of a pleasantly ethereal smelling liquid,[3] boiling at 120°, this is, singularly enough, at the same temperature at which monochloracetone boils. It has a specific gravity of 1·236 at 21°, and its vapour density is 4·32.

The constitution of dichloracetone is represented by the formula $CH_3.CO.CHCl_2$, for an isomeric compound is obtained by oxidizing dichlorhydrin (dichlorisopropyl alcohol), $CH_2Cl.CH(OH).CH_2Cl$, and accordingly has the following constitution, $CH_2Cl.CO.CH_2Cl$. It is a solid body, crystallizing in long needles, fusing at 43°. The liquid boils at 170°—171°, but evaporates at the ordinary temperature. It possesses an excessively pungent odour, the vapour attacking the eyes violently.[4]

Trichloracetone, $C_3H_3Cl_3O$, was first prepared by Bouis,[5] by the action of chlorine on a mixture of acetone and wood-spirit. Krämer[6] afterwards obtained it by treating a mixture of acetone and isobutyl aldehyde with chlorine. It is also formed, according to Bischoff, when moist chlorine is led into warmed acetone in presence of sunlight. It boils at 170°—172°, possesses a sharp smell, and yields, with water, the hydrate, $C_3H_3Cl_3O + 2H_2O$, crystallizing in fine tables which melt at 43°. When mixed with aniline and caustic potash an intense smell of phenyl carbamine is produced, and hence the constitution of the substance is $CH_3.CO.CCl_3$ or methyl-chloral.

Tetrachloracetone, $C_3H_2Cl_4O$, is produced by the action of chlorine on a mixture of acetone and ethyl alcohol. It is a liquid possessing a very strong and irritating smell, and, when brought in contact with water, it yields the crystalline hydrate $C_3H_2Cl_4O + 4H_2O$, melting at 38°—39°. As this also gives the carbamine reaction it possesses the formula $CH_2Cl.CO.CCl_3$.

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[1] *Ann. Chem. Pharm.* cx. 23.

[2] Städeler, *ib.* cxi. 277.

[3] Borsche and Fittig, *Ann. Chem. Pharm.* cxxxiii. 111.

[4] Markownikoff, *Ber. Deutsch. Chem. Ges.* iv. 562 ; vi. 1210 ; Glutz and Fischer, *Journ. Prakt. Chem.* [2], iv. 25 ; Von Hoermann, *Ber. Deutsch. Chem. Ges.* xiii. 1306.

[5] *Ann. Chim. Phys.* [3], xxi. 111.

[6] *Ber. Deutsch. Chem. Ges.* vii. 257.

Pentachloracetone, $CHCl_2.CO.CCl_3$, has not been obtained as yet from acetone, but it can be prepared by the action of chlorine on quinic acid and other aromatic compounds, as well as on albuminoid bodies and other substances. It is a mobile liquid boiling at 190°, and possessing a sharp taste, and a smell resembling that of chlorine. It forms a hydrate, $C_3HCl_5O + 4H_2O$, which melts at 15°—17°.[1]

Hexchloracetone, $CCl_3.CO.CCl_3$, is formed by the action of chlorine on an aqueous solution of citric acid exposed to the sunlight. It is an oily, pungent smelling liquid, boiling at 200°—201°, and forming with water, at 6°, the hydrate $C_3Cl_6O + H_2O$, which decomposes at 15°.[2]

Various bromine and iodine substitution-products of acetone are also known.

Nitroso-acetone is produced by the action of potassium nitrite on an alkaline solution of aceto-acetic ether which is acidified with sulphuric acid and then saturated with potash. After some days dilute sulphuric acid is added, and the compound, is extracted with ether. It is a product of decomposition of the compound nitro-aceto-acetic acid which will be described further on:

$$CH_3.CO.CH(NO).CO.OC_2H_5 + H_2O = CH_3.CO.CH_2(NO) + CO_2 + HO.C_2H_5.$$

Nitroso-acetone is easily soluble in water, and crystallizes in glistening tablets or prisms, which melt at 65°, and decompose easily at a higher temperature, but may be volatilized in a current of steam. It is an acid which dissolves in alkalis with formation of a deep yellow colour.[3]

CONDENSATION-PRODUCTS OF ACETONE.

367 Acetone forms a series of condensation-products. Some of these have been known for a long time and have been investigated by various chemists. We shall here describe only the better known of these bodies. Hygroscopic agents give rise to the following compounds:

Mesityl oxide . . .	$C_6H_{10}O$.
Phorone	$C_9H_{14}O$.
Mesitylene	C_9H_{12}.

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[1] Städeler, *Ann. Chem. Pharm.* cxi. 277.

[2] Plantamour, *ib.* xxxi. 326.

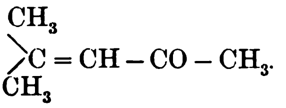
[3] Meyer and Züblin, *Ber. Deutsch. Chem. Ges.* xi. 692.

Of these, the least is a trimethyl-benzol, and will be described later on.

Mesityl Oxide, $C_6H_{10}O$. This body was discovered in 1838 by Kane.[1] He obtained it by acting on acetone with sulphuric acid or hydrochloric acid. The latter mode of preparation is recommended by Baeyer[2] as the best. Acetone is saturated in the cold with this gas, and then allowed to stand for some weeks, and the product afterwards washed with water and caustic soda. It is distilled in a current of steam, and the distillate, which still contains chlorine, treated with a small quantity of alcoholic potash and mesityl oxide and phorone obtained from the washed and dried product.[3]

Mesityl oxide is a mobile liquid smelling of peppermint, boiling at 132°, and acting like acetone. On oxidation it yields acetic acid, and when treated with phosphorus pentachloride yields a heavy liquid dichloride, $C_6H_{10}Cl_2$, which decomposes on heating. It combines with bromine to form the compound $C_6H_{10}Br_2O$, resembling the foregoing compound. When heated with dilute sulphuric acid it decomposes with assumption of water into two molecules of acetone.

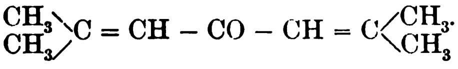
From these facts it would appear that mesityl oxide possesses the following constitution:



$$(CH_3)_2C = CH - CO - CH_3.$$

Phorone, $C_9H_{14}O$, crystallizes in large yellow prisms, which melt at 28° and boil at 190°—191°. It possesses a smell somewhat like that of geranium and not unpleasant, producing in many persons headache and sickness. In its chemical properties it resembles mesityl oxide. It is converted by oxidation into acetic acid, and bromine converts it into the tetrabromide, $C_9H_{14}Br_4O$, which crystallizes from alcoholic solution in colourless transparent flat monoclinic prisms which melt at 88°—89°.

When boiled with dilute sulphuric acid it decomposes first into acetone and mesityl oxide; its constitution may, therefore, be represented by the following formula, and this is corroborated by its formation from triacetonamine (see p. 574):



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C = CH - CO - CH = C<\!\!\begin{matrix}CH_3.\\CH_3\end{matrix}$$

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[1] *Trans. Roy. Irish Acad.* 1838 ; *Pogg. Ann.* xliv. 473.

[2] *Ann. Chem. Pharm.* cxl. 297.

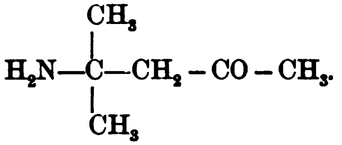
[3] Claisen, *ib.* clxxx. 1.

ACETONE BASES.

368 According to Städeler,[1] the base *acetonine*, $C_9H_{18}N_2$, is formed when a mixture of ether and acetone is saturated with ammonia at 100°. Heintz states that this base does not exist. He obtained a series of different bases[2] which have also been investigated by Sokoloff and Latschinoff.[3] These bases may be separated by means of their platinum double chlorides.

Diacetonamine, $C_6H_{13}NO$, is a colourless liquid, difficult to obtain in a pure state, as it partially decomposes on distillation into ammonia and mesityl oxide. With acids, it forms, however, a series of stable salts which crystallize well. When it is treated with potassium nitrite, mesityl oxide is formed, whilst sodium amalgam yields *diacetone alkamine*, $C_6H_{15}NO$, a liquid possessing a slightly ammoniacal smell, and boiling at 174°—175°.

Diacetonamine probably possesses the following constitutional formula:



$$\begin{array}{c} \quad\;\; CH_3 \\ \quad\;\; | \\ H_2N-C-CH_2-CO-CH_3. \\ \quad\;\; | \\ \quad\;\; CH_3 \end{array}$$

This is rendered more likely by the fact that on oxidation it yields amidodimethyl acetic acid and amidodimethyl propionic acid.

Triacetonamine, $C_9H_{17}NO$, separates out as a hydrate, $C_9H_{17}NO + H_2O$, on addition of caustic soda to the oxalate, and this crystallizes from ether in large rhombic tables which melt at 58°. The anhydrous base is obtained ftom the mother-liquors in the form of long needles which melt at 34°·6.

Triacetonamine volatilizes easily at the ordinary temperature, and can be distilled without decomposition. Its salts are also very stable. By the action of potassium nitrite on the neutral solution of the hydrochloride, *nitrosotriacetonamine*, $C_9H_{16}(NO)NO$, is obtained, and this substance is easily soluble in alcohol and hot water, crystallizing in needles which melt at 72°—73°. When warmed with caustic potash, phorone is produced.

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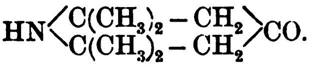
[1] *Ann. Chem. Pharm.* cxi. 277.

[2] *Ann. Chem. Pharm.* clxxiv. 133; clxxviii. 305, 326; clxxxi. 70; clxxxiii. 276, 290; clxxxix. 214; cxci. 122; cxcii. 339; cxciv. 53; cxcviii. 42.

[3] *Ber. Deutsch. Chem. Ges.* vii. 1384.

When triacetonamine is treated with sodium amalgam and water, *triacetonalkamine*, $C_9H_{19}NO$, is produced; this crystallizes from hot water in pyramids which easily volatilize, melt at 128°·5, and have a sweet burning taste.

Triacetonamine on oxidation yields the dibasic *imidodimethylacetodimethyl-propionic acid*, $C_7H_{14}(NH)(CO_2H)_2$. From this fact, and from the other reactions of the base, the following constitution may be deduced:



$$HN\left\langle\begin{matrix}C(CH_3)_2-CH_2\\C(CH_3)_2-CH_2\end{matrix}\right\rangle CO.$$

Other compounds belonging to this class have been prepared by Heintz. For their description the memoirs already cited must be referred to.

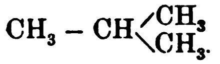
COMPOUNDS OF FOUR ATOMS OF CARBON, OR THE BUTYL GROUP.

369 THESE compounds are derived from the following paraffins:

Butane.

$CH_3 - CH_2 - CH_2 - CH_3.$

Isobutane.



$CH_3 - CH\begin{matrix}/CH_3\\ \backslash CH_3.\end{matrix}$

Four alcohols are derived from these; from butane, in the first place, one primary and one secondary; and secondly, from isobutane, one primary and one tertiary alcohol. One of these was discovered by Wurtz, in 1852, in fusel oil from potato spirit, and from beetroot molasses. This exhibits a striking analogy in its reactions with common alcohol, and, on oxidation, yields an acid which has the composition of butyric acid. Hence this alcohol was supposed to possess a constitution analogous to that of ethyl alcohol, especially as at that time even the existence of isomeric alcohols was not dreamt of. Still its low boiling-point was an anomaly, for Hermann Kopp had found that in the homologous series of alcohols, for every increment of CH_2, the boiling-point rises 19°. and hence butyl alcohol ought to boil at 116°, whereas various observers agreed that it boiled constantly at 108°—109°. In 1867 Erlenmeyer found that the butyric acid got by this oxidation is not common butyric, but isobutyric acid, $(CH_3)_2CH.CO_2H$, a body which had been obtained synthetically from secondary propyl-iodide by conversion into the nitril, and thus it appeared that fermentation butyl alcohol is derived from isobutane.

A second butyl alcohol was discovered in 1863, by De Luynes, and to it he gave the name of butylene hydrate, because it is so easily converted into butylene and water, and can also be readily obtained from butylene. This was soon recognised as being the secondary alcohol.

About the same time Butlerow prepared the tertiary alcohol by synthesis, whilst the normal primary alcohol was first prepared by Lieben and Rossi, in 1869, by the reduction of butyric acid.

NORMAL BUTANE AND ITS DERIVATIVES.

370 *Butane* or *Tetrane*, C_4H_{10}, was first prepared by Frankland in 1849, by acting with zinc[1] or mercury[2] on ethyl iodide. He termed it *ethyl*, a name which was afterwards changed to *diethyl* in order to distinguish it from butyl hydride, which Wurtz had obtained from alcohol, and which, as we now know, is isobutane.

In order to prepare pure butane, ethyl iodide, dried over phosphorus pentoxide, is heated in sealed tubes, with the requisite quantity of clean zinc, to 150°. An excess of this metal must be avoided, as otherwise zinc-butyl would be formed. According to Schöyen,[3] the zinc is best employed in the form of thin strips, and the ethyl iodide mixed with its equal volume of pure ether. After the mixture has been heated to 100°, the point of the tube is opened in the flame in order to allow the ethane to escape; this gas being formed in large or small quantity, according to the care which is taken in drying the materials. The tube is then again sealed, and heated for several hours to 130°—140°. It is then cooled with ice-water, and the point opened, when a mixture of ethane and ethylene is evolved. The cold water is now removed, and the regular stream of gas which is evolved collected over mercury. The butane thus obtained may still contain small quantities of the two other hydrocarbons, as well as of ethyl iodide. This latter, as well as the ethylene, can be removed by drying the gas with a coke pellet, saturated with fuming sulphuric acid. Pure butane is obtained after washing with caustic potash, and drying. It may, however, still contain a trace of ethane.

Butane occurs in American petroleum (see p. 140), and it is also produced when butyric acid and succinic acid are heated with from twenty to thirty times their weight of hydriodic acid

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[1] *Journ. Chem. Soc.* ii. 263; *Ann. Chem. Pharm.* lxxi. 171.
[2] *Journ. Chem. Soc.* iii. 322; *Ann. Chem. Pharm.* lxxvii. 221.
[3] *Ann. Chem. Pharm.* cxxx. 233.

for some hours to 280°.[1] Butane is a colourless gas, which can easily be condensed by cold to a liquid, which boils at + 1°, and has a specific gravity of 0·6. Under a pressure of 2·25 atmospheres the gas liquefies at 18° (Butlerow). The specific gravity of butane gas is 2·046. It is almost insoluble in water, whilst absolute alcohol dissolves at 14°·2, and under a pressure of 744·8 mm., 18·13 volumes.

In diffused daylight chlorine acts upon butane with formation of substitution-products, amongst which butyl chloride occurs. This compound is, however, not obtained pure in this way, but its presence is ascertained by transforming it into butyric acid (Schöyen). Carius obtained dibrombutane, a liquid boiling between 155° and 162°, by the action of bromine on butane.[2]

PRIMARY BUTYL COMPOUNDS.

371 *Primary Butyl Alcohol,* C_4H_9OH. In order to prepare this compound an aqueous solution of butyraldehyde obtained by distilling a mixture of calcium formate and calcium butyrate, is treated with 1 per cent. sodium amalgam, of which about 70 times the volume is needed. This is gradually added, the liquid being kept slightly acid by the addition of dilute sulphuric acid. The whole is then distilled, and the alcohol dried, first over ignited carbonate of potash, and then over caustic baryta.[3]

In the above method of preparing the aldehyde a not inconsiderable quantity of the alcohol is formed, a part of the formate being decomposed with evolution of hydrogen.[4]

Butyl alcohol is also formed by the action of sodium amalgam on butyric anhydride diluted with butyric acid.[5]

$$(C_4H_7O)_2O + 4\ H_2 = 2\ C_4H_9OH + H_2O.$$

In place of the anhydride, a mixture of butyryl chloride and butyric acid may be employed;[6] but, as in the former reaction, this does not give a good yield. On the other hand it is formed, together with other products, in tolerable quantity, by a peculiar

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[1] Berthelot, *Bull. Soc. Chim.* vii. 62.

[2] *Ann. Chem. Pharm.* cxxvi. 214.

[3] Lieben and Rossi, *Ann. Chem. Pharm.* clviii. 137.

[4] Pagliani, *Ber. Deutsch. Chem. Ges.* x. 2055.

[5] Linnemann, *Ann. Chem. Pharm.* clxi. 180.

[6] Saytzeff, *Journ. Prakt. Chem.* [2], iii. 82.

fermentation of glycerin,[1] brought about in the presence of a schizomycetes. It has also been found in the fusel oil from potato spirit.[2]

Butyl alcohol is a highly refracting, somewhat oily liquid, possessing a peculiar smell, which excites coughing. It boils at 117°, and burns with a luminous flame. At 0° it has a specific gravity of 0·8242, and dissolves in 12 parts of water, but is separated on addition of calcium chloride. Its derivatives are obtained in an analogous manner to the corresponding ethyl compounds, from which they are chiefly distinguished by their higher boiling-points.

Butyl-ethyl Oxide, $O\left\{\begin{array}{l}C_4H_9\\C_2H_5\end{array}\right.$, is formed by the action of butyl iodide on sodium ethylate, and is a mobile liquid boiling at 91°·7, and having a specific gravity at 6° of 0·7694. In the formation of this ether, α-butylene and ethyl alcohol are also formed:

$$C_4H_9I + C_2H_5ONa = NaI + C_2H_5OH + C_4H_8.$$

In order to remove the alcohol it must be rectified over powdered calcium chloride.

Dibutyl Oxide, $(C_4H_9)_2O$, is obtained in a similar way to the foregoing compound. Butylene is always evolved in its preparation, and secondary butyl alcohol is produced, which may be separated by distillation over sodium. Dibutyl ether boils at 140°·5, and has a specific gravity of 0·784.

Butyl Chloride, C_4H_9Cl, is obtained by heating the alcohol with hydrochloric acid, or the iodide with corrosive sublimate. It boils at 77°·6, and has at 0° a specific gravity of 0·9074.

Butyl Iodide, C_4H_9I, boils at 129°·6, and has at 0° the specific gravity 1·643. This body serves for the preparation of other butyl compounds, because it can be prepared from impure butyl alcohol, and the impurities can be easily got rid of by fractional distillation, whereas they are only removed from the alcohol with considerable difficulty.

The other ethers of primary normal butyl have been but slightly investigated. The alcohol dissolves in sulphuric acid, with formation of a very stable acid sulphate, which yields an easily soluble barium salt, $(C_4H_9SO_4)_2Ba + H_2O$, crystallizing in tablets.

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[1] Fitz, *Ber. Deutsch. Chem. Ges.* x. 278.
[2] Rabuteau, *Compt. Rend.* lxxxvii. 500.

Butyl Carbonate, $(C_4H_9)_2CO_3$, is formed, together with butylene and butyl oxide, by heating the iodide with silver carbonate. It is a pleasantly smelling liquid boiling at 207°.

Sulphur Compounds of Butyl. These are obtained from the corresponding potassium salts by treating them with an alcoholic solution of butyl iodide. They are mobile liquids possessing an unpleasant smell:[1]

	B.P.	Sp. Gr. at 0°.
Butyl hydrosulphide, C_4H_9SH	97°-98°	0·856
Butyl sulphide, $(C_4H_9)_2S$	182°	0·8523

Nitrogen Bases. These are obtained from the chloride by heating it with potassium cyanate and alcohol, when a solution of the carbimide is first obtained, and this is then boiled with caustic potash. The liquid obtained by distilling the product is saturated with hydrochloric acid and evaporated, and the residue distilled with lime. The distillate boils between 76° and 208° and is a mixture of three bases, of which the primary one is easily obtained pure by fractional distillation. *Butylamine*, $C_4H_9NH_2$, boils at 75°·5, has at 0° a specific gravity of 0·7553, fumes in the air, and is very hygroscopic, and its vapour easily attacks caoutchouc and cork (Lieben and Rossi).

Cyanogen Compounds. Of these the only one which is known is the mustard-oil, $CS.NC_4H_9$, a liquid boiling at 167°, and yielding a thio-urea which melts at 79°.[2]

Nitro-compounds of Primary Butyl. Normal primary nitrobutane, $C_4H_9NO_2$, is obtained by the action of silver nitrite on well-cooled butyl iodide. At the same time butyl nitrite, which has not been specially investigated, is produced. Primary nitrobutane boils at 151°—152°, and possesses the characteristic properties of the primary nitro-paraffins, but it is only a weak acid. It yields substitution products with bromine. The monobrom-compound yields, like bromnitroethane, *dinitrobutane*, $C_4H_8(NO_2)_2$, by the action of nitrous acid. This is a rather sweetly smelling liquid which decomposes on heating. It is a monobasic acid; the potassium salt forms golden-yellow tablets, and the silver salt crystallizes from hot water, in large deep-yellow scales, which exhibit a bluish-violet colour by reflected light. Neither of these salts is explosive.[3]

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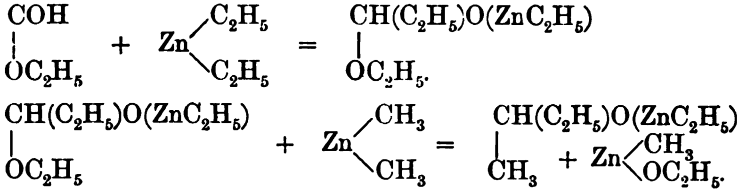
[1] Grabowsky and Saytzeff, *Ann. Chem. Pharm.* clxxi. 251.
[2] Hofmann, *Ber. Deutsch. Chem. Ges.* vii. 511.
[3] Züblin, *Ber. Deutsch. Chem. Ges.* x. 2083.

SECONDARY BUTYL COMPOUNDS.

372 *Methyl-ethyl Carbinol*, $CH_3(C_2H_5)CH.OH$, was first prepared by De Luynes.[1] He obtained the iodide by heating erythrite with hydriodic acid, and converted this into the acetic ether by the action of silver acetate, and then decomposed this by caustic potash.

Butlerow and Ossokin prepared it from ethylene-iodhydrin, $C_2H_4I(OH)$, and zinc ethyl, when the crystalline compound, $C_2H_4(C_2H_5)O(ZnC_2H_5)$, is produced. This is converted by the action of water into the secondary alcohol, zinc hydroxide and ethane. As the iodhydrin possesses the constitution $ICH_2{-}CH_2OH$, it would be expected that the primary alcohol would be obtained, but this is not the case, as it undergoes molecular interchange during the reaction.

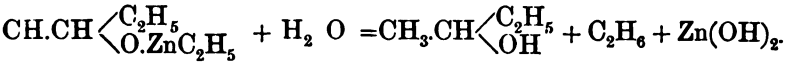
Another synthetic mode of formation was discovered by Kanownikoff and Saytzeff.[3] They found that, when a mixture of equal molecules of ethyl formate, ethyl iodide, and methyl iodide is heated with zinc and some zinc-sodium alloy, an imperfectly crystalline mass is obtained, which is decomposed by water, and thus the products, which have been already described, are obtained. From this it is clear that the product of the reaction contains the same compound as is obtained by the action of zinc-ethyl on ethylene iodhydrin. The formation probably takes place in two phases:



$$\begin{array}{l} COH \\ | \\ OC_2H_5 \end{array} + Zn\begin{array}{l} \diagup C_2H_5 \\ \diagdown C_2H_5 \end{array} = \begin{array}{l} CH(C_2H_5)O(ZnC_2H_5) \\ | \\ OC_2H_5. \end{array}$$

$$\begin{array}{l} CH(C_2H_5)O(ZnC_2H_5) \\ | \\ OC_2H_5 \end{array} + Zn\begin{array}{l} \diagup CH_3 \\ \diagdown CH_3 \end{array} = \begin{array}{l} CH(C_2H_5)O(ZnC_2H_5) \\ | \\ CH_3 \end{array} + Zn\begin{array}{l} \diagup CH_3 \\ \diagdown OC_2H_5. \end{array}$$

The same compound may be still more readily obtained by bringing together anhydrous aldehyde and zinc-ethyl.[4] Its decomposition by water is represented by the following equation:



$$CH.CH\begin{array}{l} \diagup C_2H_5 \\ \diagdown O.ZnC_2H_5 \end{array} + H_2\,O = CH_3.CH\begin{array}{l} \diagup C_2H_5 \\ \diagdown OH \end{array} + C_2H_6 + Zn(OH)_2.$$

This reaction gives a satisfactory yield.

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[1] *Ann. Chim. Phys.* [4], ii. 385; *Ann. Chem. Pharm.* cxxxii. 274. See also Lieben, *Ann. Chem. Pharm.* cl. 106.

[2] *Ann. Chem. Pharm.* cxlv. 257.

[3] *Ib.* clxxv. 374.

[4] G. Wagner, *Ann. Chem. Pharm.* clxxxi. 261.

Properties. Methyl-ethyl carbinol is a pleasantly smelling liquid possessing a burning taste, boiling at 99°, and having at 0° a specific gravity of 0·827. Oxidizing agents convert it first into *methylethylketone*, $CH_3.CO.C_2H_5$, a body which is obtained by various other reactions already mentioned[1] (see p. 182). This is a mobile liquid smelling like common acetone, boiling at 78°, and being converted by further oxidation into two molecules of acetic acid. Like dimethylketone, it yields a nitro-compound, $CH_3.CO.CH(NO)CH_3$, which crystallizes from alcoholic solution in prisms, melts at 74°, and boils at about 186° (Meyer and Züblin).

Secondary Butyl Oxide, $[CH_3(C_2H_5)CH]_2O$. This has not as yet been prepared from the alcohol, but it may be obtained by acting upon aldehyde with hydrochloric acid, when ethidene oxychloride, $(CH_3.CHCl)_2O$, isomeric with dichlorether is obtained, and this, when treated with zinc-ethyl, easily exchanges its chlorine for ethyl, and thus yields the ether, which is a mobile liquid boiling at 120°—121°, and being converted into the secondary iodide on heating with hydriodic acid.

Secondary Butyl Iodide, $CH_3(C_2H_5)CHI$. Erythrite, a body closely allied to the sugars, and occurring in a variety of plants, is the alcohol of a tetrad radical, and it yields the secondary iodide in considerable quantity when heated with an excess of concentrated hydriodic acid, amorphous phosphorus being added to prevent the formation of free iodine:

$$C_4H_6(OH)_4 + 7\,HI = C_4H_9I + 4\,H_2O + 3\,I_2.$$

The same body occurs when ethyl-chlorether is heated with hydriodic acid (see p. 339). It may also be obtained from the primary iodide, as this, when heated with alcoholic caustic potash, yields ethyl-butyl ether and α-butylene, $CH_3—CH_2—CH = CH_2$, which latter readily unites with hydriodic acid to form the secondary iodide.[2] It is a colourless liquid, boiling at 118°, which soon becomes brown on exposure to light.

Sulphur Compounds of Secondary Butyl are obtained from the iodide by reactions which have frequently been described. The mercaptan, $CH_3(C_2H_5)CH.SH$, boils at 84°—85°, and smells like asafœtida, and the sulphide $[CH_3(C_2H_5)CH]_2S$, is an unpleasant alliaceous smelling body, boiling at 165°.[3]

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[1] Fittig, *Ann. Chem. Pharm.* cx. 18; Freund, *ib.* cxviii. 3; Frankland and Duppa, *Chem. Soc. Journ.* xix. 395; *Ann. Chem. Pharm.* cxxxviii. 336; Popoff, *ib.* cxlv. 283; Grimm, *ib.* clvii. 258.

[2] Saytzeff, *Ber. Deutsch. Chem. Ges.* iii. 870.

[3] Reymann, *ib.* vii. 1257.

