VOL. XLIII 1923

TRANSACTIONS
of the
American Electrochemical Society

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H. G. Hinckley

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OF THE

American Electrochemical Society

VOLUME XLIII

FORTY-THIRD GENERAL MEETING
NEW YORK CITY
MAY 3, 4 AND 5, 1923

PUBLISHED BY
The American Electrochemical Society
AT THE OFFICE OF THE SECRETARY
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VOLUME XLIII 1923

TRANSACTIONS

OF THE

American Electrochemical Society

PROCEEDINGS

CONDENSED MINUTES AND RECORD OF THE FORTY-THIRD GENERAL MEETING OF THE SOCIETY, HELD AT THE COMMODORE HOTEL, NEW YORK CITY, MAY 3, 4 AND 5, 1923.

The total registration at this meeting was 254, of whom 168 were members and 86 guests.

PROCEEDINGS OF WEDNESDAY, MAY 2, 1923

The registration of Society members and guests began at 6.00 P. M. on the mezzanine floor of the Commodore Hotel. At 7.00 P. M. the Board of Directors met at dinner for the purpose of conducting its annual business meeting.

PROCEEDINGS OF THURSDAY, MAY 3, 1923

The meeting convened at 9.30 A. M. with President C. G. Schluederberg in the Chair. Having but recently returned from a trip to the Far East, the President expressed his gratitude at being back in the United States again, and, on behalf of the Society, heartily welcomed the members and guests present. He then called upon Dr. Wm. G. Horsch, who had arranged for the Symposium on "Electrode Potentials," to assume the Chair. Dr. Horsch briefly mentioned that the subject of electrode potentials is one which lies particularly within the field of the electrochemist, and that the papers and discussions of this session should give rise to a rather comprehensive cross-section of the line of progress at the present time. Papers by the following authors were presented and are printed, together with discussions, in these Transactions: Hugh S. Taylor; H. C. Howard; M. Knobel, P. Caplain and M. Eiseman; N. Howell Furman; A. H. W. Aten; M. Knobel; Alexander Lowy and H. S. Frank.

At 11.30 the meeting adjourned. Within a quarter of an hour, members and guests were conveyed by special buses to the plant of the McGraw-Hill Co., Inc., where a complimentary luncheon was served. This was followed by an inspection trip through the various departments of the printing and publishing plant. Moving pictures depicting the construction and operation of the Diesel engine concluded the visit, the members returning to the Commodore Hotel to attend the afternoon session.

At 2.30 P. M. President Schluederberg opened the annual business meeting of the Society. Secretary Fink presented the reports of the Board of Directors and of the Secretary. In the latter report it was pointed out that since the Baltimore meeting the Society had published and distributed four volumes of the Transactions (Vol. 39, 40, 41 and 42), thus bringing the publication work up to date. Following the presentation of this report, Dr. Hering offered the following resolution: That a vote of thanks be expressed to the Secretary and his office for having brought the volume publications up to date. The motion was unanimously carried. The above reports, together with that of the Treasurer are included in subsequent pages of the proceedings.

The next order of business included reports of Standing Committees. Dr. C. F. Burgess presented the report of his committee on dry cells, which indicated that in 1914, 17,092,438 dry cells were sold in this country at a valuation of $8,719,164, while in 1919 the number had increased to 173,754,676 at a valuation of over $25,000,000. To promote rapid work and to avoid unnecessary duplication of effort this committee made the following recommendations:

1. That a committee on dry cells be appointed for the coming year, with instructions to offer its co-operation to the Bureau of Standards in standardization of tests for dry cells in various kinds of radio service.

2. That members of the American Electrochemical Society who are engaged in dry cell manufacture, and who are desirous of contributing to and taking part in this work, indicate their desires to the Bureau of Standards.

Dr. S. C. Lind presented the report of the Radio Activity Committee, in which it was especially pointed out that in the production of radium in the United States there has been a marked cessation of activity. This is directly due to the discovery and development of a large deposit of high grade radium-bearing uranium ore in the Belgian Congo by the Katanga Copper Co. It was the recommendation of Dr. Lind's committee that the Society undertake to concentrate in its Transactions the results of numerous investigations, in the field of radio activity, which are published in such a widely scattered range of journals.

The report of the Organic Electrochemistry Committee was presented by its Chairman, Dr. C. J. Thatcher. The progress being made in this field will be discussed extensively at a symposium to be held at the Spring meeting, 1924.

Mr. A. T. Hinckley presented the report of his committee on membership. The essential data of this report are published in following pages.

Chairman FitzGerald of the Publication Committee presented a report which in part is as follows:

To the Board of Directors, American Electrochemical Society:

During the year 1922-23 your committee has received and examined 98 papers. Of these 20 were rejected, 27 were returned to the authors for revision, 48 were accepted without change and 3 were withdrawn.

Every paper is sent to *at least* 2 examiners. Some papers during the past year have been reported on by 5 examiners, and several papers have been reported on by 3 examiners, before final action by the committee. This change in the routine examination of papers has made it necessary to insist on an earlier date for the submission of papers than has formerly been the practice, and the ruling of the Publication Committee as to the latest date for receiving papers will in future be rigidly enforced.

A new rule of the Publication Committee in relation to papers submitted for symposia is that one of the two examiners to whom a symposium paper is submitted shall be the member in charge of the symposium. The object of this rule is to avoid embarrassments which are apt to arise when the member in charge of the symposium has invited papers which the Publication Committee is disposed to reject.

Prior to presenting the report of the Tellers of Election, the Chair read a communication from H. C. Parmelee in which he withdrew his name from the report in favor of A. T. Hinckley. The Chair then read

THE REPORT OF THE TELLERS OF ELECTION

The following is a list of votes cast in the election of officers for the year 1923-1924:

President: A. T. Hinckley, 246.

Vice-Presidents: Lawrence Addicks, 212; G. K. Elliott, 148; Henry Howard, 117; Dorsey Lyon, 103; W. Lash Miller, 71; W. R. Mott, 60; A. T. Hinckley, 2.

Managers: F. M. Becket, 208; C. B. Gibson, 185; R. A. Witherspoon, 149; G. B. Hogaboom, 99; D. B. Rushmore, 51; Lawrence Addicks, 1.

Treasurer: F. A. Lidbury, 240.

Secretary: Colin G. Fink, 244.

Void Ballots, 33.

(Signed) LINCOLN T. WORK
ARTHUR K. DOOLITTLE

The President announced the following elections, as the result of the Tellers' report:

President: A. T. Hinckley.

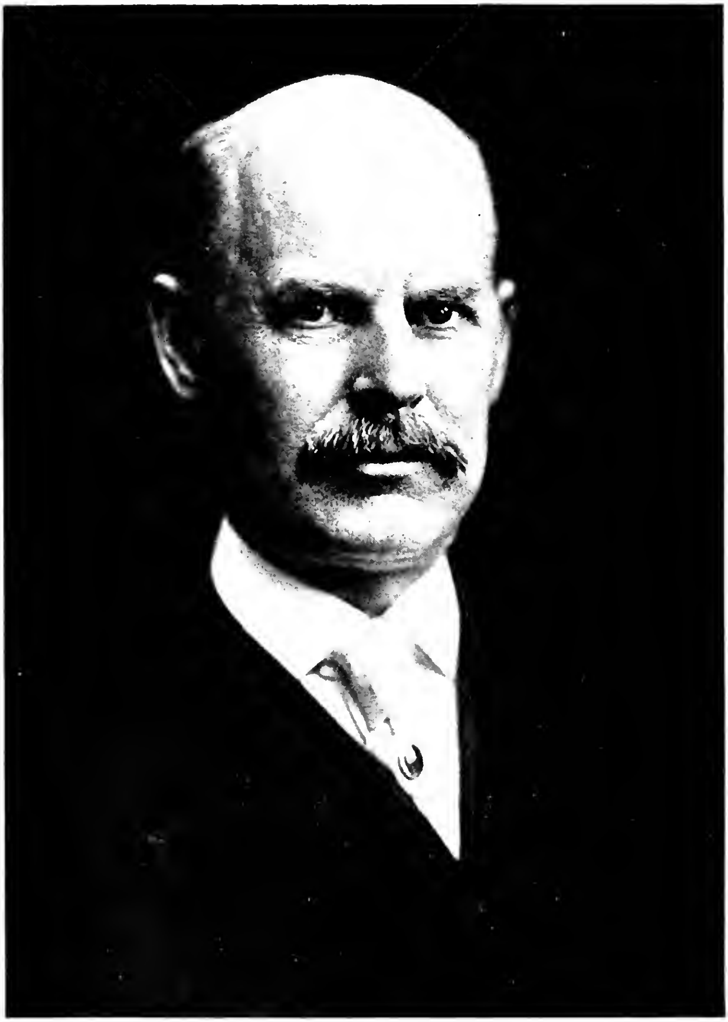
Vice-Presidents: Lawrence Addicks, G. K. Elliott, Henry Howard.

Managers: F. M. Becket, C. B. Gibson, R. A. Witherspoon.

Treasurer: F. A. Lidbury.

Secretary: Colin G. Fink.

Following this announcement the Chir requested Mr. Acheson Smith to escort President-elect Hinckley to the platform.



Edward G. Acheson

DR. EDWARD G. ACHESON MADE HONORARY MEMBER

President Schluederberg announced that, at the meeting of the Board of Directors held Wednesday evening, Dr. Edward G. Acheson was elected to Honorary Membership upon official recommendation from 15 members of the Society. Dr. Hering escorted Dr. Acheson to the platform, whereupon Mr. F. A. J. FitzGerald delivered the following introductory address on E. G. Acheson and his work.

DR. EDWARD G. ACHESON AND HIS WORK

By F. A. J. FitzGerald.[1]

The twenty-first anniversary of the American Electrochemical Society has a special significance. It is fitting that its coming of age should be marked by the conferring of its Honorary Membership on one whose name is universally known for what he has done in advancing electrochemical industry. Inasmuch as I had the good fortune to serve an eight years' apprenticeship with Dr. Edward G. Acheson when some of his inventions were made, I can perhaps contribute something in the way of an appreciation of his work in electrochemistry.

You have no doubt observed that some naive amateurs interested in industrial research seem to consider the objective of the work as something of minor importance compared with the process of reaching it; but actually the conception of an invention often demands a rarer gift than the working out of its details. Dr. Acheson's work is characterized particularly by this gift of choosing objectives to which he devotes his inventive genius.

One of his early objectives was the production of an abrasive material, the properties of which would surpass anything that could be obtained from natural sources, for he visualized clearly the vast industrial importance of such a material. So he made his well-known experiment with the arc light electrode and the plumber's soldering bowl filled with clay and powdered coke, which resulted in the discovery of carborundum and the building of a miniature electric furnace for its manufacture. This, I think,

[1] FitzGerald Labs., Niagara Falls, N. Y.

illustrates clearly what I mean by Acheson's faculty of seeing a valuable objective, the direction of experimental work which would have a great industrial future.

Acheson's subsequent work in creating the artificial abrasive industry illustrates another characteristic of his which is so frequently lacking in those who may perhaps equal him in original ideas; that characteristic is his ability to concentrate on his subject. The late William De Morgan, probably most widely known as the author of those remarkable series of novels which began with "Joseph Vance," devoted most of his life to the manufacture of pottery, and did wonderful work in that field with his inventive genius; but according to one who knew him well, "his mind was ever full of original methods and ideas on all sorts of subjects," and "it was perhaps, to some extent, the wide range of William De Morgan's inventive and creative ability which tended in a measure to hamper the success of the pottery."[2]

Like De Morgan, Acheson's mind is full of original methods and ideas; but these are not allowed to interfere with the development of any particular objective he has in mind. Note how in the early days of carborundum manufacture he observed and recognized the value of the artificial graphite produced by the decomposition of silicon carbide; how he realized the remarkable refractory qualities of silicon carbide; how he made calcium carbide in his electric furnace; but he did not allow these things to divert his attention from the great objective, the production of carborundum, which would revolutionize the abrasive industry, on a large scale.

Observe also that Acheson fully recognized the importance of basing his work on fundamental scientific principles. This may not appear a surprising thing to us at the present day, for we would certainly be astonished at an electrochemical plant that attempted to run without scientific control. But when Acheson made his first little vial of carborundum he sold it at 40 cents a carat and devoted the proceeds to the purchase of a microscope, and when he organized the Carborundum Company with its little 100-kilowatt plant in Monongahela he at once established a chemical laboratory in charge of a German chemist, in those days

[2] "William De Morgan and His wife" by A. M. W. Stirling. Henry Holt and Co., 1922.

believed to be the best variety. This was an extraordinary thing for an abrasive manufacturer in those days, and led to the designation of the Carborundum Company as a plant "run by educated blockheads."

This was the beginning of the manufacture of artificial abrasives and it is not necessary to tell you what that electrochemical industry has become; but I may note that the world production of electric furnace abrasives in 1895 came from Acheson's 100-kilowatt furnace in Monongahela, while 25 years later at Niagara Falls alone the power used in this industry amounted to 20,000 kilowatts.

In the development of Acheson Graphite, we again have an excellent example of his faculty for selecting an objective that would develop into an important industry. Acheson observed the formation of graphite in his early carborundum furnace; but it was not until several years later, after carborundum had already become an important industry and when he undertook to graphitize carbon anodes at the Carborundum Company's plant for use in the Castner caustic soda cell, that he concentrated his energy on the building up of the graphite industry. It is needless to dwell on the value of Acheson graphite in electrolytic and electrothermic processes; but it will be interesting to consider some other work relating to its development.

Persistent refusal to accept defeat is a quality of the highest value in war and in pioneer work in a new process or industry. There is another quality, however, that is perhaps rarer and equally valuable and this is the faculty of recognizing a tactical error and effecting a strategic retreat. In the development of the graphitizing industry, after much experimental work was done on the production of bulk graphite from anthracite coal, Dr. Acheson designed a furnace for its production that has since figured prominently in text books both in this country and abroad, and yet that furnace was never run commercially. On paper it looked excellent; it was built and the special electrical apparatus required for it obtained and set up; but about six hours' trial convinced Dr. Acheson that it was useless as a commercial apparatus and it was then and there sentenced to the scrap pile.

The thing I wish to emphasize is that Acheson saw at once that the design was faulty; that it would be throwing away money to try to get it to work, and that complete abandonment of the scheme was the proper course in spite of the large expenditure already incurred. It is worth noting that subsequent experience has completely demonstrated the soundness of Acheson's judgment; but there can be no question that it required a high order of courage on his part to resist the temptation of trying to make an apparatus work on which so much had been spent.

A large and important use for graphite is in the manufacture of crucibles. When Acheson started experimental work on these he found that the clay bond used in making them was imported, the reason given for this being that, while in this country we had plenty of refractory clays, none of these combined sufficiently high plasticity with refractory qualities. Acheson reacted characteristically to this, and determined to investigate the plasticity of clays. He apparently felt, as I think he always does, that it is not necessary to depend on natural sources for things of this sort, but that they can be better made by man.

He immediately began experimental work based on the effect of organic substances on clay, and two or three days later, on a Monday morning, he came into the laboratory carrying a big load of straw, which he deposited on the bench. He then told me that, on the day before, his children had been having at their Sunday School the story of the Egyptian bondage of the Children of Israel, and the difficulties they met in making brick without straw. Why, he asked, did they need straw for their brick? Surely not as a mere re-enforcement, but because the aqueous extract of the straw gave to the clay the plasticity and mechanical strength which he was seeking. He began the straw experiments that day, and I worked on big wash tubs of clay and aqueous extracts of straw nearly all night with Dr. Acheson, whose health was bad at the time, following up and directing the experiments through the long distance telephone. Thus Egyptianized clay was discovered.

It was about this time also that Acheson was working on Siloxicon; but I can not do more than mention it by name so as to leave a little time for the consideration of one more of his inventions.

I have already called attention to Dr. Acheson's keen appreciation of what is needed. At the present day we have all sorts of problems, the handling of which will profoundly affect the future of civilization. We have reparations, the disastrous effects of phrases like "self-determination," German marks, etc., but there is none of the problems more important than that of the mineral oil fields. Twenty years ago the average man was not worrying about mineral oil, today he is thinking of it seriously. But even now he is only thinking of it as a source of fuel, more particularly as supplying the wants of his motor car or his Ford.

But fuel is not the most important point; we have other sources of fuel—even our powerful army of moral uplifters can not amend the constitution of nature. Careful study of the subject shows that the great value of mineral oil lies in its lubricating qualities, and it is becoming clearer and clearer now that the strong argument for its conservation is found in its importance as a lubricant. Twenty years ago, Acheson saw this clearly, and determined to turn his inventive genius towards finding a substitute for mineral lubricating oils, or at least something that would lead to their economical use.

It would take too long to follow the development of methods of producing a nearly chemically pure non-coalescing graphite for lubrication, nor is this necessary because the technical details of this work are probably well known to most of you. It is sufficient to note that the inception of the work on deflocculated Acheson graphite was similar to that which characterizes other fields in which Acheson worked, and that in its development we find the same ingenuity, resourcefulness and persistence which distinguish his other work.

Those of you who are familiar with Acheson's work will understand how inadequate this review is. I hope, however, that I have said enough to show to those unacquainted with the details of his work why, in the history of electrochemical industry, one of the great names is that of Edward Goodrich Acheson.

Following the above address, President Schluederberg presented Dr. Acheson with a certificate of Honorary Membership. In response, Dr. Acheson spoke, in part, as follows:

"I appreciate most highly the honor you are conferring upon me. It is a matter of much gratification to me to know that I assisted in the organization and the early work of our Society. I am gratified to know that it has become a national society of considerable magnitude, with a foreign membership of which we can be proud. It has done good work in the past, and I hope and believe it will do more valuable work in the future. I hope that it will continue to hold its place among the national societies, and that we will all have good reason to be proud of having been enrolled in its membership."

President Schluederberg then invited President-elect Hinckley to assume the Chair during the presentation of his presidential address, entitled, "Opportunities for the American Electrochemist Abroad." This address is printed in full in this volume.

Thereafter papers by the following were presented for discussion: W. Blum and H. S. Rawdon; H. E. Haring and W. Blum; A. Kenneth Graham; M. R. Thompson; H. D. Hineline. These papers, with the exception of that of H. D. Hineline, will be published in Volume 44 of the Transactions. The final paper of this session was by Will Baughman, on lead vanadates. It is printed in this volume.

At 6.00 P. M. the Council of the Electrothermic Division held a dinner-meeting. This was followed by a meeting of the Advisory Committee to the Bureau of Mines on electrometallurgical work.

PROCEEDINGS OF FRIDAY, MAY 4, 1923

The session was called to order at 9.30 A. M. by President Schluederberg, and the results of the election of officers to the Electrothermic Division and the Electrodeposition Division for 1923-1924 were announced. The officers of these divisions are printed on the first pages of this volume.

The technical session began with the presentation, by title, of papers by J. C. Woodson and Frank W. Brooke. Both these papers had been read, but not preprinted, at the 42nd meeting of the Society. Then followed the presentation for discussion of papers by the following authors: M. deKay Thompson and Per K. Frölich; A. E. R. Westman; C. E. Williams, C. E. Sims and C. A. Newhall; C. W. Drury; F. C. Kelley. All the above papers, with discussions, are printed in this volume. The meeting adjourned at 11.30.

At 12 o'clock members and guests left by train for Westport, Conn. At the kind invitation of Dr. J. V. N. Dorr and Mr. H. N. Spicer, a visit was made to the Westport Mill of the Dorr Co. The members were also guests at an enjoyable luncheon served amid the beautiful and idyllic surroundings of the mill. Later in the afternoon, members and guests went on to the Westport Country Club, where a golf tournament was staged by the men, while the ladies enjoyed bridge and walks. During the dinner, which was served under the auspices of the New York Section of the Society, and for the successful arrangement of which Mr. Irving Fellner was responsible, the following golf prizes were awarded: An engraved silver loving cup, donated by Dr. Dorr, to Frank J. Vosburgh; a niblick, as booby prize, to Robert Burns. This was followed by the clever rendition of a funny song, by Messrs. Lidbury and Hinckley, which, as a parody of "Mr. Gallagher and Mr. Shean," characterized numerous members of the Society. Thereafter dancing was enjoyed by many, and it was with great reluctance that the party returned to New York later in the evening.

PROCEEDINGS OF SATURDAY, MAY 5, 1923

On Saturday, at 9.15 A. M., President Schluederberg opened the meeting by introducing Dr. F. M. Becket, who had arranged for an interesting and comprehensive session on the "Production and Application of the Rarer Metals." Dr. Becket assumed the Chair and papers were presented by the following authors: C. James; H. S. Cooper; H. W. Gillett and E. L. Mack; F. M. Becket; B. D. Saklatwalla; R. W. Moore; J. A. Holladay and T. R. Cunningham; R. P. Neville; Edward Wichers and Louis Jordan; F. E. Carter. These papers, with discussions, are printed in these Transactions. Another paper which had been contributed toward this symposium, but arrived too late to permit of its presentation at this meeting, will be printed in the subsequent volume, *viz.,* 44. This paper is entitled "The Reduction of Some Rarer Metal Chlorides by Sodium," by M. A. Hunter and A. Jones. In concluding the technical program, President Schluederberg, on behalf of the Society, thanked Dr. Becket for his successful efforts in procuring the many excellent papers for this session. He also expressed thanks to those who had contributed papers and discussion to the meeting.

Prior to adjourning the meeting, Dr. Hering offered the following

RESOLUTION OF THANKS.

Resolved: That a vote of thanks be given to the following for having made this forty-third meeting of the American Electrochemical Society such a success:

The Dorr Co., and especially to Dr. J. V. N. Dorr and Mr. H. N. Spicer.

The Westport Country Club.

The McGraw-Hill Co.

The New York Local Section.

The Local Committee, and especially to Mr. Irving Fellner, its active chairman.

ANNUAL REPORT OF THE BOARD OF DIRECTORS

To the Members of the American Electrochemical Society:

The following are some of the important items of business transacted by your Board of Directors during the past year: The following constitutional amendment, effective January 1, 1923, submitted over the signatures of 15 members, was adopted: That Article 4, Section 2, "The annual dues shall be five dollars", be changed to read "The annual dues shall be eight dollars." It was further moved and passed that commencing January 1, 1923, bound volumes be charged to members at the rate of $5.00 per year, to non-members at $6.50 per volume, and to public libraries and scientific societies at $4.00 per volume. The proposed by-laws for the Electrodeposition Division were adopted, the result of the vote being 115 in favor, 1 opposed. Mr. Acheson Smith was appointed to represent the Society on the National Research Council, June 30, 1922, to June 30, 1925. Acting on a resolution submitted and signed by seventeen members of the Society, Dr. Carl Hering was unanimously elected to Honorary Membership at the Annual Meeting of the Board. See Volume **41**, 2 (1922).

It was adopted that the price of our Transactions to members of the Faraday Society be the same as to our members. The relocation of the Society's headquarters from Bethlehem, Pa., to Columbia University, New York, was adopted by a majority two-thirds vote of the Board of Directors. The change was accordingly made August 1, 1923. At the July Directors' Meeting it was resolved that the Publication Committee hereafter be guided by a limit of about 400 pages per volume of the Transactions.

In August of last year the following measure was adopted:

That each Board of Directors of the Society prepare a tentative program for the two meetings of the subsequent year and that it appoint, not later than the fall meeting, a committee from among its members to carry such programs into effect, subject to the approval of the new Board.

The Board approved that any person whose membership was suspended during the war on account of nationality, may upon written application to the secretary, be reinstated without election or payment of the initiation fee.

SECRETARY'S ANNUAL REPORT

To the Board of Directors of the American Electrochemical Society:

GENTLEMEN: The Society held two General Meetings during 1922—one in Baltimore, Md., April 27, 28 and 29, at which the attendance was 125 members and 77 guests, total, 202; the second in Montreal, Que., September 21, 22 and 23, at which the registration was 75 members and 135 guests, total 210. The Transactions of the spring meeting, the feature of which was the session devoted to the reading and discussion of papers on "Electric Furnace Cast Iron," include 24 papers, and those of the fall meeting, embodying a symposium on "Industrial Heating," 22 papers.

The following bound Transactions of the Society have been mailed to the membership since the last Annual Meeting of the Society:

Volume XXXIX, Atlantic City Meeting, in June, 1922.
Volume XL, Lake Placid Meeting, in November, 1922.
Volume XLI, Baltimore Meeting, in February, 1923.
Volume XLII, Montreal Meeting, in April, 1923.

This brings the distribution of volumes up to date, the next volume to be issued being the one which will cover the transactions of this meeting. The edition of the above mentioned volumes of the Transactions was as follows:

Volume No.	Copies complete bound in cloth	Copies bound in paper for Faraday Society sub.	Copies for Storage	Free Copies of each paper to authors
XXXIX	1,650	350	250	10
XL	1,550	350	200	10
XLI	1,400	300	200	10
XLII	1,400	150	200	10

The stock of volumes on hand April 1, 1923, was as follows:

Volume I, 66; II, 88; III, 11; IV, 187; V, 210; VI, 208; VII, 167; VIII, 301; IX, 307; X, 242; XI, 262; XII, 252; XIII, 202; XIV, 377; XV, 345; XVI. 408; XVII, 436; XVIII, 589; XIX, 387; XX, 371; XXI, 429; XXII, 372; XXIII, 346; XXIV, 487; XXV, 491; XXVI, 479; XXVII, 230; XXVIII, 458; XXIX, 96; XXX, 421; XXXI, 87; XXXII, 322; XXXIII, 281; XXXIV, 262; XXXV, 404; XXXVI, 523; XXXVII, 358; XXXVIII, 514; XXXIX, 972; XL, 813; XLI, 787; XLII, 989. Index 1-20, 512.

Condition of Membership of the Society in 1922.

Members January 1, 1922	2,172	
Qualified as members in 1922	108	
		2,280
Deaths in 1922	14	
Resignations in 1922	111	
Dropped for non-payment of 1921 dues	194	
		319
Members, December 31, 1922		1,961
Net decrease for calendar year		211

Condition May 1, 1923.

Members January 1, 1923	1,961	
Qualified as members to May 1, 1923	28	
		1,989
Deaths	1	
Dropped for non-payment of 1922 dues	204	
		205
Members, May 1, 1923		1,784
Members, April 27, 1922		1,995
Net decrease		211

FINANCIAL STATEMENT.

The following is a statement of receipts and expenditures, as of December 31, 1922:

RECEIPTS IN 1922

Cash Balance—January 1, 1922		$ 3,537.13
Entrance Fees	$ 430.00	
Current Dues	6,745.75	
Back Dues	780.95	
Advance Dues, 1923	3,088.00	
Advance Dues, 1924	6.00	
Volumes—1921	355.00	
Volumes—1922	4,851.02	
Volumes—1923	1,117.00	
Sale of Publications—non-Members	2,841.40	
Sale of Reprints	265.10	
Sale of Preprints	139.73	
Sale of Membership Certificates	8.00	
Sale of Society Pins	46.50	
Payment of 1920 Transactions by Faraday Society	402.47	
Subscription to Faraday Society Transactions	184.50	
Advance Subscriptions to Ten-Year Index	60.00	
Sale of U. S. Victory Bond and other Liberty Bonds	8,910.67	
Sale of Phila. Electric Bonds with accrued interest	3,115.20	
Interest on Liberty Bonds	403.75	
Interest on Philadelphia Electric Bonds	155.00	
Interest on Bank Balances	65.30	
Miscellaneous—Refunds on Insurance, etc.	45.81	
Electrothermic Division	44.12	
Total Receipts, January 1 to December 31, 1922		34,061.27
Total		$37,598.40
Total Disbursements		31,545.42
Cash Balance—December 31, 1922		$ 6,052.98

EXPENDITURES IN 1922

Publication Expenses:

Printing of Volume 38	$ 3,127.64	
Printing of Discussion—Volume 38	431.40	
Printing of Volume 39	3,038.94	
Printing of Discussion—Volume 39	597.26	
Printing of Volume 40	2,528.38	
Printing of Discussion—Volume 40	389.07	
Preprints for Volume 39	834.20	
Preprints for Volume 40	2,855.72	
Preprints for Volume 41	2,525.60	
Preprints for Volume 42	1,916.82	
Engraving	677.71	
Extra Reprints	312.75	
Directory of Members (1921)	1,204.46	
Printing of Discussion—Volume 41	325.22	
Constitution and By-Laws	72.50	
Printing of Discussion—Volume 42	313.68	
Total Publication Expenses		$21,151.35

Office and General Expenses:

Secretarial Appropriation	$ 3.900.00	
Office Printing	803.75	
Office Postage	16.95	
Office Expense—Stationery and Supplies	1,107.13	
Postage on Preprints and Bulletins	817.95	
Postage on Volumes	410.59	
Freight and Express on Volumes and Preprints	81.98	
Expenses of Meetings	1,017.36	
Membership Certificates	4.42	
Membership Committee	102.85	
Publication Committee	40.10	
Booth Committee	75.00	
Local Sections	235.00	
Electrothermic Division	2.75	
Electrodeposition Division	28.00	
Moving Expense (Bethlehem to New York)	112.50	
Contribution to Annual Tables of Constants	75.00	
Storage and Insurance	279.38	
Auditing and Accounting Expenses	170.26	
Total Office and General Expenses		$ 9.280.97
Total Expenditures, January 1 to December 31, 1922		$30.432.32

Refund:

Return of Loan (with interest) to J. W. Richards' Estate	$ 1,018.46	
Walter Dalton, for overpayment of Dues	5.00	
Advance Subscription to Ten-Year Index	64.00	
Collection Charge on Canadian Checks	.39	
		$ 1,087.85

Bad Debts Charged Off:

J. B. Grenagle (check uncollectible)		$ 25.25
Total Disbursements		$31,545.42

TREASURER'S ANNUAL REPORT, 1922

January 1, 1922, Cash Balance	$ 3,537.13	
Total Receipts, 1922	34,061.27	
		$37,598.40
Total Expenditures		31,545.42
Balance, December 31, 1922		$ 6,052.98
Balance in Power City Bank, 12-31-22	$ 7,160.57	
Deposits not included in Bank Statement	360.85	
Balance retained as petty cash by Secretary's Office	50.00	
		7,571.42
Less December, 1922, checks not in		1,518.44
Balance, December 31, 1922, as above		$ 6,052.98

We have examined the above statement of accounts, receipts, and expenditures for the year 1922, and find the same to be correct.

(Signed) H. B. Coho,
(Signed) Harry J. Wolf,
Auditors.

MEMBERS AND GUESTS REGISTERED AT THE FORTY-THIRD GENERAL MEETING

Members

Franz D. Abbott
E. G. Acheson
Lawrence Addicks
A. N. Anderson
William C. Arsem
D. K. Bachofer
R. O. Bailey
A. T. Baldwin
F. M. Becket
E. O. Benjamin
M. H. Bennett
Geo. M. Berry
Edw. L. Blossom
Wm. Blum
W. H. Boynton
Robert H. Buckie
C. F. Burgess
C. O. Burgess
R. M. Burns
D. C. Burroughs
P. Caplain
D. C. Carpenter
F. E. Carter
H. Casselberry
N. K. Chaney
G. W. Coggeshall
H. B. Coho
S. J. Colvin
E. F. Cone
H. S. Cooper
W. M. Corse
J. H. Critchett
Ed. L. Crosby
Thomas S. Curtis
C. Dantsizen
F. W. Davis
Wm. Delage
P. K. Devers
Arthur K. Doolittle
E. F. Doom
J. V. N. Dorr
Wm. Dreyfus
W. F. Edwards
C. H. Eldridge
W. H. Falck
F. F. Farnsworth
Alex L. Feild
Colin G. Fink
F. A. J. FitzGerald
J. A. Fogarty
Oscar R. Foster
Gay N. Freeman
N. H. Furman
A. J. Gailey
Richard H. Gaines
W. H. Gesell
A. E. Gibbs
C. B. Gibson
H. W. Gillett
G. C. Given
J. B. Glaze
A. Kenneth Graham
Carl Hambuechen
H. E. Haring
L. O. Hart
W. G. Harvey
Carl Hering
Chas. H. Herty
A. T. Hinckley
C. D. Hocker
Geo. B. Hogaboom
E. M. Honan
A. H. Hooker
W. G. Horsch
L. E. Howard
O. Hutchins
W. C. Hyatt
John Johnston
Louis Jordan
F. R. Kemmer
E. F. Kern
R. H. Kienle
D. H. Killefer
Max Knobel
V. R. Kokatnur
C. G. Koppitz
W. S. Landis
Harry R. Lee
F. A. Lidbury
W. T. Little
E. A. Lof
J. M. Lohr
Russell Lowe
Dorsey A. Lyon
Paul McAllister
J. Y. McConnell
Robert J. McKay
Duncan MacRae
Chas. P. Madsen
Paul D. V. Manning
J. W. Marden
A. L. Marshall
M. W. Merrill
H. S. Miner
R. B. Moore
W. C. Moore
W. R. Mott
Martha E. Munzer
D. L. Ordway
N. Petinot
E. C. Pitman
H. W. Porth
R. Prefontaine
W. J. Priestley
O. C. Ralston
J. W. H. Randall
W. C. Read
H. T Reeve
C. H. M. Roberts
F. W. Robinson
C. J. Rodman
Chas. F. Roth
B. D. Saklatwalla

L. E. Saunders
C. G. Schluederberg
Louis Schneider
J. A. Seede
R. L. Shepard
Acheson Smith
W. S. Smith
J. S. Speer
H. N. Spicer
A. D. Spillman
E. C. Sprague
Reston Stevenson
M. E. Stewart
Bradley Stoughton
Haakon Styri
Henry P. Taber
E. Takagi
Floyd D. Taylor
Hugh S. Taylor
Sterling Temple
C. J. Thatcher
M. R. Thompson
F. J. Tone
A. E. Thurber
L. S. Thurston
Henry A. Tobelmann
R. Turnbull
F. M. Turner, Jr.
C. H. Tyler
M. A. Ulbrich
Mary Upshur Von Isakovics
L. D. Vorce
Frank J. Vosburgh
E. A. Vuilleumier
Helen Gillette Weir
C. J. Wernlund
A. E. R. Westman
Clyde E. Williams
Roger Williams
A. M. Williamson
Charles Wirt
W. A. Wissler
Wm. J. Wooldridge
L. T. Work
F. Zimmerman

Guests

Mrs. E. G. Acheson, New York City
Robert Aiken, Washington, D. C.
Jerome Alexander, New York City
H. A. Anderson, New York City
R. W. Baldwin, Milwaukee, Wis.
Mrs. E. O. Benjamin, Newark, N. J.
P. H. Brace, Pittsburgh, Pa.
Robert E. Brown, New York City
R. C. Burner, Bayside, N. Y.
Joseph T. Butterfield, New York City
Mrs. Fred E. Carter, Newark, N. J.
Mrs. G. W. Childs, New York City
W. H. Coy, New York City
Helen E. Dalling, New York City
Edmund S. Davenport, Bloomfield, N. J.
A. W. Davison, Troy, N. Y.
Mrs. Maude T. Doolittle, New York City
R. W. Erwin, Flushing, L. I., N. Y.
Mrs. Colin G. Fink, Yonkers, N. Y.
Charles FitzGerald, Malba, L. I., N. Y.
Mrs. F. A. J. FitzGerald, Niagara Falls, N. Y.
Mrs. Oscar R. Foster, New York City
Mrs. W. H. Gesell, Montclair, N. J.
F. R. Glenner, New York City
Max Greeff, East Orange, N. J.
E. T. Gushee, Detroit, Mich.
Mrs. Henry K. Hardon, New York City
J. E. Harris, New York City
Henry S. Haupson, New York City
George W. Heise, Bayside, N. Y.
R. E. Hickman, Maplewood, N. J.
O. K. Holderman
H. D. Holler, New York City
Mrs. A. H. Hooker, Niagara Falls, N. Y.
Mrs. W. G. Horsch, New York City
G. P. Houghland, Parlin, N. J.
H. C. Howard, Jr., Princeton, N. J.
N. Iseki, New York City
C. James, Durham, N. H.
Mrs. John Johnston, New Haven, Conn.
F. C. Kelley, Schenectady, N. Y.
D. B. Keyes, New York City
W. P. Kierman, Bloomfield, N. J.

Mrs. D. H. Killefer, New York City
H. W. Langzettel, Westport, Conn.
Mrs. H. W. Langzettel, Westport, Conn.
H. H. Lowry, New York City
W. A. Linch, New York City
C. E. MacQuigg, New York City
Wm. A. Moore, Waterbury, Conn.
Edward G. Nellis, New York City
Keizo Nishimura, New York City
W. B. Nottingham, New York City
K. L. Page, Boston, Mass.
P. G. Paris, Westport, Conn.
F. Peters, Westport, Conn.
Mrs. F. Peters, Westport, Conn.
J. M. Price, New York City
M. B. Rascovich, New York City
H. C. Rentschler, Bloomfield, N. J.
H. K. Richardson, Newark, N. J.
Mrs. F. W. Robinson, Maplewood, N. J.
Ancel St. John, Brooklyn, N. Y.
John R. Sheffield, Jr., Brooklyn, N. Y.
George Smith, New York City
Mrs. C. W. Spicer, Plainfield, N. J.
Mrs. H. N. Spicer, New York City
Mrs. E. C. Sprague, Buffalo, N. Y.
Mrs. W. A. Stedman, Westport, Conn.
T. A. Schwartz, Prince Bay, L. I., N. Y.
Theodore M. Switz, East Orange, N. J.
Stem Tiberg, New York City
Magnus Tigershield, Soderfors, Sweden
R. J. Traill, Ottawa, Canada
Miss Beryle Van Allen, New York City
H. N. Van Dansen, New York City
G. A. Vaughn, Jr., New York City
Alois von Isakovics, Monticello, N. Y.
Miss B. von Isakovics, Monticello, N. Y.
W. B. Wallis, Pittsburgh, Pa.
W. B. Williams, New York City
Mrs. A. M. Williamson, Niagara Falls, N. Y.
Mrs. Charles Wirt, Philadelphia, Pa.
J. C. Woodson, East Pittsburgh, Pa.
Mrs. L. T. Work, Yonkers, N. Y.
L. F. Yutema, New Haven, Conn.

The Presidential Address presented at the Forty-third General Meeting of the American Electrochemical Society, in New York City May 3, 1923.

OPPORTUNITIES FOR THE AMERICAN ELECTROCHEMIST ABROAD

By C. G. Schluederberg.[1]

There have appeared in the journals from time to time fairly complete reports on the development of electrochemistry in Europe, and what has been accomplished in our own country is, of course, a matter of general information. Visits to South America and the Far East during the past year have afforded opportunity for first-hand information and personal observation, and it is therefore felt that a brief summary of what has been done in these two sections, or of what the indications are for the future, may help to round out our fund of information on electrochemical development and on the opportunities abroad for the electrochemist.

Electrochemical or electric-furnace development on any commercially appreciable scale inherently requires large amounts of electric power at low cost; therefore, in considering opportunities for the electrochemist it is perforce necessary to give thought to the power resources of the locality under observation, as these are so intimately allied with the possibilities for the successful development of the industries for which the electrochemist is responsible.

In South America, the west coast countries of Peru and Bolivia, with their large mineral wealth and mining operations extending back over hundreds of years to the time of the Incas, naturally appeal to the imagination as fertile fields for electrochemical activities. Copper, silver, tin, vanadium and other ores are mined in quantities and, in the case of the copper, refined locally to a high degree of purity in large smelters of the most modern type; the final purification by electrolysis is, however, not carried out on the ground, but usually at some of the large refineries in the

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[1] Westinghouse Elec. & Mfg. Co., East Pittsburgh, Pa.

vicinity of New York, the metal as shipped containing upwards of 96 per cent copper or copper and silver.

In view of the fact that this metal is shipped in such a pure state, and that it can receive final purification in existing refineries close to the markets, there is at the present time no necessity for the investment of the additional capital which would be required for the building of an electrolytic plant on the ground. A decided change in labor or power rates of existing electrolytic refineries, or in market conditions, might possibly justify such an electrolytic plant in the future.

Water-power, while not over-abundant on the Pacific side of the Andes, is available on the eastern slopes in quantities. Present transportation facilities to the sites of such power, as well as conditions inherent to the tropical climate of that region, while bad, cannot be considered as insuperable obstacles. Many surveys have been made and it is quite certain that power developments will take place.

Considerable experimental work along electrochemical lines has been done by one of the larger companies in Peru, with a view to the working out of a satisfactory process for extracting the silver from certain of the local complex ores, which so far it has not been possible to work on a commercial scale. Should the results of this research work prove satisfactory, it is quite likely that an electrochemical plant of size would be erected in the Cordilleras of the Peruvian Andes in the neighborhood of La Oroya or Cerro de Pasco. The opportunities for the electrochemist in connection with the complex silver ores of Peru loom large indeed. Undoubtedly ores of many of the other less common metals will afford equally attractive possibilities to the electrochemist with enough pioneering spirit in his make-up not to be deterred by primitive living conditions and the discomforts of working at the high altitudes which surround the deposits of the precious metals in this country, the fabulous wealth of which was first revealed to the then civilized world by the indomitable Pizarro almost exactly 400 years ago.

In Bolivia, renowned for its large deposits of rich tin ore as well as of copper, silver, and other useful and precious metals, electric tin reduction furnaces have been tried, but, at least up to the time of my visit a few months ago had failed to prove commercially successful, the cost of carbon in the form of coal required for reduction purposes being one of the contributing factors. Here again the opportunity for the electrochemist is great. Just as in Peru, water-power is available in the tropical sections of Bolivia, and the promise of large oil developments in the central and eastern parts offers the chance of cheap fuel for steam stations, so that from the standpoint of power the establishment of electrochemical or electrothermal processes in this country so rich in natural resources is entirely feasible.

Farther south along the west coast, the northern half of Chile is another country richly endowed with minerals, and containing what is probably the largest copper mine in the world, as well as large deposits of iron ore, saltpeter, etc., but with an almost entire absence of water-power or even rain, while the southern portion, not so richly endowed with metal-bearing ores, is blessed with an abundant rainfall, water-power, and coal. However, the distances are great and present indications for long-distance electric power transmission not promising. In spite of this handicap, electrolytic refining of copper is carried out on a large scale at the Chile Exploration Company's copper mine in northern Chile, but the copper ore here is in the form of salts readily soluble, from the solution of which the metal can be obtained more readily and economically by electrolytic means than otherwise, in spite of the necessity of generating electricity at an oil-fired steam plant on the sea coast many miles distant from the mine, firing the boilers with oil transported by ship from Mexico and the transmitting of energy over high-tension lines at 110,000 volts. Even the water for lixiviation of the ore, as well as for all other purposes at this mine, has to be carried for many miles through large pipe lines from distant mountain sources.

The plant of this company represents the one outstanding electrochemical development on the west coast of South America. It is a monument to the American electrochemists, through whose efforts the many details incident to the successful development of a commercially successful process for the extraction of ore on a large-tonnage basis, not the least important of which was the production of an insoluble anode, have been satisfactorily worked out.

Indications of oil resources near the eastern boundary of Chile, as well as further developments in long-distance power transmission, give promise of additional opportunities for the electrochemist in this progressive South American republic so far-famed for its mineral resources.

So much for the west coast of South America.

In the front rank of those countries bordering on the east coast and readily reached by a two-day journey from Chile over the famous Transandine Railway is the republic of Argentina, for whose renowned wealth, however, cattle and cereals and not minerals are responsible. Argentina is almost devoid of water-powers of any size. Even in mineral resources she is almost totally lacking. It is true that near the northeastern border are the Falls of the Iguassú, reputed to be capable of delivering many hundreds of thousands of horsepower, and on the western border the waterfalls of the Andes, but these are so far removed from present centers of civilization or human activity of any kind that even modern electric transmission developments, using 220,000 volts, do not indicate that it is yet advisable to attempt the harnessing of these waterfalls. As a matter of fact, the Falls of the Iguassú, located almost at the point where Brazil, Argentina, and Paraguay touch, are nearer the center of industrial activities in Brazil than in Argentina.

The progressive republic of Uruguay very much resembles Argentina both in resources and in that at the present time there are no electrochemical or electric furnace developments, with the possible exception of one or two small steel furnaces for use in foundries, so that in neither of these countries does any immediate opportunity exist for the electrochemist.

Brazil, rich in mineral resources and with great quantities of water-power distributed over her vast area, offers much in the way of opportunity to the electrochemist. He will find here great beds of rich iron ore, immense deposits of manganese, vast stores of the rarer metals and elements so widely used in the industries, fluxes, and reducing agents in the form of charcoal from the rapidly maturing eucalyptus tree, and water-powers in abundance. These are near the sea coast and existing centers of civilization, many of them already developed with power lines extending over wide stretches of territory.

The most important electrochemical development is that of the

Brazilian Electrometallurgical Company at Ribeirão Preto, where two 30-ton electric pig-iron furnaces have been erected, together with two 6-ton Bessemer converters for the direct conversion of the hot iron ore into steel, as well as a Ludlum 6-ton electric steel furnace for the treatment of such steel as may be received from the Bessemer converters and require special doctoring in order to bring it up to the desired composition. In addition, there are rolling mills for plates and shapes, reheating furnaces, and the necessary auxiliaries. Recent reports from this operation indicate that so far the plant has worked only on scrap metal, with some pig iron, which is melted in the Ludlum steel furnace. They have rolled as much as 20 tons of round and square bars per day, which have been offered at prices 10 per cent below quotations on similar foreign material. Owing to the railroad not having been completed to the iron ore mine, no ore has yet come in, and hence reduction operations have not commenced. It is reported that the company has been able to book enough business to keep the plant busy for the next year or more.

Whereas on the west coast of South America practically all electrochemical and electrometallurgical processes and operations are carried on by Americans or Europeans, on the east coast, as in Brazil, this work is being carried on and financed in a large measure by Brazilians, although even here the apparatus, of American or European manufacture, so far has generally been installed by American or European engineers.

A second plant for the electric-cupola reduction of the local deposits of iron ore on a much larger scale is under active consideration in this same district, and it is reported that the rather large financing required is being carried out successfully and that steel rails will be the principal product.

With abundant cheap power readily available from the numerous waterfalls, and plentiful deposits of iron ore of an excellent grade, as well as manganese and other necessary alloys and fluxes, and a local market for pig iron and steel products, the only material thing which seems to stand in the way of Brazil becoming a considerable producer of iron and steel products seems to be the question of a suitable reducing agent, such as coal or coke. Here it becomes necessary to substitute charcoal usually obtained from eucalyptus trees, which mature within five years in this tropical climate, and the wood of which, planted in large numbers, regularly serves as fuel for railways and industrial plants. The fact that in the electric cupola carbon is consumed only in proportion to the amount of ore reduced, and that it does not have to serve the dual purpose of both fuel and reducing agent, is a factor of no mean importance where only such an expensive form of carbon is readily obtainable.

Outside of possibly a few electric furnaces for foundry use, the above summary covers electrolytic and electrothermal activities in six of the principal countries of the South American continent. Reports from the other countries, not visited, do not give any immediate encouragement to the electrochemist, but undoubtedly certain of the northern countries, when further developed, will offer opportunities similar to those of Peru and Bolivia.

Turning to the Far East, we find one country at least with a development along lines approaching our own or that of Europe—Japan—rich in water-powers, many of them already developed on a large scale, high-tension transmission lines everywhere, and the one idea in the minds of all her 70,000,000 people of emulating western civilization and making industrial progress as rapidly as possible, and willing to sacrifice almost every other consideration to this end. This assimilation of western civilization started not more than two generations ago, and has attained results to date which must command our admiration.

The war gave an impetus to the industries of Japan as to those of other countries; the ones already in existence increased and many others, electrochemcial and electrothermal, came into being. These include manufactures of soda, chlorate, carbide, ferro-alloys, pure pig iron, electrolytic zinc, copper, etc., along with others. As in other countries, some of them since the war had difficulty in maintaining their existence. Today general business in Japan, while quiet, is improving, but many of her electrochemical industries are working only part time or are shut down.

One plant located at Odera, 150 miles north of Tokyo, almost on the shores of Lake Inawashiro, close to the immense power plants of the power company bearing the name of that lake, one of the first large high-tension systems in Japan was established in the fall of 1916. It was completed in less than six months, and is devoted largely to electrolytic extraction of zinc and the production of ferro-alloys.

The sulfide ore for this plant is brought from a mine some fifty miles distant, and after being crushed and roasted is leached with sulfuric acid made locally in a chamber process plant, purified with zinc shavings, and deposited on prepared cathodes in cells much resembling those used in an ordinary copper refinery. Costs are, however, higher than for imported electrolytic zinc, in spite of low power and labor charges, but the purity of the product seems to be higher, as evidenced by the following analysis:

	Japanese Electrolytic Zinc	Electrolytic Zinc from U. S. A. (1918)
Zinc	99.96721	99.88205
Lead	0.01749	0.075468
Copper	0.00319	0.00796
Iron	0.00462	0.00518
Cadmium	0.00749	0.0048

The costs of the local product have, however, been considerably higher than those of the products imported. They were given as 230 yen for the zinc ore, which is higher on account of the extensive freight rates, 70 yen for electricity, 70 yen for labor, and 150 yen for overhead. (The yen equals approximately 50 cents in U. S. gold). Labor in this locality is very cheap, running from 160 yen to 180 yen (80 to 90 cents in U. S. gold) per day. The capacity of the plant is reported at 300 tons of zinc per month.

This plant also turns out a very pure grade of pig iron made in an open type electric furnace, with phosphorus of 0.021 per cent, sulfur 0.005 per cent, and copper 0.018 per cent; ferro-silicon 25, 50 and 75 per cent, and silicon 90 per cent; 60 per cent ferro-chrome, 80 per cent ferro-manganese, 18 per cent ferro-phosphorus, and cadmium of 99.5 per cent purity, obtained from the zinc shavings used in purifying the zinc sulfate solution in connection with the production of electrolytic zinc. Calcium carbide is being manufactured in fair quantities at present; the extensive fishing industries make considerable use of acetylene torches in night fishing and absorb an appreciable portion of this product.

The Cottrell process is being applied and at the present time nitrogen fixation and fertilizer manufacture is receiving much consideration.

That Japan is determined to keep to the fore in electrochemical development is evidenced not only by what she has already done in her industries, but also by the training given her young electrochemists in the various courses on electrochemistry forming part of the regular curriculum of her universities, by the amount of attention given electrochemical subjects in the local engineering and scientific journals, and also by the fact that of all foreign countries Japan is best represented in the American Electrochemical Society, which numbers in its membership about 75 Japanese members residing in Japan, as well as many others residing in this and other countries.

China, in spite of her 400,000,000 people and most ancient of civilizations, at the present time offers but little, if any, opportunity to the electrochemist. Although both rich coal and iron deposits exist, and fairly modern blast furnaces and steel plants are available for turning out pig iron and finished shapes and rails, there has been practically no electric furnace development, and electrochemistry, except as applied in a few small plating shops and possibly in the new mint in Shanghai, is an unknown quantity. There is but little water-power available or developed throughout the vast alluvial plain forming the eastern central part, or Great Middle Kingdom of China. In one or two of the more important coast cities electric furnaces have begun to be used in the foundries and shops of the larger companies. At Hongkong, in a steel foundry, a two-ton furnace of one of the better-known makes has given an excellent account of itself, albeit hand regulation of electrodes by Chinese labor melting from cold scrap has caused considerable conversation between the central station and foundry managers, with instructions from the former to the latter to keep off the line during peak hours.

Disturbed political conditions, instability of the republican form of government due to the absolute unpreparedness of the mass of the people for self-government, maintenance of separate armies by the various provincial governors in their endeavor to hold individual power, as well as a few other disturbing factors, are at present militating against industrial, economic, scientific, and all other progress. This condition applies even in South China in the province of Yunnan, far-famed for its wealth of tin, copper, zinc, and other ores and water-power. The immediate prospects of either electrochemical or electric furnace developments in China are not encouraging.

Nor in Indo-China, the northern part of which, bordering as it does on Yunnan, is rich in both coal and mineral deposits, are there any evidences of electrochemical developments having been undertaken by the French, although here, as in the Malay Peninsula, the problem of the reduction of tin is ever present.

Certainly the Yunnan Province of China, Northern Indo-China, and the Malay Peninsula offer an interesting field for the electrochemist who is not afraid to go and remain abroad amid living conditions radically different from those existing in the United States.

Philippines: What should be the outpost of American enterprise and business in the Far East and what undoubtedly will be, provided the uncertainty regarding self-government is eliminated and the United States protectorate maintained for a definitely stated period of years, the Philippine Islands, although blessed with some water-power and mineral deposits and possibly with oil resources, so far offer practically no field for the electrochemist. However, once political conditions are sufficiently stabilized to justify entry of big business interests on a worthwhile scale, there is promise for the development of many industries, in some of which undoubtedly electrochemistry will apply. There is every indication that were the United States to guarantee definitely that present supervision over the Philippine Islands would apply for a certain period of years, say thirty, fifty, or more, before a local government would be considered, there is no doubt in the minds of those most familiar with the situation that big business would come into the Philippines, which are so ideally suited for the raising of many products, and that these islands would become the important center of American activities in the Far East, which they deserve to be.

SUMMARY.

Summarizing the possibilities for electrochemical activity in South American and Far Eastern countries, it would seem that greatest immediate progress will be made in Japan, the west coast of South America, and Brazil. There will be perhaps more general research work done in Japan than elsewhere, although naturally the large companies operating on the west coast of South America will continue research along the lines pertaining to their particular operations. Certain countries with ample power but relatively few minerals, such as Japan, are especially suited to the conversion of the raw products of their neighbors into finished materials of world-wide application. The future unquestionably holds much in store for them.

Unquestionably the aggressive industrial activity of Japan will result in the establishment of many industries throughout that country, in which electrochemistry and the electrochemist will play a large part. There can be no question that the Japanese are alive to the possibilities of electrochemical development, and that their activities along this line will be just as great as the industrial and financial prosperity of the country will permit. However, it must be kept in mind that the opportunities for the electrochemist in Japan will loom especially large for the Japanese electrochemist, while in the other countries considered it is likely that Americans and Europeans will predominate.

Richly endowed, as many of these countries are, with both water-power and minerals, one cannot travel through them without being impressed by the tremendous possibilities for the development of both natural and economic resources.

It must be remembered that things move more slowly than with us, and that it takes a long time for ideas to take hold and a still longer time for definite results to follow. The electrochemist working in these countries must be of the pioneering type and possessed of infinite patience and perseverance, but once progress is initiated along sound lines the opportunities for profit present themselves in far more glowing colors than is usually the case in our own or European countries. The way is difficult and progress slow, but the possibility of reward is fully commensurate with the effort involved.

A paper presented at the Forty-third General Meeting of the American Electrochemical Society held in New York City, May 3, 1923, Dr. Wm. G. Horsch in the Chair.

NEWER ASPECTS OF IONIZATION PROBLEMS.[1]

By Hugh S. Taylor.[2]

Abstract.

A resume is presented of some recent work by Born, Fajans, Haber and others on the problem of energy changes accompanying the conversion of some solid crystalline substances and of the hydrogen halides into dissolved ions. An outline is given of the concepts of lattice energy and of the electron affinity of halogens, the quantitative side of the problem receiving detailed consideration. In the latter, small modifications of the earlier calculations have been made whenever newer material of a more reliable nature seemed to be available. Some of the lines along which progress may be anticipated have been indicated.

The modern electrochemist must survey with pride the background which his predecessors in the science provided for the more recent advances which the examination of the physics of the atom and the X-ray spectra of elements and compounds have achieved. The concept of ions as current carriers, of the existence of free ions in solution, of the mobility and hydration of ions, of potentials due to ions and the tendency to form ions were all familiar to the electrochemist before the newer ideas of electronics were formulated, and they materially aided the rapidity with which the newer developments found ready acceptance. The indebtedness is, however, mutual. In the light of modern ideas as to the structure of atoms and ions, with the aid of the quantitative relationships which the physicist has developed between the various electrical states which a substance may achieve, the electrochemist

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[1] Manuscript received February 14, 1923.

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can recast anew his own ideas, can seek new methods of attack on older problems and, mayhap, can find a clearer method of presentation of the fundamentals of this science.

THE CONCEPT OF LATTICE ENERGY AND ITS THERMOCHEMICAL APPLICATIONS.

The pioneer work of Laue and the Braggs on the X-ray spectra of elements and compounds served to focus attention on the atoms as the essential units of the crystal structure, even in the case of compounds. A cubical crystal of rock salt was shown to consist of alternate sodium and chlorine, in three dimensional space at the corners of elementary cubical units, each sodium spaced 2.81 x 10^{-8} cm. from its six neighboring chlorines, each chlorine similarly spaced from six sodiums. The distance between two similar atoms, twice the above magnitude, may be designated as the "lattice constant," δ.

By a more refined X-ray analysis, Debye and Scheerer[3] were able to show that only a fraction of this distance between atoms was actually occupied by the atoms, that the electrons surrounding the nucleus of an atom were concentrated in a relatively small space around the nucleus, of radius approximately one tenth that of the lattice constant. Further investigation by Born[4] revealed that the units of such a crystal were electrically charged, carrying each a single charge. The units were, in fact not atoms but the respective ions.

A detailed analysis of the attraction existing between oppositely charged ions so situated in space and repulsion between the electrons comprising the outer shells of such ions, led to the conclusion that the attraction varies, normally, inversely as the square of the distances. The repulsion, however, in the case of simple cubic structures, such as sodium and potassium chlorides, was shown to vary as the inverse tenth power, or the potential of the repulsive force varies as the inverse ninth power of the distance between the ions.

The connection between such attractive and repulsive forces on the one hand and the compressibility of the crystal on the other, established the approximate validity of the conclusions reached; the cohesive force of such regular crystals is purely electrical in

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[3] Physikal. Zeitsch. 19, 474 (1918).

[4] Ber. Deut. physikal. Ges., 20, 210 (1918); Ann. Physik. (IV) 61, 87 (1920).

its origin. It should be observed that the inverse ninth power relations in the case of such crystals lead directly to the assumption of a cubical atom model, such as is now familiar from the publications of Lewis,[5] Langmuir,[6] and Kossel.[7]

On the basis of these assumptions as to attraction and repulsion, Born proceeded to the calculation of the electrostatic work necessary to evaporate one mol. of the crystal into free gaseous ions, that is to say, the work necessary to remove the ions from the positions they occupied in the crystal to an infinite distance from one another. Born found that this energy was expressible by an equation

$$A = \frac{Na}{\delta} \frac{n - 1}{n}$$

where

N is the Avogadro number, 6.06×10^{23}.

δ is the lattice constant.

a, is a constant characteristic of the lattice type and in the case of the alkali halides of the cubic system $= 13.94 e^2$.

$e = 4.774 \times 10^{-10}$ electrostatic units, the charge of the electron.

$n = 9$ for the alkali halides with the exception of lithium salts, for which $n = 5$.

It is to be observed that the cubical arrangement is impossible for the lithium ion, since it has only two electrons in the outer shell. Born consequently adopted at the outset the lower value $n = 5$, demanded by the Bohr electron ring system. Typical results obtained in this way for a variety of salts are set forth in the following table, in which the unit of energy is the kilogram calorie.

Salt	LiCl	NaCl	KCl	NaBr	KBr	NaI	KI
A..........	179	182	163	171	155	158	144

An alternative method of stating these energy quantities is to regard them as the magnitude of the free energy decrease, when one gram molecule of the crystalline solid is formed from the gaseous ions.

$$(Li)^+ + (Cl)^- = [LiCl] + A_{LiCl}{}^{(8)}$$

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[5] J. Am. Chem. Soc., 38, 762 (1916).

[6] J. Am. Chem. Soc., 41, 868, 1543 (1919).

[7] Ann. d. Phys., 49, 229 (1916).

[8] Here and in following equations parentheses, ( ), refer to gaseous components, brackets, [ ], to solid substances.

An approximate test of the accuracy of these values was attempted by Born by correlating the above energy quantities with the thermal magnitudes involved in a reaction of the type,

$$[NaCl] + [KI] = [KCl] + [NaI]$$

Fajans [9] has shown that in the case of all these halides the change in total energy at ordinary temperatures, U_{300}, is approximately = 1.003A. For all practical purposes, therefore, the differences in the above magnitudes, A, will be essentially equal to the differences of the thermal magnitudes, U. The net change in the A values for the above compounds can therefore be equated to the net heat effect of the above reaction, *i. e.*,

$$A = A_{NaCl} + A_{KI} - A_{NaI} - A_{KCl} = Q_{NaCl} + Q_{KI} - Q_{NaI} - Q_{KCl}$$

where Q values are the heats of formation of the solid salts from the elementary components. A brief test will show, however, that such heat effects are small, of the order of a few kilogram calories, while the individual values are of the order of 100 Cal.; so far as the test went it was favorable to the A values obtained by Born.

A more accurate test was devised by Fajans.[9] By substituting the heats of solution of the several salts in very dilute solution for the heats of formation used by Born, the net effect of the several heats of solution could be equated to the net value of A. Thus in the reaction given above,

$$\begin{aligned}
[NaCl] &+ aq = Na^+_{aq} + Cl^-_{aq} + H_1 \\
[KI] &+ aq = K^+_{aq} + I^-_{aq} + H_2 \\
[KCl] &+ aq = K^+_{aq} + Cl^-_{aq} + H_3 \\
[NaI] &+ aq = Na^+_{aq} + I^-_{aq} + H_4
\end{aligned}$$

where H refers in each case to the heat of solution of the solid salt, to yield a very dilute solution in which it may be assumed all of the salt is dissociated. Now, since the net result as regards ionic content is the same, whether the solutions be made up from NaCl and KI or from KCl and NaI, it follows that

$$H = H_1 + H_2 - H_3 - H_4 = \Delta A = \Delta U = \Delta Q$$

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[9] Ber. Deut. physikal. Ges., 21, 542 (1919).

In this case the results were of a higher order of accuracy, since the individual H values were small as compared with the Q values used by Born. They were known to a higher degree of accuracy, and hence the test yielded by the use of such figures was more reliable. Table I illustrates the agreement obtained in a large number of examples studied.

TABLE I.

Reaction	A	H
KCl + LiBr = KBr + LiCl	+4	+3.6
KCl + LiI = KI + LiCl	+7	+7.2
KCl + NaBr = KBr + NaCl	+3	+2
KCl + NaI = KI + NaCl	+5	+3.4

The Concept of Heat of Hydration of Gas Ions.

Fajans[10] further pointed out that the heat of solution of such salts may be regarded as composed of two effects, (a) the heat energy required to convert the solid salt completely into free gas ions (*i. e.*, the heat equivalent of the lattice energy, or U = 1.003A), and (b) the heat of solution of these gas ions in water. As is readily seen from the following equation,

$$\begin{array}{c} (K)^{+} + (Cl)^{-} = [KCl] + U \\ [KCl] + aq = K^{+}_{aq} + Cl^{-}_{aq} + L \\ \hline (K)^{+} + (Cl)^{-} + aq = K^{+}_{aq} + Cl^{-}_{aq} + (U + L) \end{array}$$

this heat of hydration of the gaseous ions is the quantity (U + L) = W. Table II gives a summary of the values obtained for the heat of solution W of the gaseous ions of a variety of salts, as compiled by Fajans from Born's lattice energies and available heats of solution of alkali halide salts.

TABLE II.

Salt	$W_{Cat + An}$	Salt	$W_{Cat + An}$	Salt	$W_{Cat + An}$
LiCl	187	LiBr	178	LiI	168
NaCl	180.5	NaBr	171	NaI	159
KCl	159	KBr	150	KI	139
RbCl	150	CsCl	151	TlCl	159

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[10] Ber. Deut. physikal. Ges., 21, 549 (1919).

A check on these results was readily obtained, since it is apparent that these values should be strictly additive quantities, dependent on the values for the individual cations and anions of the several salts. Thus—

$$(\mathrm{Na})^+ + (\mathrm{Cl})^- + \mathrm{Aq} = \mathrm{Na}^+_{\mathrm{aq}} + \mathrm{Cl}^-_{\mathrm{aq}} + W_{\mathrm{Na}^+,\,\mathrm{Cl}^-}$$

$$(\mathrm{K})^+ + (\mathrm{Cl})^- + \mathrm{Aq} = \mathrm{K}^+_{\mathrm{aq}} + \mathrm{Cl}^-_{\mathrm{aq}} + W_{\mathrm{K}^+,\,\mathrm{Cl}^-}$$

or

$$(\mathrm{Na})^+ - (\mathrm{K})^+ + \mathrm{Aq} = \mathrm{Na}^+_{\mathrm{aq}} - \mathrm{K}^+_{\mathrm{aq}} + W_{\mathrm{Na}^+,\,\mathrm{Cl}^-} - W_{\mathrm{K}^+,\,\mathrm{Cl}^-} = W_{\mathrm{Na}^+} - W_{\mathrm{K}^+}$$

Now, since $W_{\mathrm{Na}^+} - W_{\mathrm{K}^+}$ must naturally be independent of the anions associated with them in the salts, it follows that

$$W_{\mathrm{Na}^+} - W_{\mathrm{K}^+} = W_{\mathrm{Na}^+,\,\mathrm{Cl}^-} - W_{\mathrm{K}^+,\,\mathrm{Cl}^-} = W_{\mathrm{Na}^+,\,\mathrm{Br}^-} - W_{\mathrm{K}^+,\,\mathrm{Br}^-} = \text{etc.}$$

In this way, Table III was obtained.

Table III.

	Cl	Br	I	Mean
$W_{\mathrm{Li}^+} - W_{\mathrm{K}^+}$	+28	+28	+29	+28
$W_{\mathrm{Na}^+} - W_{\mathrm{K}^-}$	+21.5	+21	+20	+21
$W_{\mathrm{Rb}^+} - W_{\mathrm{K}^+}$	—9	......	......	—9
	Li	Na	K	
$W_{\mathrm{Cl}^-} - W_{\mathrm{Br}^-}$	+9	+9.5	+9	+9
$W_{\mathrm{Br}^-} - W_{\mathrm{I}^-}$	+10	+12	+11	+11

As is evident, the differences between the heats of hydration of two cations or two anions are quite definite quantities, and are independent of the ion with which a given ion is associated. The additivity of heats of hydration is thus established, and the plausibility of the lattice energy calculations enhanced.

Further Refinements in Lattice Energy Calculations and a Test of the More Accurate Data.

Born's original calculations had shown that the calculation of the exponent for the repulsive force, on the basis of compressibility data, led to a value somewhat smaller for sodium than for potassium salts. For lithium a much lower exponent, n = 5, was used, the low value being attributed to the lack of cubical structure in the lithium ion. Fajans and Herzfeld,[11] accordingly, have recalculated the lattice energies of a series of alkali halides, assuming in addition to a repulsive force varying as the 9th power other terms, involving the 5th and 7th powers when the cations and anions are of different size. The lattice energies so obtained are set forth in Table IV, the older values of Born being enclosed in parentheses.

TABLE IV.

	F	Cl	Br	I
Na	210.4 (220.3)	170.0 (181.6)	159.7 (171.6)	146.7 (158.3)
K	192.2 (190.7)	159.0 (163)	150.4 (155.3)	139.1 (145.1)
Rb	......	154.6 (155.5)	146.5 (148.7)	135.8 (139.5)

The corrections throughout are greater with the sodium salts than with the potassium salts. The smaller value for repulsive force of sodium, as found by Born, receives a satisfactory explanation in the newer work. As before, the thermochemical test of these newer values can be made on the basis of additivity of the heats of hydration of the gas ions. Table V gives the results of such a test.

TABLE V.

	F	$W_{F^-} - W_{Cl^-}$	Cl	$W_{Cl^-} - W_{Br^-}$	Br	$W_{Br^-} - W_I$	I
Na	209.8	41.3	168.5	9.0	159.5	11.6	147.9
$W_{Na^+} - W_{K^+}$	14.0	....	13.9	....	14.2	....	13.9
K	195.8	41.2	154.6	9.3	145.3	11.3	134.0
$W_{K^+} - W_{Rb^+}$	....	....	4.8	....	....	....	....
Rb	....	....	149.8	....	....	....	....

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[11] Z. Physik. 2, 309 (1920).

The means of the several differences may be therefore expressed thus—

$$W_{Na^+} - W_{K^+} = 14.0 \qquad W_{F^-} - W_{Cl^-} = 41.2$$
$$W_{K^+} - W_{Rb^+} = 4.8 \qquad W_{Cl^-} - W_{Br^-} = 9.1$$
$$W_{Br^-} - W_{I^-} = 11.4$$

Agreement within 1 Cal. is obtained in each case. The values obtained by Fajans and Herzfeld by this refined calculation are, however, regarded by Born and Gerlach[12] as somewhat too low. Before their reasoning can be adduced, we must apply the concept of lattice energy to the determination of the electron affinity of halogen atoms. Before passing to this problem, however, we may indicate an alternative method, independent of the lattice theory, of testing the values obtained for the differences of the heats of hydration of the various gas ions. The method is due to Fajans[13] and makes use of various thermochemical data, the ionization potentials, heats of sublimation and of dissociation, respectively of potassium and hydrogen, in a determination of the heat hydration difference $W_{\ +} - W_{K^+}$. The method is in reality the application of Hess' law of constant heat summation, employed with the aid of the following equations:

$$[K] + Aq = K^+_{aq} + OH^-_{aq} + \tfrac{1}{2}(H_2) + 48.1 \qquad (1)$$

$$H^+_{aq} + OH^-_{aq} = Aq + 13.6 \qquad (2)$$

whence

$$[K] + H^+_{aq} = K^+_{aq} + \tfrac{1}{2}(H_2) + 62 \text{ Cal.} \qquad (3)$$

now

$$(K) = [K] + 21 \qquad (4)$$

$$(K^+) + \ominus = (K) + 99. \qquad (5)$$

$$\tfrac{1}{2}(H_2) = (H) - 45. \qquad (6)$$

$$(H) = (H^+) + \ominus - 312 \qquad (7)$$

Whence by addition, (3) + (4) + (5) + (6) + (7)

$$(K^+) + H^+_{aq} = (H^+) + K^+_{aq} - 175 \text{ Cal.} \qquad (8)$$

or since

$$(H^+) + Aq = H^+_{aq} + W_{H^+}$$

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[12] Z. Physik, **5**, 435 (1921).

[13] Ber. Deut. physikal, Ges., **20**, 712 (1918).

and

$$(K^+) + Aq = K^+_{aq} + W_{K^+}$$

the equation (8) may be written

$$W_{H^+} - W_{K^+} = 175 \text{ Cal.}$$

Equations (1) and (2) are the ordinary thermochemical equations. Equation (4) represents the heat of sublimation of potassium, (5) the ionization potential of gaseous potassium. Equation (6) gives the heat of dissociation of hydrogen and (7) the ionization potential of atomic hydrogen. All these several quantities may be experimentally determined, though the order of accuracy is not as yet high in the case of several. Nevertheless the calculation goes to show a pronounced energy difference between the heat of hydration of gaseous hydrogen ions, and that of the gaseous potassium ion. We shall return to a discussion of this magnitude at a later stage. In a similar manner and similarly independent of the concept and calculations of lattice energy Fajans and Sachtleben[14] obtained

$$W_{Na^+} - W_{K^+} = 16 \pm 4 \text{ Cal.}$$

and

$$W_{K^+} - W_{Rb^+} = 6 \pm 4 \text{ Cal.}$$

These values stand in good agreement with those noted previously as derived from lattice energy calculations. These latter therefore may be given a reasonable measure of confidence.