Secondary Butyl Thiocarbimide, $CS.NCH(C_2H_5)CH_3$. Hofmann has shown that this substance is the chief constituent of the oil of scurvy-grass (from *Cochlearia officinalis*). He obtained it artificially by heating secondary butyl iodide with ammonia, monobutylamine being the chief product, and this, which boils under 120°, can be converted into the mustard-oil by treatment with carbon disulphide and mercuric chloride. It is a sharply smelling liquid, boiling at 159°·5, and yielding, with ammonia, a thio-urea, fusing at 133°.[1] When the mustard-oil is heated with sulphuric acid, a sulphate of a secondary butylamine is obtained, and from this the base can be separated out by potash. It is a liquid, boiling at 63° (Hofmann, Reymann).

Secondary Nitrobutane, $CH_3(C_2H_5)CH(NO_2)$, is formed together with the nitrite and butylene by the action of silver nitrite on the iodide. It is a liquid boiling at 140°, which yields a pseudo-nitrol closely resembling the propyl compound, and fusing with decomposition at 58°.

ISOBUTANE AND ITS DERIVATIVES.

373 *Isobutane* or *Trimethyl Methane*, $(CH_3)_3CH$, was obtained by Butlerow, together with isobutylene, by acting with zinc on tertiary butyl alcohol in presence of water. The isobutylene can be easily removed from the gaseous mixture by means of bromine. Isobutane is a colourless gas which liquefies at −17°.

PRIMARY ISOBUTYL COMPOUNDS.

Isobutyl Alcohol, $(CH_3)_2CH.CH_2OH$, occurs in varying quantities in several fusel-oils, and is especially found in the spirit from beet-root, potatoes, and grain.[2] It is obtained from this by fractional distillation, which, when small quantities are employed, is rather a tedious operation and is not now carried on. The faints are now distilled in a rectifying apparatus, and the isobutyl alcohol separated from the propyl alcohol and other homologues

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[1] *Ber. Deutsch. Chem. Ges.* vii. 508.

[2] Wurtz, *Ann. Chim. Phys.* [3], xlii. 129; Pierre and Puchot, *Bull. Soc. Chim.* xi. 43; Chapman and Smith, *Journ. Chem. Soc.* xxii. 153.

which these faints contain.[1] In order to obtain it perfectly pure it is best to prepare the iodide from the commercial product. This can be readily purified by fractional distillation from the other iodides, and then reconverted into the alcohol.

Isobutyl alcohol is a somewhat mobile liquid possessing a spirituous smell, but at the same time a fusel-oil odour, somewhat resembling that of the flowers of the syringa (*Philadelphus coronarius*). It boils at 108°—109°, and at 0° has a specific gravity of 0·817. At the ordinary temperature it dissolves in 10 parts of water, the greater portion being separated from solution on the addition of calcium chloride, common salt, potash, &c.

Isobutyl alcohol serves as the starting point for the preparation of the various isobutyl compounds, which were first examined by Wurtz, and afterwards by a number of other chemists. They are obtained in a similar way to the ethyl compounds, and, for this reason, it is sufficient to give their chief properties in tabular form.

ETHERS.[2]

	B. P.	Sp. Gr.
Ethyl isobutyl ether, $C_2H_5.O.C_4H_9$,	70°-80°	0·7509 at —
Disobutyl ether, $(C_4H_9)_2O$,	100°-104°	— —

The latter compound has not been obtained quite pure.

ETHERS OF INORGANIC ACIDS.

[3] Isobutyl chloride, C_4H_9Cl,	68°·5	0·8953 at 0°
[4] Isobutyl bromide, C_4H_9Br,	92°·3	1·2490 „ 0°
[5] Isobutyl iodide, C_4H_9I,	120°·6	1·6345 „ 0°
[6] Isobutyl nitrate, C_4H_9NO,	130°	— —
[7] Isobutyl borate, $(C_4H_9)_3BO_3$,	212°	— —
[8] Isobutyl silicate, $(C_4H_9)_4SiO_4$,	256°-260°	0·953 „ 15°
[9] Isobutyl carbonate, $(C_4H_9)_2CO_3$,	190°	— —

ETHERS OF THE FATTY ACIDS.[10]

Isobutyl formate, $C_4H_9O(CHO)$,	98°·5	0·8845 at 0°
Isobutyl acetate, $C_4H_9O(C_2H_3O)$,	116°·5	0·8596 „ 0°
Isobutyl propionate, $C_4H_9O(C_3H_5O)$,	135°·7	0·8926 „ 0°

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[1] *Ber. Entw. Chem. Ind.* ii. 276.

[2] Wurtz, *loc. cit.*

[3] Wurtz; Linnemann, *Ann. Chem. Pharm.* clxii. 17; Pierre and Puchot, *ib.* clxiii. 276.

[4] [5] Wurtz; Linnemann, *ib.* clx. 240.

[6] Wurtz.

[7] Councler, *Journ. Prakt. Chem.* [2], xviii. 382.

[8] Cahours, *Compt. Rend.* lxxvii. 1403.

[9] Wurtz.

[10] Wurtz; Pierre and Puchot, *Ann. Chim. Phys.* [4], xxii. 234.

SULPHUR COMPOUNDS.

	B.P.	Sp. Gr.	at
[1] Isobutyl hydrosulphide, C_4H_9SH,	88°	0·8480	11°·5
[2] Isobutyl sulphide, $(C_4H_9)_2S$,	170°·5	0·8363	10°
Isobutyl trithiocarbonate, $(C_4H_9)_2CS_3$,	285°-290°		

In addition to this thiocarbonate other oxy-thiocarbonates are known.[3]

NITROGEN COMPOUNDS.

[4] Isobutylamine, $(C_4H_9)NH_2$,	67°·5	0·7357	15°
[5] Di-isobutylamine, $(C_4H_9)_2NH$,	135°-137°		
[6] Tri-isobutylamine, $(C_4H_9)_3N$,	184°-186°		
[7] Isobutyl carbamine, $C_4H_9.NC$,	114°-117°	0·7873	4°
[8] Isobutyl thiocyanate, $C_4H_9S.CN$,	174°-176°	—	—
[9] Isobutyl mustard oil, $C_4H_9.NCS$,	161°-163°	—	—
[10] Nitro-isobutane, $C_4H_9NO_2$	137°-140°	—	—

Isobutyl mustard oil forms a thio-carbamide melting at 90°—91°.

Isonitrobutane exhibits the same reactions as its lower homologues, but its nitrolic acid does not crystallize.

PHOSPHORUS COMPOUNDS.[11]

Isobutylphosphine, $C_5H_9.H_2P$,	62°	—	—
Di-isobutylphosphine, $(C_4H_9)_2HP$,	153°	—	—
Tri-isobutylphosphine, $(C_4H_9)_3P$,	215°	—	—

Hofmann has also prepared several mixed butylphosphines.

METALLIC COMPOUNDS.[12]

Zinc-isobutyl, $(C_4H_9)_2Zn$,	185°-188°	—	—
Mercury-isobutyl, $(C_4H_9)_2Hg$,	205°-207°	1·835	15°
Aluminium-isobutyl, $(C_4H_9)_3Al$,	—	—	—

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[1] Humann, *Ann. Chim. Phys.* [3], xliv. 337.

[2] Grabowsky and Saytzeff, *Ann. Chem. Pharm.* clxxi. 253.

[3] Mylius, *Ber.* v. 974 ; vi. 312.

[4] Wurtz ; Linnemann, *Ann. Chem. Pharm.* clxxii. 22 ; Gautier, *ib.* clii. 223 ; Reimer, *Ber. Deutsch. Chem. Ges.* iii. 756.

[5] Ladenburg, *ib.* xii 948.

[6] *Ib.*; Sachtleben, *ib.* xi. 733.

[7] Gautier, *Ann. Chem. Pharm.* clii. 222.

[8] Reimer, *loc. cit.*

[9] Reimer, *loc. cit.*

[10] Demole, *Ann. Chem. Pharm.* clxxv. 142 ; Züblen, *Ber. Deutsch. Chem. Ges.* x. 2087.

[11] Hofmann, *Ber. Deutsch. Chem. Ges.* vi. 292.

[12] Cahours, *Compt. Rend.* lxxvii. 1403 ; Cahours and Demarçay, *ib.* lxxxix. 68.

with formation of the acid ether, and this latter is decomposed by distillation with water into the alcohol and sulphuric acid.[1]

In order to prepare larger quantities of trimethyl carbinol an upright condenser is used, the inner cylinder of which is filled with broken lumps of glass and is closed at the top and bottom with doubly bored caoutchouc stoppers. To the lower stopper is connected a gas-delivery tube which passes into the cylinder to one-third of its height, and through which the isobutylene enters; the second opening of this stopper carries a tube which serves to run off the acid which is produced, and this is provided with a double bend so that the acid forms a liquid joint and prevents the escape of the gas. The holes of the upper stopper carry an outlet tube, and a tap funnel by means of which sulphuric acid of 75 per cent. is allowed to run in. If it is stronger than this, more or less of the isobutylene is converted into polymeric modifications. This also takes place when the temperature rises, and the whole, therefore, must be well cooled, and the acid produced is allowed to run slowly off into a large quantity of cold water. This is then distilled, and a small quantity of oily matter removed from the distillate by filtration, and the liquid shaken up with carbonate of potash and dried a second time over the ignited salt.

The tertiary alcohol is also formed when liquefied isobutylene is shaken up for some time with 50 per cent. sulphuric acid. Even water acidulated with sulphuric acid dissolves the hydrocarbon slowly, but the action then requires months for its completion.[2]

Another mode of formation of the carbinol appears at first sight remarkable. If a mixture of isobutyl iodide and glacial acetic acid be added to moist freshly precipitated oxide of silver, a mixture of trimethyl carbinol, its acetic ether, isobutyl alcohol, and isobutyl acetate is formed, whilst isobutylene is evolved.[3] In this case a part of the isobutyl iodide is converted into hydriodic acid and isobutylene, and this latter combines, apparently in the nascent condition, with water or acetic acid to form the tertiary compounds.

Trimethyl carbinol is also found in small quantities in commercial isobutyl alcohol.[4]

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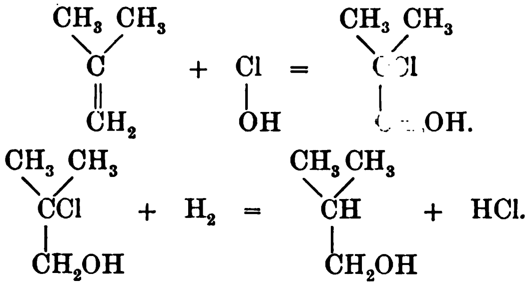
[1] *Zeitsch. Chem.* 1870, 236.

[2] Butlerow, *Ann. Chem. Pharm.* clxxx. 245.

[3] Linnemann, *Ann. Chem. Pharm.* cliv. 130; clxii. 12; Butlerow, *ib.* clxviii. 143.

[4] Butlerow, *Ann. Chem. Pharm.* cxliv. 34.

product of the reaction is isobutylene, and this reaction serves for the purpose of converting the tertiary alcohol into isobutyl alcohol. For this purpose the hydrocarbon is led into a solution of hypochlorous acid, when isobutylene chlorhydrate or monochlorisobutyl alcohol is formed. This, when treated with sodium amalgam and water, yields up its chlorine for hydrogen.[1] The following equations explain this reaction:



Trimethylcarbyl Nitrite, $(CH_3)_3C.O.NO$. Silver nitrite acts very violently on tertiary butyl iodide, and the nitrite, together with a small quantity of tertiary nitrobutane, is formed together with water and the oxides of nitrogen. The ether is a yellow oily liquid, boiling at 76°—78°. *Tertiary Nitrobutane,* $(CH_3)_3C.NO_2$, which is formed at the same time, has not as yet been obtained pure. It is a liquid smelling of peppermint, and boiling between 110° and 130°, and possessing no acid properties. It is not attacked by bromine and potash, nor does it give any reactions with nitrous acid.

The isomeric nitrites are always formed in the preparation of the nitro-paraffins, except in the case of nitromethane. Thus, by the action of silver nitrite on ethyl iodide, almost equal quantities of the two isomers are obtained. This may be explained by the fact that the ether is formed by a secondary reaction in which a part of the iodide is converted into ethylene and hydriodic acid, and this latter decomposed by the silver nitrite, whilst the liberated nitrous acid combines with the ethylene to form ethyl nitrite. The more easily an iodide decomposes into an olefine and hydriodic acid, the smaller is the yield of nitroparaffin, and this is the reason why, in the case of the primary compounds, a satisfactory yield is obtained, whilst in that of the secondary it is smaller, and, in the case of the tertiary compounds, very small.[2]

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[1] *Ann. Chem. Pharm.* cxliv. 24.

[2] Tschermiak, *Ann. Chem. Pharm.* clxxx. 155.

NORMAL BUTYRIC ACID, $C_3H_7.CO_2H$.

In the year 1811, Chevreul commenced his classical ***Recherches sur les Corps Gras,***[1] which have thrown so much light on the constitution of the fats, and on the nature of saponification. A more complete account of these researches will be hereafter given under the subject of glycerin. We here only mention that in 1818 he discovered the various volatile acids contained in butter, and four years later discriminated between them, giving to them the names of butyric, caproic, and capric acids. The name for the first is derived from its origin, and from this the expressions butyryl and the butyl compounds.

This acid occurs, however, not only in butter, but likewise in a variety of other animal fats, as, for instance, in cod-liver oil. It is also found in the muscle-plasma, in the secretions of various insects, in perspiration, and in other animal liquids. It is also widely distributed in the vegetable kingdom. Thus it has been detected in croton oil and other fatty vegetable oils, in tamarinds, the fruits of the soap-nut tree, and that of the *Gingko biloba.* Ethers of butyric acid also occur in the oils of various species of umbelliferæ.

Pelouze and Gelis showed that butyric acid also is formed in a peculiar kind of saccharine fermentation; and the acid thus obtained was afterwards investigated by them[2] and by Lerch. It also occurs in the products of many other fermentation processes, and in the putrefaction of various substances. Thus it has been detected in putrid cheese, in the sour liquors from the tan-yard, in decomposed cider, and in putrefying yeast. Together with other fatty acids, it is a frequent constituent of the products of dry distillation of various organic substances, such as amber oil, crude pyroligneous acid, &c.

In order to prepare butyric acid, the process by fermentation of sugar is usually employed, the method given by Bensch[3] yielding the best product. For this purpose about 6 kg. of sugar and 30 g. of tartaric acid are dissolved in 26 liters of boiling water, and, after some days, 250 grams of putrid cheese mixed with 8 kg. of sour skimmed-milk, are added together, as well as 3 kg. of finely divided chalk. The mixture is then so placed that the temperature of the mass shall be from 30° to 35°. The mixture is stirred up every day, and the liquid, after about

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[1] Paris, 1823; *Ann. Chim. Phys.* [2], xxiii. 23.

[2] *Ann. Chim. Phys.* x. 434.

[3] *Ann. Chem. Pharm.* lxi. 177.

a week, becomes a thick magma of calcium lactate. It is then allowed to stand longer at 35°, the whole again becoming liquid, and an evolution of hydrogen and carbon dioxide being observed, and lasting for some weeks. As soon as the evolution of gas ceases, the butyric fermentation is complete. During the whole operation the water, as it evaporates, must from time to time be renewed. The whole is then diluted with more water, and 8 kg. of crystallized carbonate of soda added to the solution, which is filtered from calcium carbonate, evaporated to 10 kg., and to this 11 kg. of dilute sulphuric acid added. The oily layer which rises to the surface is separated from the aqueous liquid, which still contains some butyric acid. For the separation of this latter the liquid is distilled, and the distillate saturated with soda, the butyric acid being separated from this by sulphuric acid, and the product added to the first portion. The crude acid contains water and sodium sulphate. This latter is removed by distillation, a small quantity of sulphuric acid being added, and care taken to prevent the separation of the normal salt, as this would produce percussive ebullition. The distillate is again dried over calcium chloride, and again distilled. The product thus obtained still contains some water as well as acetic acid and caproic acid, from which it can be separated by fractional distillation. In order to obtain the pure acid, the chief fraction boiling from 155° to 165° is dissolved in water, when the caproic acid remains behind, and the pure calcium salt is prepared from this solution.[1] This is again decomposed, as described, and from the product the pure butyric acid is obtained by means of concentrated hydrochloric acid.

The formation of butyric acid from cane sugar, $C_{12}H_{22}O_{11}$, takes place in several stages. In the first place, the sugar is converted by absorption of water into glucose, $C_6H_{12}O_6$, and this decomposes into two molecules of lactic acid, $C_3H_6O_3$, which, again, is converted. as is shown in the following equation, into butyric acid:

$$2\,C_3H_6O_3 = C_4H_8O_2 + 2\,CO_2 + 2\,H_2$$

This subject will be more fully treated under the article "Fermentation." We may here simply remark that this fermentation is produced by a species of schizomycetes, the germs of which are either added in the putrid cheese, or may be derived from the air. This, however, is not the only organism

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[1] Lieben and Rossi, *Ann. Chem. Pharm.* clviii. 145 ; Grillone, *ib.* clxv.

contained in the fermented liquid, and these bring about other decompositions of the sugar. Hence, for this reason, it is more rational to add individuals of the special ferment, instead of the sour milk and putrid cheese.

According to Fitz, potato-starch is preferable to sugar. He takes 100 grams of this to two liters of water at 40°, and to this he adds a minute quantity of the schizomycetes *Bacillus subtilis*, and for its nourishment a mixture of 0·19 potassium phosphate, 0 02 magnesium sulphate, and 1 gram of sal-ammoniac. As the fermentation proceeds only in neutral solution, 50 grams of calcium carbonate are also added, and the process is completed in about ten days. The products of this reaction are 1 gram of alcohol, 0·33 of succinic acid, about 4 of acetic acid, and 34·7 grams of pure butyric acid; whilst by the other process, Bensch obtained only 29·2 grams of crude butyric acid from 100 grams of sugar.

As acetic acid is a stronger acid than butyric acid, the latter may be obtained in the pure state from a mixture of the calcium salts by adding such a quantity of hydrochloric acid that only the butyric acid is liberated.[1]

Butyric acid has been synthetically prepared by Frankland and Duppa[2] according to the reaction described on p. 180, and Linnemann and Zotta[3] have also prepared it synthetically from butyronitril.

Butyric acid is a mobile liquid having a strongly acid and rancid smell. This is especially unpleasant in dilute solution. Its taste is strongly acid. The concentrated acid produces a white spot on the tongue, and attacks the skin like glacial acetic acid. It boils at 163°, solidifies in a freezing mixture forming a pearly glistening mass which melts at $-2°$ to $+2°$, and at 0° has a specific gravity of 0·9817, and, at 14°, 0·9601. Like acetic, butyric acid also possesses an abnormal vapour-density even at temperatures tolerably far removed from its boiling-point, a constant limit of 3·07 not being reached until a temperature of 250° is attained (Cahours).

Butyric acid is miscible with water in all proportions, and it is thus distinguished from isobutyric acid. It forms easily soluble salts, and strong acids separate it again from these as an oily layer.

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[1] *Ber. Deutsch Chem. Ges.* xi. 51.
[2] *Proc. Roy. Soc.* xiv. 198; *Ann. Chem. Pharm.* cxxxv. 217.
[3] *Ann. Chem. Pharm.* clxi. 175.

THE BUTYRATES.

376 The salts of butyric acid are more or less soluble in water, and many also are soluble in alcohol; and they are chiefly crystalline. In the dry state they possess no smell, but when moist they generally emit a smell of the acid. Several of them are wetted by water with difficulty, and exhibit a remarkable rotatory motion like that of camphor when they are thrown on to the surface of water. The most characteristic salts are the following.

Calcium Butyrate, $(C_4H_7O_2)_2Ca+H_2O$, forms transparent scales, which are more soluble in cold than in hot water. One part dissolves at 14° in 3·5, and at 22° in 5·1 parts of water. If the solution be warmed beyond this point, the salt separates out as a crystalline precipitate, this quantity being greatest at 70°. At higher temperatures it again dissolves, but even if the solution be heated in closed tubes to 110°, it does not wholly disappear. On cooling, the salt dissolves again readily if the solution has not taken place in open vessels, in which latter case some of the acid escapes and basic salts are formed.[1]

Prof. Erlenmeyer, after having shown this experiment some forty times in his lectures, observed that much less salt separated out each time than had formerly been the case; and at last no further separation took place, but on cooling the solution considerably, crystalline scales made their appearance. A careful investigation of this led to the remarkable conclusion that from 9 to 10 per cent. of the normal butyrate had been converted into the isobutyrate, and that the presence of this latter had hindered the precipitation of the crystals.[2]

The fact that calcium butyrate is less soluble in warm water than in cold has been made use of, as has been stated, to separate acetic and caproic acid from the crude butyric acid. According to Lieben and Rossi, this latter liquid is evaporated with milk of lime, and the solution evaporated down, when the salt, which is only wetted by water with difficulty, separates out as a scum, which may then be removed. The evaporation and skimming is continued until the last mother-liquors do not yield a pure product.

Zinc Butyrate, $(C_4H_7O_2)_2Zn$, forms pearly scales difficultly

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[1] Lieben and Rossi, *Ann. Chem. Pharm.* clxv. 120.

[2] *Ann. Chem. Pharm.* clxxxi. 126.

soluble in water. It appears to be most soluble in warm water, whilst the solubility at 100° is not much greater than at 0°.[1]

Silver Butyrate, $C_4H_7O_2Ag$, is thrown down as a curdy precipitate, when a tolerably strong solution of a butyrate is treated with silver nitrate. It crystallizes from the hot saturated solution, on cooling, in dendritic prisms. One hundred parts of water dissolve, at 16°, 0·413 parts of the salt.

ETHERS OF BUTYRIC ACID.

377 Some of these compounds have been prepared artificially, and some occur ready formed in the vegetable kingdom. The following are the most important:

	B.P.	Sp. Gr.	at
Methyl butyrate	101°	0·9475	4°
Ethyl butyrate	121°	0·9019	0°
Propyl butyrate	143°·4	0·8872	0°
Isopropyl butyrate	128°	0·8787	0°
Butyl butyrate	165°·5	0·8885	0°
Isobutyl butyrate	149°·5	0·8719	0°

Of these, the ethyl ether is obtained by warming a mixture of two parts of spirit, two parts of butyric acid, and one part of sulphuric acid for some time to 80°, and then pouring the mixture into water and washing the layer of ether which swims on the surface with dilute soda solution, drying over chloride of calcium and distilling. It has a pleasant fruit-like smell, resembling, especially in dilute condition, that of pine-apples. A solution of the ether in ten parts of spirits of wine goes by the name of essence of pine-apple or Ananas-oil. This serves for the preparation of artificial rum, and is added to the common sorts of this spirit as well as other liquors; it is also used in perfumery and for flavouring cheap confectionery. In place of butyric acid, a mixture of volatile fatty acids may be used, obtained by saponifying butter in a current of steam.

The other *butyryl compounds* are prepared in an exactly similar way to the corresponding acetyl compounds:

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[1] R. Meyer, *Ber. Deutsch. Chem. Ges.* xi. 1790.

second is a solid body, crystallizing in oblique rhombic prisms, melting at about 140°.[1]

Other chlorinated butyric acids are not formed directly, but may be prepared from other compounds. These will be described hereafter in connection with the bodies from which they are obtained.

Monobrombutyric Acid, $C_4H_7BrO_2$, is obtained by heating butyric acid with bromine for three to four hours to 150°.[2] It may be distilled in a vacuum, and boils under the ordinary pressure with partial decomposition at 217°. It is slightly soluble in water, possesses a pungent smell, and at 15° has a specific gravity of 1·54. When hydrochloric acid is passed into its alcoholic solution, the ethyl ether is obtained as a colourless liquid, boiling at 178°. When heated with alcohol and potassium iodide, *ethyl iodobutyrate* is formed, a heavy liquid, boiling with partial decomposition at about 192°. Free iodobutyric acid is not known in the pure state.

Dibrombutyric Acid, $C_4H_6Br_2O_2$, is obtained by heating the monobrominated acid with bromine. This crystallizes from hot water in thin prisms which melt at 65°—70°, and boil at 227° with partial decomposition. Its ethyl ether is a liquid smelling like apples, and boiling between 191° and 193°.

Other isomeric higher brominated butyric acids will be afterwards mentioned.

ISOBUTYRYL COMPOUNDS.

379 *Isobutyraldehyde*, $(CH_3)_2CH.CHO$, is obtained by oxidizing isobutyl alcohol with potassium dichromate and sulphuric acid.[3] It is a strongly refracting liquid, possessing a pungent though not unpleasant smell, boiling at 61°, and having a specific gravity at 0° of 0·8226. It easily polymerizes, like acetaldehyde, into the trimolecular para-isobutyraldehyde, $C_{12}H_{24}O_3$, a substance crystallizing from alcohol or ether in fine needles, melting at 60°, and easily undergoing sublimation.

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[1] Pelouze and Gélis, *Ann. Chim. Phys.* [3], x. 449.

[2] Naumann, *Ann. Chem. Pharm.* cxix. 115; Friedel and Machuca, *ib.* cxx. 282; Suppl. ii. 70; Schneider, *ib.* cxx. 279; Tupoleff, *ib.* clxxi. 248.

[3] Michaelson, *Compt. Rend.* l. 388; Krämer, *Ber. Deutsch. Chem. Ges.* vii. 252; Pfeiffer, *ib.* v. 699; Barbaglia, *ib.* v. 1052; Lipp. *Ann. Chem. Pharm.* ccv. 1.

standard for comparison was obtained by the oxidation of isobutyl alcohol.

Isobutyric acid has also been prepared synthetically by Frankland and Duppa by the aceto-acetic-ether reaction (see p. 181).

Isobutyric acid is found in the free state in the flowers of the *Arnica montana*,[1] as well as in the carob bean, and amongst the acids of croton oil.[2] Isobutyl ether is one of the constituents of oil of camomile (*Anthemis nobilis*).[3]

Isobutyric acid boils at 154°, and at 0° has a specific gravity of 0·9598. It has a smell resembling the normal acid, but is less unpleasant, and is not miscible with water, one part requiring for complete solution three parts of water at the ordinary temperature. It is distinguished from the normal acid, inasmuch as, when heated with dilute sulphuric acid and potassium dichromate, it is easily oxidized into acetic acid and carbon dioxide.

ISOBUTYRATES.

381 The salts of isobutyric acid resemble in general properties the butyrates, with the exception of the salts of calcium and of silver.

Calcium Isobutyrate, $(C_4H_7O_2)_2Ca + 5H_2O$, crystallizes in monoclinic needles, which dissolve at 18° in thirty-six parts of water, whilst in hot water they are more soluble, and the saturated solution solidifies on cooling to a crystalline magma. If subjected to dry distillation, isopropyl ketone as well as methyl isopropyl ketone and isobutyl aldehyde are formed.[4]

Silver Isobutyrate, $C_4H_7O_2Ag$, crystallizes from hot water in transparent scales. One hundred parts of water at 16° dissolve 0·928 parts of the salt.

Zinc Isobutyrate, $(C_4H_7O_2)_2Zn$, crystallizes in monoclinic prisms, which at 19°·5 dissolve in 5·8 parts of water. The solubility diminishes quickly with increase of temperature, and a solution saturated in the cold deposits crystals in large quantity when warmed.[5]

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[1] Sigel, *Ann. Chem. Pharm.* clxx. 345.
[2] Schmidt and Behrendes, *Ann. Chem. Pharm.* cxci. 101.
[3] Kobig, *Ann. Chem. Pharm.* cxcv. 92.
[4] Barbaglia and Gucci, *Ber. Deutsch. Chem. Ges.* xiii. 1572.
[5] R. Meyer, *Ber. Deutsch. Chem. Ges.* xi. 1790.

chlorisobutyrate, $C_4H_6ClO_2(C_2H_5)$, a liquid boiling at 147°—150°.[1]

Bromisobutyric Acid, $(CH_3)_2CBr.CO_2H$, is formed by heating equal molecules of the acid and bromine to 140°.[2] It crystallizes from alcohol and ether in white tables which melt at 48°, and boils with slight decomposition at 198°—200°. Its ethyl ether boils at 160°.

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[1] Balbiano, *Ber. Deutsch. Chem. Ges.* xi. 1693.
[2] Hell and Waldbauer, *ib.* x. 448.

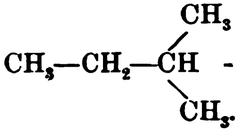
COMPOUNDS CONTAINING FIVE ATOMS OF CARBON, OR THE PENTYL GROUP.

383 THE compounds of this group are derivatives of the following isomeric paraffins:

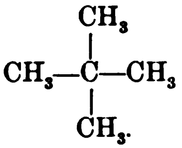
(I.)
Pentane.

$CH_3—CH_2—CH_2—CH_2—CH_3.$

(II).
Isopentane or Dimethyl-ethyl-methane.



(III).
Tetramethyl-methane.



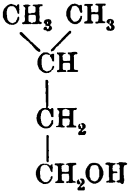
$$\begin{array}{c} CH_3 \\ | \\ CH_3—C—CH_3 \\ | \\ CH_3. \end{array}$$

Eight alcohols corresponding to these can exist, viz.:

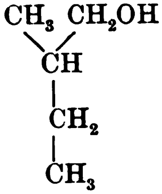
	Primary.	Secondary.		Tertiary.
	I. Pentyl Alcohol, or Butyl Carbinol (p. 603).	II. Methyl Propyl Carbinol (p. 604).	III. Diethyl Carbinol (p. 605).	
From Normal Pentane.	CH_3 CH_2 CH_2 CH_2 CH_2OH	CH_3 $CH.OH$ CH_2 CH_2 CH_3	CH_3 CH_2 $CH.OH$ CH_2 CH_3	—

From Isopentane.

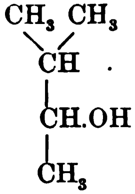
IV.
Inactive Amyl
Alcohol, or
Isobutyl
Carbinol
(p. 609).



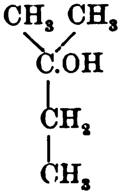
V.
Active Amyl
Alcohol, or
Secondary Butyl
Carbinol
(p. 610).



VI.
Methyl
Isopropyl
Carbinol
(p. 615).

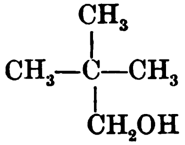


VII.
Dimethyl
Ethyl
Carbinol
(p. 616).



From Tetramethyl Methane.

VIII.
Tertiary Butyl
Carbinol (p. 617).



Of these alcohols the first seven are with certainty known.

NORMAL PENTANE AND ITS DERIVATIVES.

384 *Pentane*, C_5H_{12}, was discovered by Schorlemmer[1] in the light oil of the tar from cannel-coal. It is also found in the products of the distillation of Boghead cannel (Torbane mineral), and occurs in considerable quantity in Pennsylvanian petroleum. It is an easily inflammable liquid, possessing an ethereal smell, and boiling at 37°—39°, and having, at 17°, a specific gravity of 0·6263, that of its vapour being 2·49.

The first product of the action of chlorine on pentane is a mixture of the primary and secondary pentyl chloride.

NORMAL PRIMARY PENTYL ALCOHOL, $C_5H_{11}.OH$.

This compound, also termed butyl carbinol, or normal amyl alcohol (No. I. on the list), was first synthetically prepared by Lieben and Rossi. These chemists, starting from normal butyl alcohol, prepared the corresponding cyanide, or the nitril of

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[1] *Phil. Trans.* 1872, 111.

in which such an atom occurs, optically inactive. Le Bel, however, found that if its aqueous solution be brought in contact with a ferment such as *Penicillium glaucum*, and allowed to stand for a short time, it is converted into the lævro-rotatory alcohol.[1]

The following compounds have been prepared:

	B.P.	Sp. Gr.	
Methyl-propyl carbyl chloride	103-105°	0·9120	at 0°
Methyl-propyl carbyl iodide	145-146°	1·5390	0°
Methyl-propyl carbyl acetate	133-135°	0·9222	0°

Methyl-propyl Ketone, $C_3H_7.CO.CH_3$, is formed, together with dimethyl ketone and dipropyl ketone (butyrone) and other products, in the dry distillation of a mixture of acetate and butyrate of calcium.[2] It has also been synthetically prepared by the method already described. In smell it resembles common acetone, boils at 103°, and at 18° has a specific gravity of 0·808. Like dimethyl ketone (p. 568), it yields a nitro-compound, $CH(NO)C_2H_5.CO.CH_3$, which crystallizes from alcoholic solution in prisms which melt at 55°, the liquid boiling between 183° and 187°, with partial decomposition.[4]

DIETHYL CARBINOL, $(C_2H_5)_2CH.OH$.

386 This alcohol (No. III. on the list) is formed by heating ethyl formate with ethyl iodide and zinc; this reaction corresponding closely to the formation of methyl-ethyl carbinol (see p. 581.)

The secondary alcohol is a peculiarly smelling liquid, boiling at 116°·5, and having, at 0°, a specific gravity of 0·8315. The following derivatives have been examined:[5]

	B.P.	Sp. Gr.	
Diethyl carbyl chloride	103-105°	0·916	at 0°
Diethyl carbyl iodide	145-146°	1·528	0°
Diethyl carbyl acetate	132°	0·9090	0°

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[1] *Compt. Rend.* lxxxix. 312; *Bull. Soc. Chim.* xxxiii. 106.

[2] Grimm, *Ann. Chem. Pharm.* clvii. 251.

[3] Butlerow, *Bull. Soc. Chim.* [2], v. 19; Wislicenus, *Ann. Chem. Pharm.* clxxxvi. 187; cxc. 157.

[4] Meyer and Züblin, *Ber. Deutsch. Chem. Ges.* xi. 323 and 695.

[5] Wagner and Saytzeff, *Liebig's Ann.* clxxv. 351; clxxix. 321.

that it was a compound standing between this latter substance and an ethereal oil.[1] Dumas, who afterwards investigated the same subject, found that a large quantity of a liquid may be separated by fractional distillation, boiling at 131°·5, and this possessed the composition $C_5H_{12}O$, from which an analogy between this body, alcohol, and the ethers might be assumed. Still he thought it more probable and simpler to consider this substance as a body analogous to camphor or to the ethereal oils.[2] Some years afterwards Cahours investigated its chemical properties, and his experiments led him to conclude that this substance is isomeric with common alcohol, and belongs to the natural series of which wood-spirit and common alcohol form the two first members.[3] The further investigations of this chemist,[4] as well as those of Dumas and Stas,[5] and of Balard,[6] confirmed this view. Cahours gave to the compound the name of amyl alcohol because it had been chiefly found in spirit obtained from bodies containing starch (amylum). Balard, however, afterwards proved that it occurs in fusel oils formed in the fermentation of grape skins, and since that time it has been shown to occur in all fusel oils.

The amyl alcohol thus obtained was for a long time believed to consist of one distinct compound. Biot first drew attention to the fact that this body possesses the power of rotating the plane of polarized light to the left, but Pasteur pointed out in 1855, that the rotatory powers of different samples of amyl alcohol vary according to the sources from which they are obtained. From this he concluded that the body termed amyl alcohol is a mixture in varying proportions of an optically active and an optically inactive compound. In order to separate these two bodies, Pasteur dissolved the mixed alcohols in strong sulphuric acid and neutralized with barium carbonate. By this means he obtained two barium-amyl sulphates; the one derived from the inactive alcohol,being 2·5 times less soluble in water than the other, so that they could be separated by repeated crystallization. He next converted them into the sodium salts by addition of sodium carbonate; these he distilled with sulphuric acid, and he thus obtained the two modifications of the alcohol.[7]

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[1] *Ann. Chim. Phys.* [1], xxx. 221.

[2] *Ib.* [1], lvi. 314 ; *Ann. Pharm.* xiii. 80.

[3] *Ann. Chim. Phys.* [1], lxx. 31 ; *Ann. Pharm.* xxx. 288.

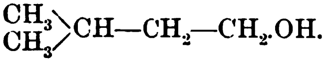
[4] *Ann. Chim. Phys.* [1] lxxv. 193 ; *Ann. Chem. Pharm.* xxvii. 164.

[5] *Ann. Chim. Phys.* [1], lxxiii. 128.

[6] *Ib.* [3], xii. 294 ; *Ann. Chem. Pharm.* lii. 311.

[7] *Compt. Rend.* xli. 296 ; *Ann. Chem. Pharm.* xcvi. 255.

by oxidation of the inactive amyl alcohol.[1] Hence its constitution is that of No. IV. on the list (p. 603), viz.:



$$\begin{matrix} CH_3 \\ CH_3 \end{matrix} \rangle CH—CH_2—CH_2.OH.$$

The accuracy of this conclusion was confirmed by the experiments of Frankland and Duppa. They proved that isopropylacetic acid obtained by synthesis is also identical with valeric acid.[2] Lastly, Balbiano found that the alcohol can be prepared synthetically from isobutyl alcohol, by the same process as that adopted by Lieben and Rossi for obtaining the normal alcohol from primary butyl alcohol.[3]

The optical properties of the inactive alcohol are almost the only means by which it can be distinguished from the fermentation-alcohol. It boils at 131°·4, and has at 0° a specific gravity of 0·8238. It occurs in camomile oil[4] as the ethers of angelic and tiglic acids. The following derivatives of the pure inactive amyl alcohol have been already prepared. They may be termed the α-amyl compounds:

		B.P.	Sp. gr. at 0°.
α-Amyl chloride,	$C_5H_{11}Cl$	98°·9	0·8928
α-Amyl bromide,	$C_5H_{11}Br$	120°·4	1·2358
α-Amyl acetate,	$C_5H_{11}O(C_2H_3O)$	138°·6	0·8838
α-Amyl valerate,	$C_5H_{11}O(C_5H_9O)$	190°.3	0.8700
[5] α-Amylamine,	$C_5H_{11}NH_2$	96°·5	—
α-Diamylamine,	$(C_5H_{11})_2NH$	185°·0	—
α-Triamylamine,	$(C_5H_{11})_3N$	237°·0	—

ACTIVE AMYL ALCOHOL.

389 This was prepared by Pasteur and by Pedler from the fermentation-alcohol in the mode already described. According to Le Bel it is also obtained from the latter compound by saturating it with hydrochloric acid, which first acts upon the inactive alcohol. The chlorides are then distilled

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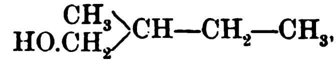
[1] *Ann. Chem. Pharm.* Suppl. v. 337.
[2] Pedler, *loc. cit.*; Erlenmeyer, *Ber. Deutsch. Chem. Ges.* iii. 899.
[3] *Ber. Deutsch. Chem. Ges.* ix. 1437 and 1692.
[4] Kobig, *Liebig's Ann.* cxcv. 99.
[5] Plimpton, *Compt. Rend.* xci. 433.

off, and the residue heated repeatedly with hydrochloric acid until about one-ninth of the original liquid remains unacted upon; this consists, to a great extent, of the levro-rotatory alcohol.[1] The first portions of the chloride can be worked up for the inactive alcohol and its derivatives. The above-named amines were obtained from a chloride obtained in this way.

Active amyl alcohol has evidently not yet been obtained pure, as the rotatory power of the different preparations has been found to be very different. It boils about 128°, and smells like the fermentation-alcohol, but has rather a more fruity flavour. The remarkable fact that the derivatives of this levro-rotatory amyl alcohol turn the ray of polarization to the right has been observed by Le Bel. Another interesting fact is, that the aqueous solution of the levro-rotatory alcohol is converted by the action of a mucor into the dextro-rotatory alcohol which boils at 127°, and yields a levro-rotatory amyl iodide.[2] When the levro-rotatory alcohol is heated for some time with soda or potash, or when it is converted into sodium amylate, the regenerated alcohol is found to have lost its optical activity; the same change occurs when it is heated under pressure. It is not improbable that a part of the alcohol is here converted into the dextro-rotatory modification, and that then a condition of equilibrium is attained, so that the optical properties of the two physical isomerides neutralize each other. The constitution of the active amyl alcohol is probably represented by the formula (No. V. on the list, page 603):



$$\begin{matrix}CH_3\\HO.CH_2\end{matrix}\!\!>CH-CH_2-CH_3,$$

and for the following reasons. Theoretically, four primary pentyl alcohols may exist independent of optical isomerides. Of these only the one possessing the above constitution contains an asymmetrical carbon atom, a well-known characteristic of optically active bodies. In addition to this, the active alcohol yields on oxidation an acid which closely resembles synthetically prepared methyl-ethyl-acetic acid, $CH_3(C_2H_5)CH.CO_2H$, which has not yet been thoroughly investigated. It is, however, distinctly different from the three other known pentylic acids whose possible existence is pointed to by theory.

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[1] *Bull. Soc. Chim.* xxv. 545.

[2] Le Bel, *Bull. Soc. Chim.* xxxi. 104.

The following derivatives of the active alcohol, which may be termed β-amyl compounds, have been prepared :[1]

		B.P.	Sp. Gr. at 0°.
β-Amyl chloride,	$C_5H_{11}Cl$	97-98°	0·886
β-Amyl bromide,	$C_5H_{11}Br$	117-120°	1·225
β-Amyl iodide,	$C_5H_{11}I$	144-145°	1·540

THE AMYL COMPOUNDS.

390 The amyl compounds derived from the fermentation-alcohol have been much more fully investigated; but inasmuch as this liquid is a mixture, its derivatives are not pure substances, the compounds of the inactive alcohol being present in largest quantity. These may be simply termed the amyl compounds.

THE AMYL ETHERS.

Ethyl-Amyl Ether, $C_2H_5(C_5H_{11})O$, was first prepared by Balard, by heating amyl chloride with alcoholic potash. It was, however, believed by him to be amyl oxide, until Williamson showed that the same compound is obtained by acting on amyl iodide with sodium ethylate[2] (see p. 329). According to Guthrie, ethyl-amyl oxide is best prepared by dissolving caustic potash in boiling amyl alcohol, and then adding ethyl iodide, when a considerable evolution of heat takes place, but at last the reaction must be aided by heat.[3] It is an ethereal-smelling liquid boiling at 112°, the vapour of which has a specific gravity of 4·042.

Methyl-Amyl Ether, $CH_3(C_5H_{11})O$, is obtained in a similar manner, and boils at 92° (Williamson).

Diamyl Ether, or *Amyl Oxide*, $(C_5H_{11})_2O$, was first prepared by de Glaubry,[4] and afterwards by Rieckher,[5] by heating the alcohol with sulphuric acid, when the oxide is formed together with a number of by-products. Williamson[6] obtained it by acting on sodium amylate with amyl iodide, and Wurtz[7] prepared it together with amylene, by acting on the iodide with

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[1] Le Bel, *Bull. Soc. Chim.* [2], xxv. 545.

[2] *Quart. Journ. Chem. Soc.* iv. 233.

[3] *Phil. Mag.* [4], xiv. 186.

[4] *Ann. Chem. Pharm.* xliv. 128.

[5] *Ib.* lxiv. 336.

[6] *Quart. Journ. Chem. Scc.* 108, 234.

[7] *Ann. Chim. Phys.* [3], xlvi. 222.

silver oxide. According to Friedel, it is best obtained by heating 10 parts of the alcohol with 1 part of amyl iodide, for several hours, to 100°[1] (see p. 331). It is an unpleasantly smelling liquid, boiling at 176°, having at 0° a specific gravity of 0·7994, that of its vapour being 5·535.

Amyl Haloid Ethers.

	B.P.	Sp. Gr.	at
[2] Amyl chloride, $C_5H_{11}Cl$	100°·9	0·8859	0°
[3] Amyl bromide, $C_5H_{11}Br$	118°·7	1·1658	16°
[4] Amyl iodide, $C_5H_{11}I$	147°·2	1·4676	0°

Amyl Ethers of Inorganic Acids.

[5] Amyl sulphite,	$(C_5H_{11})_2SO_3$	—	—	—
[6] Hydrogen amyl sulphate,	$H(C_5H_{11})SO_4$	—	—	—
[7] Amyl nitrite,	$C_5H_{11}NO_2$	99°	0·902	—
[8] Amyl nitrate,	$C_5H_{11}NO_3$	148°	1·000	7°
[9] Amyl phosphite,	$(C_5H_{11})_3PO_3$	—	—	—
[10] Amyl phosphoric acids	—	—	—	—
[11] Amyl borate,	$(C_5H_{11})_3BO_3$	254°	0·872	0°
[12] Amyl silicate,	$(C_5H_{11})_4SiO_4$	322-325°	0·868	20°
[13] Amyl carbonate,	$(C_5H_{11})_2CO_3$	226°	0·914	—

Amyl Nitrite. This important compound is obtained by passing nitrous fumes, obtained by the action of nitric acid on starch or arsenic trioxide, into amyl alcohol; or by dissolving amyl alcohol in its own volume of sulphuric acid, and heating the mixture, after it has become cold, with a solution of 26 parts of potassium nitrite in 15 parts of water, and then

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[1] *Ber. Deutsch. Chem. Ges.* ii. 715.

[2] Cahours; Balard; Buff, *Ann. Chem. Pharm.* cxlviii. 350.

[3] Cahours; Elketoff, *Ber. Deutsch. Chem. Ges.* vi. 1258.

[4] Cahours; Frankland, *Quart. Journ. Chem. Soc.* iii. 30.

[5] Carius and Fries, *Ann. Chem. Pharm.* cix. 1; Cahours, cxi. 98.

[6] Cahours; Kekulé, *Ann. Chem. Pharm.* lxxv. 275.

[7] Balard, Guthrie, *Quart. Journ. Chem. Soc.* xi. 245; Nadler, *Ann. Chem. Pharm.* cxvi. 176; Hilger, Rennard, *Jahresb.* 1874, 352.

[8] Rieckher, *Ann. Chem. Pharm.* lxiv. 336; Hofmann, *ib.* lxviii. 332; Chapman and Smith, *Journ. Chem. Soc.* xx. 581.

[9] Williamson and Railton, *Proc. Roy. Soc.* vii. 131; Menschutkin, *Ann. Chem. Pharm.* cxxxix. 348.

[10] Guthrie, *Journ. Chem. Soc.* ix. 131: Kraut, *Ann. Chem. Pharm.* cxviii. 102.

[11] Schiff, *Ann. Chem. Pharm.* Suppl. v. 187.

[12] Ebelmen, *ib.* lvii. 331.

[13] Medlock, *Quart. Journ. Chem. Soc.* i. 370; Bruce, *ib.* v. 131.

distilling. Amyl nitrite is a light yellow liquid possessing a peculiar stupefying smell, and its vapour, when inhaled in small quantity, produces a flushing of the countenance, rush of blood to the head which may increase up to insensibility, and a quickening of the pulse due to an increase in the area of the blood-vessels, and a diminution of the controlling-power of the contractile fibres. These symptoms disappear again very quickly. On account of its peculiar physiological action amyl nitrite is employed in medicine, and is said to have been beneficially employed in epilepsy, asthma, in certain cases of hypochondriasis, and in angina pectoris.

Amyl nitrite has a peculiar disagreeable smell, and its vapour, like that of ethyl nitrite, is very explosive.

AMYL ETHERS OF THE FATTY ACIDS.

		B.P.	Sp. Gr.	at
[1] Amyl formate,	$C_5H_{11}O(CHO)$	116°	0·874	21°
[2] Amyl acetate,	$C_5H_{11}O(C_2H_3O)$	137°	0·8837	0°
[3] Amyl propionate,	$C_5H_{11}O(C_3H_5O)$	155°	—	—
[4] Amyl butyrate,	$C_5H_{11}O(C_4H_7O)$	176°	0·852	15°

Amyl Acetate is obtained by warming a mixture of one part of sulphuric acid, two parts of amyl alcohol, and two parts of acetic acid, and distilling. It has an aromatic ethereal smell which, when the ether is diluted with alcohol, resembles the smell of Jargonelle pears. Hence it is used for the preparation of pear-essence. It is usually prepared for this purpose from potato fusel-oil, and 10 parts of the ether are mixed with one part of acetic ether and 80 parts of rectified spirit, and a few drops of oil of lemons or oil of bergamot added.

AMYL SULPHUR COMPOUNDS.

		B.P.	Sp. Gr.	at
[5] Amyl hydrosulphide,	$C_5H_{11}.SH$	119°·5	0·835	21°
[6] Amyl sulphide,	$(C_5H_{11})_2$	S213-214°	—	—
[7] Ethyl-amyl sulphide,	$C_2H_5(C_5H_{11})S$	160°	–	—

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[1] Kopp, *Ann. Chem. Pharm.* lv. 183.

[2] Cahours ; Kopp, *ib.* xciv. 294.

[3] Wrightson, *ib.* xc. 45.

[4] Delffs, *ib.* xcii. 278.

[5] Balard ; Krutzsch, *Journ. Prakt. Chem.* xxxi. 1

[6] Balard ; Beckmann, *ib.* [2], xvii. 440.

[7] Saytzeff, *Ann. Chem. Pharm.* cxxxix 361 ; Beckmann.

Amyl Telluride, $(C_5H_{11})_2Te$, was prepared by Wöhler and Dean by heating potassium telluride with a solution of potassium amyl sulphate. It is a reddish yellow heavy liquid, having a most unpleasant smell. It boils with partial decomposition at 198°, and is converted, on exposure to air, into the oxide $(C_5H_{11})_2TeO$.[1]

AMYL NITROGEN COMPOUNDS.

		B.P.	Sp. Gr.	at
[2] Amylamine,	$(C_5H_{11})NH_2$	95°	0·7503	18°
Diamylamine,	$(C_5H_{11})_2NH$	170°	0·7825	0°
Triamylamine,	$(C_5H_{11})_3N$	257°	—	—
[3] Amyl carbamine,	$C_5H_{11}.NC$	137°	—	—
[4] Amyl carbimide,	$C_5H_{11}N.CO$	100°	—	—
[5] Amyl thiocyanate,	$C_5H_{11}S.CN$	197°	0·905	20°
[6] Amyl thiocarbimide,	$C_5H_{11}N.CS$	183-184°	—	—

Nitropentane, $C_5H_{11}NO_2$, is formed by the action of amyl iodide on silver nitrite. It has, however, not been obtained in the pure state, as it is difficult to separate it from the amyl nitrite formed at the same time, although the latter boils 60° lower. It is a light liquid, smelling like the rest of the amyl compounds, and boiling between 150° and 160°, and dissolving only with difficulty in caustic potash.[7]

AMYL PHOSPHORUS COMPOUNDS.[8]

		B.P.
Amylphosphine,	$(C_5H_{11})PH_2$	106-107°
Diamylphosphine,	$(C_5H_{11})_2PH$	210-215°
Triamylphosphine,	$(C_5H_{11})_3P$	300°

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[1] *Ann. Chem. Pharm.* xcvii. 1.

[2] Wurtz, *ib.* lxxi. 326; lxxvi. 317; Hofmann, *ib.* lxxiv. 118; lxxv. 364; lxxviii. 279; lxxix. 20; Silva, *Compt. Rend.* lxiv. 1299.

[3] Hofmann, *Ann. Chem. Pharm.* cxliv. 114; cxlvi. 107; Gautier, *ib.* cxlvi. 119, 124.

[4] Wurtz, *Compt. Rend.* xxix. 186.

[5] Medlock, *Ann. Chem. Pharm.* lxix. 214; *Quart. Journ. Chem. Soc.* i. 373; Henry, *Journ. Pract. Chem.* xlvi. 161.

[6] Hofmann, *Ber. Deutsch. Chem. Ges.* i. 173.

[7] V. Meyer, *Ann. Chem. Pharm.* clxxi. 43.

[8] Hofmann, *Ber. Deutsch. Chem. Ges.* vi. 297.

AMYL ANTIMONY COMPOUNDS.[1]

Antimony-diamyl, $(C_5H_{11})_4Sb_2$.
Antimony-triamyl, $(C_5H_{11})_3Sb$.

AMYL METALLIC COMPOUNDS.

		B.P.	Sp. Gr.	at
[2] Zinc-amyl,	$(C_5H_{11})_2Zn$	220°	1·022	0°
[3] Mercury-amyl,	$(C_5H_{11})_2Hg$	—	1·6663	0°
[4] Lead-sesquiamyl	$(C_5H_{11})_6Pb_2$	—	—	—
[5] Tin-tetramyl,	$(C_5H_{11})_4Sn$	—	—	—
[6] Amyl-tin iodide,	$(C_5H_{11})_3SnI$	302-305°	—	—
Amyl-tin hydroxide,	$(C_5H_{11})_3SnOH$	335-338°	—	—

METHYL-ISOPROPYL CARBINOL, $(CH_3)_2CH(CHOH)CH_3$.

391 This secondary alcohol (No. VI. on the list) is formed by the action of sodium amalgam on an aqueous solution of the corresponding ketone,[7] as well as when bromacetyl bromide is treated with zinc-methyl. A thick liquid is formed after standing for several weeks, and this is decomposed by water, with formation of the secondary carbinol. The mechanism of the last reaction has not yet been explained.[8] The carbinol is a sweetly smelling liquid, boiling at 111°-113°, and having at 0° a specific gravity of 0·819.[9]

Hygroscopic substances easily split it up into water and trimethyl ethylene, $(CH_3)_2C = CH(CH_3)$, and for this reason, on treatment with phosphorus chloride, hydriodic acid, &c., it yields the tertiary alcohol, and not the corresponding ethers. Its haloid ethers may be obtained, however, by combining the hydracids with isopropyl ethylene, $(CH_3)_2CH.CH = CH_2$, which can be obtained, together with an isomeric olefine, by heating common amyl iodide with alcoholic potash.

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[1] Berlé, *Ann. Chem. Pharm.* xcvii. 316 ; Cramer, *Jahresb.* 1855, 590.

[2] Frankland, *Quart. Journ. Chem. Soc.* vi. 64 ; Frankland and Duppa, *Journ. Chem. Soc.* xvii. 32.

[3] Frankland and Duppa, *ib.* xvi. 420.

[4] Klippel, *Jahresb.* 1860, 383.

[5] Grimm, *Ann. Chem. Pharm.* xcii. 383.

[6] Cahours and Demarçay, *Compt. Rend.* lxxxix. 68.

[7] Münch, *Ann. Chem. Pharm.* clxxx. 339.

[8] Winogradow, *ib.* cxci. 125.

[9] Wyschnegradsky, *ib.* cxc. 338.

	B.P.	Sp. Gr.	at
Secondary amyl chloride, $C_5H_{11}Cl$	91°	0·883	—
Secondary amyl bromide, $C_5H_{11}Br$	115-116°	—	—
Secondary amyl iodide, $C_5H_{11}I$	137-138°	—	—

If these are heated with water and silver oxide, or lead oxide, the *tertiary* alcohol is formed.

Methyl-propyl Ketone, $(CH_3)_2C.H.CO.CH_3$, is prepared by the usual method from calcium isobutyrate and calcium acetate; and also by the decomposition of dimethyl aceto-acetic ether. It is a liquid boiling at 95°, and having at 0° the specific gravity 0·822.

DIMETHYL-ETHYL-CARBINOL, $(CH_3)_2(C_2H_5)COH$.