THE CONCEPT OF ELECTRON AFFINITY AND ITS MEASUREMENT.

Theories of atomic structure have familiarized us recently with the tendency of atoms to approach the rare gas type of structure, by the loss or gain of an electron. The energy changes involved have been less prominently put forward. The loss of a valence electron by a sodium atom, yields a sodium ion whose outer system of electrons is that of the neon atom. This loss of an electron is, however, an energy consuming process, the energy involved being given by the ionizing potential of sodium vapor, or 5.1 volts, equivalent to a heat energy input of 118 Cal. per gram atom of sodium vapor.

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[14] Cited by Fajans, Z. Physik. 2, 328 (1920).

In a similar manner, potassium reverts to the argon type with an energy expenditure of 4.3 volts or a heat equivalent of 99.6 Cal. At the other end of the groups in the periodic system the halogen atoms display a tendency to add an electron and assume the rare gas type of structure, a chloride ion being similar to argon, bromide ion to krypton, iodide ion to xenon, fluoride ion to neon. What the energy change involved in such a process is, whether positive or negative, are questions to which no direct method of determination has as yet been able to provide an answer. Several indirect methods, however, serve to show that the affinity of a chlorine atom for an electron is positive, that energy is yielded in the process of formation of a negative halide ion from a neutral halogen atom, or conversely that energy is expended in removing an electron from a halide ion.

Born[15] and Fajans[16] have indicated one method of solution of the problem, making use of the lattice energy calculations previously considered. The magnitude of the electron affinity of chlorine atoms for electrons may be deduced by the consideration of two methods, whereby solid potassium chloride may be converted into free gaseous ions, potassium and chloride ions. The one way obviously is that involving the lattice energy previously discussed. Let us assume Born's first calculation of this magnitude, 163 Cal. The alternative method consists in decomposing the solid salt into its electrically neutral constituents, metallic potassium and gaseous molecular chlorine, whereby 106 Cal. are absorbed, equal to the heat produced when solid potassium chloride is produced from its elements.

To obtain the gaseous ions from the elements it is further necessary to vaporize the metal, the heat absorbed being 21 Cal., and to ionize the vapor whereby as we have already seen a further 99 Cal. are required. Similarly the molecular chlorine must be dissociated into atoms, the heat absorbed being 31 Cal. per gram atom, and then each of the chlorine atoms attaches itself to one of the electrons set free by ionization of the potassium vapor. This last step involves the unknown electron affinity, E, of the halogen atom. Since, however, we have arrived at the same end point by two independent paths this unknown quantity E can be

[15] Ber. Deut. physikal. Ges. **21**, 679 (1919).

[16] Ibid., **21**, 714 (1919).

obtained by equating the energy quantities involved in the two steps,

$$(-163) = (-106) + (-21) + (-99) + (-31) + E$$

whence E = 94 Cal.

The method of calculation of the electron affinities of bromine and iodine atoms may be similarly deduced as Table VI shows.

TABLE VI.

	Cl	Br	I
$[KX] = (K^+) + (X^-)$ ...	—163	—155	—144
$[K] + \frac{1}{2}(X_2) = [KX]$	+106	+99	+87
$(X) = \frac{1}{2}(X_2)$	+31	+23	+18
$(K) = [K]$	+21	+21	+21
$(K^+) + \ominus = (K)$	+99	+99	+99
whence $(X) + \ominus = (X^-)$	+94	+87	+81

NOTE:—The first line of the table gives Born's original values for lattice energies. The newer data of Fajans would reduce these from 4 to 6 units. The second line gives the normal heats of reaction, probably with an accuracy of ½ per cent. The third line gives the heats of dissociation of the halogens. These are less certain. The value chosen by the writer for Cl_2 is a mean of two recent determinations (Trautz Z. anorg. Chem., **122**, 81, (1922), Q = 70 Cal. per mol.; Henglein, Z. anorg. Chem., **123**, 137, (1922), Q = 54 Cal.) The mean 62 Cal., is concordant with the value calculated by Trautz from the absorption band of chlorine. See, however, V. Halban and Siedentopf, Z. physik. Chem., **103**, 85, (1922), who dispute the existence of such a band. The bromine value is due to Bodenstein, Z. Elektrochem. **22**, 317, (1916). The iodine value is from Starck and Bodenstein, Z. Elektrochem., **16**, 961, (1910). The fourth and fifth lines are respectively the heat of vaporization and the ionization potential of potassium.

Born and Fajans both tested their calculations by a method, independent of the lattice energy concept, based on the ionization potentials of the hydrogen halides. Born assumed that HCl ionizes to give $H^+ + Cl^-$, an assumption later confirmed experimentally by Foote and Mohler,[17] who determined the ionization potential J_{HCl} to be approximately 14.0 volts. The method of

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[17] J. Am. Chem. Soc. 42, 1832 (1920).

deriving the electron affinity of the halogen is conveniently demonstrated by the following diagrammatic outline due to Haber,[18]

$$\begin{tikzcd}
(HCl) & (H),\ (Cl) \arrow[l, "Q_{HCl}"] \\
(H)^+,\ (Cl^-) \arrow[u, "J_{HCl}"'] & (H^+),\ (-),\ (Cl) \arrow[l, "E_{Cl}"'] \arrow[u, "J_H"']
\end{tikzcd}$$

The direction of the arrows corresponds with the evolution of heat. Similar diagrams may be set up for hydrogen bromide, hydrogen iodide and hydrogen cyanide. Now Q_{HCl}, which is the heat of formation of hydrogen chloride from hydrogen and chlorine atoms, also involves the heats of dissociation of corresponding molecules. For the halogens we shall use the values previously given. For hydrogen we shall use the mean of Langmuir's value and that of Herzfeld,[19] namely 90 Cal. per mol. For the ionization of hydrogen atoms the generally accepted value is 310 Cal. per gram atom or 13.4 volts. For the ionization potentials of the halides we shall use the measurements of P. Knipping,[20] as amended recently by Franck[21] and Grimm.[22] The several relationships may be expressed in the following equations:

$$\begin{aligned}
\tfrac{1}{2}(H_2) + \tfrac{1}{2}(Cl_2) &= (HCl) + 22 \text{ Cal.} \\
(H) &= \tfrac{1}{2}\,(H_2) + 45 \\
(Cl) &= \tfrac{1}{2}\,(Cl_2) + 31 \\
(HCl) &= (H^+) + (Cl^-) - 313 \\
H^+ + \ominus &= (H) + 310
\end{aligned}$$

Whence, by summation $(Cl) + \ominus = (Cl^-) + E_{Cl}$

$$\begin{aligned}
\text{Where } E_{Cl} &= 22 + 45 + 31 - 313 + 310 \\
\text{or } E_{Cl} &= 95 \text{ Cal.}
\end{aligned}$$

This value is in good agreement with that for E_{Cl} obtained from the lattice energy calculations of Born. The errors of the

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[18] Ber. Deut. physikal. Ges., **21**, 754 (1919).
[19] Z. Elektrochem. **25**, 302 (1919).
[20] Z. Physik. **7**, 328 (1921).
[21] Z. Physik. **11**, 155 (1922).
[22] Z. phys. Chem. **102**, 504 (1922).

above data are therefore of the same order as the uncertainties of the lattice energy data. Similarly

$$E_{Br} = 12.1 + 45 + 23 - 300 + 310 = 90 \text{ Cal.}$$
$$E_{I} = 1.5 + 45 + 18 - 290.5 + 310 = 84 \text{ Cal.}$$

The accuracy of these determinations amounts to ± 10 Cal. since there is an uncertainty in the ionization potential data, estimated by Knipping at ± 7 Cal., uncertainty in the dissociation values for hydrogen and chlorine, which may easily amount to ± 3 Cal. Nevertheless, both the lattice energy calculations and those based on ionization potentials serve to show the affinity of halogen atoms for electrons is a large positive quantity.

Fajans[23] has shown that the evaluation of this electron affinity for various gases has a definite utility, in indicating the probable effect of electron impacts with molecules of the various gases. Thus in the case of the halogens, the quantitative data already given lead to the following equations.

	Cl	Br	I
$(X_2) = (X) + (X)$	—62	—46	—36 Cal.
$(X) + \ominus = (X^-)$	+95	+88	+82 Cal.
whence $(X_2) + \ominus = (X) + (X^-)$	+33	+42	+46 Cal.
similarly $(X_2) = 2(X)$	—62	—46	—36
$2X + 2\ominus = 2(X^-)$	+190	+176	+164
whence $(X_2) + 2\ominus = 2(X^-)$	+138	+130	+128

It is evident therefore that the production either of atom plus ion or two ions by collision of electrons with chlorine molecules are both strongly exothermic processes. The collision of a slow moving electron with a chlorine molecule will therefore probably give a negative ion and a neutral atom in the sense of the first set of equations. If two electrons collide simultaneously, two halogen ions will result, with still larger evolution of heat. The affinity of halogen atoms for electrons is large enough to split the atomic linkage in the molecule. The existence of negative halogen molecules is therefore not probable.

One further method of measurement of electron affinity has

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[23] Ber. Deut. physikal. Ges., 21, 724 (1919).

been suggested by Franck[24] in a very suggestive paper connecting affinity with spectroscopic phenomena. This is not the place to amplify the subject. Interested readers may be referred to its treatment in the recent monograph by Foote and Mohler,[25] where additional details on all three methods of computation may be obtained. The most recent spectroscopic data give[26] for E_{Cl}, 89.3 Cal., $E_{Br} = 67.5$ Cal. and for E_I, 59.2 Cal., values therefore somewhat lower than in the preceding.

Electrode Processes and the Newer Concepts.

The importance attaching to the heats of hydration of individual gas ions prompts a closer inquiry into the determination of these quantities. Only one method of obtaining these seems to have been indicated in the literature. This method is based on the value for the absolute potentials of electrodes. The commonly accepted value for the single potential of the normal calomel electrode is + 0.56 volt. This value is based on measurements involving the dropping mercury electrode. Estimates of the accuracy of this value vary widely. By some it is regarded as accurate to within a few hundredths of a volt. Others,[27] however, claim a much greater error than this amounting to some tenths of a volt.

Ostwald, accepting the higher accuracy of the value 0.56 volt has shown[28] that with the use of this value the heats of ionization of various elements may be determined approximately. With the aid of the equation

$$nF\pi - U = nFT\frac{d\pi}{dt}$$

using for π the value for the single potential of a given electrode and for $\frac{d\pi}{dt}$ its temperature coefficient, Ostwald and Jahn[29] determined U for a number of elementary electrode processes.

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[24] Z. Physik. 5, 428 (1921).

[25] The Origin of Spectra, A. C. S. Monograph Series, Chem. Catalog Company. 1922, Chap. VIII.

[26] Angerer, Z. Physik. 11, 169 (1922).

[27] Cf. Garrison, J. Am. Chem. Soc., 45, 37 (1923).

[28] Z. physikal Chem., 11, 506 (1893).

[29] Z. physikal. Chem., 18, 421 (1895).

$$M = M^{+}_{aq}$$

For the reaction at the hydrogen electrode

$$(H_2)\ Pt = H^{+}_{aq},$$

the heat of reaction was shown to be very small, and of the order of 0 ± 1 Cal. An error of 0.25 volt in the determination of the absolute potential would involve a corresponding variation of 0.25 x 23 = ± 6 Cal. in this value for the electrode process, which is not a higher order of error than is inherent in the calculations recorded in earlier sections of this paper. Accepting Ostwald's value for the hydrogen electrode process, Fajans has associated it with the material accumulated by him with reference to the combined heats of hydration of cation and anion. The conversion of molecular hydrogen to hydrogen ions in solution takes place in a cell in which the gas is bubbled over a platinum electrode. The hydrogen ions pass into the solution, the electrons remain on the platinum side of the double layer at the junction of electrode and electrolyte. The net heat change of this electrode process, 0 ± 1 Cal. is composite of two thermal magnitudes, that of the change from molecular hydrogen to dissolved hydrogen ions and that associated with the presence of electrons in the platinum metal. This latter is equal and opposite to the energy required to evaporate electrons from the metal, a quantity which amounts, according to Born,[30] to approximately 100 Cal.[31]

We may therefore obtain the heat of hydration of gaseous hydrogen ions assuming this value by the following set of equations:

$$\begin{aligned} (H^{+}) + \ominus &= (H) + 312 \text{ Cal.} \\ (H) &= \tfrac{1}{2}\,(H_2) + 45 \text{ Cal.} \\ (H_2) + Pt + aq &= H^{+}_{aq} + Pt(-) + 0 \text{ Cal.} \\ Pt\ (-) &= Pt + \ominus - 100 \text{ Cal.} \end{aligned}$$

Hence, by addition $(H^{+}) + Aq = H^{+}_{aq} + 257$ Cal.
Now, as was shown in an earlier section

$$W_{H^{+}} - W_{K^{+}} = 175 \text{ Cal.}$$

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[30] *Loc. cit.*

[31] Most varied values are to be found in the literature for this magnitude varying between 2.5 volts for platinum containing hydrogen to 6.6 volts (Langmuir) in which special precautions were taken to ensure the absence of this gas. No high order of accuracy can therefore be assigned to this quantity.

Hence it follows that

$$W_{K^+} = 257 - 175 = 82 \text{ Cal.}$$

And, since

$$W_{K^+} + W_{Cl^-} = 159$$
$$W_{Cl^-} = 77 \text{ Cal.}$$

On the basis of such a procedure Born[32] has compiled the following table of individual heats of hydration of gas ions.

H^+	Li^+	Na^+	K^+	Rb^+	Cs^+	Cl^-	Br^-	I^-
262	110	103	82	73	74	77	68	57

The hydrogen value in this table is slightly different from that given above due to small variations in the values used for the heat of dissociation of molecular hydrogen. Especially noteworthy is the decrease in value for the heat of hydration with increase in the size of the ion.

It is apposite at this point to define more precisely the significance of the concept of hydration of gas ions. According to Fajans it is not to be regarded as involving the solution of a gaseous ion in the water with the formation of ion-hydrates of definite stoicheiometric composition. Rather has one to assume that, through the charge which the ion carried, the oppositely charged parts of the polar water molecules in its immediate neighborhood are oriented towards the ion, whereas the similarly charged portions of the water molecules are turned away from the ion, and, in their turn, act electrically upon the molecules in their immediate environment. There results, therefore, a kind of electric polarization in the solution. In the preceding table there is obviously a greater heat of hydration the smaller the gas ion. The electrical forces are operating at smaller distances. Born concludes that in every case, irrespective of the nature of the gas ion the heat of hydration of the gas ion will be a positive quantity.

In the preceding calculation of the individual value for the heat of hydration of the hydrogen gas ion, it is apparent that the calculation involves the magnitude of the heat change associated with the electron emission from the metal used as the hydrogen gas electrode, which was platinum in the example

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[32] *Loc. cit.*

considered. It was pointed out that a considerable degree of uncertainty attaches to this value. It would therefore be well worthy of experimental investigation how or whether the characteristics of the hydrogen electrode change, as a consequence of alteration in the metal used as electrode material. Of many substitutes considered, tantalum appears to us to offer possibilities of usefulness. It is known to take up many times its own value of hydrogen. Furthermore, its thermionic emission has been most carefully studied. The data for an independent check on the magnitude of the individual heats of hydration should therefore be easily obtained. We plan to obtain these if possible.

Meanwhile we must regard the data already given in the preceding table as tentative. The corresponding calculation for a potassium electrode does not yield the same value for W_{K^+} as is obtained indirectly from the above calculations, as the following equations demonstrate.

$$\begin{aligned}
[\mathrm{K}] &= (\mathrm{K}) - 21\\
(\mathrm{K}) &= (\mathrm{K}^+) + \ominus - 99\\
(\mathrm{K}^+) + \mathrm{Aq} &= \mathrm{K}^+_{aq} + W_{\mathrm{K}^+}\\
\ominus + \mathrm{K} &= \mathrm{K}(-) + 50.6
\end{aligned}$$

Now we have shown (p. 290) that

$$[\mathrm{K}] + \mathrm{H}^+_{aq} = \mathrm{K}^+_{aq} + \tfrac{1}{2}(\mathrm{H}_2) + 62$$

And since

$$\mathrm{H}^+_{aq} = \tfrac{1}{2}\,(\mathrm{H}_2) + \mathrm{Aq} + 0$$

it follows that the electrode process potassium → K^+_{aq} or alternatively 2 $[\mathrm{K}] = \mathrm{K}^+_{aq} + \mathrm{K}\,(-) + 62$ Cal. This would yield for W_{K} a value = 132 Cal., deviating most markedly from that given by the hydrogen calculation. The diversity between the two has its origin in the two equations

$$\mathrm{Pt} + \ominus = \mathrm{Pt}\,(-) + 100$$

and

$$\mathrm{K} + \ominus = \mathrm{K}\,(-) + 50.6$$

This latter is the most probable value from determinations of the photoelectric effect, and seems equally as well founded as the platinum value used by Born and Fajans.

It is evident, therefore, that the problem is only in its initial stages. Much work remains to be done, much progress to be made. In the present communication, the argument has been confined solely to the hydrogen and alkali halides, because with the aid of direct measurements of ionization potentials of the hydrogen halides, and with the readily verified calculations of lattice energy, for the relatively simple alkali halide crystal lattices a surer basis for calculations existed. The treatment is being extended to other compounds, as a recent attempt by Grimm[33] indicates. There opens up a new field of investigative work which cannot fail to have its influence on the development of electrochemical science in general.

DISCUSSION.

S. C. Lind[1]: Prof. Taylor's paper is extremely interesting. I had frequently been tempted to undertake a similar analysis to that of Prof. Taylor, and therefore it interests me all the more. At the time that many of us became members of the Society, we were entirely satisfied with the electrolytic pressure theory, or the Nernst theory, of what happens at an electrode. It has been evident to many of us for some time that it would be extremely important to study electrode phenomena from the standpoint of gaseous ionization. One of the difficulties has been to know whether the elctrolytic ion is exactly the same as the gaseous ion; and that is one of the assumptions Prof. Taylor has had to make, about which there might possibly be some question.

It will be useful in the future to use these conceptions that Prof. Taylor has brought to our attention, whether they ultimately prove to be correct or not.

John Johnston[2]: I would like to support the idea Dr. Taylor is emphasizing, namely, that the usual picture of the process of ionization in solution is not satisfactory, and that, so far as I know, no one has outlined a satisfactory picture of the process of forming an ion at the electrode in solution.

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[33] Z. physikal. Chem., **102**, 113 and 504 (1922).

[1] Chief Chemist, U. S. Bureau of Mines, Washington, D. C.

[2] Yale University, New Haven, Conn.

S. C. LIND: Those of us who have believed for a long time that gaseous ions might be chemically active have met opposition on the part of physicists, who have pointed out that in the case of the electrolytic ions, the sodium ion and the chlorine ion, we have a special case. That, for example, in the case of the sodium ion with one positive charge, and the chlorine ion with one negative charge, under the Lewis-Langmuir theory leads to the rare gas configuration, which we all admit to be inert. In other words, if the assumed electrolytic sodium ion were present as a gaseous ion, you would not expect it to be chemically active, except through an electrical attraction for the electrical opposite. Therefore, if that is true, we would not expect the sodium ion with one negative charge to be active toward electrically neutral water, nor would we expect it to lead to a reaction with high heat of reaction. I merely want to ask Prof. Taylor what explanation he would give of that objection of the physicist. It is not one that I am raising at all, but one that has been raised to theories that I hold.

H. S. TAYLOR: I do not know what the answer to such an objection is. The chlorine ion is certainly a peculiarly stable system. At one time I (along with Dr. Lind and some others who had been working in the field before) thought that if I could succeed in getting the chlorine ion in a hydrogen chlorine mixture I could get a reaction. In view of what has accumulated with regard to the nature of chlorine ion, I myself am skeptical now. I would agree with the physicist in saying that the chlorine ion is something akin to a noble gas, except in so far as you have an excess negative charge, and thereby can have electrical attraction such as is present in solid sodium chloride. This is one of the problems that certainly needs the intense co-operation of the physicist and the electrochemist.

W. C. MOORE[3]: A number of years ago I was interested in gaseous conduction, particularly with reference to the flaming arc. I looked up the literature on the subject and found that Prof. H. A. Wilson, who at that time was doing considerable work on conduction in gas flames, had discovered that potassium ion in potassium chloride vapor carried three positive charges; whereas,

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[3] Research Chemist, U. S. Industrial Alcohol Co., Baltimore, Md.

we suppose we know that it carries one charge only, in solutions in water.

There is an interesting discrepancy here; we need some means of determining how the number of charges on a potassium ion vary in raising the temperature from that of a bunsen burner to that of the flaming arc.

H. C. Howard[4]: The same objection could be urged against the activity of the electrolytic potassium ion, because that also reverts to the rare gas type.

S. C. Lind: It is correct that many of the electrolytic ions follow a special class, and fall into the rare gas series. On the other hand, it does not follow that we can not have some kind of a chlorine negative ion as, for instance, Cl_2, with one negative charge, which will not fall into that class. We have in the gaseous ions a much wider variety in nature than in electrolytic ones, and we should not be hasty to conclude that there is no such thing as a chemically active gaseous ion.

H. S. Taylor: The little section on page 43 tends to show that the existence of negative halogen molecules is not probable. I think the evidence on that point is fairly conclusive, since the magnitudes of the heat quantities involved are so tremendously large.

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[4] Princeton, N. J.

A paper presented at the Forty-third General Meeting of the American Electrochemical Society held in New York City, May 3, 1923, Dr. Wm. G. Horsch in the Chair.

OXYGEN OVERVOLTAGE OF ARTIFICIAL MAGNETITE IN CHLORATE SOLUTIONS.[1]

By H. C. HOWARD.[2]

ABSTRACT.

Attempts were made to oxidize sodium chlorate to perchlorate electrolytically at a magnetite anode. Negative results were obtained. The oxygen overvoltage of a magnetite anode in N sodium chlorate was measured and found to be from 0.4 to 0.6 volt lower than that of smooth platinum.

Several years ago, in the course of a study of the electrolytic oxidation of sodium chlorate to perchlorate, some time was devoted to an attempt to find a substitute for the expensive platinum anodes usually employed.

All of the common and many of the rarer metals were tried and all, except those of the platinum group, were found to corrode very rapidly when used as anodes in a sodium chlorate electrolyte. Carborundum and the various high silicon alloys were shown to be valueless and the oxide electrodes, such as lead peroxide and manganese dioxide, which have been used effectively as insoluble anodes in certain cases, decomposed very quickly under the conditions present in this electrolysis.

It was known that an artificial magnetite had been used with success in some of the German alkali-chlorine cells, and we were anxious to test this material. Finally we obtained samples of such electrodes, through the courtesy of the Chile Exploration Co. These artificial magnetite electrodes proved to be very

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[1] Manuscript received February 2, 1923.

[2] Contribution from the Chemical Laboratory of Princeton University.

resistant to corrosion, and in this respect appeared to offer a good substitute for platinum. Analysis of the electrode in which these anodes had been tested showed, however, that no perchlorate had been formed during the electrolysis, and this was found to be the case in all later experiments, even under the most favorable conditions for perchlorate formation, such as low temperature and high current density.

At the time, this was explained by assuming that the overvoltage of oxygen at magnetite is very much lower than at smooth platinum, and hence, at anodes of the former material, oxygen evolution takes place in preference to the oxidation of the chlorate ion to the perchlorate.

TABLE I.

Oxygen Overvoltage of Magnetite in Sodium Chlorate.

Electrolyte, *N* sodium chlorate. Temperature, 20° C. Area of the anode was 36 sq. mm. in each case. The potentials are referred to *N* calomel electrode as zero, and are all positive.

Smooth Platinum Anode		Magnetite Anode		
c. d. amp./sq. dm.	anode potential v.	c. d. amp./sq. dm.	anode potential v.	magnetite potential*
3.0	2.04	1.4	1.58	1.58
5.5	2.10	2.8	1.61	1.61
8.3	2.17	5.5	1.66	1.65
11.0	2.23	11.0	1.72	1.69
22.3	2.46	16.6	1.79	1.75
		22.8	1.86	1.80

* Potential of the magnetite, corrected for the voltage drop in the electrode itself. The resistance of the electrode and contact was 0.78 ohm. The resistance of the platinum electrode was negligible.

A search of the literature revealed no data on the oxygen overvoltage of magnetite, and since lack of time prevented further experimental work, a test of the explanation offered was not then possible.

Recently a few measurements of the oxygen overvoltage of magnetite in sodium chlorate have been made in this laboratory. The results of these measurements are presented in Table I and Fig. 1.

These data and curves show clearly that the oxygen overvoltage of magnetite is much lower than that of smooth platinum.

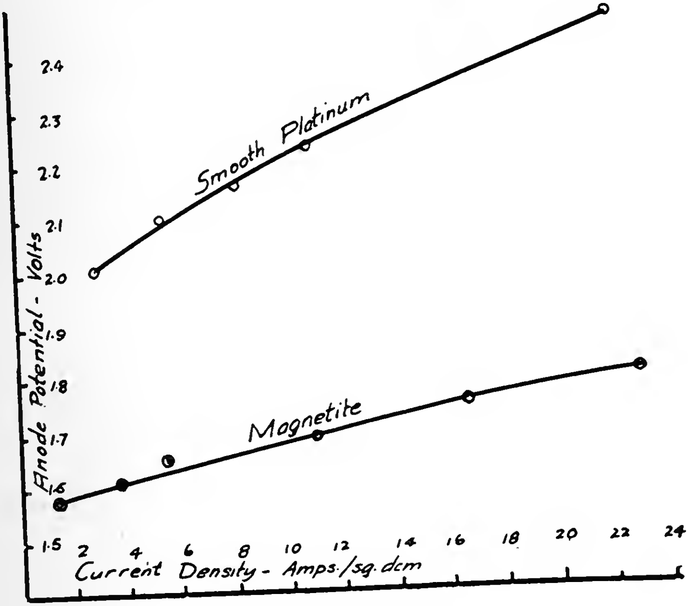

FIG. 1. Potentials of platinum and magnetite in N sodium chlorate.

CONCLUSION.

The failure to oxidize chlorates to perchlorates at a magnetite anode, together with the fact that such an anode has been shown to have a much lower oxygen overvoltage than a smooth platinum one, at which such an oxidation takes place readily, afford further confirmation of the hypothesis that there is a direct relationship between the overvoltage of an electrode and its oxidizing or reducing power.

DISCUSSION.

COLIN G. FINK[1]: Mr. Howard's paper is interesting and brings up the general subject of the insoluble anode. In electrolytes such as we have studied, particularly with SO_4 ions present, a number

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[1] Consulting Metallurgist, New York City.

of reactions occur. The ultimate anode reaction is the liberation of oxygen gas. Now anything that will hasten the evolution of oxygen gas in preference to the dissolution of the metal of the anode, will cut down the corrosion of the anode under investigation. In other words, you finally come to a point where you can use a very soluble anode, providing you have on the surface a thin film of a catalyzer, which will hasten the discharge of the SO_4 ions and the formation of oxygen gas in preference to the formation of metal compounds.

In other words, the overvoltage phase of the insoluble anode is a phase which has not always been taken into account, because primarily the metals have been studied from the purely chemical solubility point of view.

M. Knobel[2]: Regarding the relation between oxidizing or reducing power and overvoltage, while one can find a good many cases in the literature where a high overvoltage metal does give a greater oxidation or reduction than a low overvoltage metal, one can also find as many cases where this relation does not hold.

W. G. Horsch[3]: Since Dr. Bancroft is not here, it may be safe to quote him as stating that oxidation at an anode may be linked up with high overvoltage, but is not necessarily a consequence thereof.

I took the liberty to subtract the reversible potential of the calomel-oxygen cell from Mr. Howard's results and compare the overvoltages thus obtained with those of Dr. Knobel in the next paper on our program, and I get 0.3 to 0.4 of a volt difference at practically all points in the curve. The curves as determined by these two authors thus show good agreement as to shape.

H. C. Howard: My results are referred to the calomel electrode, as zero. The potential of the calomel electrode has already been subtracted. Whereas, Dr. Knobel's results represent real overvoltages. You would obtain more nearly comparative values if you subtracted the reversible potential of oxygen from my results.

W. G. Horsch: What I meant was platinum in terms of oxygen.

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[2] Mass. Inst. of Technology, Cambridge, Mass.

[3] Chile Exploration Labs., New York City.

A paper presented at the Forty-third General Meeting of the American Electrochemical Society held in New York City, May 3, 1923, Dr. Wm. G. Horsch in the Chair.

THE EFFECT OF CURRENT DENSITY ON OVERVOLTAGE.[1]

By M. Knobel, P. Caplan, and M. Eiseman[2]

INTRODUCTION.

There are numerous references[3] in the literature on the effect of current density on overvoltage, but they are in general more or less isolated values and for comparatively small current densities. The experimental conditions are so different also that it would be difficult to compile a comparable set of data. On account of the great technical importance of this phase of overvoltage, and also for the theoretical interpretation of overvoltage, it was thought desirable to have extensive and consistent data in this field. In the following work we have attempted to include all the more common metals and alloys as cathodes, and to determine oxygen and halogen overvoltages on as many electrodes as possible. While the overvoltage values obtained may not be acceptable as absolute values, they should at least be comparable as the experimental conditions were maintained the same in all cases.

METHOD OF MEASUREMENT.

We have accepted as our definition of overvoltage "the potential necessary in excess of the reversible potential to discharge the product in question, both potentials being measured under identical conditions as external hydrogen pressure, temperature and concentration of solution." Thus the hydrogen overvoltage on a lead

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[1] Manuscript received November 4, 1922.

[2] Contribution from the Rogers Laboratory of Physics, Electrochemical Laboratory, Massachusetts Institute of Technology.

[3] Tafel, Z. Physik. Chem. **50**, 641 (1904); Ghosh, J. Am. Chem. Soc. **36**, 2333 (1914); **37**, 733 (1915); Rideal, J. Am. Chem. Soc. **42**, 94 (1920); Newbery, J. Am. Chem. Soc. **109**, 1051, 1066 (1916); Sacerdotti, Z. Elektrochem. **17**, 473 (1911); Tainton, Trans. Am. Electrochem. Soc. **41**, 389 (1922); Reichinstein, Z. Elektrochem. **17**, 85 (1911); Coehn & Osaka, Z. anorg. Chem. **34**, 86-102 (1903); Foerster & Yamasaki, Z. Elektrochem. **16**, 321 (1910); Bennewitz, Z. Physik. Chem. **72**, 202 (1910); Lewis & Jackson, Z. Physik. Chem. **56**, 193 (1906); Coehn & Dannenberg, Z. Physik. Chem. **38**, 609 (1901); Gockel, Z. Physik. Chem. **32**, 607 (1900); Nutton & Law, Trans. Far. Soc. **3**, 50 (1907).

cathode at a given current density will be the potential difference between that lead cathode and the solution, minus the potential difference between a reversible electrode (practically platinized platinum with no current flowing) and the same solution at the same temperature and pressure. We believe this to be the generally accepted definition.

There are two methods of measuring overvoltage, and the question arises as to which gives the overvoltage just defined. The first is to insert a reference electrode with the tip against the cathode and measure the electrode potential while the current is flowing. The second or commutator method, which has been championed principally by Newbery[4] on the other hand, allows for shutting off the electrolyzing current while the electrode potential measurement is being made; it alternately allows the electrolyzing current to pass and then connects the cell to the potentionmeter. The main argument for use of the commutator is that all ohmic resistance drops are eliminated; but let us defer the discussion of this point until we have analyzed the commutator method to see whether it gives correct values.

The potential measured in the commutator method depends on the concentration of the electrode products stored up during the period of electrolysis. The curves determined by LeBlanc[5] with an oscillograph and a commutator throw light on this point. The typical curves obtained by him for the variation of electromotive force across the cell (ordinates) with time (abscissæ) are shown in Fig. 1, 2 and 3. Fig. 1 is for the electrolysis of a normal iodine and potassium iodide solution between platinum electrodes; Fig. 2 is for $0.05N$ iodine and potassium iodide in one normal sulfuric acid, and Fig. 3 for one normal sulfuric acid. In all of these curves the portions A are for the time when the electrolyzing current is on, portions B when the current is shut off and the oscillograph only is connected to the cell; and portions C when the electrolyzing current is passing in the reverse direction. A difference in LeBlanc's procedure and Newbery's must be noted in that the electrode products must supply current to operate the oscillograph in LeBlanc's arrangement when the outside current

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[4] Trans. Far. Soc. **15** (1919); J. Am. Chem. Soc. **42**, 2007 (1920).

[5] "Die Elektromotorischen Krafte der Polarization und ihre Messungen mit Hilfe les Oszillographen" Hall, 1910.

is shut off, while Newbery takes no current from the cell in this interval.

Fig. 1 indicates that no polarization has occurred, neither in the nature of overvoltage nor concentration polarization in the solution. The fact that portion B is directly on the zero potential axis means that the two electrodes are in the same condition, that is, have the same potential difference with respect to the solution, and the flatness of portion A shows that the electrolysis is occurring at constant potential. The distance of A and C from the axis is presumably due to ohmic resistance drop in the whole cell. This electrolysis is therefore reversible as far as the electrodes are concerned.

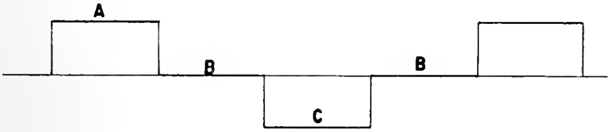

Fig. 1

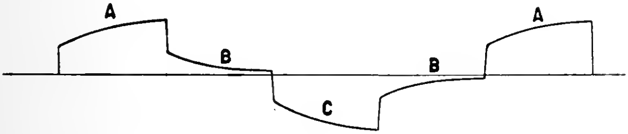

Fig. 2

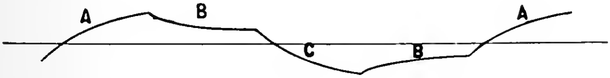

Fig. 3

Fig. 2 indicates the existence of some polarization due to accumulation of electrode products, as hydrogen and oxygen, or concentration differences in the electrodes. This curve is typical of all LeBlanc's measurements on oxidation reduction cells such as the ferri-ferro ion electrode, etc. The form of Fig. 3 is without doubt caused by the accumulation of H_2 and O_2 on the electrodes. During the time represented by A the electromotive force gradually increases as the gas concentration increases. The maintenance of the potential at B has its source in the gases at the electrodes yielding current by going back into solution.

It is the electromotive force represented by B that the commutator method should measure. For the low current densities used by LeBlanc in his work (about 0.0045 ampere per sq. cm.) the commutator should give essentially correct results. If no current were taken from the cell during the time B, that portion of the curve would probably be more nearly horizontal, which of course it should be, to allow accurate measurement on a potentiometer, and to have a definite meaning.

In consideration of the very small time interval (about 0.019 second) when the electrolyzing current is on and off, and of the small current used, the gases liberated at the electrodes cannot attain high pressures and will not tend to diffuse away appreciably. They should then have essentially the same concentration as when the current is passing, and B should give the back electromotive force or the overvoltage (of both electrodes) according to the definition previously given. In support of this reasoning is the fact that at low current densities Newbery's values obtained by the commutator, are the same within the limits of reproducibility of overvoltage, as those obtained by the direct method.

However, at high current densities and with electrodes other than platinum the above relations cannot hold. It is well known that platinum has a much greater power to occlude or adsorb gases than other metals. At the opposite extreme is mercury which probably adsorbs only extremely small quantities of gas. The gas accumulation at a mercury electrode must then occur in a layer of solution under which conditions the gas may easily be carried away by convection or diffusion. A curve analogous to Fig. 3 for mercury electrodes would show a sharp drop in the portion B and the overvoltage measured by the potentiometer would be much lower than the back electromotive force when the current was passing. Newbery in fact gives values for mercury overvoltage at low current densities, obtained by the commutator method, considerably lower than those obtained while the current is passing.

At high current densities the stirring effect of the evolved gases will also cause portion B to drop sharply from its maximum. For large currents the gas pressure is comparatively much larger, which in itself will tend to increase the loss of gas by diffusion. Of probably much greater importance however is the violent stirring of the solution directly at the electrode surface by the evolved gas. Most of the gas which is in the solution, possibly in a super-saturated state, will be swept away so that it is no longer in contact with the electrode. Again this explanation is supported by the very low values obtained by Newbery at high current densities, at mercury as well as at other electrodes.

The time interval in which this must occur is small. For the speed of 2,500 revolutions per minute of the commutator as used by Newbery the current is broken only 0.012 second, but LeBlanc's time interval is 0.019 second, and an appreciable drop has occurred in the case in Fig. 3 where the drop is least to be expected. Some of these points have been tested experimentally recently by Tartar & Keyes[6] and all their results directly confirm the conclusions drawn here. Other investigators[7] have criticized this commutator method, but we will not attempt to discuss their criticisms here. We believe the method can fairly be rejected. The extensive tables of Newbery[8] are of little value if the objections to the commutator method are valid.

The question of eliminating ohmic resistance drop in the closed circuit method is a serious one. Obviously the reference electrode tip cannot be situated any large distance from the electrode surface, or the potential drop in the solution will be measured with the overvoltage. One method, which unfortunately has been rather widely used in an attempt to obviate this difficulty[9], is to place the reference electrode behind the cathode, that is, on the opposite side from the anode. This is obviously in error for the current density is indefinite and much smaller on the back face of the cathode and the potential so measured bears no relation to the potential difference between the electrode and the solution in contact with the front face. While the electric potential of the whole electrode is the same, the solution in front of and behind the electrode need by no means have

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[6] J. Am. Chem. Soc. 44, 557 (1922).

[7] Tainton, Trans. Am. Electrochem. Soc. 41, 389 (1922); MacInnes, J. Am. Chem. Soc. 42, 2233 (1920).

[8] J. Chem. Soc. 109, 1051, 1066 (1916) 111, 470 (1917).

[9] See for example Nutton and Law, Trans. Far. Soc. 3, 50 (1917); Pring and Curzon Ibid. 7, 237 (1911).

the same electric potential, and therefore the potential difference between electrode and electrolyte will be different on the two sides. While seemingly unnecessary we have tested this point experimentally and confirmed the statement made.

If the reference electrode tip is placed on the front side it disturbs the current flow lines in the small region near the tip. A large tip or one pressed too closely to the surface would cause an appreciable decrease in current density in the electrolyte immediately between the tip and the electrode, and too low overvoltage values will result. It would appear that the smallest possible tip would be desirable. This was tested out experimentally by a series of tips of different diameters. They were moved up to an electrode from some distance out in the solution

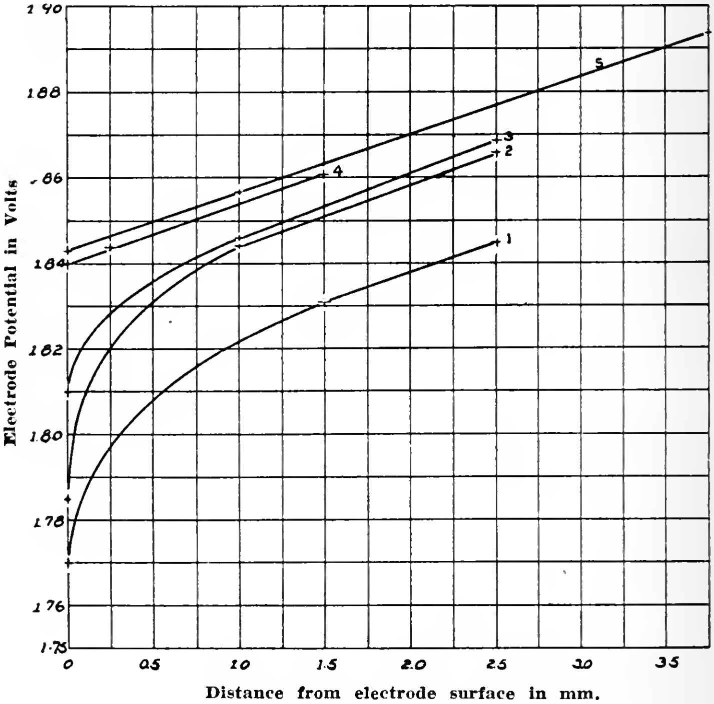

FIG. 4. Showing effect of varying size of electrode tips.

and the potential plotted as a function of the distance. As uniform a current density as possible of 0.5 ampere per square centimeter was maintained.

An auxiliary reference electrode held at a constant position with respect to the lead cathode used, indicated the constancy of the latter. The results are shown in Fig. 4. The ordinate scale is the electrode potential in volts with an arbitrary zero. The abscissæ indicate the distance of the tip from the electrode surface, measured in mm. The tip sizes corresponding to the numbers on the curves are as follows:—No. 1, 4.6 mm. in diameter; No. 2, 3.1; No. 3, 2.3; No. 4, 1.3; No. 5, 0.08. The slope of the curves is of course due to the resistance of the electrolyte. For the larger tips the drop in potential in excess of the ohmic resistance drop, as the tip approaches the electrode, is marked. The use of a tip as large as the first, pressed against the electrode would introduce an error as large as 0.04. If the tip is one millimeter or less in diameter, however, we concluded it would give essentially correct values practically independent of the tip diameter.

Another experiment with a mercury cathode proves conclusively the lowering of the potential measured by the lowering of the current density in the above manner. The tip was lowered from a point out in the solution until it was some distance under the mercury surface. The electrode potential decreased at a constant rate, due to the change in the ohmic resistance in the electrolyte until the tip had made a slight depression in the mercury. When the tip was pushed still further into the mercury, the electrode potential dropped very quickly to a value not far from the hydrogen electrode potential, and was not influenced at all by changes in the current density on the remainder of the mercury surface. A small electrode tip was also pushed into soft lead sufficiently to cause a marked lowering in potential.

We therefore have used tips of approximately one millimeter or less in diameter and have pressed them directly but lightly against the active electrode surface during measurements. A small piece of cotton is inserted in the end of the tip to prevent bubbles entering the tube and breaking the electrical circuit.

APPARATUS.

The electrolyzing vessel was a U-tube of 3.8 cm. (1.5 in.) tubing, the anode and cathode being in opposite arms, and the cross tube plugged with cotton wool to prevent mixing of the solutions. The electrode under investigation was placed directly opposite the cross arm and was sufficiently small (usually one centimeter square) so that a uniform current density was obtained. Three ammeters of different ranges were placed in the electrolyzing current line to measure accurately small and large currents. The potential measuring apparatus was an ordinary potentiometer sensitive to 0.1 millivolt. The reference electrodes used were Hg, Hg_2SO_4, H_2SO_4 $(2N)$[10] with sulfuric acid solutions Hg, HgO, KOH $(1N)$ with alkaline solutions[11] and the normal calomel electrode with the salt solutions, each being checked against the standard hydrogen electrode occasionally.

The electrodes were always, when possible, made of square sheets, exactly one centimeter on each side. A projection left on this sheet or a stout wire soldered to the back, passed up through a glass tube. The back and connecting strip up to the glass were heavily coated with asphalt. This was found to be very satisfactory, the asphalt being unattacked in all the solutions used and having no tendency to peel off as paraffine does. In every case the actual resistance of the electrode and lead itself was determined and corrections made for the ohmic resistance drop if it were appreciable.

The surface wherever possible, was polished with No. 0000 emery paper. Any further polishing seemed useless as the surface is so soon roughened after passing the electrolyzing current. All measurements were made with the apparatus in a thermostat at 25°C., regulated to within 0.2°C.

MATERIALS.

All hydrogen overvoltages were measured in pure two-normal sulfuric acid, care being always taken to saturate the solution first

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[10] 98 g. H_2SO_4 per 1,000 g. of water.

[11] In calculating the oxygen overvoltages the electromotive force of the hydrogen-oxygen cell was taken as 1.227 volts. See Lewis and Randall J. Am. Chem. Soc. 36, 1969 (1914).

with hydrogen. Oxygen overvoltages were determined in one normal potassium hydroxide. No particular effort was made to saturate this solution with oxygen as the results were too unsteady to warrant it and were not improved by preliminary saturation. For the halogen overvoltages, saturated solutions of the sodium or potassium halide were used, saturated further with the pure halogen. The strong solutions were used to give a good conducting solution and to avoid depletion of ions at the electrode. The saturation with the halogen is obviously necessary since the equilibrium potential with no current will only be obtained under that condition.

Wherever possible the pure metals were obtained for electrodes. No extraordinary care was exercised however as the measurements could not be made with a precision to necessitate it.

The procedure in making a run was to set the current at the desired value and make the electrode potential determination within one minute, then raise the current and make the next measurement, etc. The objection will immediately be raised against this procedure that insufficient time is allowed for the electrode to come to a constant value, but it was found without question that more nearly reproducible values could be obtained on the increase and decrease of current in this way. If five or ten minutes were allowed at each step the electrode had so changed by the time a complete run had been made, from the lowest current to the highest and back, that the last value was several tenths of a volt different in some cases from what it had been for the same current at the start. Particularly with the higher currents the measurements were made quickly to avoid destroying the surface and to prevent excessive heating. In general measurements were made both on the increase and decrease of current, but only the values for increasing current are listed. Check runs on newly made electrodes were made in every case; these were considered satisfactory if the forms of the curves were similar and the deviation of the two not more than 0.1 volt. One of the runs only is listed and not an average of the two as the form of the curve is believed to be more important than absolute values.

RESULTS.

The results are listed in Tables I to V and shown graphically in Fig. 5 to 9. The current density is given in milliamperes per square centimeter and the overvoltage in volts. The overvoltage is given to tenths of a millivolt where the steadiness of the individual values seemed to warrant it, although it is unlikely that the measurements could be reproduced to better than two to three

TABLE I.

Hydrogen Overvoltages at 25° C.

Current density mili. amp. per sq. cm.	Overvoltage in Volts.						
	Au	Cd	Cu	Plat-inized Pt	Smooth Pt	Al	Graph-ite
0	....	0.466	....	0.000	....	....	0.0022
0.1	0.122	0.651	0.351	0.0034	....	0.499	0.3166
1	0.241	0.981	0.479	0.0154	0.024	0.565	0.5995
2	....	....	....	0.0208	0.034	0.625	0.6520
5	0.332	1.086	0.548	0.0272	0.051	0.745	0.7250
10	0.390	1.134	0.584	0.0300	0.068	0.826	0.7788
50	0.507	1.211	....	0.0376	0.186	0.968	0.9032
100	0.588	1.216	0.801	0.0405	0.288	0.996	0.9774
200	0.668	1.228	0.988	0.0420	0.355	1.176	1.0794
500	0.770	1.246	1.186	0.0448	0.573	1.237	1.1710
1000	0.798	1.254	1.254	0.0483	0.676	1.286	1.2200
1500	0.807	1.257	1.269	0.0495	0.768	1.292	1.2208

Current density mili. amp. per sq. cm.	Overvoltage in Volts.						
	Ag	Sn	Fe electrode	Chem-metal	Brass	Monel metal	Dur-iron
0	.....	0.2411	0.2026	0.2824	.....	.....	0.1680
0.1	0.2981	0.3995	0.2183	0.3160	0.3832	0.1911	0.1710
1	0.4751	0.8561	0.4036	0.6592	0.4967	0.2754	0.1970
2	0.5787	0.9469	0.4474	0.7249	0.5346	0.3022	0.2136
5	0.6922	1.0258	0.5024	0.7885	0.5960	0.3387	0.2443
10	0.7618	1.0767	0.5571	0.8349	0.6459	0.3832	0.2856
50	0.8300	1.1851	0.7000	0.9322	0.8011	0.5345	0.5096
100	0.8749	1.2230	0.8184	0.9696	0.9104	0.6244	0.6129
200	0.9379	1.2342	0.9854	0.9989	1.1088	0.7108	0.7240
500	1.0300	1.2380	1.2561	1.0407	1.2318	0.8619	0.8591
1000	1.0890	1.2306	1.2915	1.0682	1.2544	1.0716	1.0205
1500	1.0841	1.2286	1.2908	1.0859	1.2491	1.2095	1.1400

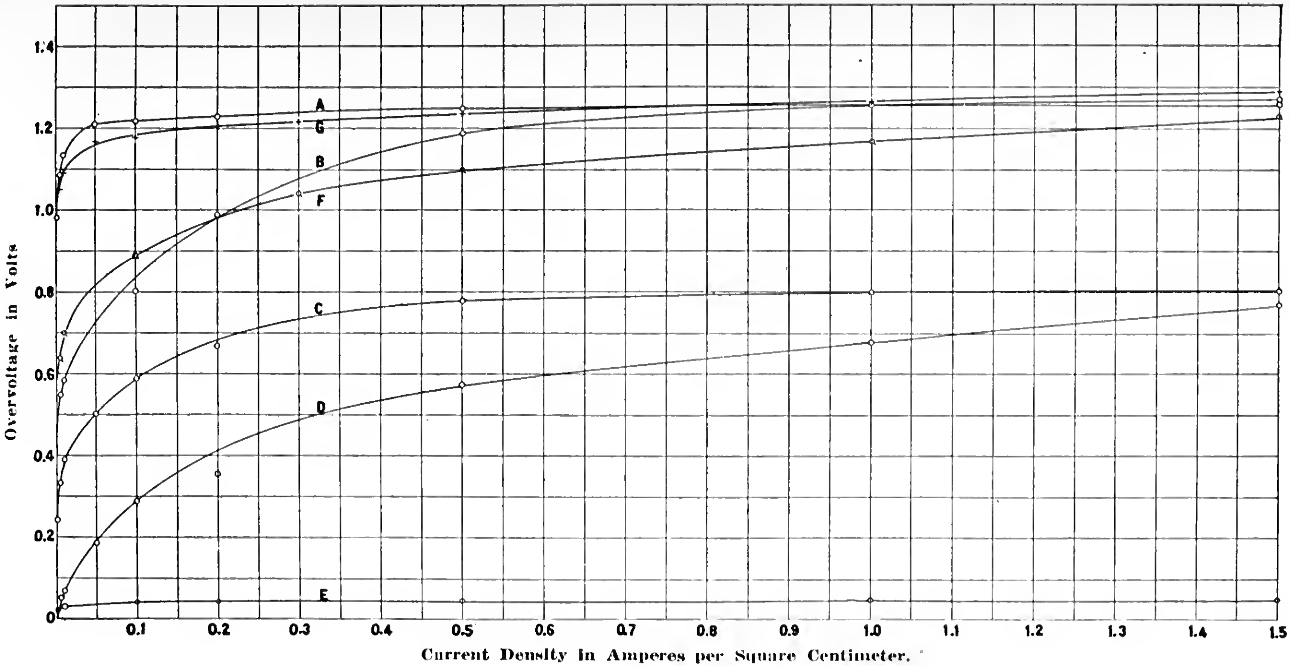

FIG. 5. Hydrogen overvoltages: A, cadmium; B, copper; C, gold; D, smooth platinum; E, platinized platinum; F, carbon; G, lead.

millivolts. At the higher current densities the potential often became rather variable and was recorded therefore in some cases only to hundredths of a volt.

The values for hydrogen overvoltage on zinc, bismuth and nickel are not plotted, but the form of the curves for zinc and nickel is not dissimilar to that of graphite, and the form of the bismuth curve resembles that of lead.

TABLE I.—*Continued*

Hydrogen Overvoltages at 25° C.

Current density in mili. amp. per sq. cm.	Overvoltage in Volts				
	Zn	Carbon	Bi	Ni	Pb
1	0.716	...	0.78	0.563	0.52
2	0.726	...	....	0.633	
5	0.726	0.64	0.98	0.705	1.060
10	0.746	0.70	1.05	0.747	1.090
50	0.926	0.82	1.15	0.890	1.168
100	1.064	0.89	1.14	1.048	1.179
300	1.168	1.04	1.20	1.130	1.217
500	1.201	1.10	1.21	1.208	1.235
1000	1.229	1.17	1.23	1.241	1.262
1500	1.243	1.23	1.29	1.254	1.290

Current density	Overvoltage Hg	Current density	Overvoltage Te	Current density	Overvoltage Pd
0.00	0.2805	0.000	.....	0.000	.....
0.0769	0.5562	0.416	0.0504	0.227	0.0546
0.769	0.8488	0.832	0.3505	1.135	0.1392
1.54	0.9295	1.667	0.4162	2.27	0.1820
3.87	1.0060	4.16	0.4405	4.54	0.2349
7.69	1.0361	8.32	0.1530	11.35	0.3165
38.7	1.0634	41.6	0.4705	22.7	0.4034
76.9	1.0665	83.2	0.4733	113.5	0.7205
154	1.0751	166.7	0.4986	227	0.8607
387	1.1053	416	0.5370	454	0.9521
769	1.108	832	0.5940	1135	1.0513
1153	1.126	1250	0.6590	2270	1.1168
				3400	1.1570

The following notes supplement the table of hydrogen overvoltages:

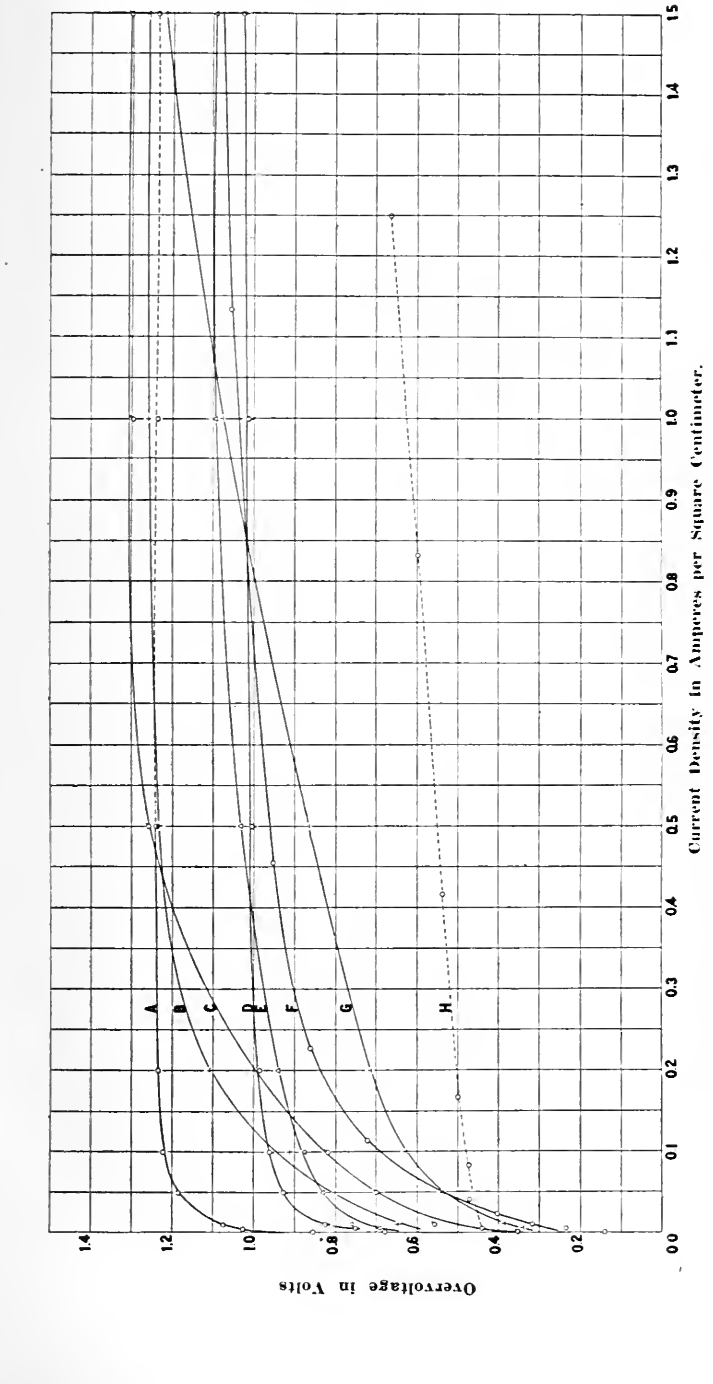

FIG. 6. Hydrogen overvoltages: A, tin; B, brass; C, electrolytic iron; D, chemmetal (values not listed in the table); E, silver; F, palladium; G, monel metal; H, tellurium.

The graphite was a very soft variety, the exposed surface of which was rubbed with No. 0 emery paper.

The tellurium was badly attacked by the acid so that the results are probably of no value.

TABLE II.

Chlorine Overvoltages at 25° C.

Platinized Pt		Smooth Pt		Graphite	
Current density mili. amp. per sq. cm.	Overvoltage	Current density mili. amp. per sq. cm.	Overvoltage	Current density mili. amp. per sq. cm.	Over-voltage
1.1	0.0060	1.1	0.008	40	0.186
5.7	0.0140	5.7	0.0199	70	0.193
14.5	0.0180	11.4	0.0299	100	0.251
21.7	0.0190	22.8	0.0378	200	0.298
38.8	0.0210	43.0	0.0457	500	0.417
60	0.024	100	0.0540	740	0.466
100	0.026	200	0.0870	980	0.489
200	0.035	500	0.161	1131	0.535
520	0.050	750	0.212		
1340	0.089	1000	0.236		
1490	0.103	1350	0.263		

TABLE III.

Bromine Overvoltages at 25° C.

Platinized Platinum		Smooth Platinum		Graphite	
Current density mili. amp. per sq. cm.	Overvoltage	Current density mili. amp. per sq. cm.	Overvoltage	Current density mili. amp. per sq. cm.	Overvoltage
10	0.002	20	0.002	10	0.002
30	0.005	30	0.004	30	0.008
50	0.007	50	0.006	50	0.016
100	0.012	230	0.033	100	0.27
200	0.025	300	0.357	200	0.54
300	0.041	360	0.113	300	0.81
420	0.056	400	0.156	390	0.108
500	0.069	420	0.164	550	0.163
590	0.082	440	0.178	740	0.218
760	0.130	520	0.266	840	0.253
940	0.202	720	0.379	990	0.329
				1110	0.356
				1210	0.400

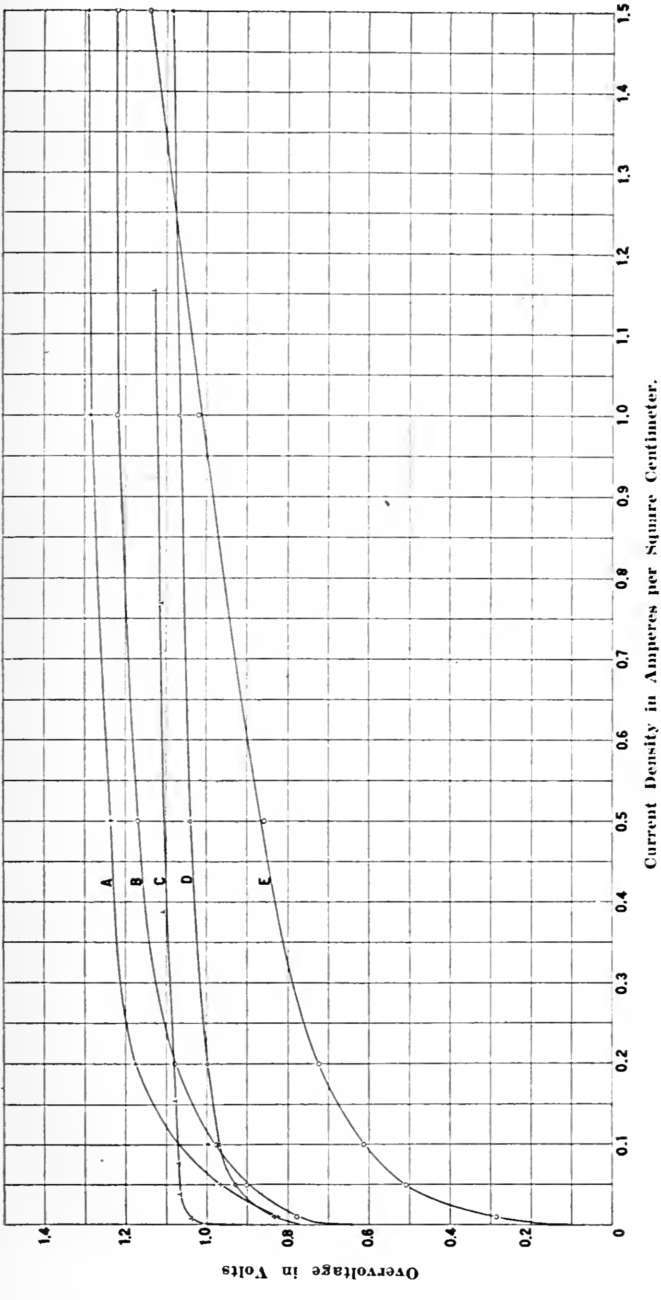

Fig. 7. Hydrogen Overvoltages: A, aluminum; B, graphite; C, mercury; D, chemmetal; E, duriron.

The zinc was obtained from a dry cell casing. It was sufficiently pure so that it would not dissolve in the acid.

The bismuth sample was a piece of the crystalline metal, coated with asphalt except for approximately one square centimeter of its surface. No attempt was made to smooth the surface.

TABLE IV.

Iodine Overvoltages at 25° C.

Platinized Platinum		Smooth Platinum		Graphite	
Current density mili. amp. per sq. cm.	Overvoltage	Current density mili. amp. per sq. cm.	Overvoltage	Current density mili. amp. per sq. cm.	Over-voltage
10	0.006	12.3	0.0039	1.2	0.002
20	0.012	23	0.0070	5.7	0.007
40	0.022	50	0.0127	11.7	0.0139
110	0.032	90	0.0216	19.7	0.0239
220	0.050	130	0.0353	34.8	0.0348
400	0.070	200	0.0510	50	0.0538
710	0.118	310	0.0744	100	0.0974
810	0.130	520	0.120	200	0.175
1000	0.196	690	0.150	400	0.315
1300	0.216	1030	0.220	590	0.451
1460	0.266	1160	0.245	840	0.645
		1330	0.277		
		1500	0.292		

TABLE V.

Oxygen Overvoltages at 25° C.

Current density mili. amp. per sq. cm.	Overvoltage in Volts								
	Soft Graphite	Au	Cu	Ag	Chem-metal	Smooth Pt	Plat'z'd Pt	Smooth Ni	Spongy Ni
1	0.525	0.673	0.422	0.580	0.55	0.721	0.398	0.353	0.414
5	0.705	0.927	0.546	0.674	0.90	0.80	0.480	0.461	0.511
10	0.896	0.963	0.580	0.729	1.02	0.85	0.521	0.519	0.563
20	0.963	0.996	0.605	0.813	....	0.92	0.561	....	....
50	....	1.064	0.637	0.912	1.10	1.16	0.605	0.670	0.653
100	1.091	1.244	0.660	0.984	1.084	1.28	0.638	0.726	0.687
200	1.142	....	0.687	1.038	1.101	1.34	....	0.775	0.714
500	1.186	1.527	0.735	1.080	1.127	1.43	0.705	0.821	0.740
1000	1.240	1.63	0.793	1.131	1.154	1.49	0.766	0.853	0.762
1500	1.282	1.68	0.836	1.14	1.175	1.38	0.786	0.871	0.759

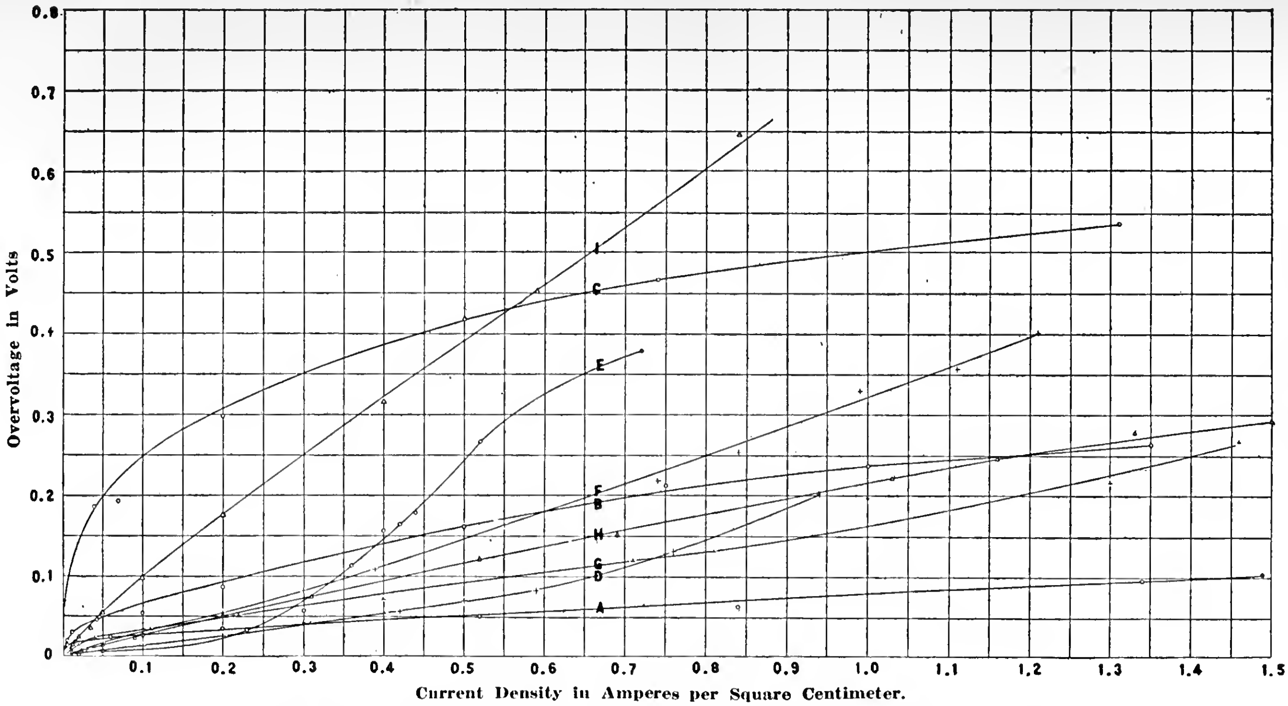

FIG. 8. Halogen overvoltages: A, Cl_2 on platinized platinum; B, Cl_2 on smooth platinum; C, Cl_2 on graphite; D, Br_2 on platinized platinum; E, Br_2 on smooth platinum; F, Br_2 on graphite; G, I_2 on platinized platinum; H, I_2 on smooth platinum; I, I_2 on graphite.

The nickel was electrolytically deposited on a platinum sheet from a pure nickel sulfate solution.

The brass sample was a piece which contained 60 per cent copper and 40 per cent zinc.

The palladium became coated with a dense black layer which could be wiped off, or which cleared up entirely on standing a few minutes, restoring the original bright surface.

The tin sample also became covered with a black layer, similarly to palladium, but this layer was adherent and did not disappear on standing.

The gold, cadmium, copper, aluminum, silver, mercury, palladium, platinum and tin electrodes were of metal which was "chemically pure."

The following note applies to the oxygen overvoltages:

The gold was strongly attacked by the oxygen. After the run it was a bright copper red color. On account of the extraordinarily high overvoltage on gold, these values were checked at three separate times and the figures given appear to be correct. It is possible that the oxide coating (which appears to be very adherent) introduces an ohmic resistance, and that there is a partial valve action as on aluminum.

We will leave the theoretical discussion of these results for a later article, in which a theory of overvoltage will be outlined. The following general observations may be made on the hydrogen overvoltages:

1. The general form of the current density overvoltage curve is similar to that of a logarithm curve. Except in a few cases, however, a simple logarithm equation cannot be fitted to the entire curve. Such an equation which is valid for very low and very high currents would show a much sharper bend in the current density range from 10 to 200 milliamperes per square centimeter, than the observed curves.

2. Metals generally specified as having a high overvoltage, as lead, mercury and cadmium, rise sharply to a high overvoltage at low current densities and then increase but little with increasing current.

3. Metals of "low" overvoltage, as copper and gold, show a more gradual increase of overvoltage with current, but in

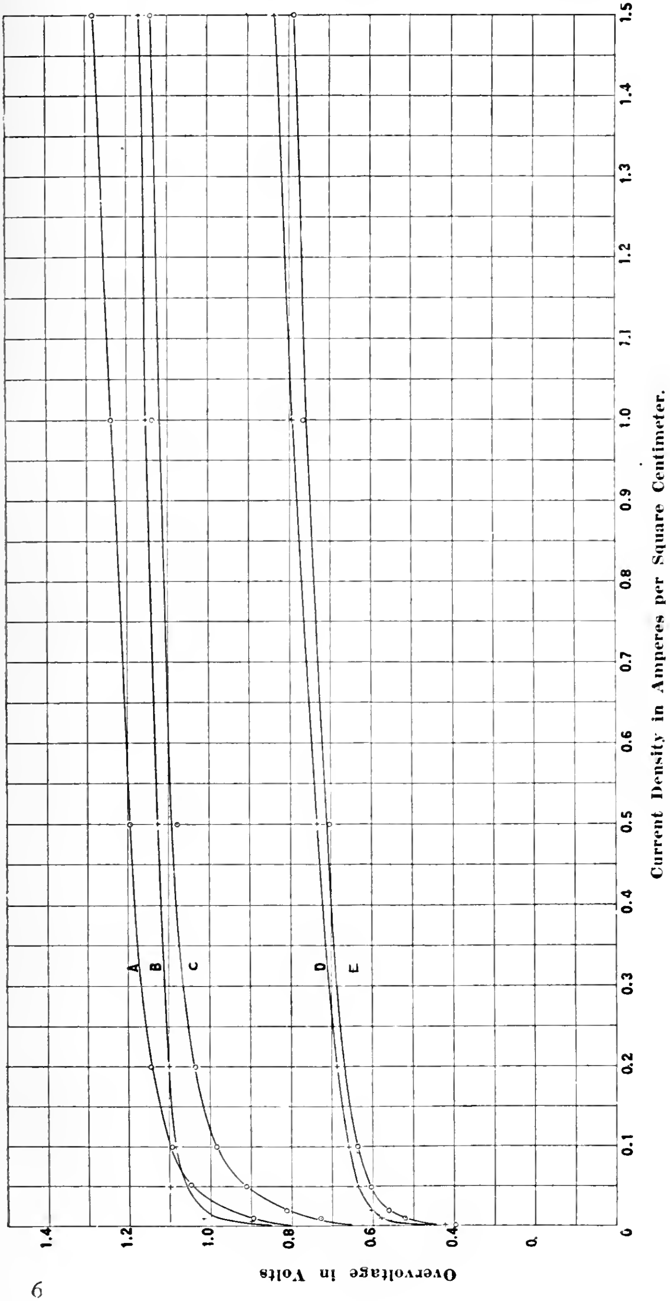

FIG. 9. Oxygen overvoltage: A, graphite; B, chemmetal; C, silver; D, copper; E, platinized platinum.

general with the exception of platinum and gold, finally attain as high an overvoltage as "high overvoltage" metals.

4. No hydrogen overvoltages measured by us exceed the value of about 1.30 volts[12], but the trend of most of the curves is toward this value.

5. Platinized platinum holds a unique position among these other smooth metals in that it maintains its low overvoltage even at exceedingly high current densities. In another experiment, not listed, the current through a well platinized electrode was increased until a spark passed from electrode to solution (at a current density of 14 amperes per square centimeter) and the overvoltage just before this point was reached was only 0.50 volt.