392 This tertiary alcohol (No. VII. on the list) is formed in an analogous way to tertiary butyl alcohol by acting upon propionyl chloride with zinc-methyl, and decomposing the crystalline product by water.[1] It may be more easily prepared from commercial amylene, obtained from the fermentation-alcohol, which contains, together with the above-mentioned isopropyl ethylene, its isomeride, trimethylethylene. This latter combines with slightly diluted sulphuric acid on shaking in the cold, and if the solution be then distilled with water, the tertiary carbinol is obtained.[2] The carbinol was obtained at an earlier date by Wurtz, but mixed probably with an isomeric alcohol. He obtained it by treating the above-mentioned mixture of amylenes with hydriodic acid, and acting upon the products with moist silver oxide in the cold.[3] He called this new isomeride of the fermentation-alcohol *amylene hydrate*. It was afterwards considered to be a secondary alcohol, until further investigation revealed its true nature.

Tertiary amyl alcohol is a peculiar aromatic-smelling liquid, boiling at 102°·5, solidifying in a freezing mixture, forming long white needles which melt at 12°, and having a specific gravity at 0° of 0·827.

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[1] Popoff, *Ann. Chem. Pharm.* cxlv. 292; Wyschnegradsky, *ib.* cxc. 336.

[2] Wyschnegradsky, *loc. cit.*; Flawitzky, *ib.* clxxix. 343; Osipoff, *Ber. Deutsch. Chem. Ges.* viii. 542, 1240.

[3] *Ann. Chem. Pharm.* cxxv. 114, cxxvii. 236; cxxix. 365.

		B.P.	Sp. Gr.	at
Tertiary amyl chloride,	$C_5H_{11}Cl$	86°	0·889	0°
Tertiary amyl bromide,	$C_5H_{11}Br$	108-109°	—	0°
Tertiary amyl iodide,	$C_5H_{11}I$	127-128°	1·524	0°
Tertiary amyl acetate,	$C_5H_{11}O(C_2H_3O)$	125°	—	0°
Tertiary amylamine,	$C_5H_{11}NH_2$	78·5	—	0°

TETRAMETHYL METHANE AND ITS DERIVATIVES.

393 *Tetramethyl Methane*, $C(CH_3)_4$, is formed by acting with zinc-methyl on tertiary butyl iodide or on propidene dichloride, $(CH_3)_2CCl_2$, a body obtained by treating dimethyl ketone with phosphorus pentachloride. It is a mobile liquid boiling at 9°·5, and solidifying when placed in a freezing mixture to a mass of delicate crystals which melt at —20°.[1]

The derivatives of this paraffin have not as yet been directly prepared from the hydride. By the action of chlorine, the first substitution-product is said to be a primary chloride from which other compounds might be prepared, such as the alcohol $(CH_3)_3C.CH_2OH$, whose corresponding acid, trimethylacetic acid, is known and will be subsequently described.

THE PENTOIC OR VALERIC ACIDS.

394 *Pentoic*, or *Normal Valeric Acid*, $C_4H_9.CO_2H$, was prepared by Lieben and Rossi by heating one of the haloid ethers of normal butyl with alcohol and potassium cyanide for two days to 100°—101°, when pentonitril, C_4H_9CN, is formed, a liquid which has a specific gravity at 0° of 0·8164, and boils at 140°·4.[2] For the purpose of preparing the acid it is not necessary to obtain the nitril in the pure state, but the product of the reaction is distilled in order to remove potassium iodide, and the distillate is boiled with caustic potash in connection with an inverted condenser as long as ammonia is evolved. The alcohol is then removed by distillation, and the acid separated from the residue by means of sulphuric acid.[3] It is also obtained, together with paraffins and normal homologous acids, when fats are distilled

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[1] Lwow, *Zeitsch. Chem.* vi. 520 ; vii. 257.
[2] *Ann. Chem. Pharm.* clviii. 171.
[3] *Ann. Chem. Pharm.* clix. 58.

Valeric acid was formerly obtained by distilling valerian root with water. The distillate which, in addition to the acid, contains an ethereal oil, is neutralized with soda, the aqueous solution concentrated and decomposed by sulphuric acid. The acid is now obtained by oxidizing fermentation amyl-alcohol when it is obtained with a larger or smaller admixture of optically active acid; and this, for the objects for which it has to be employed, does not signify. In order to prepare it, a mixture of one part of amyl alcohol and 3·9 parts of sulphuric acid, is gradually added to a mixture of 5·1 parts of potassium dichromate and four to five parts of water, and the mixture distilled. An aqueous solution of the acid comes over, together with valeraldehyde and amyl valerate, which separate out as a light oily layer. The whole distillate is then neutralized with carbonate of soda and shaken up until the aqueous solution has a slightly alkaline reaction. This is then separated from the upper layer, concentrated by evaporation, and valeric acid liberated from the residue by means of sulphuric acid.[1] In order to obtain the pure acid, either the pure inactive alcohol must be used, or the acid must be synthetically prepared from isobutyl iodide, which is first transformed into the nitril, and this then decomposed by alkali.[2] For this purpose the following is the best process to adopt. The iodide is dissolved in half its weight of strong alcohol, and water added until an opalescence occurs, which is then again removed by the addition of some alcohol. Ten parts of this solution are then heated in a water-bath for two days with three parts of powdered potassium cyanide, when a thick crystalline magma is produced owing to the formation of potassium iodide. The nitril is removed from this by a vacuum filter, the filtrate distilled, and again heated in an upright condenser with caustic potash as long as ammonia is evolved, the alcohol distilled off, and valeric acid prepared from the residue by the addition of sulphuric acid. It is then dried over dehydrated glauber-salt, and afterwards over phosphorus pentoxide.[3]

Inactive valeric acid is a mobile oily liquid boiling at 175° and having a specific gravity at 0° of 0·9536. It has a strongly acid taste and caustic action. It has an unpleasant pungent smell resembling old cheese, and dissolves in about thirty

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[1] Lawrose and Jazukowitsch, *Zeitsch. Chem.* 1864, 83.
[2] Erlenmeyer and Hell, *Ann. Chem. Pharm.* clx. 264.
[3] Schmidt and Sachtleben, *Ann. Chem. Pharm.* cxciii. 87.

parts of water. The specific gravity of its vapour at temperatures considerably removed from its boiling-point is 3·67 (Dumas and Stas). Like acetic acid, it possesses, at lower temperatures, a higher specific gravity, though it does not exhibit so great a divergence as the latter acid.

The ethereal oil obtained by distilling valerian root which occurs together with other bodies in the process of preparing valeric acid, is used in medicine, whilst the acid obtained from amyl-alcohol is used for preparing the ammonium and zinc salts, which are also employed in pharmacy.

THE VALERATES.

395 Many of the older statements respecting the salts of valeric acid are found to be contradictory, inasmuch as it frequently happened that for their preparation the acid containing the active compound was employed. The investigations of Erlenmeyer and Hell as well as those of Schmidt and Sachtleben have, however, placed this subject in a clear light. The salts of the alkali- and alkaline-earths-metals are easily soluble in water, whilst those of the other metals are less soluble. When freshly prepared they are, in the dry state, almost odourless, but on keeping, especially on access of air, the smell of the acid becomes noticeable, as they are partly decomposed into basic salts, a decomposition which also takes place when they are heated with water.

Calcium Valerate, $(C_5H_9O_2)_2Ca + 3H_2O$, crystallizes in long needles on evaporation of the solution.

Barium Valerate, $(C_5H_9O_2)_2Ba$, easily crystallizes in triclinic scales or tables.

Zinc Valerate, $(C_5H_9O_2)_2Zn + 2H_2O$, forms large glistening laminæ.

Silver Valerate, $C_5H_9O_2Ag$, is difficultly soluble in water, and crystallizes from the hot saturated solution in glistening scales.

ETHERS OF VALERIC ACID.

		B.P.	Sp. Gr.	at
Methyl valerate,	$CH_3O(C_5H_9O)$	116°·5	0·885	17°
Ethyl valerate,	$C_2H_5O(C_5H_9O)$	134°·5	0·866	18°
Amyl valerate,	$C_5H_{11}O(C_5H_9O)$	188°	0·879	0°

The last named of these compounds is obtained as a by-product in the preparation of valeric acid from amyl-alcohol (see p. 619), and it is also easily produced when the acid or the sodium salt is warmed with amyl-alcohol and sulphuric acid. Its dilute alcoholic solution has a pleasant smell of apples, and is used as an apple-essence in cheap confectionery.

VALERYL COMPOUNDS.

[1] Valeryl oxide, $(C_5H_9O_2)_2O$.
[2] Valeryl chloride, C_5H_9OCl.
[3] Valeryl bromide, C_5H_9OBr.
[4] Valeryl iodide, C_5H_9OI.

Divaleryl, $(C_5H_9O)_2$, is formed by the action of sodium on valeryl chloride diluted with ether, and is a yellow oily liquid possessing a fruity smell, and it may be distilled under diminished pressure without decomposition.[5]

Valeryl Cyanide, $C_5H_9O(CN)$, is produced when the chloride is heated with silver cyanide. It forms a thick liquid, which smells like celery, boils at 145°—148°, and is slowly decomposed by water into valeric and hydrocyanic acids.[6]

Valeramide, $C_5H_9O(NH_2)$, is formed by the action of concentrated aqueous ammonia on the methyl or ethyl ether,[7] and also by heating the acid with ammonium thiocyanate.[8] It is easily soluble in water, alcohol, and ether, crystallizes in large thin tables melting at 126°—135°, and sublimes below its boiling point at 230°—232°.

Valeronitril, C_5H_9CN, was first discovered by Schlieper amongst the products of oxidation of glue.[9] Dumas obtained it by heating the amide with phosphorus pentoxide, or by passing the vapour of the former compound over red-hot lime.[10] For its preparation the method already mentioned (see p. 619) may be employed. The alcohol is first distilled off and the residue then heated more strongly in order to drive over the nitril, which contains small quantities of the iodide. It is, therefore,

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[1] Chiozza, *Ann. Chem. Pharm.* lxxxiv. 106.

[2] Béchamps, *Compt. Rend.* xlii. 224; Moldenhauer, *Ann. Chem. Pharm.* xciv. 100; Brühl, *Ber. Deutsch. Chem. Ges.* xii. 314.

[3] Béchamps, *loc. cit.*

[4] Cahours, *Ann. Chem. Pharm.* civ. 111; *Compt. Rend.* xliv. 1252.

[5] Brühl, *loc. cit.*

[6] Hübner and Cunze, *Ann. Chem. Pharm.* cxxxi. 74.

[7] Dumas, Malaguti, and Leblanc, *Compt. Rend.* xxv. 475, 658; Schmidt and Sachtleben, *Ann. Chem. Pharm.* cxciii. 102.

[8] Letts, *Ber. Deutsch. Chem. Ges.* v. 672.

[9] *Ann. Chem. Pharm.* lix. 1.

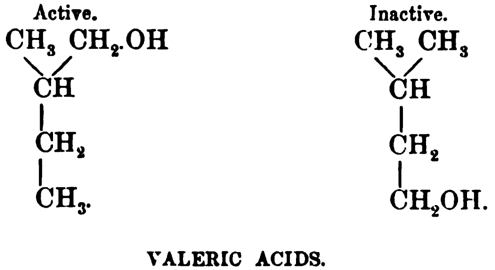
[10] *Loc. cit.*

re-distilled in a current of steam, when the latter compound passes over first. Valeronitril is a liquid having a smell resembling oil of bitter almonds, boiling at 126°—128°, and having a specific gravity at 0° of 0·8826.

396 *Active Valeric Acid*, $C_5H_{10}O_2$, is formed by the oxidation of the lævro-rotatory amyl alcohol and turns the plane of polarization to the right.[1] It has a smell resembling ordinary valeric acid, but boils at a temperature 2°—3° lower, and is easily converted by oxidation into acetic acid, carbon dioxide, and water. The barium salt is the most characteristic. This, on account of its solubility, remains behind as a thick syrup, in which, on standing for some time, small crystals are formed, consisting probably of the salt of the inactive acid which may be present, whilst the mother-liquor dries up to an amorphous varnish.

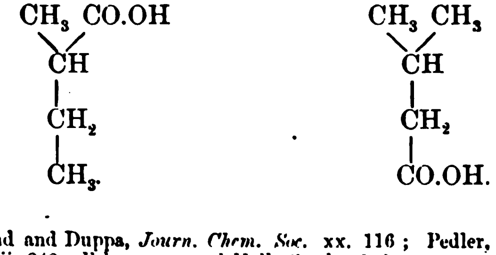
Active valeric acid appears to possess an identical constitution with methyl-ethyl-acetic acid, $(CH_3)C_2H_5.CH.CO_2H$. But this latter, obtained by the aceto-acetic-ether reaction is, like other synthetically prepared compounds, not optically active. It boils at 175°.[2] If this be the case, as appears extremely probable for a variety of reasons, it follows that the inactive and active alcohols and valeric acids are derivatives of isopentane.

AMYL ALCOHOLS.



Active. Inactive.

VALERIC ACIDS.



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[1] Frankland and Duppa, *Journ. Chem. Soc.* xx. 116 ; Pedler, *Ann. Chem. Pharm.* cxlvii. 243 ; Erlenmeyer and Hell, *ib.* clx. 282.

[2] *Ann. Chem. Pharm.* clxxxviii. 257.

397 *Tertiary Valeric Acid,* or *Trimethylacetic Acid,* $(CH_3)_3C.CO_2H$. This acid is the first example of a fatty acid which contains a tertiary alcohol radical (dibutyryl). It was discovered by Butlerow, who obtained it synthetically from tertiary butyl iodide.[1] This is first converted into the nitril by bringing it in contact with the double cyanide of mercury and potassium in the cold, and allowing it to stand until the reaction is complete. If the mixture becomes heated, isobutylene and its polymerides are formed, together with other products, such as tertiary butylamine, the formation of which can never be completely prevented. Pure *trimethyl acetonitril,* $(CH_3)_3C.CN$, has a pungent smell resembling that of bitter-almond oil. It boils at 105°—106°, and solidifies on cooling to a crystalline mass which melts at 15°—16°. In order to prepare the acid, the crude nitril is heated with an equal volume of fuming hydrochloric acid in a closed vessel to 100°, the product diluted with water in order to dissolve the sal-ammoniac, the oily acid drawn off, and the aqueous liquid distilled, as it contains some acid which can then be recovered from the distillate by the addition to it of glauber-salt. The crude acid is then treated with caustic soda, the insoluble portion removed, and the solution evaporated to dryness. The residue is next treated with alcohol, the filtrate again evaporated, and the pure sodium salt thus obtained decomposed with tolerably concentrated sulphuric acid. The acid which is thus liberated is dried over anhydrous glauber-salt, and then over phosphorus pentoxide and afterwards rectified. It boils at 163°·7—163°·8, and solidifies on cooling to a mass of crystals which appear to belong to the regular system as they do not produce any action on polarized light. They have, however, not been obtained in very definite form, as the fused salt absorbs air, and this, on solidification, is evolved in small bubbles. When cooled down to 0° it is converted into a snow-like mass of needles, which at the ordinary temperature gradually changes into a transparent amorphous mass. It melts at 35°·4, has a strongly acid taste, and smells of acetic and valeric acids. Its specific gravity at 50° is 0·905, and its coefficient of expansion for 1° between 50° and 75° is 0·00112.

Trimethylacetates. Those of the alkali-metals are very easily soluble in water, and form, like acetic acid, so-called acid salts.

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[1] *Ann. Chem. Pharm.* clxv. 322; clxx. 151; clxxiii. 355.

Calcium Trimethylacetate, $(C_5H_9O_2)_2Ca + 5 H_2O$, is more easily soluble in hot than in cold water, and crystallizes in silky prisms.

Barium Trimethylacetate, $(C_5H_9O_2)_2Ba + 5 H_2O$, forms flat transparent prisms.

Zinc Trimethylacetate, $(C_5H_9O_2)_2Zn + H_2O$, is a very characteristic salt. It is only very slightly soluble in water, and separates out from dilute solutions in crystalline scales. When a solution saturated in the cold is heated, a basic salt separates out, and the pasty mass which is formed has a strongly acid reaction. If an escape of the free acid is prevented, the mass becomes almost perfectly clear on cooling. The salt is tolerably soluble in alcohol, and crystallizes from this in silky needles.

Silver Trimethylacetate, $C_5H_9O_2Ag$, is difficultly soluble in water, crystallizing on spontaneous evaporation in glistening flat needles.

COMPOUND ETHERS.

		B. P.	Sp. Gr. at 0.
Methyl trimethylacetate,	CH_3O,C_5H_9O	100–102°	—
Ethyl trimethylacetate,	C_2H_5O,C_5H_9O	118°·5	0·8773
Trimethylcarbyl trimethylacetate,	C_4H_9O,C_5H_9O	134–135°	—

In addition the following compounds have been prepared by Butlerow:

	B. P.
Trimethylacetyl oxide	190°
Trimethylacetyl chloride . . .	105–106°
Trimethylacetamide	—

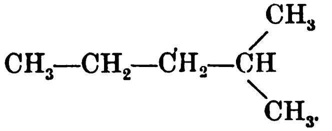
COMPOUNDS WITH SIX ATOMS OF CARBON, OR THE HEXYL GROUP.

398 According to theory five paraffins may exist of the formula C_6H_{14}, and the whole of these are known:

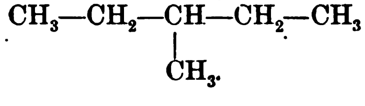
I. Hexane.

$$CH_3—CH_2—CH_2—CH_2—CH_2—CH_3.$$

II. Isohexane, or Dimethylpropyl Methane.

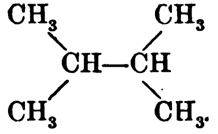


III. Methyl-diethyl Methane.

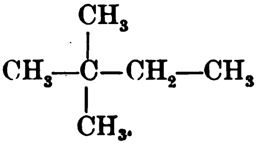


$$CH_3—CH_2—\underset{\displaystyle CH_3.}{\underset{|}{CH}}—CH_2—CH_3$$

IV. Tetramethyl Ethane.



V. Trimethyl-ethyl Methane.



$$CH_3—\underset{\displaystyle CH_3.}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}—CH_2—CH_3$$

NORMAL HEXANE AND ITS DERIVATIVES.

399 *Hexane*, C_6H_{14}, was first observed by C. Greville Williams in the products of the distillation of Boghead cannel, and was believed by him to be the free radical propyl.[1] Cahours and Pelouze next found that this same hydrocarbon occurs in large quantities in the volatile portions of Pennsylvanian petroleum, and they termed it "hydrure de caproylène" or "hydrure

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[1] *Journ. Chem. Soc.* xv. 130.

d'hexyle."[1] Lastly, Schorlemmer proved that it occurs in the naphtha from cannel coal.[2]

Normal hexane is also formed when suberic acid, $C_8H_{14}O_4$, is heated with caustic baryta.[3] The yield is, however, in this case only small, owing to the large number of by-products formed.[4] It is likewise produced by heating secondary hexyl iodide, obtained from mannite, with zinc and water or alcohol.[5] This decomposition takes place, however, more satisfactorily when the iodide is brought in contact with zinc and water, and hydrochloric acid gradually added. In this way some hexylene, C_6H_{12}, is always formed together with dihexyl or dodecane, $C_{12}H_{26}$ (see p. 138). The latter compound, which boils at 202°, can readily be removed by distillation. The two other hydrocarbons, both of which boil at 69°, may be separated by addition of bromine when the difficultly volatile hexylene bromide is obtained, and the hexane can be distilled off, and afterwards obtained in the perfectly pure state by allowing it to remain for some time in contact with a mixture of concentrated sulphuric and nitric acids. It is then washed with water, dried over caustic potash, and lastly rectified over sodium.[6]

Hexane can be synthetically obtained by heating primary propyl iodide with sodium.[7] It is a mobile liquid, possessing a weak but pleasant smell, boiling at 69°, and having at 17° a specific gravity of 0·663, whilst that of its vapour is 2·98. If chlorine be allowed to act upon it in diffused daylight, the first product obtained is a mixture of the primary and secondary chlorides.[8] Bromine on the other hand yields only secondary hexyl bromide.[9]

Primary Hexyl Alcohol, $C_6H_{13}OH$, was first prepared by Pelouze and Cahours, but mixed with the secondary alcohol. They regarded this, as well as the other derivatives of hexane, as pure compounds. Schorlemmer, however, proved that this is not the case.

Hexyl alcohol occurs in the form of ethers in nature. Thus the oils of the seeds of *Heracleum giganteum* consist principally

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[1] *Ann. Chem. Pharm.* cxxiv. 289 ; cxxvii.

[2] *Journ. Chem. Soc.* xv. 422.

[3] Riche, *Ann. Chim. Phys.* [3], lix. 432.

[4] Dale, *Journ. Chem. Soc.* xvii. 258 ; *Ann. Chem. Pharm.* cxxxii. 243.

[5] Erlenmeyer and Wanklyn, *Journ. Chem. Soc.* xvi. 227 ; *Ann. Chem. Pharm.* cxxxv. 136.

[6] Schorlemmer, *Phil. Trans.* 1872, 118.

[7] Schorlemmer, *ib.* ; Brühl, *Ann. Chem. Pharm.* cc. 183.

[8] Schorlemmer, *loc. cit.* and *Lieb. Ann.* cxcix. 139.

[9] Schorlemmer, *Phil. Trans.* 1878, p. 1.

of the isomeric ethers, hexyl butyrate, and octyl acetate, which cannot be separated by distillation as they boil at almost the same temperature. By collecting the portion boiling between 201° and 206°, and heating it with caustic potash, the alcohols are obtained, and these may then be dried over ignited carbonate of potash, and easily separated.[1] Hexyl alcohol may also be obtained from normal caproic acid by reduction.[2] It is a pleasantly aromatic-smelling liquid boiling at 157°, and having at 0° a specific gravity of 0·8333. The following derivatives are those which have been most accurately examined:

		B.P.	Sp. Gr.	at
Ethyl-hexyl ether,	$C_2H_5(C_6H_{13})O$	134-137°	—	—
Hexyl bromide,	$C_6H_{13}Br$	155°·5	1·1935	0°
Hexyl iodide,	$C_6H_{13}I$	181°·4	1·4607	0°
Hexyl acetate,	$C_6H_{13}O(C_2H_3O)$	169°·5	0·8890	17°

400 *Methyl-butyl Carbinol*, $(CH_3)C_4H_9.CH.OH$, was first prepared by Erlenmeyer and Wanklyn,[3] and termed by them β-hexyl alcohol. They obtained it by acting upon the iodide, which is about to be described, with silver oxide and water, when, together with the alcohol, hexylene and secondary hexyl oxide are formed. A better method is to convert the iodide into hexylene by heating with alcoholic potash, and then to shake up this with an equal volume of a mixture of three volumes of sulphuric acid and one volume of water until the hydrocarbon is dissolved, taking care to keep it cool during the whole operation. On the addition of water the larger portion of the alcohol separates out, and a further quantity is obtained by distilling the aqueous liquid. It is an oily liquid, possessing a pleasant, refreshing smell, boiling at 136°, and having a specific gravity at 0° of 0·8327.

Secondary Hexyl Iodide, $C_6H_{13}I$. This compound, which is the starting-point for the hexyl compounds derived from methyl-butyl carbinol, is formed on heating mannite or its isomeride dulcite with concentrated hydriodic acid:[4]

$$C_6H_{14}O_6 + 11\,HI = C_6H_{13}I + 6\,H_2O + 5\,I_2.$$

As the presence of free iodine acts deleteriously in this reaction its formation is prevented by the addition of amorphous

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[1] Franchimont and Zincke, *Ann. Chem. Pharm.* clxiii. 193.

[2] Lieben and Janecek, *ib.* clxxxvii. 126.

[3] *Journ. Chem. Soc.* xvi. 230.

[4] Erlenmeyer and Wanklyn, *loc. cit.*; Hecht, *Ann. Chem. Pharm.* clxv. 146.

phosphorus. According to Hecht, 95·7 grams of iodine are covered with 86 cc. of water, and 20 grams of yellow phosphorus are gradually added, and then a further 10 grams of red phosphorus. The air is displaced by carbonic acid, and the whole gently warmed, and 50 grams of mannite or dulcite added gradually in small portions; 10 grams of amorphous phosphorus are then introduced, and the whole is distilled in a current of carbon dioxide. It is perhaps simpler to gently warm a mixture of mannite and red phosphorus with an excess of fuming hydriodic acid, to distil the iodide off, and again to add mannite and phosphorus. In this way the operation may be conducted for some time, care being taken to pour back again from time to time the hydriodic acid which comes over (Schorlemmer).

The secondary iodide is a colourless liquid, which soon becomes brown on exposure, boils at 167°, and at 0° has a specific gravity of 1·4526.

SECONDARY HEXYL COMPOUNDS.

		B.P.	Sp. Gr.	at
[1] Hexyl oxide,	$(C_6H_{13})_2O$	203°·5-2 ?	—	—
[2] Hexyl chloride,	$C_6H_{13}Cl$	125-126°	—	—
[2] Hexyl bromide,	$C_6H_{13}Br$	143-145°	—	—
[1] Hexyl hydrosulphide,	$C_6H_{13}SH$	142°	0·8856	0°
[3] Hexylamine,	$C_6H_{13}.NH_2$	116°	0·7638	—
[3] Hexyl thiocyanate,	$C_6H_{13}.SCN$	206-207°·5	—	—
[3] Hexyl thiocarbimide,	$C_6H_{13}N.CS$	197-198°	0·9253	—
[1] Hexyl acetate,	$C_6H_{13}O(C_2H_3O)$	155-157°	0·8778	0°

Ethyl-butyl Ketone, $C_2H_5(C_4H_9)CO$, is formed by oxidizing the secondary alcohol, and was formerly described as β-hexylaldehyde. It is a pleasantly-smelling liquid, boiling at 127°, and being converted by further oxidation into acetic acid and normal butyric acid. This fact supplies the means of ascertaining the constitution of the hexyl alcohol from mannite. The ketone forms a crystalline compound with sodium sulphite.

Ethyl-propyl Carbinol, $C_2H_5(C_3H_7)CH.OH$. This second normal secondary hexyl alcohol is formed by the action of sodium amalgam and water on the corresponding ketone,[4] described hereafter. It boils at 134°, and at 0° has a specific gravity of 0·8343. It has a pleasant aromatic smell. When

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[1] Erlenmeyer and Wanklyn, *loc. cit.*

[2] Schorlemmer.

[3] Uppenkamp, *Ber. Deutsch. Chem. Ges.* viii. 55.

[4] Völker, *Ber. Deutsch. Chem. Ges.* viii. 1019; Oechsner de Coninck, *Bull Soc. Chim.* [2], xxv. 7.

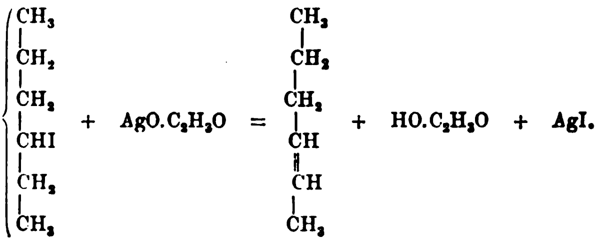
heated with hydriodic acid the iodide is formed, boiling at 164°—166°. The acetate is a pleasantly-smelling liquid, boiling between 149° and 151°.