No generalizations of importance are apparent in regard to the halogen overvoltages, except that platinized platinum shows the lowest and graphite the highest values. The forms of the curves are widely different, some being nearly linear.

The oxygen overvoltages are rather less reliable than either the hydrogen or halogen overvoltages, due to unaccountable variations with time. Even after long polarization at a given current, the overvoltage may vary by a tenth of a volt or more. The shape of the curves is in general logarithmic.

SUMMARY.

Values of the hydrogen overvoltage at twenty-two cathodes; of the chlorine, bromine and iodine overvoltages at three anodes; and of the oxygen overvoltage at nine anodes, have been determined and tabulated at various current densities from one milliampere to one and one-half amperes per square centimeter. All measurements were made at 25°C. ± 0.2°C.

An investigation of the method of measuring overvoltage has led to the conclusion that the use of a small glass tip less than one millimeter in diameter, pressed against the active electrode surface while the current is passing, will give correct results.

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[12] While higher values may be found in the literature, we believe they are due to imperfect elimination of ohmic resistances.

DISCUSSION.

W. G. Horsch[1]: In connection with this overvoltage work, has Dr. Knobel ever attempted to analyze the commutator method by applying equations similar to those that have been developed for expressing the rise and decay of current in the ordinary copper wire circuits?

M. Knobel: I have done just that with the curves of overvoltage as a function of the time. The course of these curves is a function of the concentrations of the gas; and deducting the theoretical equation and making the equation fit that curve, constants are obtained which involve the concentration of hydrogen on the electrode. I hope soon to publish the results.

P. Caplain: I think it important to emphasize something that Dr. Knobel has pointed out. Ultimately, it appears, there is no such thing as a high or low overvoltage electrode. If you increase the current sufficiently, and permit a sufficient lapse of time, the hydrogen overvoltages of the metals investigated apparently tend to rise to the same maximum value, provided no secondary reactions take place. The literature of the past has considered low and high overvoltage metals, but the results, in the last analysis, seem to indicate that this is a fallacy.

M. Knobel: I have tried all possible methods and have spent considerable time trying to get reproducible overvoltage measurements, but it seems almost impossible. There are unaccountable variations with time which apparently can not be eliminated.

E. O. Benjamin[2]: I would like to ask Mr. Caplain whether the condition that he approaches, in saying that the overvoltage of all these metals would be nearly alike, is not an approach to a true gas electrode, in eliminating the characteristics of the metallic elements?

P. Caplain: That is what the results seem to indicate. I should not go much further, because Dr. Knobel is personally working on the problem. Assuming that the electrode does become saturated with gas, and applying the gas laws, a value of overvoltage may be calculated which corresponds to that obtained experimentally.

E. O. Benjamin: In carrying on the work of electrolysis

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[1] Chile Exploration Labs., New York City.

[2] Consulting Engr. and Chemist, Newark, N. J.

of water on a large scale, in dealing with a square meter electrode, taking a characteristic volt-ampere curve, we obtain at zero current flow about 1.5 volts as the potential between a nickel anode and an iron cathode in a sodium hydroxide solution. The volt-ampere curve generally assumes a form similar to the curve shown in Fig. 1. We reach point "e" where the curve nearly assumes the form of a straight line, and it seems that from the point "e" to the point "f," we have full saturation of the electrodes. Below "e" we have a partial saturation of the electrodes, and are gradually building up the gas film. Above "f" the resistance seems to increase, due to the formation of molecular gas on the electrodes and the accumulation of gas bubbles in the elec-

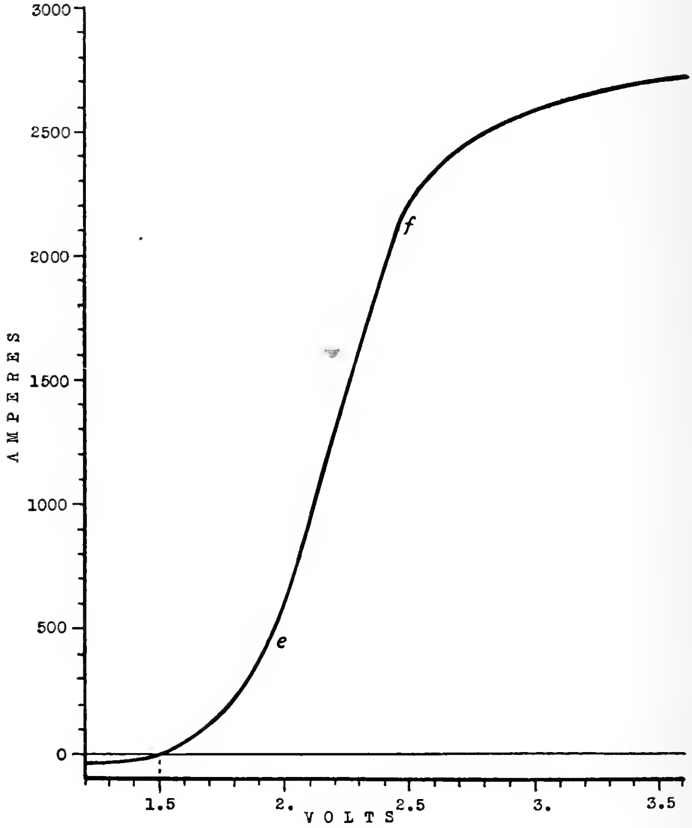

FIG. 1.

trolyte, thereby reducing the effective cross-section of the electrolyte.

This may have some bearing on the fact that a gas electrode is actually formed at a point above "e," which we may assume to be the saturation point of the electrode. In many cases this curve has been referred to as the decomposition characteristic of a cell; and with the same conditions as to electrolyte, temperature, etc., but regardless of pressure, we never vary more than about 0.02 volt.

In a large electrode we do not necessarily have a complete film of the gas, and below that point when a portion of the metallic electrode is exposed, it is what I refer to as an unsaturated condition, meaning that there is metallic surface which can be coated or that will hold a gas film.

M. KNOBEL: That is quite in accord with some results which I am getting. I think it will appear that the maximum overvoltage occurs when there is a single molecular layer of gas on the electrodes; when you start to build up a second layer you are then forming practically free monatomic hydrogen at the maximum overvoltage.

CARL HERING[3]: When the electrode is covered with a molar film of gas, the voltage rises fifty to a hundred fold, and produces an arc over the whole surface, as I showed in a paper some years ago. If the electrode is covered completely with a film of gas, this arc heats the electrode so quickly that one can melt steel under water.

A. H. W. ATEN[4] (*Communicated*): From experiments on the scattering of lead cathodes I concluded in 1916[5] that the overvoltage for hydrogen evolution might be ascribed to a slow combination of hydrogen atoms to hydrogen molecules. If the result of the present authors, that the overvoltage at high current densities approaches a limiting value of 1.3 volt, independent of the nature of the metal (except in the case of plantinized platinum) is considered from this point of view, this would mean that 1.3 volt possibly corresponds to the potential of atomic hydrogen of one atmosphere. Now the potential of atomic hydrogen is given by the formula:

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[3] Consulting Electrical Engr., Philadelphia, Pa.

[4] Prof. of Chemistry, University of Amsterdam, Holland.

[5] Proc. Roy. Acad. Sci., Amsterdam, 18, 1379 (1916).

$$V_H = E_H + 0.058 \log_{10} C_{H^+} - 0.058 \log_{10} P_H \qquad (1)$$

and the potential of molecular hydrogen by

$$V_{H_2} = E_{H_2} + 0.058 \log_{10} C_{H^+} - 0.029 \log_{10} P_{H_2} \qquad (2)$$

where $E_{H_2} - E_H$ is, according to the assumption made above, equal to 1.3 volt.

If one mol of hydrogen, at a pressure of one atmosphere, is dissolved into atoms at constant volume, the pressure will be two atmospheres. The decrease in free energy, in transforming this atomic hydrogen galvanically into molecular hydrogen, will, according to (1) and (2) be given by

$$2F\ (E_{H_2} - E_H) + 2F \times 0.058 \log_{10} 2. \qquad (3)$$

P_{H_2} being $= 1$ and $P_H = 2$.

The value of the second term lies within the experimental uncertainty, and we can put the decrease of the free energy equal to 2 x 96,500 x 1.3 joules = 250,000 joules = 60,000 cal.

The value of 60,000 cal. for the molal dissociation energy of hydrogen is rather low. This figure is calculated from the Bohr-Debyes model of the hydrogen molecule, but the experimental values are higher.

Langmuir[6] finds 84,000 cal., and Isuardi[7] 95,000 cal., whereas Franck, Knipping and Kruger[8] calculate 81,300 ± 5,700 cal. from ionization potentials. Assuming these latter values to be correct, it should be concluded that even at the highest current densities the concentration of H atoms at the cathode remains less than that corresponding to one atmosphere.

M. KNOBEL (*Communicated*): The discussion by Prof. Aten brings up a point of which we were aware, but had excluded from the present article, planning to discuss it with other theoretical interpretations of the data in connection with a theory of overvoltage. In view of the uncertainty in the experimental and calculated values of the free energy of formation of H_2 from H_1, we believe one can conclude that the monatomic hydrogen is at a pressure of approximately one atmosphere, when the maximum overvoltage is reached.

[6] Z. f. Elektrochemie, **23**, 217 (1917).

[7] Z. f. Elektrochemie, **21**, 405 (1915).

[8] Ber. Deut. physik. Ges. **21**, 728 (1919).

A paper presented at the Forty-third General Meeting of the American Electrochemical Society held in New York City, May 3, 1923, Dr. Wm. G. Horsch in the Chair.

ELECTROTITRATION WITH THE AID OF THE AIR ELECTRODE.[1]

By N. Howell Furman.[2]

Abstract.

A brief report of further progress in the study of some uses of the air electrode is given. The results indicate clearly that the air electrode is capable of giving satisfactory results in electrotitration, either in the presence or absence of oxidizing agents.

INTRODUCTION.

The results of a preliminary study of some applications of cells composed of a *N* calomel electrode in conjunction with some one of the electrodes:

(A) Oxygen Electrode,
(B) Air Electrode,
(C) Platinized Platinum Electrode,
(D) Burnished Platinum Electrode,

have been presented in a recent communication.[3]

It was shown in a general way that the oxygen electrode-*N* calomel electrode cell may be used to construct titration curves which are in large measure analogous to those which are obtained in the familiar hydrogen electrode titrations. Special emphasis was placed upon the use of the oxygen electrode in the acidimetry and alkalimetry of solutions which contained strong oxidizing agents.

The majority of the results which were there presented were obtained with the aid of the oxygen electrode. A number of

[1] Manuscript received January 31, 1923.

[2] Contribution from the Chemical Laboratory of Princeton University.

[3] Furman, J. Am. Chem. Soc., 44, 2,685 (1922).

results which were obtained by means of the other electrodes (B, C and D) were included. After a brief preliminary study, the burnished platinum electrode was found to be extremely sensitive to minute variations in the details of handling. Recently van der Meulen and Wilcoxon[4] have described the conditions under which the burnished platinum electrode may be employed successfully.

The air electrode is very slightly influenced by minor changes in the mode of manipulation, in which respect it is superior to the platinized and burnished platinum electrodes. The potential of an air electrode toward any given solution is subject to the well-known drift in value which is ordinarily ascribed to the process of oxide formation.[5] Nevertheless satisfactory titration curves may be obtained either in the presence or absence of oxidizing agents. Furthermore, a fair approximation of the hydrogen ion concentration may be obtained by making an empirical calibration of the electromotive force of the air electrode-N calomel electrode cell with the aid of a series of solutions of known hydrogen ion concentration.

Arthur and Keeler[6] have described a continuous recording apparatus for the measure and control of the alkalinity of boiler feed water by means of the air electrode-0.1 N calomel electrode combination. The electromotive force readings of this cell were calibrated in terms of grains of alkalinity per gallon of water. They state that this method involving the air electrode was more reliable under continuous operating conditions that the colorimetric method in the hands of unskilled operators.

EXPERIMENTAL.

The apparatus, mode of procedure, details of standardizing reagents, and general technique were described in the previous paper. It is perhaps well to repeat that the electromotive force values were repeatedly referred to the value of a Weston saturated type standard cell by means of a potentiometer set of moderate precision.[7]

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[4] Van der Meulen and Wilcoxon, Ind. and Eng. Chem., **15**, 62 (1923).

[5] A brief review of the literature relating to the oxygen and air electrodes was given in the previous paper (ref. 3) p. 2686. Data were given relating to the magnitude of the drift to be expected.

[6] Arthur and Keeler, Power. **55**, 768 (1922).

[7] Leeds and Northrup students' type potentiometer, and a galvanometer of current sensitivity 2 mm. per micro-ampere.

A number of curves typical of those obtained are plotted in Fig. 1. It should be noted that the form of the apparatus made it necessary to dilute the solutions somewhat before the titrations were commenced. The volume was ordinarily 75 cc. at the start of each titration.

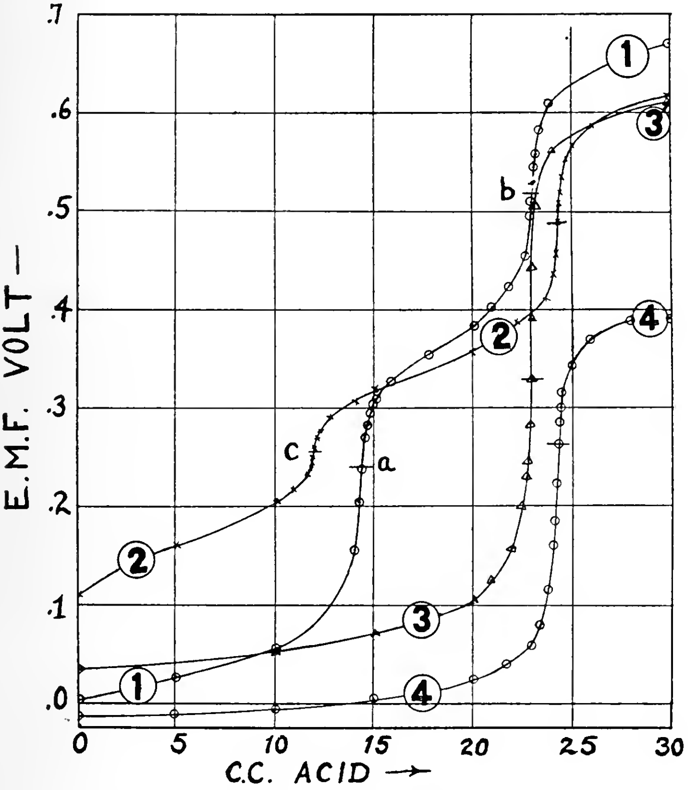

FIG. 1. Air Electrode Titrations.

(1) Titration of 15.87 cc. of 0.09123 *N* alkali and 8.33 cc. 0.1000 *N* Na_2CrO_4 with 0.09986 *N* HCl.
Cal. 14.50, found 14.55 cc. acid to neutralize free alkali.
Calc. 8.34, found 8.43 cc. acid to transform chromate into dichromate (distance *a* to *b* curve 1).

(2) 25 cc. of 0.5000 *N* Na_2CO_3 titrated with 0.5176 *N* H_2SO_4.
Point *c* (bicarbonate point) calc. 12.07, found 12.19 cc. of acid.
Second inflection (complete neutralization) calc. 24.15, found 24.20 cc. of acid.

(3) Titration of 25 cc. 0.09123 *N* NaOH with 0.09986 *N* HCl. Calc. 22.84, found 22.93 cc.

(4) Titration of 25 cc. 0.4937 *N* NaOH with 0.5050 *N* acetic acid. Calc. 24.44, found 24.40 cc.

A qualitative measure of the difference in hydrogen ion concentration of 0.1 *N* hydrochloric acid, as contrasted with 0.5 *N* acetic acid, is given by the relative positions on the voltage scale of the end portions of curves (3) and (4) respectively. Point *c* curve (2) represents the completion of the conversion of sodium carbonate into bicarbonate. Point *a* curve (1) represents the neutralization of free alkali in the presence of chromate; while point *b* represents the completion of the conversion of chromate into dichromate.

Fig. 2 contains titration curves for nitric (1) and perchloric

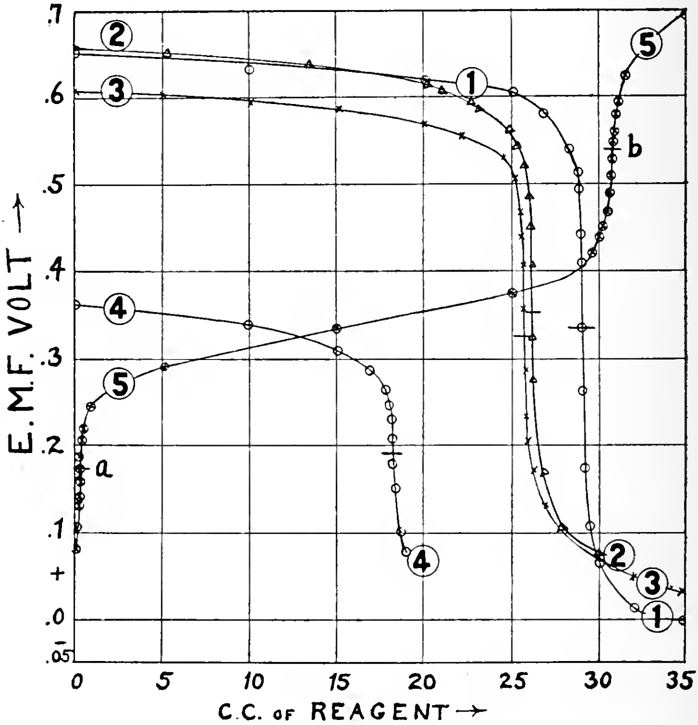

FIG. 2. Air Electrode Titrations.

(1) 25 cc. 0.5285 *N* nitric acid titrated with 0.4541 *N* NaOH. Calc. 29.10, found 29.15 cc.

(2) 24. cc. of 0.09986 *N* HCl titrated with 0.09123 *N* NaOH. Calc. 26.27, found 26.25 cc.

(3) Titration of 25 cc. of 0.09497 *N* $HClO_4$ with 0.09123 *N* NaOH. Calc. 26.02, found 25.98 cc.

Data showing the results of No. (4) and (5) will be found in exp. 7, Table I.

(3) acids, together with a curve for hydrochloric acid (2) for purposes of comparison. A salt bridge of approximately 0.1 *N* sodium nitrate was interposed between the solution and the calomel electrode during the titration of the nitric acid. Curve (4) represents the titration of dichromate, in a mixture of chromate and dichromate, with alkali. At the end of this titration all of the chromate was converted into dichromate by means of standard acid. The distance *a* to *b* (curve 5) represents the amount of acid required.

In the previous paper[8] it was shown that an accurate determination of free alkali in the presence of chromate (providing the carbonates were absent), or of free acid in the presence of dichromate, could be made with the aid of the oxygen or air electrodes. The method may be extended to the analysis of mixtures of chromate and dichromate as the following results will serve to show.

Solutions of chromate and dichromate were prepared. Each solution was standardized against freshly standardized ferrous sulfate by the electrometric method of Forbes and Bartlett.[9] Known portions of the solutions were mixed. The mixture was then analyzed by one of the following methods.

(A) The amount of acid necessary to convert the chromate, which was present in the mixture, into dichromate, was determined electrometrically. The total amount of dichromate was then determined electrometrically either (1) by means of standard alkali, or (2) by means of freshly standardized ferrous sulfate, after the addition of a large excess of acid. Total alkali requirement minus acid equivalent to chromate equals alkali equivalent to dichromate present.

(B) The amount of alkali necessary to convert dichromate into chromate was determined. The total acid requirement was then found (1) by direct titration with standard acid (distance *a* to *b* curve 5, Fig. 2) or (2) by reduction with standard ferrous sulfate after strongly acidifying the solution. Then, total acid requirement minus alkali equivalent to dichromate equals acid equivalent to chromate.

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[8] Furman, J. Am. Chem. Soc., 44, 2,685 (1922).

[9] Forbes and Bartlett, J. Am. Chem. Soc. 35, 1,527 (1913).

All of the electrometric methods, as well as a number of other physico-chemical methods, agree in finding two sharply defined changes in the neutralization curves of chromic acid or of acidified chromate solutions. Similar changes appear in the curves for the acidification of alkaline chromate solutions. Margaillan[10] investigated the neutralization of $M/30$ solutions of chromic acid, both by means of conductance titration and hydrogen electrode titration. By both methods a sharp change was revealed when one mole of sodium hydroxide per mole of chromic anhydride (CrO_3) had been added; a second sharp change appeared when two moles of alkali per mole of chromic anhydride had been added. Hughes[11] who has recently investigated the glass cell (glaskette), with an improved apparatus similar to that of Haber and Klemensiewicz[12], presents an interesting curve for the neutralization of chromic acid. The two inflections which the author obtained with the aid of the oxygen or air electrodes appear at hydrogen ion concentrations (empirically estimated) which are in fair agreement with those obtained by Hughes. His method seems to be the most reliable which has thus far been devised for measuring hydrogen ion concentrations in solutions of highly colored oxidizing agents.

TABLE I.

Electrometric Analysis of Mixtures of Chromate and Dichromate.

Results No. 1 to 3 are calculated to 0.1 N; No. 4 to 8 to 0.5 N.

No.	1 Dichromate Taken cc.	2 Dichromate Found cc.	3 Chromate Taken cc.	4 Chromate Found cc.	5 Method Used (see above)
1	8.33	8.44	18.05	17.93	B 2
2	16.67	16.72	18.05	17.96	B 2
3	8.33	8.44	7.19	7.24	B 1
4	16.85	16.89	7.19	7.20	A 1
5	16.85	16.79	14 38	14.45	A 1
6	33.70	33.78	14.38	14.44	A 1
7	16.85	16.80	14.38	14.39	B 1
8	33.70	33.71	7.19	7.24	B 1

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[10] Margaillan, Compt. rend., **157**, 994 (1913).

[11] Hughes, J. Am. Chem. Soc., **44**, 2,860 (1922).

[12] Haber and Klemensiewicz, Z. physik. Chem., **67**, 385 (1909).

These physico-chemical results have been used as arguments for or against (depending upon the view-point of the individual) one or the other of the two stoichiometrically equivalent sets of reactions:

$$\text{I} \left\{ \begin{array}{lll} \text{(a)} & H_2CrO_4 + NaOH & = NaHCrO_4 + H_2O \\ \text{(b)} & NaHCrO_4 + NaOH & = Na_2CrO_4 + H_2O \end{array} \right.$$

$$\text{II} \left\{ \begin{array}{lll} \text{(a)} & \tfrac{1}{2}(H_2Cr_2O_7 + 2NaOH & = Na_2Cr_2O_7 + 2H_2O) \\ \text{(b)} & \tfrac{1}{2}(Na_2Cr_2O_7 + 2NaOH & = 2Na_2CrO_4 + H_2O) \end{array} \right.$$

In this work the second set (II) has been adopted as being more probable and convenient in picturing the relations at the two points of inflection.[13]

TABLE II.

Variation of E. M. F. of Air-N Calomel Cell with Changes in Hydrogen Ion Concentration.

Time Min.	Approx. Normality		E. M. F. Volt	Time Min.	Approx. Normality		E. M. F. Volt
	Acidic	Basic			Acidic	Basic	
0.	0.007	....	0.640	25.	....	0.004	0.077
2.5	0.007	....	0.643	27.5	....	*0.004	0.086
5.	0.007	....	0.644	30.	....	0.004	0.088
6.	....	0.006	0.037	30.5	0.007	....	0.630
7.5	....	0.006	0.029	35.	0.007	....	0.632
10.	....	0.006	0.038	36.	....	0.003	0.118
10.5	0.007	....	0.615	38.	....	0.003	0.101
12.5	0.007	....	0.618	40.	....	0.003	0.101
14.	0.007	....	0.617	41.	0.007	....	0.634
17.	0.007	....	0.616	45.	0.007	....	0.633
20.	0.007	....	0.615	50.	0.007	....	0.630
21.	....	0.004	0.076	185.	0.007	....	0.625
22.5	....	0.004	0.073				

* Change caused by one drop of approx. 0.5 *N* acid.

The experience of Arthur and Keeler, as well as numerous observations made in the course of this work, point to a field of usefulness of the air electrode in approximate hydrogen ion concentration measurement and control. Some idea of the readiness of response of the air electrode to repeated variations in

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[13] A comprehensive discussion of the nature of chromic acid, and the equilibrium relations in chromate and dichromate solutions, together with abundant literature references are to be found in Abegg's Handbuch der anorg. Chem., IV, 1, 2nd half, pp. 306-311, Pub. by S. Hirzel, Leipzig, 1921.

hydrogen ion concentration may be obtained from the results in Table II. Known quantities of acid and alkali were alternately added to a given volume of solution.

It should be noted that the readings in alkaline solution are more sluggish in coming to a state of gradual drift than are those in acid solution.

DISCUSSION.

M. R. THOMPSON[1]: Prof. Furman's paper supplies information on an interesting phase of electrode potential measurements, and is an important contribution to this subject.

In his previous paper mentioned, a more extended discussion was given of the irreversibility of the electrode. If the oxygen (or air) electrode were really reversible, indicating a definite equilibrium for oxygen (or equivalent hydroxyl) ions, the measurements obtained should be complementary to those of hydrogen ion concentrations by the reversible hydrogen electrode and would readily serve to calculate the latter concentrations. This depends, of course, upon the well-known equilibrium of hydrogen and hydroxyl ions in water, giving at about 25° C. the relationship

$$C_{H^+} = \frac{10^{-14}}{C_{OH^-}}$$

Or in Sorensen units, pH = 14 — pOH. Physico-chemical neutrality exists at pH = pOH = 7 (which is the end point only when strong acids and bases are combined), and in the diagrams this point is represented roughly by an e. m. f. not far from 0.3 volt.

Actually, Prof. Furman and others have shown that the oxygen (or air) electrode is not quite reversible and that measurements by means of it only serve, at best, to calculate approximate hydroxyl and hydrogen ion concentrations, if the latter are desired. This condition does not interfere, however, with extensive applications of the electrode for relative determinations, such as the accurate establishment of the end points in certain classes of

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[1] Assoc. Chemist, Bureau of Standards, Washington, D. C.

titrations and the paper has demonstrated this fact satisfactorily. We may expect a rapidly increasing field of usefulness for the air electrode.

N. H. FURMAN: I hope that the accuracy of this method of measuring hydrogen and hydroxyl ion concentrations will not be taken too seriously. The experience of the research department of Leeds & Northrup Co.[2] and my own seem to point out that about all you can hope for is an accuracy of one-half of a Sorensen (pH) unit.

I did not wish to give the impression that this electrode will give values for hydrogen or hydroxyl concentration of the same order of accuracy as the hydrogen electrode. It does serve as a rough substitute for the hydrogen electrode in some cases, where the solution is exposed to air and must remain so. It has some usefulness in rough control work.

O. C. RALSTON[3]: For over a year we have been using an air electrode one centimeter square and heavily platinized at the Pacific Experiment Station of the Bureau of Mines (Berkeley, Calif.) for the purpose of following the course of hydrolytic reactions, either on the large scale or during titration in the laboratory. It is of great use in following hydrolytic purification of electrolytes of zinc sulfate, copper sulfate, or in preparing iron-free aluminum sulfate solutions.

We found it necessary to study the air electrode in much the same way that Prof. Furman has done and we agree, I think, almost entirely with his conclusions. The most important thing about it is that the air electrode can not be used as an exact measure of hydrogen ion (or hydroxyl ion) concentration, but as an indicator of the end of certain reactions, due to changes in direction of the voltage-titration curve or voltage-time curve, it is very satisfactory. I had hoped to present a paper at this meeting on the more practical applications of the air electrode, but will have to postpone its presentation.

For such a reaction as the separation of ferric iron from a copper sulfate solution, using powdered limestone or copper oxide for hydrolyzing the ferric sulfate, the voltage-titration curve is

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[2] Private communication from Dr. I. B. Smith of Leeds & Northrup Co.

[3] U. S. Bureau of Mines, Berkeley, Calif.

almost horizontal till nearly all the iron has been precipitated as a basic salt, and then the voltage suddenly drops, indicating the end of the reaction. Chemical control of this hydrolysis is difficult, because if a sample of the pulp is filtered at this point the iron stays in the filtrate as a colloidal compound which makes the solution look like coffee. Under these conditions it is difficult for the chemist to determine if all the iron in true solution has been hydrolyzed.

The air electrode, of course, functions in oxidizing solutions where the hydrogen electrode fails, especially solutions containing ferric iron. Since most technical operations with inorganic compounds in solution are complicated with the presence of iron in the solution, the hydrogen electrode has previously found little use in this field. On the other hand, the air electrode is not only satisfactory but more easily manipulated, because the solutions in practice are usually saturated with air or are stirred or agitated with air so that the form of air electrode that can be used is extremely simple.

W. G. HORSCH[4]: In studying methods of this sort, starting out possibly with pure solutions and then trying to apply the results to solutions that contain other constituents, we must be careful that the method is peculiar to the reaction that we are studying or to the endpoint that we wish to obtain.

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[4] Chile Exploration Labs., New York City.

A paper presented at the Forty-third General Meeting of the American Electrochemical Society held in New York City, May 3, 1923, Dr. Wm. G. Horsch in the Chair.

THE HYDROGEN ELECTRODE IN ALKALINE SOLUTIONS.[1]

By A. H. W. Aten.[2]

Abstract.

When a hydrogen electrode, saturated with hydrogen, is in equilibrium with 0.1 *N* HCl, it is in the same state of equilibrium with 1.0 *N* HCl, and *vice versa*. This is not the case, however, when the solution of an alkali is used in place of an acid. When a hydrogen electrode in equilibrium with 1.0 *N* NaOH is put in 0.1 *N* NaOH, or the reverse, a considerable time period is required to reach a new equilibrium. The same phenomenon is observed in a more marked degree when the electrode is changed from 0.1 *N* NaOH to 0.1 *N* HCl, or the reverse. The explanation suggested is that the electrode must absorb Na or give it off, as the case may be, in order to reach an equilibrium with the final solution. [C. H. E.]

In the course of an investigation, in which a hydrogen electrode was brought into contact with solutions of varying alkalinity, it was found that the potential in a given solution was markedly affected by the alkalinity of the preceding solution. This phenomenon was further examined, and the following is an account of part of the results.

In the apparatus shown in Fig. 1 the tube A, containing the hydrogen electrode, is filled with a solution of a given alkalinity, say 0.1 *N*, and the tube B with a solution of different alkalinity, say 1.0 *N*. After the hydrogen electrode has reached equilibrium in the 0.1 *N* solution, this solution is removed through the tap C, and the 1.0 *N* solution, which has been saturated with hydrogen, is introduced through the tap D. The potential of the hydrogen

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[1] Manuscript received January 15, 1923.

[2] Prof. of Chemistry at the Univ. of Amsterdam.

electrode is measured against a decinormal calomel electrode. The liquid junction is made by a saturated solution of potassium chloride. The values given are those immediately measured, without attempting to correct them further for liquid potentials.

The temperature was room temperature, about 18° C. The electrodes consisted of gold sheet, 0.5 x 3 cm., covered with palladium black by electrolyzing a solution of palladium chloride (0.3 per cent palladium) with 0.1 amp. for 5 min. Then these electrodes were cathodically polarized in a solution of sulfuric acid, in order to reduce the absorbed palladium chloride, and to charge them with hydrogen.

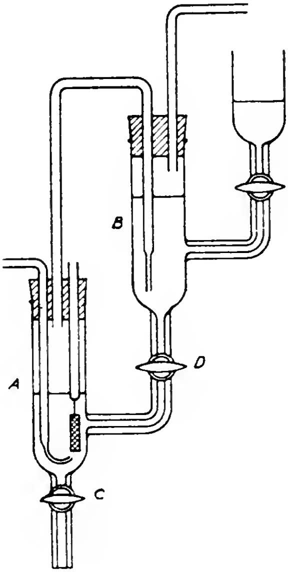


FIG. 1

When an electrode thus treated was brought into contact with 0.1 *N* HCl, contained in tube A, the potential rose in 8 min. from +0.340 to +0.400. In contact with 1.0 *N* HCl it rose from +0.288 to +0.343 in 14 min. Under these circumstances the equilibrium was reached in a short time. It should be observed that, in bringing the electrode into the tube A, the entering of some air could not be avoided. Hence the potential is initially too negative.

When now, after equilibrium was reached in 0.1 *N* HCl, this solution was replaced by 1.0 *N* HCl, which had been saturated with hydrogen in the tube B, the potential was immediately +0.343. In the same way, when 1.0 *N* HCl was replaced by 0.1 *N* HCl, the potential was immediately +0.401. These are sensibly the equilibrium potentials.

From this observation it follows that, when a hydrogen electrode, saturated with hydrogen, is in equilibrium with 0.1 *N* HCl, it is in the same state in equilibrium with 1.0 *N* HCl, and *vice versa.* This is no longer the case when a solution of an alkali is used in place of an acid.

If a hydrogen electrode, which is in equilibrium with 1.0 *N* NaOH, is brought into 0.1 *N* NaOH, the potential is at the beginning some 20 millivolts too positive, and reaches after some time the equilibrium potential for 0.1 *N* NaOH.

On the other hand, when an electrode, which is in equilibrium with 0.1 *N* NaOH, is brought into contact with a solution of 1.0 *N* NaOH, its potential is at first some 20 millivolts too negative and falls more or less slowly to the equilibrium potential. The same phenomenon is observed, and in a more marked degree, when a hydrogen electrode is brought from 0.1 *N* NaOH into 0.1 *N* HCl.

It is evident that a hydrogen electrode in an acid should behave otherwise than in an alkali, since in an acid the only active substance on the electrode is hydrogen, while in sodium hydroxide sodium also may be electromotively active.

If metallic sodium forms a solid solution with palladium, the electrode cannot be in equilibrium with a solution of sodium hydroxide, unless it contains metallic sodium at a certain concentration, which is determined by the hydrogen potential, *i. e.,* by the hydroxyl ion concentration, and also by the sodium ion concentration. The electrode is therefore a sodium electrode as well as a hydrogen electrode.

Let us suppose that the potential of the sodium-palladium electrode is a logarithmic function of the sodium content, then the potential will be given by an equation of the form:

$$E_{Na} = \epsilon_{Na} - 0.058 \log_{10} C_{Na} + 0.058 \log_{10} C_{Na^+} \qquad (1)$$

where C_{Na} denotes the concentration of the metallic sodium in the palladium, and C_{Na^+} the concentration of sodium ions in the solutions. ϵ_{Na} is a constant.

The potential of the hydrogen electrode is given by

$$E_H = \epsilon_{OH} - 0.058 \log_{10} C_{OH^-} \tag{2}$$

When we put $C_{Na} = 1$ for an electrode which, both with respect to hydrogen and to sodium, is in equilibrium with a solution for which $C_{Na^+} = 1$ and $C_{OH^-} = 1$, then it follows, while E_{Na} must be equal to E_H,

$$\epsilon_{Na} = \epsilon_{OH}$$

Hence the sodium concentration of an electrode in equilibrium with a solution of sodium hydroxide of the concentration C_{OH^-} and C_{Na^+} must be:

$$C_{Na} = C_{Na^+} \cdot C_{OH^-} \tag{3}$$

If now an electrode, which is in equilibrium with a solution of the concentration $C'_{Na^+} \cdot C'_{OH^-}$ is brought into contact with a solution of the concentration $C''_{Na^+} \cdot C''_{OH^-}$ its hydrogen potential will be:

$$E_H = \epsilon - 0\ 058 \log_{10} C''_{OH^-} \tag{4}$$

and its sodium potential

$$E_{Na} = \epsilon - 0.058 \log_{10} C'_{Na^+} C'_{OH^-} + 0.058 \log_{10} C''_{Na^+} \tag{5}$$

and the difference:

$$E_{Na} - E_H = 0.058 \log_{10} \frac{C''_{Na^+} \cdot C''_{OH^-}}{C'_{Na^+} \cdot C'_{OH^-}} \tag{6}$$

If thus an electrode, charged with hydrogen at one atmosphere, is brought from 0.1 *N* HCl into 0.1 *N* NaOH, the electrode is not in equilibrium with this latter solution, because it contains no sodium. It will therefore, in an alkaline solution, lose hydrogen and take up sodium, according to the equation:

$$H + Na^+ \rightarrow H^+ + Na$$

If this reaction takes a certain time, the electrode will at first be too negative, and approach the equilibrium potential, as the above given reaction proceeds.

In the same way, if an electrode is brought from 1.0 *N* NaOH into 0.1 *N* NaOH, it will be, according to the equations (4) and (5) 0.058 volt more positive, if it behaves fully as a sodium electrode, and 0.058 volt more negative, if it acts fully as a hydrogen electrode. Now neither of these is probable, so one will find a value that lies between the potential of the sodium electrode, and that of the hydrogen electrode. In any case, however, the potential must at first be more positive than the equilibrium potential.

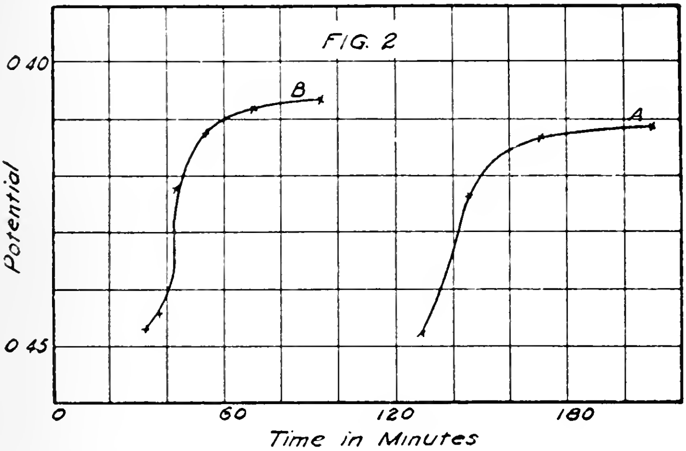
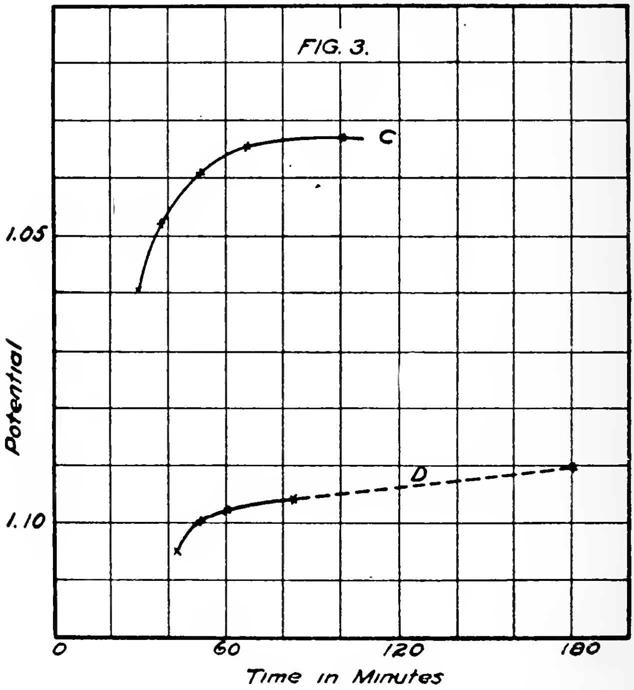


Fig. 2 shows two curves which give the potential as a function of time for two electrodes which had been in contact with a solution of sodium hydroxide, and were then brought into 0.1 *N* HCl. "A" relates to an electrode covered with platinum black, that had been in contact with 1 *N* NaOH for three days, during which time a slow current of hydrogen was passed through the apparatus. "B" is the curve for an electrode, covered with palladium black, which was left in 0.1 *N* NaOH for thirty hours. Both electrodes were completely immersed in the liquid. It is seen that the potential is at first some 40 or 50 millivolts too positive and that, after an hour, the equilibrium potential is approached, though not yet fully reached.

The same behavior is found when an electrode is brought from a stronger alkaline solution into a weaker one. In Fig. 3 the curve

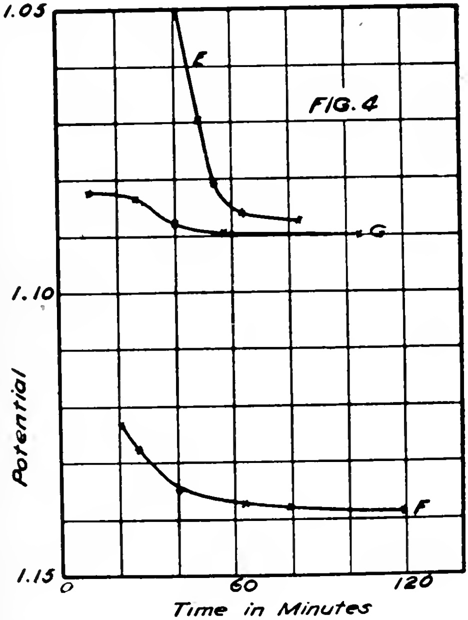
"C" represents the potential for an electrode which has been in contact with 0.1 N NaOH and is then put into a 0.01 N solution. Curve "D" gives the potential, when a 1.0 N solution of NaOH is replaced by a 0.1 N solution. In the latter case the potential was, after an hour, still 0.008 volt too positive. Next morning the equilibrium potential was reached. The total difference between the potential immediately found and the equilibrium potential is here less than for the curve "C," because this electrode had been in contact with the 1.0 N NaOH for two hours only, while the electrode C remained thirty hours in the 0.1 N solution.

FIG. 3.



The reverse is observed when an electrode is brought from an acid solution into an alkaline solution, or from a weaker alkaline solution into a stronger one. This is shown by the curves in Fig. 4, of which "E" relates to an electrode which was brought from 0.1 N HCl into 0.1 N NaOH. "F" gives the potential, when passing from a 0.01 N solution of NaOH to a 1 N solution, and "G" when a solution of 0.01 N NaOH is replaced by a 0.1 N solution.

The same phenomena are observed when the electrode has been charged with hydrogen and sodium by cathodic polarization. The apparatus, shown in Fig. 5, permits polarizing an electrode "A" in a solution of NaOH, while a current of hydrogen is passed through this solution, and through a second solution, contained in the tube B, which is in this way freed from oxygen. When the electrode "A" is polarized for 10 min. with a current of 10 milliamperes and the current is then broken, the potential, immediately after polarization, is found too positive.



The deviation from the equilibrium potential increases with increasing dilution of the alkali as follows:

Concentration of NaOH	Deviation millivolts
1.0 N	0
0.49 N	4
0.21 N	6
0.083 N	13

This may be explained by observing that during the electrolysis the liquid in contact with the electrode is more strongly alkaline than the bulk of the liquid, because of the discharge of hydrogen ions at the cathode. This concentration polarization gives the cathode a too positive potential. In consequence the electrode takes up more sodium from the solution than corresponds to the equilibrium potential. The electrode remains, therefore, some time after polarization, too positive.

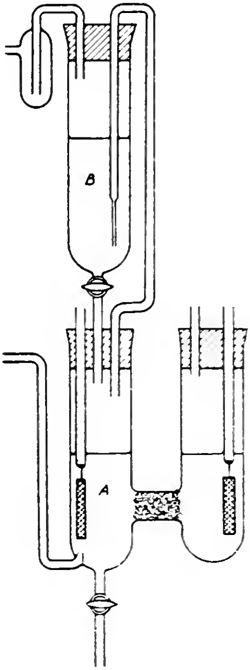


FIG. 5

As the relative increase in alkalinity during electrolysis is greatest for the more dilute solutions, the effect on the potential will be greatest in solutions with small alkali content.

When now, a short time after polarization, the solution is diluted with its own volume of water, the potential is again found too positive. This can be ascribed to the fact that the electrode is still too positive as a result of the polarization.

If, on the other hand, the electrode was polarized in 0.005 *N*

NaOH, and then, immediately after polarization, a strong solution of NaOH was introduced, the potential was found 22 millivolts too negative, when the resulting solution was 0.3 *N*. This experiment is more decisive, because it shows that the electrode, though at first too positive, becomes too negative by greatly increasing the alkali content. The most certain proof that a hydrogen electrode in alkali acts partly as a sodium electrode would be given if it were possible to show that in increasing the alkali content the electrode takes temporarily a more negative potential. This would mean that by increasing the alkali content ten times, the electrode should be more than 58 millivolts too negative. So great a value was never found.

One can however leave the hydroxyl ion concentration almost unchanged, and increase the sodium ion concentration by adding a strong solution of NaCl to a weak solution of alkali.

In this case the potential of an electrode must, according to equation (5) become more negative if it behaves as a sodium electrode, and remain approximately constant if it acts as a hydrogen electrode. Now it was found that the potential of an electrode, covered with smooth palladium, after polarization in 0.01 *N* NaOH fell as much as 30 millivolts, when a strong solution of sodium chloride was added, so as to make the liquid 0.2 *N* with respect to sodium chloride.

When the electrode is polarized in a solution containing NaCl + NaOH, the potential after polarization is about 20 millivolts more positive than in a solution which is only 0.01 *N* to NaOH, corresponding to a greater sodium content of the electrode. Now it is evident that the electrode should take up more sodium in this latter experiment, because polarization in a solution of NaOH with a great excess of NaCl gives rise to a stronger alkalinity at the cathode than in NaOH alone. In the first case the hydroxyl ions are removed by diffusion only, in the second case by diffusion and by the current.

The same experiment was repeated with an electrode covered with palladium black, because smooth palladium contains a relatively small quantity of hydrogen, and the electrode is therefore very sensitive to oxygen. So a trace of oxygen, contained in the solution of sodium chloride, might give the electrode a too negative potential. Here a saturated solution of NaCl was used, which had been boiled, and saturated with hydrogen for two hours. Only a small quantity of this liquid was introduced into 0.01 *N* NaOH. The potential fell immediately from +1.043 to +1.012 volt and rose afterwards very slowly to the equilibrium potential.

A paper presented at the Forty-third General Meeting of the American Electrochemical Society held in New York City, May 3, 1923, Dr. Wm. G. Horsch in the Chair.

THE REACTIONS OF THE LEAD STORAGE BATTERY[1]

By M. Knobel[2]

Abstract.

The theories of the lead storage battery are discussed. The results of the author's investigations, together with the work of MacInnes, Adler and Joubert, complete the evidence in favor of the Gladstone and Tribe theory of the reactions in the lead storage battery. The claim of Fèry that only one mol of sulfuric acid is used per two faradays on discharge is not supported, which tends to disprove the theory he proposes.

The theory of the reactions of the lead storage battery proposed by Fèry[3] is represented by the following equation for discharge:

$$Pb + H_2SO_4 + Pb_3O_7 = PbSO_4 + H_2O + 3PbO_2 \qquad (1)$$

or possibly

$$Pb + H_2SO_4 + Pb_2O_3 = PbSO_4 + H_2O + PbO_2 \qquad (2)$$

It differs from the generally accepted theory of Gladstone and Tribe[4] represented by the equation

$$Pb + PbO_2 + 2H_2SO_4 = 2PbSO_4 + 2H_2O \qquad (3)$$

in the supposition that there is a higher oxide of lead than the peroxide on the anode which changes over to the peroxide on discharge. A consequence of this supposition is that only one

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[1] Manuscript received November 22, 1922.

[2] Contribution from the Rogers Laboratory of Physics, Electrochemical Laboratory, Massachusetts Institute of Technology.

[3] Lumiere Elec., **34**, 305 (1916); J. Physique, **6**, 21 (1916); Bull. Soc. d'en. Ind. Nat., **118**, 92 (1919).

[4] "The Chemistry of the Secondary Batteries of Plante and Faure," MacMillan, 1883. For a discussion of this reaction see also Dolezalek "The Theory of the Lead Accumulator," Translated by Von Ende.

mol of sulfuric acid should be used for every two faradays on discharge, instead of two mols, as Gladstone and Tribe's theory requires. Fèry supports his theory by the claims that the higher oxide of lead can be shown to exist on the fully charged plate by chemical analysis; that lead peroxide will not give the potential of the storage battery anode; and that only one mol of sulfuric acid per two faradays is actually used on discharge. The careful experiments of MacInnes, Adler and Joubert[5] cast considerable doubt on the first two of these claims. They found by analysis that the material on the positive plate coincided closely in composition with lead peroxide. They also found that PbO_2 formed chemically and electrochemically on a platinum sheet gave the same electromotive force in sulfuric acid as the storage battery anode, contrary to the experiments of Fèry.

TABLE I.

Amp.	Time of discharge in hr.	ϕ
5	6	1.40
4	9	1.48
3	14	1.56
2	24	1.69
1	59	1.79

In regard to the last mentioned claim of Fèry, existing data are at variance and are quite inconclusive. MacInnes, Adler and Joubert found that a quantity of sulfuric acid between one and two mols per two faradays is used on discharge, the values varying from 1.34 to 1.79 mols. W. Kohlrausch and Heim[6] conclude that 2 mols per two faradays are used, but their work is of doubtful accuracy. Scheneck and Farbaky[7] find on the average 1.23 mols for the same quantity. The work of Pfaff[8] in this connection is

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[5] Trans. Am. Electrochem. Soc., **37**, 641 (1920).

[6] Electrotechnische Zeit., **10**, 327 (1889). These authors used a hydrometer for the specific gravity determinations and no mention is made of temperature control.

[7] Dingler's Polytech. Jour., **257**, 357 (1885).

[8] Centralblatt fur. Accumulatoren, **11**, 73, 173 (1901).

the most useful, in that he has taken into account the other variables which might affect the quantity of H_2SO_4 used. He determined the quantity of acid used per two faradays (which will hereafter be designated by ϕ) at successive intervals during the course of a single discharge, and also during several discharges at different current densities. The latter data are reproduced in Table I.

These figures are significant, showing as they do how greatly ϕ varies with the current. The tendency of ϕ, as seen best from a curve, is to approach, at sufficiently small current densities, the theoretical value two, required by the Gladstone and Tribe equation. On account of the importance of this point in determining which reaction takes place in the battery it was thought desirable to ascertain whether ϕ would not be found equal to 2 at very small current densities.

EXPERIMENTAL.

The first experiments were made with a positive and two negative pasted plates[9] of the following specifications:

Dimensions, 14.5 cm. wide, 12.5 cm. in height and 0.25 cm. thick; weight of unpasted grid 225 g.; weight of dry pasted positive 366 g.; and of dry negatives 347 g.; rated capacity 20 amp.-hr. They were put in a jar of such a size that about 1,000 g. of electrolyte just covered the plates. A rubber cover was used on the cell to prevent loss of electrolyte. A copper coulometer was used to determine the number of faradays passed. The specific gravity determinations were made at 25° C. with a 10 cc. pycnometer and the percentages of sulfuric acid were interpolated from the tables of Landolt and Börnstein. From one-half to two hours, with occasional stirring, was allowed for the electrolyte to become uniform in composition after a run, the longer time being for runs at higher currents. All measurements were made at a temperature of 26°C. ± 2°C.

The results on these pasted plates are listed in the first six runs of Table II, the headings of which are self-explanatory. In every

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[9] These plates were obtained through the kindness of the American Storage Battery Co., manufacturers of the "Harvard" battery and are designated by them as Type A.

case the values of ϕ were found approximately equal to two,[10] including the run at 10 amperes, which is five times the rated current for the cell. The high values of ϕ in the first two runs are probably due to local action of the acid on the new grids. The deviations in the calculated value of ϕ may be as large as 3 per cent, for although the density determinations are comparatively precise, the quantity of acid consumed is determined as the difference in two large numbers and the percentage error in the difference becomes large.

TABLE II.

Consumption of H_2SO_4 in Storage Battery Discharge

Run	Current amp.	Time of discharge hr. (approx).	Density of acid		Weight of electrolyte g. (beginning)	Weight of H_2SO_4 used	Faradays	Weight of H_2SO_4 theoretical	ϕ
			beginning	end					
1	0.10	53.0	1.1245	1.1106	986	21.1	0.2018	19.79	2.13
2	0.50	20.0	1.1299	1.1031	950	39.0	0.3719	36.47	2.14
3	1.0	16.0	1.1394	1.1000	967	58.3	0.5905	57.91	2.01
4	2.0	4.0	1.1440	1.1230	957	31.2	0.3159	30.98	2.01
5	5.0	2.5	1.1465	1.1187	949	41.8	0.4218	41.37	2.02
6	10.0	0.7	1.1872	1.1772	1400	21.0	0.2093	20.55	2.04
7	0.5	10.0	1.1775	1.1679	920	14.5	0.1760	17.26	1.68
8	0.5	12.5	1.1679	1.1561	906	18.2	0.2319	22.75	1.60
9	0.5	5.0	1.1561	1.1537	888	3.5	0.0724	7.11	0.98
10	0.5 to 0.1	16.0	1.1537	1.1522	882	2.1	0.0695	6.80	0.62
11	0.1	65.0	1.1893	1.1741	941	23.0	0.2445	24.00	1.92

Run 8 is a continuation of run 7; run 9, of run 8; run 10, of run 9.

Experiments were made next with a Planté type positive[11] (Manchester plate) of the same superficial area, with the same two pasted negatives. The results on this plate are listed in Runs 7 to 11 of Table II. Runs 7 to 10 are for successive periods in a single discharge, and it is seen that the quantity of acid used decreases

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[10] ϕ was calculated from the equation:

$$\phi = \frac{WF\ (a - b)}{C\ (49 - 40b)}$$

in which W is the weight in grams of the electrolyte before the run, F equals 96,500, C is the number of coulombs passed, a and b are percentages (x 0.01) of H_2SO_4 before and after the run respectively.

[11] MacInnes, Adler and Joubert used a Manchester plate.

constantly as the discharge continues. Run 11 is at a lower current density than Runs 7 to 10 and for the same part of the discharge as Run 8. It is seen that the value of ϕ (1.92) at the lower current is much nearer to 2 than at the higher current, which confirms the results of Pfaff previously given. It was thought unnecessary actually to discharge the Manchester plate at a current low enough to make ϕ equal to 2 since the experiments on the pasted plate showed that 2 is the correct value.

DISCUSSION OF RESULTS.

The explanations which have been suggested for the small amount of acid used on discharge, with the exception of the theory of Fèry, are based primarily on the supposition that there exists a lack of sulfate ions in the pores of the positive plate. The present results confirm this hypothesis. On the pasted plate the material is so porous and the reaction proceeds to such a small depth that a large concentration difference of acid cannot exist. While the sulfate ions migrate out of the plate, they are easily replaced by diffusion.

The construction of the Manchester plate, with the inserted lead ribbon buttons, however, is such as to produce ideal conditions for the depletion of sulfate ions in the inner parts of the plate. The acid can diffuse only very slowly into the narrow and deep channels of the button. This effect should become greater as the discharge continues and the reaction proceeds farther into the plate and the experimental values of ϕ do in fact decrease as the discharge continues as seen in Runs 7 to 10. At lower current densities the migration outward of the ions is less and the time for diffusion of acid back into the plate is greater so that the concentration decrease in the pores should be less than at higher currents. The high value of ϕ in Run 11 confirms the above statement. It is probably only on the Manchester or similar plate which contains such deep channels that the above effect will be observed.

Just what reaction takes place when less than the theoretical amount of acid is used is still somewhat uncertain. It is probable that a mixture of lead oxide and lead sulfate is formed, varying in proportions as the lack of sulfate ions becomes greater. When this condition exists the free energy of the reaction will be less and the voltage of the cell should become less. On the pasted anode, the voltage was constant until near the end of the discharge, when it dropped rapidly. With the Manchester plate, however, the decrease in voltage during discharge was much more gradual, and a large fraction of the discharge (Run 10) was obtained after the voltage had fallen below 1.7. A part of this decrease in voltage is due, of course, to the decrease in acid concentration, and part to the increasing resistance of the cell on discharge, but a part may be due to the decreased free energy of the reaction.

SUMMARY.

It has been found that under proper conditions the amount of acid used on discharge of the lead storage battery corresponds to that required by the Gladstone and Tribe theory. The evidence in favor of the latter theory is thus completed and the theory proposed by Fèry appears untenable.

DISCUSSION.

Helen Weir[1]: May I ask Dr. Knobel what evidence he has that any other compound is formed than lead sulfate, as a part in the discharge?

M. Knobel: From the number of faradays passed through the battery, the amount of lead peroxide reduced is known, but less acid is used than there would be if only lead sulfate were formed.

Helen Weir: As I understand no analyses have been made; is there not a possibility of an experimental error there?

M. Knobel: Since the value of ϕ came out as low as 0.6, the percentage error would have to be as large as 70 per cent, which is improbable.

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[1] Union Carbide and Carbon Res. Lab., Long Island City, N. Y.

HELEN WEIR: You will remember Dolzalek substantiated the double sulfate theory by thermo-dynamic relations, and those relations need no modification to support the theory.

M. KNOBEL: I do not see that thermodynamic calculations have anything to do with the present question; it is a matter of Faraday's Law and the quantity of materials used.

HELEN WEIR: But in the slow discharges where you have the most ideal condition for diffusion and can get the most accurate determination, you come nearest to finding that you do use two mols per faraday. Do you not think that this is evidence that a lead sulfate is formed rather than an intermediate or additional compound?

On your lower rates of discharge your sulfate is formed throughout the pores of the plate and into the interior, so that you can get an ideal condition for your determination, but on a high rate where you have it formed on the surface, it is possible that you may have sulfuric acid trapped in the pores which diffuses out very slowly.

M. KNOBEL: In answer to that point I may say that when the density determination was made one hour after the run and then again two hours later, there was found to be no appreciable difference.

HELEN WEIR: How do you explain recuperation then? At any high rate of discharge you can get remarkable recuperation in two hours, due presumably to diffusion of acid.

M. KNOBEL: That is in the voltage.

HELEN WEIR: Ampere-hour capacity also. It is an interesting phase of the storage battery subject, and I would like to see some more work on it.

M. KNOBEL (*Communicated*): A further point may be mentioned in regard to Mrs. Weir's question of the possibility of experimental error. If acid were trapped in the pores of the plate and came out slowly, a density determination made a long time after the run should be larger than one made just after the run and would therefore result in a still smaller value of ϕ.

Recuperation may be explained by diffusion of the acid back into the plates. The first result of this would be to build up the voltage. The capacity would then increase, but only because the voltage has increased, the capacity being limited by an arbitrary low voltage.

A paper presented at the Forty-third General Meeting of the American Electrochemical Society held in New York City, May 3, 1923, Dr. Wm. G. Horsch in the Chair.

ELECTROLYTIC AND CHEMICAL CHLORINATION OF BENZENE.[1]

By Alexander Lowy and Henry S. Frank.[2]

Abstract.

One of the processes to which the electrolytic method applies is the chlorination of benzene, and it seemed advisable to investigate this reaction because (1) only a limited amount of work has been done on this subject, (2) reports in the literature are often contradictory, and (3) investigation of this kind might throw additional light on the mechanism of chlorination.

HISTORICAL.

A considerable amount of research work has been done on the chlorination of benzene. A number of important references for the chlorination of benzene by the chemical method, under variable conditions, are given below.[3]

Concerning chlorination of benzene by the electrolytic method, Mühlhofer[4] stated that benzene is not appreciably affected by electrolytic chlorine. Mühlhofer found, however, that when 20 g. toluene was stirred vigorously into 250 cc. conc. HCl, and the mixture electrolyzed, a good current yield of chlorotoluene was obtained (30 per cent ortho, 70 per cent para). The addition of

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[1] Manuscript received January 26, 1923.

[2] Contribution from the Dept. of Chemistry, University of Pittsburgh, Pittsburgh, Pa.

[3] Pogg. Ann. **29**, 231 (1833); **31**, 283 (1834); Ann. chim. **26**, 59 (1834); **63**, 41 (1836); Comptes rendus des travaux de chimie (1849) 429; Proc. Royal Soc. 7, 18. 94 (1854); J. C. S. **15**, 41 (1862); **16**, 76 (1863); Ann. chim. (4) 15, 186 (1868); Ber. 8, 1400 (1875); Ann. 225, 199 (1884); Compt. rend. 127, 1,026 (1898); 126, 1212 (1898); **170**, 1319, (1920); Bull. soc. chim. 29, 283 (1903); J. Soc. Chem. Ind. 35, 1130 (1916); Chem. Soc. Proc. **24**, 15-16 (1908); Germ. pat. 219,242; U. S. Pat. 1,180,964; U. S. Pat. 1,189,736, and corresponding foreign patents; Compt. rend. **170**, 319 (1920); J. Am. Chem. Soc. **36**, 1007-11 (1914).

[4] Dissertation "Über die Einwirkung elektrolytisch erzeugter Halogene auf Organischen Verbindungen." Technische Hochschule, Munich, (1905).

iodine did not influence the products in nature or amount. Benzyl chloride was not formed.

Schluederberg[5] electrolyzed benzene in ether saturated with $ZnCl_2$, removing 76 to 80 per cent of the chlorine from inorganic combination. When benzene was floated on a layer of Oettel's solution (160 g. NaCl, 140 g. H_2SO_4 made up to 1 liter with water) and electrolyzed, the rotating anode being entirely in the benzene layer, an efficiency of only 2.29 per cent was obtained. Analogous experiments with toluene gave efficiencies ranging from 4.07 to 38.25 per cent. Of the chlorine acting, 76 to 96 per cent substituted in the ring and the rest in the side chain.

Van Name and Maryott[6] electrolyzed benzene in a glacial acetic acid solution of LiCl, and found that chlorination took place. It also took place, however, when chlorine was bubbled through the solution and electrolysis in addition to this bubbling produced no added effect.

Fichter and Glanzstein[7] used glacial acetic acid to prepare a homogeneous solution containing benzene and concentrated aqueous HCl. Electrolysis of this solution gave, under various conditions, chlorobenzene, p-dichlorobenzene, sym-tetrachloro and hexachloro benzene and in addition pentachlorophenol and chloranil. The relative amounts of these substances present in the product depended regularly upon the current density employed, (in addition to other determining conditions, such as temperature) which indicates that an electrochemical reaction was taking place.

Neminski and Plotnikow[8] electrolyzed the molecular compound $AlBr_3 . 3C_6H_6$, and observed that the hydrocarbon separated at the cathode, and bromination took place at the anode.

Some additional light on whether or not the chlorination is electrochemical is shown by the work of Cohen, Dawson and Crosland.[9] They electrolyzed toluene with a carbon anode over a layer of conc. HCl. As in Schluederberg's later work, substitution was largely in the ring. When, however, chlorine was bubbled through the same mixture under the same conditions, substitution was almost entirely in the side chain.

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[5] J. Phys. Chem. **12**, 595 (1908).

[6] Am. J. Sci. **35**, 130-70 (1913).

[7] Ber. **49**, 2473-89 (1916).

[8] J. Russ. Phys. Chem. Ges. **40**, 391-96 (1908).

[9] J. Chem. Soc. **87**, 1034 (1905).

THEORETICAL.

The work described in the references cited above seems to indicate that in the absence of carriers, chlorine does not substitute for hydrogen in benzene, and most text books make this, or an equivalent statement. They then define a carrier as a substance which catalyzes the substitution of halogens into the ring in aromatic hydrocarbons. Most lists of carriers include I, Fe, $FeCl_3$, $SbCl_3$, $SbCl_5$, $MoCl_5$, Al or $AlCl_3$, PCl_5, S, $ZnCl_2$, and Sn. For other halogens the corresponding halides are used.

The mechanism of the action of carriers seems to be fairly well agreed upon; the carrier forms an addition compound with the halogen, which it then liberates in a more active state than before. This view is supported by the fact that benzene can be chlorinated, for instance, by ICl, ICl_3, $FeCl_3$, $SbCl_5$, $MoCl_5$, etc., in the absence of any free chlorine. The function of the chlorine in these processes seems therefore to be regeneration of the original compound (ICl_3, etc.).

This concept of the mechanism of chlorination has been extended by Schluederberg[10] to include electrolytic chlorination. as follows: Benzene is chlorinated by the action of negatively charged Cl^-, and any source of negatively charged chlorine will therefore act as a chlorinating agent. He points out that each of the carriers mentioned dissociates, furnishing a negative chlorine, as:

$$ICl \rightarrow I^+ + Cl^-$$
$$FeCl_3 \rightarrow FeCl_2 + Cl^-$$

and so on. Moreover, the fact that electrolytic chlorine may be considered negatively charged explains why benzene can be chlorinated by electrolytic methods.

According to another theory, however, halogens that substitute in the nucleus in aromatic compounds bear a positive charge. This is derived by Fry[11] from his electronic conception of the structure of benzene, and his argument is that each of the substances mentioned as carriers is a possible source of positive halogen. He also points out that in the case of toluene, the presence of moisture promotes substitution in the ring, anhydrous halogens, in the

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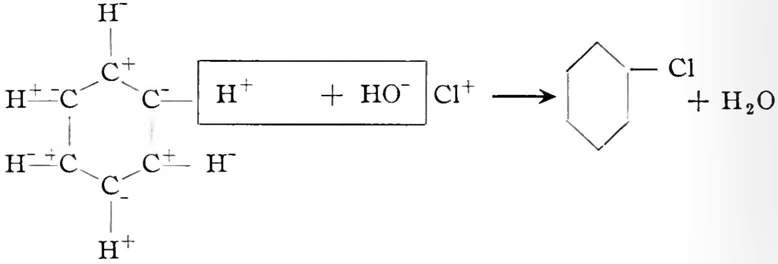
[10] J. Phys. Chem. 12, 595, (1908).

[11] Fry "Electronic Conception of Valence."

absence of carriers, tending to substitute in the side-chain. He suggested the following mechanism to explain this: the chlorine (for instance) first reacts with the water

$$Cl_2 + H_2O \leftrightarrows HCl + HOCl$$

The HO^-Cl^+ then acts as a source of positive chlorine which replaces a positive hydrogen in the benzene:



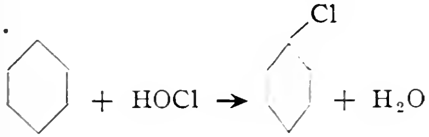
In this as in the ordinary interpretation of the reaction, half the original chlorine is converted to HCl.

Work done in the course of this investigation confirms Fry's hypothesis that water may act as a halogen carrier, as far as chlorine is concerned. With chlorine and benzene in the presence of water, substitution was obtained. Under identical conditions, with anhydrous materials, no substitution took place, but a considerable amount of benzene hexachloride was produced. As the results with water were duplicated when light was excluded from the system, there was obviously no photochemical action, and the effect was due entirely to the water, which probably acts as suggested by Fry.

A point in favor of this theory is the fact that the yield was nearly doubled by allowing the charge to stand overnight at the conclusion of the experiment. The additional chlorination here was undoubtedly effected by the chlorine that had been in solution.

According to the above, the electrolytic chlorination cannot be an electrochemical phenomenon since electrolytic chlorine at the moment of liberation is negative. According to Fry's hypothesis, the chlorination in the electrolytic cell would have to be called a secondary reaction depending upon the previous liberation of molecular chlorine, Cl_2, and possible only on account of the water present, the action being,

$$Cl_2 + H_2O \rightleftarrows HCl + HOCl$$



If, however, the chlorination is not electrochemical, it is difficult to explain the fact that the electrolytic reaction furnishes some more highly chlorinated products, which the non-electrolytic reaction does not give under the same conditions. Indeed, the latter fact points strongly to direct anodic depolarization as the explanation of the electrolytic process.

It would appear that the true explanation of what takes place in the chlorination of benzene must be sought further, and it is not hard to understand the disagreement among the men who have chlorinated benzene electrolytically, as to whether the phenomenon is chemical or electrochemical; the results obtained point to both conclusions.

The addition of iodine as a carrier to the system where aqueous chlorination was taking place increased the extent of the chlorination, but not to anything like the degree in which it would have done so, had the system been anhydrous.

EXPERIMENTAL PART.

(A) *Electrolytic Methods.*

The electrolytic experiments were conducted in the apparatus represented in Fig. 1. Particular attention is called to the water seal arrangement, and to the glass tube by which the porous cup cathode cell was suspended. The former made it possible to introduce or remove a charge easily and quickly without interfering with the stopper, which was permanently set up and insured an entirely gas-tight system. The glass tube conducted the hydrogen from the cathode directly to the outside atmosphere, preventing the formation of an explosive mixture inside the cell.

An experiment was made as follows: 750 cc. of 12 per cent

HCl (sp. gr. 1.06) and 75 cc. of pure benzene were placed in the beaker (4 on Fig. 1), and fitted into the cell. The mixture was agitated vigorously by means of a bell-type stirrer, and current was passed. Under the conditions of agitation the mixture resembled an emulsion.

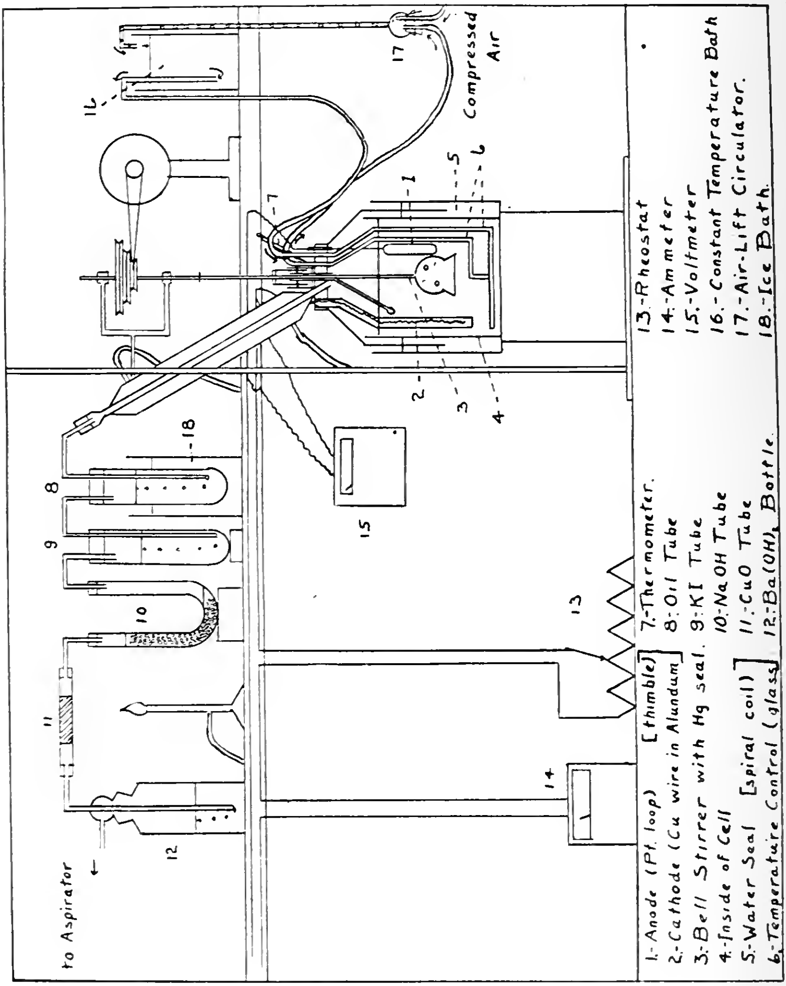


Fig. 1.

A stream of air was maintained through the system by means of an aspirator bottle. The air inlet in the stopper is not shown, but was equipped with a soda-lime tube through which the air passed before entering. The possible constituents of the vapor passing up the condenser were chlorine, hydrogen chloride, benzene vapor, oxygen, nitrogen, hydrogen (perhaps by diffusion through the porous cup), water, CO_2, CO. The two latter were formed by anodic oxidation of the benzene. The oil-tube, (8), contained heavy lubricating oil cooled to 0° C., the function of which was to absorb the benzene vapor. Tube (9) contained aqueous KI. The water removed any HCl in the vapors, and the KI completely removed the chlorine. As the experiment continued, this solution gradually colored up to a deep red. The U tube (10) contained NaOH solution, which absorbed CO_2. The NaOH was about 0.5 *N*, of undetermined strength, and was always present in excess. At the conclusion of the experiment the contents of the U tube was washed into a beaker, and the solution neutralized to phenolphthalein with HCl of undetermined strength. Two drops of methyl orange were then added, and the solution titrated with standard HCl to a fairly strong end-point. The hydrochloric acid used here was equivalent to half the CO_2 evolved during the electrolysis.

The remaining constituents of the gas, CO, O_2, H_2 and N_2 were passed over hot CuO in tube (11), where the CO was oxidized to CO_2. This was absorbed by an excess of standard $Ba(OH)_2$ in the wash-bottle (12), and the excess back-titrated to phenolphthalein with standard oxalic acid. This gave a figure for the CO produced by the electrolysis. The use of two oil-absorbing tubes did not always prevent the escape of some benzene vapor, which was then burned over the CuO and determined as CO. For this reason the CO figure is not always trustworthy. It will be noted that a possible escape of HCl or Cl_2 into the NaOH in tube (10) could not harm the CO_2 determination as long as sufficient NaOH was present to be alkaline to phenolphthalein at the end of the experiment, which was always the case. It is reasonably certain, however, that no Cl_2 or HCl did escape in this way.

The cell was kept at the desired temperature by circulating water from the constant temperature bath through the glass spiral coil (6). Control within one degree was obtained in this way, and it was possible to run at any temperature between 12° and 70° C.

After an experiment was completed, the charge was allowed to stand over night in place, after which the layers were separated and the aqueous layer extracted once with benzene. The benzene extract was added to the oily layer and rendered alkaline, made up to about 500 cc. with water, and steam distilled. The distillate was separated, and the lighter oily layer, consisting of benzene and substituted chlorobenzenes subjected to fractional distillations three times, the fractions collected being below 90°, 90-120°, 120-135°. The latter fraction contained the chlorobenzene. A trace of charred residue was left in the distilling flask although the distillation was made from an oil bath.

The residue from steam-distillation was extracted twice with ether, and the residue left on evaporating off the ether, weighed as the alkali-insoluble product. It consisted of more highly chlorinated products. The residue from the ether extraction was acidified, and again extracted twice with ether. The residue remaining this time on evaporating off the ether was weighed as the alkali-soluble product. It was a tarry mass with a strongly phenolic odor.

A number of electrolytic experiments were performed under different conditions, giving different results. The purpose of each experiment, its results and conditions are given in Table I.

(B) *Non-Electrolytic.*

The first non-electrolytic experiments were conducted in the same apparatus, the chlorine being bubbled in through a capillary in contact with the platinum anode. In order to discover whether the results were in any way due to the presence of the platinum, or of the alundum porous cup, etc., the rest of the purely chemical experiments were made in a glass bottle containing nothing but a glass inlet tube, a glass outlet tube, and a glass bell stirrer, The latter was also equipped with a mercury seal, but precautions were taken to prevent contamination of the charge with mercury. The chlorine was generated by dropping an excess of HCl on a weighed amount of $KMnO_4$. It was bubbled through water to remove HCl, and in one case through conc. H_2SO_4 to remove moisture.

The charge was the same as in the other series, except that in

TABLE I.

Experiments in the Electrolytic Chlorination of Benzene.

Expt. No.	Factor Studied	Amp.	Anode amp. c. d. per sq. dm.	Volts	Curent passed amp. hr.	Anolyte per cent.	Temp. °C.	Stirring
1[1]	....	5.2	116-120	8.0	16.2	12 HCl	30	500 r.p.m.
2[2]	Temp.	5.2	116-120	8.7	16.2	12 HCl	15	500 r.p.m.
3	Temp.	5.2	116-120	9.4	16.2	12 HCl	20	500 r.p.m.
4[3]	Temp.	5.2	116-120	7.4	16.2	12 HCl	55-60	500 r.p.m.
5	Temp.	5.2	116-120	8.0	16.2	12 HCl	40	500 r.p.m.
6[4]	Temp.	5.2	116-120	10-11	16.2	12 HCl	12-15	500 r.p.m.
7	Stir'g	5.2	116-120	7.6	16.2	12 HCl	50	300 r.p.m.
8	Stir'g	5.2	116-120	8.0	16.2	12 HCl	30	300 r.p.m.
9[5]	Temp.	5.2	116-120	6.6	16.2	12 HCl	70	500 r.p.m.
10	Carrier	5.2	116-120	6.4	16.2	12 HCl	70	500 r.p.m.
11	Stir'g	5.2	116-120	6.4	16.2	12 HCl	70	300 r.p.m.
12	Carrier	5.2	116-120	8.0	16.2	12 HCl	20	300 r.p.m.
13[6]	Anolyte	5.2	116-120	12-12.4	16.2	20 NaCl	50	300 r.p.m.
14[7]	C. D.	2.6	58-60	7.0	16.2	12 HCl	20	300 r.p.m.
15[8]	C. D.	8.1	171-180	13.2	16.2	12 HCl	20	300 r.p.m.
16[9]	Stir'g	5.2	116-120	8.8	16.2	12 HCl	20	300 r.p.m.

Expt. No.	Carrier	Benzene used g.	Distillate 120°-135° g.	Alkali insol. g.	Alkali sol. g.	CO_2 g.	CO g.
1[1]	None	65	14.0	0.04	0.16	0.232	0.056
2[2]	None	65	13.0	0.01	0.19	0.123	0.048
3	None	65	13.5	0.04	0.14	0.13	0.074
4[3]	None	65	17.5	0.20	0.18	0.23	0.10
5	None	65	16.3	0.02	0.07	0.20	0.15
6[4]	None	65	11.8	0.01	0.07	0.119	...
7	None	65	19.2	0.13	0.22	0.21	0.12
8	None	65	17.5	0.03	0.16	0.176	0.12
9[5]	None	65	9.6	1.34	1.87	0.25	...
10	1 g.I_2	65	11.8	0.53	0.38	0.29	0.16
11	None	65	12.4	0.09	0.35	0.31	0.15
12	1 g.I_2	65	18.6	0.16	0.18	0.13	0.12
13[6]	None	65	7.3	0.66	0.66	0.21	0.19
14[7]	1 g.I_2	65	10.7	0.14	0.13	0.209	...
15[8]	1 g.I_2	65	15.82	3.28	0.50	0.10	0.146
16[9]	None	65	15.8	...	...	...	...

[1] Oily layer was orange color.

[2] Oily layer lemon yellow.

[3] Oily layer orange red.

[4] Yellow oily layer.

[5] Red oily layer.

[6] Color was pale green.

[7] Expt. conducted twice as long as others.

[8] Run two-thirds as long as others.

[9] Worked only for Chlorobenzene.

The anode was in every case a platinum wire loop of 4.5 sq. cm. area.

Remarks as to color, etc., are made only in typical instances, and are indicative of a general trend.

most cases distilled water replaced the hydrochloric acid. The chlorine was bubbled through at a uniform rate and the charge was well stirred. The product of an experiment after standing over night, was separated, and the oily layer washed free of chlorine with NaOH. It was then fractionated for chlorobenzene just as before. There were no higher chlorination products, either alkali-soluble or alkali-insoluble formed, or at most, mere traces.

The results of the various experiments as well as their purposes, and the conditions under which they were made, appear in Table II.

TABLE II.

Non-Electrolytic Chlorination of Benzene.

Expt. No.	Factor studied	Benzene used g.	Other component	Distillate 120-135° g.	Remarks
18	Chemical action	65	12 per cent HCl	22.6	Experiment conducted in electrolytic cell. Excess Cl_2 used. Qualitative experiment.
19	Quantitative relations	65	12 per cent HCl	19.8	Same as No. 18 except Cl_2 generated from 19 g. $KMnO_4$ (equivalent to 16.2 amp. hr.)
20	Foreign material	65	12 per cent HCl	20.6	New apparatus used. Nothing present except reactants. Same amt. Cl_2 as in No. 19.
21	Function of HCl	65	Dist. H_2O	12.7	Worked up immediately instead of standing overnight as in all other expt. + same Cl_2.
22	Effect of standing	65	Dist. H_2O	20.4	Same as No. 21, but stood overnight.
23	Effect of light	65	Dist. H_2O	21.4	Same as No. 22, except that light was excluded.
24	Effect of moisture	65	Materials were anhydrous	..	No substitution took place. Benzene hexachloride was obtained. Same amount of Cl_2 used.

DISCUSSION OF RESULTS AND SUMMARY.

1. It is possible to chlorinate benzene by stirring it in with aqueous HCl and electrolyzing. Aqueous NaCl can also be used.

2. The yield of chlorobenzene increases with increase of temperature up to 60°.

3. The yield of chlorobenzene is affected by the rate of stirring.

4. The introduction of iodine as a carrier increases the yield of chlorobenzene.

5. The amount of higher chlorinated products formed increases in general with rise in temperature.

6. The amount of benzene decomposed to CO_2 by anodic oxidation increases with the temperature.

7. Increase in current density rapidly increases the alkali-insoluble product.

8. Water acts as a carrier in the chemical chlorination of benzene.

9. No substitution takes place when dry chlorine is passed into dry benzene. However, chlorine forms addition products of the type of benzene hexachloride.

10. Mühlhofer[12] states that the addition of iodine as a catalyzer does not alter the course of the electrolysis. The above experiments show that under the conditions cited, iodine seems to catalyze the chlorination.

11. A new form of apparatus was devised for this type of electrolytic work.

12. A preliminary series of experiments was conducted to study the electrolytic chlorination of benzene. A more detailed study of this process under variable conditions, as well as electrolytic bromination and iodination, will be reported in subsequent papers.

[12] Dissertation cited, quoted in Haber and Moser "Die elektrolytischen Prozesse der organischen Chemie." p. 97.

A paper presented at the Forty-third General Meeting of the American Electrochemical Society held in New York City, May 3, 1923, G. B. Hogaboom in the Chair.

NOTES ON THE ELECTRODEPOSITION OF IRON[1].

By HARRIS D. HINELINE.[2]

ABSTRACT.

Experiments were carried out to determine the type of plating bath that would give good deposits of iron on rubber. Particular attention was given to baths of high "throwing" power. Various formulas were tried out. A saturated bath of ferrous and calcium chlorides, containing chromous chloride and hydroquinone as reducing agents, gave the best results. Further investigation is encouraged. [A. D. S.]

The problem presented was that of depositing a substantial thickness of iron onto rather irregularly shaped rubber articles, this involving a process for preparing a conducting coating, a plating bath which would give good heavy deposits, in thicknesses up to 12.5 mm. (½ in.), and have a high throwing power to ensure filling the crevices. The conducting coating on the rubber was easily obtained by varnishing it, and then brushing in graphite, repeating the application of graphite at intervals until the varnish was too dry to take on any more.

The ferrous ammonium sulfate bath suggested by D. R. Kellogg[3] was tried out, but found to be unsatisfactory, as it is too easily rendered useless by organic extractives from the rubber. The deposit was badly pitted. Kellogg, too, records the failure of his bath when organic compounds entered it.

The best summary of work done on iron plating baths is that by Mr. W. E. Hughes.[4] From this summary we concluded that

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[1] Original Manuscript received Sept. 5, 1922.

[2] Pittsburgh Park, Pittsburgh, Pa.

[3] Trans. Am. Inst. Min. and Met. Eng., Feb., 1922.

[4] Trans. Am. Electrochem. Soc., 40, 185, *et seq.*, (1921).

the Fisher-Langbein, ferrous calcium chloride bath would probably be the most promising for our problem. However, this bath caused serious pitting and corrosion on both iron and rubber cathodes. A simple ferrous chloride bath, (150 g./L.) was equally bad, suggesting that the trouble might be due to the presence of ferric chloride. A bath made up of 150 g./L. of ferrous chloride and 100 g./L. of sodium acid sulfite to insure complete reduction of all the iron, gave a very good deposit for several days, reaching a thickness of about 0.24 mm. (3/32 in.). Corrosion then began, due partly to exhaustion of the sulfite, and partly to high acidity.

No mention is made in Mr. Hughes' paper of any trials of a bath made up of ferrous sulfite. A solution was therefore prepared by treating a suspension of ferrous carbonate in water with sulfur dioxide. A solution containing about 50 g./L. of iron was obtained, probably present as ferrous acid sulfite. On electrolysis, no iron deposit was obtained, but instead, a thick mass of material at the cathode, which seemed to be a mixture of ferrous sulfite and sulfide. The mass, on treatment with dilute acid, first evolving sulfur dioxide and then hydrogen sulfide, dissolved completely.

Since the addition of the sulfite to the ferrous chloride solution gave a good deposit it did seem that a reducing agent in the bath would improve conditions. A canvass of available reducing agents suggested hydroquinone as a possibility. A bath containing 250 g./L. of ferrous chloride, a little ferrous carbonate and 5 g./L. of hydroquinone gave a deposit free from corrosion and pitting. A solution of 150 g./L. of ferric chloride was then reduced with an excess of hydroquinone. The lower solubility of the resulting quinone caused it to crystallize out.

The solution with its suspended crystals was then electrolyzed at a c. d. of about 2.7 amp./sq. dm. (25 amp./sq. ft.). It yielded an excellent deposit, free from corrosion and treeing, but very brittle, due probably to high acidity from the reduction of the ferric salt. Large gas bubbles were evolved at the cathode, but they did not produce gas pits. A solution containing 200 g./L. of ferrous chloride, 200 g./L. calcium chloride and 10 g./L. hydroquinone gave an excellent deposit, and after electrolysis over a period of a month, during which a deposit 3 mm. (1/8 in.) in thickness was made, the bath was still working well. Anode corrosion had liberated considerable sludge, so the bath was filtered. The filtered bath again gave much trouble due to corrosion, but the addition of 10 g./L. of hydroquinone restored the bath to good working condition.

In plating baths a wide variety of addition agents, both organic and inorganic, is used. Glue, glycerine, gum arabic and dextrose were tried in a Fisher-Langbein bath containing hydroquinone, but all were rapidly destroyed, yielding a sludge and breakdown products which ruined the bath. In one case 20 g./L. of glue were added, giving a bath of such high viscosity that the hydrogen liberated at the cathode was held in place. The iron was deposited between the bubbles, resulting in a bulky deposit of fine iron crystals.

Chromous chloride being a good reducing agent, a bath was made up containing 10 g./L. of it, and 200 g./L. each of ferrous chloride and calcium chloride. This gave a very good deposit at a c. d. as high as 8 amp./sq. dm. (75 amp./sq. ft.) even when continued over a period of a month, although some trouble was experienced with treeing. Manganous chloride gave a similar result, but required much larger quantities. Antimony, added as chloride, plated out before the iron; zinc was without effect.

A bath containing, per L., 350 g. of ferrous chloride, 225 g. of calcium chloride, 20 g. of chromous chloride, and 5 g. of hydroquinone, was chosen as having about the best proportion among its various constituents. This was used at a temperature between 60 and 70° C. It showed no corrosion, no pitting, only a little treeing and fair metal quality. Deposits as thick as 12.5 mm. (1/2 in.) were made which had about the strength of a mediocre grade of cast iron. The individual crystals of metal were very large, some extending entirely through the deposit.

In most of the trials made in search of a suitable bath flat rubber or iron sheets were used as cathodes. It was soon noticed that although rubber is a good insulator, a "strike" of deposited metal over its surface could be obtained without special preparation. A sheet of rubber simply suspended in the bath by a metal clamp, so that part of the clamp was submerged, would take a "strike" over its entire surface in a very short time. This fact seriously complicated the problem of filling the grooves and crevices in the specimens. The plating bath we developed does not "throw" its deposit at all well, in fact none of the iron baths will "throw" as well as zinc and copper cyanide baths will.

We were not able to prepare a conducting line with varnish and graphite at the bottoms of the crevices and keep the deposit on it. In a very short time the metal would strike over the entire rubber surface, whereupon it ceased to deposit in the crevices. Rubber being a good insulator, this was most unexpected. The physical character of the surface of the rubber or perhaps the interfacial tension between rubber and solution may account for the phenomenon.

A variety of expedients were tried to overcome the difficulty. Small anodes placed within the crevices, so as to shorten the current path, were ineffective because of lack of anode area. Strongly charged shields, covering the projecting portion, showed possibilities, but an adequate insulating covering for the shields was not available. Anodes in contact with the projection forced the deposit into the grooves, but did not fill them to the bottom. Hard rubber shields to control the path of current flow worked, until the deposit was thick enough at some point to touch the shield, a strike then took place over the shield, and it got all the deposit. A rapid stream of electrolyte, impinging on the surface of the projection would keep the deposit off of it, but the stirring of the solution was too great, and a knobby deposit resulted.

It finally became evident that it would be necessary to cover the entire rubber surface with stopping off material; a tung oil baking varnish, lightly baked, was found to be adequate. Conducting lines were then put in the bottom of the crevices, and it was found that if the applied voltage did not exceed 0.45 volt the deposit did not creep, and the crevices could be filled completely before any metal deposited on the tops of the projections. With the crevices filled, a slightly higher voltage would cause the deposit to strike over the entire surface. An observation that should be recorded is the effect of various hydro-carbons on the bath. Saturated petroleum products, such as gasoline, kerosene, or machine oil, produce bad treeing of the deposit, even when present in exceedingly small quantities, while turpentine, in considerable quantity, is without effect on the deposit.

The bath made up as first indicated worked reasonably well, but proved to be a little too dilute. Better results were obtained from a bath made up with equal parts of ferrous chloride and calcium chloride in such a quantity as to make the bath saturated at a temperature of about 30° C., to which was added about 20 g./L. of chromous chloride, and about 5 g./L. of hydroquinone. This bath worked best at a temperature of 60° to 70° C. Lower temperatures gave a poorer deposit, less strength and more inclusions, while higher temperatures showed rather too much evaporation. The material in the bath appears to be present in the form of a double salt of iron and calcium chloride in which the ferrous ion is much reduced in concentration. The solution is much lighter in color than the equivalent solution of ferrous chloride alone, and the salts crystallizing out are also much lighter in color than ferrous chloride crystals and different in crystal habit.

It is of primary importance that the iron in the bath be kept in the ferrous condition. It is difficult to determine the amount of ferric iron in any given bath, but the permissible amount in a satisfactory bath is certainly below 1 g./L. and probably below 0.1 g./L. This low concentration of ferric iron may be maintained by the use of hydroquinone in the solution, in spite of the high partial pressure of oxygen at the surface of the solution, and in spite of oxygen liberated at the anode, when anode corrosion is less than 100 per cent. The hydroquinone has a higher reduction potential than ferrous chloride, and a comparatively small concentration of it will keep the ferric iron content sufficiently low. The hydroquinone is oxidized to quinone, which, although not as soluble as the hydroquinone itself, is still somewhat soluble, so as to bring a low concentration to the cathode surface. The hydrogen, which was always liberated at the cathode to a certain extent, is taken up by the quinone to reform hydroquinone, thereby maintaining the hydroquinone content.

The hydroquinone may be considered as a carrier of hydrogen from the cathode to the solution, thereby taking care of the hydrogen which otherwise might form gas pits on the cathode. Likewise the quinone may be considered as a carrier of oxygen from the anode, to obviate the difficulties due to less than 100 per cent anode corrosion. The hydroquinone and its oxidation product will remain in the solution without further destruction for a period of months. There appeared to be no electrode reactions which were sufficiently powerful to cause further reaction with the ring nucleus of the compound. A concentration of hydroquinone of 5 to 20 g./L. appears to be ample as long as anode corrosion efficiency does not get too low. It is possible that an anode corrosion efficiency of less than 95 per cent will ruin the solution regardless of any treatment.

The action of the small percentage of chromous chloride is not so readily explained nor is it as conspicuous. The chromium appears to be plated out slowly. Analysis of a typical deposit showed 0.3 per cent chromium, which is probably in the metallic condition, since the amount of inclusions of electrolyte in the deposit were far too small to account for such a quantity of chromium. It was first considered that the chromium served as a carrier of oxygen and hydrogen in the same way as the hydroquinone. However the evidence in support of this view is not strong, since oxidation of the chromium seems to proceed through an intermediate step when the chromium precipitates.

It is more probable that the chromium plates out slowly to give a slight breaking up of the iron crystal structure somewhat after the idea of interleaved nickel in copper deposits.[5] This point should be checked up, for if it proves to be correct it is possible that the addition of other metal salts, perhaps nickel chloride, cobalt chloride, or some similar salt might yield a deposit which would have finer crystal structure and better strength than the iron deposits so far obtained.

Control of the acidity of the plating solution is not of the critical importance that is required in the control of the reduction of the bath. The solution should be slightly acid, sufficiently so to prevent the precipitation of ferrous hydroxide or ferrous carbonate. The minimum satisfactory acidity is probably about 0.01 per cent and it may go to about 0.5 per cent of HCl. The acidity of the bath is satisfactory when the bath is made up from good

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[5] Trans. Am. Electrochem. Soc. 40, 307, (1921).

grades of ferrous chloride and calcium chloride, and it will stand the addition of about 2 g./L. of concentrated HCl without producing a deposit which is excessively brittle. The addition of ferrous carbonate, calcium carbonate or caustic is permissible to reduce the acidity of the bath, but if continued to the point where iron precipitates as a carbonate or hydroxide, the bath immediately gives treeing deposits.

Another method of keeping the bath reduced to the ferrous condition was under trial, but without conclusive results. Early experiments showed that the presence of sulfur dioxide in the plating bath was not harmful. It did not seem possible to add the gas directly, since the oxidation product, being sulfate, would precipitate a portion of the calcium from the bath and liberate an excess of hydrochloric acid. It does seem possible, however, to add to the bath small quantities of normal calcium sulfite made by suspending calcium hydroxide in water and passing in the weighed quantity of sulfur dioxide gas. This would yield a precipitate of calcium sulfate, which is harmless, and would not change either the calcium content or the acidity of the plating bath. Results at this time have not been continued far enough to show whether this is practical or not.

The foregoing experiments are somewhat desultory in character and do not follow, as rigorously as might be desired, a definite line of logical research. It is hoped, however, that other workers interested in similar work will find suggestions of value in this paper.

A paper presented at the Forty-second General Meeting of the American Electrochemical Society, held in Montreal, and brought up for discussion at the Forty-third meeting in New York City, May 4, 1923, President Schluederberg in the Chair.

HEAT INSULATING MATERIALS FOR ELECTRICALLY HEATED APPARATUS[1].

By J. C. Woodson[2].

INTRODUCTION.

Heat and heat processes enter into practically every form of manufacture and the industry is indeed scarce that does not somewhere in its organization, utilize this form of energy to fashion or perfect its product. This has been true of industry since its inception, yet only within the last two decades has there been any real effort to conserve or reduce the heat lost in these processes. Even today, there is very limited data available on the subject of heat insulating material, except for certain specific temperatures and under conditions which do not necessarily hold for other conditions.

While the attempt will be made in this paper to be as general as possible on this subject, attention is called to the fact that most of the data and curves given refer to heat insulating material used in connection with electrically heated apparatus. It is vital and absolutely necessary to conserve all the heat possible with such apparatus, which also requires careful attention to other characteristics of insulating material ordinarily considered unimportant. The rapid and almost phenomenal increase in the commercial use of electrically heated apparatus, ovens, furnaces and machines, indicates that all other forms of heat and heat treatment will sooner or later be supplanted, to a large extent, by electric heat. This change is now and will continue to be, dependent, to a greater or less degree, upon the available heat insulating mediums and the ability of engineers and manufacturers to apply them properly.

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[1] Original manuscript received August 8, 1922.

[2] Electric Heating Engineering Dept., Westinghouse Elec. and Mfg. Co., E. Pittsburgh, Pa.

TEMPERATURE RANGES CONSIDERED.

Low temperatures, such as 80°F. (27°C.) or lower will be considered only briefly, and for convenience we will divide our temperature ranges into the 5 divisions shown in Table I.

TABLE I.

Division	Range	Application
1	0° to 200° F. —18° to 93° C.	Refrigeration, cooling, water heating, drying, presses, air heating, various liquids.
2	200° to 350° F. 93° to 177° C.	Steam pipes, drying, color enamel, presses, baking.
3	350° to 600° F. 177° to 315° C.	Japanning, core baking, bread baking, presses, appliances, liquids.
4	600° to 1,000° F. 315° to 538° C.	Tempering, annealing, solder, babbitt, tin melting.
5	1,000° to 2,000° F. 538° to 1,093° C.	Heat treating, drawing, forging, melting, enameling.

To cover these five ranges, there are numerous commercial grades of insulating material of various trade names and ratings; a great many for divisions one and two and tapering off to only two or three reliable grades for division five. Practically all of these commercial grades can be located in three classes by fundamental composition as stated in Table II.

TABLE II.

Class	Division	Composition
A	1	Hair, wool, felt, wood pulp, animal and vegetable fiber, asbestos paper, cork.
B	2, 3, 4	Asbestos, magnesia, sponge, earths, mineral wool.
C	4, 5	Diatomaceous earth, mineral wool, earths, silicates.

From this Table, it is evident that there is no clear or definite dividing line between either the temperature division or the classes by composition, as there is a certain amount of overlapping. Certain combinations of these fundamental ingredients also produce distinct grades of insulation, entirely different from any of the component parts. Also, certain ingredients are used in one class as insulating material, and in another class as a mechanical binder or strengthener of the true insulation, such as asbestos in classes B and C and mineral wool in class C.

There are numerous qualities desired in heat insulating materials and different applications require different qualities, but in general a good heat insulating material should have the following characteristics.

1. Low heat conductivity.
2. Low specific heat.
3. Low specific gravity.
4. Non-inflammable.
5. Strong and durable mechanically.

Low conductivity to reduce radiation losses; low specific heat to save as much power in heating up period as possible and make apparatus faster; low specific gravity to keep down unnecessary weight and save heating up power as No. 2; non-inflammable as most insulations are subjected to periodic or locally high temperatures; No. 5 for length of life and reliability.

Other attributes to be desired are:

6. Electrical non-conduction.
7. Have no chemical action on metals.
8. Easily shaped or formed.
9. Permanent in setting (no shifting or settling).
10. Impervious to action of liquids, (water, acids, oil)[3].

Practically all commercial insulations have most of these qualities in some degree, the two last being the ones most often left out. In the writer's experience, No. 10 is not attained by any present day insulations; though several grades will stand drenching in water and after being thoroughly dried prove to be practically as good as ever. However, while still wet, this insulation is almost useless[3].

[3] Weidlein, Chem. and Met. Eng., 24, 295, (1921).

An evacuated space is the best thermal insulator of conducted heat known, while gases under certain conditions are probably next. Air is a good insulator if it can be entrapped in small enough spaces to prevent convection currents, and to this fact and arrangement most present day heat insulators owe their value as such. This minute honey-combing of the structure places multitudes of confined dead air spaces in series opposing the heat flow, with only minute point contact of the material fibers or crystals for direct conduction.

Heat transfer by radiation through insulating material is problematical, as these radiations are stopped by the insulation and the heat carried by conduction; or with some insulations the rays are to a certain extent refracted so that the penetration is relatively shallow. At temperatures beginning with 300°C. this characteristic is important.

The law of heat flow through resisting materials is analogous to Ohm's law for electrical circuits, expressed as $I = E/R$ where I is the current, R the resistance and E the voltage pressure or difference between two points. Likewise the amount of heat flowing between two points of different temperatures can be expressed as

$$W = \frac{Td}{R} \qquad (1)$$

where W is watts flowing as heat, Td is temperature difference and R is the thermal resistance of the path of flow. This means that the rate of heat flow is directly proportional to the temperature pressure or difference, and inversely proportional to the resistance of the path or material composing the thermal circuit.

From the above, it follows that

$$R = \frac{Td}{W} \qquad (2)$$

In formulas 1 and 2, Td is expressed in °C. R is the total thermal resistance of the circuit. Therefore

$$R = \frac{L}{A} r = \frac{L}{A} \cdot \frac{1}{c} \qquad (3)$$

Where

R = total resistance of circuit in thermal ohms

L = length of circuit in inches

A = area of path in sq. in.

r = specific resistance of circuit in thermal ohms per inch cube

c = thermal conductivity in watts per inch cube per °C. ($r = 1/c$)

By substituting in formula No. 1, we have

$$W = \frac{A}{L} \cdot \frac{Td}{r} = \frac{A}{L} \cdot c \cdot Td^{(4)} \qquad (4)$$

Where W is watts flowing per unit of time. Tables III, IV, and V, give the values of r for a number of building and insulating materials.

The above simple formulae are little recognized and seldom used, due to the many awkward and arbitrary units ordinarily used by engineers, so that while the rule remains simple, the means of applying and using it are often complicated and involved. In this country, the usual unit used is the British thermal unit, and the method of expressing heat flow is given by the equation

$$Q = KAt \left(\frac{T_1 - T_2}{th}\right) \qquad (5)$$

Where Q is the quantity of heat flowing through a path of area A in time "t" the length of the path is "th" with a temperature difference of $T_1 - T_2$. K is the coefficient of thermal conductivity of the material of the circuit. These units are ordinarily expressed as follows.

Q = B. t. u. transmitted

A = sq. ft.

t = hours

th = inches

$T_1 - T_2$ = °F.

K = B. t. u. per sq. ft., per inch of thickness, per hr., per °F. temperature difference

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[4] C. P. Randolph, Trans. Am. Electrochem. Soc. **21**, 545. (1912).

TABLE III.

Material	Density lb. per cu. ft.	Spec. Heat	K B. t. u. per sq. ft. etc.	r. thermal ohms per cu. in.	At temp. °F.	Authority
Air	0.08	0.240	0.175	1560.0	77	Van Dusen
Air-cel asbestos	8.8	0.281	0.500	546.0	77	Van Dusen
Balsa wood	7.5		0.350	780.0	77	Van Dusen
Cabot quilt	16.0		0.321	851.0	77	Van Dusen
Calorox	4.0		0.221	1235.0	77	Van Dusen
Cork board	6.9	0.44	0.279	979.0	77	Van Dusen
Cotton wool	7.0	0.362	0.291	938.0	77	Van Dusen
Cypress wood	29.0		0.666	410.0	77	Van Dusen
Eiderdown	6.77		0.1345	2030.0	212	Randolph
Eiderdown	0.134		0.438	623.0	212	Randolph
Fibrofelt	11.3		0.329	830.0	77	Van Dusen
Gimco thermalite ...	17.0	0.20	0.272	1013.0	93	General Ins. and Mfg. Co.
Ground cork	9.4	0.48	0.296	923.0	77	Van Dusen
Hair felt	17.0	0.40	0.246	1110.0	77	Van Dusen
Hard maple (wood).	44.0		1.124	242.3	77	Van Dusen
Insulite	11.9		0.296	923.0	77	Van Dusen
Kapok	0.88		0.237	1151.0	77	Van Dusen
Keystone hair felt ...	19.0	0.40	0.271	1008.0	77	Van Dusen
Linofelt	11.3		0.300	910.0	77	Van Dusen
Lith board	12.5	0.32	0.379	721.0	77	Van Dusen
Mahogany wood	10.2	0.50	0.304	898.0	150	Armstrong Cork and Insulation Co.
Nonpareil corkboard.	34.0		0.916	298.0	77	Van Dusen
Oak wood	38.0	0.57	1.000	273.0	77	Van Dusen
Pulp board			0.458	596.0	77	Van Dusen
Remanit (charred silk)			0.274	996.0	300	Stott
Sheep's wool	6.9		0.246	1110.0	300	Van Dusen
Tar-paper roofing ...	55.0		0.708	386.0	300	Van Dusen
Vacuum			0.041	6666.0	300	Van Dusen
Virginia pine	34.0		0.958	285.0	300	Van Dusen
White pine	32.0	0.67	0.792	345.0	300	Van Dusen
Wool felt	21.0	0.39	0.363	752.5	300	Van Dusen

TABLE IV.

Material	Density lb. per cu. ft.	Spec. Heat	K B. t. u. per sq. ft. etc.	r. thermal ohms per cu. in.	At temp. °F.	Authority
Air-cel asbestos	8.8	0.292	0.500	546.0	77	Van Dusen
Air-cel asbestos	15.6		0.683	399.0	0 to 392	Randolph
Asbestos felt	30 to 40		0.549	497.0	400	Franklin Mfg. Co.
Asbestos fiber	12.5 to 18.7		0.608 to 0.497	448.0 to 548.0	932	Randolph
Asbestos fire felt	27.6		1.093	249.0	370	McMillan
Asbestos lumber	123.0		2.710	100.5		Van Dusen
Asbestos mill board	61.0		0.833	328.0		Van Dusen
Asbestos paper	50 to 70	0.300	1.250	218.5	150	Marks
Asbestos sponge felted			0.509	537.0	400	Stott
Asbestos sponge felted	34.4		0.329	830.0	392	Randolph
Carey carocel			0.540	506.0	370	McMillan
Carey duplex			0.636	429.0	370	McMillan
Carey 85% magnesia	18.0		0.546	500.0	370	McMillan
Carey 85% magnesia	18 to 24	0.312	0.500	546.0	300	Wiedlien
Carey 85% magnesia	18 to 24	0.312	0.585	467.0	600	Wiedlien
Carey serrated			0.682	401.0	370	McMillan
Celite powder	10.6	0.289	0.309	883.0	77	Van Dusen
Diatomaceous earth and asbestos	20.7		0.497	549.0	0 to 750	Randolph
85% magnesia	13.5		0.455	600.0	0 to 750	Randolph
Fire felt roll	43.0		0.624	438.0	77	Van Dusen
Fire felt sheets	26.0		0.583	468.0	77	Van Dusen
Fullers earth	33.0		0.708	386.0	77	Van Dusen
Gypsum plaster	56.0	0.26	2.250	121.4	77	Van Dusen
Insulex	29.0		0.916	298.0	77	Van Dusen
J. M. asbestocel		0.281	0.549	497.0	400	McMillan
J. M. asbestos sponge felted	12.0 42.0		0.468	583.0	370	McMillan
J. M. 85% magnesia	13 to 16	0.312	0.507	538.0	370	McMillan
J. M. 85% magnesia	16.8		0.444	615.0	470	J. M. Co.
J. M. fine corrugated asbestos	15.6		0.538	507.0	470	J. M. Co.
J. M. indented			0.666	409.0	370	McMillan
J. M. moulded asbestos			0.778	351.0	370	McMillan
J. M. vitrobestos	21.6		1.087	251.0	370	McMillan
K. & M. air-cel asbestos	12.5		0.680	402.0	370	Stott
Laminated cork		0.48	0.433	631.0	400	Stott
Mineral wool	12.5	0.198	0.275	993.0	77	Van Dusen
Mineral wool	26.6	0.198	0.479	570.0	932	Randolph
Nonpareil H. P.	22.56	0.20	0.470	581.0	370	McMillan
Nonpareil H. P. block	27.0	0.20	0.543	502.5	370	McMillan
Plastic 85% magnesia			0.587	465.0	370	McMillan
Poplox	1.43		0.384	712.0	572	Randolph
Poplox	5.80		0.463	589.0	932	Randolph
Rock cork			0.350	780.0	77	Van Dusen
Sallmo wool felt			0.510	536.0	370	McMillan
Silica	106.0		1.775	153.8	932	Randolph
Solid cork		0.45	0.418	653.0	400	Stott
Thermo fiber	10.0	0.20	0.320	853.0	200	F. D. Farnum and Co.
35% magnesia	29.8		0.569	480.0	0 to 750	Randolph
Vitrified Monarch block	40 to 45		0.842	324.0	400	Franklin Mfg. Co.

TABLE V.

Material	Density lb. per cu. ft.	Spec. Heat	K B. t. u. per sq. ft. etc.	r. thermal ohms per cu. in.	At temp. °F.	Authority
Alundum brick	127 to 149		7.26 to 4.03	37.5 to 67.7	1112	Randolph
Bauxite brick	118.0		9.41	29.0	1832	Randolph
Carborundum	128.0		40.8	6.69	2072	Randolph
Chromite brick	128.0	0.174	7.19 to 19.5	38.0 to 14.0	2072	Randolph
Concrete	170 to 180	0.20	6.38	42.8		McMillan
Feldspar			16.05	17.0	212	Randolph
Fire brick	111 to 178	0.253	10.1 to 12.4	27.0 to 22.0	2072	Randolph
Gas retort brick			11.03	24.7		Marks
Glass	150 to 170	0.18	7.00	39.0		McMillan
Glass			4.33	63.0	78	Randolph
Graphite brick	112.0		71.9	3.8		Randolph
Infusorial earth	43.0		0.583	468.0	77	Van Dusen
Insulbrix	36.0	0.19	0.84	325.0	1000	Quigley Fur. Spec. Co.
Iron	480.0	0.118	420.0	0.65		Marks
Lime stone	170.0	0.217	15.0	18.2		McMillan
Magnesia brick	125.0	0.324	17.05	16.0	2072	Randolph
Nonpareil brick	27.0	0.20	1.10	248.0	1600	Armstrong Cork Co.
Nonpareil brick	25.8	0.295	0.477	572.0	470	McMillan
Retort brick	116.0		10.95	24.9	2072	Randolph
Sand	110.0	0.195	2.70	101.0		McMillan
Silica brick	98.5	0.29	5.81	47.0	1832	Randolph
Silo-cel brick	30.0	0.225	0.67	407.0	470	McMillan
Silo-cel brick	31.0	0.2089	0.745	366.0	1600	Celite Prod. Co.
Silo-cel powder	12 to 15	0.2089	0.300	910.0	77	Celite Prod. Co.
White building brick.	118.0		10.90	25.0	1832	Randolph

Many of the materials given in the Tables III, IV and V are not heat-insulating materials in the ordinary sense of the term, but are given only for purposes of comparison. The authorities given refer to the value of K. K is expressed as B. t. u. per hour, per square foot, per inch of thickness, per ° F. difference.

For flat surfaces of sufficient area so that the end or edge effect is relatively small, this formula can be used as given, though only approximately correct. McMillan gives this formula as

$$Q = \frac{ts - ta}{\frac{x}{k} + \frac{1}{a}} \tag{6}$$

Where

Q = B. t. u. per sq. ft., per hr. transmitted
ts = temperature of hot surface, °F.
ta = temperature of surrounding air °F.
x = thickness of insulation in inches
a = surface transmission factor (1/a = surface resistance)
k = conductivity of material.

This takes into account, not only the absolute mean conductivity of the insulation, but also the resistance that is offered by the surface of the material to the transmission of heat. This factor 1/a varies between wide limits, and has been determined for only a few materials, so that for ordinary calculations 0.5 is taken as the value of 1/a for still air conditions and a good grade of insulating material at medium temperatures.

From formula No. 5 it is evident that the factor $\frac{T_1 - T_2}{th}$ is the determining variable, and expresses the rate of temperature drop with distance through the material, and its limiting value or dT/dth is the "temperature gradient" of any point in the path of flow, assuming that K is a true constant for the full thickness of the materials.

For cylindrical surfaces such as steam pipes, tanks, boilers, etc., it can be shown that the heat loss is equal to

$$Q = \frac{K\,(T_1 - T_2)}{R \log_e \frac{R_2}{R_1}} \tag{7}$$

Where

R_1 is inside radius of covering in inches
R_2 is radius of outside of covering (or insulation) in inches

R is outside radius of pipe in inches (usually taken equal to R_1 in above equation)
Q is rate of heat flow per in. B. t. u. per sq. ft., per hr.
T_1 is temperature of inside of pipe in °F.
T_2 is temperature of outside of insulation °F.

This is the formula generally used for all cylindrical surfaces and Table IV gives the value of K for a number of different insulations commonly used for such surfaces. T_2 is ordinarily taken as the temperature on the outside surface of the covering or even room temperature, whereas it actually refers to the temperature of the outside of the insulation, which for steam pipes would be under the canvas sheathing.

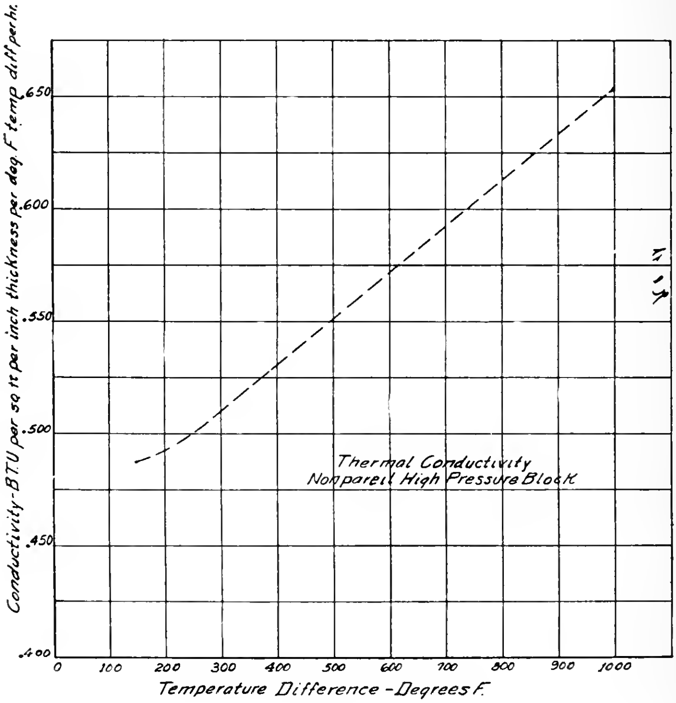
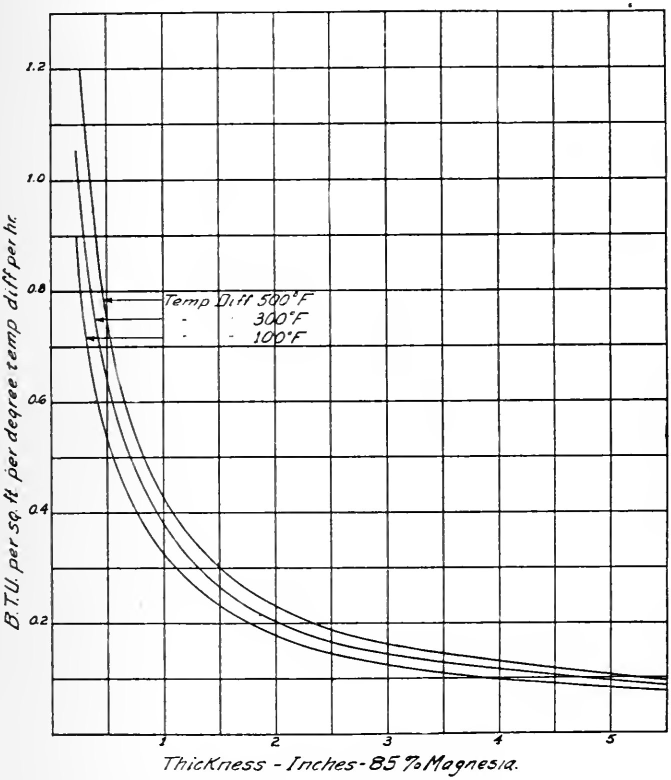


FIG. 1.

In the above formulæ, numbers 4, 5, 7, etc., two assumptions are made which are not strictly correct; first, that K is constant in value throughout the thickness of the insulation, and second, that the value of K varies inversely with the thickness. The value of K varies with the temperature as shown in Fig. 1, so that it presents a curve between T_1 and T_2. It is a matter of common knowledge that the insulating value does not increase directly with the thickness, but so far no general law has been worked out. Stott[5] attempted this and states that for 85 per cent. magnesia, the law is



Variation of heat transmission for various thicknesses of material on flat surfaces

FIG. 2.

$$\frac{K_1}{K_2} = \frac{\sqrt[2]{th_2}}{\sqrt[2]{th_1}} \qquad (8)$$

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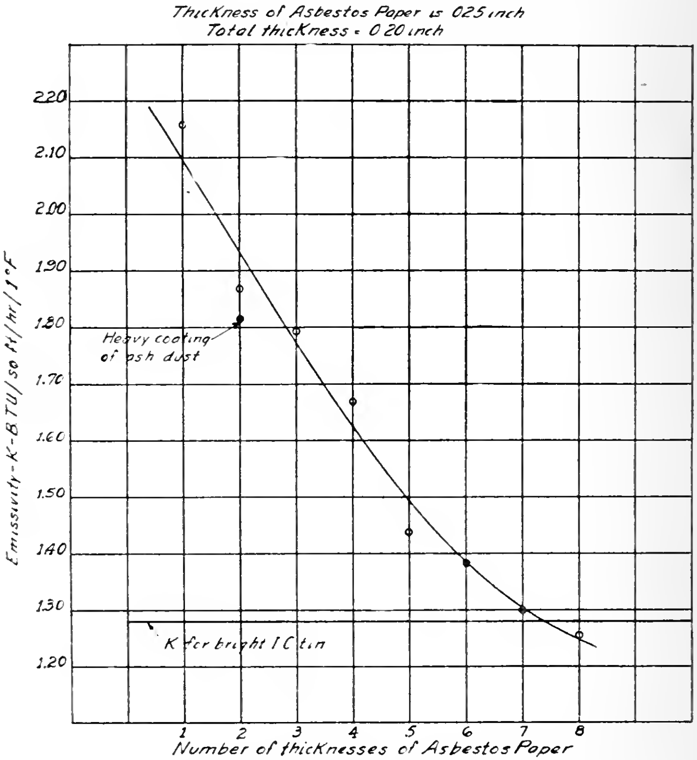
[5] Power, 1902.

Where K_1 and K_2 are the coefficients of conductivity and th_1 and th_2 are the thicknesses, while for every other material a different constant is required. These have not been accurately determined as yet. Fig. 2 shows this general relation for 85 per cent magnesia on flat surfaces. Stott's law will not hold for flat surfaces as it takes into account the increased radiating surface on a pipe or cylinder.



Curve showing ineffectiveness of Comercial Asbestos Paper for insulation of Bright Tin Pipes

FIG. 3.

From the above, it will be seen that these two conditions tend to counteract each other, so that the result is a curve that will vary for each temperature and each insulating material. Common practice is to follow the inverse square root law for cylinders, and use a multiplier for flat surfaces, such as ovens, which really depend more upon the mechanical construction of the oven than upon the characteristics of the insulation. This multiplier for formula No. 5 varies from 1.2 to 2.5, depending on conditions.

For many applications, such as medium temperature ovens and high temperature furnaces, it is customary to construct the walls of layers of different materials having different internal resistances. The heat loss from such a flat wall can be calculated by the following formula; using the notation and form of formula No. 5 we have

$$Q = At \frac{T_1 - T_2}{\frac{th_1}{k_1} + \frac{th_2}{k_2} + \frac{thn}{kn}} \tag{9}$$

where th is the thickness of the various layers and K the conductivity; or more accurately this is given by McMillan as

$$Q = \frac{ts - ta}{\frac{x_1}{k_1} + \frac{x_2}{k_2} + \frac{x_3}{k_3} + \ldots + \frac{1}{a}} \tag{10}$$

using the same notations as formula No. 6. For cylindrical surfaces this becomes

$$Q = \frac{ts - ta}{\frac{r_s \log_e r_2/r_1}{k_1} + \frac{r_s \log_e r_3/r_2}{k_2} + \ldots + \frac{1}{a}} \tag{11}$$

in which r_s is radius of outside surface of insulation r_1 is outside radius of cylinder and r_2 equals r_1 plus thickness of first layer of insulation, r_3 equals r_2 plus thickness of second layer, etc.

APPLICATION TO APPARATUS.

The materials in class A Table II are used successfully only for quite low temperature work, and due to this fact the heat loss is generally low regardless of insulation used. For this reason, little attention is paid to the proper selection and too often a few layers of asbestos paper is used, as this is easy to obtain almost anywhere. It has been shown that the heat loss from a bare bright tin pipe is less than from the same pipe covered with 7 layers of 0.025-

inch (0.64 mm.) asbestos paper at approximately 180° F. (82°C.) in the pipe (Fig. 3)[6]. So it is obvious that it would be better economy to use some of the fibrous or spongy insulations given in Table III even though the first cost and cost of installation was higher than for the asbestos paper.

Class B, Table II, is by far the most important class, as most commercial and industrial applications fall within it. To meet this demand there are dozens of grades and brands of commercial insulations on the market. Table IV gives only a few representative grades of this class. Much care should be exercised in the selection of an insulation in this class, as many are good under certain conditions and poor under other conditions at the same temperatures. For instance some will stand soaking in water and when dried out are apparently as good as ever. Others disintegrate and fall to pieces under the action of water or any other liquid. Some grades will stand up and hold their place and position under con-

Fig. 4.

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[6] University of Ill. Bulletin No. 117.

tinual jarring and vibration, others settle down and leak out of their retaining walls and leave an air space. So other considerations besides thermal characteristics are important, depending upon the particular application[7].

In the application of these insulations to electrical apparatus, the largest per cent will go on tanks, boilers, etc., and on ovens, drying cabinets, etc. These are shown in figures 4 and 5. On the former the insulation is usually applied exactly as pipe covering, with an outer surface of canvas, while with ovens the insulation is ordinarily confined between two thin sheet metal walls. In building such ovens, care should be exercised so to construct them that there is a minimum of continuous through metal from inside to outside of the wall; that all joints are tight and well

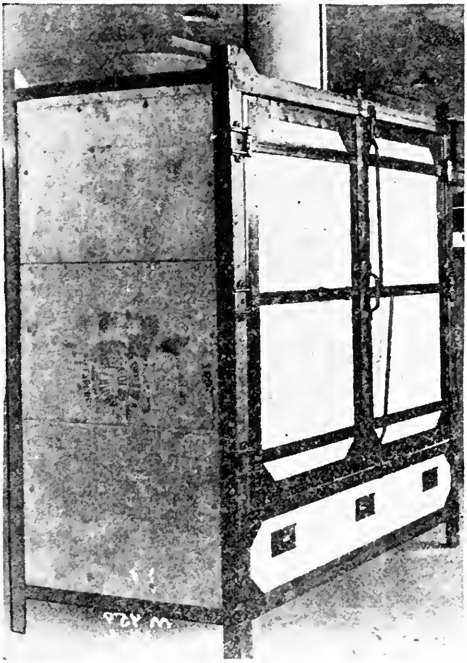

FIG. 5.

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[7] E. R. Weidlein, Chem. and Met. Eng. 24, 295, (1921).

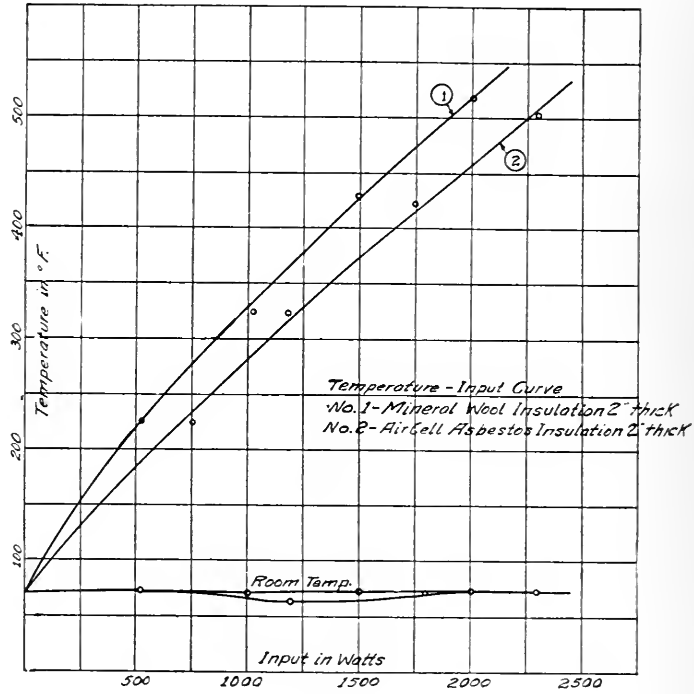

Temperature in °F
100
200
300
400
500
Input in Watts
500
1000
1500
2000
2500
Room Temp.
①
②
Temperature - Input Curve
No. 1- Mineral Wool Insulation 2" thick
No. 2- Air Cell Asbestos Insulation 2" thick

FIG. 6.

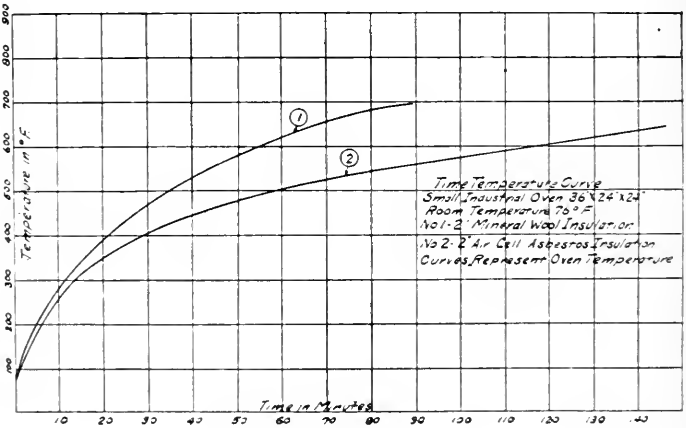
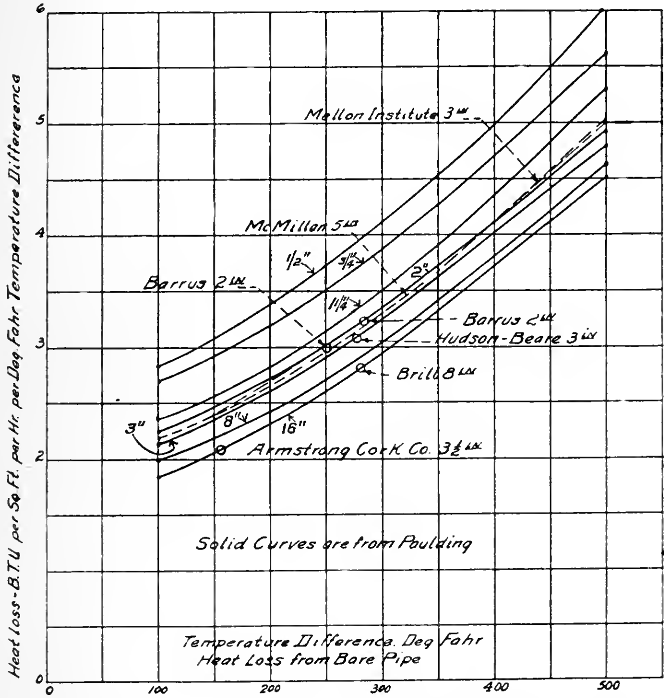

Temperature in °F
100
200
300
400
500
600
700
800
900
Time in Minutes
10
20
30
40
50
60
70
80
90
100
110
120
130
140
①
②
Time Temperature Curve
Small Industrial Oven 36"x24"x24"
Room Temperature 76° F
No 1- 2" Mineral Wool Insulation
No 2- 2" Air Cell Asbestos Insulation
Curves Represent Oven Temperature

FIG. 7.

packed; and that the outer surface of the oven is one that does not radiate the conducted heat readily. Cases are on record of similar ovens in which one was finished in black iron and one in bright galvanized iron. At 500°F. (260°C.) the black oven showed a radiation loss 30 per cent greater than the galvanized oven. Other conditions may have contributed to this difference, but it is believed the different character of surface was the main cause. In ovens of several hundred square feet radiating surface, this is a feature to be watched closely.



Heat Loss from Bare Iron Pipe as determined by various Investigators

The figures ½", ¾", etc., indicate the diameter of the pipes.

FIG. 8.

As brought out previously, it is essential that the specific heat or heat absorbing power of an insulation be taken into considerations as well as its conductivity. Fig. 6 and 7 show curves of identical ovens, one with a commercial grade of mineral wool, the other with a commercial grade of aircel asbestos insulation. It will be noted that the former not only has a lower constant loss, but comes up to temperature more rapidly, thus storing less power to be lost when the oven is shut down at night.

Some of the insulating materials in Table V can be, and often are, used for temperatures as low as 300°F. (149°C.) but their real field lies in furnace work, where temperatures of 1,000 to 3,000°F. (538 to 1,650°C.) are encountered.

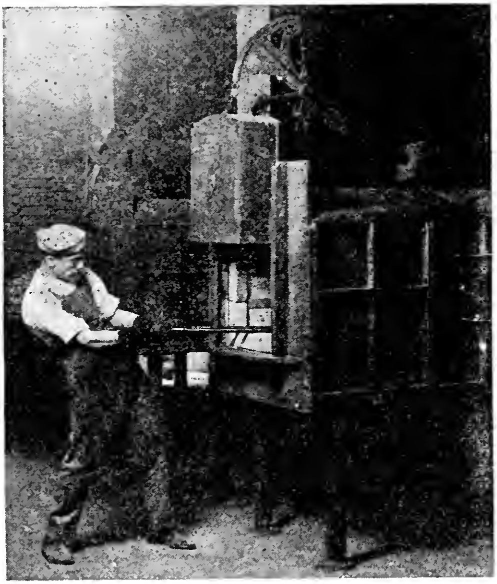


Fig. 9.

While these insulators will stand direct contact with the heating elements and temperatures of 2,000° F., it is better practice to line the inside of the furnace with a good grade of refractory fire brick, and place the insulating brick outside of these. As these insulating brick are not strong mechanically, a layer of building brick or red brick outside of them will protect them and insure permanent insulating value. Fig. 9 shows one of the large electrical furnaces insulated in this manner.

Due to the fact that the absolute mean conductivity of air is considerably lower than any present day commercial insulation, industrial plant engineers often try to increase the efficiency of furnaces and boiler settings by including air spaces in the walls. The results are invariably the opposite from those desired. This is due to the fact that even thin air spaces readily set up convection currents, and that the radiant heat leaps across the air space with little opposition, especially if the air space is close to the inside of the furnace.

Tests by the U. S. Bureau of Mines, proved that a wall of solid fire brick or building brick lost less heat than a similar wall with a 2-inch (51 mm.) air space enclosed in it[8]. Therefore this practice is poor and should be abandoned entirely where medium and high temperatures are involved.

CONCLUSIONS.

While there are numerous grades of heat insulations on the market, there are none that can compare with electrical insulators. Of all the different grades, there are only a few fundamentally different sorts, as some half dozen items will cover the raw materials successfully used. In all these materials the true insulation value lies almost entirely in the entrapped dead air spaces of their structure. The difference between grades then really goes back to the physical structure of the crystals or cells. This fact leads many engineers astray in the use, in furnace and oven walls, of air spaces, which actually increase rather than decrease the heat loss.

The application of poor insulation can have the same effect as the air spaces mentioned above, as shown by the University of Illinois in tests of asbestos paper on hot air pipes. See Fig. 2.

While the conductivity of an insulation is of primary importance, other thermal characteristics must be considered, such as specific heat and specific weight. The application also has to be considered with regard to the physical properties of the material.

The laws of heat flow are simple and follow closely those for electrical energy, but are little used or understood. This probably is due in part to the fact that there are few reliable data available on the subject, and of these the values given by different authors vary over wide limits.

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[8] Bureau of Mines Bulletin No. 8.

It is the writer's opinion that a great deal more research and development work should be done along the lines of heat insulation engineering, as we have about come to a stop and have accepted our present standards by saying "there is bound to be a certain amount of heat lost, and this is as good as we can do."

I believe that if there was a wider distribution of available data and a broader dissemination of the laws and character of heat flow and its prevention, it would help to conserve the national coal supply and result in better insulation methods being developed. The progress of electrically heated apparatus is dependent to a large extent upon the efficiency of its insulation, and warrants the keenest attention of electrical, chemical and mechanical engineers, as well as of heating and ventilating engineers.

DISCUSSION.

CARL HERING[1]: Mr. Woodson spoke of the thermal ohm. This is decidedly the best unit to use for electrical engineers, who deal with energy in electrical units but it is not the most convenient unit to use when you are dealing with B. t. u.'s and calories, as in the case of steam pipes. It is something like using the circular mil and the square mil; each of them is the best unit to use under particular circumstances, because the conversion factor is then unity.

I do not know whether Mr. Woodson called attention to another point, namely the effect of joints in the insulation, which is quite important. For instance, if in the wall of a furnace the bricks are placed on edge, you get a much better insulation than if placed flat, because there is an extra joint, and a joint is a very important heat insulator. I have seen the material on one side of a joint red hot, while on the other side it was black. There is great heat insulation in a joint.

He refers to the spaces in finely divided material. The late Mr. Stanley,[2] of the General Electric Company, made researches with such material several years ago, and found the interesting results

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[1] Consulting Electrical Engr., Philadelphia, Pa.

[2] Personal communication.

that as such material is compressed, which means that the air spaces become smaller, the heat insulation at first improves, but after reaching a certain point, if you compress it still more, the heat insulation again diminishes. There is a maximum point to which one should compress such granular or fluffy material.

Foundrymen have discovered that if they whitewash the outside of a furnace, it makes them feel more comfortable, which to us means that whitewashing the outside of a furnace adds quite a little to the heat insulation; it is hotter to the touch, but emits less heat.

F. A. J. FITZGERALD[3]: Joint heat insulation referred to by Dr. Hering is particularly noticeable in carbon electrodes. For example, in an Acheson graphite electrode, while a well-made joint may have a very low electrical resistance, the resistance of the flow of heat is extremely high. In furnaces with metallic resistors, where the terminals are made of some metal, it would be interesting to find out if one could get a low electrical resistance with a high heat resistance.

J. C. WOODSON (*Communicated*): The matter of surface or joint resistance to heat flow is gone into on page 135 on this paper, and is largely responsible for increased insulating value of insulation when this insulation has several distinct joints or parallel surfaces. This is also a partial explanation of the increased efficiency found in insulated walls using more than one kind of insulating medium in the same wall. More definite data should be made available on the true value of the surface resistance of insulating materials under varying conditions.

[3] FitzGerald Labs., Niagara Falls, N. Y.

A paper presented at the Forty-second General Meeting of the American Electrochemical Society held in Montreal, and brought up for discussion at the Forty-third meeting in New York City, May 4, 1923, President Schluederberg in the Chair.

METHODS OF HANDLING MATERIALS IN THE ELECTRIC FURNACE AND THE BEST TYPE OF FURNACE TO USE[1]

By Frank W. Brooke[2]

Abstract.

The author discusses, in general, the design of various electric furnaces, such as the plain box type, the special box type, the car type, the recuperative and continuous furnaces, and refers to their advantages and disadvantages. Attention is drawn to the method of handling materials for these furnaces, so that a uniform temperature and high furnace efficiency may be maintained.

[A. D. S.]

The outstanding engineering features that have made the modern electric furnace for temperatures up to 980° C. (1800° F.) so successful are the drawn nickel-chromium resistance elements and the high standard of thermal insulation. Those who have read the many interesting papers presented at various times, especially by such authors as Mr. E. F. Collins, will realize the careful study and pioneer work that has been given to these subjects, and the accurate data that have been compiled by those interests that are successfully pushing the electric heat-treating furnace.

One problem, however, that will not be standardized for many years to come is the method of handling the material to be treated both while it is in the furnace and out of the furnace. The efficiency of the best design of furnace can be entirely ruined by poor handling methods. On the other hand, given a particular method of handling the material, it becomes a problem for an experienced furnace engineer to design the furnace to meet this method.

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[1] Original manuscript received September 20, 1922.

[2] Chief Engineer, Wm. Swindell & Bros., Pittsburgh, Pa.

Take, for instance, the handling of very light materials in many of the existing fuel-fired furnaces. Strength and resistance, as long as possible to scaling, has necessitated a high ratio of the weight of the handling medium in the furnace to the work being treated. It is quite common to meet cases where this ratio is 2 to 1, or more, which means that twice as much fuel is expended in heating the holding or carrying device as in heating the work.

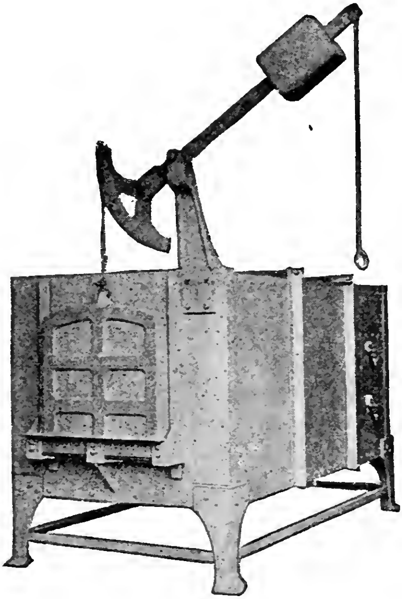

FIG. 1

The electric furnace designer has met these cases in a proper engineering manner. The whole of his furnace engineering is taken from accurate mathematical data. The heat input is exact and constant. He studies specific heats not only at room temperatures but along the range of his working temperatures. He calculates the heat losses and so forth. Besides, he is not confronted with the eating away of his holding devices by oxidation to the same extent.

It is the object of this paper to point out some of the advantages and disadvantages of various furnace designs and methods employed in the handling of materials for electric furnaces at the higher temperatures.

The plain box type of furnace having, say, one door: This design is simple and the many methods of handling material for it are too well known to require description. It allows for high grade thermal insulation, and care need only be taken to provide against the door losses. This is done by making a well-sealed door, and by doubling up resistance elements at the door ends. See Fig. 1.

Special box type: In electric furnaces the volume of the furnace chamber is not restricted to the same degree as in the fuel-fired furnace, and therefore lends itself to the use of special design, such as is shown in Fig. 2. This furnace is designed for the accurate heat treatment of steel products having varied lengths, where the output does not warrant the use of a different length of furnace for each different length of product.

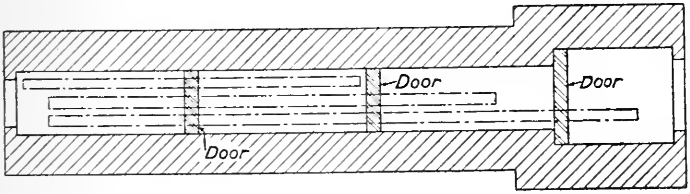

FIG. 2

It is fitted with three partition doors, each having a special seal, and the heating units are so placed that there is a uniform heat distribution under all conditions of operation. The end doors face into two different shops and give an extremely flexible arrangement for the class of work for which it was designed, at a first cost and an operating cost both much lower than if separate furnaces were used.

Another interesting variation of box type furnace is one in which a preheating chamber is put back to back with the high temperature chamber, having in this case only one partition wall. This is used for vitreous enameling work, or for heat treating fine tools. In the latter case the low temperature chamber can also be used for drawing.

For vitreous enameling a special form of hearth is used, either for facilitating the handling of the work, as in thin sheet work, or for allowing a large amount of the heat to be applied at the bottom of the work to be treated. It is essential, as in bath tub work, for the enameling to be done "through the work" as well as from the upper surface.

Car type: This gives a much better handling arrangement, especially for large pieces handled by the crane. In considering its use, it should be borne in mind that when the car is withdrawn from the furnace the entire hearth bottom is exposed to rapid heat loss. In order to give high thermal efficiency and uniformity of temperature, an electric furnace car bottom is much more massive than that used in the ordinary fuel-fired furnace, and when exposed to direct radiation loss it loses a greater quantity of heat.

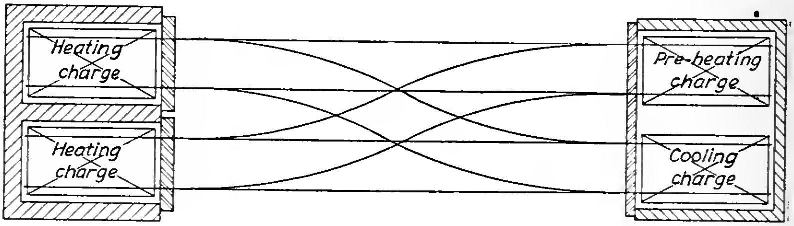

Fig. 3.

For this reason the time cycle of electric car type furnaces should be arranged to ensure the car being rapidly unloaded and reloaded, or else a dummy furnace should be provided, as shown in Fig. 3, whereby there is an exchange of heat not only between the cooling of a hot charge to a cold charge but also from car to car. For heat treatments requiring a long time of heating, holding and cooling in the furnace, it is advantageous to build the door directly on to the car.

Recuperative furnaces: Fig. 3, already referred to, is perhaps the simplest form of this type of furnace. Providing the time between heats is not too long and the output warrants two furnaces, its use invariably pays. Where the heats are of long duration, the steady radiation loss of the dummy furnace defeats its economy.

A better form of recuperative furnace is shown in Fig. 4. This arrangement allows for recuperation from one heating chamber, but on the other hand requires three chambers per unit. It requires also considerable rail switching, but has given excellent fuel economy.

Still another form of recuperation is shown in the counter-flow type of furnace, the various designs of which are too numerous to illustrate. Fig. 5 shows a car type of counter-flow furnace, now used in the annealing of gray iron castings.

The furnace is divided into seven sections, each corresponding to a car length. Only the middle section is equipped with heating units and has a short dividing wall. The heating units are suspended on the four walls so that each preheated car is heated from both sides. On either side of the heating section are two cooling and two preheating sections.

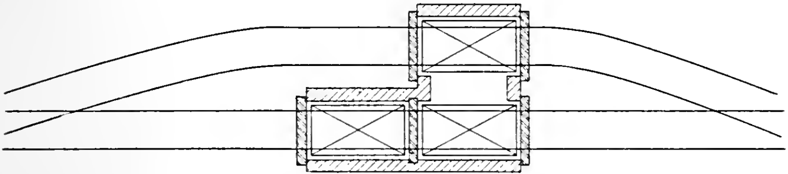

FIG. 4

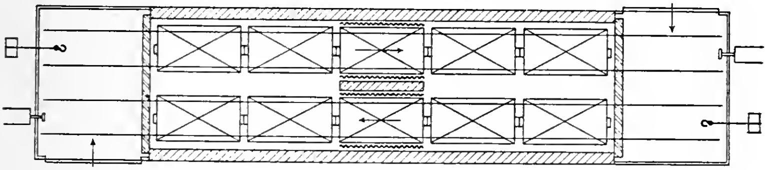

FIG. 5.

The trains of parallel cars move in opposite directions, and each moves one car length at equal intervals of time. Therefore a heated car and its charge leaving a heating section is placed directly beside a car and its charge partially preheated, and is given a period of interchange of heat. It then moves forward another car length, and some of its remaining heat is given up to a cold car and its charge coming from the transfer chamber. There is also a transfer chamber at either end, enclosed in lightly insulated walls, as the cars after being reloaded still retain a considerable amount of heat well worth conserving.

It is interesting to note that the first electric furnace installed of this design had a partition wall running the entire length of the furnace, in which port holes had been left at the top and bottom. The design of this furnace was taken from a previous fuel type design, but the engineers built the partition wall in such a way that the portions in the recuperative chambers could be readily removed if necessary, They soon found this to be necessary. It was also found that instead of longitudinal partition being necessary, transverse partitions between each section were absolutely essential for temperature uniformity and efficient heat exchange. The work which is small and of very thin gray iron castings is placed on superimposed trays, and one end of each tray forms part of the transverse partition.