Ethyl-propyl-carbyl Ethyl Ether, $\left.\begin{array}{r} C_2H_5(C_3H_7)CH \\ C_2H_5 \end{array}\right\} O$, has been already described as biethyl ether (page 339). It is formed by heating dichlorethyl ether with zinc-ethyl under pressure:

$$\left.\begin{array}{r} CH_2Cl.CHCl \\ C_2H_5 \end{array}\right\} O + Zn(C_2H_5)_2 = \left.\begin{array}{r} CH_2(C_2H_5).CH(C_2H_5) \\ C_2H_5 \end{array}\right\} O + ZnCl_2.$$

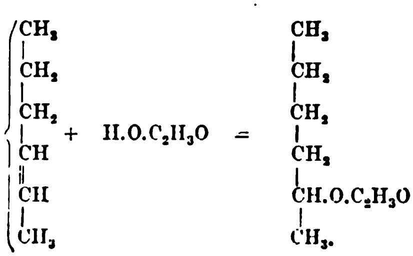
The product gives the pure ether on heating with sodium. This boils at 131°, and at 0° has a specific gravity of 0·7856. When heated with fuming hydriodic acid under pressure, ethyl and hexyl iodides are formed, which latter is converted by the action of acetic acid and silver acetate into hexyl acetate, a body boiling at 154°—157°. When heated with caustic potash this does not yield ethyl-propyl carbinol, but methyl-butyl carbinol. Consequently in the reaction an intermolecular interchange takes place, which may be explained in a variety of ways. Thus, by the action of silver acetate a small quantity of hexylene is always formed, and it is probable that in this reaction the iodide is first converted entirely into this hydrocarbon, which is methyl-propyl ethylene, and that this latter in the nascent condition, when brought in contact with acetic acid, unites with it to form the acetate of the mannite alcohol. The following equations show these reactions:

(1)



$$(1)\quad \left\{\begin{array}{l} CH_3 \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CHI \\ | \\ CH_2 \\ | \\ CH_3 \end{array}\right. + AgO.C_2H_3O = \begin{array}{l} CH_3 \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CH \\ \| \\ CH \\ | \\ CH_3 \end{array} + HO.C_2H_3O + AgI.$$

(2)



$$(2)\quad \left\{\begin{array}{l} CH_3 \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CH \\ \| \\ CH \\ | \\ CH_3 \end{array}\right. + H.O.C_2H_3O = \begin{array}{l} CH_3 \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CH.O.C_2H_3O \\ | \\ CH_3. \end{array}$$

According to theory, isohexane yields two secondary alcohols, which, however, have not as yet been prepared, although the ketones corresponding to them are known.

Isobutyl-methyl Ketone, $(CH_3)_2C_2H_3.CO.CH_3$, was prepared by Williamson, though not in the pure state, by distilling a mixture of potassium valerate and sodium acetate.[1] Frankland and Duppa obtained it by decomposing isopropyl-aceto-acetic ether with baryta-water.[2] It is a liquid having a strong smell of camphor, boiling at 114°, and having a specific gravity of 0·819 at 0°.

Dimethyl-propyl Carbinol, $(CH_3)_2C_3H_7.COH$, was obtained by the action of zinc-methyl on butyryl chloride. It is a thick liquid which has a faint smell of camphor and boils at 122°·5—123°·5. Its chloride boils at 100°, and its iodide boils with decomposition at 142°.[3]

METHYL-DIETHYL METHANE AND ITS DERIVATIVES.

402 *Methyl-diethyl Methane*, $CH_3(C_2H_5)_2CH$, was obtained by Le Bel by acting on a mixture of methyl iodide and active amyl iodide with sodium. It is a liquid boiling at 60°, and is optically inactive, not containing any assymetrical carbon atom.[4]

Methyl-diethyl Carbinol, $CH_3(C_2H_5)_2COH$, is prepared by the action of zinc-ethyl on acetyl chloride. It is a thickish liquid, smelling of camphor, boiling between 121° and 125°, and yielding only acetic acid on oxidation.

TETRAMETHYL ETHANE AND ITS DERIVATIVES.

403 *Tetramethyl Ethane*, $(CH_3)_4C_2H_2$, was obtained by Schorlemmer by heating secondary propyl iodide with sodium in presence of ether, and he termed it *di-isopropyl*.[5] It is a liquid smelling like normal hexane, boiling at 58°, and at 10°

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[1] *Quart. Journ. Chem. Soc.* iv. 238.

[2] *Journ. Chem. Soc.* [2], v. 106.

[3] Butlerow, *Zeitsch. Chem.* 1865, 617; Jawein, *Ann. Chem. Pharm.* cxcv. 253.

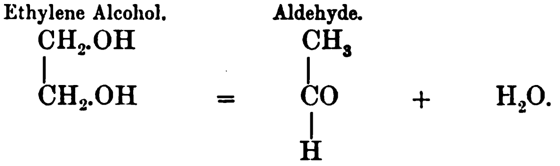
[4] *Bull. Soc. Chim.* [2], xxv. 546.

[5] *Proc. Roy. Soc.* xvi. 34.

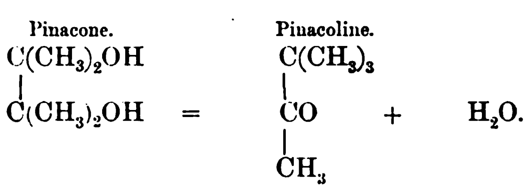
This body will be treated of more fully hereafter. When it is dissolved in moderately dilute sulphuric or hydrochloric acid, it is converted into *pinacoline*, $C_6H_{12}O$, and this is capable of uniting with nascent hydrogen to form pinacolyl alcohol. This latter body is a liquid smelling like camphor, boiling at 120°—121°, and having at 0° a specific gravity of 0·8347. On cooling it solidifies to long silky needles melting at 4°.[1] On oxidation it is converted into pinacoline, which is its ketone.

	B.P.	Sp. Gr. at 0°.
Pinacolyl chloride, $C_6H_{13}Cl$	112°·5-114°·5	0·8991
Pinacolyl bromide, $C_6H_{13}Br$	140-144°	1·4739
Pinacolyl acetate, $C_6H_{13}O(C_2H_3O)$	140-143°	—

Pinacoline or *Trimethylcarbyl-methyl Ketone*, $(CH_3)_3C.CO.CH_3$. This liquid has a smell resembling peppermint, boils at 105°·5 to 106°·5, and has a specific gravity at 0° of 0·83.[2] On oxidation it yields, together with carbon dioxide, an acid which was first called pinacolinic acid,[3] until Butlerow showed that it is trimethylacetic acid[4] (see p. 623). The formation of the acid in which three methyl groups are linked to one carbon atom from pinacoline, the constitution of which has been already given, appears at first difficult to understand, although similar intermolecular interchanges are known. Ethylene alcohol or common glycol is converted into aldehyde by hygroscopic bodies, a reaction which is quite similar to the formation of pinacoline:



$$\underset{\text{Ethylene Alcohol.}}{\begin{matrix} CH_2.OH \\ | \\ CH_2.OH \end{matrix}} = \underset{\text{Aldehyde.}}{\begin{matrix} CH_3 \\ | \\ CO \\ | \\ H \end{matrix}} + H_2O.$$



$$\underset{\text{Pinacone.}}{\begin{matrix} C(CH_3)_2OH \\ | \\ C(CH_3)_2OH \end{matrix}} = \underset{\text{Pinacoline.}}{\begin{matrix} C(CH_3)_3 \\ | \\ CO \\ | \\ CH_3 \end{matrix}} + H_2O.$$

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[1] Friedel and Silva, *Compt. Rend.* lxxvi. 226.
[2] Fittig, *Ann. Chem. Pharm.* cxiv. 57.
[3] *Compt. Rend.* lxxvii. 48.
[4] *Ann. Chem. Pharm.* clxx. 162; clxxiii. 358.

the acids occurring in fats, and certainly in those produced by fermentation, as the properties of these bodies exactly coincide with those of the substance obtained by oxidation of normal hexyl alcohol as well as with those of the synthetically prepared acid. This latter substance was obtained by Lieben and Rossi by heating normal pentyl iodide with potassium cyanide and alcohol. The solution of the nitril thus obtained was boiled with caustic potash until no more ammonia was evolved, and the potassium salt obtained on evaporation was decomposed by sulphuric acid.[1]

Normal caproic acid is best obtained from the crude fermentation-butyric acid by fractional distillation, the portion passing over above 180° being separated and washed repeatedly with six times its volume of water, when butyric acid alone passes into solution. The pure acid may be obtained from the residue by fractional distillation.[2] It boils at 205° and has a specific gravity at 0° of 0·9450.

Calcium Caproate, $(C_6H_{11}O_2)_2Ca+H_2O$, crystallizes in long very thin glistening laminæ. 100 parts of a solution saturated at 18°·5 contain 2·7 parts of the anhydrous salt. When mixed with calcium formate and heated, *caproyl aldehyde,* $C_5H_{11}.COH$, is obtained together with other products. This substance has a pungent smell, boils at 127°·9, has a specific gravity at 0° of 0·850 and readily absorbs oxygen with formation of ozone.

Barium Caproate, $(C_6H_{11}O_2)_2Ba$. This deposits in six-sided laminæ often united in coxcomb-like tufts. 100 parts of the solution saturated at 18°·5 contain 8·49 parts of the anhydrous salt. The acid derived from hexyl alcohol yields a salt crystallizing in scales or thick tablets containing one molecule of water of crystallization.[3] Kottal, however, obtained a salt from the fermentation-acid which contained three molecules of water and crystallized in bushy needles.[4]

Ethyl Caproate, $C_6H_{11}O(C_2H_5O)$, separates out as a light layer of liquid when a mixture of two parts of absolute alcohol and two parts of the acid is allowed to stand for some time together with one part of sulphuric acid. It is a pleasantly-smelling liquid boiling at 167°, and having at 0° a specific gravity of 0·8898.

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[1] *Ann. Chem. Pharm.* clix. 75 ; clxv. 118.
[2] Grillone, *Ann. Chem. Pharm.* clxv. 132 ; Lieben, *ib.* clxx. 89.
[3] Franchimont and Zincke, *Ann. Chem. Pharm.* clxiii. 193.
[4] *Ann. Chem. Pharm.* clxx. 97.

the preparation of the above compounds. Very probably it was that obtained from amyl alcohol.

Isocaproylamide, $C_6H_{11}O.NH_2$, is formed by the action of ammonium carbonate on the chloride. It crystallizes in small pearly glistening scales which have a fatty smell and boil at about 255°[1]

Isocaproyl Nitril, $C_6H_{11}N$, was first prepared by Balard[2] by heating amyl oxalate or potassium amyl sulphate with potassium cyanide. He termed it *éther cyanhydramylique*, but did not investigate it more fully. Frankland and Kolbe prepared it by the latter reaction, and ascertained its properties.[3] Williamson showed later on that it can be obtained by heating amyl iodide with potassium cyanide and alcohol;[4] and Wurtz, who obtained it in a similar way, proved that it, like all the derivatives of the common laevro-rotatory alcohol, turns the polarized ray to the right.[5]

It is a colourless liquid, having a pungent smell, boiling at 155° (Wurtz), and its vapour has a specific gravity of 3·335 (Frankland and Kolbe). Like other nitrils, it unites with various metallic chlorides to form crystalline compounds,[6] and by the action of potassium a base corresponding to cyanethine (p. 562) is formed.[7]

407 *Diethylacetic Acid*, $(C_2H_5)_2CH.CO_2H$, was first prepared by Frankland and Duppa[8] by the successive action of sodium and ethyl iodide on acetic acid. Saytzeff[9] obtained it from diethylcarbinol by converting this into the iodide and then heating it with alcohol and potassium cyanide. The product was distilled, and the distillate boiled with caustic potash. The potassium salt thus prepared was decomposed by sulphuric acid after the alcohol had been driven off.

Diethyl-acetic acid is a liquid possessing a pleasant smell, but slightly resembling that of caproic acid. It boils at 190°, and at 0° has the specific gravity 0·9355.

The calcium and barium salts of this acid crystallize only with difficulty. The silver salt forms glistening needles, and is more readily soluble than are those of the two preceding

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[1] Henry, *Ber. Deutsch. Chem. Ges.* ii. 494.

[2] *Ann. Chim. Phys.* [3], xii. 294.

[3] *Ann. Chem. Pharm.* lxv. 297.

[4] *Phil. Mag.* [4], vi. 205.

[5] *Ann. Chim. Phys.* [3], li. 358.

[6] Henke, *Ann. Chem. Pharm.* cvi. 280.

[7] Medlock, *Quart. Journ. Chem. Soc.* i. 379; *Ann. Chem. Pharm.* lxix. 229.

[8] *Phil. Trans.* 1866, 50.

[9] *Ann. Chem. Pharm.* cxciii. 350.

acids. Its ethyl-ether boils at 151°, and at 0° has a specific gravity of 0·8826.

Methyl-propyl-acetic Acid, $CH_3(C_3H_7)CH.CO_2H$, is prepared from methyl-propyl-carbinol in a corresponding manner. It boils at 193°, at 0° has the specific gravity 0·9414, and both it and its salts closely resemble diethylacetic acid. Its ethyl-ether boils at 153°, and at 0° has a specific gravity of 0·8826 (Saytzeff).

Dimethyl-ethyl-acetic Acid, $(CH_3)_2C_2H_5.CH.CO_2H$, is prepared from dimethyl-ethyl carbinol exactly as trimethylacetic acid is got from tertiary butyl alcohol (p. 623). It is a colourless liquid, boiling at 187°, having a faint smell of the fatty acids, and on cooling in a freezing mixture forms crystalline scales which melt at —14°.

Barium Dimethyl-ethyl-acetate, $(C_6H_{11}O_2)_2Ba+5H_2O$, crystallizes in scales or transparent tablets which effloresce on exposure to air.

The very soluble calcium salt forms long, thin, glistening needles.[1]

Markownikoff[2] obtained a caproic acid from amyl iodide obtained by the combination of ordinary amylene and hydriodic acid and subsequently making use of the nitril reaction. This acid he believed to be methyl-isopropyl-acetic acid, as the iodide from which it was obtained must be looked upon as secondary amyl iodide. This, however, as has been stated, is a tertiary compound, and the acid obtained from it, which has not been more nearly investigated, ought, therefore, to be identical with dimethyl-ethyl acetic acid. As, however, ordinary amylene is itself a mixture of isomeric bodies, it is probable that this is also the case with the caproic acid obtained from it. Hence it therefore merits further investigation.

As has been stated (p. 630), hexyl alcohol from oil of camomile yields a caproic acid by oxidation, which is different from the other known acids. Its calcium salt crystallizes in small silky needles, which do not contain any water of crystallization; 100 parts of the solution saturated at 15° contain 16·5 parts of the salt, which is partly deposited on warming the solution.

[1] Wischnegradsky, *Ann. Chem. Pharm.* clxxiv. 56.
[2] *Zeitsch. Chem.* 1866, 502.

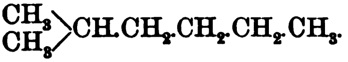
COMPOUNDS CONTAINING SEVEN ATOMS OF CARBON, OR THE HEPTYL GROUP.

408 Nine paraffins of the formula C_7H_{16} may exist according to theory. Of these only the following are, however, known with certainty:

Normal Heptane.

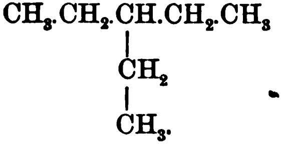
$CH_3.CH_3.CH_2.CH_2.CH_2.CH_2.CH_3.$

Isoheptane, or Dimethyl-butyl Methane.



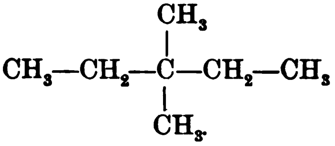
$$\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle CH.CH_2.CH_2.CH_2.CH_3.$$

Triethyl Methane.



$$\begin{matrix}CH_3.CH_2.CH.CH_2.CH_3\\ \quad\quad\;\; | \\ \quad\quad\;\; CH_2 \\ \quad\quad\;\; | \\ \quad\quad\;\; CH_3.\end{matrix}$$

Dimethyl-diethyl Methane.



$$\begin{matrix} & & CH_3 & & \\ & & | & & \\ CH_3— & CH_2— & C & —CH_2— & CH_3 \\ & & | & & \\ & & CH_3. & & \end{matrix}$$

NORMAL HEPTANE AND ITS DERIVATIVES.

409 *Heptane*, C_7H_{16}, was first discovered by Schorlemmer in cannel-coal naphtha,[1] and he afterwards showed that this paraffin is contained in large quantity in the Pennsylvanian petroleum;[2] this liquid, however, contains another isomeric heptane boiling at 90°,[3] the presence of which renders the purification of the normal compound boiling 8° higher very difficult.[4] The heptyl hydride obtained by Pelouze and Cahours[5] from the same source, and boiling at 92°—94°, is a mixture of these two heptanes.

Normal heptane also occurs largely in the distillation-products of lime-soaps of the Menhaden oil, and together with other

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[1] *Journ. Chem. Soc.* xv. 423.

[2] *Journ. Chem. Soc.* xvi. 216.

[3] Warren, *Chem. News.* xiii. 74; Schorlemmer, *Proc. Roy. Soc.* xvi. 367.

[4] Schorlemmer, *Phil. Trans.* 1872, [1], 120.

[5] *Ann. Chim. Phys.* [4], i. 1.

products in the dry distillation of a mixture of azelaic acid, $C_7H_{14}(CO_2H)_2$, and caustic baryta.[1]

A remarkable occurrence of this paraffin in the vegetable kingdom remains to be noticed. On the low mountain chains running parallel to the coast of California, as well as on the slopes of the foot-hills of the Sierra Nevada, the nut-pine or digger-pine (*Pinus Sabiniana Dougl*) grows in magnificent profusion. This tree, the fruit of which is used as an article of food by the Digger Indians, yields a turpentine which has become an article of commerce. For the purpose of procuring the exudation, the tree is notched and guttered during winter at a convenient height from the ground, and the resin obtained subjected to distillation. This yields a very volatile liquid which was recognised by Wenzel as a hydrocarbon, to which he gave the name of *abietene*. It has also received the names of *aurantine* and *theoline* in the San Francisco market, and it is used instead of benzoline or petroleum benzene for the removal of grease-stains and also as an insecticide. The crude hydrocarbon is a mobile, almost colourless liquid, having a smell resembling oranges, and its vapour produces anæsthetic effects on inhalation. When subjected to distillation it begins to boil about 100°, by far the larger portion coming over at 101°. The residue leaves on further evaporation a brown resin, which has a strong and persistent smell of oranges. When the liquid is shaken up for some time with sulphuric acid this smell disappears, and the purified *abietene* consists entirely, as Thorpe has shown, of pure normal heptane whose physical constants he has most carefully determined.[2] It boils at 98°·4, and at 0° has a specific gravity of 0·70048, whilst that of its vapour is 3·464. It is remarkable that the substance obtained from petroleum and purified as carefully as possible, exhibits a higher specific gravity than that from *Pinus Sabiniana*. This appears to depend upon the fact that petroleum purified by the action of sulphuric and nitric acid, though consisting principally of the normal paraffins, also contains small quantities of isomeric and homologous hydrocarbons which cannot be removed, and that the heptane obtained from this source containing some of these thus has a higher specific gravity.

Heptane behaves towards chlorine and bromine exactly like hexane (p. 626).[3]

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[1] Dale, *Chem. Soc. Journ.* xvii. 258.

[2] *Chem. Soc. Journ.* 1879 (I.), 296.

[3] Schorlemmer, *loc. cit.*; Venable, *Ber. Deutsch. Chem. Ges.* xiii. 1649.

410 *Primary Heptyl Alcohol*, $C_7H_{15}.OH$. The point of departure for this compound is the corresponding aldehyde which can be easily obtained by the distillation of castor-oil, and is known under the name of œnanthyl alcohol. The first attempts to convert this body into œnanthyl alcohol were made by Fittig. By heating œnanthol with slaked-lime he obtained, together with œnanthylic acid and other products, a liquid which undoubtedly contained the alcohol in question, but he did not succeed in preparing it in the pure state.[1]

Bouis and Carlet then heated œnanthol with glacial acetic acid and zinc under somewhat increased pressure and thus obtained an acetate, which, when heated with alkali, yielded an alcohol-like liquid, and this, according to their description, was probably an impure hexyl alcohol.[2]

The pure alcohol was first prepared by Grimshaw and Schorlemmer, who employed Lieben and Rossi's method for the reduction of the aldehyde. The aldehyde was brought into contact with water and sodium amalgam, care being taken that the liquid should always remain neutral by addition of dilute sulphuric acid.[3] By this process large quantities of condensation-products of œnanthol are also obtained. The quantity of these may, however, be diminished, as Schorlemmer has shown, if instead of using water, strong acetic acid in which œnanthol has been dissolved be employed.[4] This method was worked out first by Cross[5] and afterwards by Jourdan.[6]

According to this latter observer, a solution of two parts of œnanthol in one part of acetic acid is taken, and to this is added a small quantity of 50 per cent. acetic acid. From 170 to 180 parts of a 2 per cent. sodium amalgam is next gradually added to the cold liquid, whilst from time to time a small quantity of glacial acetic acid is poured in. The whole is then diluted with water, neutralized with carbonate of soda, and the oily layer which separates out twice heated with acetic acid and sodium amalgam, and the oil then obtained boiled with caustic potash in order to decompose the acetate which is formed. The liquid is then dried over ignited carbonate of potash and the product fractionally distilled under diminished pressure.

Heptyl alcohol is a colourless pleasantly smelling liquid

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[1] *Ann. Chem. Pharm.* cxvii. 76.

[2] *Ib.* cxxiv. 352; *Comptes Rendus*, xv. 140.

[3] *Chem. Soc. Journ.* xxvi. 1073.

[4] *Ann. Chem. Pharm.* clxxvii. 303.

[5] *Chem. Soc. Journ.* 1877, ii. 123.

[6] *Ann. Chem. Pharm.* cc. 102.

boiling at 175°·5, and having a specific gravity of 0·838. Cross prepared the following derivatives:

	B.P.	Sp. Gr. at 16°.
Heptyl-ethyl ether, $C_7H_{15}(C_2H_5)O$	165°	0·790
Heptyl chloride, $C_7H_{15}Cl$	159°·2	0·881
Heptyl bromide, $C_7H_{15}Br$	178°·5	1·133
Heptyl iodide, $C_7H_{15}I$	201°	1·346
Heptyl acetate, $C_7H_{15}O(C_2H_3O)$	191°·5	0·874

Methyl-pentyl Carbinol, $CH_3(C_5H_{11})CH.OH$. This is prepared from normal heptane, but has not as yet been obtained in the pure state. It boils at 160°—162°, and yields a ketone boiling at 150°—152°. It is converted on oxidation into acetic and normal pentylic acids (Schorlemmer). The chloride boils at about 145°, and the bromide at 165°—167°.

Dipropyl Carbinol, $(C_3H_7)_2CH.OH$, is obtained from the corresponding ketone. Water is added to the ketone and then sodium in small pieces, the whole being well shaken up. It is a peculiarly smelling liquid boiling at 149°—150°, and having a specific gravity of 0·814 at 25°.[1]

Dipropyl Ketone, $(C_3H_7)_2CO$, Chevreul was the first to obtain this compound in the impure state by the dry distillation of certain salts of butyric acid. It was then described as a liquid oil having a smell of certain species of *Labiatæ*. Chancel investigated it more exactly, and recognised it as a ketone of butyric acid, giving to it the name of *butyrone*.[2] In order to prepare it, calcium butyrate is subjected to distillation in small quantities and at as low a temperature as possible. The crude product always contains other ketones,[3] from which butyrone is separated by fractional distillation. It is a highly refracting liquid, having a pleasant smell and a burning taste. It boils at 144°, and at 20° has a specific gravity of 0·82, whilst that of its vapour is 3·99. It does not yield any compounds with the acid sulphites of the alkali metals, and decomposes on oxidation into propionic acid and butyric acid. By the action of hot concentrated nitric it is converted into dinitropropane, $C_3H_6(NO_2)_2$, a body which was formerly supposed to be nitro-propionic acid.[4]

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[1] Friedel, *Ann. Chim. Phys.* [4], xvi. 310; Kurtz, *Ann. Chem Pharm.* clxi. 205.

[2] *Ann. Chim. Phys.* [3], xii. 146.

[3] Friedel; Kurtz, *loc. cit.*

[4] Chancel, *Ann. Chem Pharm.* lxiv. 331; *Compt. Rend.* lxxxvi. 1405; Kurtz, *Ann. Chem. Pharm.* clxi. 209.

ISOHEPTANE AND ITS DERIVATIVES.

411 *Isoheptane*, or *Dimethyl-butyl Methane*, $(CH_3)_2CH.C_4H_9$, was first obtained by Wurtz by acting with sodium upon a mixture of ethyl and amyl iodides, and was termed by him *ethyl-amyl*.[1] In order to prepare it, a mixture of equal parts of ethyl bromide and amyl bromide is gradually treated with the requisite quantity of sodium, care being taken that the temperature does not rise above 25° and does not fall below 20°. As soon as all the sodium has been added, and the reaction slackens, the mixture is heated to 100°, and kept for some time at this point. It is then distilled, and the distillate fractionated in order to separate the tetramethylmethane (diamyl) which is formed at the same time. During this process more sodium is added in order to remove more completely the bromides which are formed. The portion boiling from 85° to 90° is then further purified by shaking with sulphuric acid, with which it is allowed to remain in contact for some time. It is then washed with water, dried over caustic potash, and afterwards rectified over sodium.[2]

Isoheptane boils at 90°·3, and at 0° has a specific gravity of 0·6969 (Thorpe). Chlorine acts easily upon it in diffused daylight; as a first substitution-product a mixture of the primary and secondary chlorides is obtained. These cannot be separated by fractional distillation, but the alcohols obtained from them may be thus separated.

Primary Isoheptyl Alcohol, $(CH_3)_2C_5H_9OH$, boils at 163°—165°, has a smell like fusel-oil, and on oxidation yields isoheptylic acid, which will be afterwards described. Faget[3] has separated out heptyl alcohol boiling at 155°—165° from the fusel-oil of wine brandy, and this perhaps is the substance under consideration.

Secondary Isoheptyl Alcohol, or *Methyl-amyl Carbinol*, $(CH)_2C_3H_5(CH.OH)CH_3$, boils about 148°, and on oxidation yields methyl-amyl ketone, $(CH_3)_2C_3H_5CO.CH_3$, boiling at 148° (Grimshaw). This may also be easily obtained in the pure state by treating isobutyl acetic ether with baryta water. In contact

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[1] *Ann. Chim. Phys.* [3], xliv. 275.

[2] Grimshaw, *Chem. Soc Journ.* xxvi. 309.

[3] *Ann. Chem Pharm.* cxxiv. 355; *Bull. Soc. Chim.* 1862, 59.

with nascent hydrogen it is again converted into the secondary alcohol, which has a sweetish smell and a specific gravity at 17° of 0·8185[1] (Faget).

It has been already stated that American petroleum not only contains normal heptane, but also an isomeric paraffin boiling at 90°. This substance has been investigated by Schorlemmer, who found that the derivatives obtained from it closely resemble those of isoheptane, but differ inasmuch as the ketone obtained from the secondary alcohol yields on oxidation only acetic acid. Hence it is evident that the above paraffin is not isoheptane.[2]

TRIETHYL METHANE AND ITS DERIVATIVES.

412 *Triethyl Methane*, $CH(C_2H_5)_3$, was discovered by Ladenburg,[3] by the action of zinc-ethyl on sodium and ethyl orthoformate:

$$2\,CH(OC_2H_5)_3 + 3\,Zn(C_2H_5)_2 = 2\,CH(C_2H_5)_3 + 3\,Zn(OCH)_2.$$

This reaction however does not occcur so simply as above described, inasmuch as several by-products are formed. In order to separate the paraffin, the portion boiling at about 100° is treated with concentrated sulphuric acid, and the liquid which is not attacked is purified by washing with water, then dried and rectified. Triethyl-methane has a faint smell of petroleum, boils at 96°, and at 27° has a specific gravity of 0 689.