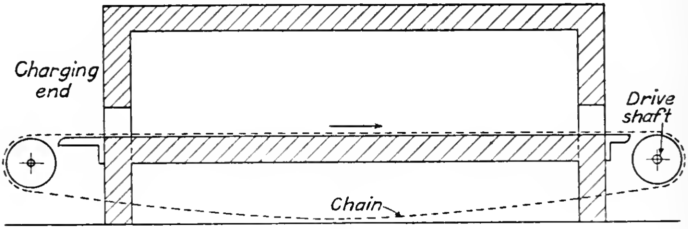

FIG. 6.

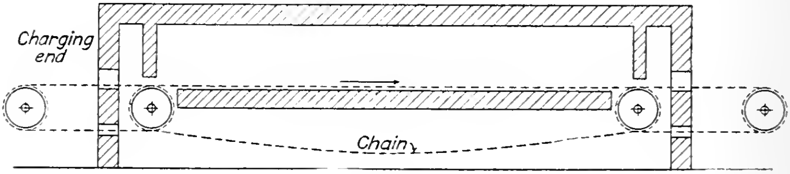

FIG. 7.

Continuous furnaces: In electric furnace salesmanship it has been the author's experience that the prospective electric furnace user thinks first of all of a continuous furnace to do the work, feeling that a continuous furnace is a labor-saving furnace, a fuel saver, routes his work better and is more modern. There are, however, many points of electric furnace engineering to be considered before a complete knowledge of these points can be given, and it is surprising how often it can be shown (excepting in such cases as producers of large quantity of uniform products as in the motor car industry) that a continuous furnace is not the best all-round furnace to install, often proving a disappointment to the prospective customer.

Fig. 6 shows a continuous furnace used for heat treating light flat discs, and working satisfactorily. The limiting feature of such a design is the temperature of the conveyor. If carried above 650° C. (1200° F.) the stretch becomes a serious consideration.

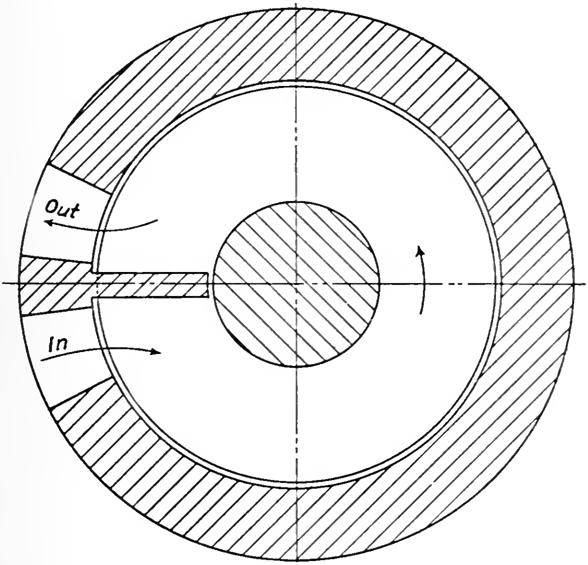

FIG. 8.

A surprising feature in such a design is the loss of heat caused by the exposed ends of the chain. It is easy to see that the loss would be material, but actual experiments in one particular design show a thermal efficiency of about 18 per cent. This can be greatly improved by the proper boxing-in of the ends, but where chain area must be available for loading and unloading this enclosing is limited.

A better arrangement for carrying light work through the furnace is shown in Fig. 7. This consists of three chain systems, only the middle one of which is always inside the highly insulated walls of the furnace. The charging and discharging systems do not attain a temperature sufficiently high to cause a serious heat loss. When a chain system is totally enclosed in the way shown, it must be remembered that this chain attains the temperature of heat balance of the furnace, which is decidedly higher than the chain shown in Fig. 6. It is also more difficult to take care of heat losses through the journals when higher shaft temperatures and stretch adjustment must be taken care of.

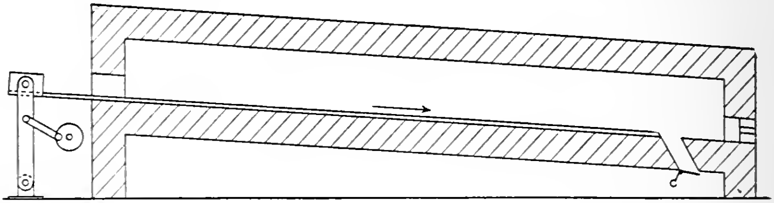

FIG. 9.

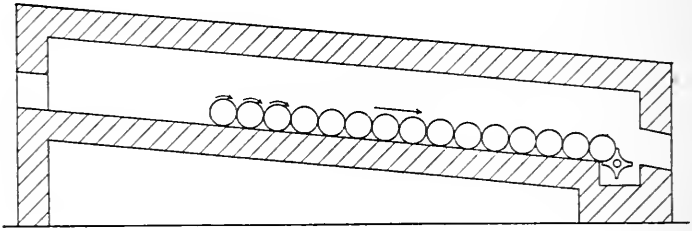

FIG. 10.

The author is at the present time engaged in the designing of three different types of electric furnaces, in each of which the mechanical handling of the material is of vital importance, as the material must not be marked and furnace efficiency and temperature uniformity is of utmost importance. He is not at liberty to publish these designs now, but hopes at some future occasion to give a paper on this subject.

For the continuous conveying of work through an electric furnace at the higher temperatures, the so-called "doughnut" furnace offers an excellent method of carrying out the operation. A plan diagram of this is shown in Fig. 8. It has many advantages. The conveying hearth is made of refractory materials, and can therefore handle materials at the limiting temperatures of electric furnace heat treatment. The charging and discharging doors are adjacent, and in many operations one man can attend to both. The thermal efficiency is high, as only the hearth seals under the furnace offer any insulating difficulty. It is used to special advantage in the heat treatment of gears and small machine parts. When the work to be treated is of a uniform character, automatic loading chutes can be adapted, and the work can be "swept-out" at the discharge end.

The "push" type of furnace is perhaps one of the most efficient types of continuous furnaces used, and is shown in Fig. 9. It is restricted to work of a uniform shape, and work which will push in a long column without bridging. This tendency to bridge can be lessened by inclining the furnace and thus lessening the friction to push. It is an excellent method of conveying such parts as small connecting rods, push rods, small cylindrical pieces, etc., and fits in with production heat treatment for small parts. The speed of travel can be varied through a wide range and the discharge end can be sealed in the quenching tank.

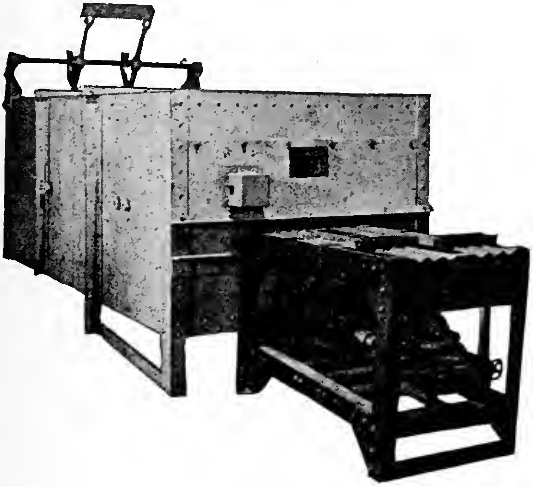

FIG. 11.

The "gravity roll" type of furnace has the same degree of efficiency and usefulness as the "push" type, but is still further restricted to products that will roll by gravity. The feed through the furnace can be regulated by a discharge timing gear, shown in its simplest form in Fig. 10.

The "push" furnace is simple in construction, has a low operating cost, and has a lower first cost than the many other types of furnace. See Fig. 11.

The "walking beam" type of furnace forms one of the fascinating means of handling materials through an electric furnace. It is restricted to uniform shapes and sizes, such as automobile crankshaft, connecting rods, bars of steel, etc. In the more simple type of walking beam, shown in Fig. 12, the beams are lined with refractory material, but the continuous top surfaces of the beams must be kept in a true horizontal plane, so that the points of contact with the work are made with each beam simultaneously; otherwise the work will creep more along one side of the furnace than the other. A good beam mechanism which ensures work temperature uniformity and furnace efficiency adds considerably to the first cost of the furnace.

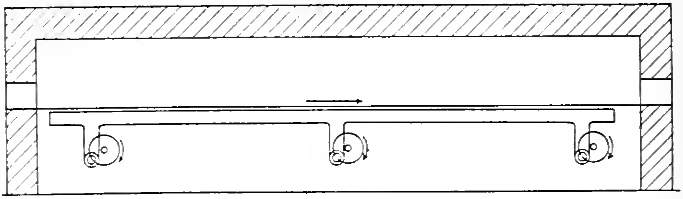

Fig. 12.

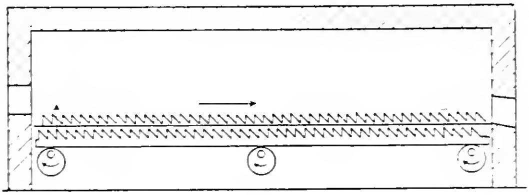

Fig. 13.

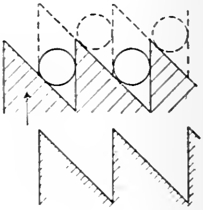

Fig. 14.

An interesting variation of the "walking beam" furnace is the type shown in Fig. 13, designed to treat shells, crankshafts, short shafts, axles, etc., in such a way that the axes of the work are always parallel and there can be no jamming in the furnace. The way the work progresses through the furnace is clearly shown in Fig. 14.

For the heat treatment of steel balls and similar materials, a design, such as is shown in Fig. 15, offers an excellent method. The author does not know of any furnace of this type in which electricity is used as a fuel, but there is no reason why electric resistance units cannot be applied to give all the inherent values of the electric furnace.

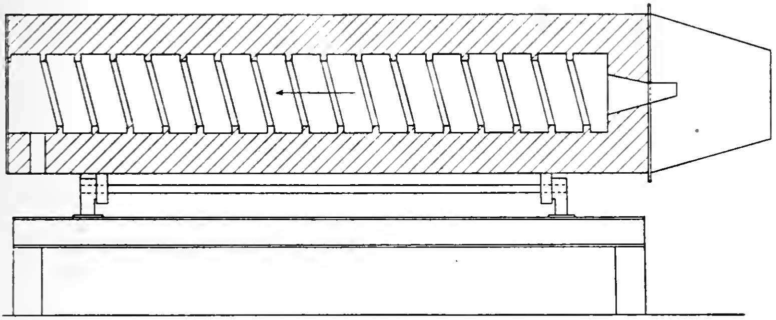

FIG. 15.

The figures shown and types referred to are very general. It would be difficult to give references that would be complete and fair.

A paper presented at the Forty-third General Meeting of the American Electrochemical Society held in New York City, May 4, 1923, President Schluederberg in the Chair.

THE CONVERSION OF DIAMONDS TO GRAPHITE AT HIGH TEMPERATURES.[1]

By M. DeKay Thompson and Per K. Frölich.[2]
Microscopic Work By J. L. Gillson.

Abstract.

It is shown conclusively that diamonds change slowly at 1650° C. to a substance that gives the Brodie test for graphite, and that the velocity of this reaction is increased about 26 times by an increase of 100° above this temperature.

INTRODUCTION.

In looking over the previous work on this subject, there is found quite a lack of agreement in the results obtained by different investigators. This may be accounted for by inaccuracy in the temperature measurements, as in many cases it is not clearly explained how these were made, and in others it is stated that temperatures were only estimated. The object of the present investigations was to determine at what temperature diamonds change to some other form of carbon with appreciable velocity, and to determine whether or not this other form is graphite. It would be hopeless to attempt to verify experimentally the calculations of Weigert[3] and of Pollitzer[4], according to whom the temperature below which diamond is stable is respectively 372° and 340° C., because the reaction velocity is too slow at

[1] Manuscript received February 1, 1923.

[2] Contribution from the Electrochemical Laboratory of the Rogers Laboratory of Physics, and Geological Laboratory, Massachusetts Institute of Technology, Cambridge.

[3] Abegg's Handbuch der anorg. Chem. III, 2, p. 47 (1909).

[4] Die Berechnung chemisher Affinitäten nach dem Nernstschen Warmetheorem. p. 136 (1912).

such low temperatures. According to Boeke[5], if the heats of combustion determined by Roth and Wallasch[6] are used in this calculation in place of those of Berthelot, used by Weigert and by Pollitzer, the result is that at atmospheric pressure diamond is unstable at all temperatures down to the absolute zero.

All of these calculations were made by the Nernst heat theorem, the data for which are the specific heats of diamond and graphite down to temperatures near the absolute zero, and the total energy change of the reaction: diamond → graphite.

PREVIOUS WORK.

The references in the foot note[7] are to the most important previous work on this subject, but in order to save space they will not be considered at length. They may be briefly summarized as follows:

Diamond changes to graphite in the arc, but, according to Moissan, not at 2000° C.; according to Doelter, diamonds are only blackened in the surface up to 2500° C., while Vogel and Tammann say diamond changes to graphite at 1200°. It was on account of these discordant results that the following work was undertaken.

EXPERIMENTAL.

A small Arsem[8] vacuum furnace was used for heating the diamonds. These were placed in the center of a carbon crucible on a small carbon plate as shown in Fig. 1. In the first experiment the cover over the diamond was omitted. The crucible had a cover with a hole through which the temperature was taken with a Leeds and Northrup optical pyrometer, which was compared with a standard optical pyrometer, and the small correction applied. The temperature had to be taken through a mica window in the top of the furnace. The effect of the mica

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[5] Centralbl. Min. Geol. und Paläontologie 321 (1914).

[6] B. d.d. chem. Ges. 46, 896 (1913).

[7] Moissan, Le Four Electrique, 157 (1897); Parson and Swinton, Proc. Roy. Soc. 80, 784 (1907-8); Vogel and Tammann, Z. phys. Chem. 69, 600 (1910); Doelter, Monathaft f. Chemie 32, 280 (1911).

[8] Trans. Am. Electrochem. Soc. 9, 153 (1906).

window on the temperature indication was determined by reading the temperature of another furnace with the window between the hot body and the pyrometer, and without the window. It was found that at 1260° with the window in place the correction to be added is 40°, at 1550° the correction is 60°, and at 1710° it is 75°. Corresponding corrections were applied to the readings through the window. The temperature of the plate covering the diamond was taken. This must have been very nearly under black body conditions. It is believed that temperatures are correct to within 30° C.

The furnace was evacuated to only 5 mm. in the first four runs. after this two pumps were connected in series, and the vacuum was reduced to less than 1 mm. In any case there was little chance of any oxygen getting at the diamond with so much other carbon present, and all of the oxygen present could not have burnt more than a small fraction of the diamond if it burnt nothing else.

The power in the furnace was kept constant by means of a carbon plate resistance and was read by a wattmeter. With constant power the temperature remained constant.

The method of procedure decided on was to heat for a given time to different temperatures and examine the product microscopically and chemically. The chemical test consisted in the Brodie test for graphite, by oxidizing in a solution of nitric acid and potassium chlorate.[9] For microscopic examination a small piece was cracked off and immersed in a solution of sulfur in methylene iodide, which has a high index of refraction.

The method of carrying out the Brodie test was to digest the sample at 60° C. with finely ground potassium chlorate and concentrated nitric acid for 24 hours. It was washed, dried and the treatment repeated. Three treatments changed a sample of graphite to yellow graphitic oxide. Acheson graphite was tested and gave a yellow product, while coke dissolved completely giving the solution a yellow color, probably due to iron.

The results are contained in Table I.

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[9] For the description of the Brodie test see Moissan, The Electric Furnace, 50 (1904); Donath, Der Graphit, 15 (1904); Selvig and Ratliff, Trans. Am. Electrochem. Soc. 37, 121 (1920).

TABLE I.

Effects of Heating Diamonds to High Temperature.

No.	Time required to reach highest temperature	Duration of heating at highest temp.	Highest temp. °C.	Vacuum
1	....	3 hr.	2060-2090	5 mm.
2	30 min. to 800° 1 hr. at 800°	2 hr.	1000-1015	5 mm.
3	30 min.	2.5 hr.	1150-1200	5 mm.
4	30 min.	5.5 hr.	1135-1155	5 mm.
5	30 min.	6.5 hr.	1250	less than 1 mm.
6	In 20 min. raised to 1250° 40 min., 1250-1350	6 hr.	1350	less than 1 mm.
7	30 min.	4.5 hr.	1680	less than 1 mm.
8	25 min. to 1530	25 min.	1535	less than 1 mm.
9	30 min. to 1520	5 hr.	1535	less than 1 mm.
10	....	9.5 hr.	1650	Less than 1 mm.
11	....	12 hr.	1650	Less than 1 mm.
12	30 min.	2.5 hr.	1865	Less than 1 mm.
13	25 min.	2 hr.	1760	Less than 1 mm.
14	25 min.	1 hr.	1760	Less than 1 mm.

REMARKS.

Exp. 1. Diamond completely destroyed. Product gave Brodie test.

Exp. 2. Diamond No. 2. Light grey color. Transparent; dark spot appeared in center. No superficial change.

Exp. 3. Diamond No. 2. Dark grey. Filled with small dark spots. Small piece cracked off showed double refraction. This small sample contained a dark spot.

Exp. 4. Diamond No. 2. No appreciable change.

Exp. 5. Diamond No. 2. No superficial change. Looked darker. More internal dark spots.

Exp. 6. Diamond No. 2. More spots and larger. Under microscope they had a brown color and spongy appearance. The dark color of the diamond seemed to be due to many cracks which totally reflected the light in air, but in the sulfur solution in methylene iodide the diamond was clear except for the spots.

Exp. 7. Diamond No. 2. Completely black. Blackened paper slightly. The spots inside now black, not brown as at first. The black spots have a metallic luster when observed in reflected light under the microscope identical with that of graphite.

Exp. 8. Diamond No. 3. Slightly grey.

Exp. 9. Diamond No. 4. Turned black.

Exp. 10. Diamond No. 2. Brittle and easily broken. Part of surface shiny, rest dull black. Blackened paper like a pencil. One small corner still transparent in small piece examined under microscope. Still hard enough to scratch steel.

Exp. 11. Diamond No. 2. Diamond was cracked into a number of pieces. All treated with HNO_3 and $KClO_3$. Small ones changed to graphitic acid. The large pieces did not dissolve, but were of lighter color. Total duration at 1650°, 26 hr.

Exp. 12. Diamond No. 5. Black residue. Gave Brodie test.

Exp. 13. Diamond No. 6. Diamond was split to pieces.

Exp. 14. Diamond No. 7. Diamond appeared at about the same degree of change as No. 2 after 26 hr. at 1650°. Parts were found thrown out from the central hole in the plate, as though the diamond exploded.

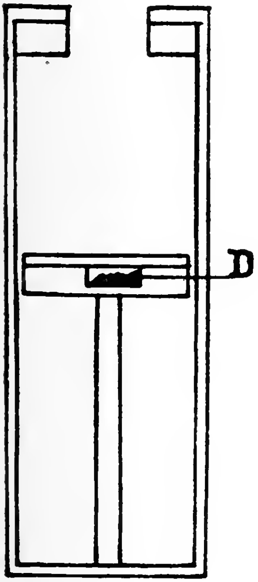

Fig. 1

Fig. 2

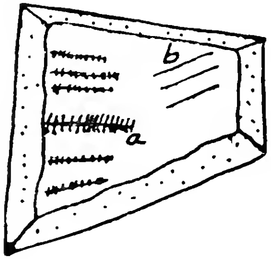

Fig. 3

Fig. 1. Diamond (D) in Graphite Crucible.

Fig. 2. Diamond No. 7. Fragment of diamond lying with outside face uppermost. Heavy coating of graphite on the outside with numerous specks of graphite scattered through the still transparent but cracked interior. Heavy cross-hatching represents the graphite coated surface; the light represents the interior of the clear diamond. x 150.

Fig. 3. Diamond No. 2 after Exp. No. 7. Cleavage Face broken from diamond shows dendritic development of graphite on the face, as at "a," and the development along incipient cleavage planes, as at "b." Dots on edges are graphite developing in the interior of the diamond. Somewhat generalized. x 300.

DISCUSSION OF RESULTS.

The above experiments show conclusively that diamonds change slowly at 1650° C. to a substance that gives the Brodie test. This change takes place about 26 times as rapidly by raising the temperature 100°. Diamonds turn dark at 1000°, but this is largely due to numerous cracks causing absorption of light from total reflection. The cracks were probably produced by the small black spots. These spots are doubtless the beginnings of change to graphite, producing strains and double refraction. Doelter also found double refraction in diamonds that had been heated. Experiments 8 and 9 show these cracks are not due alone to thermal expansion and contraction, for if they were the two diamonds would have had the same appearance.

DISCUSSION.

W. C. ARSEM[1]: There seems to be a great deal of confusion in regard to the nature of the different forms of carbon that we meet with. There is no question about what we mean by diamond or pure graphite. They are definite crystalline substances, and X-ray analysis has shown them to have definite molecular structure and definite lattices. When we consider the different so-called amorphous carbons and so-called graphites of indefinite character, there is some doubt.

It seems to me that when carbon is set free from an organic compound or derived from some different form by heat, if the conditions are not favorable for an arrangement or rearrangement of the atoms to form a definite crystalline structure, we must have a mixed lattice structure.

Amorphous carbon derived from sugar will not have a definite crystalline structure. It will be a heterogeneous arrangement of atoms. You may have different characteristic groupings here and there throughout the whole mass or solid particle, but no definite repeated chain or pattern structure, such as you have in a crystalline substance. In the same way we would expect, on heating

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[1] Consulting Chemical Engr., Schenectady, N. Y.

the diamond to temperatures far below the point of mobility, that the atoms can not rearrange themselves to form a definite lattice structure. So that we would not expect to get pure graphite by heating the diamond any more than we would expect to get pure graphite, from heating certain amorphous carbon to a high temperature.

Now, as to the Brodie test, I believe that when pure crystalline graphite is oxidized, that the so-called graphitic acid, the yellow organic substance which is formed, has a definite chemical structure, and can be identified, but when obtained from a carbon with a mixed lattice structure, the same as we would expect to get on heating most amorphous carbons or the diamond, the yellow oxidation product does not have a definite structure. It may be a mixture of substances, or it may be a complex organic compound with a mixed lattice structure corresponding to the structure of the carbon from which it is derived.

The Brodie test, in the light of our present knowledge of molecular structure can not be regarded as a satisfactory test for graphite, or even for the presence of graphitic structure, until more is known of the chemical nature of the yellow oxidation products obtained with different carbons.

I presented a paper before the Society some years ago, and mentioned the heating of a diamond to 3,000°. I found a specific gravity of the product that was about 1.8, whereas, pure graphite should have a specific gravity of 2.25. I do not think that pure graphite can result from heating the diamond under these conditions, and I do not believe that the data given in the present paper support that conclusion.

Colin G. Fink[2]: I should like to refer briefly to experiments recently carried out at the laboratories of the Siemens-Halske Company.[3] They started out with amorphous carbon in fine thread form, and heated this up to temperatures of 3,000 to 3,600°. What they obtained was a graphite of 2.23 specific gravity.

They tested these fine filaments, and curiously enough they could be rolled, and their length extended by 10 per cent. Furthermore, they could take the filaments and wind them into a

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[2] Consulting Metallurgist, New York City.

[3] Z. Elektrochem. **29**, 171 (1923).

very small coil, and then straighten them out again just as though they were made of lead.

F. A. J. FitzGerald[4]: I understand from Dr. Fink that the Siemens-Halske graphite filaments had a positive temperature coefficient of electric resistivity like the Gem filaments, on which Dr. Whitney was working some years ago at Schenectady.

Does Mr. Arsem consider the Brodie test a definition of graphite as Berthelot suggested? It is probable that the best test for graphite is found in a study of the lattice structure by X-ray examination.

W. C. Arsem: On some of the work on Gem filaments we produced a graphite with a specific resistance one-third that of mercury and a pronounced positive temperature coefficient. Some of this was produced in thin sheets that had the characteristics of tin foil and could be rolled up, but I never succeeded in rolling any of it thinner and extending its length. I had hopes of doing so, but about that time we lost interest in it, because the tungsten lamp looked more promising, and all efforts were devoted to that work.

S. C. Lind[5]: It seems to me the important thing in connection with this paper is, whether the spots that Prof. Thompson has found can be examined by the X-ray method. We agree it is perfectly satisfactory for graphite or diamond, but if it can not be used on the spots as they exist in diamond, I do not see that it would be of much use in that connection.

I would like to mention one or two points in connection with some observations we have recently made. I do not wish to go fully into the matter because we are publishing the results in the Journal of the Franklin Institute next month. In connection with some work in the coloring of diamonds with alpha rays, we found under some conditions that "carbon spots" were produced. I will not call these spots graphite, because we have not proved they are. The results were produced at ordinary temperature, showing that high temperature is not necessary to convert diamond into some other form of carbon. These spots were small, round spots in the interior of the diamond, which does not

[4] FitzGerald Labs., Niagara Falls, N. Y.

[5] Chief Chemist, U. S. Bureau of Mines, Washington, D. C.

support the idea that they are produced directly by alpha rays. In some instances they appeared to grow from a center. There was a halo surrounding the round spot, which made us think they grew from a center acting as a seeding point in the diamond.

Furthermore, at the temperature of a blast lamp they disappeared and reverted to diamond. Whether this reversion will satisfy Dr. Fink or not, I do not know, but it satisfied the jewelers who had furnished the diamonds, because otherwise they would have stood a considerable financial loss. These spots disappeared absolutely and went back to perfect diamonds, showing, I think for the first time, that there is some form of carbon other than diamond, which will revert, under conditions we have always supposed were not characteristic of diamond in the stable form, into diamond. Whether or not this controverts the phase rule, I will leave to you to decide.

ANCEL ST. JOHN[6]: Regarding the question as to whether the X-ray would be able to tell about the change from diamond to graphite, I can say that it would. But I do not know how soon the work on this will be completed.

I have on my desk a few rather small diamonds. They are unfortunately not as large nor as numerous as I would like to play with, but they will do. For with a very small quantity of material you can get results by the X-ray method which are incontrovertible. Thus, in a photograph of the pattern from diamond, A. W. Hull[7] has obtained twenty-five of the twenty-seven lines calculated for the structure assigned to diamond, and in a pattern from graphite, nineteen of the forty lines required by its proposed structure. By mounting specimens in a different way, I have recorded thirty of these graphite lines in a single pattern.

One of the problems I want to attack when I get time is to find out just what happens to the crystal structure when a diamond is heated until it goes through some of the transformations mentioned.

COLIN G. FINK: Dr. Lind says you can get the spots at low temperature by the action of alpha rays on the diamond. Does

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[6] Union Carbide and Carbon Research Lab., Inc., Long Island City, N. Y.

[7] Physical Review, 10, 695 (1917).

he mean to infer that in the Arsem furnace rays from the incandescent crucible may have had some effect? That it was not the heat alone, but radiation from the hot crucible that may have brought about the spots?

S. C. LIND: I did not intend to draw such an inference. All I meant to point out was that it is evidently possible, under some conditions other than high temperatures, to change diamond into some other form of carbon. I did not mean to question Prof. Thompson's results.

A paper presented at the Forty-third General Meeting of the American Electrochemical Society held in New York City, May 4, 1923, President Schluederberg in the Chair.

THE RELATION BETWEEN CURRENT, VOLTAGE AND THE LENGTH OF CARBON ARCS[1]

By A. E. R. Westman[2]

Abstract.

An account of the early work on the electric arc has been given by Mrs. Ayrton[3], and a summary of present knowledge by Steinmetz[4]. Each of these writers is the author of a formula connecting current, voltage, and arc length; but in the experiments on which these formulas were based the currents only ran up to 30 amperes or so, and it seemed desirable to add to the experimental material. The present paper gives an account of measurements made with currents up to 770 amperes.

I. INSTRUMENTS AND APPARATUS.

The voltage over the arc was measured directly by a Weston model 45 voltmeter with scale 0-150 volts (V_1 Fig. 1). In addition, in order to get closer readings, a second voltmeter (V_2) of the same type but with scale 0-3 volts was used to measure the difference between the e. m. f. of a storage cell (B) and the p. d. over 70 ohms, forming part of a resistance of 1,000 ohms in parallel with the arc; in the run of March 8th referred to later, the voltage over the arc was given by the relation:

$$e = 28.0 + 0.340 \text{ div.} \tag{1}$$

where "div." is the reading V_2 in fiftieths of a volt.

The current was measured by a Weston millivoltmeter model 45 (M Fig. 1) in conjunction with appropriate shunts (S). The

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[1] Original Manuscript received August 21, 1922.

[2] Department of Electrochemistry, Univ. of Toronto, Toronto, Ont.

[3] H. Ayrton, "The Electric Arc," Electrician Pub. Co., London, 1908.

[4] Chem. and Met. Eng., 22, 458 (1920).

millivoltmeter, the shunts, and the voltmeters mentioned above, were all calibrated by comparison with Weston standards.

The current was derived from a 100 kw. 110 v. d. c. compound wound generator driven by a steam turbine in the power house of the University; during my experiments no other load was carried on this generator. Owing to a breakdown in the power house, however, many of the measurements (including those of March 8th) had to be made with power supplied by the Toronto Electric Light Company.

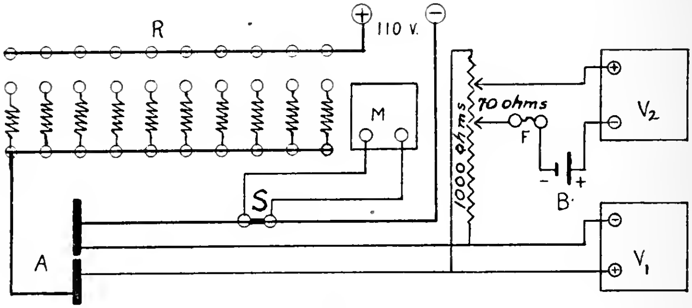

FIG. 1

The rheostat (R Fig. 1) in series with the arc consisted of ten parallel coils of No. 12 iron (telegraph) wire immersed in running water. Each coil had a resistance when new of about half an ohm, and was provided with its own switch; the resistance in series with the arc could thus be varied from 0.5 to 0.05 ohm. The relation between current i, and voltage over the arc, e, is given by

$$e = E - iR \tag{2}$$

where E is the voltage at the source of supply, and R the resistance of the rheostat. If the temperature of the rheostat wires, and hence their resistance, were independent of the current, and if there were no voltage drop in the leads carrying in the current, R and E would be constants, and the relation between current and voltage over the arc would be linear so long as the setting of the rheostat remained unchanged; this is the relation assumed by Mrs. Ayrton and others in their work with low amperage. Under the conditions of my own experiments, however, the temperature of the rheostat wires was far from independent of the current, the water flowing hot from the wire box; and yet a graph of the 200 current and voltage readings of the run of March 8th referred to below shows a straight line from $e = 20$ to $e = 55$ volts, with the equation

$$e = 137.4 - 0.292\, i \tag{3}$$

There were no greater variations (± 3 per cent of the current) than can be ascribed to fluctuations in the line voltage, but this was in the neighborhood of 110 volts, not 137.4. The following discussion may serve to clear this matter up, although the simple conditions postulated below are of course not strictly fulfilled in practice.

Since the heat generated in the rheostat was carried off by a constant flow of water, the average temperature of the latter would be:

$$t_w - t_o = aRi^2 \tag{4}$$

where t_o is the temperature of inflowing water, R the resistance of the wires, and a a constant depending on the rate of flow.

When a steady state has been attained, the difference between t (the temperature of the wires) and t_w will be proportional to the flow of heat through the stationary film of water at their surface, or

$$t - t_w = bRi^2 \tag{5}$$

Finally, the resistance of the wires may be expressed by

$$R = [1 + c\,(t - t_o)]\,.\,R_o \tag{6}$$

where R_o is the resistance at the temperature t_o, and c the temperature coefficient of the resistance of iron wire.

From equations 4, 5 and 6 may be found an expression for R as a function of the current; this when introduced into equation (2) gives:—

$$e = E - R_o i \,/\, [1 - c\,(a + b)\,R_o i^2] = E - Ai/(1 - Bi^2) \tag{7}$$

Setting $E = 110$, and choosing A and B so that for $e = 20$ and $e = 55$ the values of i are those given by the empirical relation of equation (3), there results:

$$e = 110 - 0.1720\, i/(1 - 1.403 \times 10^{-6}\, i^2) \tag{8}$$

The following table gives for a number of values, of e, the values of i calculated from the rational formula (8) and those from the convenient empirical formula (3). Between 280 and 400 amperes, that is, while the p. d. over the cell varies from 55 to 20 volts, the greatest difference is 5 amperes; thus for the purpose of calculating the current, Mrs. Ayrton's straight line construction is accurate enough even though the conditions for which it was originally deducted are not fulfilled; if it be used to calculate the potential difference from the current, however, an error of 1.4 volts would be introduced at $e = 35$.

TABLE I.

p. d. over arc	Amp. Eq. 8	Amp. Eq. 3	Diff.
110.00	0.0	94.0	94.0
92.47	100.0	154.0	54.0
73.41	200.0	219.5	19.5
55.00	282.5	282.5	0.0
50.63	300.0	297.6	— 2.4
43.96	325.0	320.4	— 4.6
36.76	350.0	345.0	— 5.0
29.26	375.0	370.8	— 4.2
20.00	402.5	402.5	0.0

Assuming $c = 0.0055$ and $t_0 = 10°$ C, the values and A and B chosen above lead to a temperature of 53° C. for the wire when $e = 55$, and to a temperature just below 100° C. when $e = 20$. This corresponds to the experimental conditions; for the amount of water sent through the rheostat was just sufficient to prevent rumbling with the heaviest current it was proposed to employ.

The arc in my experiments was struck between a stationary vertical anode and a vertical cathode carried by a jib; thus the cathode was always above the anode. Both electrodes were four inches in diameter and were manufactured from a petroleum coke base by the National Carbon Company.

The jib holding the cathode was raised and lowered by an electric winch motor set. Each revolution of the armature of the motor raised the jib 0.553 mm., and by attaching a Veeder revolution counter to the armature the position of the electrode could be known to half a millimeter; owing to the great weight of the jib, 365 kg. (800 lb.), and smooth bearings, there was very little slack. After trial, however, this method was discarded in favor of measurement with a cathetometer. This was an upright instrument provided with telescope and vernier, manufactured by Becker, Hatton Wall, London; it was sighted on a very fine line ruled with india ink on drawing paper attached to the cathode holder. Readings were made to 0.01 mm. which was closer than necessary, and perhaps rather beyond the accuracy of the instrument.

II. CONDITIONS FOR A STEADY ARC.

By far the greater part of the time so far devoted to this investigation has been spent in finding conditions under which a steady arc can be maintained; for no measurements at all are possible unless the voltmeter readings are definite and show no variations except the steady rise due to the electrodes burning away. The principal difficulties met with and overcome were those due to air draughts, magnetic flux from the cables, eccentric arcs, "humming," and "groaning"; minor difficulties, due to spontaneous shifting of the arc, still remain. Owing to the heavy currents used in my work, the disturbances from these sources were incomparably greater than those met with by previous experimenters.

Air draughts: At first, a circular wall of silica firebrick was built around the arc, no "bond" (mortar, etc.) being used in the construction; then a top of firebrick was added, and as it appeared that each added protection improved the arc, the brick wall was replaced by a steel furnace shell 76 cm. in diameter and 91 cm. high (30 x 36 in.) lined with clay firebrick and covered with large firebrick blocks and sheet asbestos. To increase the heat insulation, the space between lining and shell was filled with crushed firebrick. Finally, the iron column described below, which acted as magnetic shield, was almost closed at the bottom with brick. With this arrangement, the air draught was reduced to a slow, evenly distributed stream moving parallel to the electrodes; any further reduction of the air supply resulted in irregular currents, which blew the arc sideways.

Magnetic disturbances: An arc, being a flexible conductor carrying a current, is blown to one side by any magnetic flux at an angle to the direction of the arc. Such a flux was set up by the loop of the circuit of which my arc was a part; and as no convenient arrangement of the cables could be found with which the disturbance from this source was not noticeable, I resorted to the use of iron shields. After experimenting with various arrangements of iron pipes and sheets, satisfactory results were obtained by surrounding the arc with a laminated iron column 38 cm. high (15 in.), 3.8 cm. thick (1.5 in.) and 30.5 x 30.5 cm. (12 x 12 in.) in (rectangular) cross section, built up of fifteen square iron window frames. The "magnetic shield" so constructed offers a path of low reluctance in the horizontal direction, and only after it was installed could the arc be steadied sufficiently for accurate readings.

Centering the arc: If new electrodes be used, with ends turned flat in the lathe, it may be hours before the arc settles down to burn steadily in one place, and the crater thus formed is seldom in the center of the anode. If the anode surface be covered with powdered carbon, the arc chooses its final position more quickly, but seldom selects the center. If a small hole (10 mm. in diameter, 15 mm. deep) be drilled in the anode, the arc will stay in that spot if it happens to run into it.

Having obtained a centered arc by the use of such a hole, I allowed it to burn for six hours; and using the resulting cratered anode and pointed cathode as patterns, turned a pair of new electrodes to the same shape and size in a lathe, making the crater, however, only about a quarter as deep as that of the used electrode. The anode was then mounted in the furnace and powdered carbon poured over it, filling the crater and covering the flat top to the depth of 5 or 6 mm.; the carbon powder obtained by dusting off the electrodes after a run proved best for this purpose. When the arc was struck (using one coil, about 0.5 ohm, in the rheostat) it centered at once, and all the carbon dust burned out of the crater in a few minutes. In all subsequent experiments, artificially shaped electrodes were employed; by the use of a tool made for the purpose in the University machine shop, the anode could be reshaped without removing it from the furnace.

Low voltage arcs: When, after the arc had been struck as described, the current was increased by lowering the resistance in the rheostat, it often happened that the arc was blown to one side and extinguished. In the end I found that this could be avoided by lowering the cathode until the potential difference over the arc was only about twenty volts before raising the current to the desired amperage.

The general belief, in which I shared, that an arc between carbons cannot be maintained at less than about 40 volts, kept me from discovering this method sooner; as a matter of fact, there is no difficulty in maintaining a 20-volt arc for well on to an hour under the conditions of my experiments. Both Mrs. Ayrton's formula[5]:

$$e = 38.88 + 2.074\, l + (11.66 + 10.54\, l)/i \qquad (9)$$

and Steinmetz's formula[6]:—

$$e = 36 + 52\ (l + 0.8)/\sqrt{i} \qquad (10)$$

contain a constant term (38.88 or 36 volts respectively) commonly referred to as the "counter electromotive force of the arc." These formulas are in good agreement with the results of experiment up to currents of thirty amperes, but it is obvious that if this interpretation is to be adhered to, the counter e. m. f. must decrease with increase of current.

Humming arcs: When the arc gave out a humming noise (direct current, not alternating current was used,) inspection through colored glasses showed that it was flickering, *i. e.*, that the luminous part of the arc was enlarging and contracting periodically. A high note accompanies rapid pulsation of the arc, but very slow changes in volume (4 or 5 times per second) are inaudible. Once begun, the humming usually gets louder and louder, but without much change in note.

In a humming arc the voltage over the electrodes oscillates; if the hum is loud, the needle of the voltmeter is set in rapid vibration and may, in addition, swing over a range of 10 to 15 volts every couple of seconds. If the hum is not loud, voltage readings may be secured; but instead of rising at the usual rate as the electrodes

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[5] *Loc. cit.*, p. 184; l gives arc length in mm.

[6] Trans. Am. Inst. Elec. Eng. **25**, 803 (1906), and Chem. and Met. Eng. **22**, 462 (1920). In equation (10) above l gives arc length in cm.

burn away, the voltage may remain almost stationary for half an hour or more. Stationary voltage over the arc may be accepted as indicating an approaching hum.

A humming arc always left the cathode with a very pointed tip, like those observed by Mrs. Ayrton in her "hissing arcs." The only cure is to shut off the current, cool the cathode, and rasp off the tip, preferably to a diameter of about 30 mm. (see below).

Swinging arc: On one occasion I was bothered for days by an arc which emitted a note rising in pitch when the cathode was lowered and falling when it was raised. At first I took this for a "humming" arc, but reshaping the cathode failed to remove the trouble. In the end, a vertical saw cut through the anode, which had become elliptical in horizontal section, revealed a crack in the carbon across the bottom of the crater; the arc had travelled backwards and forwards along this crack, and dug out a trench with a craterlet at each end.

Groaning arcs: When the arc is burning normally the whole crater is so hot that it is impossible to distinguish a specific anode spot; but if the arc *groans,* inspection shows that a white hot spot is jumping from the bottom to the edge of the crater and back again; when the spot is on the edge, the arc is blown outwards (away from the center of the crater) and the "groan" is heard. At first the spot stops only two or three seconds in each position; but this period soon lengthens, rising in four or five minutes to about ten seconds, whereupon the groan rises to a shriek, and the arc is extinguished.

In a groaning arc the voltage over the electrodes falls about thirty volts each time the anode spot reaches the edge of the crater, and rises again when it returns to the bottom.

It is evident that an arc can "groan" only if the cathode is too near the edge of the crater in comparison with its distance from the bottom. The groaning can be stopped (1) by making the cathode narrower at the point, (2) by widening the crater throughout, (3) by bevelling the edge of the crater, thus making the latter wider at the top, or (4) by cutting down the edge of the crater, thus making the latter more shallow. All four methods have their limitations. If the cathode is too narrow at the tip, the arc will hum; if the crater is too wide, the arc will burn small craterlets in the bottom and jump from one to the other; if its walls are too much bevelled, the same thing will occur; and if the crater is too shallow, the arc will not remain in it. Electrodes cut to the dimensions of the accompanying section (Fig. 2), which is drawn from the templates used in the laboratory, will give a good arc for 4 or 5 hours with currents up to 300 or 400 amperes.

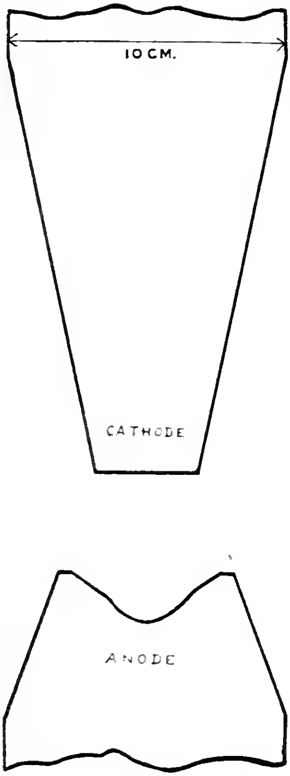

FIG. 2

III. DIRECT DETERMINATION OF ARC LENGTH.

In Mrs. Ayrton's work the "length of the arc" was defined to be the vertical distance between the point of the cathode and the horizontal plane drawn through the edge of the crater; length zero did not mean that the carbons were in contact, but that the point of the cathode was just entering the crater. It is obvious that in an arc between unformed carbons burning with constant current and "constant arc length" so defined, the vertical distance between the electrodes will not be constant at all, but will keep increasing until the crater attains its final dimensions. This did not escape Mrs. Ayrton, who studied the changes in voltage accompanying the formation of the crater; nevertheless, she adhered to her own definition of "*l*," and measured it on an image of the arc projected by a lens. In my own work, the depth of the crater was such a large fraction of the whole distance between the electrodes—it often reached 35 mm., while the total length never exceeded 60 mm.—and the voltage so evidently depended on the total length and not on that above the crater's edge, which moreover with my high currents was too irregular to afford a fixed point for the measurements, that I decided to measure the total vertical length as the "length of arc." This quantity, of course, is greater than Mrs. Ayrton's "l"; to avoid confusion I indicate it by the capital letter "L".

Measurement of L: When a steady arc had been secured the height of the cathode was determined (by revolution counter or cathetometer), voltage and current were read, and the circuit broken. To protect crater and tip from burning away, powdered carbon was then poured down a pipe into the crater, and the cathode was lowered until its tip was also protected by the powder. The furnace was then allowed to cool (about ten hours was required), the carbon was blown out, the height of the cathode measured again, and a plastic ball of moistened fire clay was squeezed into place so as to take an impression of crater and tip. When the clay had hardened, the length of the arc when the circuit was broken (L, as defined above) was determined by caliper measurements of the clay model *plus* the difference between the two cathetometer readings. With care, such measurements can be made within a millimeter or two; if the electrodes are too hot, the surface of the model will be rough; if they have cooled to room temperature, the clay takes three or four hours to harden, and a good model results.

Every such measurement involved shutting down the furnace for at least twelve hours; I have obtained, so far, eight fairly good results, besides a number of failures. In Table II, those marked with a star were measured with the cathetometer, the other two with the revolution counter.

For comparison, the values of l from Mrs. Ayrton's formula (Eq. 9) and from Steinmetz's formula (Eq. 10) are given in Table II, both of them in millimeters.

IV. DETERMINATION OF CHANGES IN VOLTAGE CONSEQUENT ON KNOWN CHANGES IN ARC LENGTH.

With a view of obtaining results more rapidly, it was decided to measure the changes in voltage caused by lowering or raising the cathode small measured distances. Such determinations should give a series of values of de/dL (or de/dl, which is the same thing) under the condition that $di = -\,k.de$ (see Eq. 3); from these by integration, using results with the clay model as integration constants, the relation between e and L might be determined. A number of fairly good runs were made with currents from 300 to 400 amperes, of which that of March 8, 1922, was the best, *i. e.*, showed the smoothest burning arc. Four others were made with currents from 700 to 800 amperes, but in none of them was the arc steady enough to give satisfactory results by this method; I hope to get better results soon.

TABLE II.

i amp.	watts	e volts	L mm.	l Ayrton mm.	l Steinmetz mm.
280	148×10^2	53.0	56	6.7	46.7
*311	135×10^2	43.5	42	2.2	17.4
*350	147×10^2	42.0	42	1.5	13.6
*385	119×10^2	31.0	30	— 3.8	—10.9
390	168×10^2	44.5	42	2.1	24.2
*712	356×10^2	50.0	55	5.42	63.8
*732	315×10^2	43.0	49	2.0	28.4
*770	262×10^2	34.0	43	— 2.3	2.7

In each of these runs, current, voltage over the arc, and "divisions" on the second voltmeter were recorded every minute; Table III gives "divisions" and time in minutes after striking the arc for the run of March 8th; the voltage over the arc can be obtained from the number of divisions by means of Eq. (1), and the current by Eq. (3). Below 28 volts the second voltmeter could not be used; the numbers entered in Table III under "volts" give the readings of the first voltmeter (scale 0-150 volts).

Table IV gives the cathetometer readings (in millimeters) for March 8th; when the cathode was raised the cathetometer reading increased. At $t = 57$, *i. e.*, 57 minutes after striking the arc, the cathode was moved to the left in the hope of steadying the arc; at $t = 111$, it was moved again to the left to stop humming; at $t = 138$ it was shifted again to stop groaning. The effect on arc length caused by these movements can only be guessed.

For $t = 231$, a clay model gave $L = 42$ mm.; values of L for other values of t (above $t = 138$) were calculated from the cathetometer readings, C, on the assumption that the carbons burn away at the uniform rate of 9.0 mm. per hour irrespective of the wattage. Thus for $138 < t \leqq 231$ $L = C - 782.6 + 0.15\,t$.

Table III.

Time min.	Volt	Time min.	Div.	Time min.	Div.	Time min.	Div.	Time min.	Div.	Time min.	Div.
17	21.2	50	14.8	87	52.0	121	60.0	156	70.0	197	38.0
18	21.2	51	15.0	88	53.0	122	42.5	157	70.5	198	38.0
18	21.2	52	34.2	89	54.0	123	43.5	165	71.5	199	38.0
19	21.2	53	33.5	90	40.2	124	43.8	166	73.0	200	37.5
20	21.3	54	34.0	90	35.0	125	45.5	167	73.5	201	17.0
21	21.7	55	34.0	91	38.0	126	47.0	168	74.5	202	17.0
22	21.9	56	44.0	92	40.0	127	48.2	169	75.5	203	17.5
23	21.6	59	44.5	93	41.2	128	48.0	170	53.0	204	18.0
24	21.5	60	44.8	94	42.0	129	48.0	171	53.5	205	18.5
25	21.6	61	45.0	95	43.0	130	48.5	172	54.0	206	44.0
26	21.6	62	45.9	96	70.0	131	49.2	173	54.5	207	43.0
27	23.7	63	46.2	97	69.5	132	49.8	174	55.0	208	43.0
28	24.0	64	46.5	98	69.5	133	51.0	175	37.0	209	42.5
29	24.2	65	47.0	99	69.5	134	23.0	176	39.5	210	42.2
30	28.6	66	47.2	100	69.5	135	23.7	177	44.5	211	42.5
min.	Div.	67	37.0	101	59.5	136	25.5	178	45.0	212	42.5
31	3.0	68	36.5	102	60.5	137	27.0	179	46.0	213	4.0
32	3.5	69	37.5	103	61.0	139	15.0	180	46.0	214	3.5
33	3.5	70	38.0	104	62.2	140	17.0	181	47.0	215	3.5
34	5.7	71	38.5	105	63.0	141	18.0	182	47.5	216	3.5
35	6.1	72	39.2	106	63.0	142	19.0	183	28.0	217	4.0
36	7.0	73	39.4	107	40.5	143	19.5	184	29.0	218	4.5
37	7.9	74	40.5	108	43.0	144	20.0	185	30.0	219	27.5
38	8.5	75	40.7	109	46.0	145	20.0	186	31.5	220	28.5
39	9.0	76	40.5	110	49.0	146	20.5	187	32.5	221	29.0
40	10.0	77	50.0	112	54.5	147	48.0	188	33.2	222	30.0
41	10.2	78	51.0	113	55.0	148	47.0	189	34.5	223	31.0
42	10.6	79	52.0	114	56.0	149	46.5	190	7.0	224	2.0
43	11.0	80	52.7	115	57.0	150	46.5	191	7.0	225	2.0
44	12.0	81	53.8	116	55.2	151	47.0	192	7.2	226	2.0
45	12.0	82	43.5	117	58.0	152	47.5	193	7.8	227	2.0
46	12.5	83	47.2	118	58.5	153	48.0	194	8.0	228	45.5
47	13.0	84	48.5	119	59.0	154	70.0	195	8.2	229	45.0
48	13.8	85	50.0	120	60.0	155	70.0	196	37.5	231	44.5
49	14.0	86	51.0								

For $110 < t < 139$, I have replaced the subtrahend 782.6 by 780.4, thus making an allowance of 2.2 mm. for the adjustment of the cathode at $t = 138$. For $58 < t < 139$, the subtrahend 783.1 is used, which is within half a millimeter of the first. Before

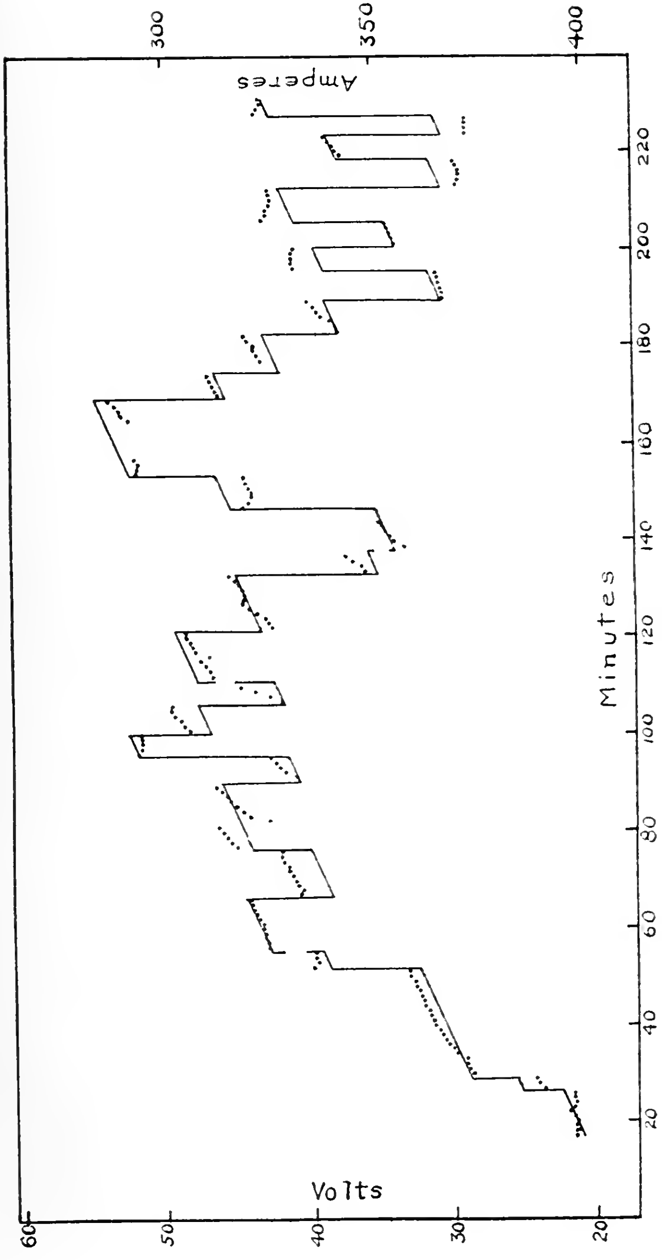
Amperes
300
350
400
Volts
60
50
40
30
20
Minutes
20
40
60
80
100
120
140
160
180
200
220

FIG. 3

$t = 57$, the subtrahend is 788.1. These last three values had to be chosen arbitrarily, and there is no independent check, as the adjustment consisted in moving the cathode sideways in order to secure a steady arc; but the value employed for calculating the last hour and a-half of the run was obtained from the direct determination with the clay model.

Table IV.

Note: The cathode was moved to give the new cathetometer reading C millimeters about half a minute after the time entered under t.

t	C	t	C	t	C
16	806.4	107	809.4	183	792.1
27	809.3	111	(moved)	190	783.8
30	813.0	112	819.4	196	791.3
52	812.8	122	804.6	201	785.6
57	(moved)	134	795.2	206	791.7
59	817.9	138	(moved)	213	780.5
67	812.4	139	794.3	219	786.8
77	816.7	147	802.7	224	778.8
91	811.0	154	810.9	228	790.0
96	820.9	170	801.8	231	(model)
101	815.4	175	797.3		

Fig. 3 reproduces the data of Table III, with scales of voltage and current. The lines are "calculated" values, based on the assumption that a change of one millimeter in L causes a change of 3 divisions, or 1.02 volts, in the potential difference over the arc. In most cases where the voltage rises or falls more than on this assumption should correspond to the movement of the cathode, the instantaneous change is followed by a slower movement towards the calculated value; the obvious explanation is that the points of origin of the arc, or one of them, have shifted along the electrodes. At $t = 90$ there is direct evidence of such a shifting of the arc; the cathode was lowered 5.7 mm. and the voltage dropped 4.8 volts at once, but within half a minute fell another 1.7 volts, most of which was recovered in the next couple of minutes; and at $t = 82$ there was a sudden drop of 3 volts without any motion of the cathode at all, this again was quickly recovered. The figure also gives examples of the stationary or falling voltage which accompanies humming, for instance at $t = 140$, 180, and 204; between $t = 157$ and $t = 175$ the humming was so loud that no voltage readings could be secured.

Taking the results as a whole, there can be no doubt that the assumptions made are justified at least as a good first approximation; and that for currents between 300 and 400 amperes, where $e = 137.4 - 0.292\,i$, de/dL is very close to one volt per millimeter. Mrs. Ayrton's formula (Eq. 9) by differentiating and introducing the relation between current and voltage given in Eq. 3, leads to $de/dl = 2.1$ volts per mm., and although L is different from l, the changes in these two quantities consequent on raising or lowering the cathode are the same. Steinmetz's formula (Eq. 10) leads to $de/dl = 0.33$ volt per mm. for 300 amperes, and 0.44 for 400 amperes. Thus these two formulas, while in accordance with the experimental results up to 30 amperes or so, can evidently not be relied upon for currents of 300 amperes or more.

SUMMARY.

Conditions have been found under which a steady arc can be maintained between carbon electrodes with currents of 300 to 400 amperes, and a fairly steady arc with currents up to 800 amperes. Humming, swinging and groaning arcs have been described, together with a way to avoid them.

A 20-volt arc can easily be maintained, and has been introduced as part of the routine of building up the arc.

A straight-line construction may be used to represent the relation between current and potential difference over the arc when the rheostat consists of water-cooled iron wire.

Direct determinations of the distance between the electrodes for various currents and voltages have been made by the use of cathetometer and clay models.

Changes in the voltage caused by raising or lowering the cathode for measured distances have been determined.

For currents between 300 and 400 amperes and potential difference over the arc 55 to 20 volts, the p. d. in volts is approximately equal to the distance between the electrodes in millimeters; for currents of 700 amperes or so the voltage is less than the distance.

The formulas proposed by Mrs. Ayrton and by Steinmetz for low currents are not in agreement with the experimental results for high currents.

These experiments were carried out in the Electrochemical Laboratory of the University of Toronto during the winter of 1921-22; my thanks are due to Professor W. Lash Miller for the interest he has taken in the work.

University of Toronto,
August, 1922.

DISCUSSION.

F. G. Dawson[1] (*Communicated*): It would appear that some variables in the environment of an arc not recorded in this paper might affect its characteristics. The temperature of the enclosure and the constancy of conditions of the gaseous atmosphere in the enclosure are certainly not without effect on an alternating current arc. In operating the experimental indirect arc steel furnace of the Bureau of Mines[2] the writer was impressed by the marked effect of these two factors on the stability and length of the a. c. arc. There was a critical temperature in the preheating of the empty furnace, below which the arc would not hold steadily without constant electrode adjustment, but above which its stability was high.

If the furnace was luted up so as to avoid any draft at all within the furnace, and consequently to build up a slight pressure within the furnace, and to avoid any sudden influx of air, the temperature at which the arc became fully steady was lowered. An opening the size of a pin head would allow change of pressure and change of the composition of the atmosphere, with tiny fluctuations of the arc due to disintegration of the graphite electrode, which would notably increase the voltage necessary to hold the arc. It is not certain that the results obtained by Mr. Westman would have been the same in the absence of a positive flow of air.

At operating temperatures, a tiny opening had no appreciable

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[1] Detroit Electric Furnace Co., Detroit, Mich.

[2] H. W. Gillett, and E. L. Mack, Experimental production of certain alloy steels. Bur. Mines Bull. 199, 1922, p. 14.

effect on the Bureau of Mines' steel furnace, and when the furnace was so hot that ionizing vapors were present by volatilization from the refractories, or at a much lower temperature if sodium silicate had been used in repairing the lining, the voltage required to hold the arc would fall off to certainly well under 20 volts.

There is no statement in the paper as to whether or not the lining glazed or showed any signs of decomposition, but the empty furnace used must have been very hot after running 6 hr. From Fig. 3, one would calculate that some 80 Kw.-hr. had been put into the furnace.

The current density in the electrodes, and their composition, *i. e.,* whether carbon or graphite, must affect the temperature of the electrode tips. With a positive flow of air, the burning away of the tip must have altered conditions throughout the run.

If Steinmetz's experiments were done in a fairly tight enclosure, the differences between his formula and Mr. Westman's results may be at least partly accounted for.

Electric furnace men would welcome a similar study of a. c. arcs in which not only the variables studied by Mr. Westman on d. c. arcs, but also the others mentioned above, are included.

A. E. R. WESTMAN (*Communicated*): The work presented was undertaken as a necessary preliminary to the study of arcs under such practical conditions as high current densities, graphite electrodes, alternating current, etc. An experimental study of these factors is now under way in this laboratory.

In Dr. Steinmetz's experiments[3] he presented his equation as an approximation, and added that more recent and extended investigation seems to show that it is not rigidly correct. My conditions were in accordance with Steinmetz's definition of a normal arc, in which no mention is made of the degree of ionization of the surrounding gases. There seems to be no good reason to believe that such ionization would affect a heavy current arc, or that it would be materially increased by partially surrounding the arc with screens as in my experiments.

Mr. Dawson reports that with a furnace thoroughly sealed, he found no trouble from air draughts in his apparatus. The top of the magnetic shield was quite open, and when I sealed it at

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[3] Chem. and Met. Eng. 22, 248, (1920).

the bottom, down draughts and irregular currents interfered. Mr. Dawson's data and his description of his work with an enclosed arc are welcome; there is next to no information of this kind in the literature.

There is no statement in my paper to the effect that 20 volts is the minimum voltage for holding an arc. With electrodes shaped as shown on page 179, it is evidently impossible for L (as defined on page 180) to be less than about 15 mm. For this reason I have not been able to run below 17 volts.

J. KELLEHER[4] (*Communicated*): On pages 175 and 176, Mr. Westman describes a magnetic shield used to eliminate the effect of magnetic disturbances caused by the electrical circuits of the furnace. As no drawing is given showing the position of this shield with regard to the arc, I shall suppose that the arc was formed midway between the top and bottom of the shield. It seems to me that if this were the case, then with a mean furnace input of about 20 kw., (see Table II) the temperature of these laminations would soon rise and reach that point at which iron loses its magnetic properties. This I believe to be about 780° C. If this happened, the shield would be of little value, except when the furnace was cold. It would be of interest in this relation to know if the shielding effect decreased as the furnace temperature increased. In my own work on arcs I found great difficulty in maintaining a long steady arc until the electrodes between which the arc was formed and the surrounding furnace walls, etc., had reached a high temperature.

If this is not the case this same shield which I imagine consists of cast iron might be responsible for the humming arcs as described on page 177. If some variation in the current occurred, and a certain amount of residual magnetism was present in the shield, oscillations in the current might be set up causing an alternating potential which would increase or decrease the volume of the arc core, this again increasing or decreasing the volume of the gas surrounding the core. If an oscillograph were connected in the furnace circuit to indicate both current flowing and the potential across the arc, the humming arc and perhaps the groaning arc might be explained.

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[4] Chippawa, Ont., Canada.

The use of a cathetometer seems slightly in excess of the requirements of accuracy, as I notice no corrections have been made for thermal expansion in the determination of "L" on page 180.

This interesting work I hope will be continued, and instead of using two carbon electrodes a bath of some metal such as iron might be substituted for the anode and a comparison made of the behavior of the arcs as described and those occurring where the anode is a metal.

A. E. R. Westman (*Communicated*): The magnetic shield did not reach a temperature higher than 800° C. in most of these runs, as there was always a current of air between the arc and the shield. I can not say whether the shielding effect decreased during a run, as other circumstances such as the deepening of the crater tended to make the arc unsteady near the end of a run.

The cathetometer was used more especially for measuring the movements of the cathode, which were sometimes as small as 4 mm.; these movements would cause no appreciable change in the temperature of the electrodes, and so no error from thermal expansion would be introduced. However, these results are only a first approximation, the results of more accurate measurements will be reported later.

A paper presented at the Forty-third General Meeting of the American Electrochemical Society held in New York City, May 4, 1923, President Schluederberg in the Chair.

ELECTRIC FURNACE DETINNING AND PRODUCTION OF SYNTHETIC GRAY IRON FROM TIN-PLATE SCRAP.[1]

By C. E. Williams,[2] C. E. Sims,[3] and C. A. Newhall.[4]

Abstract.

Experiments were conducted in a small electric furnace in which tin-plate scrap was melted with various addition agents in attempts to remove the tin from the iron. Sodium chloride, iron sulfide, and an oxidizing slag were used under various conditions. The conclusions reached were that in the electric furnace complete detinning is impossible, and any detinning impractical. Melting tests conducted in the cupola showed that the amount of detinning was dependent upon the amount of surface of metallic tin exposed to the oxidizing gases, and will be somewhere between the limits of 0 and 50 per cent. Test bars, prepared by melting pig iron with various quantities of tin, were subjected to physical tests. The results showed that a tin content of one per cent or less did not seriously affect the properties of gray iron. Synthetic cast iron made from tin-plate scrap was used successfully in making commercial castings of good quality.

INTRODUCTION.

The investigation here described was conducted at the Northwest Experiment Station of the U. S. Bureau of Mines, in cooperation with the College of Mines of the University of Washington. The object of the study was to determine the possibilities of converting tin-plate scrap or used tin cans into a marketable

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[1] Published by Permission of the Director, U. S. Bureau of Mines. Manuscript received February 1, 1923.

[2,3] Metallurgist and Electrometallurgist, respectively, North-west Experiment Station, U. S. Bureau of Mines, at Seattle, Wash. in cooperation with College of Mines, University of Washington.

[4] Washington Elcetrochemical Co., Seattle, Wash.

steel or iron product by electrothermal means. Most of the tin-plate scrap produced in this country is detinned and subsequently melted in the open-hearth furnace, producing steel; a small quantity of it is melted with other iron scrap in the cupola for the manufacture of sash weights and similar low-priced castings; and some is used in certain hydrometallurgical plants to precipitate metals from solutions. A small quantity of used tin cans is treated similarly to tin-plate scrap, as above described. There are three established methods of detinning, namely: the chlorine, electrolytic alkali and the alkali-saltpeter processes, producing respectively tin tetrachloride, metallic tin and tin oxide.

A plant utilizing one of the established detinning processes, to be profitable, must be operated on a comparatively large scale, the minimum capacity having been variously estimated as between 50 to 100 tons of tin-plate scrap per day. In some localities the quantity of tin-plate scrap or old cans available may be so small, or the market for the recovered tin so limited, that another process of utilizing these waste materials would be required. In districts near can factories there may be an oversupply of tin-plate clippings and punchings, and in cities where efficient methods of collecting old cans are in vogue, such materials may be available at much lower prices than the cost of steel scrap. In such cases a method of using this cheap form of iron in a more profitable manner than for conversion into sash weights would be desirable.

The weight of the tin coating on tin plate varies between wide limits. Results of the analysis by the National Canners' Association[5] of many thousands of cans showed weights of from 0.53 to 6.37 lb. of tin per base box containing 112 sheets and weighing 100 lb., the grand average of all analyses being from 0.81 to 2.94 lb. per base box. During the past few years,[6] the tin recovered by detinning clean tin-plate scrap amounted to 1.6 lb. for each 100 lb. treated. Hence, assuming a recovery of 95 per cent, the average tin content of tin-plate scrap would be 1.7 per cent, which probably represents the average content fairly closely. The tin content of used cans will be usually found a

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[5] Relative value of different weights of tin coating on canned food containers. National Canners' Assn., Washington, D. C., 1917.

[6] Secondary Metals in 1919, 1920, and 1921. J. D. Dunlap. Mineral Resources of the United States. U. S. Geological Survey.

few tenths less than this, due to losses by mechanical abrasion and by solution in the foodstuff contained in the can, although if solder were used in sealing the can the tin content might be above 1.7 per cent.

Not much information is available regarding the effect of tin upon the properties of steel or cast iron. In detinning, the attempt is made to produce a product containing less than 0.1 per cent tin, although during the war this limit was not insisted upon by purchasers of detinned scrap. In the present investigation no time was spent on chemical or electrolytic detinning, but attempts were made to remove the tin by some action during the process of melting the scrap. The impracticability of removing a large proportion of the tin in this manner was soon determined, and a study was then made to determine the possibilities of using tin-plate scrap in producing gray iron without removing the tin. With this in view a study was made of the effect of various quantities of tin on the properties of gray iron.

EXPERIMENTS ON DETINNING.

The physical and chemical properties of tin and its compounds are such as to offer little encouragement to the possibility of detinning iron in the electric furnace. The popular belief, that tin is volatilized when iron containing it is melted, is not founded on fact, because the boiling point of tin is 2270° C. Tin is found in gases from cupolas in which tin-plate scrap is being melted, but its presence is probably due to the burning of the tin to oxide which is then carried mechanically through the stack by the escaping gases. Although the melting point of tin is only 232° C. and that of iron 1500° C., the tin coating on most tin plate is so thin that the tin, although above its melting point, will not flow off and thus permit separation.

The volatility of the chlorides of tin suggests the use of sodium chloride. The reaction would require oxidizing conditions and would undoubtedly produce stannous chloride whose boiling point is 603° C. The most obvious time to conduct this reaction would be before fusion of the iron, in order to permit the maximum contact of salt and air with the tin coating. The facts that stannous sulfide boils at 1230° C. and that it can be made by the action of iron sulfide on metallic tin offer the possibility of detinning with pyrite. The reaction would have to be complete enough to permit the use of only a slight excess of pyrite and thus avoid the introduction into the iron of too much sulfur.

It has been suggested that detinning could be accomplished by melting under an oxidizing slag, thereby oxidizing the tin and slagging it off. Complete removal of the tin, however, could not be expected by this means, because tin is lower in the electromotive series than iron and would be kept in a reduced condition by the metallic iron. Tin is soluble in iron up to 19 per cent,[7] and hence, molten tin-plate scrap would contain tin in a dilute solution (about 1.7 per cent), which would contribute to the difficulties of removing it by a chemical reaction.

A preliminary study of the reaction with salt at a temperature below the melting point of iron was first made. Strips of tin plate placed in fire clay roasting dishes were heated in a muffle and treated with fumes of sodium chloride. Tin was volatilized at temperatures above 500° C. when the atmosphere was kept strongly oxidizing, but the resultant iron sheet was badly oxidized and unfit for conversion into steel or iron.

The subsequent tests were carried out in a basic-lined single-phase series-arc stationary furnace. The hearth was 23 x 38 cm. (9 x 15 in.) in cross section and conveniently held the 50-lb. charges used. Test No. 4 was made in a carbon-lined, direct-heating, single-arc, stationary furnace. The tin-plate scrap, which consisted of clippings and rejected can ends, varied greatly in tin content and much difficulty was had in obtaining true samples of the charges to the furnace. A fairly uniform feed was obtained by using only the can ends of uniform gauge.

Numerous analyses showed that the average tin content was 1.25 per cent, although the tin content of some charges probably varied as much as 10 or 15 per cent from this average value. Hence, great accuracy is not claimed for the results given below, which show the extraction of tin obtained by the different treatments. However, these results do show approximately the magnitude of the detinning obtained, and the relative effectiveness of the various methods tried. In order to make the results compara-

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[7] Tammann, Z. f. anorgan. Chem., 53, 281-295 (1907).

ble, the conditions were kept as nearly uniform as possible in all tests. The furnace was preheated before charging and the molten charge held in the furnace for at least a half hour in order to superheat the metal and permit any reactions to go to completion.

Tin-plate scrap was first melted with carbon in the electric furnace. The results, one of which is entered in Table I, show that no tin was removed by the treatment. A series of experiments using sodium chloride with various other reagents was conducted. A large excess of salt, amounting to 10 per cent of the weight of the scrap was charged with the scrap into the furnace. In some cases reducing and in others oxidizing conditions were maintained during the test. Table I shows the essential data of these experiments.

TABLE I.

Tests on Chloride Volatilization.

Run No.	Charge					Tin in pig per cent	Per cent tin removed	Remarks
	Tin plate scrap lb.	Salt lb.	Iron ore lb.	Silica lb.	Carbon lb.			
1	50	..	..	..	4	1.25	0	Reducing
2	50	5	..	..	4	1.20	4	Reducing
3	50	5	..	..	4	1.22	2	Reducing
4	50	5	..	..	..	0.96	23	Slightly oxidizing
5	50	..	15	..	..	1.13	10	Oxidizing
6*	50	5	15	3	..	0.74	41	Oxidizing slag
7	50	5	15	3	..	1.02	18	Oxidizing slag
8	50	5	5	..	Carbon lining	1.02	18	Oxidizing, then reducing

* This charge forced its way out of tap hole before the run was complete.