Triethyl Carbinol, $(C_2H_5)_3COH$, is obtained by the action of propionyl chloride on zinc-ethyl.[4] It is a liquid having a smell of camphor, boiling at 140°—142°, and having a specific gravity at 0° of 0·8593. When oxidized by potassium dichromate and weak sulphuric acid, acetic and propionic acids are obtained; the greater part, however, is converted by loss of water into heptylene, which may be looked upon as diethyl-methylethylene, $(C_2H_5)_2C=CH.CH_3$.

Diethyl-dimethyl Methane, $C(CH_3)_2(C_2H_5)_2$. The compound $C_3H_6Cl_2$ is obtained by the action of phosphorus pentachloride on acetone, and this when warmed with zinc-ethyl gives the above-named paraffin together with other products:

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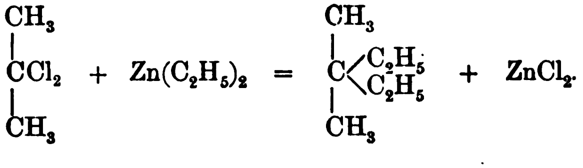
[1] Rohn, *Ann. Chem. Pharm.* cxc. 309.

[2] *Journ. Chem. Soc.* xxvi. 319.

[3] *Ber. Deutsch. Chem. Ges.* v. 752.

[4] Ladenburg, *Ber. Deutsch. Chem. Ges.* v. 752.



$$\begin{array}{l}CH_3\\ |\\ CCl_2\\ |\\ CH_3\end{array} + Zn(C_2H_5)_2 = \begin{array}{l}CH_3\\ |\\ C\begin{cases}C_2H_5\\ C_2H_5\end{cases}\\ |\\ CH_3\end{array} + ZnCl_2.$$

By careful rectification, the pure product is obtained, boiling at 86°—87°, and having a specific gravity of 0·7111 at 0°.[1]

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413 The other heptyl compounds which have been prepared are derived from unknown paraffins.

Di-isopropyl Carbinol, $[(CH_3)_2CH]_2CH.OH$. This secondary alcohol is prepared from the following ketone, which is dissolved in benzene, the solution poured upon water, and sodium gradually added, the whole being kept cool. Di-isopropyl carbinol is a liquid with a pleasant smell resembling peppermint, boiling at 131°—132°, and having at 17° a specific gravity of 0·8323.

Di-isopropyl Ketone, $[(CH_3)_2CH]_2CO$, is obtained by the fractional distillation of the product of the dry distillation of calcium isobutyrate. It is a liquid having a strong ethereal smell somewhat resembling that of camphor, boiling at 124°—126°, and having a specific gravity at 17° of 0·8254.[2]

Isobutyl-dimethyl Carbinol, $(CH_3)_2C_2H_3(CH_3)_2C.OH$, was first prepared by Markownikoff from isopropyl-dimethylethylene, $(CH_3)_2CH.CH = C(CH_3)_2$, by combining this with hydriodic acid and treating the iodide with moist silver oxide. The tertiary alcohol is also formed by the action of zinc-methyl on valeryl chloride, the product being treated with water.[3] It boils at 129°—131°, smells like camphor, and yields isobutyric acid and acetic acid on oxidation.

Propyl-ethyl-methyl Carbinol, $C_3H_7(C_2H_5)(CH_3)C.OH$, is obtained by the action of zinc-methyl and zinc-ethyl on butyryl chloride, and boils at 135°—138°.[4]

Isopropyl-ethyl-methyl Carbinol, $(CH_3)_2CH(C_2H_5)(CH_3)C.OH$, is prepared in a corresponding way from isobutyryl chloride, and boils at 124°—127° (Pawlow).

Trimethylcarbyl-dimethyl Carbinol, $(CH_3)_3C(CH_3)_2C.OH$. This tertiary alcohol was first prepared by Butlerow, and termed by

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[1] Friedel and Ladenburg, *Ann. Chem. Pharm.* cxlii. 310.

[2] Münch, *Liebig's Ann.* clxxx. 327.

[3] Pawlow, *Ann. Chem. Pharm.* clxxiii. 192.

[4] *Ib.* clxxxviii. 122.

chemists found that the body in question can be obtained in large quantity from wine-lees, and they showed that it is the ethyl-ether of an acid having the formula $C_{14}H_{26}O_2 + H_2O$, and to which they gave the name of *œnanthic acid* (οἶνος wine).[1]

Tilley, in 1841, obtained an acid by the oxidation of castor-oil, to which he gave the formula $C_{14}H_{26}O_3 + H_2O$, and supposed that it contained the same radical as œnanthic acid, and gave it therefore the name of *œnanthylic acid*, suggesting that the acid whose ether is contained in wine should be termed *œnanthylous acid.*[2]

Further investigation has shown that Tilley's acid is normal heptoic acid, and that œnanthic ether is a mixture of the ethyl ethers of higher acids, especially of capric acid, under which heading a further description will be found.

Heptaldehyde, Œnanthaldehyde, or *Œnanthol,* $C_6H_{13}.CHO$, was first prepared by Bussy by distilling castor-oil,[3] and then further investigated by several other chemists.[4] Castor-oil consists essentially of the glycerin ether of ricinoleic acid, and on heating, it undergoes a somewhat complicated decomposition by which, in the first place, acraldehyde and œnanthaldehyde are formed, and these may be separated by fractional distillation owing to their difference in boiling point.

According to Erlenmeyer and Sigel the best mode of preparing heptaldehyde is to distil 500 grams of the oil quickly in a large glass retort, the operation being stopped when the mass becomes resinous. The distillate is rectified, and the portion coming over between 90°—180° shaken up with a solution of acid sodium sulphite. The whole is then warmed on the water-bath, and the hot solution filtered; on cooling, the compound $C_7H_{14}O + HNaSO_3 + H_2O$ separates out in fine scales. These are freed on a filter-pump from the mother-liquor, and dried between filter-paper. On distillation of these crystals with soda solution, pure œnanthol is obtained, and this may be dried over anhydrous glauber-salt.

A better yield is obtained when the castor-oil is distilled under a diminished pressure of 100 mm. In this case it is almost completely converted into œnanthal and hendecatoic acid:

$$C_{18}H_{34}O_3 = C_7H_{14}O + C_{11}H_{20}O_2.$$

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[1] *Ann. Chem. Pharm.* xix 241.

[2] *Chem. Soc. Mem.* i. 1.

[3] *Ann. Chem. Pharm.* lx. 246.

[4] Tilley, *Phil. Mag.* [3], xxxiii. 81; Schiff, *Zeitsch. Chem.* 1870, 74; Erlenmeyer and Sigel, *Ann. Chem. Pharm.* clxxvi. 341.

These bodies may be separated by two or three rectifications under diminished pressure.[1]

When castor-oil is distilled under ordinary pressure hendecatoic acid remains behind as a spongy mass, which on more strongly heating splits up into heptane and its homologues.[2]

Œnanthol is a highly refracting liquid boiling at 154°, having a specific gravity at 16° of 0·823, and possessing an aromatic pungent smell. It absorbs dry ammonia with evolution of heat, a thick liquid having the composition $C_7H_{14}O,NH_3$ being formed (Erlenmeyer and Sigel).

415 *Normal Heptoic Acid*, or *Œnanthylic Acid*, $C_6H_{13}.CO_2H$. This acid was first obtained in the impure state by oxidizing oleic acid with nitric acid, and termed by Laurent[3] "acide azoléique." Tilley then obtained it in a similar way from castor-oil,[4] and Bussy by the oxidation of œnanthol.[5] It was then investigated by various chemists,[6] and synthetically prepared by Franchimont,[7] as well as by Lieben and Janecek,[8] from normal hexyl alcohol by the nitril reaction.

For its preparation crude œnanthol boiling at 150°—160° is used, and 300 grams of this are gradually added to a warm mixture of 300 grams of potassium dichromate, 450 grams of sulphuric acid, and 900 grams of water. As soon as the action has moderated, the mixture is heated for some hours in a flask with a reversed condenser. When cold, the oily liquid swimming on the top is dissolved in caustic soda. The acid aqueous liquid, which also contains œnanthylic acid in solution, is distilled, and the product also neutralized with carbonate of soda. The solutions of sodium œnanthylate are then evaporated, and the acid liberated from the residue by sulphuric acid. The pure acid may be readily obtained by repeated fractional distillation and rectification of the distillate over phosphorus pentoxide (Grimshaw and Schorlemmer). Œnanthylic acid is also found amongst the products of the distillation of fats in superheated steam. It is an oily liquid which when cold has a faint smell, but on heating acquires a more pungent odour. It boils at 223°—224°, and solidifies at a low temperature, either in tablets or in broad

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[1] Krafft, *Ber. Deutsch. Chem. Ges.* x. 2034; xi. 2218.

[2] Amato, *Gazz. Chim.* 1872, 6.

[3] *Ann. Chim. Phys.* [2], lxvi. 173.

[4] *Loc cit.*

[5] *Ann. Chem. Pharm.* lx. 246.

[6] Williamson, *ib.* lxi. 38; Tilley, *loc. cit*; Redtenbacher, *Ann. Chem. Pharm.* lix. 41; Schneider, *ib.* lxx. 107; Arzbacher, *ib.* lxxiii. 199; Grimshaw and Schorlemmer, *Chem. Soc. Journ.* xxvi 1073.

[7] *Ib.* clxv. 237.

[8] *Ib.* clxxxvii. 126.

needles, melting at $-10^\circ\cdot5$. It has a specific gravity at 0° of 0·9345.

The heptoates of the alkali-metals are easily soluble in water, and separate after concentration or cooling, usually in the form of a jelly. The sodium salt can be obtained in thin interlaced needles.

Calcium Heptoate, $(C_7H_{13}O_2)_2Ca + H_2O$, crystallizes from hot-water in thin bushy needles.

Barium Heptoate, $(C_7H_{13}O_2)_2Ba$, crystallizes in bright needles or in thin scales.

The heptoates of zinc, lead, and silver are white precipitates. The two latter may, however, be crystallized from boiling water, in which they are slightly soluble.

Copper Heptoate, $(C_7H_{13}O_2)_2Cu$. This characteristic salt is insoluble even in boiling water, but crystallizes from absolute alcohol in short silky lustrous needles or short prisms.

Ethyl Heptoate, $C_7H_{13}O_2(C_2H_5)$, is obtained like the hexoate. It has a pleasant fruity smell, boils at 189°, and has a specific gravity of 0·8879 at 0°.

Heptyl Heptoate, $C_7H_{13}O_2(C_7H_{15})$, boils at 270°—275°, and has a pleasant fruity smell.

Heptoyl Oxide, $(C_7H_{13}O)_2O$. This anhydride, obtained in the usual way,[1] is a liquid boiling at 268°—271°, and at 21° having a specific gravity of 0·932.

Heptamide, $C_7H_{13}O.NH_2$, is prepared by the action of ammonia on the anhydride as well as by heating the acid with potassium thiocyanate. It crystallizes in needles, which melt at 94°—95°, and when quickly heated it distils between 250°—258°.

Heptonitril, $C_7H_{13}N$, is obtained together with the amide in the second method of preparation of the latter body. It is a slightly aromatic smelling liquid boiling at 175°—178°, and have at 22° a specific gravity of 0·895 (Mehlis).

Isoheptoic Acid, or *Isoœnanthylic Acid*, $(CH_3)_2C_4H_7.CO_2H$, is obtained by the oxidation of the corresponding alcohol. It is an unpleasantly smelling acid liquid, boiling at 210°—213°. The barium salt forms an amorphous mass, whilst the calcium salt, $(C_7H_{13}O_2)_2Ca + 2\,H_2O$, crystallizes in small needles.

Methyl-butyl-acetic Acid, $CH_3(C_4H_9)CH.CO_2H$, is prepared from secondary hexyl iodide, obtained from mannite. It is converted into the nitril by the action of cyanide of potassium, and this decomposed by boiling with caustic potash. The acid

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[1] Chiozza, *Ann. Chem. Pharm.* xc. 102; Mehlis, *ib.* clxxxv. 370.

sphondylium). This consists chiefly of octyl acetate, but also contains the free alcohol together with the caproic ethers, and its higher homologues, as well as some hexyl acetate.[1] It has already been stated that octyl acetate occurs together with hexyl butyrate in the fruit of *Heracleum giganteum* (p. 626), whilst the oil from the seeds of the common parsnip (*Pastinacca sativa*) chiefly contains octyl butyrate.[2] Several of these oils also contain small quantities of methyl and ethyl compounds.

In order to prepare octyl alcohol, the portion of cow-parsnip oil, boiling between 206°—208° is heated with caustic potash, the crude liquid dried over fresh caustic lime, and purified by fractional distillation. It is a colourless, oily, pungently aromatic-smelling liquid, boiling at 196°—197°, and having a specific gravity at 16° of 0·830.

The following derivatives of primary octyl alcohol have been more accurately examined:

	B.P.	Sp. Gr.	at
[3] Ethyl-octyl ether, $(C_2H_5)(C_8H_{17})O$	182-184°	0·7940	17°
[3] Dioctyl ether, $(C_8H_{17})_2O$	280-282°	0·8050	17°
[4] Octyl chloride, $C_8H_{17}Cl$	179°·5-180°·5	0·8802	16°
[4] Octyl bromide, $C_8H_{17}Br$	198-200°	1·1160	16°
[4] Octyl iodide, $C_8H_{17}I$	220-222°	1·138	16°
[4] Octyl acetate, $C_8H_{17}O(C_2H_3O)$	206-208°	0·8717	16°
[4] Octyl valerate, $C_8H_{17}O(C_5H_9O)$	249-251°	0·8624	16°
[4] Octyl caproate, $C_8H_{17}O(C_6H_{11}O)$	268-271°	—	—
[3] Octyl sulphide, $(C_8H_{17})_2S$	—	0·8419	17°
[6] Octyl nitrite, $C_8H_{17}O(NO)$	175-177°	0·8620	17°
[5] Nitro-octane, $C_8H_{17}NO_2$	205-212°	—	—
[5] Octylamine, $C_8H_{17}.NH_2$	185-187°	—	—
[4] Octylphosphine, $C_8H_{17}PH_2$	184-187°	0·8209	17°
[4] Mercury-octyl, $(C_8H_{17})_2Hg$	—	1·342	17°

417 *Secondary Octyl Alcohol*, or *Methyl-hexyl Carbinol*, $CH_3(C_6H_{13})CH.OH$, was discovered in 1851 by Bouis, who obtained it by the distillation of castor-oil or of ricinoleic acid with caustic soda, and termed it caprylic alcohol, $C_8H_{18}O$.[6] Soon afterwards he came to the conclusion that this liquid is œnanthylic alcohol, $C_7H_{16}O$;[7] and this appeared to be confirmed by

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[1] Zincke, *ib.* clii. 1; Möslinger, *ib.* clxxxv. 26.

[2] Renesse, *Ann. Chem. Pharm.* clxvi. 80.

[3] Möslinger, *loc. cit.*

[4] Zincke, *loc. cit.*

[5] Eichler, *Ber. Deutsch. Chem. Ges.* xii. 1879.

[6] *Ann. Chem. Pharm.* lxxx. 304.

[7] *Ib.* 306.

chiefly of the sodium salt of ricinoleic acid, and this, under the above conditions, undergoes the following decomposition:

$$C_{18}H_{33}NaO_3 + NaOH + H_2O = C_8H_{18}O + C_{10}H_{16}Na_2O_4 + H_2.$$

The crude alcohol contains octylene, boiling at 125°, and other bodies, together with the products of the decomposition of the sodium suberate, and these occur in larger quantities if the heat has been applied for any length of time (Schorlemmer).

Neison,[1] who has also investigated this subject, obtained chiefly methyl-hexyl carbinol when he distilled castor-oil soap by itself. Another preparation yielded large quantities of œnanthol, and on distilling with excess of alkali, only products containing eight atoms of carbon were formed, varying quantities of the ketone being produced; this, according to Schorlemmer, not being the case when the distillation is carried on rapidly. In place of castor-oil, the oil obtained from the fruit of the *Curcas purgans* may be used for this preparation.[2]

In order to purify the crude alcohol, it is subjected to repeated fractional distillation, with addition of caustic potash, and then rectified over sodium. It is an aromatic-smelling liquid, boiling at 179°·5, and having at 20° a specific gravity of 0·8913.

The following derivatives have been obtained:

	B.P.	Sp. Gr.	at
[3] Methyl-capryl ether, $CH_3(C_8H_{17})O$	160-161°	0·830	16°
[3] Ethyl-capryl ether, $C_2H_5(C_8H_{17})O$	177°	0·791	16°
[3] Amyl-capryl ether, $C_5H_{11}(C_8H_{17})O$	220-221°	0·680	20°
[4] Capryl chloride, $C_8H_{17}Cl$	175°	—	—
[4] [5] Capryl bromide, $C_8H_{17}Br$	190-191°	—	—
[4] [6] Capryl iodide, $C_8C_{17}I$	220-221°	1·338	16°
[3] Capryl sulphuric acid, $C_8H_{17}SO_4H$	—	—	—
[3] Capryl nitrate, $C_8H_{17}NO_3$	—	—	—
[4] [7] Capryl acetate, $C_8H_{17}(C_2H_3O_2)$	191-192°	—	—
[4] Capryl sulphide, $(C_8H_{17})_2S$	—	—	—
[4] [6] [8] [9] Caprylamine, $(C_8H_{17})NH_2$	165°	—	—
[9] Capryl thiocyanate, $C_8H_{17}.SCN$	242°	—	—
[9] Capryl mustard oil, $C_8H_{17}NCS$	234°	—	—

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[1] *Journ. Chem. Soc.* 1874, 301, 507, 837.

[2] Silva, *Compt. Rend.* lxvii. 1251.

[3] Wills.

[4] Bouis.

[5] Berthelot, *Ann. Chem. Pharm.* civ. 185; *Comptes Rendus*, xliv. 1350.

[6] Squire.

[7] Dachauer

[8] Cahours, *Ann. Chem. Pharm.* xcii. 399; *Comptes Rendus*, xxxix. 254.

[9] Jahn, *Ber. Deutsch. Chem. Ges.* viii. 803.

gated by Carleton-Williams,[1] who obtained the hydrocarbon by the action of sodium on isobutyl bromide. By passing chlorine into the vapour of the boiling paraffin he obtained a mixture of chlorides which could not be separated by fractional distillation. The chief portion, boiling between 170°—180°, was then heated with potassium acetate and glacial acetic acid, when the acetic ethers, as well as an octylene, C_8H_{16}, boiling at 122°, is formed. The acetates, boiling between 170°—205°, cannot be separated by distillation, but on heating them with concentrated caustic potash the alcohols are obtained, and these can be fairly well separated by repeated fractionation.

Primary Isoctyl Alcohol, $(CH_3)_2C_4H_6(CH_3)CH_2OH$, is a liquid smelling like oranges, boiling at 179°—180°, and having a specific gravity of 0·841 at 0°. It yields an acid on oxidation which will be described hereafter.

Secondary Isoctyl Alcohol, or *Isopropyl-isobutyl Carbinol,* $(CH_3)_2C_2H_3(CH.OH)CH(CH_3)_2$, is only formed in small quantity. It has a fainter smell than the primary alcohol; boils at 160°—163°, and has a specific gravity at 15° of 0·820. On oxidation it yields the corresponding ketone, boiling at 159°—161°, which on further oxidation chiefly yields acetic acid, though at the same time a small quantity of another acid which appears to be isobutyric acid is formed. According to theory, the latter acid should be produced, and that this is not the case is probably due to the fact, as Erlenmeyer has shown, that isobutyric acid is easily oxidized to acetic acid and carbon dioxide, and this naturally takes place more easily when the acid is in the nascent condition.

TERTIARY OCTYL COMPOUNDS.

419 *Diethyl-propyl Carbinol,* $(C_2H_5)_2(C_3H_7)COH$, is formed by the action of zinc-ethyl on butyryl chloride. A sticky mass is obtained, which is decomposed by water. It yields a liquid smelling like camphor, boiling between 145°—155°.[2]

Isodibutol, $(CH_3)_3C.CH_2.C.OH(CH_3)_2$. The iodide of this tertiary alcohol is formed by the union of hydriodic acid with di-isobutylene, C_8H_{16}, which will be described under the octylenes. By the action of moist oxide of silver on the resulting iodide it is converted into the carbinol, a thick liquid smelling like

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[1] *Journ. Chem. Soc.* 1877, i. 541; 1879, i. 125.

[2] Butlerow, *Zeitsch. Chem.* 1865, 617.

camphor, boiling at 146°·5—147°·5, and solidifying in needles at — 20°, and having at 0° a specific gravity of 0·8417.[1]

HEXMETHYL ETHANE, $C(CH_3)_3C(CH_3)_3$.

420 This hydrocarbon is formed by the action of sodium on tertiary-butyl iodide. It is a crystalline substance melting at 96°—97°, and boiling from 105°—106°.[2] No derivatives have as yet been prepared.

THE OCTOIC ACIDS.

421 *Normal Octoic* or *Caprylic Acid*, $C_7H_{15}.CO_2H$. The volatile fatty acids which occur in cow's butter, and were discovered by Chevreul, have since been carefully investigated by Lerch.[3] He found a new acid amongst them which, according to its composition, stands between caproic acid and capric acid, and to this he gave the name of *caprylic acid*. The same acid is found, together with other fatty acids, in large quantity in cocoa-nut oil,[4] and it has also been detected in other fats, as in human fat. It is also found, together with its homologues, in old cheese, and in the products of distillation of the fats in superheated steam; it also occurs, partly in the free state and partly in the form of ethers, in various fusel oils and in the acid aqueous distillate from *Arnica montana*.

That the eight-carbon acid contained in fats, &c., is normal caprylic acid is proved by the fact that its properties are identical with those of the acid obtained by the oxidation of the primary alcohol.[5]

In order to prepare it, cocoa-nut oil is treated with caustic soda having a specific gravity of 1·12, and after the soap which swims on the surface is solidified, it is removed and well mixed with dilute sulphuric acid, and the mixture quickly distilled in a copper retort. The distillate, which chiefly consists of caproic and caprylic acids, is neutralized with baryta, and the solution evaporated to crystallization. After cooling, barium caprylate separates out, whilst the mother-liquor, on further concentration,

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[1] Butlerow, *Liebig's Ann.* clxxxix. 53.
[2] Lwow and Chrapowicki, *Bull. Soc. Chim.* xxxv. 169.
[3] *Ann. Chem. Pharm.* xlix. 212.
[4] Fehling, *Ann. Chem. Pharm.* liii. 399.
[5] Zincke, *Ann. Chem. Pharm.* clii. 1; van Renesse, *ib.* clxxi. 381.

yields barium caproate. Both salts are purified by recrystallization and decomposed by dilute hydrochloric acid. The oily layer which separates is dried, and the acid obtained in the pure state by repeated fractionations.

Pure caprylic acid is a liquid which, especially when hot, has a smell resembling that of sebacic acid and of perspiration. On cooling it crystallizes in needles or scales, which melt at 16°—17°. It boils at 235°—237°, at 0° has a specific gravity of 0·9139, and is soluble in 400 parts of boiling water, separating out almost completely in crystalline scales from this solution on cooling.

The octoates or caprylates of the alkali-metals, and those of he alkaline-earth metals, are soluble in water; those of the other metals are sparingly soluble or insoluble in water, but, as far as they have been investigated, are all soluble in alcohol.

Calcium Octoate, $(C_8H_{15}O_2)_2Ca + H_2O$, is a salt difficultly soluble in cold water, crystallizing in long, thin, silky needles.

Barium Octoate, $(C_8H_{15}O_2)_2Ba$, is somewhat more soluble, and forms fatty tablets or thin flat needles, or, when slowly crystallized, yields long prisms.

Methyl Octoate, $C_8H_{15}O_2(CH_3)$, is a strongly aromatic-smelling liquid.

Ethyl Octoate, $C_8H_{15}O_2(C_2H_5)$, possesses the smell of pineapples, boils at 208°, and has a specific gravity at 16° of 0·8728.

Octyl Octoate, $C_8H_{15}O_2(C_8H_{19})$, is a liquid boiling at 297°—299° and having a specific gravity at 16° of 0·8625.

Caprylamide, $C_8H_{15}O(NH_2)$, is formed by the action of aqueous ammonia on ethyl octoate. It forms pearly glistening scales, melting at 110°, and boiling with decomposition above 200°.

Octoyl Oxide, or *Caprylic Anhydride*, $(C_8H_{15}O)_2O$, was prepared by Chiozza by acting with phosphorus oxychloride on barium octoate. It is an oily liquid which boils with partial decomposition at 280—290°, is slowly acted upon by water, and has a disagreeable smell resembling that of the carob.[1]

Octonitril, or *Caprylonitril*, $C_8H_{13}N$, is a liquid smelling of camomile, obtained by heating the ammonium salt with phosphorus pentoxide. It boils at 194°—195°.[2]

Isoctoic Acid, $(CH_3)_2C_4H_6(CH_3)CO_2H$. This, as has been stated, is the oxidation-product of isoctyl alcohol. It is an oily liquid which, when warmed, has a smell of old cheese. It

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[1] *Ann. Chem. Pharm.* lxxxv. 229; *Comptes Rendus*, xxxv. 865.

[2] Felletar, *Jahresb.* 1868, 624.

boils at 218°—220°, and does not solidify at —17°. At 0° it possesses a specific gravity of 0·926.

Calcium Isoctoate, $(C_8H_{15}O_2)_2Ca + H_2O$, crystallizes in scales which have a stellated form, and is more easily soluble in cold than in warm water.

The *barium* salt does not crystallize, but the solution, on drying, gives an amorphous mass.

The *ethyl ether* boils at 175°, and has a peculiar penetrating smell.

A *third octoic acid* is formed in small quantity, together with trimethyl-acetic acid and acetone, by the oxidation of di-isobutylene. It has a smell resembling trimethyl-acetic acid, but somewhat weaker, and boils at 215°. Its constitution has not been satisfactorily determined, but the mode of its formation is strictly analogous to that of isobutyric acid from trimethyl carbinol.[1]

COMPOUNDS CONTAINING NINE ATOMS OF CARBON, OR THE NONYL GROUP.

422 The compounds of this group have been but imperfectly investigated. Pelouze and Cahours obtained *nonane*, C_9H_{20}, a body boiling at 136°—138°, from petroleum, and termed it *palargyl hydride*. This substance is, however, evidently a mixture, as, indeed, were all the paraffins obtained by them from petroleum (p. 132). On the other hand, Thorpe and Young obtained a series of liquid paraffins by the distillation of solid paraffin, and as the lower members of these certainly belong to the normal series, the higher homologues, doubtless, are also normal.

Normal Nonane, C_9H_{20}, is a liquid boiling at 147°—148°, and having at 13°·5 a specific gravity of 0·7279, whilst that of its vapour is 4·587.[2]

Tetramethyl-pentane, $(CH_3)_2C_5H_8(CH_3)_2$, was obtained by Wurtz by acting on a mixture of amyl iodide and isobutyl iodide with

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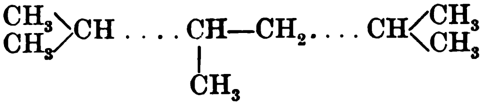
[1] Butlerow, *Liebig's Ann.* clxxxix. 70.

[2] *Chem. Soc. Journ.* xxiv. 342.

sodium, and described by him as butyl-amyl. It is a liquid boiling at 132°, and having at 0° a specific gravity of 0·7247.[1]

Pentamethyl-butane, $(CH_3)_2(C_2H_2(CH_3)CH_2.CH(CH_3)_2$, was obtained by Silva, together with a small quantity of di-isopropyl (p. 565), propane, and propylene, by heating secondary propyl iodide with sodium amalgam.[2] In order to explain the formation of this paraffin, which boils at 130°, it must be assumed that the radicals propylene and secondary propyl combine together when in the nascent condition:



The *Nonyl Alcohols* have been only slightly investigated. The alcohol obtained from petroleum-nonane, and boiling at about 200°, is certainly a mixture.

By acting on amyl valerate with sodium, and treating the residue with water, Lourenço and d'Aguiar obtained an oily liquid which, according to them, is a mixture of various homologous alcohols, the lowest member consisting of nonyl alcohol, $C_9H_{20}O$, boiling at 205°—212°.[3]

Di-isobutyl Ketone $[(CH_3)_2C_2H_3]_2CO$. This compound, commonly known as *valerone*, is formed in small quantity, together with a larger amount of valeraldehyde and other products, by the dry distillation of calcium valerate. It is an ethereal smelling liquid which boils at 181°—182°, has a specific gravity at 20° of 0·833, and does not combine with the acid sulphites of the alkali metals.[4]

Dinitro-isobutane, $(CH_3)_2C_2H_2(NO_2)_2$, first obtained by the action of hot nitric acid on this substance, has acid properties, and was originally described as nitro-butyric acid.

THE NONOIC ACIDS, $C_8H_{17}CO_2H$.

423 In 1827 Recluz showed that *Pelargonium roseum* owes its peculiar odour to an ethereal oil;[5] and this was more accurately examined in 1846 by Pless, who, by distilling the plant with water, obtained an acid distillate which, on saturation with

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[1] *Ann. Chem. Pharm.* xcvi. 371; *Ann. Chim. Phys.* [3], xliv. 290.

[2] *Ber. Deutsch. Chem. Ges.* v. 984.

[3] *Zeitsch. Chem.* 1870, 404.

[4] E. Schmidt, *Ber. Deutsch. Chem. Ges.* v. 600.

[5] *Journ. Pharm.* xiii. 529.

baryta water left a neutral insoluble oil whilst the aqueous liquid contained the barium salt of a new acid.[1] Almost simultaneously Redtenbacher found an acid having the same composition amongst the products of the action of nitric acid on oleic acid, and to this he gave the name of *pelargonic acid.*[2] Gerhardt[3] as well as Cahours,[4] also obtained an acid by the oxidation of oil of rue from *Ruta graveolens*, and this substance they believed to be identical with pelargonic acid. The same body was afterwards more exactly examined by Fittig and Giesecke.[5]

The statements concerning the melting-points and boiling-points of the pelargonic acids obtained from these various sources are not concordant. It is, however, probable that they all consist of the normal acid.

Normal Nonoic Acid was synthetically prepared by Zincke and Franchimont from octyl iodide: this substance being heated for some days in contact with spirit of wine and potassium cyanide, and the crude nitril formed being decomposed by alcoholic potash. The acid is then prepared from this and purified by well-known processes.[6]

The same acid is obtained together with other products by the oxidation of stearolic acid, $C_{18}H_{32}O_2$,[7] as also by the action of hexyl iodide on the sodium compound of aceto-acetic ether and decomposition of the product by means of potash.[8]

It is an oily, slightly smelling liquid boiling at 253°—254°, and having a specific gravity of 0·9065 at 17°·5. On cooling it crystallizes to a scaly mass, which melts at 12°—12°·5 and solidifies again at 11°.

The salts of nonoic acid are very similar to those of the different pelargonic acids. They are most of them difficultly soluble in water. Those of the heavy metals dissolve readily in alcohol. The salts of the alkali metals on the other hand are readily soluble, and crystallized in tablets.

Calcium Nonoate, $(C_9H_{17}O_2)_2Ca$, crystallizes from hot alcohol in glistening scales and is very difficultly soluble in water.

Barium Nonoate, $(C_9H_{17}O_2)_2Ba$, separates out from a hot aqueous or alcoholic solution in similar scales.

Ethyl Nonoate, $C_9H_{17}O_2(C_2H_5)$, boils at 227°—228°, and at

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[1] *Ann. Chem. Pharm.* lix. 54 (*foot-note*).

[2] *Ib.* lix. 52.

[3] *Compt. Rend.* xxvi. 226.

[4] *Ib.* xxvi. 262; xxxi. 143.

[5] *Zeitsch. Chem.* 1870, 429.

[6] *Ann. Chem. Pharm.* clxiv. 193.

[7] Limpach, *Liebig's Ann.* cxc. 294.

[8] Jourdan, *Ann. Chem. Pharm.* cc. 107.

17°·5 has a specific gravity of 0·8635; whilst *methyl nonoate*, $C_9H_{17}O_2(CH_3)$, boiling at 213°—214°, has at the same temperature a specific gravity of 0·8765.

The peculiar odour of the quince is due to an ethereal oil,[1] which, according to R. Wagner, is perhaps ethyl pelargonate; and this ether is obtained on the large scale by oxidizing the acid contained in oil of rue. It is employed in the manufacture of common brandy and wines, &c.[2]

From this pelargonic acid the *chloride*, $C_9H_{17}OCl$, is obtained by the action of phosphorus pentachloride. It is a liquid fuming in the air and boiling at 220°.[3] If the sodium salt be acted upon by this chloride, *nonoic anhydride*, $(C_9H_{17}O)_2O$, is obtained, and this is purified by solution in ether. On evaporation the anhydride remains as a slightly rancid oil, which on cooling crystallizes in needles melting at + 5°.[4]

If methyl-nonyl-ketone obtained from oil of rue be heated with nitric acid of specific gravity 1·2, and the oily layer which remains when the action is completed be removed and shaken up with concentrated potash, a crystalline precipitate is formed which is increased on the addition of water. If this be then filtered off and washed with ether in order to remove any neutral oil and crystallized from hot alcohol, glistening yellow rectangular tables are obtained which decompose on addition of a dilute mineral acid with separation of a yellow liquid, known as *nitrous-oxide-pelargonic acid*, $C_9H_{18}O_2(NO)_2$.[5] There can however be little doubt that this compound is *dinitrononane*, $C_9H_{18}(NO_2)_2$. It decomposes on heating with evolution of nitric oxide and combustible gases, whilst its difficultly soluble and yellow salts deflagrate when heated. The formation of this compound is analogous to that of dinitro-propane from dipropyl ketone (p. 642.)

424 *Isononoic Acid*, or *Methyl-hexyl-acetic Acid*, $CH_3(C_6H_{13})CH.CO_2H$. If secondary octyl iodide be boiled with alcohol and potassium cyanide, isononononitril separates out on the addition of water as a brown oil. On heating the crude product for some time with alcoholic potash isononamide, $CH_3(C_6H_{13})CH.CO(NH_2)$, is produced, which crystallizes from hot water in scales or needles melting at 80°—81°. Boiling alcoholic potash only acts slowly upon this with formation of isononoic acid.

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[1] Wöhler, *Ann. Chem. Pharm.* xli. 239.

[2] *Journ. Prakt. Chem.* lvii. 440.

[3] Cahours, *Compt. Rend.* xxxix. 257.

[4] Chiozza, *Ann. Chem. Pharm.* lxxxv. 231.

[5] *Ib.* lxxxv. 235; Alezeyeff, *Zeit. Chem.* 1865, 736.

This substance is a liquid boiling at 244°—246°, and does not solidify at —11°. At 18° its specific gravity is 0·9032.

The salts of the alkali-metals are easily soluble in water, and separate out as a saponaceous mass on the addition of common salt.

Calcium Isononoate, $(C_9H_{17}O_2)_2Ca + H_2O$, is obtained as a flocculent precipitate on the addition of calcium chloride to the sodium salt. This however soon becomes crystalline, and may be obtained in fine needles from hot alcohol.

Ethyl Isononoate, $C_9H_{17}O_2(C_2H_5)$, is a liquid having a pleasant fruity smell, boiling at 213°—215°, and having at 17° a specific gravity of 0·8640.[1] On heating with concentrated ammonia it yields *nonamide*, a body analogous to that obtained from the nitril, but not melting below 105°.[2]

Isoheptyl-acetic Acid, $(CH_3)C_5H_{11}.CH.CH_2.CO_2H$, was obtained by Venable by heating isoheptyl-malonic acid, $CH_3(C_5H_{11})CH.CH(CO_2H)_2$, a body which will be subsequently described. It decomposes into carbon dioxide and isoheptyl-acetic acid, a liquid boiling at 232°.[3]

COMPOUNDS CONTAINING TEN ATOMS OF CARBON, OR THE DECATYL GROUP.

425 *Normal Decatane*, $C_{10}H_{22}$, also doubtless occurs in Pennsylvanian petroleum and other liquids containing its lower homologues, although it has not been obtained from this source in the pure state. On the other hand, a hydrocarbon, having the composition $C_{10}H_{22}$, was obtained by Thorpe and Young by the decomposition of the solid paraffins, and this is no doubt normal decatane. It boils at 166°—168°, and at 13°·5 has a specific gravity of 0·7394, that of its vapour being 5·03.[4] It also appears to occur in common coal-tar naphtha.[5]

Dimethyl-heptyl-methane, $CH(CH_3)_2C_7H_{15}$, was prepared by Wurtz by the electrolysis of a mixture of potassium valerate

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[1] Kullhem, *Ann. Chem. Pharm.* clxxiii. 319.

[2] *Ib.* clxxvi. 308.

[3] *Ber. Deutsch. Chem. Ges.* xiii. 1652.

[4] Thorpe and Young, *Ann. Chem. Pharm.* clxv. 22.

[5] Jacobsen, *ib.* clxxxiv. 202.

and potassium œnanthylate, and termed by him *butyl-caproyl;* it is a liquid boiling at 160°.[1]

Tetramethyl-hexane, $(CH_3)_2C_6H_{10}(CH_3)_2$, was first prepared by Frankland, and described as *amyl.* It is obtained together with amylene and amyl hydride (isopentane) by heating amyl iodide with zinc to 160°—180°.[2]

Brazier and Gossleth obtained the same hydrocarbon by the electrolysis of sodium isocaproate,[3] and Wurtz showed that it is also easily formed when amyl iodide is warmed with sodium.[4] In place of the iodide, amyl bromide may be employed.[5]

Diamyl, as this paraffin is usually termed, boils at 160°, and has at 0° a specific gravity of 0·7413.

The action of chlorine on the hydrocarbon has been investigated by Schorlemmer[6] and Grimshaw. As first product, a mixture of monochlorides is obtained, boiling between 198°—217°. By heating this with acetate of lead and glacial acetic acid it is converted into acetates, which on treatment with concentrated potash are retransformed into the alcohols, and these may with difficulty be separated into two parts, the larger boiling at 202°—203°, and the smaller at 211°—213°. They possess an agreeable smell, especially the higher boiling portion, somewhat resembling the flowers of the *Daphne odorata.* Besides these two other decatyl alcohols have been briefly described.

Isocapric Alcohol, $C_{10}H_{21}.OH$, is formed, together with amyl alcohol, valeric acid, and other products, by the action of sodium on valeraldehyde. It is a pleasantly smelling liquid boiling at 203°·3, and having at 0° a specific gravity of 0·8569. When heated with glacial acetic acid under pressure, an aromatic smelling acetate, boiling at 220°, is formed. The oxidation-products of this alcohol show it to be a primary compound.[7]

An isomeric alcohol is also formed, together with other products, by the action of sodium amalgam on amyl valerate (p. 620); it boils at 225°—230°.

Isoctyl-methyl Ketone, $CH_3(C_6H_{11})CH.CH_2.CO.CH_3$, was prepared by means of the acetic-ether-reaction from secondary heptyl bromide. It is a pleasantly smelling liquid, boiling at 196°—198°.[8]

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[1] *Ann. Chim. Phys.* [3], xliv. 291; *Ann. Chem. Pharm.* xcvi. 371.
[2] *Quart. Journ. Chem. Soc.* iii. 33. [3] *Ib.* 222.
[4] *Ann. Chem. Pharm.* lxxv. 249.
[5] Grimshaw, *Journ. Chem. Soc.* 1877, ii. 260. [6] *Journ. Chem. Soc.* xvi. 427.
[7] Borodin, *Jahresb.* 1864, 338; *Zeit. Chem.* 1870, 415.
[8] Venable, *Ber. Deutsch. Chem. Ges.* xiii. 1651.

THE CAPRIC OR DECATOIC ACIDS.

426 *Capric Acid*, $C_9H_{17}.CO_2H$. This acid, as has been stated, was discovered by Chevreul (p. 634), but more accurately examined by Lerch.[1] It is found not only in butter, but in many other fats, as, for instance, in cocoa-nut oil,[2] and generally occurs together with caproic and caprylic acids. In combination as the ethers of various alcohol radicals, as well as in the free state, it forms one of the constituents of the high-boiling portions of the several fusel oils.[3] Hungarian wine also contains a considerable quantity of amyl caprate.[4] It is also formed together with other acids in the products of the distillation and oxidation of oleic acid,[5] as well as in the oxidation of the higher fatty acids.[6] The synthesis of capric acid has been effected by the introduction of normal octyl in place of one atom of hydrogen in acetic acid.[7]

Capric acid is a crystalline mass of scales or needles. It possesses a goat-like smell, which is faint when cold, but becomes strong on heating the acid. It melts at 30°, and boils at 268°—270°. It is somewhat soluble in boiling water, but separates out, almost completely, in scales on cooling.

The caprates of the alkali metals are easily soluble in water. Those of the other metals are difficultly soluble or insoluble. A few, however, dissolve with difficulty in alcohol.

Calcium Caprate, $(C_{10}H_{19}O_2)_2Ca$, crystallizes from hot water or alcohol in fine, glistening, thin plates.

Barium Caprate, $(C_{10}H_{19}O_2)_2Ba$, separates out from the same solvent in nacreous needles.

Methyl Caprate, $C_{10}H_{19}O_2(CH_3)$, has a pleasant, fruity smell, and boils at 223°—224°.

Ethyl Caprate, $C_{10}H_{19}O_2(C_2H_5)$, boils at 243°—245°, and has a specific gravity of 0·862. It has already been stated that this ether forms the chief portion of œnanthic ether (p. 647), occurring in old wines, and obtained on the large scale by the distillation of wine-lees[8] or the after-brandy[9] of grape-

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[1] *Ann. Chem. Pharm.* xlix. 223.

[2] Görgey, *ib.* lxvi. 290.

[3] Rowney, *Edin. Phil. Trans.* vol. xx. part ii.; Fehling, *Dingl. Polyt. Journ.* cxxx. 77; Wetherill, *Journ. Prakt. Chem.* lx. 202; Johnson, *ib.* lxii. 252; Fischer, *Ann. Chem. Pharm.* cxviii. 307.

[4] Grimm, *ib.* clvii. 254.

[5] Gottlieb, *ib.* lvii. 63.

[6] Redtenbacher, *ib.* lvii. 150; lix. 54.

[7] Guthzeit, *Ann. Chem. Pharm.* cciv. 1.

[8] Liebig and Pelouze, *Ann. Chem. Pharm.* xix. 241.

[9] Schwarz, *ib.* lxxxiv. 82.

marc. These lees containing wine are diluted with half their volume of water and distilled, and the distillate, which contains about 32 per cent. by volume of alcohol, is distilled again, when a liquid containing 60 per cent. of alcohol first passes over, and then the œnanthic ether. Four thousand parts of wine contain about one part of this ether (Liebig and Pelouze). The commercial product is an oily liquid, frequently coloured green by copper, and possessing a strong alcoholic smell. It is used for the preparation of artificial brandy, and for giving an aroma to common wines.

Delffs, who investigated a sample of œnanthic ether which had been prepared in Kreuznach, came to the conclusion that the chief constituent was the ethyl-ether of pelargonic acid.[1] On the other hand, Fischer who examined another sample obtained from Neustadt, could not detect this acid, but found that the ether contained chiefly capric acid, together with small quantities of caprylic acid.[2]

Isocapric Aldehyde, $C_9H_{19}.CHO$, is obtained by the gradual oxidation of isocapric alcohol. It is a mobile, aromatic-smelling liquid, boiling at 169°, and having a specific gravity of 0·828.[3]

Isocapric Acid, $C_9H_{19}.CO_2H$, is obtained by the further oxidation of the aldehyde as an oily, slightly-smelling liquid, having an unpleasant, burning taste. It boils at 241°·5, and does not solidify at $-37°$, and its specific gravity is 0·9096.

Its salts usually crystallize with difficulty. The barium salt forms an oily or wax-like mass.

Calcium Isocaprate, $(C_{10}H_{19}O_2)_2Ca$, is a white precipitate, crystallizing from hot water in needles.

COMPOUNDS CONTAINING ELEVEN ATOMS OF CARBON, OR THE HENDECATYL GROUP.

427 *Hendecatane*, $C_{11}H_{24}$, also probably occurs, together with its isomerides, in petroleum and other oils containing the paraffins; but it has not yet been prepared in the pure state. Amato obtained a body, boiling at 180°—185°, which is probably the normal compound, by distilling the spongy residue left in the

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[1] *Pogg. Ann.* lxxxiv. 505; *Ann. Chem. Pharm.* lxxx. 290.

[2] *Ann. Chem. Pharm.* cxviii. 307.

[3] Borodin, *loc. cit.*

preparation of œnanthol from castor-oil (p. 647). Lourenço and d'Aguiar obtained an hendecatyl alcohol, boiling at 245°—255°, from amyl valerate.

Methyl-nonyl Carbinol, $CH_3(C_9H_{19})CH.OH$, is formed by the action of sodium amalgam and water on the corresponding ketone. It is a very thick liquid, which boils at 228°—229°, and at 19° has a specific gravity of 0·8628.[1]

Methyl-nonyl Ketone, $CH_3(C_9H_{19})CO$, forms the chief constituent of the essential oil of rue from *Ruta graveolens*, occurring together with hydrocarbons and other bodies. This oil was first examined by Will, who first ascertained its chemical constitution.[2] According to Gerhardt[3] and Cahours[4] it chiefly consists of capric aldehyde, as on oxidation it yields an acid which they believed to be capric acid. If this has really been produced, it shows the presence of an admixture. Greville Williams also examined this oil, and came to the conclusion that it contains hendecatoic aldehyde, $C_{11}H_{22}O$, together with lauraldehyde, $C_{12}H_{24}O$.[5] The analytical numbers obtained by Hallwachs indicate the existence of the former compound, but he considered it to be a ketone rather than an aldehyde.[6] Strecker then threw out the suggestion that it is methyl-nonyl ketone (methyl-caprinyl); and this view was confirmed by the investigations of Fittig and Giesecke,[7] as well as those of Gorup-Besanez and Grimm.[8] The two first of these chemists distilled 500 grams of the oil, which contained scarcely any hydrocarbons, and thus obtained 300 grams of a liquid boiling at 225°—226°, and this on oxidation yielded acetic acid and pelargonic or nonoic acid. The two other chemists obtained the ketone synthetically by submitting calcium acetate and calcium caprate to dry distillation, the product being repeatedly rectified. The portion boiling between 210°—245° is mixed with liquid ammonia, and the solution saturated with sulphur dioxide, when it becomes warm, and on cooling the compound $C_{11}H_{22}O + H(NH_4)SO_3 + H_2O$ separates out in shining, white, pearly crystalline scales, and these are decomposed by warming with a solution of carbonate of soda. The ketone thus obtained is an oily, highly refracting liquid, possessing a pleasant smell

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[1] Giesecke and Fittig, *Zeit. Chem.* 1870, 428.

[2] *Ann. Chem. Pharm.* xxxv. 235.

[3] *Compt. Rend.* xxvi. 226; *Ann. Chim. Phys.* [3], xxiv. 96.

[4] *Thèse présenté à la faculté des Sciences*, le 15 Janvier, 1845; *Compt. Rend.* xxvi. 262.

[5] *Phil. Trans.* 1858, 199.

[6] *Ann. Chem. Pharm.* cxiii. 107.

[7] *Zeitsch. Chem.* 1870, 428.

[8] *Ann. Chem. Pharm.* clvii. 275.

resembling that of garden rue. It boils at 224°, and at 17° has a specific gravity of 0·8295. On cooling it solidifies, as also does that obtained from oil of rue, to crystals which melt at 15°—16°.

Diamyl Ketone, or *Caprone*, $(C_5H_{11})_2CO$, is obtained by distilling calcium isocaproate. It is a liquid having a pleasant smell, boiling at 220°—221°, and having at 20° a specific gravity of 0·822.[1] On warming with concentrated nitric acid it yields a crystalline compound which deflagrates on heating, and possesses acid properties, and is probably dinitro-isopentane.

Hendecatoic or *Undecylic Acid*, $C_{10}H_{21}.CO_2H$, was first prepared by Krafft by heating hendecalenic acid, $C_{10}H_{19}.CO_2H$, with phosphorus and hydriodic acid,[2] and he afterwards prepared it by oxidizing undecatyl-methyl ketone.[3] It forms a scaly, crystalline mass, having a faint smell of caproic acid, is insoluble in water, and melts at 28°·5. Under diminished pressure it distils without decomposition, and it boils under a pressure of 100 mm. at 212°·5. Its salts and derivatives have not as yet been examined.

Dipseudo-butyl-methyl-acetic Acid, $[(CH_3)_3C]_2CH_3.C.CO_2H$, was obtained by Butlerow by the oxidation of tri-isobutylene. $C_{12}H_{24}$. It is a crystalline mass, fusing at 66°—70°, easily soluble in alcohol, and boiling at 266° without decomposition.[4]

COMPOUNDS CONTAINING TWELVE ATOMS OF CARBON, OR THE DODECATYL GROUP.

428 *Normal Dodecatane*, $C_{12}H_{26}$, was first prepared by Brazier and Gossleth[5] by electrolysis of potassium œnanthylate. A hydrocarbon identical with this appears to be formed as a by-product in the preparation of normal hexane from secondary hexyl iodide (p. 626). It also appears to occur in petroleum (Pelouze and Cahours), and in the distillation-products of Boghead cannel (Greville Williams). It is a mobile liquid, boiling at 202°, and having a faint ethereal smell (Schorlemmer).

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[1] E. Schmidt, *Ber. Deutsch. Chem. Ges.* v. 604.

[2] *Ber. Deutsch. Chem. Ges.* xi. 2218. [3] *Ib.* xii. 1664. [4] *Ib.*

[5] *Quart. Journ. Chem. Soc.* iii. 224; see also Wurtz, *Ann. Chem. Pharm.* xcvi. 372.

COMPOUNDS CONTAINING THIRTEEN ATOMS OF CARBON, OR THE TRIDECATYL GROUP.

429 Neither paraffins nor alcohols containing thirteen atoms of carbon have hitherto been prepared.

Dihexyl-ketone, or *Œnanthone*, $(C_6H_{13})_2CO$, is formed, together with other bodies, in the dry distillation of calcium heptoate. It crystallizes in scales melting at 30°, and boiling at 264°.[1]

Methyl-undecyl Ketone, or *Methyl-hendecatyl Ketone*, $CH_3(C_{11}H_{23})CO$, is formed when a mixture of calcium acetate and calcium laurate is distilled under diminished pressure. It is a crystalline mass, melting at 28°, and boiling at 263°.[2]

Tridecatoic or *Tridecylic Acid*, $C_{12}H_{25}.CO_2H$, obtained by the oxidation of methyl-tridecatyl ketone (p. 674), is a scaly crystalline body, insoluble in water, but dissolving in alcohol. It melts at 40°·5, and boils, under a pressure of 100 mm., at 236°.[3]

COMPOUNDS CONTAINING FOURTEEN ATOMS OF CARBON, OR THE TETRADECATYL GROUP.

430 The following acid, occurring in nature, is the only one of this series known:

Myristic Acid, $C_{13}H_{27}.CO_2H$. This body was discovered by Playfair[4] in the nutmeg-butter of *Myristica moschata*. It also occurs, together with other fats, in the otoba-fat of the *Myristica otoba*, which contains the glycerine ethers of oleic acid and myristic acid (Uricöchea).[5] According to Oudemans, one half of the fatty acid contained in Dika-bread consists of myristic

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[1] Uslar and Seekamp, *Ann. Chem. Pharm.* cviii. 179.

[2] Krafft, *Ber. Deutsch. Chem. Ges.* xii. 1667.

[3] *Ib.* 1668.

[4] *Phil. Mag.* [3], xviii. 102.

[5] *Ann. Chem. Pharm.* xci. 369.

An acid of the same composition occurs in a fungus (*Agaricus integer*). It crystallizes in small needles, which melt at 69°·5—70°; its properties have not been more particularly examined.[1]

COMPOUNDS CONTAINING SIXTEEN ATOMS OF CARBON, OR THE HECDECATYL GROUP.

432 *Normal Hecdecatane*, or *Di-octyl*, $C_{16}H_{34}$, is formed, together with octane, by the action of sodium-amalgam and water on octyl iodide. It boils at 278°, and solidifies on cooling to pearly glittering scales, which melt at 21°.[2]

This paraffin is probably a constituent of oil of roses. Dioscorides mentions such a ῥόδινον ἔλαιον; this, however, was only olive-oil, in which rose-leaves had been steeped in order to give it an agreeable odour. Up to the end of the last century this preparation was known in Europe under the name of *Oleum rosateum.*

An odoriferous water, obtained by distilling the flowers with water, is frequently described by Oriental poets, and appears first to have been prepared on the large scale in Persia. It was prepared in such quantities that, in 1772, 20,100 gallons of rose-water, of the value of 3,500*l.*, were imported into Bombay. The traveller Kämpfer, who visited Persia in the year 1683-4, states that a kind of fat, in appearance like butter, was obtained from rose-water, and that this was known under the name of *œttrgyl.* That a volatile oil is obtained by distilling roses was first stated by Geronimo Rossi[3] in 1582, and Baptista Porta in 1589 says, "Omnium difficillimæ extractionis est rosarum oleum atque in minima quantitate sed suavissimi odoris."[4] In the price lists of the German apothecaries in 1614 this substance is also mentioned.[5] The discovery of otto of roses in the East is thus described by Langlès. "On the occasion of the marriage of the Great Mogul Jehan Ghir with the Princess Nur-jehan,

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[1] Thörner, *Ber. Deutsch. Chem. Ges.* xii. 1635.

[2] Zincke, *Ann. Chem. Pharm.* clii. 1; see also Schorlemmer, *Phil. Trans.* 1872, 122.

[3] *Hieronymi Rubei Rav. De Destillatione*, Ravennæ, 1582.

[4] *De Distillatione*, Romæ, 1608.

[5] *Valor sive Taxatio omnium materierum medicarum . . . quæ in officinâ pharmaceuticâ scinphordianâ venundantur*, Giessen, 1614.

in the year 1612, a canal in the garden of the palace was filled with rose-water, and the bride noticed that a scum deposited on its surface. This, having an admirable fragrance, was collected, and to it the name Atar-jehanghiri, or the perfume of Jehan Ghir, was given."[1] The Arabic word *ʿătr* (or more properly *ʿĭtr*) is used throughout the East, and, combined with the Persian word *gul* (rose), is *atrgul*, or otto of roses. Oil of roses is still made in the East, wherever the flower grows in abundance; and that which comes into the English market chiefly comes from Roumelia and the lower slopes of the Balkans. There the peasants cultivate the *Rosa damascina*, and this plant flowers in April and May. The flowers are cut off before sunrise, and distilled in a rough copper still. The first portion of the distillate is used for a second operation, and from this second product the oil separates out on standing. One part of rose-oil is obtained from about 2,500 parts of the flowers.[2]

Rose-oil is a varying mixture of liquid oil, and a solid, odourless body, known as rose-camphor or solid rose-oil. This latter substance was analyzed by Saussure in 1820, and by Blanchet in 1833, and shown to belong to the family of the olefines (C_nH_{2n}). This fact has been since confirmed by Flückiger.[3] Analysis, however, can only decide with difficulty whether a body containing a large number of carbon atoms belongs to the olefine or to the paraffin series. The fact that it is only slowly attacked by boiling and fuming nitric acid would rather point to its belonging to the latter class. It melts at 32°·5, and begins to boil at 272°, but soon becomes brown and carbonizes; from this it would seem that it is a mixture, and the boiling-point indicates that it contains normal hecdecane.