Practically no tin was removed by melting with salt and carbon, the reducing atmosphere caused by the carbon undoubtedly preventing the formation of tin chloride. About 23 per cent of the tin was volatilized by melting the mixture of tin-plate scrap and salt without carbon, and about 10 per cent elimination of the tin was effected using an oxidizing slag. In two tests, using an oxidizing slag with sodium chloride, 18 and 41 per cent of the tin was removed, but the larger result can not be stressed too much because the furnace was tapped before the charge was completely melted. In no case was the elimination of tin complete or the results encouraging enough to give promise of success on a larger scale.

The results of the experiments in which the attempt was made to volatilize the tin as sulfide are summarized in Table II. Mixtures of tin-plate clippings and pyrites in various ratios were melted with carbon. In one case gypsum was substituted for pyrite. Runs 9 and 10 show that both the elimination of tin and the amount of sulfur introduced into the iron are proportional to the amount of pyrite used. The removal of the tin was not complete in any test and became less rapid as the concentration of the tin in the iron became less. The relatively small elimination obtained in Runs 11 and 12 was due to the basic slag which kept the sulfur from dissolving in the iron. As a result of these tests, it seems that although tin dissolved in molten iron may be converted to sulfide and volatilized, complete elimination is probably impossible and the removal of even small amounts of tin by this means introduces a large amount of sulfur into the iron. These preliminary experiments were not sufficiently encouraging to warrant further work along this line.

TABLE II.

Tests on Sulfide Volatilization.

Run No.	Charge							Analysis of pig		Per cent tin removed
	Tin plate scrap lb.	Pyrite lb.	Gypsum lb.	Lime lb.	Silicon lb.	Fe-Si lb.	Carbon lb.	S per cent	Sn per cent	
9	25	0.25	....	....	....	1	3	0.21	0.80	36
10	25	0.50	....	....	....	1	3	0.43	0.67	46
11	50	1.50	....	3	1.5	2	6	0.09	1.20	4
12	50	....	5.5	....	....	2	6	0.06	1.07	14
13*	50	2.00	....	....	....	2	2.5	0.36	0.95	24

* The metal in this test was treated with a desulfurizing slag before tapping.

In order to make the data more complete tests were made in which iron, coated with both tin and lead (terne plate), and galvanized scrap were melted with carbon. In the melt using scrap containing 1.9 per cent tin and 2.5 per cent lead, practically no elimination of the tin and complete elimination of the lead were obtained. Some of the lead was vaporized and the rest of it, on tapping, ran out of the furnace ahead of the molten iron in which it was insoluble. In the test using galvanized scrap containing 8.22 per cent zinc, the resultant metal contained only 0.20 per cent zinc. Thus, unlike tin, lead and zinc are both readily removed from iron by melting in the electric furnace.

Cupola Tests.

In order to determine the degree of detinning possible in the cupola, the following experiments were conducted.

Charges consisting of 25 lb. of tin-plate scrap, 75 lb. of gray iron and a large excess of coke were melted in a small cupola 45.5 cm. (18 in.) in diameter. In one case, when a strong blast was used, the resultant metal contained only half of the tin charged. In another instance, in which a light blast was used, the temperature of the metal was consequently low and a viscous melt was obtained with practically no elimination of tin. A sample obtained from the castings made at a local sash-weight foundry by melting four parts gray iron and one part baled tin-plate scrap in a large cupola was analyzed and found to contain 0.37 per cent tin. Assuming that the tin-plate scrap contained 1.7 per cent tin (the average for all scrap detinned in 1921), a recovery of practically 100 per cent of the tin was obtained.

One thousand pounds of synthetic cast iron was made in the electric furnace from tin-plate scrap and used as the iron in a regular cupola melt at a local foundry. The iron before melting in the cupola contained 1.25 per cent tin, and after melting 1.23 per cent tin, thus showing practically no elimination.

It is apparent from the above study that some elimination of tin, probably up to 50 per cent, may be effected by melting thin sheets in a strongly oxidizing atmosphere, that there is practically no loss of tin when melting large pieces of iron containing tin in solid solution, and that the tin removed in cupola melting is dependent upon the conditions of melting and the state in which the tin is present.

SYNTHETIC CAST IRON FROM TIN-PLATE SCRAP.

Effects of Tin in Cast Iron.

Believing it to be impractical to effect detinning in the electric furnace or the cupola, experiments were then conducted to determine what effect tin had on cast iron, and whether suitable castings could be made from synthetic cast iron made from tin-plate scrap. Test bars containing quantities of tin varying from 0.05 per cent to 5.0 per cent were cast from pig iron melted with the required proportions of tin in an electric furnace. The tests on these bars showed that tin increases the hardness and decreases the transverse, compressive and tensile strengths, as well as the resistance to impact. Chemical analyses showed a decrease in graphitic carbon as the tin content increased, and microscopic examination gave evidence that less than 1 per cent of tin has no effect upon the size and shape of the graphite. These effects of tin are in direct proportion to the amount present, and roughly, 1 per cent of tin will reduce the strength of gray iron 15 per cent. The effect on hardness and graphitic carbon will not be over 10 per cent. When the tin content is 2 per cent or more, the molten iron appears dirty, does not fill the mold well, and the castings are rough and porous.

It seems, therefore, that tin-plate scrap or old tin cans can be used in the production of synthetic gray iron for the ordinary grade of castings provided the tin content of the product can be kept to 1 per cent or less. If the scrap contains more than 1 per cent of tin it should be mixed with enough tin-free scrap to bring the average tin content to about this figure.

Commercial Tests.

In order to obtain more data on the value of tin-plate scrap as a raw material in the manufacture of synthetic cast iron, one thousand pounds of it were melted and carburized in a basic-lined, single-phase, roofed Heroult furnace. The composition of the product is shown in Table III. It was taken to a local foundry and used in one of the regular cupola melts. Both heavy sections and thin ornamental castings were made from it. All parts of the molds were well filled, and the castings without exception were smooth and sound. A machining test was made by the manager, who was well satisfied with the iron and gave the following report:

"Depth of chill, nil. Very soft. Cuts readily with hack saw. Drills easily with ordinary carbon drill. Turns readily in lathe at considerably over ordinary speed. On facing cut run at 36.6 m. per min. (120 ft. per min.), 1.6 mm. (1/16 in.) depth of cut, 0.79 mm. (1/32 in.) feed with Rex AA high speed steel. No difficulty to make deep cut with parting tool. Fracture very fine, dense, close grain, rather dark in color. Elasticity good."

Five hundred pounds more of synthetic iron of the same composition was made and submitted to another foundry for a similar test; another favorable report was returned.

Table III.

Composition of Synthetic Iron Made from Tin-Plate Scrap before and after Melting in a Cupola.

	Before melting per cent	After melting per cent
C	3.85	3.78
Si	1.34	1.13
Mn	0.83	0.60
P	0.45	0.56
S	trace	trace
Sn	1.25	1.23

CONCLUSIONS.

1. It is impossible to remove most of the tin in tin-plate scrap or similar material by any of the electric furnace melting processes tried; moreover, it is impractical to attempt any detinning by these means.

2. No tin is volatilized, ordinarily, when iron scrap containing it is melted in the electric furnace.

3. The amount of tin volatilized during melting in the cupola may be as much as 50 per cent in some cases, whereas in others it may be practically nil, depending upon the amount of surface of metallic tin exposed, and the oxidizing condition of the blast.

4. Lead can be removed completely from iron coated with lead,

and likewise, zinc can be largely removed from galvanized scrap by melting in the electric furnace.

5. A tin content of 1 per cent or less does not seriously affect the physical properties of cast iron.

6. Under conditions prevailing in many parts of the country, tin-plate scrap and used tin cans can not be profitably treated by any of the established detinning processes. This potential waste material can probably be recovered most usefully and efficiently by treating it in the electric furnace to produce synthetic cast iron, using low-grade, tin-free scrap for dilution to reduce the tin content of the product to within safe limits.

ACKNOWLEDGMENTS.

The authors are grateful for the helpful co-operation of the College of Mines, University of Washington, and also to Mr. Lyall Zickrick, graduate student in metallurgy at the University of Washington, for assistance with the physical examination of the cast iron test bars; to Messrs. R. J. Anderson and G. M. Enos, of the Pittsburgh Station of the Bureau of Mines, for a microscopic study of the cast iron specimens containing tin, and to Messrs. E. P. Barrett and J. D. Sullivan, of the Northwest Experiment Station of the Bureau of Mines, for the large amount of analytical work done in connection with this investigation.

DISCUSSION.

E. L. Crosby[1]: There are several processes which look feasible from the electric furnace operating standpoint, affording possibilities of using sheet scrap, which do not work out so well in practice. The instant a plant starts in a certain community, where a cheap supply of scrap is available, the law of supply and demand operates. The cost of the material goes up, and it does not allow for any commercial margin.

C. G. Schluederberg[2]: I would like to have further light on just what the market is for some of this low-grade cast iron. Is

[1] Vice-Pres. and Gen. Mgr., Detroit Elec. Furnace Co., Detroit, Mich.

[2] Westinghouse Elec. and Mfg. Co., East Pittsburgh, Pa.

there enough of a market to justify large operations in recovery of this material?

H. W. GILLETT[3]: On the economic end, may I ask whether this refers purely to selected scrap, clean scrap, or whether it is possible to pick up old tin cans and shove them into the furnace and use them; in other words, whether somewhat oxidized scrap would be feasible for use or not? When this proposition came up years ago, every community was to have a tin can wagon to collect them, and instead of having them go to the garbage man they were all to be picked up. I wonder if that point of view still obtains.

C. E. WILLIAMS: In regard to Mr. Crosby's point regarding supply and demand, and that brought up by Dr. Gillett, we are looking tô the future in this case just as much perhaps as any question in which we are involved.

Much of the tin-plate scrap is treated by the chlorine detinning process, which produces tin tetrachloride used in weighting silk. We are not sure but that a cheaper or better substitute for tin tetrachloride will be developed. Such a development would liberate a large quantity of scrap. Moreover, there are times when the spread between the cost of tin-plate scrap and of detinned scrap is not sufficiently large to make detinning by present methods profitable.

Large cities are developing efficient methods of garbage collection and disposal, in which large picking bands are operated, old tinned containers being segregated and baled at a low cost. This practice will furnish a large potential supply of cheap scrap iron for use in producing foundry iron by the method described in this paper. A foundry in Los Angeles is now operating on a fairly large scale using baled cans collected in this manner and produces white cast iron therefrom. This company recently put into operation an electric furnace for producing gray iron, but I do not know what success they have had.

H. W. GILLETT: Have you ever tried to use your tin-plate scrap as part of the iron base for semi-steel? If your gray iron is not up to the mark on account of the presence of tin, for most uses

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[3] U. S. Bureau of Mines, Ithaca, N. Y.

you can improve the quality by going down on the carbon and making semi-steel out of it.

C. E. Williams: We have not investigated the properties of semi-steel containing tin. However, it would probably be all right unless the physical properties of that semi-steel are affected more than the properties of gray iron are affected by tin.

We know that tin has a decided action upon steel when present in very small quantities, and that it does not have much effect on gray iron even when it is present in fairly large quantities. So as you go from gray iron down to steel, the deleterious effect of tin would probably increase. Hence it might be that semi-steel containing a few tenths per cent of tin would be affected to a greater extent than is gray iron. However, this is something that should be investigated.

A paper presented as an introduction to the session devoted to the reading and discussion of papers on "Rarer Metals," at the Forty-third General Meeting of the American Electrochemical Society, held in New York City, May 5, 1923, Dr. F. M. Becket in the Chair.

PRESENT STATUS OF THE PRODUCTION OF RARER METALS.[1]

By C. James[2].

Many years ago, while attending a lecture in London University, I heard of the work of Waldron Shapleigh, of the Welsbach Company. The lecturer described some of the work that was done in the days before the modern thorium mantle was evolved. Shapleigh had separated large amounts of lanthanum, praseodymium, etc., in very pure form. The enthusiastic description of the beautiful salts, the mystery which enshrouded them, and the immense opportunities for research among the rare metals converted me completely.

Although this section of chemistry has appealed to many, because of the thought that there must be something unique about these substances, yet most of the work in the past has been devoted to their chemical characteristics. Notwithstanding the fact that much time has been spent searching for methods for detecting and for the quantitative determination of these elements, we find that in many cases good methods are completely lacking. The separation of tantalum and columbium is such an one. Even the determination of the mixed oxides requires great care, since these substances tend to retain both alkalies and acids. The acid solutions used during the work are liable to carry away some of the metallic acids. The errors act in opposite directions, the first tending to increase, and the latter to decrease the per cent. In working with these two elements along these lines, some of us have passed through discouragingly gloomy periods. However, many experiments along qualitative lines indicate that, after all, there appears to be quite a difference between these elements as regards their chemical properties.

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[1] Introductory paper to the session on "Rarer Metals."

[2] Professor of inorganic chemistry, New Hampshire College, Durham, N. H.

Cupferron is a reagent that can be used for precipitating tantalum and columbium together from acid solution. The oxalic acid solution, strongly acidified with sulfuric acid, or the hydrofluoric acid solution containing considerable sulfuric acid, is readily precipitated by cupferron. The precipitation should be carried out in very cold solutions. The precipitate can be readily washed and the oxides, obtained by igniting this precipitate, appear to be very pure. The results seem to be exact.

When solutions of pure tantalum and pure columbium, under the same conditions, are treated with cupferron, a great difference is observed in the behavior of the precipitate. Tantalum gives no trouble in filtering and washing, while columbium is thrown down as a sticky semi-liquid mass. It will probably take some time before the conditions for an exact separation of tantalum from columbium can be achieved.

Recently some interesting observations have been made with regard to the effect of solutions of organic substances, such as bases, benzidine, quinoline, hexamythelene tetramine, piperazine hydrate, quinine, etc., upon solutions of tantalum and columbium dissolved either in oxalic acid solution or in a solution of methylamine or some similar substance. Qualitative experiments have shown that tantalum is usually more readily precipitated than columbium. However, there are cases where columbium solutions have been precipitated while those of tantalum have remained clear. The oxide of tantalum obtained by some of these tests is extremely white.

So far as quantitative analysis is concerned, the greatest problem is found in the case of the cerium and yttrium groups of metals. The separation of the two groups is an extremely tedious matter, which is rarely carried out. The precipitation performed with sodium or potassium sulfates is far from accurate. The precipitated cerium group may be as much as fifty per cent too high, while only a small fraction of the yttrium group may be separated as such.

The most accurate method for separating these elements is to stir the sulfate solutions with potassium sulfate until the solution no longer shows any neodymium absorption. The precipitated double sulfates are filtered off and washed with a solution of potassium sulfate. The filtrate is precipitated with oxalic acid. The oxalates are filtered off, washed, dried, ignited, the resulting oxides boiled out with water, filtered and washed with hot water. These oxides are dissolved in the least amount of hydrochloric acid, the solution boiled and precipitated again with oxalic acid. These oxalates upon ignition give a portion of the yttrium oxides. The other portion is separated from the precipitated double sulfates by converting to hydroxides or oxides. These are then dissolved in nitric acid. A similar amount of nitric acid is then neutralized by magnesium oxide and the solution added to the rare earth nitrates. The liquid is then evaporated to crystallization. The mother liquor is poured off, a quantity of bismuth magnesium nitrate added, together with some concentrated nitric acid. The mass is heated and allowed to crystallize. The original crystals are also recrystallized. A short fractional crystallization is carried out. All mother liquors that fail to show neodymium or samarium absorption bands are placed aside. When no more mother liquors of this type can be obtained, the process is stopped. The mother liquors are then diluted, the bismuth removed by hydrogen sulfide, and the yttrium earths precipitated by oxalic acid. This precipitate is filtered off, washed and ignited. This oxide, together with that obtained from the potassium sulfate solution represents the total yttrium earths originally present. The yttrium earths at the gadolinium end give double sulfates that are almost insoluble in potassium sulfate solution.

Some metals may have been neglected either because they were considered to be absolutely useless, or because they appeared to be too rare. When an element is condemned as being useless, it is evident that its characteristic properties are deeply hidden. Many years ago, thorium oxide was a very rare substance, and, one would suppose, considered useless. When it was found to be an ideal substance for the Welsbach mantle, a search was made for new mineral locations. At first the occurrence seemed to be very limited, and the production of a cheap mantle seemed to be out of the question. Finally the search for new raw material was rewarded by the discovery of monazite sand. Today large amounts of sand are obtained from Brazil and Travancore. Many other deposits are known, but most of them possess a lower thorium content than those mentioned. At the present time there is enough thorium for mantles and for other purposes, if such can be found.

If we search the literature for work on germanium, we shall find little, apart from that at the time of its discovery, and that done during the last two or three years. This substance, which once seemed so useless, is attracting much attention in the medical world, because of its action on the blood. According to several authorities, it should be of great value in certain cases of anæmia. This element occurs in argyrodite and canfieldite (which appear to be very rare), and to a very minute extent in some zinc ores. That occurring in the zinc ores is concentrated in the regenerated zinc oxide, which is obtained from the retort residues. Even after concentration, the amount of germanium dioxide is still very small.

Recently it has been stated to occur in a copper ore in Africa. Some of this mineral, which is said to occur in considerable quantity, was obtained and examined. The mineral proved to be rich in germanium, which is easily extracted in an exceedingly pure condition. There is therefore a possibility that this metal may become sufficiently plentiful so that its effect upon metals and alloys may be determined. It alloys quite readily with copper; 5 per cent gives a pale gold colored alloy.

G. Urbain informed me, at the New Haven meeting last April, that he treated several tons of zinc ore and obtained only a few grams of germanium dioxide. This was finally loaned to a doctor, who returned two decigrams. Germany, I understand, has forbidden the export of germanium and its compounds.

Will thulium ever be of any use? It must be admitted that it is very rare and extremely troublesome to separate. The oxide certainly possesses characteristic properties, for it glows when heated. With careful heating it gives a beautiful carmine colored light, which changes as the temperature is raised, becoming yellow and then almost white. I am optimistic enough to believe that all these very rare elements will prove to be of great importance in the future. Much work may have to be done, and we must not be discouraged by stone age talk in the time of super-steel.

On the other hand there are some of the so-called rare elements occurring fairly commonly in nature which have been subjected to considerable research, and which, unfortunately, are still unconquered. Metallic beryllium is a good illustration of this group.

Beryl, $3BeO \cdot Al_2O_3 \cdot 6SiO_2$, occurs in the United States in New Hampshire, etc., and in many other parts of the world. It would seem that in the case of this element there are perhaps three reasons why the metal is not well known. The mineral, beryl, is not readily decomposed; the separation of beryllium from aluminum is not an easy matter, and the reduction of beryllium compounds presents great difficulties.

Perhaps the simplest way to decompose beryl is to heat with sodium hydroxide in the following manner: The mineral ground to 200 mesh is mixed with 1.5 parts of sodium hydroxide, and heated over a powerful oil burner. The mass first softens, then fuses and boils, after which it dries to a friable, bluish earthy mass. During the drying, the whole should be well stirred so as to yield a fine powdery product. Care should be taken to prevent a second fusion in which a glass would result. Under good conditions nearly complete decomposition of the beryl is obtained (98 per cent). This friable product is found to be superior to the glassy mass obtained by a second fusion, since it is easily leached by water. Careful extraction by water removes about 30 per cent of the total silica, and a considerable amount of sodium hydroxide. The amount of beryllium found in solution is negligible. This leaching is best carried out by grinding with water in a ball mill. It is considered advisable to make this extraction in order to save mineral acid in the next stage of the process where the alkali is removed by treatment with acid.

The powdered product of the fusion, or the residue from the leaching is stirred with water, sulfuric acid being added from time to time to neutralize the alkali. It is essential that the liquid be neutral or slightly alkaline towards the end of the stirring, the desired result being the removal of the soda, leaving the beryllium, aluminum and silica in the residue. The mass is then filtered, washed and treated with dilute sulfuric acid to extract the beryllium and aluminum. The solution is filtered off, evaporated to dryness and gently heated to render the silica insoluble. The residue is taken up with water, and the resulting solution contains the beryllium and aluminum originally present in the ore.

A solution of the sulfates is tested for the amount of mixed $Al_2O_3 + BeO$. Assuming that the oxides exist in solution in the same ratio as they occur in beryl, about three times as much ammonium sulfate is added as is required by theory to convert the aluminum sulfate to ammonia alum,

$$Al_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 24H_2O.$$

The solution is concentrated and cooled to 10° C., when, if the concentration has been sufficient, practically the whole of the aluminum separates out in the form of alum. The liquid upon examination is found to be almost entirely free from aluminum.

A small amount of iron still remains, and this is separated by diluting the solution, heating to boiling, and oxidizing the iron if necessary by potassium bromate or some other suitable oxidizing agent. The liquid is then neutralized by ammonium hydroxide, and the iron precipitated by ammonium acetate and a slight amount of acetic acid. If too much acetic acid is liberated, more ammonium hydroxide is added to neutralize the great excess. When a sample upon filtering and treating with ammonium sulfide gives a white precipitate, it is concluded that all iron has been removed. The whole is then filtered, the filtrate boiled and the beryllium precipitated as basic carbonate by means of ammonium carbonate or sodium bicarbonate. The basic carbonate is filtered off, washed with boiling water and gently dried.

This method, when carefully carried out, gives a product which is almost chemically pure. The regaining of the ammonium sulfate is an important matter, which has not been completed at present. Many thanks are due to H. C. Fogg, J. F. Cullinan and D. A. Newman for carrying out this work.

The reduction of beryllium compounds such as the oxide by calcium and magnesium, the chloride by sodium and calcium; and the electrolysis of fused salts and salt solutions is still under investigation. Before we can make much more progress with regard to beryllium, it is essential that we know more about its constants, and that we have a simple method for its quantitative determination. Such knowledge would allow us to study solubility curves and alloys with rapidity.

A few years ago the difficulties of a zirconium determination were as great as those of beryllium are now. However, as zirconium grew in commercial value, so the accuracy of its determination improved.

During recent years new reagents have been recommended from both inorganic and organic divisions. The organic section seems to be rich in reagents which may be applied to the titanium, zirconium, cerium, thorium family. Phenylarsonic acid is one which is being thoroughly examined at the present time. The substituted phenylarsonic acids act similarly. This substance precipitates zirconium and titanium from solutions very acid with hydrochloric acid, while cerium and thorium remain in solution. There seems to be considerable difficulty in driving off all the arsenic on ignition. Igniting in a current of hydrogen rapidly removes all arsenic.

Phenylarsonic acid precipitates thorium from solutions containing ten per cent acetic acid and a slight excess of ammonium acetate. Under the same conditions the metals of the cerium and yttrium groups are not precipitated. Cerium must be in the cerous state. However, the thorium carries down a small amount of the rare earths, and it is necessary to make a second precipitation. This is easily performed by dissolving the thorium phenylarsonate in a little hydrochloric acid, diluting and adding acetic acid until the solution contains about ten per cent. The thorium is then reprecipitated by adding an excess of ammonium acetate, and a little more phenylarsonic acid. This second precipitate is once again dissolved in hydrochloric acid, the solution diluted, and the thorium thrown down as oxalate. The oxalate is filtered off, washed, dried and ignited to oxide. Thorium phenylarsonate can be ignited directly to oxide, if a current of hydrogen be used to reduce any arsenic remaining after the first ignition.

When hydrogen peroxide is added to a solution of cerium nitrate containing a little acetic acid, an excess of ammonium acetate and phenylarsonic acid, a precipitate of the ceric compound rapidly forms. The quantitative nature of this reaction has not been ascertained as yet.

Phenylarsonic acid can be easily prepared according to the method recommended by Roger Adams (Journal American Chemical Society, 1922).

We must not forget that long list of elements known as the rare earths, which includes the members of the cerium and yttrium groups. It seems unfortunate that these substances, which are obtained in considerable quantities as a by-product during the extraction of thorium, have not found many uses commercially. It is true that some are used to a certain extent, however a large amount goes to waste. If we except cerium, the chemistry of the remaining elements is a little section all by itself. These rare earth elements resemble a homologous series of carbon compounds in many respects. Many properties when plotted against the atomic weights give interesting curves. If the solubilities of a set of isomorphous compounds, containing the same amount of water of crystallization are examined, it is usual to find that they lie upon a smooth curve. On the other hand a set of compounds possessing two or three states of hydration will give a curve resembling that of a single substance at various temperatures where two or three states of hydration are met.

Unfortunately, in this family the separation of the elements from each other is no simple matter. With few exceptions, quantitative analysis is unknown. The exceptions include cerium and those members which lie at opposite ends of the series. Cerium can be separated by converting it into the ceric condition, when its properties become similar to those of thorium.

Lanthanum, which occurs at one end, can be separated from erbium, which occurs near the opposite end of the series, by stirring the solution of the nitrates with magnesium nitrate and an excess of bismuth magnesium nitrate. Lanthanum magnesium nitrate is precipitated out, being insoluble in the bismuth magnesium nitrate solution. Erbium remains in solution in the form of the simple nitrate.

There is therefore little trouble in separating two elements that lie far apart in the series. It is an easy matter also to separate one element, such as lanthanum, from several elements occurring at the opposite end by the above method. The greatest difficulties are encountered when an attempt is made to separate two or three consecutive elements such as lanthanum, praseodymium and neodymium. In this case the praseodymium comes between the lanthanum and neodymium when the double ammonium nitrates are fractionated. Lanthanum ammonium nitrate is the least soluble, while the neodymium salt is the most soluble. Praseodymium ammonium nitrate tends to accompany both.

The three elements presenting the greatest difficulty are dysprosium, holmium and yttrium. In certain cases, the scarcity of an element makes the problem still more difficult. This is recognized in the cases of europium, terbium and thulium.

Many members of the rare earth group can be obtained in large amounts and at a reasonable cost whenever required. This statement applies especially to cerium, lanthanum, praseodymium, neodymium and yttrium. Of course it is evident, when a use is found for the elements mentioned, that those which are rarer will be more easily obtained.

Although we often come across the statement that the rare earths are no longer rare, we must realize that this is not general. In fact europium, terbium, thulium and celtium are exceedingly rare. Some zinc ores contain more gallium than monazite sand contains europium.

Since the separation of these elements is based upon slight differences, the process has to be repeated many times. In some cases thousands of operations have to be carried out before some of the desired salt can be obtained pure. Fractional crystallization or fractional precipitation can be employed. The former is usually selected because it is cheaper and more efficient in the long run with large amounts. Perhaps the cases of lanthanum and yttrium are exceptional, for in these cases precipitation plays a big part.

With regard to fractional crystallization there are two special lines which are being examined at the present time: (a) Solubility curves of various salts in various solvents; and (b) the effect of one rare earth salt upon another. In addition to this large amounts of dysprosium, holmium, erbium, thulium, ytterbium and lutecium are being separated in order to prove whether there are any other elements occurring in minute amounts in this series. Welsbach believes that some of these elements, such as terbium, thulium, etc., are complex. This is rather against the theory of Urbain, and the problem should be settled. It is evident therefore, that the rare earths require considerable investigation, for as yet we know little about them. Only a few of the metals have been obtained in a fused state. We have learned much with regard to the structure of atoms from the radio-active elements, and it is highly probable that the rare earths will give us a whole lot more.

Rare earth research is slow and tedious, but it is simple compared with what it used to be. That which required years in the time of Crookes can be done now in about as many weeks.

Gallium and indium, two other elements of group III, should be mentioned. If only gallium could be obtained in quantity, it would without doubt find many uses, for it has a low melting point, and when pure has many properties approaching those of the noble metals. A few years ago, after the discovery made by the Bartlesville Zinc Company, it looked as though there would be enough material to supply all those who desired to work upon it. However, the ore containing gallium occurs only in pockets. Upon purifying this crude zinc by redistillation, a leady residue was obtained, which was rich in gallium and indium. Unfortunately, this process has been discontinued.

Indium occurs much more commonly in certain zinc by-products. Some flue dusts have shown about 0.5 per cent of this element. All this material passes through the smelters and the indium is lost.

When we study a list of rare metals, we note that many elements, such as titanium, zirconium, etc., are commoner than many of the metals with which we come in contact every day. These elements form stable compounds that are reduced with difficulty. Moreover, the metals when finely divided are very active, combining with oxygen, nitrogen, carbon, silicon, etc. This great activity and a melting point beyond the range of most furnaces easily account for the stupendous work required for solving such matters.

It is not long since we had to use the greatest of care in handling tungsten lamps. It would be a nightmare to a man accustomed to the use of ductile tungsten, to be placed in a lamp factory under the old conditions. Some of us doubtless remember those old times with the huge amount of labor involved. The production of ductile tungsten at one time seemed remote, although the number of investigators was comparatively great. Finally this difficult matter was solved, and not until then did the tungsten lamp really become commercial. Today tungsten and molybdenum can be worked as may be desired.

Tantalum, which was originally worked by Siemens-Halske, is now being produced by the Fansteel Company in a ductile form. They also state that columbium can be put on the market in a similar state.

It is especially interesting to observe that with improved methods, both zirconium and uranium metals give melting points very different from the figures obtained by earlier workers. The problem is being attacked in the correct manner at the present time. The first aim is to obtain pure metal, regardless of the cost of the process, in order to study its properties. When these have been outlined, it will be much easier to reason out a simpler plan.

Zirconium is an element occurring generously in nature, so its commercial possibilities are considerable. One of the great costs is the purification of the salts and oxide. The cost of production is, however, much less than it used to be. The indexes of the various journals are a good gauge of the attention that the various elements are receiving. If the number of patents mean anything, the future of zirconium should be assured.

Uranium, a by-product obtained during the extraction of radium salts, is easily purified. The new deposits of the Congo indicate that there will be no shortage of this element in the near future. Probably long before this new region is exhausted, others will be discovered. Since uranium is a member of the tungsten, molybdenum and chromium family, it ought to have commercial value.

The rare elements will also have many uses when in the form of compounds. Probably some will be used as catalysts. Thallous chloride acts as an excellent chlorine carrier, especially in the chlorination of hydrocarbons. Benzyl chloride is not produced when toluene is used. Zirconium has a tendency to remove hydrogen from compounds.

Many of the rare metals are thoroughly established in the commercial field, but we must realize that some are completely discarded. If the minerals are not being used, of course it does not matter much, for they can be mined when wanted. It is sad, however, when many rare metals, obtained as by-products, have to be thrown away.

As time goes on the remaining territory of the rare metals will become more and more difficult to explore, since the easier ones fall before the steadily increasing power of the investigators. It is highly probable that in all difficult tasks, the worker, at times, is liable to become discouraged. However, we have many fine illustrations in the past where the problems seemed hopeless, but where the work was finally crowned with success. It is especially interesting to read the work of Crookes upon his search for certain elements giving phosphorescent spectra.

We who are interested in the commercial application of the rare metals, ought to be thankful that we are working at this period, for these substances are being launched upon their journey through the commercial world as never before. It is our duty to assist in this project. What greater reward can we have than to learn that they have proved seaworthy, and are steadily going ahead.

A paper presented at the Forty-third General Meeting of the American Electrochemical Society held in New York City, May 5, 1923, Dr. F. M. Becket in the Chair.

THE PREPARATION OF FUSED ZIRCONIUM.[1]

By Hugh S. Cooper.[2]

INTRODUCTION.

In the course of certain alloy investigations a considerable quantity of zirconium was needed to pursue the work. This metal is a rather scarce commodity, and therefore its preparation in the laboratory became necessary. Although nothing novel is claimed for the process described herein, yet there are a number of interesting features and essential precautions involved in the production of the metal, which are considered of sufficient importance to be published in some detail. The experimental data on the establishment of the melting point of zirconium metal are also given, as well as a brief description of some new alloys.

After due consideration of the various methods employed in the past for making zirconium, it was decided to adopt the method in which zirconium tetrachloride is reduced by sodium, because this seemed to be the most promising. Previous experience in producing anhydrous chlorides also influenced this decision to some extent. Although some zirconium chloride was made by passing chlorine over the oxide in the presence of carbon, the yields were rather unsatisfactory. By far the major portion of the work was carried out by the action of chlorine upon zirconium carbide, a procedure which gave satisfactory results.

The carbide chlorination scheme has been used heretofore by Moissan and Lengfeld,[3] and also by Wedekind,[4] but a brief description of the apparatus used in the laboratory, as well as the results obtained, will be given because of some rather important considerations involving the purity and physical character of the

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[1] Manuscript received February 14, 1923.

[2] Kemet Laboratories Co., Inc., Cleveland, O.

[3] Moissan and Lengfield. Compt. Rend. 122. 651 (1896).

[4] Wedekind, Preparation of Zirconia and Tetrachloride Z. anorg. Chem. 33, 81.

chloride, the latter greatly influencing the yield of zirconium metal during reduction.

PREPARATION OF ZIRCONIUM TETRACHLORIDE.

The furnace, as shown in the accompanying illustration, Fig. 1, is of the horizontal, wire-bound tube type in which temperatures up to 1000° C. are obtainable. The carbide is placed in silica or alundum boats approximately 7.6 x 15 x 2.5 cm. (3 x 6 x 1 in.) deep. These boats hold approximately 228 g. (8 oz.) of material each and are inserted in a fused silica tube which fits snugly into the furnace. The diameter of this vitreosil tube is about 7.6 cm. (3 in.) and the length about 92 cm. (3 ft.) One end of the tube is fitted into a terra cotta condenser by means of a thick rubber stopper. The other end of the condenser is also sealed with a rubber stopper of equal size, in the center of which is an opening for the chlorine outlet tube. This condenser is approximately 30 cm. (12 in.) in diameter by 46 cm. (18 in.) long.

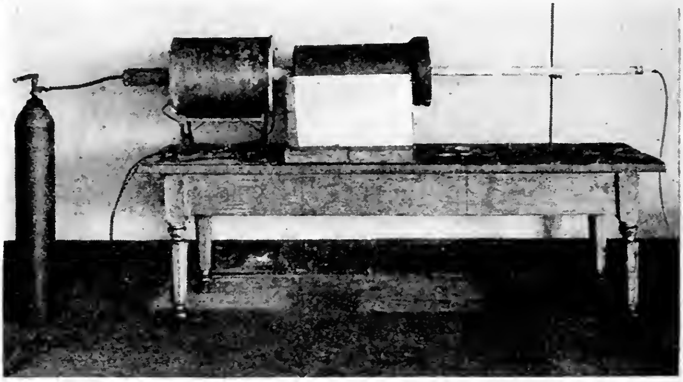

FIG. 1.
Chlorination Furnace.

After placing the carbide in the boats the tube is sealed and the current applied until a temperature of 500° C. is indicated by a thermo-electric pyrometer, the couple being adjacent to the outside wall of the silica tube. At this time a stream of chlorine is allowed to pass over the carbide, the temperature being held as close to 500 or 550° C. as possible, since this seems to be the optimum temperature from the standpoint of selective separation of the iron. The physical condition of the chlorine depends upon the temperature at which it is condensed, and this determines to a great extent the yield of zirconium metal which is obtained upon reduction. For example, that chloride which has been condensed in the terra cotta pipe is in a fine state of sub-division, due probably to the rapid cooling at normal temperature, whereas, that in the end of the silica tube near the entrance to the condenser consists of a heavy dense mass of large crystals. The temperature at this point is about 200° C. as a maximum. As soon as the carbide has been converted to chloride, which usually takes four or five hours, the respective chlorides above mentioned are removed separately and placed in glass stoppered bottles. The voluminous finely divided material is very hygroscopic, rapidly absorbs moisture, and in so doing assumes a lemon-yellow color characteristic of the oxychloride. The heavy crystalline material, on the other hand is much less affected by moisture and can be transferred many times with slight absorption of water.

NATURE OF CARBIDE.

An analysis of some of the carbide used in some of these experiments is given below:

	No. 1	No. 2
Zr	73.88	83.78
Fe	0.63	1.00
Ti	0.41	0.48
Si	0.10	1.40
C	23.50	12.96
	98.52	99.62

Many experiments have conclusively demonstrated that carbide containing some free graphite, similar in analysis to No. 1, is more readily attacked by chlorine and at much lower temperatures than material of the second type which more nearly approaches ZrC in composition. As a matter of fact, ZrC shows only a superficial attack at temperatures of 800° C. and is a very dense, heavy material. The former is of a light porous nature, is friable and gives practically the theoretical recovery of the metal as chloride.

A representative analysis of zirconium oxide made from chloride, by exposing the same to the action of steam with subsequent ignition, follows:

	Per Cent
$Zr O_2$	99.44
$Ti O_2$	0.12
Fe_2O_3	0.28
$Si O_2$	0.08
	99.92

REDUCTION OF ZIRCONIUM CHLORIDE.

The furnace depicted in Fig. 2 is 55 cm. (21.5 in.) in height and has an outside diameter of 15 cm. (6 in.) It consists of two parts, the upper containing the periscope for observing the temperature of the reaction and a tube connecting with the vacuum pump. The lower part of the furnace consists essentially of a cylindrical tube having an inside diameter of 13 cm. (5 in.) and 13 mm. (0.5 in.) wall, to which a base is welded, the upper part having a 13 cm. (5 in.) opening with a welded steel collar. The height of the cylinder is 33 cm. (13 in.) and the collar is 41 mm. (1 5/8 in.) in diameter. Just below this collar is a threaded plug in which the terminals are placed which conduct the current to the inside of the cylinder. A lead gasket is used between the top and base to make an absolutely air-tight joint.

The heating unit consists of an alundum core wound with nichrome and is 5 cm. (2 1/8 in.) inside diameter by 23 cm. (9 in.) long. Between the outside wall of this core and the steel shell the space is insulated with sand. The steel cylinders in which the zirconium chloride and sodium are packed are 21 cm. (8 1/4 in.) long by 45 mm. (1 3/4 in.) in diameter, and are provided with screw tops. Dense crystalline zirconium chloride only is employed to make the metal, since it is more permanent in air and permits a greater weight of material to be used per charge, due to the smaller volume. The amount of chloride and sodium used for each reaction is based upon the equation:

$$ZrCl_4 + 2Na_2 \rightarrow 4NaCl + Zr$$

The theoretical amounts would therefore be 232 g. of chloride plus 92 g. of sodium, this yielding about 90 g. of metal. In actual practice 230 g. of chloride and 92. g. of sodium are used, as the slight excess of sodium can be easily washed out and a complete reduction of the chloride is thus assured.

Zirconium chloride and sodium in the proportions given above are rapidly placed in alternate layers in the iron cylinder, the cap is tightly screwed on, and the cylinder inserted in the furnace. The furnace top is then bolted tightly on and the cylinder is then exhausted. At this stage the current is applied and within a short time a temperature of 500° to 600° C. will have been reached. Close observation at this point will show a sudden rise in temperature, the cylinder reaching about 900° to 1000° C. It is held at this temperature for a short time, current is turned off, when the cylinder has become cold the pump is cut off and the

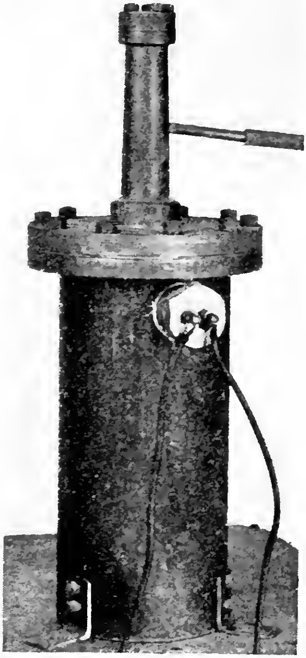

Fig. 2.
Reduction Furnace.

furnace opened. It is extremely important not to remove the cap from the cylinder until the temperature has dropped to normal because of the extreme activity of the metal, which ignites upon the slightest friction. When the cylinder has been opened a black skeleton-like mass is exposed to view. This is slowly added in successive portions to a large volume of cold water. It will be immediately found that the heavy lamellar material sinks to the bottom while the powder remains suspended, and in this manner an easy separation is effected. The metal is thoroughly washed with cold, and finally hot, water until entirely free from sodium salts; it is next dried for several days at a temperature not exceeding 85° C. If this procedure is carefully followed, metal having the following approximate analysis will be obtained:

	Per Cent
Zr	99.28
Fe	0.14
Ti	0.13
Si	0.07
	99.62

The metal suffers little loss either in concentrated or in dilute hydrochloric or nitric acid, even when boiled therein. It is also practically insoluble in dilute sulfuric acid, but dissolves completely in boiling concentrated sulfuric.

EXPERIMENTS TO DETERMINE THE MELTING POINT OF ZIRCONIUM METAL.

The melting point of zirconium is not known with certainty even at this late day. According to Von Bolton this point lies in the neighborhood of about 2350° C. Burgess states that three experiments gave 1529°, 1533°, 1523°, and he decided on 1530° C. as the melting point. According to Guertler the melting point is around 1700° C. Having a considerable amount of metal on hand, with ample equipment at our disposal, it was decided to make a few experiments in an attempt to correct these discrepancies. The melting experiments were carried out in argon and hydrogen, as well as *in vacuo*. Two types of furnaces were used. One of these was an Arsem furnace, in which the metal was melted in especially prepared zirconium oxide crucibles, the other of a type used in treating tungsten and molybdenum rods, one end of the metal being clamped to the upper electrode, the other dipping into a pool of mercury which acts as the lower electrode.

The zirconium metal, in large pieces which have been carefully dried for several days at the prescribed temperature, is weighed in lots of 35 grams each. These lots, placed successively in a die and subjected to a pressure of about 35 tons, yield rods about 6 mm. (1/4 in.) square and 25 cm. (10 in.) long. The heating of these rods in the tungsten treating furnace in an atmosphere of argon or hydrogen, has been only partially successful up to this time, and the experiments are being continued. Traces of oxygen still remaining in argon, as well as moisture in both gases, has prevented obtaining full-length bars of completely sintered zirconium having a clean surface similar in appearance to that of tungsten or molybdenum. Nearly all such rods showed superficial oxidation, although in some instances short lengths of well-fused metal have been obtained. These experiments indicate that if practically dry hydrogen were employed it should be possible to make solid bars of metal by this method, and it is also believed that once the metal reaches a fused state the hydride will not be formed at the lower temperatures upon cooling.

The melting experiments in the Arsem furnace, utilizing zirconium oxide crucibles, gave some gratifying results. The temperature measurements were made with a Leeds & Northrup optical pyrometer, especially calibrated for temperatures up to 3000° C. The curve supplied with the furnace, in which the temperature is plotted against the power input, enabled us to check the temperature readings closely. An accurate check was also obtained by use of molybdenum and tantalum, which have well-defined melting points.

In the first experiment a rod of pure molybdenum metal was placed on one end of a zirconia slab, and on the other end a rod of pressed zirconium metal. Previous tests in alundum crucibles had shown that the melting point of the metal was above that of alundum. The first optical reading was taken at 2420° with 8.5 kw. input, which gave 2475° on the chart. A final reading was taken at 9.5 kw., corresponding to 2600°, and at this temperature one end of the molybdenum rod had melted to a small button. The optical reading at this time gave a temperature of 2630° C. Upon removal from the furnace the metal rod was observed to possess a well-sintered appearance, but it was not fused.

In the next experiment several grams of metal were placed in a zirconium oxide crucible. The temperature reached 2650°, with a power input of 11 to 11.5 kw. The zirconium in this instance was well-sintered, but showed no signs of fusing and no loss in weight.

In the third trial the metal was placed on one end of a zirconium oxide slab, with a piece of pure tantalum on the opposite end. At 2800° the zirconium had partially fused into small, flat sections without showing a complete melting, the tantalum had begun to "sweat," indicating a temperature close to the melting point. This was checked with a further and similar experiment. The temperature in this experiment reached 2865° C. The tantalum showed distinct fusion on one corner, and the zirconium had flowed rather freely over the sides of the slab. This was checked closely in a further test in which no tantalum was used. In the sixth test several grams of metal were placed in the zirconia crucible and heated to 2910°. At this point the zirconium melted and took the shape of the crucible. These experiments led to the conclusion that the melting point of zirconium metal is above that of molybdenum and very close to that of tantalum, probably about 2800° C.

ALLOYS OF ZIRCONIUM.

Probably the most interesting alloys of zirconium yet discovered are those with tin and with nickel. The former alloys are exceedingly pyrophoric when the zirconium content exceeds 60 per cent, and in this respect resemble the well known cerium-iron alloys.

Tin and zirconium alloy readily with evolution of heat at about 800° C., giving alloys of very high melting points. A composition containing approximately 25 per cent Zr and 75 per cent Sn is very soft; when heated to about 2000° C. most

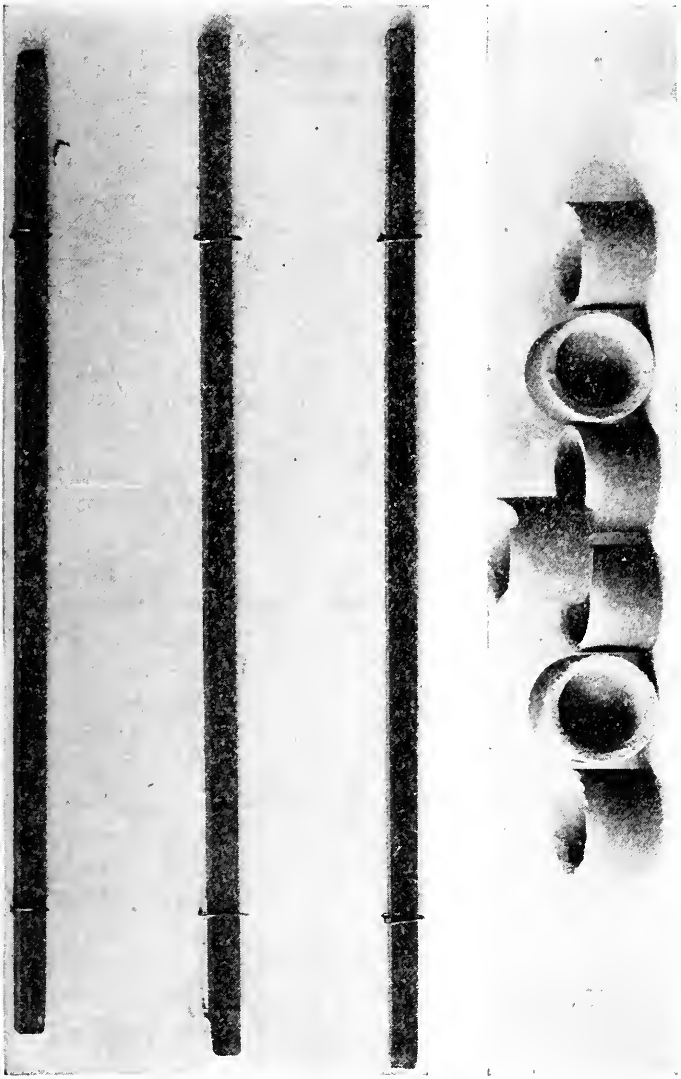

Fig. 3.
Zirconium Metal and Zirconium Oxide Crucibles.

of the tin can be removed, the zirconium being left behind as an unfused mass. When 40 to 50 per cent Zr is present, the alloy begins to show pyrophoric properties when rubbed across a file, and at 60 to 80 per cent the action is marked. At 70 to 80 per cent Zr the alloys probably equal the cerium-iron alloys in their scintillating effect. Because of their high melting point, it is not possible to produce rods and the like by casting, but these can be readily made by first pressing the zirconium metal into the desired forms and then heating these in the presence of powdered or ingot tin, the latter being rapidly absorbed. Compositions containing as high as 90 per cent Zr can be made in this manner and these appear suitable for ignitors, etc.

When used in percentages up to about 15, with small amounts of aluminum, silicon and tungsten or molybdenum, and with a base of nickel, excellent machine cutting tools are produced which retain their cutting edge at a red heat.

Ternary alloys have also been made using manganese or antimony in connection with zirconium and tin, but these do not seem to offer any advantage over the binary compositions.

Fairly high percentages of zirconium can be added to nickel before malleability is lost. The range of toughness probably extends up to about 30 per cent. A 20 per cent alloy can be drilled and machined; but when the zirconium approaches 50 per cent considerable hardness is manifested, together with some brittleness. These latter alloys can be produced only at a temperature around 1700° C.

With gold, zirconium forms straw-colored brittle alloys for the production of which high temperatures are also required. The zirconium can be almost entirely removed from the gold by heating in an oxy-hydrogen flame. Attempts to make alloys with antimony and zinc were unsuccessful, as the metals volatilized away from the zirconium before alloying occurred. At about 1500° C. zirconium dissolves in copper. The effect is to increase the hardness with little change in color. Few alloys with lead were made and these seemed to disintegrate when exposed to the air for some time. Alloys with aluminum have been made in nearly all proportions, the action taking place at about 1100° C. When the zirconium content is relatively low, considerable toughness is manifested, but above 35 per cent brittleness prevails. Unlike the tin-zirconium series, the alloys exhibit no pyrophoric properties. The effect of zirconium on aluminum appears to be similar to that of silicon.

Zirconium has been alloyed with magnesium by reduction of the oxide *in vacuo,* using a large excess of magnesium. Treatment with hydrochloric acid removes the magnesium without affecting the zirconium. If the zirconium is not too high the malleability of magnesium is not affected by addition of the latter. Alloys of tungsten can be produced by pressing the powdered mixed metals into briquettes. In this manner as much as 25 per cent Zr has been introduced. Forging properties of this series have not yet been investigated.

DISCUSSION.

J. W. MARDEN[1]: The paper given by Dr. Cooper is of interest to the speaker because, in collaboration with Mr. M. N. Rich, he tried to make zirconium metal by the identical method described, using the Arsem furnace. The results of these investigations (which were made in 1919), were published in Bulletin 186, U. S. Bureau of Mines, 1921. Although we had some success, we found that it was nearly impossible to avoid some contamination when the zirconium was heated in the Arsem furnace. In more recent work in the laboratories of the Westinghouse Lamp Co., much better results have been obtained using an especially constructed high-frequency high-vacuum induction furnace, which has been described by Rentschler and Marden before the American Physical Society, April 20, 1923.

Attempts were made to fuse zirconium in the Arsem furnace as described by Dr. Cooper, and the reasons for failure have been given on page 82 of the above bulletin, which dealt briefly with the impossibility of completely excluding oxygen and carbon in this kind of apparatus. Even when extreme precautions were observed, using a slow stream of pure dry H_2 at the low pressure of a few mm., the introduction of carbon from the heating helix

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[1] Westinghouse Lamp Co., Bloomfield, N. J.

and oxidation from the moisture always given off from the large amount of metal surface enclosing the furnace could not be eliminated. It is well known that the presence of oxide will raise the melting point considerably.

Zirconium oxide crucibles were also used in some of the above experiments. The preparation of these crucibles is described in Bulletin 186.

Bars of sintered zirconium were made in a vacuum treating furnace in the laboratory of the Westinghouse Lamp Company many months ago. The vacuum used for this work must be of the highest type, using mercury diffusion pumps and liquid air traps. These bars have no superficial coating of oxide. It is of interest to bring out some of the points about the purity and the methods of analysis of the metal powder. The analysis of a metal powder is attended with extreme difficulty due to the volatile gas, either in free or adsorbed state. Wedekind has found that in a good vacuum these volatile gases can not be all removed from zirconium even at 1,000° C. We have found that zirconium powder often contains 2 to 9 per cent of moisture, hydrogen, loosely bound nitrogen, etc. Since zirconium increases only about 30 per cent in oxidation there is often enough gas present in weighing the sample to indicate many per cent. of ZrO_2. In the very painstaking work of Weiss and Neumann, they found for example that 0.1006 g. of zirconium yielded 0.1333 g. ZrO_2. This corresponds to 98 per cent total zirconium, but only 91 per cent free metallic zirconium.

Four years ago the writer could not obtain over 92.5 per cent free zirconium by the best methods of preparation. The purity of the powder was undoubtedly greater than that indicated, but the methods of analysis are not yet satisfactory for this work. Analyses should be stated in terms of free metal and not total metal. According to the results we obtained the method of desiccation described by Dr. Cooper would not remove all of the gases.

The melting point determination of zirconium, as with certain other of the rare metals, should be done with extreme accuracy, and these determinations must be made under conditions which preclude the possibility of the presence of oxygen or carbon. The metal which is used for this must be analyzed for oxygen and the per cent of oxide in the sample not inferred by difference, but be actually determined analytically. The melting point given by Dr. Cooper is near that of the oxide or the carbide. The melting point has been determined in the laboratory of the Westinghouse Lamp Company, and is not nearly as high as the value given by Dr. Cooper. Our metal melted sharply and did not show any gradual softening. The blistering or sweating of the high melting point metals in the Arsem furnace may have been indicative of carbide formations.

Ruff[2] has suggested the formation of carbide under such conditions as Dr. Cooper worked. This carbide was partially avoided in the work of Bulletin 186, U. S. Bureau of Mines, by the use of purified dry hydrogen to sweep away hydrocarbon vapors from the heating helix and moisture from the walls of the container. The melting point of pure zirconium is discussed on page 97, Bulletin 186.

When the melting points of the metals are plotted against the atomic numbers, a regularity is observed which would indicate the melting point of zirconium about 1,700° C., or about 2,000° Abs. This may be somewhat too high or too low, but roughly indicates where it should be if the atomic number and atomic weight assigned to this element are correct.

Lastly, the sintering of mixtures of tungsten and zirconium has been tried by the writer, and it is found that zirconium in a high vacuum distils away from tungsten at temperatures high enough for treating this metal. Pure metallic zirconium volatilizes rapidly below 2,800° C., where tungsten is treated before working.

H. S. COOPER: It has been stated that the melting point determinations in the Arsem furnace were in effect comparisons between zirconium carbide and molybdenum and tantalum, because it was thought that the zirconium would be converted to carbide in the atmosphere which prevails in a furnace of this type. There is no evidence, up to this time, that this occurs when zirconium is the metal used. Our analyses have shown that there is only an absorption of carbon to an extent of about 0.2 per cent

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[2] Z. Electrochemie, 24, 157 (1918).

when the metal is heated to its melting point, and it is unlikely that this amount of carbon would materially affect the results in either direction.

In all of our work we have been careful not to use amorphous zirconium, as we have found that this grade of metal is apt to contain oxygen to an appreciable extent. Two grades of metal exist after reduction, and we have been careful to pick clean, bright samples, which are then pressed into the rods which I have described. When such rods are used in the Arsem, I seriously question whether there can be any combination with oxygen, as the furnace atmosphere is decidedly reducing, which is evidenced by the discoloration that you have noted on the zirconium oxide crucibles. This change of color on the crucibles is not due to carbon or carbide, but is an actual reduction of the oxide to metallic zirconium, which has been proved.

Mr. Marden's criticism on the use of the Arsem furnace for these experiments seems to me to be rather misdirected, in view of his statements under the title of "Preparation of Coherent Metal in Arsem," on pp. 94 and 96 of the Bureau of Mines Bulletin No. 186—"Thus the experiment had accomplished what had been considered impossible, namely, the fusion of the amorphous metal." The analyses with this statement is what might be expected by the use of amorphous metal.

It is rather strange that having a product of a purity indicated by the various analyses discussed in the bulletin, that Mr. Marden was unable to produce an alloy of zirconium with tin, as these alloys are simply prepared. If I have correctly interpreted the remarks made by this gentleman there appears to be some doubt in his mind that the zirconium-tungsten alloys can be prepared in the manner outlined, since he has stated "that in his experience the former metal boils away from the latter before alloying occurs." In this connection I wish to state that we have prepared a great many alloys of zirconium and tungsten. These were made by thoroughly blending the powdered zirconium with powdered tungsten, pressing the product into rods, sintering the rods in vacuo and then heating the same by their own resistance up to about 2,200° C. There can be no doubt that alloys of any desired percentage of either metal can be prepared in this manner, and contrary to Mr. Marden's statement, if any evaporation of the zirconium does occur the amount is so slight as to be invisible on the surface of the glass enclosure in which the experiments were conducted.

W. C. Arsem[3] (*Communicated*): It should be remembered that in a vacuum furnace the character of the results depends on the maintenance of a vacuum as good as can be obtained. The best results are not to be expected unless the pressure is kept low, probably around 1 to 10 microns. It is not sufficient to maintain a fairly good vacuum by an efficient pump acting against a continuous leak in the furnace. Leaks should be absent. In order to guard against leaks it is necessary to make sure of the absolute tightness of both electrode and cover gaskets by appropriate tests. The technique for realizing this condition should be quite obvious, although it is often carried out imperfectly through failure to recognize its importance.

A furnace with graphite parts, allowed to stand open to the air when not in use, absorbs and condenses a considerable amount of air and moisture, and to avoid this condition it should be kept exhausted when not in use. When experiments are to be tried in high vacuum it is best to run the furnace under experimental conditions without a charge until gases are well removed and a high vacuum can be maintained at a high temperature, then let it cool under exhaust and open it with the temperature of the cooling water above the dew-point to avoid condensation of moisture. Then insert the charge, exhaust immediately and continue to exhaust at low temperature until a high vacuum is obtained before applying the current.

The presence of oxygen or water in the interior means that the atmosphere will eventually be chiefly carbon monoxide. This is not a "reducing" atmosphere except under special conditions.

With many of the metals whose oxides are extremely stable we have at high temperatures the following reactions:

$$\mathrm{CO} + \mathrm{M} \leftrightarrows \mathrm{MO} + \mathrm{C}$$

and

$$\mathrm{CO} + 2\mathrm{M} \leftrightarrows \mathrm{MO} + \mathrm{MC}$$

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[3] Consulting Chemical Engineer, Schenectady, N. Y.

The action which takes place is really more complex than the equations indicate, but the net result is that a mixture of oxide and carbide can be formed at least superficially by heating certain metals in an atmosphere of CO.

It would be advisable in reporting results of research of this kind to include in the paper a complete log of each furnace run, including pressure readings. Absence of these data may lead to much misunderstanding and uncertainty.

A paper presented at the Forty-third General Meeting of the American Electrochemical Society held in New York City May 5, 1923, Dr. F. M. Becket in the Chair.

EXPERIMENTS WITH URANIUM, BORON, TITANIUM, CERIUM AND MOLYBDENUM IN STEEL

By H. W. Gillett and E. L. Mack.*

Abstract.

Of U, B, Ti, Zr, Ce and Mo used as alloying elements in heat-treated steels, only Mo has a decided and consistently beneficial effect. In the types of steel in which the other elements were used they were either of slight effect one way or the other, or decidedly harmful.

U probably has a slight strengthening effect, but similar results can be obtained by cheaper means. B and Ce are harmful. Ti and Zr have about as much effect as equal amounts of Si. Mo is a real and potent alloying element.

When the Bureau of Mines was actively studying radium production it was thought desirable to study the preparation of ferro-uranium, and this work was assigned to the writers.[2] This gave a stock of ferro-uranium. On account of reported German use of U steel, the Watertown Arsenal requested that an experimental series of U steels be made up and supplied to the arsenal for study. Later, further series of W, Mo and other steels were requested. Since the Bureau was equipped for this sort of small-scale work, the navy then requested the preparation of some high Si-Ni steels, containing Zr. In that connection, Ce and B were also added to this Ni-Si steel.

In the above work, the Bureau merely prepared and analyzed

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[1] Published by permission of the Director of the Bureau of Mines. Manuscript received January 30, 1923.

* Department of Interior, Bureau of Mines, Ithaca, N. Y.

[2] Gillett, H. W., and Mack, E. L., Preparation of ferro-uranium, Tech. Paper 177, Bur. of Mines 197.

the steels, the testing being done by other departments or bureaus.[3-4] Co-operative agreements were later made with the Welsbach Co. for a further study of Ce steel, and with the Vanadium Corporation of America for a study of various types of Mo steel. These latter series have been tested by the Bureau of Mines and a comprehensive series of endurance tests on them is still under way. As regards data on the physical properties of the other steels, these are wholly lacking in the case of the steels prepared for the arsenal, and in the case of most of the steels of the Ni-Si-Zr series they are fragmentary, in that only normalized specimens and specimens subjected to a single heat treatment and that at a very low draw temperature were tested.

Detailed data on the preparation of the steels, especially in regard to recovery of the alloying elements, have been fully given elsewhere,[5] and will be only briefly touched on here.

The steels were made up in 50 to 100-lb. heats in an indirect arc furnace. Ferro-alloys of readily oxidizable alloying elements were usually added at the end of the heat, just before pouring. Armco iron was used as the base, by which means sulfur was held to 0.035 per cent, usually below 0.030 per cent and P to below 0.02 per cent, usually below 0.015 per cent.

URANIUM.

Since the arsenal desired a number of steels of high U content, attempts were made to prepare these. Steels analyzing 2 per cent U and over were prepared, but usually shattered in forging. Steels analyzing over 0.55 per cent U were slushy when poured, although very hot, and all such steels showed terrific segregation in different parts of the ingot. To get a uniform U content of 0.35 to 0.50 per cent U it was necessary to add over 1 per cent of U as ferro-uranium, ferro-uranium alloy low in C and high in U giving the best results.

Physical tests (Bureau of Standards, small round test bars cut from plates one-half in. thick) were made only on some of

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[3] Wheeler, H. E., Nitrogen in Steel and the Erosion of Guns, Trans. Am. Inst. Min. and Met. Eng. **47**, 257 (1922).

[4] Burgess, G. K., and Woodward, R. W., Manufacture and Properties of Steel Plates containing Zirconium and other elements, Tech. Paper 207, Bur. of Standards, 1922.

[5] Gillett, H. W., and Mack, E. L., Experimental Production of Alloy Steels, Bull. 199, Bur. of Mines, 1922.

the non-segregated Ni-Si steels, to which uranium was added. These are given in Table I, together with a couple of comparison steels without U.

TABLE I.

Physical Tests on Alloyed Steels.

Normalized from 800 to 840° C.

Steel No.	C	Si	Mn	Ni	U	Yield Point	Tensile	El
1244	0.43	1.30	0.90	3.00	0.34	134,000	184,000	6
1229	0.45	1.05	0.75	3.00	0.36	234,000	240,000	3
1228	0.63	1.20	0.84	3.00	0.37	169,000	176,000	0.5
1327	0.45	2.42	0.70	2.92	0.52	*		
1227	0.40	1.45	0.84	3.10	....	97,000	134,000	18.5
1237	0.49	2.20	0.94	3.05	....	108,000	156,000	14.5

Steel No.	Red.	Brinnell	Heat Treated. Quenched from 800-840° C. in oil; 175° C. draw.				
			Yield Point	Tensile	El.	Red.	Brinnell
1244	13	290	195,000	310,000	10.5	35	625
1229	8.5	315	192,000	283,000	2.5	8.5	530
1228	2.5	305	......	300,000	1	3.5	620
1227	52	265	205,000	286,000	8.5	39	555
1237	41	315	258,000	313,000	8	25	530

* Broke in rolls.

The normalized U steels showed a martensitic pattern, and were stronger and less ductile than the comparison normalized steels. The heat-treated steels with U show on the average no appreciable improvement over those without. The U steels contain characteristic blue inclusions. While great claims have been made for U in high speed steel and in ordinary steels, the first seem open to grave question and the second seem to be covered by the comment of Poluskin[6] to the effect that, while U may somewhat increase tensile strength and toughness without loss of ductility, it does nothing that cannot be done with cheaper alloying elements. He thinks much of the U in steel is present as oxide.

The cost of U, the difficulty of introducing it without excessive loss and without the formation of dangerous inclusions, together

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[6] Poluskin, E. Les aciers a l' uranium. Rev. de Met., **17**, 421 (1920). Iron Trade Rev., **68**, 413 (1921). Iron Age, **106**, 1512 (1920).

with the cessation of mining of domestic carnotite, make uranium steel arouse little enthusiasm at present. Were its alleged advantages more outstanding or the supply of U larger, it would deserve further study. It might have use as a scavenger, but it has not impressed us as promising on this score, as its oxidation products do not appear to be readily released by the steel.

BORON.

Since B is reputed to give great hardness to steel some C-B and Ni-Si-B steels were made up. The only ferroboron available was the thermit product. One lot contained two-thirds as much Al as B and another one-third as much. The ferro-alloy was readily taken up. Adding it at the end of the heat, 90 per cent of the B or better was recovered. Even when charged at the start of the heat, an 80 per cent recovery was made. Analyses of different parts of the ingots showed no segregation of boron.

The B steels with around 0.10 per cent B, and with a C content of 0.15 to 0.70 per cent, had an amazing freezing range. They started to solidify about the usual temperature, but did not become fully solid till the temperature dropped down, somewhere around the melting point of cast iron.

During the long freezing range the ingot was plastic, and when poked it acted like pie crust under the cook's thumb. There is plainly a very low-melting carbon-iron-boron eutectic. This is clearly shown metallographically. Moreover the first couple of ingots of boron steel rolled by the Bureau of Standards fell to pieces of their own weight when heated to the usual rolling temperature and picked up by tongs, so that the preheating temperature had to be reduced.

With 0.30-0.50 per cent B even low carbon steels lost a great deal of their ductility, and even 0.06 per cent B spoiled a 0.45 per cent C steel for heat treating. The B eutectic in the cast material is a network, but this can be broken up and spheroidized by hot working (possibly also by thermal treatment), and in that state the steel is not so brittle. Heating to a normal temperature for quenching causes a network to reappear and gives a brittle product.

It is within the bounds of possibility that the steels might be handled so as to be good for something, but hot-working processes as used on other steels do not produce anything worth having. A purely scientific study of the Fe-B-C system would be highly interesting. One wonders what B might do in cast iron.

If B is to be used as an alloying element, the steels will have to be given special treatment, and, lacking a detailed preliminary scientific study, it is hard to see how they can be commercially useful.

In regard to boron as a scavenger, the fact that it gives a high recovery even when added at the start of the heat indicates that it cannot be expected to have strong deoxidizing action. If it will act as a deoxidizer it might, by the formation of the oxide, tend to flux out other oxides and hence be beneficial. One thinks at once of boron nitride and of the possibility that it would remove nitrogen. In a British patent, Walter,[7] a German, says that, while 0.2 per cent or more B causes brittleness, anywhere from 0.001 to 0.10 per cent B causes astonishing grain refinement in steel, and that similar amounts in cast iron give stronger material with graphite in spherical form. One would be more impressed by his claims if he did not state also that from 0.007 to 0.01 per cent B in a C steel makes it self-hardening.

The writers are inclined to feel that, while, on the face of returns, boron does not appear to be of any use in steel, a systematic study of B in steel might show greater possibilities than can be seen at present. This view is based on the fact that B has a real effect and gives a product with peculiar properties, which might conceivably be utilized.

TITANIUM.

For comparison with Zr steels, which carry some Ti, various plain Ti and Ni-Si-Ti steels were made, using a thermit ferro-titanium containing about one-fourth as much Al as Ti. Adding this at the start of the heat, around 20 per cent of the Ti was recovered, while, by adding it at the end of the heat, around 65 to 70 per cent was recovered. Steels were made with up to 2 per cent Ti. Segregation of Ti was not troublesome. The steels containing Ti as alloying element were certainly no better, and generally somewhat less ductile than comparison steels without

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[7] Walter, R., British Pat. 160, 792, Aug. 25, 1921.

Ti. Steels with only a few hundredths per cent of Ti showed no superiority over the comparison steels.

ZIRCONIUM.

The work on Zr was required because of the high recommendation given a Ni-Si steel carrying Zr, by Mr. W. H. Smith of the Ford Motor Co. While "zirconium steel" was loudly heralded, it is only fair to say that Mr. H. T. Chandler, formerly with the Ford Motor Co., the metallurgist in actual charge of the Ford experimental work with Zr, considered the value of this steel to lie chiefly in the Ni-Si combination, with the possibility that Zr added something to that combination.

As a result of the agitation for Zr steel, much baddeleyite was imported from Brazil at a time when shipping was precious, and ferro-alloy manufacturers had to displace the production of ferro-alloys of proven value for that of ferrozirconium. The navy was not stampeded by the agitation, but decided to find out what, if any, virtue lay in the Zr.

In the work done by the Bureau of Mines for the navy, some 75 Zr steels, and an equal number of comparison steels without it, were made in the preliminary work in which the steels were rolled, heat treated (normalized and given a quench and a single low temperature draw) and tested for mechanical properties by the Bureau of Standards. In the later work a series of some 30 steels, with and without Zr, was made by the Bureau, rolled, and each given three or four different heat treatments by the Halcomb Steel Co. and tested for mechanical properties by the navy.

Although thermit ferrotitanium was found to give fair recovery of Ti, thermit ferrozirconium did not, the recovery of Zr averaging not over 10 per cent.

Various electric furnace ferro-alloys reduced by C, and carrying considerable C, made by the Bureau of Mines and by the Southern Manganese Co. also gave a low recovery, averaging under 5 per cent.

Electric furnace ferro-alloys made by the Bureau, using Si as reducing agent, gave 60 to 80 per cent recovery. An electric furnace ferro-alloy, low in Si, made by the Electro Metallurgical Co., with Al as reducing agent, gave around 10 per cent recovery, but an alloy similarly made but in place of Fe containing 55 per cent Ni, gave 40 per cent recovery, while the Electro Metallurgical Co's Si-Zr (30 per cent Zr-45 per cent Si, reduced by C in the presence of Si) gave a 55 per cent recovery.

In the second series, using Electro Metallurgical Co's ferro-alloy, the Si-Zr gave a 50 per cent recovery, Ni-Zr 50 per cent and a Si-Ni-Zr (27 per cent Zr, 22 per cent Ni, 35 per cent Si) made by melting together Si-Zr and Ni-Zr, 65 per cent.

To get these recoveries, the Zr alloy had to be added at the end of the heat. If added at the start, the steel contained only traces of Zr. When remelting crop ends containing 0.20-0.25 per cent Zr and 0.03 per cent Ti, the steels came out with no trace of Zr and under 0.01 per cent Ti.

When we consider the loss of Zr in making the ferro-alloy from ore, that from ferro-alloy to steel, and that in remelted scrap containing Zr, the recovery from ore to finished steel would not be over 40 per cent and probably well under that figure.

No matter what the Zr alloy used, steels finishing with from 0.30 to 0.80 per cent Zr regularly showed a segregation of Zr, the top of the ingot containing say 30 per cent more Zr than the butt.

The Ni and Si introduced by the Ni-Zr, Si-Zr or Ni-Si-Zr alloys did not show segregation. With not over 0.25 per cent in the finished steel, segregation of Zr is negligible. Full details as to recoveries and segregation can be found in the report[8] on the preparation of these steels.

The physical tests on the Ni-Si-Zr and comparison steels of the first series can be found in the report of the Bureau of Standards.[9]

The sum total of the tests by all the co-operating government agencies led to the conclusion that the Ni-Si steels have good mechanical properties; that these properties, measured by the ordinary tensile and impact tests, are not materially injured by the introduction of small amounts of zirconium. Neither did it appear that the properties were materially enhanced. A steel of 0.40 C, 1.45 Si, 0.85 Mn, 3.00 Ni, rolled to one-half in. from a 3 x 3-in. ingot, normalized from 840° C., gives, on 0.3-in. diameter by 2-in. gauge length round specimens, a yield point of

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[8] Gillett, H. W. and Mack, E. L., Experimental Production of Alloy Steels, Bull. 199, Bur. of Mines 1922.