433 *Hecdecatyl Alcohol*, or *Cetyl Alcohol*, $C_{16}H_{33}OH$. Spermaceti is found in peculiar cavities in the head of *Physeter macrocephalus*, *P. Tursio*, and in *Delphinus edentulus.* During the life of the animal the spermaceti is kept in solution in the sperm oil by the animal heat, but it crystallizes out after death. It is freed as much as possible from oil by filtration and treatment with potash-lye, and then melted. The commercial product is a white, scaly, brittle mass, soft to the touch; and from this the pure spermaceti fat (cetin) was obtained by Chevreul by

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[1] *Recherches sur la découverte de l'essence de rose.* Paris, 1804.

[2] Flückiger and Hanbury, *Pharmacographia*, 233.

[3] *Pharm. Journ.* 1869, p. 74.

repeated crystallizations. Spermaceti is also found in small quantity in the blubber of the *Balæoræa rostrata*, and also in the oil of *Delphinus globiceps*.

In 1818 Chevreul found that this fat is decomposed, by heating with caustic potash, into an acid which he had already observed in other fats, and a neutral body. This latter substance he analyzed, and gave to it the name *ethal*, a name composed of the first syllables of the words ether and alcohol, because he believed this body to be composed of olefiant gas and water.[1] Ethal was first recognised to be an alcohol by Dumas and Peligot.[2]

Spermaceti consists chiefly of the cetyl-ether of palmitic acid, $C_{16}H_{32}O$; but it also contains small quantities of lauric, myristic, and stearic acids, in the form of the ethers of the following alcohols, which have not yet themselves been obtained in the pure state:[3]

Lethal, $C_{12}H_{26}O$.
Methal, $C_{14}H_{30}O$.
Stethal, $C_{18}H_{38}O$.

In order to prepare pure cetyl alcohol, a solution of 10 parts of purified spermaceti in 30 parts of alcohol is boiled for some time with 4·5 parts of caustic potash, and then precipitated with barium chloride. The whole is next filtered, and the hot residue pressed and moistened two or three times with alcohol, and again pressed. The alcoholic residues are then distilled, and the cetyl alcohol which was dissolved is found in the residue, and this is then dissolved out by ether. The ethereal solution is again distilled, and the residual compound purified by repeated crystallizations from alcohol.

Cetyl alcohol crystallizes from hot spirit of wine in small scales, melting at 49°·5, and solidifying on slow cooling in glistening laminæ. It boils at about 400°, but evaporates perceptibly at the temperature of boiling water. Heated with caustic potash to 250°, it forms potassium palmitate:

$$C_{16}H_{34}O + KOH = C_{16}H_{31}KO_2 + 2\,H_2.$$

434 *Cetyl Oxide*, or *Dicetyl Ether*, $(C_{16}H_{33})_2O$, was obtained by Fridau by dissolving sodium in fused cetyl alcohol until the evolution of hydrogen ceased, and heating the product with cetyl iodide to 110°. Cetyl oxide crystallizes from alcohol or

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[1] *Ann. Chim. Phys.* [1], vii. 157.

[2] *Ib.* lxii. 5.

[3] Heintz, *Pogg. Ann.* lxxxi. 267, 553.

Tricetylamine, $(C_{16}H_{33})_3N$. This was obtained by Fridau by passing ammonia over cetyl iodide, heated to 150°, the temperature being gradually raised to 180°. It crystallizes from alcohol in white needles, melting at 39°, and forms salts which are insoluble in water. The hydrochlorate, $(C_{16}H_{33})_3NHCl$, crystallizes from hot alcohol in glistening needles. Its solution yields with platinic chloride a cream-coloured precipitate, having the formula, $2(C_{16}H_{33})_3NHCl + PtCl_4$.

Palmitaldehyde, $C_{16}H_{32}O$, is formed, according to Friedel, by heating cetyl alcohol with potassium dichromate and sulphuric acid. A better process is to distil a mixture of calcium palmitate and formate under diminished pressure. It crystallizes from ether in glistening scales which melt at 58°·5, and boils under a pressure of 100 mm. at 239°—240°.[1]

PALMITIC ACID, $C_{15}H_{31}.CO_2H$.

435 So early as the year 1813, Chevreul pointed out that the soap obtained by saponification of pig's lard yields on decomposition two fats having acid properties, one of which is solid and the other liquid. The former of these, on account of the pearly character of its potash salt, he termed *margarin* (*μάργαρος*, pearl-shell). In a subsequent investigation in 1816, he came to the conclusion that saponification depends on the combination of a fatty acid with the alkali and the simultaneous separation of glycerin. To the two above fatty acids he then gave the names of *acide margarique* and *acide oléique*. The subsequent investigation of many other fats showed that the consistence of these bodies depends on the proportion of the solid and of the fluid fat which they contain. To the first of these he gave the name of *stearin* (from *στεάρ*, tallow) and to the other that of *eliene* (from *ἔλαιον*, oil). Lastly, in 1820, he distinguished two kinds of fatty acids, namely, *acide margarique* and *acide margareux*, to the last of which he afterwards gave the name of *acide stéarique*. Chevreul did not, however, believe that any real distinction between the two acids existed, and he threw out the idea that margaric acid would after all turn out to be a mixture of stearic acid with some easily fusible acid. Nevertheless, margaric acid was usually considered to be a definite compound, and to it the formula

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[1] Krafft, *Ber. Deutsch. Chem. Ges.* xiii. 1416.

bodies of men and animals. Other fatty acids are also contained in this material. The first mention of this substance is found in a letter, dated November 17, 1664, from Henry Oldenburg, then Secretary of the Royal Society, to Robert Boyle. "Mr. Howard produced a substance taken out of the grave of a man who had been dead thirty years, and was in a manner all wasted, but that a piece of fat remained about the place of his belly, of which this present was a small portion, which being put upon the fire, burned and smelled like fat."[1] The above name was given to this substance by Fourçroy as standing half-way between fat and wax.

Ethyl Palmitate, $C_{16}H_{31}O_2(C_2H_5)$, is obtained by passing hydrochloric acid into a hot saturated alcoholic solution of the acid. It crystallizes in hard prisms, melting at 24°.

Cetyl Palmitate, $C_{16}H_{31}O_2(C_{16}H_{33})$, is the chief constituent of spermaceti; from which it may be obtained by repeated crystallizations from hot alcohol and ether, when it is deposited in the form of thin glistening scales, melting at 53°·5.

Isopalmitic Acid, or *Diheptylacetic Acid*, $(C_7H_{15})_2CH.CO_2H$, is obtained by the decomposition of the diheptylacetic ether. It forms a white, hard, crystalline mass, melting at 26°—27°, and boiling under a pressure of 80—90 mm. between 240° and 250°.[2]

COMPOUNDS CONTAINING SEVENTEEN ATOMS OF CARBON.

436 *Pentadecatyl-methyl Ketone*, $CH_3(C_{15}H_{31})CO$, is obtained by the dry distillation of a mixture of barium acetate and barium palmitate under diminished pressure. It yields colourless crystals which melt at 48°, and boils under the normal pressure at 319°—320 (Krafft).

Margaric Acid, $C_{16}H_{33}.CO_2H$, was obtained synthetically by distilling a mixture of potassium cetyl sulphate and potassium cyanide. The crude margaronitril thus obtained was decomposed by boiling with alcoholic potash, and the acid separated from the product.[3] Krafft obtained this acid by the oxidation

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[1] Boyle, *Opera*, vi. 176.

[2] Jourdan, *Ann. Chem. Pharm.* cc. 112.

[3] Becker, *Ann. Chem. Pharm.* cii. 209 ; Heintz, *Pogg. Ann.* cii. 272.

is also suitable for the preparation of stearic acid, inasmuch as the substance only contains stearic and oleic acids.[1]

Stearic acid crystallizes from hot alcohol in nacreous laminæ or needles, which melt at 69°·2, to a colourless oil, again solidifying on cooling to a fine, white, scaly, crystalline mass. It can be distilled, but under the normal pressure suffers partial decomposition. Under a pressure of 100 mm. it boils constantly at 287° (Krafft). Its specific gravity from 9° to 11° is equal to that of water (H. Kopp).

Potassium Stearate, $C_{18}H_{35}O_2K$, crystallizes from hot alcohol in needles or scales. It dissolves in ten parts of water at the ordinary temperature, forming a mucilaginous mass. On heating, however, the solution becomes clear, and when poured into a large volume of cold water the so-called acid stearate, $C_{18}H_{35}O_2K + C_{18}H_{36}O_2$, separates out in delicate white pearly laminæ.

Sodium Stearate, $C_{18}H_{35}O_2Na$, forms the chief constituent of ordinary tallow soap. It crystallizes from hot alcohol in forms similar to the potassium salt, and like this is decomposed by a large volume of cold water into free alkali and the acid salt. This method may be employed for the preparation of pure stearic acid by dissolving good tallow soap in six parts of hot water and adding to this fifty parts of cold water, when a mixture of sodium palmitate and sodium stearate is precipitated. This is then dissolved in hot alcohol, and on cooling the stearate first separates out, and this is decomposed by hydrochloric acid, and the acid purified by recrystallization.

The stearates of the *alkaline earths* are crystalline precipitates insoluble in water. The magnesium salt, which is obtained in the form of a white flocculent precipitate, crystallizes from alcohol in delicate laminæ. The stearates of the other metals form imperfectly crystallized or amorphous precipitates.

By the dry distillation of a mixture of the pure calcium salts of acetic and stearic acids *methyl-heptdecatyl ketone*, $CH_3(C_{17}H_{35})CO$, is formed. This body melts at 55°·5, and distils at 266°·5 under a pressure of 100 mm.

When calcium stearate is distilled alone, a variety of products are formed, amongst which stearone, $(C_{17}H_{35})_2CO$, occurs. This body crystallizes from ether in laminæ which melt at 87°·8.[2]

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[1] H. L. Buff, *Gmelin's Handbook*, xvii. 1041 ; Oudemanns, *Journ. Prakt. Chem.* lxxxix. 215.

[2] Bussy, *Ann. Chem. Pharm.* ix. 270.

Lignoceric Acid, $C_{23}H_{47}.CO_2H$, is found in paraffin and in beechwood tar. It crystallizes from hot alcohol in interlaced needles melting at 80°·5.[1]

An acid of the same composition, but melting at 45°—47°, was obtained by Pouchet by oxidizing solid paraffin with fuming nitric acid. He gave to this the name of paraffinic acid.[2]

Hyænasic Acid, $C_{24}H_{49}.CO_2H$, was found by Carius in the anal glandular pouches of the striped hyæna (*Hyæna stricta*). It crystallizes from alcohol in granules consisting of microscopic curved needles, and from ether in more distinct crystals. It melts at 77°·5.[3]

The existence of these acids, with the exception of arachic and lignoceric acid, is somewhat doubtful.

THE WAXES.

439 Professor John, in Berlin, who in 1812 was the first to examine beeswax, found that it could be separated into two constituents by boiling alcohol. The easily soluble portion he termed *cerin*, and the more insoluble *myricin*. Other chemists occupied themselves with investigations of the various kinds of wax, but Brodie's investigations first threw a clear light upon this subject.[4]

Ceryl Alcohol, $C_{27}H_{53}O$. Chinese wax is produced by the puncture of an insect (*Coccus ceriferus*) on the various species of *Rhus*, *Ligustrum*, and *Hibiscus*, and that of *Coccus Pela*, on *Fraxinus chinensis*. Chinese wax consists almost entirely of cerotyl cerotate, $C_{27}H_{53}O_2(C_{27}H_{55})$. It can be purified by recrystallization from solution in the lighter tar-oils and alcohol. It melts at 82°.

In order to obtain the alcohol from this substance, the wax is melted with caustic potash, the fused mass treated with boiling water, and barium chloride added, the solution filtered, and the washed precipitate, consisting of a mixture of barium cerotate, and ceryl alcohol, washed and dried. The latter substance is then dissolved out by boiling alcohol, to which a small quantity of benzol has been added, and crystallized from a solution in a mixture of alcohol and ether. It forms a waxlike mass

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[1] Hell and Hermanns, *Ber. Deutsch. Chem. Ges.* xiii. 1713.

[2] *Bull. Soc. Chim.* xxiii. 111.

[3] *Ann. Chem. Pharm.* cxxix. 168.

[4] *Phil. Trans.* 1848, i. 159.

resinous body with myricyl- and probably ceryl-ethers.[1] By repeated treatment with strong alcohol at 20°—25° the colouring matter is removed, and the residue is then heated with alcoholic potash. The residue remaining on evaporation is boiled with a solution of acetate of lead, and the mixture of lead salts and wax-alcohols thus obtained is well dried, and treated with pure ether free from alcohol. On cooling, myricyl alcohol separates out, and is purified by recrystallization.

Myricyl alcohol is a crystalline silky mass, melting at 85°, and solidifying as a fibrous crystalline mass on cooling. It is scarcely soluble in cold ethyl alcohol.

Melissyl Chloride, $C_{30}H_{61}Cl$, is formed by heating the alcohol with phosphorus pentachloride, when the ether separates out as a waxlike mass, melting at 64°·5.

Melissyl Iodide, $C_{30}H_{61}I$, is obtained by the action of iodine and phosphorus on fused melissyl alcohol. It separates out from alcohol in the form of crystalline grains, melting at 67°. When heated in a current of ammonia to 120° a mixture of the primary, secondary, and tertiary bases is obtained, which have not as yet been obtained pure.

Melissyl Hydrosulphide, $C_{30}H_{61}SH$, is formed by boiling the chloride with alcohol and potassium sulphide. It is a yellow amorphous powder, without taste or smell, and melting at 94·5°.

Melissic Acid, $C_{29}H_{59}.CO_2H$, does not occur in nature, but is obtained as a crystalline mass by heating the alcohol with potash-lime to 220° as long as hydrogen is evolved (Brodie, Pieverling). It crystallizes from alcohol in small, fine, silky needles, which melt at 88°·5. Its alcoholic solution has a faintly acid reaction.

Potassium Melissate, $C_{30}H_{59}O_2K$, crystallizes from alcohol in glistening needles, and dissolves in about 20 parts of water, forming a turbid, gummy liquid, from which the acid salt is precipitated on addition of an excess of water.

Lead Melissate, $(C_{30}H_{59}O_2)_2Pb$, is formed as an amorphous precipitate, but crystallizes from boiling toluol in glistening needles.

Ethyl Melissate, $C_{30}H_{59}O_2(C_2H_5)$, is obtained by boiling the silver salt with ethyl iodide. It is easily soluble in alcohol and ether, and is a waxlike, odourless mass, melting at 73°.

442 *Theobromic Acid*, $C_{63}H_{127}.CO_2H$, is found, together with other acids, in cocoa-butter. It crystallizes from alcohol in

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[1] Maskelyne, *Journ. Chem. Soc.* [2], vii. 87; Pieverling, *Lieb. Ann.* clxxxiii. 344.

latter can be separated by a repetition of the method of partial neutralization, and the valerianic acid can be removed by distillation. By a repetition of these operations a mixture of two, or even more, of these volatile fatty acids can be completely separated from one another.

In the oxidation of the ketones which contain methyl, acetic acid is formed together with another fatty acid. If the dilute aqueous solution be distilled, the latter acid passes over first, the acetic acid remaining almost completely in the residue. By a repetition of this operation it is also possible to separate these acids completely from one another.[1]

The solid fatty acids can be separated by the method of *fractional precipitation* proposed by Heintz.[2] An alcoholic solution of acetate of barium, magnesium, or lead is added to the alcoholic solution of the acids, when the fatty acid richest in carbon is first precipitated, care being taken that the precipitant is added in quantity sufficient only to throw down a small portion of the acids present. The filtrate is then treated in a similar way, and the various precipitates thus obtained are decomposed by hydrochloric acid. The acids thus separated out are again treated in a similar way, until a pure compound is obtained, this being ascertained by the melting-point. If the melting-points of the different fractions are found to be identical, and correspond with that observed in the previous partial precipitation, it may be concluded that the pure acid has been obtained, especially if the point of solidification is identical with the melting-point, for, in the case of a mixture, the melting-point and point of solidification do not fall together, the first being generally lower than that of the more easily fusible constituent. Besides, the texture of the mixture is a totally different one from that of the pure acid. The following examples illustrate this:

Mixture of Stearic Acid	& Palmitic Acid	M.P.	Point of Solidification.	Texture on Solidification.
100	0	69°·2	69·°2	Crystalline scales.
80	20	65°·3	60°·3	Fine needles.
60	40	60°·3	56°·5	Non-crystalline.
40	60	56°·3	54°·3	Large plates.
30	70	55°·1	54°·0	Non-crystalline.
20	80	57°·5	53°·8	Ill-defined needles.
0	100	62°·0	62°·0	Scales.

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[1] Schorlemmer, *Phil. Trans.* 1872, i. 121.

[2] *Journ. Prakt. Chem.* lxvi. 1 ; *Pogg. Ann.* xcii. 588.

It was formerly believed that the melting-point in this series also regularly rose with the increase of molecular weight; but Baeyer[1] has shown that this takes place in an irregular manner, inasmuch as an acid with an uneven number of carbon atoms always possesses a lower melting-point than the preceding member of the series containing an even number of carbon atoms. The following table is arranged to show this periodic increase and diminution of melting-point:

Œnanthylic acid,	$C_7H_{14}O_2$	. . − 10°·5
Caprylic acid,	$C_8H_{16}O_2$	. . + 16°·5
Pelargonic acid,	$C_9H_{18}O_2$	. . 12°·5
Capric acid,	$C_{10}H_{20}O_2$	. . 30°·0
Hendecatoic acid,	$C_{11}H_{22}O_2$	. . 28°·5
Lauric acid,	$C_{12}H_{24}O_2$	. . 43°·5
Tridecatoic acid,	$C_{13}H_{26}O_2$	. . 40°·5
Myristic acid,	$C_{14}H_{28}O_2$	. . 53°·8
Pentadecatoic acid,	$C_{15}H_{30}O_2$	. . 51°·0
Palmitic acid,	$C_{16}H_{32}O_2$	. . 62°·0
Margaric acid,	$C_{17}H_{34}O_2$	. . 59°·9
Stearic acid,	$C_{18}H_{36}O_2$	. . 69°·9
Nondecatoic acid,	$C_{19}H_{38}O_2$	. . 66°·2
Arachidic acid,	$C_{20}H_{40}O_2$	. . 75°·0
Medullic acid,	$C_{21}H_{42}O_2$	. . 72°·5
Behenic acid,	$C_{22}H_{44}O_2$	. . 76°·0
Lignoceric acid,	$C_{24}H_{48}O_2$	. . 80°·5
Hyænasic acid,	$C_{25}H_{50}O_2$	. . 77°·5
Cerotic acid,	$C_{27}H_{54}O_2$	. . 81°·5
Melissic acid,	$C_{30}H_{60}O_2$	. . 88°·5
Schalfejew's acid,	$C_{34}H_{68}O_2$	. . 91°·0

We have already seen that most of these acids occur in nature, especially those which contain an even number of carbon atoms in the molecule. Many are found in the free state, although the larger number occur as ethers of the various alcohols, especially as those of glycerin, $C_3H_5(OH)_3$. The fats and oils occurring in the vegetable and animal kingdom usually consist of mixtures of the normal ethers of this alcohol, and, together with the fatty acids, they also usually contain acids of the series $C_nH_{2n-2}O_2$, and especially oleic acid, $C_{18}H_{34}O_2$.

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[1] *Ber. Deutsch. Chem. Ges.* x. 1286.

second century, and ascribed to Geber, we find the statement that soap was prepared from various kinds of tallow with potash-lye and lime. German soap is described as the best and most fatty; and then came the Gallic. It is stated that soap is used as a medicine, and that by means of it all dirt could be removed from the body and clothes. That the German soap was softer depended, of course, upon the fact that it was prepared from wood-ashes containing potash, whereas the French soap was made from the ashes of sea-plants containing soda.

It was only, however, by slow degrees that soap came into general use as a cleansing agent. In place of soap potash-lyes were frequently used, the ancients cleansing in this way not only their wine and oil casks, but also the marble statues of their gods. Natural carbonate of soda and the ashes of sea-plants were also used for this purpose, but the cheapest material used as a cleansing agent was putrid urine. The fullers in Rome were obliged to live beyond the walls, or in districts removed from the fashionable portion of the city, in consequence of the disagreeable nature of their trade.

That the Romans, at least in later times, employed soap is rendered certain by the discovery at Pompeii of a complete soap-boiling establishment, together with some soap in a perfect state of preservation.

Certain plants were employed for washing, such as the Saponaria, Gypsophila, &c., in early days, and are used even at present in certain localities. The juice of these plants forms a kind of soap-like lather with water, produced by the saponin which is contained in the substance.

Little is known concerning the soap industry up to the seventeenth century. The use of soap had then become pretty general, and its manufacture has increased from year to year. It received an important impetus from Chevreul's discovery of the decomposition of the fats, and from Leblanc's discovery of the artificial preparation of soda on the large scale.

In former days soap was prepared in northern countries entirely from tallow, whilst in other places olive-oil was employed. When, however, soap came to be used not merely for washing purposes, but was needed in very large quantities in many industries, such as in bleaching and calico-printing, it was necessary to seek for other sources of the fatty acids, and these were found in cocoa-nut oil, palm-oil, and other vegetable fats and oils.

becomes saponified, after which the soap is separated by the addition of common salt. In France, Spain, and England, the kelp was frequently used in place of wood-ashes.

In the year 1823 artificial soda was first employed in the making of soap. The alkali was manufactured from common salt on the large scale in England according to Leblanc's process by James Muspratt. The Lancashire soap-boilers were long before they would believe that this artificial soda could replace that to which they had so long been accustomed, and Muspratt had to give away his soda by scores of tons in order to convince them that by using his purer article both time and labour were spared. After a time, however, the tide turned, and so great was the demand for the new and purer soda, that it was packed off to the soaperies in iron waggons whilst still hot from the furnace.

Up to within a recent period soap-boilers made their own caustic lye from soda-ash. At present, however, caustic soda prepared in the alkali-works is almost entirely used for the preparation of soap. The process employed in the manufacture of soap depends greatly on the character of the fat and the nature of the soap which has to be prepared. When a fat is boiled with caustic alkali and the whole well mixed together, an emulsion is formed when a certain degree of concentration is reached. If common salt be then added to this, the soap separates out as a liquid layer, solidifying to a granular or imperfect soap, whilst glycerin and the alkali salts, termed the *spent lyes*, remain in solution. This imperfectly-made soap is then boiled with water or weak alkali, when the contents of the pan are brought into a state of homogeneous mixture called the *close-state*. In this process the soap takes up more water, and, on addition of common salt, it separates out as *curd soap*.

After the spent lyes have been removed from under the curd soap, it is boiled again with an excess of caustic soda solution to insure perfect saponification. The soap is now allowed to settle for about twelve hours. The excess of soda solution is removed and the curd soap is boiled with a small proportion of water till the whole is "close" and homogeneous. This process is called "fitting." After this the pan of soap is left at rest for two or three days, during which time an impure and dark-coloured soap (called "nigre") separates out at the bottom, and a light and frothy portion (termed the "fob") rises to the top. The pure (or upper soap) is removed into forms (frames), cooled and cut is much more soluble in salt-water than the other soaps, and it is therefore used on board ship, and receives the name of *marine soap.* This soap is very similar to *castor-oil soap,* which is hard but very brittle.

Resin Soaps. The resin left behind in the distillation of turpentine contains a number of compounds having acid properties, and these when heated with alkalis form resin soaps. These are usually mixed with fatty soaps, and are commonly employed in soap used for bleaching.

Silicate Soap is prepared by stirring up a solution of silicate of soda or soluble glass with the liquid soap in the forms before solidification sets in. The addition of silicate of soda greatly lessens the price of the soap without diminishing, at any rate in the same ratio, its detergent properties, as silicate of soda, like the fatty acid, holds the alkali in a feeble state of combination.

449 *Soft Soaps* are obtained by the saponification of a cheap oil or fat with caustic potash, oleic acid or fish oil being usually employed. Soft soap forms a thick transparent emulsion, which is more or less darkly coloured. It contains an excess of alkali, and also all the glycerin which is contained in the fat. The soft soap obtained from Belgium and Germany is green, and as this green soap is in many places in demand, common brown soft-soaps are frequently coloured with indigo. Soft soaps made from clear fish-oil are also commonly coloured brown artificially. Soft soap is chiefly used for fulling, and for scouring, and in the cleaning of woollen goods and wooden vessels; it is also employed in linen-bleaching works.

Lead Soap. If oxide of lead be employed for the saponification of fats, a mixture of the lead salts of the fatty acids is obtained, and this is used in pharmacy, and serves as diachylon plaster. Such a preparation has been known for a long time. The ordinary lead-plaster, which is obtained by boiling olive-oil with litharge, was said to be discovered by the Roman physician Menecrates, in the middle of the first century. It was likewise known to Pliny, who writes as follows: "*Molybdæna cocta cum oleo, jecinoris colorem trahit. . . . Usus in liparas, ad lenienda refrigerandaque hulcera; emplastrisque quæ non alligantur. Composito ejus est libris tribus, et ceræ libra unas olei tribus heminis.*"

The purifying action of soap depends upon the fact that it is decomposed by a large quantity of water into free alkali and an insoluble acid salt. The first of these takes away the fatty dirt on washing, and the latter forms the soap lather, which envelops the greasy matter and thus tends to remove it.

A solution of soap in dilute alcohol is used for the determination of the hardness of water (Vol. 1. p. 250), as when the whole of the salts of calcium and magnesium are precipitated a permanent lather is obtained, and this point can be readily ascertained.

Soap is also employed in medicine, both internally and externally. As an internal medicine it should be prepared from the best olive-oil and pure caustic soda. It acts like a mild alkali, and is sometimes mixed with other medicines in the form of pills. Soap-water, which can readily be prepared, acts as an excellent antidote in the case of poisoning with the stronger acids.

Externally it is used in many forms of skin diseases, soft soap being most frequently used for this purpose.

The soaps which occur in commerce vary very much in their composition, as is shown in the following table:

	Fatty Acids.	Potash, K_2O.	Soda, Na_2O.	Water.	Salt and other admixtures.
I. HARD SOAPS—					
Old mottled soap … … …	81·25	1·77	8·55	8·43	—
New tallow soap … … …	61·0	—	8·4	28·8	2·3
Marseilles soap … … …	67·0	—	7·8	21·2	4·0
Palm-oil soap, yellow .. …	65·2	—	9·8	19·9	1·1
Do. bleached… …	61·2	—	9·7	24·8	1·3
Tallow soap … … .. …	42·8	—	8·8	39·1	—
Cocoa-nut oil soap (marine soap) … … … … …	22·0	—	4·5	73·5	—
Palm-oil soap… … … …	49·6	—	8·0	35·4	1·1
II. SOFT SOAPS—					
Common soft soap…	49·5	9·1	—	48·0	—
London do.	[illegible]	8·5	—	46·5	—
Belgian green do. ..	[illegible]	[illegible]	—	57·0	—

450 *Statistics of British Soap.* A well known soap manufacturer, the late Mr. Wm. Gossage, states that in 1852, when the excise duty on soap was finally abolished, the total production of soap in Great Britain was 1,000 tons per week, less than one-half of which was produced in the Lancashire district. He also

concludes that the production in Lancashire in 1870 is fully equal to the total production in the year 1852, and that hence during the eighteen years the production of British soap was doubled. From information furnished us by his son, Mr. Frederick H. Gossage, we learn that the British make at the present time (1881) has reached the enormous amount of 4,500 tons per week, or taking fifty weeks to the year 225,000 tons per annum.

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