[9] Burgess, G. K., and Woodward, R. W., *loc. cit.*

around 100,000 and a tensile strength of around 140,000 lb. per sq. in., with an elongation of say 15 per cent and a reduction of area of say 40 per cent with a Brinnell hardness of around 270. On quenching from 840° C. and drawing 3 hours at 175° C., it gives a yield point of around 240,000 and a tensile strength around 280,000 pounds per sq. in., with an elongation of about 9 per cent and a reduction of area of 30 per cent, a Brinell of around 550, and (on a standard Izod bar) around 9 to 12 foot-pounds on the Izod test. The elongations would be higher on a standard 0.505-inch tensile bar.

With 0.10-0.40 per cent Zr similar steels show a tendency toward higher tensile strength and hardness, and lower ductility in the normalized state, and approximately the same properties with perhaps lower ductility under the heat treatment given. The better Zr steels of this class do not contain much over 0.15 per cent Zr. The tests on Zr steels show rather more variation among steels of about the same composition than those on plain Ni-Si steels. Since the problem was concerned with these steels, and it was necessary to use Si-Zr alloys which introduced a good deal of Si, nothing was done with plain C low Si steels containing Zr. A few high Si-C steels were made with and without Zr, but these, like the Ni-Si steels, show no regular beneficial effect due to Zr.

A few tests on the addition of Mo or V to the Ni-Si steels did not materially change the results either on the normalized steel or on that given the quench and low draw.

So far the evidence was against any beneficial effect from Zr at least in the Ni-Si steels, but another series was made on which each steel had three or four different treatments, higher draw temperatures being used. These steels were cast in 3 x 6-in. ingots and were rolled to plates one-quarter inch thick, being spread to a little over 12 in. wide by cross-rolling, then straight-rolled, reheated and finished by straight-rolling.

For the physical tests, made by the navy, tensile bars 0.5 in. wide by 0.25 in. thick by 2 in. gauge length, were cut from the plates with a 0.06 in. emery wheel, being finished by hand. The bars were shouldered and held in wedge grips. Izod specimens were also cut, 10 mm. wide by thickness of the plate. The notch was cut by a shaper tool, being 2 mm. deep with 1 mm. radius at the bottom (Mesnager notch). The direction of impact was parallel to the surfaces of the plate. The Izod values were computed to standard square Izod bar size by means of the ratio of standard 10 mm. width to the plate thickness. Two notches were tested on each Izod bar. Both tensile and impact specimens were taken in both longitudinal and transverse directions.

Steels of 0.35-0.40 C and 1.50-2.25 Si (or Si + Zr + Ti) gave very uniform results between longitudinal and transverse bars on ductility and Izod tests. With higher carbon or silicon (or Si + Zr + Ti) or both, the transverse bars generally fell below the longitudinal ones on these tests. Tensile strength and elastic limit were of course closely the same on bars taken in either direction on all the steels.

If we assume that Zr or Ti are approximately equal to equivalent amounts of Si, and plot the properties of the different classes, we get, for the average compositions given in Fig. 1, the properties plotted, for bars taken longitudinally. By comparison with the data obtained by the Bureau of Standards[10] for some similar steels drawn at 175° C. and from some Navy data not plotted in Fig. 1, it will be found that with draw temperatures below 400° C., the strength continues to increase while the ductility remains about the same as at the 400° draw. Raising the C or Si too high causes the ductility to increase with increasing draw temperature only slightly, and gives a dip in the Izod curve with a minimum around a 525° C. draw.

The navy Izod figures are on bars with the Mesnager notch (1 mm. radius at base) and were taken on rectangular bars and calculated to a 10 mm. square bar. The Bureau of Standards' Izod figures are on round bars, with the one-quarter mm. radius V notch, computed to the standard round bar of 1 sq. cm. area.

The British automobile steel research committee, whose results on alloy steels would be interesting to compare with this steel, used square bars with one-quarter mm. radius notch. Conversion factors, especially between the two notches, are so unsatisfactory that no direct comparison can be made of the Ni-Si steels and other alloy steels as to impact results. Also, because the Ni-Si steels had to be tested in flat bars, the ductility figures do not compare exactly with data on other steels from round bars.

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[10] Burgess, G. K. and Woodward, R. W., *loc. cit.*

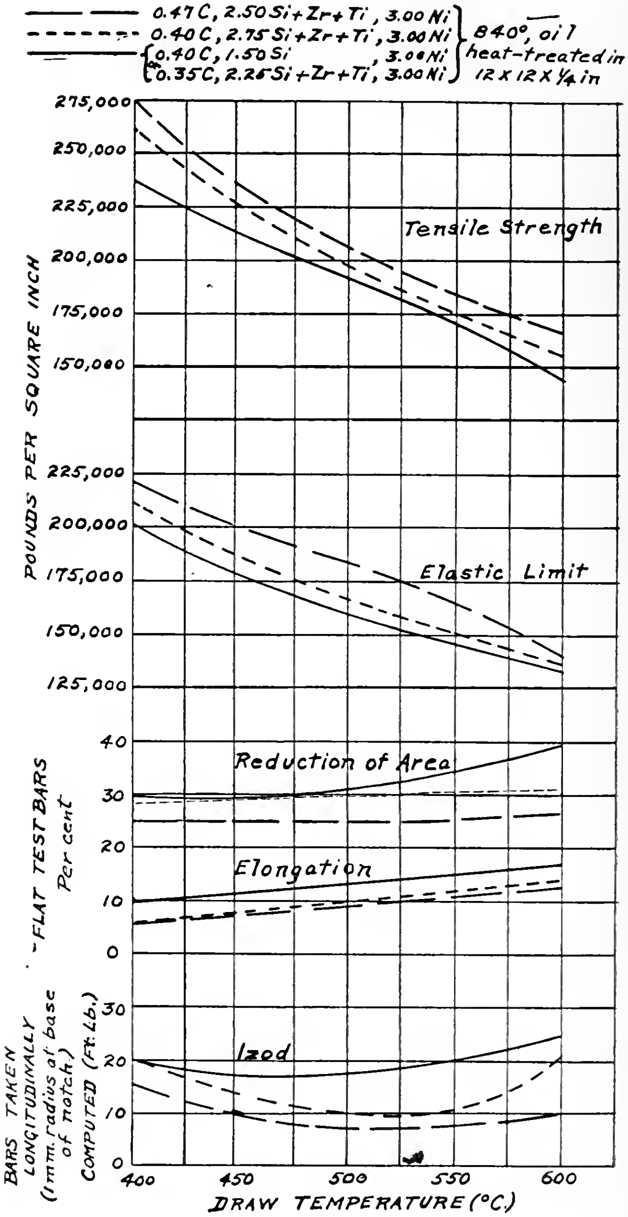
0.47 C, 2.50 Si+Zr+Ti, 3.00 Ni
0.40 C, 2.75 Si+Zr+Ti, 3.00 Ni
0.40 C, 1.50 Si, 3.00 Ni
0.35 C, 2.25 Si+Zr+Ti, 3.00 Ni
840°, oil heat-treated in 12 X 12 X ¼ in
POUNDS PER SQUARE INCH
275,000
250,000
225,000
200,000
175,000
150,000
Tensile Strength
225,000
200,000
175,000
150,000
125,000
Elastic Limit
FLAT TEST BARS Per cent
40
30
20
10
0
Reduction of Area
Elongation
BARS TAKEN LONGITUDINALLY (1 mm. radius at base of notch.)
COMPUTED (Ft. Lb.)
30
20
10
0
Izod
400
450
500
550
600
DRAW TEMPERATURE (°C.)

FIG. 1.

The steel requires higher draw temperatures to soften it than plain Ni, or the ordinary Ni-Cr steels. It will therefore be possible to draw the steel at temperatures high enough to make fairly certain that quenching stresses are released, and still get a high tensile strength combined with good ductility and toughness. The steels are especially attractive at draw temperatures around 400° C., for springs, and possibly for gears, or other use, where great strength or hardness combined with toughness is desired. Moreover, around this draw temperature, there is a fair range of compositions through which about the same physical properties are obtained.

The steels rolled well and, in the simple shape in which they were heat treated, did not show quenching cracks. We do not know what they would do in complicated shapes.

All the Ni-Si or Ni-Si-Zr steels within the limits of composition tested gave good and uniform results at the 400° draw. Results at draw temperatures of around 500° C. were less uniform.

Up to around 0.30 per cent Zr the effect of Zr seems to be negligible, or at any rate no more noticeable than the addition of an equal percentage of silicon. Putting in 0.40 to 0.75 per cent Zr consistently decreased the toughness and such steels, as well as those with too much C or Si gave much more erratic results, especially on transverse bars. One might expect that these high Si steels would tend to throw out graphite readily and that the impaired toughness of the higher C, high Si steels might be due to this cause. Microscopic examination, however, has not shown any deposition of graphite in these steels.

The steels lower in C and Si can just be machined in the normalized condition. Cooling in lime made it possible to crop all the ingots, of whatever composition, by sawing, though those high in C and Si would be classed as steels difficult to machine.

The results of the second series of Zr steels agreed with the indications of the first, to the effect that the virtues of the so-called "Zirconium" (Ni-Si-Zr) steels were due to the combination of Ni[11] and Si rather than to Zr. Zr probably has no greater effect in this type of steel than so much Si. Zr leaves tiny, sharp-

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[11] Compare Hoyt, S. L. Metallography Part II, p. 358, 1921, for properties of similar steels without nickel.

cornered inclusions in the steel, and it is more desirable to have a steel free from such inclusions.

As to the possibilities of Zr as a scavenger, some very good steels were made by remelting crop ends containing Zr, the resulting steels coming out with only a few hundredths of one per cent Zr. On the other hand, equally good plain Ni-Si steels, into which no Zr entered, were also made. Johnson[12] has studied the Ni-Si steels and has also concluded that Zr and Ti did not have any beneficial effects. The compositions of his steels are given in general terms only, so that no real comparison with our results can be made.

CERIUM STEELS.

Cerium being in the same group in the periodic system as Zr and Ti, some work on Ce was done in connection with that on Zr. Since the early work showed that Ce had a desulfurizing action, further work on this point and on its possibilities as an alloying element was done in co-operation with the Welsbach Co. Some "mopping up" on endurance tests on this problem is still under way.

Mix metal (Ce, La, Nd, Ph and Sa) was used to introduce Ce, and the word "cerium" and all calculations involving percentages of "cerium," hereinafter refer to the Ce group of metals thus introduced.

By adding 0.50 to 1.0 per cent Ce to the steel just before pouring, we have reduced S from 0.155 per cent to 0.067 per cent, from 0.085 per cent to 0.45 per cent and from 0.035 per cent to 0.015 per cent. A strong SO_2 odor and the rising of a reddish slag indicates that S combines with Ce and rises to the surface, where the S burns out. When less than 0.50 per cent Ce is added, desulfurization is slight. Adding 1 per cent Ce as soon as the charge is melted removes only a little S and no Ce is found in the steel.

Desulfurization by Ce thus appears to require the addition of so much Ce at the end of the heat that some will be left in the steel, and its use would depend on what the residual Ce does to the steel. Somewhere from 5 to 45 per cent of the Ce added at the end of the heat is all that is retained in the steel, and if much is retained it segregates badly. Such figures as 0.60 per cent Ce

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[12] Johnson, C. M., some alloy steels of high elastic limit, their heat treatment and microstructure, Trans. Am. Soc. for Steel Treat., 2, 501 (1922).

in the top and 0.30 per cent in the butt of a 70-lb. ingot are common. If not over 0.25 per cent Ce is retained, there is little segregation.

We have not been able to make steels containing over 0.30 to 0.40 per cent Ce in 3 x 6-inch ingots of 75 to 100 lb. without having the ingots unsound through the formation, at least in the top of the ingot, which freezes last, and often clear to the butt, of very tiny hair cracks not visible without smoothly machining the cross section of the ingot. Microscopic examination shows that there are literally myriads of tiny inclusions in a Ce steel, and that if there is enough Ce present and enough time given for it to act, these inclusions tend to coalesce and rise. If enough large coalesced inclusions are present to be collected between the crystals as the steel freezes, they cause these inter-crystalline hair cracks. Possibly if enough time could be given, all the inclusions would coalesce and rise, but, working with not over 100 lb. of steel, it could not be held long enough in the ladle.

The inclusions, under high magnification, are grayish, sometimes mottled with orange. They are roundish in the ingot. On rolling or forging the steel the inclusions smash up a trifle so as to have more irregular outlines, but are still more or less roundish. They do not draw into hair-like or knifeblade-like forms during the rolling of rods and plates as manganese sulfide does. Incidentally, the woody fracture of a transverse specimen of a rolled plate that contains ordinary inclusions may be due to the fact that the inclusions roll out too, for one such plate which is very dirty from inclusions of Ce does not show a woody fracture, while companion plates, free from Ce and immeasurably freer from inclusions, all showed woody transverse fractures. Rolling or forging, while it does not flatten or draw out the individual inclusions, often spreads the shattered inclusions in well-defined lines, so that rods of Ce steel are often seamy and plates laminated.

It is probable that the S of the Ce steel is held in these inclusions not as manganese sulfide, as in ordinary steel, for the inclusions are larger and in greater mass though not usually in greater numbers, in the top of the ingot, and the S is often decidedly higher in the top of the ingot than in the butt, the ratio of segregation being usually higher than that of the Ce present.

Starting with material of 0.03 per cent S, it was rare that the butt of an ingot of Ce steel would run over 0.01 per cent S.

On the other hand, if all the inclusions contain S, the percentage of S in them must be very low. It could not be present as any orthodox cerium sulfide and account for the great mass of inclusions. The inclusions are probably of complex composition, and one would naturally suppose them to be mostly oxides. That the S is combined with the Ce is probable from the behavior of a couple of steels in which the Mn was kept as low as possible (and in one case extra S added) and the steel treated with 1 per cent Ce. One of these, a 0.30 per cent C steel, was made up for 0.069 per cent S. It came out with 0.032 per cent S, 0.06 per cent Mn and with 0.05 per cent Ce left out of 1.10 per cent Ce added. Theoretically, 0.055 per cent Mn is required to combine with the S present. Practically, on account of mass action, it is generally considered that much more Mn would be required to prevent the presence of FeS, so that such a steel would be expected to be red-short. However, the steel forged nicely. Physical tests show no difference from any steel of that general composition. No Al or other special deoxidizer was used, but the Si was raised to 0.65 per cent to compensate, in killing the steel, for the low Mn. Some tests have been made using 0.01 to 0.03 per cent Ce as final deoxidizer which produced dead, de-gasified steel on high silicon steels, but 0.06 per cent Ce failed to kill a low Si steel. Ce is not as strong a deoxidizer and de-gasifier as aluminum.

Part of the Ce, or at least of some one or more of the Ce group, of metals, is probably present as carbide, for the steels containing more than something between 0.10 and 0.20 per cent Ce have a decided acetylene-like odor. Steels high in Ce give out a strong odor on machining. All one has to do to pick out such a Ce steel from among others is to rub it with emery paper or even with a rubber eraser, so as to remove some invisible film, and the characteristic odor will be easily detected.

With the low and irregular recovery of Ce, irregular desulfurization, the prevalence of cracked ingots and the great number of inclusions, it is difficult to get steels by which one can determine the real alloying effect, if any, of Ce. In the Ni-Si and in Ni-Cr steels, there is some evidence that 0.20 per cent Ce increases the propensity toward air-hardening, *i. e.,* that it acts as a true alloying element. But the ever present inclusions so complicate matters by reducing ductility that we are unable to state what would be the properties of a steel containing Ce as alloying element and none as non-metallic inclusions.

Tests have been made on plain Ce, Cr-Ce, Ni-Si-Ce, and Ni-Cr-Ce steels. A 0.45-per cent C, 1.30-per cent Si, 2.95-per cent Ni steel tested by the Bureau of Standards gave (oil quenched and drawn at 175° C.) 311,000 lb./sq. in. tensile and 37 per cent reduction of area at a Brinnell of 555. On this 0.02 per cent Ce was used as final deoxidizer. Other steels containing more Ce showed similar strength but lower ductility. A couple of these showed very good impact tests and hence all the Ce steels made since have been given the Izod test on samples drawn at low temperatures. However, none of these other Ce steels have shown any exceptional impact results.

Generally speaking, the forged or rolled Ce, Cr-Ce and Ni-Cr-Ce steels, containing 0.20 to 0.50 per cent Ce quenched and tempered, are practically indistinguishable on tensile, impact or repeated impact tests from similar steels without Ce, when test bars taken longitudinally are considered. Transverse test bars from plates fall down on ductility, doubtless due to the inclusions.

When we come to the "fatigue" test, endurance against repeated bending, the Ce steels regularly fall down in comparison with similar steels free from Ce, and this is the more noticeable the harder the steel. This test is probably more sensitive to the presence of inclusions than any of the other mechanical tests, and the poor behavior of the Ce steels is obviously due to the inclusions. In fact, if one looks at a micrograph of a Ce steel, taken from a polished but unetched section to show inclusions (see Fig. 2-5) he wonders why such dirty steel does not give poorer results on all tests than it does. The endurance tests show that, due to the inclusions, the cerium steels, especially when treated to a high hardness, are highly unreliable against repeated bending.

It is possible that some means might be found to control and

FIG 2. Unetched Cross Section of Cerium Steel. x 100.

FIG. 3. Unetched Longitudinal Section Cerium Steel. x 100.

FIG. 4. Unetched Cross Section Chromium-cerium Steel. x 100.

FIG. 5. Unetched Cross Section Chromium-cerium Steel. x 100.

utilize the desulfurizing action of Ce without doing more harm than good by the retaining of inclusions. We came close to this with a couple of steels low in manganese, but would be unwilling to attempt it on a production basis.

Cerium has been claimed to increase the ductility of aluminum alloys, and we tried[13] it out in various light aluminum casting alloys, including the duraluminum type, both as cast and heat-treated, but were unable to find any improvement of any sort due to cerium.

MOLYBDENUM

After working with U, Zr and Ce, which give low and variable recoveries, leave inclusions in the steel, segregate and either have little effect on or do actual harm to the steel, it is a relief to work with an alloying element that enters the steel without loss, does not segregate, and has a positive and very beneficial effect on the steel.

Most of the elements above mentioned are not available in this country in large quantities. Mo, on the other hand, is an element of which the United States has an an ample supply, and a complete understanding of just what it does in steel is important in the development of our Mo resources.

Present-day alloy steels for such uses as automobiles and aircraft require one or more of the following elements—Mn, Si, Ni, Cr, V. The first two are not usually classed as alloying elements, since they are present in all steel, but in amounts above the normal, they do exert an influence that justifies classing them as alloy elements.

The great bulk of the Ni used is mined in Canada. The V comes from Peru. Though we can, at a pinch, supply some Cr and Mn, the Cr usually comes from New Caledonia, Rhodesia and Asia Minor, and the Mn from Brazil and Caucasia. Fe, C and Si are domestic.

The development of a home supply of an alloying element which can, in whole or in part, replace or supplement the elements of foreign origin, is of obvious importance. One deposit in Colorado contains enough Mo to make some 20 million

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[13] Gillett, H. W., and Schnee, V. H., Cerium in Aluminum Alloys, soon to be published in Ind. Eng. Chem.

tons of Mo steel of the usual Mo content.[14] The Bureau of Mines is therefore interested in Mo steel both from the point of view of preparedness and avoidance of dependence on foreign raw materials and from that of development of a national mineral resource that is as yet so little used as to justify including Mo among the rarer elements despite the size of the deposits.

Much work[15] has recently been done on Mo steels, almost all, save the pioneer work of Swinden that has been done by observers not primarily interested in the sale of Mo, having been published in the last two or three years. When the Bureau started its work on Mo steels, very little data that was definitely free from possible bias was available. Now, however, there is such a mass of well agreeing data that there is little chance for argument as to the facts.

The Bureau's objective in the work on Mo was, incidentally, to check up the outside data on ordinary tests, but primarily to get some idea of how far Mo can replace other alloying elements, and to secure data on the resistance of Mo steel to shock and fatigue, points of increasing importance to the engineer and on which strong claims of excellence have been made by advocates of Mo.

For two years the work was carried on under a co-operative agreement with the Vanadium Corporation of America, producers

[14] Compare Moore, R. B., Molybdenum. Political and Commercial Control of the Mineral Resources of the World, Bur. Mines Mimeographed Report No. 5 of War Minerals Investigations Series, August 25, 1918.

[15] Bullens, D. K., Steel and its Heat-Treatment 354 (1916).

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of Mo. For the last six months it has been carried on by the Bureau alone, and it will take at least six months more to complete the time-consuming endurance tests which are the central point of the investigation.

In the preparation of Mo steels, by adding ferromolybdenum to the charge at the beginning of the heat, the recovery was found to be quantitative and no segregation was found.

The most important property of Mo in steel is the control it gives of the development by heat-treatment of the properties desired. Comparing C steels with alloy steels as a class, the carbon steels are not so readily brought over by quenching, to the metastable, hardened state. Carbon steels require drastic quenching with its attendant stresses and dangers, they do not harden throughout in large pieces, and if heated too high before quenching in order to increase the hardening effect, they deteriorate on account of excessive grain growth. The introduction of alloying elements, such as Mn or Ni, alone or in combination with Cr or V, makes the steel much more readily hardened, even in large pieces, and the evil effect of over-heating diminishes. The introduction of a sufficient quantity of the proper alloys makes the steel so sluggish that even cooling in the air produces a self-hardening or air-hardening steel. By proper adjustment of the alloy content and the carbon content, any gradation between a C steel that will not harden at all and an air-hardening steel can be made.

The best classification of steels, which was made by Aitchison[16] in his excellent book, is on the basis of the properties that can be developed in them, or, what is almost the same thing, their relative propensity toward hardening, rather than on chemical composition.

From this point of view, Mo is—C excepted—the most active and potent element used in steel. The propensity toward hardening can be shown by varying the rate of cooling or by varying the maximum temperature to which the steel is heated, and cooling at a constant rate, since raising the initial temperature aids in suppressing the stable change and producing undercooling or hardening, much as increasing the cooling rate does. In either

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[16] Aitchison, L., Engineering Steels, Van Nostrand, 1921.

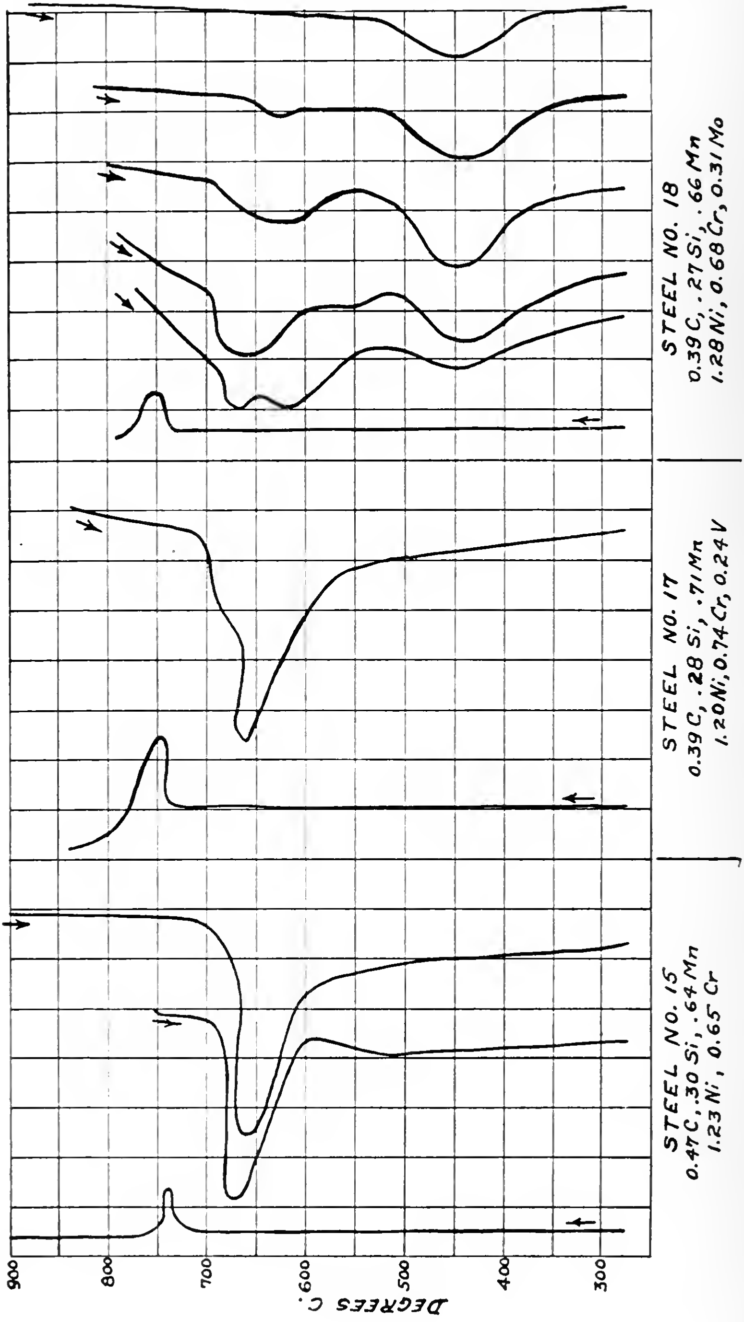
STEEL NO. 18
0.39 C, .27 Si, .66 Mn
1.28 Ni, 0.68 Cr, 0.31 Mo
STEEL NO. 17
0.39 C, .28 Si, .71 Mn
1.20 Ni, 0.74 Cr, 0.24 V
STEEL NO. 15
0.47 C, .30 Si, .64 Mn
1.23 Ni, 0.65 Cr
900
800
700
600
500
400
300
DEGREES C.

FIG. 6.

method the lowering and "splitting" of the critical points on cooling will show the propensity toward hardening.

Fig. 6 shows differential heating and cooling curves of steels of about 0.40 per cent C, 1.25 per cent Ni, 0.70 per cent Cr. No. 15 has higher C, but the comparison of the steels is not altered thereby.

On either the plain Ni-Cr or the Ni-Cr-V steel, the critical point on cooling at the slow rate used (about 75 min. to cool to 300° C.) is not appreciably altered (slightly lowered) by raising the maximum temperature from 775° to 900° C. But with the addition of 0.31 per cent Mo, cooling at the same rate from 770° C., gives a weaker critical point at the normal temperature, and a new weak one starting about 525° C. and with a maximum at 450° C. At the upper point the austenite goes over to primary troostite, which at the ordinary rate of cooling immediately goes over to pearlite; but some austenite is retained unchanged, which at the lower critical point goes over into martensite. This martensite is not stable at the temperature at which it is formed, and in turn goes over to secondary troostite or sorbite on slow cooling.

As the maximum temperature is raised, the upper critical point becomes slightly lowered and progressively weaker, and the lower point becomes stronger, till at 900° C. maximum temperature the upper point is wholly wiped out and the steel shows only the low critical point corresponding to the formation of martensite, *i. e.,* is wholly air-hardening. The propensity toward hardening is so great that many Mo steels will harden throughout on oil-quenching in sizes which would not harden at the center on water-quenching without the Mo.

This same effect is shown by Mo in all combinations. If we leave out the Ni and Cr and raise the Mo to say 0.75 per cent, we get a similar family of cooling curves. As we raise the C, the Mn or the Ni, it takes less Mo to shift the steel from the behavior of a plain C steel on cooling toward that of an air-hardening steel. With combinations of Cr and Mo the effect of Mo is not quite so marked, but it is still evident.

Whatever the composition of the steel in which it is used, the presence of Mo tends to make the steel require less drastic quenching and to make it harden to a greater depth on a given quench. This slowing up of the transformation gives much better control over the hardening operation, and this control is given in good degree by quite small percentages of Mo, 0.20 per cent Mo having a definite effect. If the steel is to be used in the normalized condition, the air-hardening properties may be a decided drawback. Even if the steel does not become difficult to machine, the normalized steel is not very good as to elastic limit, ductility or single-blow notched-bar test. When the Mo is over say 0.40 per cent and normalized, plain V or Cr-V steels appear more desirable than normalized Mo or Cr-Mo steels, unless tensile strength is the prime aim. Molybdenum steels should be used in the heat-treated condition to secure the maximum beneficial effect.

Vanadium does not, in itself, produce a strong tendency toward air-hardening. However, the greater hardening due to quenching from a higher temperature can safely be made use of in V steels, because of the marked ability of V to inhibit grain growth of austenite at temperatures that would give fatally coarse grain in C steel. Most alloying elements have this property in some degree, and Mo shows it strongly, though the effect is probably not quite so great as with V.

Vanadium steels generally show a higher elastic ratio than other alloy steels. In this respect, Mo has very nearly the same effect as V. The individual good properties of both Mo and V are still in evidence when other alloying agents are present, and they may both be used together. For example, the addition of V to a Cr-Mo steel produces a steel of remarkable toughness.[17]

The effect of Mo is shown not only in the behavior on quenching, but in tempering also. A hardened Mo steel does not soften on tempering with the facility of a similar steel without Mo. To bring the steel to a given strength or hardness, it has to be tempered at a higher temperature or for a longer time than one without Mo. Steels high in Mo, especially in the presence of a good deal of other alloying elements at first change in properties at a slow rate with increasing draw temperature, and more rapidly at very high draw temperatures so that at the highest draws it may require very accurate temperature control to get

[17] See Sargent, G. W. *loc cit.* p. 596.
Crucible Steel Co. Booklet, Al-Mo Steels, 39 (1919).

the same results on consecutive draw heats. But, if the Mo content is not too high, so that the properties desired are obtained in the range of draw temperatures through which the properties change slowly (and this is the case with most commercial Mo steels) less accurate control is required and consecutive heats produce more uniform results than with most other alloy steels.

The resistance to tempering shown by Mo steels holds promise for these steels for use at temperatures above normal, but no extended study of their properties at higher temperatures seems to have been made. Another advantage in the sluggish nature of a Mo steel is that the higher draw temperature for a given hardness or strength means a better release of quenching stresses.

Table II gives some of the data secured on heat-treated Mo and comparison steels. These figures are all on specimens heat treated in 1 inch diameter or less. Were larger specimens used, say 3-inch diameter, the depth-hardening properties of Mo would give the Mo steels an advantage that is not shown by the table.

A cursory examination of the table will show that Mo has a real strengthening effect and that the heat-treated Mo steels combine good strength with good ductility and toughness.

With 2.5 per cent Ni, 0.8 per cent Cr and 0.75 per cent Mo, one can get results of the same general order as with 3.5 per cent Ni, 1.5 per cent Cr. Cr-V and Cr-Mo steels each have nearly the same properties. On the other hand, Mo finds its chief use as an addition together with Cr, Ni, or Ni-Cr. Quite good alloy steels, decidedly ahead of plain C steels, can be made with up to 1 per cent Mo, especially by increasing simultaneously the Mn per cent.

From the results of a couple of Ni-Si plus Mo steels, given the 175° draw, the Bureau of Standards concludes[18] that these steels would be superior with the Mo omitted, while Johnson[19] secured good results in such steels with Mo, but says that it is not certain that the improved showing was due to the Mo. In the second series of Ni-Si steels made for the navy, one was included which contained Mo. This showed the normal effect of Mo in increasing the strength at high draw temperatures without, however, appreciably altering the ductility. This steel had rather

[18] Burgess, G. K., and Woodward, R. W., *loc. cit.* p 153.

[19] Johnson, C. M., *loc. cit.* p. 501.

TABLE II.

Physical Data for Alloyed Steels. Heat Treated.

No.	C	Si	Mn	Ni	Cr	Mo	V	Quenched from °C	In	Drawn at °C	Brinnell	Yield point* in 1000 lb. sq. in.	Ultimate tensile in 1000 lb. sq. in.	Elongation per cent in 2 in.	Reduction of Area at neck	Stanton test No. blows	Izod test Ft. lb.
1	0.40	0.29	0.77	...	...	...	...	870	H_2O	360	405	170	194	9	30.5	8400	14.5
3	0.38	0.35	0.71	...	...	0.37	...	870	H_2O	420	375	170	187.5	13.5	52	6800	26
2	0.41	0.42	0.72	...	...	0.67	...	870	H_2O	500	370	160	178	14.5	54.5	5800	28
41	0.46	0.43	0.75	...	...	1.05	...	900	oil	600	400	180	194.5	16	49	6200	36
42	0.36	0.40	0.67	...	...	2.05	...	875	oil	550	430	187.5	210.5	14	49	†	27
44	0.36	0.30	0.65	...	...	3.00	...	900	oil	500	415	195	198	13.5	42	8800	20
55	0.50	0.16	0.84	...	...	...	0.20	840	oil	475	360	155	171.5	15.5	55	4600	44.5
6	0.44	0.30	1.05	...	...	...	...	875	oil	400	380	150	187	8.5	24	7600	15
8	0.44	0.33	1.29	...	...	0.34	...	875	oil	450	400	170	195	11.5	37	7900	15
7	0.43	0.46	1.24	...	...	0.73	...	875	oil	550	370	157	182	17	49	5800	32
9	0.35	0.35	0.62	...	0.94	...	...	900	oil	525	340	131	158	16.5	54.5	5300	55
45	0.40	0.12	0.65	...	0.88	0.30	...	820	oil	525	360	143	166	15	53	6500	26
11	0.41	0.28	0.63	...	0.89	0.36	...	900	oil	525	375	155	178	15	52	5600	33.5
10	0.40	0.40	0.62	...	0.95	0.68	...	900	oil	525	390	165	203.5	13	46	6700	33.5
12	0.40	0.31	0.64	...	0.93	...	0.20	900	oil	525	360	156	165	16.5	54.5	5700	42
47	0.15	0.12	0.36	...	0.73	0.28	...	925	H_2O	425	320	130	155	14	55.5	5400	53
46	0.22	0.14	0.59	...	0.79	0.34	...	850	H_2O	425	320	124	137	13.5	52	5800	32
49	0.25	0.19	0.48	...	0.95	0.73	...	925	oil	530	365	140	165	19	62	6500	59
48	0.42	0.19	0.55	...	0.55	0.39	...	925	oil	530	365	162	175	17	55	6800	51
50	0.52	0.16	0.71	...	0.95	0.39	...	815	oil	525	365	157	188	17.5	54	6500	19
15	0.47	0.30	0.64	1.23	0.65	...	...	825	oil	525	345	147	160	15.5	54.5	5300	47
17	0.39	0.27	0.66	1.28	0.68	0.31	...	825	oil	525	355	160	168.5	15	54.5	6900	27
16	0.41	0.41	0.64	1.27	0.67	0.83	...	825	oil	625	380	171.5	182.5	14.5	52	5900	34
18	0.39	0.28	0.71	1.20	0.74	...	0.24	825	oil	525	340	156	160	13	54.5	6100	44
21	0.36	0.33	0.65	2.56	0.83	...	...	810	oil	425	375	177	191	14	54.5	7900	23
23	0.46	0.32	0.61	2.45	0.88	0.35	...	810	oil	525	385	158.5	182.5	15.5	52	6800	34
22	0.41	0.31	0.60	2.49	0.79	0.76	...	810	oil	525	410	180	200	14.5	45	5000	23
26	0.50	0.44	0.63	2.39	0.86	0.75	...	790	oil	525	425	190	210	11.5	37	4900	18
24	0.40	0.28	0.61	2.52	0.84	...	0.20	810	oil	525	345	158	170	16.5	54.5	5300	35

* Or "elastic limit" if yield point is not marked. † Not tested.

TABLE II.—*Continued.*

Physical Data for Alloyed Steels. Normalized.

No.	Air Cooled from °C	Brinnell	Yield Point (or elastic limit)	Tensile	Elongation per cent in 2 in.	Reduction of area at neck	Stanton test No. blows	Izod test Ft. lb.
3	900	200	67.5	107.5	24	54	1600	22
	840	210	65.5	104	25	54.5	1500	27
2	900	230	62.5	121.5	16	46.5	1500	11.5
	840	230	71	119	21	51.5	2200	14
41	900	280	75	140	17.5	43.5	1500	7
42	900	275	75	143	20	49	2600	11
44	900*	205	67.5	112.5	22.5	39.5	400	6
55	900	260	97	125	25	54	2000	19
45	900	245	60	127	17.5	50	†	†
11	900	280	57.5	129.5	18	45.5	1800	7.5
	840	250	57.5	129.5	16.5	44	2400	12
10	900	320	47.5	160	5	4.5	2300	7.5
	820	285	38.5	148.5	15	20	1600	6
12	900	245	82.5	113.5	21.5	62	1500	33.5

* Steel No. 44 cooled in furnace with door open. † No test.

too much Si to show best results from the addition of another hardening element.

Some fairly good Mo high speed steels have been made, and it is possible that they will be tamed and used some day. So far, the results are too erratic, and Mo does not appear to be a serious competitor of W for this purpose.

On the single-blow notched bar Izod tests (on the standard round bar, V notch 0.25 mm. radius at base) and on Stanton repeated impact tests (5-lb. hammer, 2-in. fall, square notch, 0.05 in. wide, 0.05 deep, 0.01 in. radius at corners) the Mo steels show properties similar to other alloy steels of their respective classes, when due consideration is given to the effect of tensile strength, C content and other variables outside of Mo in these tests. (Our thanks are due to Mr. J. H. Nelson, of the Wyman Gordon Co., for making the Stanton and Izod tests).

The repeated bending endurance tests, made on Upton-Lewis machines (kindly made available for our use by Sibley College, Cornell University) are still incomplete, although a large number have been made. It has been claimed in technical and advertising literature that Mo steel is in a class by itself as to endurance against repeated or vibratory stresses. Similar claims have been made for a long time for V steel, and no text-book discussion of V is complete without the statement that V in steel enables steel to withstand vibratory stress. And in practice, it is found that both these steels do give good service under conditions of severe repeated stress.

The claims for Mo steel against fatigue were largely based on the evident asumption that since Mo steel has a high ductility for a given tensile strength, the toughness must give good endurance.

But the work of Moore[20] and McAdam[21] has shown that the resistance to repeated bending, at least in sorbitic and pearlitic steels, is strictly proportional to the tensile strength, while the elastic limit, yield-point and ductility have no direct relationship to endurance. Published data of endurance tests on alloy steels are incomplete, but there are indications that any sound, clean steel is equivalent in endurance of any other sound, clean steel of the same tensile strength.

Our work indicates that this relation between tensile strength and endurance limit is a good first approximation, at least for a pretty wide range of alloy steels. There are often greater deviations from this relationship in sister bars of the same steel than among different steels of widely different types. Slight differences in surface finish or in the cleanliness of the steel make great differences in the results. The only place that we can see any effect of ductility is in very hard steels as compared to softer steels, the former being more sensitive to surface scratches or non-metallic inclusions.

We are led to believe from our work that the cleanliness of a steel, its uniformity of composition and structure, and its freedom from internal stress have far more effect on its life under repeated stress than its composition. The quality of the steel has more to do with the endurance than the question of whether it is a C steel, a Mo steel or a V steel.

Of course, if the comparison is made between, say a plain Cr and a Cr-Mo steel having received the same heat treatment, the one containing Mo will be superior, simply because it is

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[20] Moore, H. F., and Kommers, J. B., An Investigation of the Fatigue of Metals, Univ. of Ill., Bull. No. 8, **19**, (1921), Eng. Expt. Sta., Bull. No. 124.

[21] McAdam, D. J., Jr., Endurance of Steel Under Repeated Stress, Chem. and Met. Eng., **25**, 1,081 (1921).

stronger for the same draw. There is probably one real advantage in Mo, in that a Mo steel of given strength requires a higher draw temperature than one without Mo, and hence internal stresses which quite certainly reduce endurance are more fully relieved,[22] As to V, it is probable that, although it is only added to steel for its alloying effect, its use makes for cleanliness in steel, because of its strong affinity for oxygen and nitrogen, and it is certain that since V and Mo are both rather expensive, the steelmaker normally will not put either into a heat of steel without taking particular pains with that heat. This psychological effect on the steelmaker probably causes these steels to be better made than the average steel, and hence they give better endurance and reliability in practice.

We are comparing the endurance of different classes of similar heat-treated steels in which the variable alloying elements are Ce, Mo and V; the latter as a basis for the comparison. So far the steels containing Ce and therefore full of inclusions, fall down badly on the comparison, especially when in a very hard condition. In the grand average to date Mo steels are a trace ahead of V steels, but consideration of the data shows that this is due to one open-hearth Cr-V steel supplied by a commercial producer which shows up poorly on most heat treatments. The V and Mo steels made by the Bureau show equally good endurance at equal tensile strength.

Hence, while the exaggerated claims for Mo steel in regard to endurance cannot be corroborated, it seems, nevertheless, true that a well-made Mo steel is at least as good in endurance as any other well-made steel.

Abbott[23] has summed up the situation in a few words. He says that there is no one type of alloy steel that resists fatigue better than any other, that there is no alloy steel which is markedly superior to all others, each alloy steel requiring its own particular heat treatment, and the choice of an alloy steel depends largely on the ease with which the necessary heat-treatment can be given it. He says that on this basis the outlook for more extensive use of Mo steel is good.

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[22] Compare Aitchison, L., Engineering Steels, 204 (1921).

[23] Abbott, R. R., The Heat Treatment of Automobile Steels, Iron Age, **106**, 1,110 (1920).

Wood,[24] basing his conclusions on wide experience with results in Liberty engines, says that Cr-Mo and Cr-V steels are equivalent.

From every point of view it appears that Mo is an alloying element in steel, which in value stands with Ni, Cr, and V. Only inertia keeps it from wide use. Enough is known of Mo steel to make its good qualities evident. There is, of course, valid objection by steelmaker and user to adding another type of steel to the list instead of following the general trend of standardization and simplification. Since the first cost of Mo steel today is no more than that of any other alloy steel of equivalent properties, and its use is often attended with reduction in machining costs, it will undoubtedly be more widely employed. Tests to date on the use of U, B, Ti, Zr and Ce as alloying elements have not given consistently satisfactory results. In fact, in view of the non-metallic inclusions attendant on the use of all these except B, and of the eutectic formed with B, we feel that their use is more likely to be definitely harmful than definitely advantageous.

DISCUSSION.

H. W. GILLETT: I would like to add a word that is not in my paper. The market quotations for steel bars show that it is not any more expensive to produce a given set of properties with molybdenum steel than with chrome-vanadium or nickel-chrome. Personally, I am much sold on molybdenum steel. I do not feel quite in the frame of mind of one advertisement I saw a couple of days ago, however, where a firm advertised: "Steel—Super-Steel—Molybdenum Steel!" Nevertheless, I think it is a valuable alloying element.

BRADLEY STOUGHTON[1]: I think this paper of Dr. Gillett's is a valuable and interesting one. He has given us a lot of new light on two matters particularly. I refer to the question of segregation and sonims. By sonims I mean solid non-metallic impurities in steel. They may be anywhere from almost molecu-

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[24] Wood, H. F., Progress in Metallurgy of Alloy Steels, Amer. Drop Forger, Jan. 1920, p. 25.

[1] Consulting Engineer, New York City.

lar size up to particles that are plainly visible under the microscope. But whatever they are, they are common in almost all steel, and they make steel that is not clean.

There are and always have been two grades of steel. There is good steel and super-excellent steel. For years there was only one type of super-excellent steel and that was crucible steel. The reason for that was freedom from segregation, freedom from gases and freedom from sonims.

Now electric steel is attempting to invade the field of super-excellent steel. Whether it succeeds or not depends upon the amount of care and the amount of money that the electrical furnace people are willing to spend on the manufacture of their steel. They have not made their steel carefully enough. They have not observed precautions that should be observed to make steel free from segregation and sonims.

At the present time, very good steel is made by the acid open hearth process, and you can get, by several processes, steel that is low in sulfur, low in phosphorus, low in gases and all other impurities, except sonims. The authors of this paper have studied really the question of sonims, and they have only scratched the field where we must have someone plow deep and harrow and till and cultivate the crop. That is no criticism of their paper. It is a good paper, but it only begins to scratch the field that needs to be greatly worked.

A paper presented at the Forty-third General Meeting of the American Electrochemical Society held in New York City, May 5, 1923, President Schluederberg in the Chair.

SOME EFFECTS OF ZIRCONIUM IN STEEL

By F. M. Becket[1].

Abstract.

This paper refers briefly to the commercial development of various alloys of zirconium. Certain specific effects of zirconium in steel are described as determined in an extensive series of experiments. Outstanding effects include the ability of zirconium to eliminate oxygen, nitrogen and sulfur; the remarkable effect of zirconium in overcoming red-shortness in high sulfur steels; and the striking improvement in physical properties of plain carbon steels brought about by the presence of zirconium in relatively small proportions.

The title of this paper purposely expresses considerable limitation and implies brevity. At this time the principal object is to describe some of the specific effects of zirconium, as determined in the course of an investigation which has involved 350 experimental heats of steel made for this particular purpose. It is intended that a much more detailed discussion of the results will be presented in the near future, including descriptions of the procedures of the steel making, the physical testing, the metallographic studies and other phases of the work.

Numerous experiments on the reduction of zirconium ores and the preparation of zirconium alloys were conducted at the Niagara Falls plant of the Electro Metallurgical Co. during the period of a few years immediately preceding the entry of United States into the world war. These endeavors confirmed in a general way the published data relating to the properties of some of the zirconium compounds; but, more particularly, they devel-

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[1] Chief Metallurgist, Union Carbide Co., New York City.

oped a few important, unforeseen results, which enabled the author to relate much more closely than he had previously found possible the properties of zirconium and certain zirconium compounds to the properties of other more thoroughly understood refractory materials.

Early in the year 1918, having been influenced by apparently authentic reports concerning the use by Germany of remarkable ordnance steels containing zirconium—reports which were later considered groundless, if the author has been correctly informed—the War Industries Board decided upon an intensive program of experimentation with zirconium in steel for light armor, the direct object being the earliest possible large scale production, and the Electro Metallurgical Co. was requested to furnish zirconium alloys with this end in view. A vast amount of energy was then expended in the way of comparatively large scale experimentation on the production of a variety of zirconium alloys, and the Ford Motor Co. assiduously attacked the problem of zirconium steel with high ballistic qualities. At the date of the armistice considerable tonnages of zirconium-silicon alloy were being shipped to designated steel companies for the purpose of large scale manufacture, this particular alloy having been selected as the most efficacious after trial heats with many other zirconium alloys. As a result of the armistice, the major portion of the alloy in these shipments did not find its way into the nickel-silicon steel for which it was intended. However, this additional experimentation on the production of zirconium alloys brought still more forcibly to the mind of the author certain peculiarities of zirconium.

The United States Navy also became interested in zirconium steels, and requested the co-operation of the Bureau of Mines and of the Bureau of Standards. According to H. W. Gillett and E. L. Mack, in Bulletin 199 of the Bureau of Mines, 1922, entitled "Experimental Production of Alloy Steels," production heats of a series of zirconium and other similar steels began in September, 1918. In this Bulletin are described fully the methods involved in making the experimental heats (50 lb.) of zirconium steel, and valuable information is contributed concerning the recoveries of zirconium obtained from several different zirconium alloys. Technologic Paper, No. 207, of the Bureau of Standards, 1922, entitled "Manufacture and Properties of Steel Plates Containing Zirconium and Other Alloys," by G. K. Burgess and R. W. Woodward, reports in detail the properties of the zirconium steels made by the Bureau of Mines. It is the author's understanding that as part of the zirconium phase of the investigations reported in the Governmental papers just mentioned, it was greatly desired to determine whether the exceptional properties of some of the steels made under the direction of the Ford Motor Co. during the summer of 1918 could be properly attributed to zirconium. The conclusions drawn by the authors of Technologic Paper, No. 207, are to the general effect that no particular enhancement of desirable physical characteristics are to be ascribed to zirconium, at least in the types of steel tested, and that the effects of this addition agent may be detrimental.

The foregoing statements have been made to explain that a tenacious enthusiasm for zirconium was the result of information acquired during the smelting of zirconium-bearing materials, the production of various alloys of zirconium, and the refining of some of these alloys. So impressed was the author in respect to certain properties of zirconium, that an extensive program of experimentation on zirconium-treated steels was instituted, and has since been continuously maintained with increasing encouragement. This program was launched with knowledge of the decidedly skeptical attitude the steel fraternity had acquired concerning the value of zirconium additions to steel in general, and in particular the role of this element in the excellent steels that had occasionally been produced by the Ford Motor Co.

The practice followed in the steel heats of the present investigation has involved in the great majority of cases the melting of a 200 to 350-lb. charge of cold scrap-steel in a basic-lined electric furnace. Duplicate or triplicate ladles have been tapped from each heat in order to permit of a reliable comparison between the effect of the zirconium alloy addition and that of an equivalent addition of ordinary ferro-silicon. Whether rolled or forged, the ingots from any given heat have been treated identically so far as was possible during hot working, and all annealing, normalizing, and heat treating operations on the finished product have been likewise conducted so as to insure strictly comparable results. The rolling and forging of the ingots have been performed under ordinary mill conditions by experienced operators.

ZIRCONIUM AS A DEOXIDIZER AND SCAVENGER.

Zirconium has a greater affinity for oxygen than has silicon, and due to this fact increased recoveries of silicon in the finished steel are obtained by the use of zirconium-silicon alloys. This greater recovery of silicon is quite marked when an alloy of 35 per cent zirconium is employed. For example, in a series of 40 heats of basic electric furnace steel an average silicon recovery of 98 per cent was realized, as compared with a recovery of 84 per cent for ordinary ferro-silicon added under identical conditions and in equivalent percentages of added silicon to duplicate ladles. This particular series resulted in a 56 per cent average recovery of zirconium, ladle additions of 0.15 per cent zirconium having been made in all cases.

The rate of the reducing action of zirconium on the impurities present in molten steel is not only more rapid than that of silicon, but zirconium is the more efficacious in removing the final traces of oxygen and nitrogen. This scavenging power of zirconium is demonstrated in the partial or complete elimination of the banded structure in rolled or forged products, and in an increased rate of coagulation of emulsified slag. Zirconium-treated steels possess a cleanness which appears to be the result of a far more deep-seated action than characterizes the well-known deoxidizing and scavenging agents. There seems to be abundant experimental evidence to justify this assertion, but the relative brevity of this paper precludes a discussion of this side of the subject.

Brief reference may be made to the analytical evidence relating to the deoxidizing power of zirconium. By means of new methods of analysis developed by the Bureau of Standards for the determination of oxygen and nitrogen in steel, reliable data have been obtained in co-operation with the Bureau on four heats of steel treated with zirconium-silicon (0.15 per cent added Zr) and with ferro-silicon in duplicate ladles. The analyses show that the zirconium treatment eliminated from 12 to 84 per cent of the total oxygen present in the steel (including oxygen as

FeO, MnO, SiO_2, ZrO_2 and silicates), the average being 54 per cent. Or, expressed in another manner, the zirconium-treated steels showed a reduction in oxygen content of 54 per cent as compared with the steels treated with ordinary ferro-silicon. Analyses on another similar series of 4 heats gave 0.0035 per cent nitride nitrogen for the zirconium-treated steels as compared with 0.0072 per cent for the ferro-silicon-treated steels.

No indication of the occurrence of inclusions of zirconium oxide has been observed in the course of this investigation. All the evidence obtained points to the conclusion that oxidized zirconium forms with silica and oxide of manganese a fusible slag, which quickly rises to the surface of the ladle. Analyses of ladle slags have confirmed this conclusion.

Minute, yellow, cubic crystals of zirconium nitride are generally observed in steels treated with zirconium in excess of approximately 0.10 per cent. They are strictly limited in number and represent that residuum of the nitrogen content of the steel which was fixed by zirconium, but not slagged off prior to solidification. These crystals as such do not exert a harmful effect on the steel; for instance, they were present in their usual amount in the heat-treated steels whose properties are mentioned later in this paper.

Fatigue tests to failure under rotary alternating stress have been made on 23 heats treated in duplicate ladles with zirconium-ferro-silicon (0.04 per cent added Zr) and 50 per cent ferro-silicon. The average effect of 0.04 per cent added zirconium has been an increase in the endurance limit by 1,125 lb. per sq. in. This is particularly significant in view of the recognized detrimental effect of non-metallic inclusions upon endurance limit.

ZIRCONIUM AND SULFUR.

When zirconium is added to steel in excess of approximately 0.15 per cent, this element assumes a new role by chemically combining with sulfur to form an acid-insoluble compound not detected by means of the ordinary evolution method of analysis, and under any given set of operating conditions a linear relation exists between the percentage of sulfur thus fixed and the amount by which the added zirconium exceeds 0.15 per cent. It has been reasonably well established that for basic practice when the zirconium-silicon alloy is added in the ladle, every part by weight of zirconium added in excess of 0.15 per cent fixes 0.10 part by weight of sulfur as an acid-insoluble, zirconium-sulfur compound. This chemical combination proceeds in as quantitative a degree when the steel contains normal sulfur and manganese contents, as it does in those instances where the steel is sufficiently high in sulfur and low in manganese to give rise to an appreciable proportion of iron sulfide. In other words, zirconium has a greater affinity for sulfur than has manganese. The difference here in affinity favorable to zirconium is probably greater than the corresponding difference between manganese and iron.

A 5-ton acid open-hearth heat and a 10-ton basic electric furnace heat may be cited as examples of the influence of zirconium on sulfur as determined by the evolution method. In the former case an addition of 0.27 per cent zirconium as silicon-zirconium lowered the percentage of sulfur from an initial value of 0.040 per cent to a final value of 0.025 per cent; in the latter a 0.22 per cent addition of zirconium diminished the sulfur from 0.020 to 0.009 per cent, leaving 0.15 per cent zirconium in the finished product.

Under favorable conditions the zirconium-sulfur compound may be actually eliminated from the steel by fairly heavy additions of zirconium-silicon alloy. Steels containing 0.08 per cent total sulfur have been reduced by ladle additions to a total sulfur of 0.048 per cent, and a corresponding sulfur content of 0.037 per cent as determined by the evolution method. Actual desulfurization by zirconium is a field more limited and much less important commercially than the field covered by the effect of zirconium on the hot-rolling qualities of high sulfur steels now to be described.

In order to obtain the full beneficial effect upon hot-rolling properties, the zirconium alloy need be added only in amount sufficient to eliminate the iron sulfide constituent responsible for red-shortness. Ingots containing 0.185-0.200 per cent sulfur and only 0.15 per cent manganese have been rolled to plate and sheet free from cracks and seams when the steel had been treated with 0.22 per cent Zr. With steels containing sulfur up to 0.260-0.290 per cent similar results have been obtained by the addition of 0.43 per cent Zr. The untreated ingots of these steels have broken to pieces in every case on their first pass through the rolls.

ZIRCONIUM IN HEAT-TREATED STEELS.

The beneficial effect of small additions of zirconium is strikingly demonstrated in the case of heat-treated, ordinary carbon steels. To illustrate, a heat of 0.70 per cent carbon steel was treated in one ladle with 0.15 per cent zirconium as a zirconium-silicon alloy, and in the other ladle with an equivalent amount of ordinary ferro-silicon. After forging the ingots to one-inch round bars the test data recorded in Table I were obtained on the steels quenched from 825° C. in water and drawn at the temperatures indicated. Standard S. A. E. specification for a much used nickel-chromium steel (2.75 to 3.25 per cent Ni; 0.60 to 0.95 per cent Cr) are also tabulated for the purpose of comparison.

TABLE I.

	0.70 per cent C 0.15 per cent Zr	0.70 per cent C without Zr.	S. A. E. 3450 Ni-Cr
Drawing Temperature	375° C.	375° C.	....
Per cent Elongation	8.3	5.2	....
Per cent Reduction of Area	23.3	6.6	....
Yield Point	185,952	128.125	....
Ultimate Strength	227,203	197,800	....
Izod Number	7.5	7.5	....
Brinnell Hardness	414	433	....
Drawing Temperature	412° C.	412° C.	427° C.
Per cent Elongation	12.7	7.5	12.5
Per cent Reduction of Area	45.8	22.9	51.0
Yield Point	172,620	180.180	175,000
Ultimate Strength	198,828	207,144	200,000
Izod Number	14.8	10.5	....
Brinnell Hardness	407	418	....

It may be observed from Table I that ordinary carbon steels in which a small percentage of zirconium has been incorporated may be made to possess by suitable heat-treatment physical characteristics approaching those of the highest grade, heat-treated alloy steels.

Additional experimentation has demonstrated that the properties of a number of the well-known alloy steels may be improved through the use of zirconium, and also that by zirconium treatment it is sometimes possible to use advantageously the ordinary alloying elements in less than normal proportions.

The author does not consider as relevant matter for this paper a discussion of the commercial aspects of zirconium in the manufacture of steel, nor does he wish to engage in concrete prognostications. Therefore it must suffice here to state that several steel companies to whom zirconium alloys were introduced have taken advantage regularly during the past two or three years of the excellent scavenging properties of zirconium. The effects of zirconium on sulfur and in heat-treated steels have been drawn to the attention of a few steel manufacturers only within a comparatively recent period.

However, there appears to be reasonable justification for the optimistic comment in conclusion, that in consideration of the specific effects herein mentioned and the experimental intimation of other effects now awaiting recognition, zirconium will probably contribute its fair share toward the progress of civilization through assistance to the steel and other metal industries.

The author acknowledges the co-operation of his associates, Alexander L. Feild, J. H. Critchett, and J. A. Holladay. Mr. Feild has contributed many valuable suggestions, and he has been throughout in immediate charge of the experimental steel manufacture and laboratory testing. Mr. Critchett, by way of suggestion, has rendered much assistance, especially in connection with the manufacture of zirconium alloys; and Mr. Holladay deserves much credit for original work on the quantitative determination of zirconium in ores and steels, and for his supervision of the analytical work involved in this investigation.

DISCUSSION.

E. F. CONE[1]: I can not refrain from saying that I think this Society is unusually fortunate in hearing what seems to me to be an epoch-making presentation of a subject that is, particularly in the future, going to be extremely important, especially with reference to the question of sulfur in rolling, and other points of equal importance.

H. W. GILLETT[2]: Have you data on the ductile properties on test pieces taken transversely instead of longitudinally? The

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[1] Assoc. Editor, Iron Age, New York.

[2] U. S. Bureau of Mines, Ithaca, N. Y.

difference in ductility really ought to show up more strikingly in this.

F. M. Becket: These particular tests did not involve transverse sections. In other work, however, transverse testing has brought out directly the point you mention, and the effect of zirconium on the transverse properties has been rather marked in improvement.

H. W. Gillett: That seems to indicate a cleaner steel when the transverse properties are good.

E. F. Cone: What is the composition of these silicon-zirconium alloys you use?

F. M. Becket: The composition of the alloys used both commercially and in this experimental work varies considerably, according to just what was attempted—the class of steel it was desired to produce.

Naturally, with a silicon-zirconium alloy, you are limited by the silicon content desired in the finished product. In cases of small additions of zirconium, it has been used pretty largely as an alloy containing approximately 10 per cent zirconium and 40 to 75 per cent silicon. When it has been desired to introduce considerable zirconium in relation to the proportion of silicon introduced, an alloy of 35 to 38 per cent of zirconium and 50 to 55 per cent silicon has been employed.

H. W. Gillett: At still higher temperatures is there the same improvement in ductility?

F. M. Becket: Up to the moment, the improvement at higher drawing temperatures has not been so marked. It follows fairly well the characteristics of your nickel-chrome and other alloy steels, but I do not think the effect is so forcibly brought out as at temperatures referred to here.

A paper presented at the Forty-third General Meeting of the American Electrochemical Society held in New York City, May 5, 1923, Dr. F. M. Becket in the Chair.

INHERENT EFFECT OF ALLOYING ELEMENTS IN STEEL.[1]

By B. D. SAKLATWALLA.[2]

ABSTRACT.

The importance of the effect of alloying elements on the purely physical changes occurring among the constituents of steel is brought out. Stress is laid on the study of the physical conditions and their alterations by alloying elements, during the period of solidification. Attention is drawn to the importance of the effect of alloying elements on surface tension of the solidifying constituents. The idea is expressed of the possibility of coordination and equivalence among alloying elements based on the periodic system, especially referring to atomic volume.

Steel at the ordinary temperature is a heterogeneous conglomerate of various crystalline constituents cemented together by the intervention, between the crystal faces, of a medium existing in an indefinitely known physical state. The composition, physical structure, and relative proportions of these constituents are governed not only by their chemistry, but also by the thermal life-history of the metal. The different phases are in the main made up of a metallic (ferritic) and a carbide (cementitic) constituent. Owing to this heterogeneity, it is apparent that the physical forces, not only those at play in the individual components, but also those existing between the phases, will be of greater importance, from an engineering standpoint, than the chemical composition. Undoubtedly through change in the chemical constitution of the components, as a means to an end, the physical changes are brought about.

If, thus, to the ordinary constituents, consisting of metallic

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[1] Manuscript received January 30, 1923.

[2] Gen. Supt. Vanadium Corporation of America, Bridgeville, Penna.

iron and an iron carbide, other elements are added, changes in the physical relations of these constituents will take place. The influences exerted by these elements constitute the metallurgy of alloy steels. The purpose of this paper is to survey such influences on the physical relations of the constituents, and to direct attention to their study from a physico-chemical standpoint, devoting special attention to the period immediately preceding solidification of the steel, an interval in its life-history hitherto rather neglected.

The remarkable properties conferred by carbon upon iron, making it steel, are due to the physico-chemical interactions between iron carbide and iron. A wide range of physical properties suitable for particular engineering problems are obtainable from the same chemical composition of the metal by merely varying the physical heat treatment. A plain carbon steel can be made exceedingly brittle and glass hard by quenching in cold water from a high temperature, or made ductile and malleable by allowing it to cool gradually from the same temperature. The discovery that additions of other metallic elements influence these changes and produce different results has been more or less of an accidental nature, and the development of alloy steel metallurgy has been more or less empirical.

The constantly increasing number of alloy steels brought out in commerce makes it opportune to establish some scientific basis for the relative influence of the several elements depending on some equivalence in physical properties among them. Undoubtedly some such equivalence of the elements exists, as several chemically different alloys can be made to produce steels of more or less similar physical properties under a divergence of heat-treatment. In order to investigate systematically the influence of these elements on the properties of the steel components, it seems logical to start such study at a period prior to the solidification of the metal. The physico-chemical activity of the constituents, and the change suffered by the addition of alloying elements, will be more pronounced, and less influenced by extraneous physical conditions, in the liquid, or during the solidifying, rather than in the final solid state. It will not be an exaggeration to assert that such a study of the inherent influence of alloying elements has been greatly neglected.

The splendid work of Bakhuis Roozeboom, Willard Gibbs, and others, has given us wonderful insight into the phenomena of solidification from the standpoint of thermo-dynamics and chemical constitution. We have applied these principles to the study of steels, and have been able to chart the solidifying phenomena and establish thermal analysis. We are thus in position to picture the constitution of the components in steel and further verify our picture by the aid of the microscope. It does not appear sufficient, however, to know the presence of these constituents and their chemical nature, without being able to correlate scientifically their chemical composition to their physical properties, and the changes occurring during their solidification to the engineering properties of the solidified steel.

The inherent physical effects of chemical elements undoubtedly start in the liquid stage, and, as the physical properties of the liquid from which crystallization takes place determine to a great extent the properties of the crystallized solid, the influence of the alloying elements should be studied in relation to the physical changes occurring prior to or during solidification. While undoubtedly, by the proper thermal treatment, much can be achieved in solid steel, yet it will be right to assert that the inherent characteristics of the steel are defined up to solidification in the ingot stage, and that all later thermal manipulations are of secondary importance.

Solidification in a metallic alloy such as steel occurs selectively during an interval, the crystal growth starting from several nuclei in the melt. According to Quincke, a separation of the melt in two liquid phases takes place, the one in very much smaller quantity, the "oily" phase, forming cell walls for the other, the whole forming a "foam structure" with several points or nuclei for crystal growth. The application of X-ray analysis to crystal structure has shown us that the atoms of the crystals are arranged in definite characteristic space lattices in contra distinction to an indefinite arrangement in a liquid.

Among the immeasurably large number of atoms of the liquid melt there will be some which will chance to have an arrangement corresponding to the space lattice arrangement of the solid crystals, or closely approaching it. We can readily see that such atoms will selectively assume the solid state ahead of the others, and hence act as nuclei for crystal growth. Solidification from these nuclei will proceed, at the same time continuously diminishing the quantity of the molten mother magma, until the amount of liquid, or the spaces left between the grown crystals, will be so small as not to allow further crystallization. This residual material will therefore fill up the capillary interstices between the crystals forming the so-called "intercrystalline cement medium."

As to the exact nature of this medium there is considerable uncertainty. On account of it not following the crystallization of the first successive solidifying part of the melt, it has been commonly called "amorphous." Recent observations with the X-ray spectograph on the amorphous metals would lead us to assume the presence of extremely fine crystal bodies combined with colloids in this "intercrystalline medium." Its remarkable properties can be explained more satisfactorily on this assumption than on that of it being "amorphous." Owing to the importance of this medium from an engineering standpoint, it deserves further close study from the standpoint of colloid phenomena and X-ray analysis.

The crystallization from nuclei and the growth of individual crystals will depend on the chemical composition of the melt, its degree of under-cooling, heat conductivity and diffusion capability of the resulting crystals, etc. In these several factors, the presence of other alloying elements in the melt will exert a great influence on the progress of crystallization. For instance, slight impurities in the melt have been found to check the velocity of crystallization. The impurity adsorbs on the surface of the growing crystal, thus checking the velocity of its growth. If the adsorption on the different faces of the crystal is of a different degree, the crystallization velocity will be different in different directions, and consequently the solidified crystal can be altered completely, for instance, from a polygonal to a dendritic form. Hence we can readily see that the presence of a small amount of another element in liquid steel can materially influence the size and shape of the primary crystals and alter the structure in the solidified steel. We are all aware of the importance of the primary ingot structure in engineering practice.

Another property of growing crystals is that they eject any impurities to the surface of the crystal. The presence of another element may alter the solubility of such impurity in the crystal and consequently influence the degree of its ejection. This ejection brings such impurities present, not only to the surface of the crystal, but into the "intercrystalline cementing medium." Thus, the presence of another alloying element may appreciably alter the amount of such impurity in this medium, and hence influence in a marked manner, in the finished steel, those physical properties which are a function of the "intercrystalline medium," such as elastic and endurance limits.

Another influence of the ejection of foreign elements by growing crystals can be seen in the case of non-corrosive steel alloys. It appears remarkable that the non-corrosiveness is brought about when a definite sharply recognized percentage of the alloying element is present. For example, 10 to 14 per cent chrome steel may be cited. This phenomenon is probably due to the fact that the growing crystal is capable of keeping in solution a certain percentage of the element, and starts ejecting it to its surface after this saturation is reached. The surface of the crystal can thus have a high percentage of the element requisite to give it the necessary protection against corrosion.

Also in connection with other physical properties we are aware that the percentage of the alloying element has to be beyond a certain range. As examples may be cited 3.5 per cent nickel steel and 12 per cent manganese steel. The influences of these percentages can probably be similarly explained on the basis of ejection of these elements to the surface by the growing crystals, thus altering their surface properties of adhesion, etc., also introducing a necessary amount into the "intercrystalline cement," altering its properties. From this standpoint it is also apparent why the presence of non-metallics in the fluid steel exerts such dastardly pernicious effect on the physical properties of the solidified metal. They not only influence the process of crystallization, but through ejection get disseminated in the vital constituents of the steel.

Whether we agree with Quincke on the separation of two liquid phases prior to solidification, or believe in crystallization growing from the nuclei only, it is easy to see that the surface tension, with its dependent properties, of the molten magma will be of extremely great importance. Considerable work has been done on measurements of surface tension of liquid metals by several different methods. It has also been assumed, since the property of surface tension of a liquid depends so intimately on the cohesion of the molecules, and since the properties of liquids and solids show signs of continuity in the two phases, that some relation exists between the surface tension of the fluid metal and cohesion and tenacity in the solidified state.

Also in studying liquids definite relations of other physical properties to surface tension have been established. As such properties of the liquids may be mentioned: molecular volume, compressibility, coefficient of thermal expansion, vapor pressure and solubility. Transferring these correlation of properties to the solid state, we find the important relation of surface tension to the factors which we generally term "hardness." Also we are aware from experimental data that "hardness" more than any other physical property forms a criterion for the endurance limit. Hence we see the importance of a study of the surface tension qualifications of a metal in the liquid state, and the influence of foreign elements on the surface tension in order to arrive at engineering merits after solidification.

It is easy to understand that a property, so inherently a function of the molecule itself as surface tension, should be very sensitive to the presence of a foreign element molecule. Molecular forces of cohesion naturally act with greater energy between two unlike than like molecules. Consequently the presence of a foreign molecule will increase the cohesive forces. This increase can be of such magnitude as to constitute chemical affinity, and bring about a chemical combination of the metallic elements, forming inter-metallic compounds. It can be of lesser intensity, constituting physical action only, bringing about an inter-atomic rearrangement with a decrease of the total volume, increasing hardness.

It is our practical experience that the hardness of a metal is generally increased by the addition of another metal to it. Also the properties and nature of solid solutions find an explanation in the intermolecular cohesive forces dependent on surface tension. Further, the modern ideas of allotropy seem to be finding explanation in the different cohesive forces in the atoms causing the presence of physically different but chemically identical matter, the differing atoms being capable of interaction on one another. If we assume such explanation for the critical points in iron, we can readily understand how the presence of foreign molecules will change cohesive forces, and exert an influence on these points, which, in turn, will alter the reactions depending on these points, such as thermal reactions during heat treatment. Herein we can find an explanation of the great susceptibility of alloy steels for thermal treatment.

Another influence, important from a practical standpoint, which alloying elements can exert is their influence on the non-metallic impurities in steel. The viscosity and surface tension of the melt can be altered by the alloying elements to allow a better mechanical separation, or the diffusion capability of the melt can be influenced so as to hinder or accelerate segregation of the non-metallics. It is also probable that slight additions of elements can greatly influence the colloidal properties of the non-metallics, inasmuch as their presence can bring about a flocculation or dispersion of the impurities, rendering their effect less harmful.

In the above considerations we have enumerated the effects brought about by the presence of alloying elements from a physical standpoint, without entering into any considerations of a purely chemical nature. In the introductory remarks we have hinted at chemical equivalence of the alloying elements. Undoubtedly the principle of periodicity among elements as initiated by Medeleeff, and expounded by Lothar Meyer, Crookes and others, which has given us such wonderful insight into the workings of pure chemistry, can be applied, with modifications in light of our newer knowledge of atomic structure, to metallurgy.

If the elements are arranged as a function of atomic weight to atomic volume, or of atomic number to atomic volume, they form a series of connected curves, each one representing a group of elements and consisting of an ascending and descending branch. The properties of the elements so arranged seem to bear marked relation to their neighbors on the same curve. For instance, the melting points, hardness, ductility and brittleness, electronic properties, surface tension, seem to be coordinated by these curves. It appears from this that the atomic volume, as an inherent characteristic of the atom, more than any other property is of paramount importance. It undoubtedly is the criterion of the physical qualifications of material.

In light of our present knowledge of the structure of the atom we can see that the atomic volume will be made up, not only of the masses of the electronic constituents, but also the intra-electronic spaces and the intra-atomic spaces. The action between atoms is known to be dependent on their relative arrangements in space lattices, and as these are brought about by forces acting over intra-atomic spaces we can readily see why the atomic volume should be a criterion of these changes. In this arrangement, according to atomic volume, it is remarkable that the steel alloying elements group themselves close together. Attempts at generalization among these elements have been made, such as the theory put forward by Osmond that elements with greater atomic volumes than that of iron tend to raise and those with atomic volumes less than that of iron tend to lower the transformation points, Ar_3, Ar_2, and Ar_1. Also the elements producing marked effects in steel possess high melting points, a characteristic also dependent on atomic volume.

In practical application of these considerations extreme caution should be used, as the formation and presence of definitely formed chemical molecules in place of the individual atoms introduce a new phase in the chemico-physical equilibrium. In such cases we are confronted not with atomic but with molecular volumes, and the effect exerted by the addition of the element is that of the compound formed and not the element itself.

In the absence of definite theoretical knowledge from a physico-chemical standpoint, we are obliged to judge the merits of alloying elements from the results achieved by them. Undoubtedly the use of alloying elements has wonderfully advanced our engineering practice in steel construction. The role of these elements has sometimes been minimized with the argument that their presence only retards or accelerates the thermal changes bringing about refinement of structure. It is not beyond the pale of possibility that similar refinement can be brought about by other and perhaps purely physical means. Until such time, however, we can not get away from the fact that alloying elements in steel have served indirectly as a means to an end to bring about these physical conditions. Have they not then fully and justifiably played the part credited to them?

As to the merits of the different elements it appears that each one has a definite role assigned to it to bring out more pronouncedly than the rest, certain definite physical characteristics in the steel. The sole criterion of the accomplishment of these characteristics remains today, service. Let us hope that more scientific study of the role of alloying elements in steel will not only give us insight into the workings of the alloying elements, but help to bring out newer types and compositions of steels, thus advancing not only the art of metallurgy, but the hopes and aspirations of our rapidly striding civilization.

A paper presented at the Forty-third General Meeting of the American Electrochemical Society held in New York City, May 3, 1923, G. B. Hogaboom in the Chair.

NOTES ON THE METALLURGY OF LEAD VANADATES.[1]

By WILL BAUGHMAN.[2]

LEAD VANADATE ORES OF THE SOUTHWESTERN UNITED STATES.

Vanadium is widely distributed throughout the arid regions of California, Arizona, New Mexico and Nevada. The principal minerals are vanadinite, descloizite and cupro-descloizite. Minor amounts of psittacinite, volborthite, eosite, endlichite, calcio-volborthite and vanadiolite are also found. These minerals are commonly associated with cerrusite, wulfenite, pyromorphite, stolzite and crocoite.

The writer has compiled a list of over 400 occurrences of vanadium in the four southwestern States. There are 343 in Arizona, 28 in New Mexico, 25 in California and 19 in Nevada. All but 8 are occurrences of lead vanadate and similar minerals. Of the 64 deposits that show commercial possibilities, 43 occur in shattered zones at or near the contact of limestone and either rhyolite, basalt, diorite or diabase. One of the largest deposits consists of lenticular masses up to 40 ft. wide, 5 ft. thick and 100 feet long (12.2 x 1.5 x 30.4 m.). The strike of these ore lenses is almost at right angles to that of intruding dikes of diabase and basalt.

In all the lead vanadate deposits, the minerals are limited to the secondary zone only, and as a rule these secondary zones are rather shallow. Only twelve of the deposits extend beyond a depth of 250 ft. (76 m.). In all cases no vanadium is found below water level. In the old Exchequer mine water was not encountered till a depth of 900 ft. (274 m.) had been reached, and then within 50 ft. (15.2 m.) the cupro-descloizite and vanadinite that had persisted, in large, well-defined lodes, from the sur-

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[1] Manuscript received January 27, 1923.

[2] Consulting Electro-Metallurgist, Los Angeles, Calif.

face, disappeared altogether and were replaced by galena, chalcopyrite, sphalerite and pyrites.

A. Ditte[3] attributes the formation of the various vanadates to percolating vanadiferous waters acting on other compounds, principally those of lead. Arthur L. Flagg and the writer have determined that the igneous rocks, associated with the large majority of the lead vanadate deposits, contain from 0.04 to 0.11 per cent of vanadium trioxide and up to five per cent of sodium oxide. It is easy to suppose that such rocks could readily become a source of sodium vanadate solutions. And as a proof of this supposition, great enrichment is generally found at those places where such infiltering waters would have met ascending mineralizing solutions or previously formed bodies of cerrusite and allied minerals.

Arthur L. Flagg, in his examination of the U. S. Vanadium Company's deposits, found an unknown black mineral, in the diabase, that contains a large percentage of vanadium. Work is still being done on this mineral to determine its characteristics. At present it appears to be ilmenite with part or all of the titanium oxide replaced by vanadium trioxide.

CONCENTRATION OF LEAD VANADATE ORES.

The concentration of lead vanadate ores is limited to gravity methods. Some attempts have been made, on an experimental scale, to use oil flotation on sulfadized minerals. Unless heat, pressure or a large excess of sodium sulfide is employed one, more or all, it is very hard to sulfadize any large amount of the lead vanadates. In fact one method of separation of wulfenite from vanadinite, both of which have substantially the same specific gravity, is to sulfadize and float the lead molybdate and leave the lead vanadates in the residue.

At S. G. Musser's 300 tons per day flotation plant, where wulfenite was being concentrated, the ratio of molybdenum oxide in the heads was three to one. But the ratio in the concentrates was twenty-five of molybdenum trioxide to one of vanadium pentoxide. The ore contained some lead tungstate, stolzite, which sulfadized readily. The concentrates often contained two per cent of tungsten trioxide.

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[3] Compt. Rend. 138, 1303.

The lead vanadate minerals are all non-conductors and cannot be separated by electrostatic methods.

The lead vanadate minerals have specific gravities ranging from 6.0 to 7.0 and the majority of the gangue minerals have specific gravities of only half that. It would seem that such ores would be amenable to gravity concentration, and several have attempted to use wet and dry gravity methods of concentration. Little success has been had with these methods, because of the great tendency of the lead vanadate to form slimes during the crushing and grinding. Often, too, the crystals are so small as to be almost microscopic, but even the large specimen crystals will "slime" readily. All the lead vanadate minerals are very brittle.

A common mistake has been to employ ball mills for pulverizing of lead vanadate ores. Six different mills using this method of pulverizing have proved failures. None has made a recovery of more than 50 per cent of the vanadium, when making concentrates containing 6 per cent or over of vanadium pentoxide. Many reports, made on some laboratory experiment, have stated differently, but none has made good in practice. R. L. Grider, at the Vanadium Mines Corporation's[4] deposits in New Mexico, used rolls and with careful classification was able to recover 69 per cent of the vanadium in a rather low-grade concentrate. The Dragon Mining Company was unable to raise the grade of concentrates beyond 4 per cent in vanadium pentoxide, nor to make a recovery in excess of 43 per cent from ball feed. Changing to rolls raised their extraction to nearly 60 per cent and the grade of the concentrates to 5.5 per cent of vanadium oxide.

The Black Buttes ore contains vanadinite, wulfenite, and cerrusite as valuable minerals, with minor amounts of galena, stolzite and crocoite. The gangue is primarily calcite and quartz with barytes, fluorspar and iron and manganese minerals. The vanadinite crystals are very large, often being 12 mm. (0.5 in.) long and 3 mm. (⅛ in.) in diameter. The writer made tests on a one-ton scale with this ore. Ball mills, highspeed rolls, and a centrifugal impact pulverizer were used for crushing and grinding. The classified pulp was then fed to an Isbell table, to a Senn pan motion concentrator and a Plumb pneumatic jig. The results are given in Table I.

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[4] Min. Sci. Press, **113**, 389-391.

The high recoveries made by the centrifugal impact mill are due to the fact that it pulverized the ore without the formation of a large amount of slimes. This mill works on the principle of the Varpart disintegrator and schuledenmuhle, briefly described in Richards' Ore Dressing. The mill has no real field for pulverizing, except where it is desired to reduce slime losses, as in this case. In this field it is supreme.

TABLE I.

Efficiency of Grinding Mills on Vanadinite Ores.

Mill	Mesh	Percentage Recovered on		
		Isbell Table	Senn Table	Plumb Jig
Herman Ball	40	41	45	..
Hardinge Ball	40	40	47	38
Rolls, H. S.	30	62	68	59
Marks Mill Centrif. impact	40	83	89	80

The Marks mill resembles a centrifugal separator in general construction details. In place of a basket a table with thrower blades or guides is suspended on the shaft. The table or disc revolves at 2,000 r. p. m. The ore is fed to the center and rapidly passes to the edge whence it is thrown 7.6 cm. (3 in.), at a speed of 4.8 km. (3 mi.) per min., against a heavy, sectional cast iron shoe. The impact against this shoe shatters the ore along natural cleavage lines and lines of crystallization. The shattered rock immediately falls to the screening apparatus, the oversize being returned for further pulverizing. Primary feed may be in 5 cm. (2 in.) cubes. The shoes are kept clean by the blast of air caused by the whirling table, and, as the ore is hit but one blow before being screened, a close sizing of the product can be obtained.

The disadvantages of the mill are that "rusty" gold is not given the scouring or cleaning rub or twist that ball mills or stamps give. It is this same rub or twist that produces slimes. The wear on the shoes is also rather high. The obvious objection "that it will fly to pieces" as yet has had no grounds. Over 40 of these mills have been installed and none has had that trouble so far. Several have been in steady use for 10 years. A mill costs about $2,000, requires only 10 horsepower to run it with its accessory feeder, screen and elevator, and is capable of pulverizing 30 tons of hard quartz, per day of 24 hours, to 40 mesh.

One promising field of investigation was not followed out according to the writer's wishes; that is the adjustment of the speed of the table so as to shatter the more brittle vanadinite to a size permitting its passage through a certain mesh screen that would retain the less brittle gangue minerals. The manufacturers of the mill have conducted extensive experiments in which they separated galena and sphalerite in this manner. They also have separated, commercially, strontianite and calcite, recovering over 90 per cent of the strontium in a product 87 per cent pure.

PRODUCTION OF VANADIUM FROM THE BLACK BUTTES ORES.

The metallurgy of the lead vanadate ores of the southwest is more of an economic problem than a technical one. There is a large amount of low-grade vanadium ore available, most of which also carries valuable amounts of gold, silver and base elements. In fact, one mine has been shipping vanadium concentrates to the smelters for the recovery of gold, silver, copper, and lead, as they could find no financially responsible buyer who would pay for the vanadium and the precious and base elements as well.

The Flett-Baughman Company became interested in the Black Buttes, and first worked out the concentration problem. These concentrates averaged 7.14 per cent vanadium pentoxide, 6.0 per cent molybdic oxide, 52.4 per cent metallic lead, 2.2 per cent combined chromium and tungsten oxides, and $5.00 gold and 42 oz. silver per ton. Only small traces of phosphorus and arsenic were found.

In spite of the fact, that at that time, there was considerable activity in rare elements, and a great many rare element extraction plants were being operated, constructed or projected, the writer was uable to find any kind of a reasonable market for the concentrates.

The following described experiments were conducted to ascertain which was the best and most economical method of extracting the various valuable elements from the concentrates. The investigation also took into consideration the fact that the ferro-vanadium market is closely controlled through long term contracts, by three or four corporations. This rendered it imperative that some new product be developed. At first it was planned to produce C. P. vanadic oxide, which was quoted at over $10.00 per lb. in the trade journals. However, the market for this product is very limited. The writer's investigations indicate an annual consumption of not over 500 lb.

The writer then started a series of investigations in the production of pure metallic vanadium, although, in view of his present knowledge of the rare element business, he can not at present see where he expected any large market for the pure metal. For additions to steel the standard 30 to 40 per cent ferro-vanadium is supreme. Iron has a melting point of 1530° C. and vanadium 1720° C. while the alloy (30 to 40 per cent) has a melting point of about 1440° C. It will be seen that the addition of pure vanadium metal to steel would only raise the melting point and offer no compensating advantages.

The writer is not the only one who has made this mistake. To his personal knowledge over twenty companies have been formed to produce vanadium oxide on a large scale, all of which expected to sell all their product at the quoted prices for the C. P. oxide. One corporation spent $700,000 and another $250,000 in the same vain attempts. None of these companies planned to use a process that would produce an average product better than 85 per cent pure, and some even expected to sell the vanadium oxide in iron vanadate at the quoted figures. The preparation of 99 per cent pure vanadium oxide is not the easy matter that it would appear to be; in fact it is a very difficult chemical operation.

Hereafter the writer describes the results of his investigations in

1. Chloride volatilization applied to Buttes concentrates.
2. Baughman process for same ores.
3. Chloridizing roasting of the U. S. Vanadium Co's ores.
4. Sodium sulfide leaching of the "Signal" ores.
5. Production of metallic vanadium.

CHLORIDE VOLATILIZATION OF THE BLACK BUTTES ORES.

By using a centrifugal impact pulverizer and gravity concentration, the Black Buttes ore yielded a high grade concentration, and a high extraction was also made. There was ample water not only for mill purposes but also for power, so that the logical thing was to concentrate and then determine a suitable method of handling the concentrates.

The Flett-Baughman Co. had been experimenting for some time on complex lead-copper-zinc ores, and among other plans had done a great deal of work in applying chlorine direct to the ores. The idea of chloride volatilization was attractive. Splendid results could be easily obtained on a laboratory scale, so that 20-lb. scale tests were conducted as described below:

A rotating silica tube 5 ft. long and 13 in. in diameter (1.5 m. x 0.32 m.) and heated by an electrical resistance coil was used. The volatilized elements were caught in a stoneware baffle tower 15 ft. (4.5 m.) high and 6 in. (15 cm.) in diameter. Temperatures from 200 to 800° C. were employed. The majority were run at 400.° The gases from the tower were dried by passing over sulfuric acid and through calcium chloride, and returned to the volatilization tube.

Sodium Chloride. Temperatures of 200 to 600° C. were used. Percentages of salt between 20 and 40. Time, up to 24 hours. The best extraction was 38.5 per cent of the vanadium volatilized, and 36 per cent converted to soluble sodium vanadate. This was done at 600° with 25 per cent salt and required 24 hours.

Magnesium Chloride. Hydrated magnesium chloride is decomposed, by heating, to magnesium oxide and hydrogen chloride,

$$MgCl_2 + H_2O = MgO + 2HCl$$

Some magnesium oxychloride is also formed, which is in turn decomposed by oxygen in the air into magnesium oxide and chlorine,

$$2MgO + 2HCl = MgO \,.\, MgCl_2 + H_2O$$
$$MgO \,.\, MgCl_2 + O = 2MgO + Cl_2$$

Thus a supply of chlorine and hydrogen chloride are generated in the tube.

The best extraction obtained was 43 per cent of the vanadium volatilized and 36 per cent of the molybdenum, while 27 per cent of the vanadium and 33 per cent of the molybdenum formed magnesium vanadates and molybdates. These salts are soluble in hot water and re-precipitated on cooling; but this gives two totally different classes of product to treat further and refine.

Calcium chloride. Two runs only were made with this reagent. Some calcium molybdate and vanadate were formed, and some oxychlorides volatilized, but the results were so small that analyses to determine percentages recovered were not made.

In all three of the above series of experiments a gentle stream of hot dry air was passed through the tube and absorption tower.

Ferric Chloride. This is a very expensive reagent to use for the purpose of chloride volatilization. Both ferric chloride and ferric sulfate with magnesium and calcium chloride to form ferric chloride, by interaction, were tried. These are known as the Gin methods. Ferric sulfate and calcium or magnesium chloride interact thus, to produce calcium sulfate and ferric chloride.

$$Fe_2(SO_4)_3 + 3CaCl_2 = 3CaSO_4 + 2FeCl_3$$

Extractions in excess of 90 per cent of the molybdenum and vanadium were obtained. Some magnesium or calcium vanadates and molybdates were formed. The high cost of the reagents precludes the commercial use of this method at present. Considerable lead chloride also volatilized, and by interaction in the tower reproduced lead vanadates and molydates.

Carbon Tetrachloride. One run was made with this reagent. An extraction of 98.5 per cent of the vanadium and 98 per cent of the molybdenum was obtained. A temperature of 400 to 450° C. was employed. Seven hours time was required. The cost of this chemical makes the process prohibitive; also a large excess, over that theoretically required, must be used.

Chlorine and Hydrogen Chloride Gases. Chlorine alone does not give a good extraction. It is necessary partially to reduce the ore, preferably by reducing gases, before applying the chlorine. Hydrogen chloride alone gives a splendid extraction of the molybdenum, but does not give as satisfactory results for vanadium. The method used was as follows:

The concentrates were first heated for 2 hr. at 400° C. in an atmosphere of natural gas. Equal portions of chlorine and hydrogen chloride gas were then passed through the tube for 4 hr. longer. The reactions are rather complex but may be expressed as:

$$
\begin{aligned}
xV_2O_5 + CyHz &= xV_2O_4 + pCO + qCO_2 + rH_2O \\
V_2O_4 + 3Cl_2 &= 2VOCl_3 + O_2 \\
V_2O_5 + 6HCl &= 2VOCl_3 + 3H_2O \\
MoO_3 + 2HCl &= MoO_2Cl_2 + H_2O \\
WO_3 + 2HCl &= WO_2Cl_2 + H_2O \\
CrO_3 + 2HCl &= CrO_2Cl_2 + H_2O
\end{aligned}
$$

The last four are reversible and on catching the volatilized elements in water in the absorption tower, they are re-converted into their respective oxides and the acid is regenerated. Considerable heat is evolved at the same time.

Some of the molybdenum and tungsten oxides were reduced during the preliminary reduction. These reduced oxides interact with chlorine as follows:

$$
\begin{aligned}
MoO_2 + Cl_2 &= MoO_2Cl_2 \\
WO_2 + Cl_2 &= WO_2Cl_2
\end{aligned}
$$

The large amount of regenerated acid causes the re-solution of a large portion of the precipitated oxides, and in addition to this some very complex rare element compounds are formed, which give all kinds of trouble in later refining steps. The most serious objection was the large amount of gas required to conduct the operation. Most of the silver was also volatilized and formed silver vanadates that made its recovery more expensive. Lead chloride volatilized also, although most of the lead was reduced in the first step to metal and remained in the residue as fine pellets.

From an economic standpoint these experiments were failures. Technically a large percentage of the rare elements were recovered. The best run was at 400° C.; time 2 hr.; reduction, 4 hr. chloridizing volatilization; vanadium recovered 96.5 per cent; molybdenum recovered 98 per cent.

BAUGHMAN'S PROCESS FOR THE TREATMENT OF LEAD VANADATES.

After the failure of the chloride volatilization experiments, the Flett-Baughman Co. initiated some new experiments on the Black

Buttes ore. The method selected was first to smelt the concentrates, producing a vanadiferous slag and a lead bullion containing the gold and silver. This step was analogous to the first steps of Gin's process and to Grider's process.

The concentrates were smelted in an electric furnace of a tilting type. It was constructed along the lines of the Girod tilting resistance furnace described in Bulletin 77 of the Bureau of Mines page 109. In addition to the resistance heating, provision was also made for using it as an arc furnace by placing three 5 in. (12.7 cm.) graphite electrode stubs, well rammed with magnesite and tar in the bottom, and suspending a 3 in. (7.6 cm.) graphite electrode, through a hole in the cover, from the ceiling, by wires, attached to the electrode holder. The electrode was raised and lowered by passing these wires through pulleys to a hand operated winch and drum. The furnace also had a tap hole at the bottom, the use of which will be seen later. The melting chamber was 15 in. (39 cm.) in diameter by 22 in. (54 cm.) high. Alternating current was used to heat the resistors, and direct current from a motor generator set with two generators of 40 to 60 volts each and capable of being connected in either series or parallel supplied the arc current. The generators were each capable of supplying a current of 900 amp. The furnace, however, drew only 500 amp. except during the starting period.

The method of operation was to charge 150 lb. (68 kg.) of concentrates, 15 lb. (6.8 kg.) of pulverized coke and 30 lb. (13.6 kg.) of soda ash, thoroughly mixed, into the furnace and melt the same by the resistance heaters. Two-thirds of the above charge was put in the furnace at the start, and the balance as soon as the first portion was melted.

At the end of 1.5 hr. the lead was tapped from the bottom notch, and as soon as this was completed a pipe was inserted in the notch and quickly luted with fire clay. A blast of air at 20 lb. (9.1 kg.) pressure supplied by a large Crowell blower was then forced through the slag. The slag changes from green to blue in color, when cooled for tests, by plunging slag rod in water. The furnace was then tilted and the molten slag poured into hot water to granulate it and render it more soluble. Up to this point the process is substantially the same as those of Gin and Herrenschmidt.

The solution in which the slag was poured was filtered off and the residue mixed with one fourth its weight of caustic soda. This mass was then roasted at a low temperature, about 300° to 400° C., for 2 hr. It was then digested 2 hr. with the original solution from which it was first filtered. The solution was filtered again and the residue, which contained less than 3 per cent of its original vanadium content, was discarded. To assist in the formation of the metavanadate of soda, peroxide of hydrogen was added at first, later the same results were obtained by using ozone. This ozone was made from oxygen, from the electrolytic cells used in a later step in this process, passed through an ozonater.

A calculated amount of sodium sulfide was also added to the solution while the roasted slag was being digested. This is to sulfadize, thus rendering it insoluble, any zinc or lead that might have remained in the slag. Sodium aluminate, also in calculated amounts, was used to precipitate the phosphorus. The digester was made of half inch sheet steel; it was mechanically agitated and steam heated.

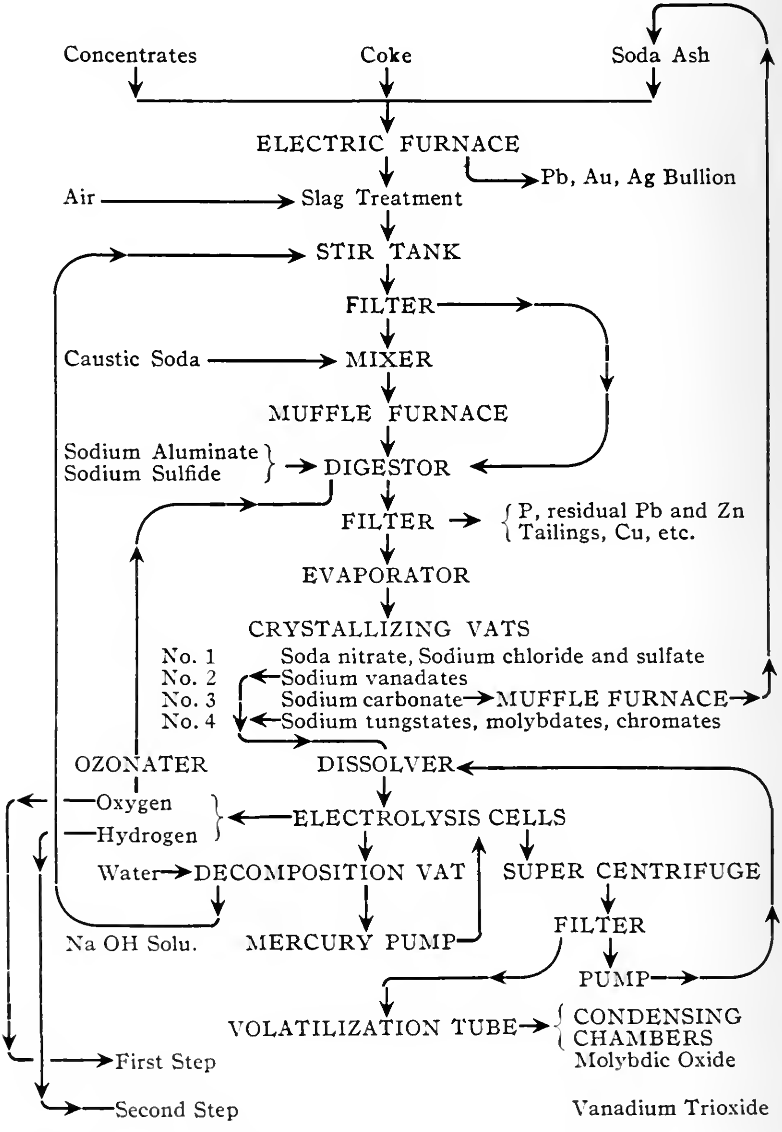
Fractional Crystallization.

After the solutions were filtered from the residue, they contained sodium chloride, vanadate, sulfate, carbonate, molybdate, tungstate, chromate, hydroxide and aluminate. This solution was then evaporated in a triple effect evaporator to 22° Bé., and the sodium sulfate, aluminate and chloride allowed to crystallize out and be removed. The next fraction was removed at 26° Bé. and contains most of the vanadium as the various sodium vanadates. However, this fraction is not pure, as it contains some molybdenum and chromium as complex molybdo-chromo-sodium vanadates. The third crystallization is at 30° Bé. and it contains some sodium vanadate with sodium carbonate. These salts, after calcining, are used for the original flux in smelting the ore. Thus no vanadium is lost in the cycle of the process. The last fraction is obtained at 33° Bé. It yields the sodium molybdates, chromates and tungstates with some vanadium as complex salts. The second and last fractions are mixed together and used in the next step.

Since these experiments, the writer has developed a system

Flow Sheet.

Baughman Process for Treating Complex Lead-Rare Element Ores.



Residue: Metallic Tungsten, Chromium and Titanium oxides and metal of fractional crystallization for such complex mixtures, that yields each salt separately and in pure condition. He has also found the method of preventing the formation of the complex molybdenum-chromium-vanadium compounds with sodium. This system is rather complicated and is too lengthy to describe here.

Electrolysis of Sodium Salts.

The mixed vanadates, chromates, molybdates and tungstates of sodium were then dissolved to a 20° Bé. solution. This was done in a small tank with a mechanical stirrer. From there the solution went to the electrolysis cells, which were similar to the mercury cathode Solvay cells for producing chlorine and caustic soda. The salts are decomposed, the sodium entering the cathode and the rare element oxides remaining in a semi-colloidal form in the electrolyte.

The sodium amalgam was kept in constant circulation between the electrolysis cells and outside decomposition vessels by a mercury pump. The amalgam was decomposed by the action of water in this outside vessel, to mercury and caustic soda; considerable hydrogen was also evolved.

The reactions in the electrolytic cell might be expressed;

$$2NaVO_3 + \text{electricity} = 2Na\ (\text{in Hg.}) + V_2O_5 + O$$

and the decomposition of the amalgam as:

$$Na_yHg_x + zH_2O = x\text{Hg} + y\text{NaOH} + zH_2$$

The regenerated caustic soda was used again in the previous steps of the process.

The electrolyte was also kept in constant circulation. It was passed through a Sharples centrifuge and then filtered. This eliminated serious trouble that had been encountered previously, due to the semi-colloidal condition of the suspended oxides of the rare elements. The filtrate is used to dissolve fresh amounts of the crystallized salts from the previous step of fractional crystallization.

A current of 8 volts was used. The cells required 1,800 amp. Seven were connected in series. The anodes were of platinum gauze, but fused iron oxide would have been as satisfactory.

Arrangements were made for collecting the hydrogen and oxygen evolved, for use in refining the oxides.

The electrolysis of sodium vanadate solutions in diaphragm cells has been proposed by W. F. Bleecker[5] and investigated by S. Fischer.[6] The writer used a mercury cathode cell, because the oxides produced in diaphragm cells always contained impurities from the disintegration of the diaphragms.

Separation of the Oxides.

The filtered oxides were washed and dried and then treated by one of the two following methods:

Electrolytic Method. The mixed oxides were dissolved in a stoneware agitator, by dilute hydrochloric and sulfuric acids. This solution, as near neutral as possible, was again electrolyzed in a mercury cathode cell. The tungsten, molybdenum and chromium passed into the amalgam, the vanadium again separated as the oxide, considerable chlorine was given off and both phosphorus and arsenic, which had been added for purpose of testing, were completely volatilized. Some vanadium remained in solution. The mercury was pumped through a chamois skin amalgam filter instead of into the outside decomposition vessel. Excess mercury was strained and pressed out of the amalgam, which was then retorted. The mixed chromium, molybdenum and tungsten metals remaining in the retort were then ignited to the oxide, (they were highly pyrophoric) and the molybdenum oxide removed from the chromium and tungsten, which was discarded, by volatilization. This is identical with the first step of the other method of separation of the rare element oxides and will be described later.

Volatilization Method. The volatilization tube previously described was used. The separation was conducted in two steps. In the first the molybdenum trioxide was volatilized in a current of oxygen. The oxygen was a by-product of the electrolysis of the rare element sodium compounds. The molybdenum trioxide was completely volatilized in 6 hr. at a temperature of 800° C. Increasing the temperature beyond this point favored the forma-

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[5] Met. and Chem. Eng. 9, 503 (1911).

[6] Trans. Am. Electrochem. Soc. 30, 175 (1916).

tion of molybdo-vanadates, and at 850° only 85 per cent of the molybdenum trioxide was volatilized.

In the second step, hydrogen from the decomposition cell of the electrolysis cells was passed over the mixed oxides of vanadium, tungsten and chromium. At the same time the temperature was raised to 1400° C. The hydrogen gas was preheated as was the oxygen gas used in the previous step. In this step the tungsten and chromium were reduced, the former to metal and the latter to sub-oxide and metal. Titanium was also reduced to the lower oxide. The vanadium pentoxide was reduced to the trioxide and then became volatile. At the end of 18 hr. it was completely volatilized. The tungsten-chromium residue was discarded.

Removal of Phosphorus and Arsenic.

The Black Buttes ore contained no trace of arsenic and very little phosphorus. A large majority of the lead vanadates contain these impurities. From acid solutions arsenic may be completely removed by passing over copper, copper arsenide being formed. Where the solution is further treated by passing over iron, to reduce the vanadium so as to make precipitation easier, the copper dissolved by the excess acid will be re-precipitated. From acid solutions, preferably hydrochloric, the phosphorus can be completely removed by precipitation as zirconium phosphate. This precipitation can be obtained from quite strong acid solutions. Zirconium hydrate (crude) prepared from zirkite is dissolved in hydrochloric acid and used as a precipitant.

From alkaline solutions sodium aluminate, made by dissolving aluminum shot in concentrated caustic soda solution, secures a complete precipitation of the phosphorus and also a little of the arsenic.

From neutral solutions, strontium nitrate, made by dissolving the mineral strontianite in commercial nitric acid, will precipitate all the phosphorus and arsenic, together with most of the tungsten and molybdenum present, but it precipitates very little vanadium.

The electrolysis of any acid solution containing chlorides secures the complete volatilization of the arsenic and most of the phosphorus.

CHLORIDIZING ROASTING AND LEACHING OF LEAD VANADATE ORES.

At several of the vanadium deposits, of the southwestern part of United States, there are valuable amounts of gold and silver in the ores, that are not recovered by concentration, and not infrequently there is so much barytes present that it is impossible to obtain a high grade concentrate. Where such conditions exist and there is a large amount of low grade ore available, chloridizing roasting and leaching is an ideal treatment method.

These experiments were first tried on the Buttes ore, but abandoned when suitable concentration methods were found. Later the process was the subject of an extensive investigation by the U. S. Vanadium Development Company, under the direction of the writer. Later the Consolidated Vanadium Company built a 25 ton per day plant to use the same method, they being cognizant of the U. S. Vanadium Co's experiments.

Chloridizing roasting and leaching has been in successful use in an ever expanding plant at Park City, Utah, at a cost of about $3.00 per ton. The ore treated there contains 6 to 14 oz. silver per ton, $1.00 in gold, a couple of pounds of copper and small amounts of lead and zinc. Recoveries as high as 95 per cent have been made, 85 to 90 per cent being common practice. This process is very simple, is economical on a large scale, and is capable of handling very low grade ores.[7] Briefly described it consists of roasting with admixed fuel in a shaft furnace, and leaching with tower acid, precipitating silver and gold on copper, copper on iron, and later electrolytically recovering the lead.

Roasting.

A mixture of 6 to 9 per cent salt, 1 to 3 per cent coal dust, 1 to 2 per cent manganese dioxide, and 2 to 8 per cent pyrites is thoroughly mixed, moistened with tower acid till the mixture will retain the imprint of the fingers when tightly pressed. This moisture varies from 5 to 10 per cent according to the fineness of the ore.

A deep bed of coals is started in the bottom of the shaft roaster and the roast mix charged to a foot of depth. As soon as the roast shows through 3 ft. (0.9 m.) more of charge is added, and at

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[7] The method is fully described in Trans. Am. Inst. Min. and Met. Engr., 49, 183-197, and has also been the subject of several articles in various mining journals.

the next appearance of the roast 4 ft. (1.2 m.) more, which is about the maximum depth to which the blower can supply air. The bottom of the shaft is all a grate, with a wind box underneath. Air is supplied at about 1 lb. (0.45 kg.) pressure.

Temperature is controlled by rate of blast. It is better to roast too slowly than too fast. Temperature range may be between 600 and 800° C. For the U. S. Vanadium ores 650 to 750° C. was found best. Too high a temperature causes clinkers and melts the salt, forming a thin glaze on the ore particles. However, caked masses are a sign of good roasting. Slimes and fines cake, not clinker, readily at the proper temperatures, and form an easily leached product.

Were a dry charge used, a great deal of the valuable elements would be volatilized, but the moisture is concentrated about a foot ahead of the roasting zone and thus entraps any volatilized elements, so that the only volatilization occurs at the end of the roast when the temperature is lowest. Even then the volatilized elements are caught in the absorption tower, where the barren mill brine is returned in order to catch the acids of the roasting fumes.

The reactions during roasting are very complex. In general the following may be said to occur:

Chlorine is produced by interaction of salt and sulfur trioxide, obtained from the pyrite, at elevated temperatures,

$$2NaCl + 2SO_3 = Na_2SO_4 + SO_2 + Cl_2$$

Chlorine is also obtained from salt, silica and oxygen,

$$2NaCl + SiO_2 + O = Na_2SiO_3 + Cl_2$$

This nascent chlorine acts strongly on metals and sulfides present, and to a lesser degree on oxides,

$$Au + 3Cl = AuCl_3$$
$$Cu_2S + 4Cl + 3O = 2CuCl_2 + SO_3$$

Some metallic chlorides are formed direct,

$$2NaCl + PbSO_4 = PbCl_2 + Na_2SO_4$$

Sulfur dioxide may be converted in part to trioxide by catalysis by silica or peroxidized by iron oxide,

$$2SO_2 + 3O + SiO_2 = 2SO_3 + O_2 + SiO_2 + 22{,}600 \text{ cals.}$$
$$SO_2 + 3Fe_2O_3 = SO_3 + 2Fe_3O_4$$

After reduction of the vanadium from the penta to tetra state it is readily attacked by the chlorine (in the roaster) to form the volatile oxychlorides thus,

$$V_2O_5 + C = V_2O_4 + CO$$
$$V_2O_4 + Cl_2 = 2VO_2Cl$$
$$V_2O_4 + 3Cl_2 = 2VOCl_3 + O_2$$

These are decomposed by the water in the absorption tower, and redissolved by the excess acid,

$$2VO_2Cl + H_2O = V_2O_5 + 2HCl$$
$$2VOCl_3 + 3H_2O = V_2O_5 + 6HCl$$

In the tower chlorine and sulfur dioxide form sulfuric and hydrochloric acids,

$$Cl_2 + SO_2 + 2H_2O = H_2SO_4 + 2HCl$$

Steam and silica interacting with salt form hydrochloric acid in the roaster,

$$2NaCl + SiO_2 + H_2O = Na_2SiO_3 + 2HCl$$

Sulfur trioxide, steam, and salt also form hydrochloric acid in the roaster,

$$2NaCl + SO_3 + H_2O = Na_2SO_4 + 2HCl$$

In turn the sulfuric acid in the brine acts upon the salt, so that the free acid is hydrochloric,

$$H_2SO_4 + 2NaCl = Na_2SO_4 + 2HCl$$

While unable to prove it in every way the writer has strong evidence that salt and vanadium pentoxide form sodium vanadate,

$$2NaCl + V_2O_5 + O = 2NaVO_3 + Cl_2$$
$$6NaCl + V_2O_5 + 3O = 2Na_3VO_4 + 3Cl_2$$

Roasting in reverberatories or mechanical furnaces does not give the results that the Holt shaft roaster does. The slower heating and the much longer cooling is the reason for this. At

Park City, Theodore P. Holt used ore through 0.25 in. (0.64 cm.) mesh, but the writer has determined that the ore should be crushed to 0.0625 in. (1.6 mm.) mesh at least when treating vanadium ores.

The addition of manganese is the result of the writer's investigations. In his work on complex lead-zinc-copper sulfide ores he found that he could convert over 90 per cent of these metals to sulfates during the roast by adding manganese dioxide in the form of pyrolusite to the charge. These complex ores were afterwards leached with dilute sulfuric acid to remove the copper, which was precipitated as cuprous chloride, and the zinc which was precipitated, after purification of the solution, by electrolysis. The lead, gold and silver were dissolved by a strong brine. The precious metals were precipitated on copper and the lead by electrolysis, at the same time regenerating the chlorine in the brine, by which the gold was attacked and made soluble. The difficult step of this process lay in the roasting so as to form a maximum amount of sulfate, without forming insoluble ferrites or excessive oxide. The accidental addition of manganese dioxide gave such wonderful results that the writer tried it in chloridizing roasting also. For vanadium ores it acts as an oxidizer, and assists in releasing a large amount of acid. Many large and small experiments have proved its value.

Lixiviation and Precipitation.

For the U. S. Vanadium Co's ores a pulp ratio of one to five was found best. A strong acid brine with a gravity of 20 to 24° Bé was used. The temperature was to be maintained at 60° C. by the use of steam. The brine was applied in counter current to the ore.

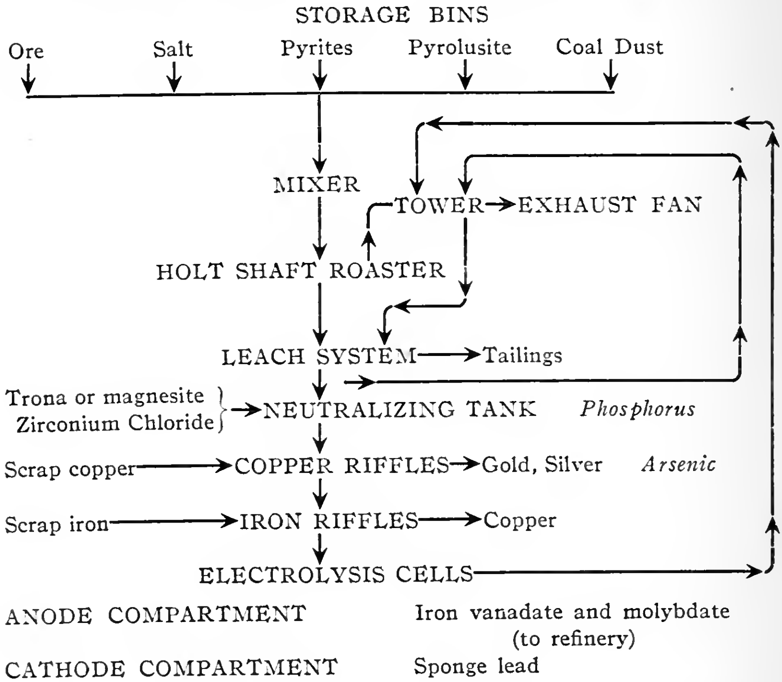
The greenish yellow solution was returned to the tower and leaching vats till it was a strong green in color and contained 10 g./L. of vanadium or over. The acid solution was then partly neutralized and passed over copper riffles to precipitate the gold and silver. This step also removes the arsenic as arsenide of copper.

The solution was next passed over scrap iron and the copper precipitated. At the same time the nascent hydrogen from the action of the excess acid on the iron, and in fact the iron itself, reduced the vanadium from the penta to tetra state and the molybdenum to the molybdous state. The solution became a dark blue.

The next step was the electrolytic recovery of the lead, as sponge lead, at the same time the vanadium was further reduced to the tri-valent state. Insoluble anodes were used for the sponge lead electrolysis at first.

Flow Sheet.

Chloridizing Plant for U. S. Vanadium Development Co.



A mixture of vanadium and molybdenum oxides together with manganese, iron, lime and other elements as hydroxides and carbonates was obtained by using crude trona as a precipitating agent. The writer found later that calcined magnesite was cheaper, gave a higher grade precipitate, and that the precipitate was easier to filter than that from the soda precipitation.

Later on soluble iron anodes were used, in order to lower the power requirements for the precipitation of the lead. We were surprised to find that the vanadium and molydenum were completely precipitated as iron vanadates and molybdates by purely anodic processes. No extra power was required, although a diaphragm to prevent the mixing of the anode products and the sponge lead was necessary.

The mixed vanadates and molybdates are of a much higher grade than any obtained by chemical precipitation. They are also very granular and easily filtered and washed.

A certain amount of the brine should be run to waste on each cycle to prevent the fouling of solution by sulfates. The wash water and the salt added with each roast will in general keep the brine up to standard.

The disadvantages of the process are that it can not be applied to ores containing any large amount of calcium or magnesium, and that for its economic operation plants should have a capacity of at least 50 tons per day.

The Consolidated Vanadium Co. built a 25-ton plant using this process, as worked out by the writer, which was closed for internal and legal reasons shortly after its initial operation. The best run they made gave an extraction of 76 per cent of the vanadium in an ore cotaining only 0.16 per cent vanadium pentoxide. The gold and silver recoveries approximated those of Holt at Park City.

The phosphorus in the ore was eliminated at the time of neutralizing the leach solution. This was done by adding a solution of zirconium chloride, which was prepared by dissolving crude zirconium hydroxide in hydrochloric acid. The zirconium hydroxide may be prepared in any manner from zirkite. The phosphorus is precipitated completely, even from highly acid solutions, as zirconium phosphate.

Chloridizing roasting has been used successfully for many years in Colorado for the treatment of roscoelite.

The precipitation of iron vanadate and molybdate by anodic reaction is analogous to the old Luckow paint processes for preparing lead carbonate and chromate. Warren F. Bleecker has patented[8] certain phases of the precipitation of vanadium by this method.

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[8] U. S. Patent 1,105,469.

The Consolidated Vanadium Co. also developed a soluble anode, which consisted of a wooden basket in which machine shop turnings worth only $6.00 per ton were used. The plates used before had cost $50.00 per ton.

The U. S. Vanadium Co's ores contained an average of $2.00 in gold and 4 oz. silver per ton, 0.57 per cent vanadium oxide and 0.52 per cent molybdic oxide. They have a tremendous amount of this grade of ore. It also contains small amounts of copper, lead, arsenic and phosphorus.

The tests for adaptability of these ores to chloridizing roasting and leaching were concluded on 200-pound scale experiments. Extractions ranging from 72 per cent to 76 per cent of the rare elements, and 90 to 95 per cent of the precious metals, were readily obtained.

Sodium Sulfide Leaching.

The vanadium minerals of the "Signal" ores are primarily cuprodescloizite and vanadinite, with minor amounts of vanadiolite and volborthite. The gangue is principally calcite with fair amounts of barytes and quartz. A typical analysis is: Gold $19.00, silver 6 oz. per ton; copper 2.5 per cent; lead 3.5 per cent; vanadium pentoxide 2.25 per cent; lime 25 per cent; barytes 18 percent; P, As, Ti, Mo, W, none.

The large amount of lime prevents the use of chloridizing roasting. Concentration is seriously interfered with on account of the barytes present; also the gold and silver are not amenable to concentration. Certain economic factors had to be considered in designing a process for these ores. The plant had to be simple in construction and operation. The first cost was to be kept as low as possible. It was also desired that the vanadium be recovered as a readily marketed compound, so that the expense of a refinery and ferro-alloy plant could be dispensed with.

Alan Kissock[9] has successfully employed sodium sulfide for the extraction of molydenum from wulfenite. S. G. Musser also built a plant using this process. Kissock used counter current decantation for treating the ore. Musser used theoretical proportions and applied heat and pressure. The reaction is substantially,

$$PbMoO_4 + Na_2S = PbS + Na_2MoO_4$$

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[9] U. S. Patent 1,403,035.

Both of them pecipitated the molydenum by calcium chloride. This was a by-product of S. G. Musser's plant for treating residual brines from the extraction of salt from sea water.

$$Na_2MoO_4 + CaCl_2 = CaMoO_4 + 2NaCl$$

Alan Kissock[10] has patented the process of using calcium molybdate so produced as a direct addition to steel, the carbon in the bath reducing the oxide, which readily alloys with the metal. Parenthetically, it may be remarked here that calcium vanadate can not be employed in a similar manner. Both Mr. Kissock and his assistants and the writer have repeatedly tried to achieve this end, but have failed in all cases. The writer has used scheelite concentrates ($CaWO_4$) in a like manner for adding tungsten to steel.

Warren F. Bleecker and W. L. Morrison[11] have described experiments in which they added calcium vanadate, with suitable reducing agents as aluminum or silicon, direct to the bath. They obtained splendid results.

Because of the great ease with which molybdenum could be extracted from wulfenite by sodium sulfide, the writer initiated experiments to ascertain whether or not the "Signal" ores could be treated in a similar manner.

Laboratory tests soon showed that simple counter current lixiviation was not sufficient. Heat, pressure and agitation all increase the efficiency. For some ores it is necessary to add sodium polysulfide, in order to take care of the cerrusite and similar minerals that also consume sulfur by becoming sulfadized. Other ores particularly those containing vanadiolite and calcium vanadates require the addition of caustic soda. The sulfadizing and formation of sodium vanadate reactions are very complex, but for simplicity's sake may be expressed thus:

$$\underset{\text{cuprodescloizite}}{(Cu\,.\,Pb\,.\,Zn)_2\,V_2O_7} + 2\,Na_2S = 2\left\{\begin{matrix}Zn\\Pb\\Cu\end{matrix}\right\}S + Na_4V_2O_7$$

$$\underset{\text{vanadinite}}{3Pb_3(VO_4)_2\,.\,PbCl_2} + 10Na_2S = 10PbS + 6Na_3VO_4 + 2NaCl$$

The use of sodium sulfide as a solvent for vanadium formed part of a patented treatment method of G. Fester.[12] Its similar

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[10] U. S. Patent 1,385,072.

[11] Met. and Chem. Eng. 13, 492-494 (1915).

[12] German Patent 294,932 (1917).

use has been recently patented in the United States by one of S. G. Musser's former laboratory assistants.

After the usual laboratory and small scale experiments, the writer specified the following procedure, which was carried out in a 2½-ton per day scale at S. G. Musser's plant. The ore was pulverized to 0.025 in. (0.63 mm.) mesh in a ball mill. It was then charged into a rotating drum made of 0.5 in. (12.7 mm.) boiler plate, which was 8 ft. (2.4 m.) long, and 3.5 ft. (1.1 m.) in diameter. It had a tight fitting manhole cover and hollow axles, so that steam could be supplied for heating and pressure. Several blades on the inside of the drum aided agitation as the drum was revolved. Three solutions were successively employed, the one containing the least sodium sulfide first and the strongest sodium sulfide liquor last.

The second solution became the first solution for the next lot of ore to be treated, and the third solution the second. A new third or strong sodium sulfide solution was prepared, by dissolving commercial sodium sulfide in water to saturation at average temperature, and then diluting with an equal amount of water. The ore was digested for 4 hours, 0.5 ton to the lot. A temperature of 90° C. and a pressure of 120 lb. was maintained. At the end of this period the ore was discharged and filtered. The residue can be easily treated by oil flotation for the recovery of both the precious and base metals. Experiments in this case were made with a K & K laboratory flotation machine.

The filtered solution was then evaporated in a single effect evaporator to 20° Bé. and sent to the crystallizing tanks, where the sodium sulfate and chloride were crystallized out. It was then evaporated to 26° Bé. and crystallized, yielding a mixture of sodium ortho, pyro, and meta vanadates.

For a plant situated on the desert, where the vanadium deposits are, the best evaporator would be spray ponds. These evaporators consist of parallel pipes, with many small perforations on the top side, which are suspended about 10 ft. (3 m.) above a shallow pond. The hot dry desert wind blowing through the spray causes a very rapid evaporation. A centrifugal pump keeps the solution in circulation. A 3 in. (7.6 cm.) centrifugal pump will supply an evaporator capable of evaporating 20,000 lb. (9,071 kg.) of water per day of average desert weather. The writer has used such evaporators successfully in evaporating borax, potash, trona, potash alum and nitrate liquors at desert deposits.

The residual liquor from the sodium vanadate crystallization contains some sodium vanadate, sulfide, sulfite and hypo sulfite. It is returned to the leach system with the new or strong sodium sulfide liquor.

The mixed sodium vanadates are a commercial product. They can also be converted into the oxide by treating with either sulfuric or nitric acids, baking to dryness, and then washing or rather leaching and filtering to remove the soluble sodium nitrate or sulfate, and recovering the insoluble vanadic oxide. This process has splendid possibilities in its limited field. The cost of plant and of operation are both low. This method can not be used if the ore contains phosphorus, molybdenum, tungsten or other impurity forming soluble compounds with the sodium sulfide. These impurities would render the product worthless.

The writer has developed a method of using such mixed sodium vanadates with some iron oxide and metal and aluminum for production of ferro vanadium by the metallo-thermic method or with silicon in the electric furnace. This method will be described at some future date.

Metallic Vanadium.

The writer has developed a method of making pure metals from difficultly reduced oxides. He has prepared vanadium which was over 99 per cent pure by this method, and has also produced very pure lithium, tantalum, titanium, thorium and cerium by the same method. The writer had hoped to be able to describe this method in this paper but business reasons have prevented, and he can only hope to make it the subject of some future paper. In the development of a process for making metallic vanadium the writer duplicated the work of previous investigators, and devised a method of reduction with lithium metal. His experiments along these lines are described hereafter.

Sefstrom's Method. Sefstrom, the discoverer of vanadium, found that on dissolving iron containing vanadium with dilute hydrochloric acid, that the vanadium remained in the residue with the graphite and other insoluble matter. Ferrovanadium may be dissolved in dilute hydrochloric acid, while passing a stream of carbon dioxide, and about one half of the vanadium content of the ferro-alloy will be recovered as vanadium metal. The vanadium carbide and graphite present in the ferro is also insoluble, and will be an impurity in the vanadium residue. Working with ferro prepared from pure materials in magnesite crucibles by the alumino-thermic method, and dissolving the alloy with C. P. acid, the writer was able to prepare vanadium metal over 90 per cent pure. This method has been used for some time in Germany, to prepare the vanadium metal sold to experimenters and colleges. It is in the form of fine glistening scales, much resembling graphite in appearance. It can be fused *in vacuo* only, and even then contains a large percentage of vanadium monoxide. It oxidizes readily in the atmosphere.

Roscoe's Method. This method is fully described in Roscoe and Schorlemmer's Treatise on Chemistry pp. 279 to 282. The writer attempted to duplicate this method on a 1 lb. (0.45 kg.) scale. He used a rotating silica tube 4 in. (10 cm.) in diameter and 3 ft. (90 cm.) long, which was heated electrically by a resistance coil. The hydrogen train and other accessories were the same as specified by Roscoe only of suitable size. At the end of 6 days less than half the chloride had been reduced to metal, but on substituting a smaller tube and using a silica boat containing one gram, nearly 90 per cent of the chloride was reduced to metal in 48 hr. The preparation of the chloride is a very difficult matter in itself, and as this method offered no commercial possibilities, no further experiments were conducted.

Prandtl and Bleyer's Methods. They describe a method[13] of preparing metallic vanadium up to 94 per cent pure. They used a can 10 in. (25 cm.) high and 5 in. (12 cm.) in diameter. In the bottom of this they tamped a layer of fluorspar 1.5 in. (4 cm.) thick. They then placed a glass tube 10 in. (25 cm.) long and 2 in. (5 cm.) in diameter in the center and tamped fluorspar around this tube. The next step was to tamp a mixture of calcium, aluminum and vanadium oxide inside the tube and withdraw the tube by twisting and turning. The mixture was then ignited by a "thermit cherry."

No data were given as to the size of the particles of aluminum and calcium nor the proportions of reducing agent and vanadium

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[13] Z. anorg. Chem. 64, 217-224.

oxide, save that there are to be 69 parts of calcium for 31 parts of aluminum. It is assumed that they planned on the following reaction:

$$15Ca + 10Al + 6V_2O_5 = 5Ca_3Al_2O_6 + 12V$$

The degree of comminution of the various ingredients in a metallo-thermic reaction is of prime importance. Both the temperature and speed of reduction can be controlled within certain limits, solely by regulating the sizes of the different elements and compounds used. Dr. Saklatwalla[14] has shown that vanadium oxide may be reduced to metal in the form of ferro, without the excessive formation of carbide or the reduction of silica to silicon, even though carbon and silica be present in large amounts. These results were obtained solely by paying attention to size of materials. This explains why certain investigators have been unable to duplicate the work of others. Different sizes of materials were used, hence a different temperature and rate of reduction.

Prandtl and Bleyer recommend the use of old slag where more than 100 g. of vanadium oxide are reduced, to keep down the temperature; but the writer obtained better results when no slag was used. The writer also used dead burned magnesite, fused in the electric furnace and then pulverized, instead of fluorspar in several runs.

The writer used a can 20 in. (51 cm.) high and 12 in. (30 cm.) in diameter and rammed the fluorspar around a tube 18 in. (45 cm.) long and 6 in. (15 cm.) in diameter. The fluorspar or magnesite should be well vented. The charge consisted of 600 g. of small calcium shavings, 270 g. of minus 40 mesh aluminum powder and 1100 g. of 80 mesh vanadium pentoxide that had been freshly fused and pulverized.

A considerable portion of the vanadium entered the slag as calcium vanadate, and in 8 runs the best metal was only 85 per cent pure. The impurities were calcium and aluminum. Remelting the regulus from the 8 runs in an electric furnace and treating the melt with more vanadium oxide, removed the remaining calcium and aluminum, but the product contained a high percentage of vanadium monoxide.

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[14] Trans. Am. Electrochem. Soc., 37, 341 (1920); Jour. Ind. and Eng. Chem. 14, 968-972.

Vogel and Tammann[15] produced vanadium metal 95 per cent pure by using pure dry ammonium-free vanadium pentoxide in the regular alumino-thermic method. The writer used the apparatus of Prandtl and Bleyer, described above, and 40-mesh aluminum dust with 80-mesh vanadium pentoxide. Out of 4 runs the best obtained was 78 per cent vanadium metal, the balance was aluminum with a little vanadium monoxide. The point anent the oxide being pure, dry, and ammonium free is important. Possibly another reason why the writer was unable to make the same grade of vanadium that they did, is that his aluminum dust contained some sodium and oxygen. The sizes of the materials used may have been different also.

The writer also duplicated the methods of Prandtl and Manz[16] who used vanadium trioxide instead of pentoxide for the calcium aluminum reduction. Vanadium trioxide gives much better results. There is less slag loss, and as a result of 4 runs a metal from 89 to 94 per cent pure was obtained, which on treating in the electric furnace with more trioxide gave a metal 96 per cent pure. Aside from the Baughman lithium method described hereafter, the reduction of vanadium trioxide by calcium and aluminum gave the best results of any method tried.

Prandtl and Bleyer[17] also produced a 95 per cent metal by using 100 parts of pure, fused and pulverized vanadium pentoxide, 49½ parts of aluminum powder, and 20 parts fluorspar in a magnesium crucible. The writer attempted to duplicate this but obtained only an 81 per cent vanadium metal.

Ruff and Martin's Methods. They describe[18] three methods:

1. Reduction of trioxide by aluminum and a small amount of carbon.
2. Reduction by carbon in the electric furnace.
3. Reduction of vanadium trioxide by vanadium carbide.

None of these methods appealed to the author because of the use of carbon, as he was searching for a way of preparing a carbon-free product. One run was made in a resistance furnace at a temperature of about 1700° C., using the third method. Over

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[15] Z. anorg. chem. **64**, 225

[16] *Ibid.* **79**, 209-22.

[17] Ber. **43**, 2602-3.

[18] Z. anorg. chem. **25**, 39-56.

three-fourths of the vanadium was lost by volatilization of the trioxide. The regulus contained 86 per cent vanadium metal, and contained both carbon and oxide as vanadium monoxide.

The writer has found that some vanadium monoxide is formed before decarburization is complete in any heat where decarburizing of vanadium carbide is attempted.

Muthmann and Weiss Method.[19] This method consists of reduction with "misch metal," a mixture of cerium and other rare earth metals. The writer was unable to obtain, at the time of these experiments, any misch metal but did obtain some cerium metal. He made three 100 g. runs with the best product containing 84 per cent vanadium.

Baughman's Lithium Method. Theoretically, lithium should be a better reducing agent than calcium, aluminum or cerium, as shown by the following:

$$\begin{aligned}3V_2O_5 + 10Al &= 5Al_2O_3 + 6V + 638{,}500 \text{ cal.}\\ 3V_2O_5 + 15Ca &= 15CaO + 6V + 648{,}000 \text{ cal.}\\ 3V_2O_5 + 7\tfrac{1}{2}Ce &= 7\tfrac{1}{2}CeO_2 + 6V + 360{,}000 \text{ cal.}\\ 3V_2O_5 + 30Li &= 15Li_2O + 6V + 825{,}000 \text{ cal.}\end{aligned}$$

This proved to be the case. The writer used lithium pellets about the size of BB shot in the same apparatus as was used for the previous experiments in calcium and aluminum reduction. A metal containing 95 to 97 per cent vanadium is readily obtained. An excess of vanadium oxide must be used, as a considerable amount is lost in the slag as lithium vanadate. The reduction is so rapid, however, that very little vanadium is lost by volatilization even when the trioxide is used.

Lithium is such an expensive reducing agent that the writer then turned his attention to making metallic lithium from lepidolite, lithia mica, of which there are large deposits in California. He finally worked out a method of producing lithium metal within reasonable cost and was planning to use the lithium reduction method to produce large amounts of vanadium metal, when the thought occurred that vanadium oxide might be reduced to the metal by the same method. With minor changes the method was successful. It was also found applicable to reducing

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[19] Liebig Ann. 337, 370; 355, 58.

titanium, thorium, uranium, cerium, and tantalum from their oxides. On account of business reasons the writer cannot describe this method, nor the technic that he has worked out of using sodium vanadate, iron oxide, and metal and aluminum shot for producing ferrovanadium.

Werner von Bolton's Method.[20] This is a method of reducing columbium or tantalum oxides to metal. It consists in preparing the oxide in the form of filaments with paraffine, calcining, and then heating by an electric current in a high vacuum. The writer used vanadium trioxide, which is a conductor, but was unable to obtain the metal. The trioxide was reduced to monoxide and dioxide but not to the metal.

The writer also attempted to produce metallic vanadium by electrolysis of vanadyl salts with a mercury cathode cell, in the same manner that metallic chromium, tungsten and molybdenum can be prepared. The experiments all gave negative results. Vanadium does not form amalgams and in aqueous solutions it is always anodic in properties.

Other methods for making metallic vanadium are those of Gin, Beckman and Cowper Coles. Dr. S. Fischer[21] investigated Cowper Coles' electrolytic method, and found it to be the formation of a coating of platinum hydride instead of metallic vanadium.

Beckman's Method. Dr. Beckman's method[22] consisted of using an igneous electrolyte of fused calcium oxide, and adding excess vanadium oxide while passing direct current. The writer used the furnace described before for smelting the Black Buttes ore. Instead of trying to produce the metal the writer attempted to produce a ferrovanadium. Scrap steel weighing 50 lb. (22.7 kg.) was first melted, then 50 lb. (22.7 kg.) of crude calcium vanadate charged on top and melted. At 20 min. periods for 4 hr., 20 lb. (9 kg.) of vanadium pentoxide was added. At the end of this period the metal was tapped and cast in pigs. It contained 2.67 lb. (1.21 kg.) of vanadium metal and carbide. A direct current of about 500 amp. at 80 volts was used.

Dr. Beckman gave no operating data in his paper on this

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[20] Zeit. elecktrochem. **11**, 45 and 722.

[21] Inst. Min. and Met. Eng. 1898-99 pp. 198-200.

[22] Trans. Am. Electrochem. Soc. **19**, 171 (1911).

method, and as apparently insignificant details determine the success or failure in this class of work, the writer decided to drop this line of investigation.

Gin's Methods. Gustave Gin describes his two methods, in detail, in his "Memoir on Vanadium,"[23] to which the reader is referred. The first method consists of electrolyzing molten calcium and vanadium fluorides, adding vanadium tetroxide from time to time. The second uses a calcium and ferrous fluoride electrolyte, and vanadium is supplied to the bath by special anodes composed of vanadium trioxide and carbon. The cathodes in both methods are iron, copper or other metal with which it is desired to alloy the vanadium, or lead, which is later volatilized if vanadium metal is desired. This latter is an object that is difficult to achieve. The methods are better suited for producing ferrovanadium.

It was the writer's privilege to be Dr. Gin's assistant when he was developing these two processes. In modified form the second method was later used at the works of Paul Girod at Ungine, France. Technically both methods are operative, but are not in wide use at present because the electrically fused alumina linings often failed before a run was half completed. The amount of carbon tetrafluoride formed at the anode, while not large in proportion to the amount of fluorine in use in the bath, was still enough to require the use of tight fitting goggles and aspirators by the furnace operators. Instead of using calcium fluoride in the second method calcium vanadium fluoride, as made for the first process, was found necessary and the addition of tetroxide of vanadium was found desirable, so that the final process became a combination of the original two. The cost of manufacture by these methods is high. In fact it can not compete with electric furnace reduction, using silicon as reducing agent, or with the alumino-thermic method.

DISCUSSION.

B. D. SAKLATWALLA[1]: The first thing that is remarkable is the large number of various occurrences which the author de-

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[23] Trans. Am. Electrochem. Soc. **16**, 439 (1909).

[1] Vanadium Corp. of America, Bridgeville, Pa.

scribes. Vanadium is one of the most widely disseminated elements that we know. It occurs on every continent of the globe. To find scattered occurrences of vanadium, therefore, should not appear strange, but the difficulty has been that we do not find them as commercial deposits. They are of an erratic nature and do not persist.

Now the metallurgy of lead vanadates has not been commercially developed, not because it is a difficult problem from a metallurgical standpoint, but because it had no particular commercial application.

As to the leaching methods and treatment, Mr. Baughman is right when he considers all these roundabout leaching processes as not commercial, because the losses are high.

He then describes his method of smelting out lead, and then taking the slag and fusing it with sodium hydrate and making a sodium vanadate. I am inclined to believe that is superfluous. The slag that you can get by reducing the lead out of the lead vanadates would be perfectly amenable to reduction directly, either by means of aluminum or silicon, or by carbon in the electric furnace. So the problem of getting vanadium out of lead vanadates is not a difficult metallurgical problem. It has not been commercially exploited for the reason that there are no lead vanadates to exploit commercially. But at the present time, since the radium industry has been practically shut down in this country, and which was a source of vanadium obtained as a by-product, there has been activity in development of other vanadium minerals, and probably this impetus to search might reveal larger deposits of lead vanadates or other vanadates.

COLIN G. FINK[2]: Formerly all ferro-vanadium was made by the Goldsmith process. Dr. Saklatwalla has recently published a paper in the "Electrical World,"[3] on the production of ferro-vanadium in the electric furnace. It is another ferro-alloy which has submitted to electric furnace methods, an alloy which for years has been thought impossible to produce by any but the alumino-thermic method.

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[2] Consulting Metallurgist, New York City.

[3] Electric Furnace makes Ferro-Vanadium by B. D. Saklatwalla and A. Anderson. Electrical World, February, 1923.

W. C. Arsem[4]: About sixteen years ago I made some vanadium on a laboratory scale and determined the melting point to be 1,650° C. This was made by reducing the tri-chloride with magnesium, in a vacuum, similar to the classic research followed by Sir Henry Roscoe, who reduced the di-chloride and tri-chloride with sodium in hydrogen.

Will Baughman (*Communicated*): The statement that 64 lead vanadate deposits show commercial possibilities is not only the writer's opinion but is based upon reports made by competent mining engineers, familiar with the characteristics of the lead vanadates, who have examined a majority of these deposits at various times.

Lead vanadates generally occur in well defined veins and should not be confused with carnotite or roscoelite deposits that occur in small, irregular, scattered pockets. To those who have made a study of the genesis of the lead vanadates, the probable existence of lead vanadate ore chutes can be determined with as much assurance as the probable existence of the commoner metals.

No vanadium deposit persists in depth. All stop at the zone of ground waters. In the arid regions of United States this may mean a considerable depth. At least one lead vanadate mine extends to 900 ft. vertical depth, or 1300 ft. on the ore body. The wonderfully rich and unique deposit in the Peruvian Andes is no exception. In fact it is a rather shallow and superficial deposit, the zone of ground waters being at 100 to 150 ft. depth.[5]

The lead vanadate deposits of United States have not been developed, because of economic conditions, not a lack of potential ore. Of the several attempts made in the past to develop these ores all failed for reasons other than lack of ore, save one project.

The lead vanadate miner can not ship his concentrates to some treatment plant. He must refine, manufacture and then market his product, which is a serious undertaking.

One company owns a deposit of ore that is practically free of impurities, that is readily concentrated by mere roasting and which contained at first seven times as much vanadium as the best run of mine lead vanadates. Through being the first large pro-

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[4] Consulting Chemical Engr., Schenectady, N. Y.

[5] Miller and Singewald. Mineral Deposits of South America. D. F. Hewett. Vanadium in Peru. Trans. A. I. M. E. Vol. 40.

ducers, and selling under contract systems, this company offers a problem in financing and competition, for which the writer knows no parallel.

Before the discovery of the unique deposit owned by this company, the lead vanadates were the principal source of supply. As soon as this deposit is reduced to low grade ore, so that the production costs will be higher than they were a few years ago, then the lead vanadates may again become the principal source of vanadium.

Hewett's description of this property shows that the very rich ore occurred as shallow gash veins in a lense shaped mass 300 ft. long, 28 ft. wide, and 200 ft. on slope to ground waters. On an optimistic basis this would indicate less than 100,000 tons of 1 to 20 per cent ore, while consular reports show over 12,000 tons of 40 per cent concentrates have been shipped. This would indicate that this deposit is approaching exhaustion. Also the first material mined ran as high as 20 per cent vanadium oxide, which was raised to as high as 80 per cent by roasting. This roasted material has steadily fallen off in grade. Consular reports show that concentrated material recently shipped contained only 16 to 20 per cent.

During the period that the highest grade ore was being mined, this company sold ferro for less than $2.50 per lb. of vanadium content, or about $1.00 less than the writer estimated that the more favorably situated lead vanadate deposits could produce it.

On the other hand, the use of vanadium may fall off. The same development of electric furnace practice that allows Dr. Saklatwalla to produce ferro-vanadium in the electric furnace, has also made it possible to use titanium. or other cheap nitrogen and oxygen removers, and with better furnace control, produce a steel for many purposes superior to the old vanadium steel. The Ford Motor Co., formerly one of the largest vanadium users, has used little for some time past.

The writer did not intend to infer that he considered all the methods discussed in the paper as non-commercial. He considers the chloride volatilization method, ball mill grinding, and the ideas of producing 99 per cent vanadium oxide or vanadium metal, in order to avoid competition, as impractical. He considers chloridizing roasting for ores difficult to concentrate and low in lime or magnesia, sodium sulfide leaching for similar ores high in lime or magnesia, and the smelting, refining method for concentrates, as methods having excellent commercial possibilities.

Dr. Saklatwalla suggests the direct reduction of slag, from smelting lead vanadates, to ferro vanadium. The lead vanadates all contain one or more of the elements phosphorus, molybdenum, arsenic, tungsten, copper, and chromium. These elements would enter the final product, making it worthless. Some kind of refining system is absolutely necessary.

A paper presented at the Forty-third General Meeting of the American Electrochemical Society held in New York City, May 5, 1923, Dr. F. M. Becket in the Chair.

PREPARATION OF METALLIC URANIUM.[1]

By R. W. Moore.[2]

Abstract.

A method for the preparation of metallic uranium in a very pure state is described, also a method of fusing the metal to form buttons or small pigs, which may be rolled down to give thin sheets.

For the preparation of this metal in a state of high purity, the old method of the reduction of the anhydrous chloride with metallic sodium seems to be the one giving the best results. This method has been used by a number of investigators, including Peligot,[3] Zimmerman,[4] Moissan,[5] Mixter,[6] Roderburg,[7] Fischer,[8] and Lely and Hamburger.[9]

The method which we have used is in general that outlined by the last named investigators, with several modifications which make for simplification. As Lely and Hamburger point out, there are several conditions which must be fulfilled if high purity of the metal is to be attained. These are, in brief, the production of the chloride in a pure, dense form, which does not take up moisture rapidly. This eliminates the action of water during the reduction, and the attack of moist chlorides *i. e.,* hydrochloric acid) on the reduction bomb. The purer the chloride, the higher is the temperature produced during reduction and the coarser the particles of metal produced. This condition is desirable since it results in less oxidation taking place during the removal of the

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[1] Manuscript received February 1, 1923.
[2] Research Laboratory, General Electric Co., Schenectady, N. Y.
[3] Ann. Chim. Phys. (4,) 17, 368.
[4] Ber. deutsch. Chem. Ges. **13**, 348 (1882).
[5] Compt. rend. **122**, 1088.
[6] Z. anorg. Chem. **78**, 231 (1912).
[7] Z. anorg. Chem. **81**, I, 122.
[8] Z. anorg. Chem. **81**, II, 189.
[9] Z. anorg. Chem. **87**, 209.

other products of the reduction. If the chloride is pure the heat of the reaction is sufficient to fuse part of the metal product into the form of small pellets.

PREPARATION OF THE CHLORIDE.

The preparation of UCl_4 is most easily carried out by the reaction of S_2Cl_2 on uranium oxide, (U_3O_8), a method similar to that used by Arsem[10] for making $ThCl_4$ and also used by Matignon and Bourion,[11] Colani,[12] and Lely and Hamburger.[13] An easy method of carrying out this reaction was found to be as follows: The oxide of uranium was placed in quartz or porcelain boats,

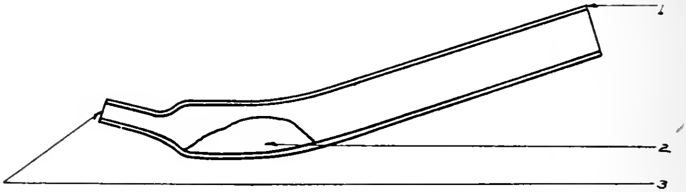

FIG. 1

1 HARD GLASS TUBE.
2 CRUDE UCL_4
3 INLET FOR CL.

and these were inserted into a 5 cm. (2 in.) porcelain tube, resistance furnace. In one end of this tube, an empty boat was placed and redistilled S_2Cl_2 was allowed to flow into this drop by drop through a tube connected to a separatory funnel. The other end of the furnace tube was closed with a rubber stopper with a large outlet tube opening under S_2Cl_2 contained in a bottle.

The furnace was inclined towards the outlet end to allow any excess S_2Cl_2 condensing in the cool end of the tube to flow out. The tube was brought up to 200°-300° C., the S_2Cl_2 started dropping in, and the temperature of the furnace gradually raised to 500° C., at which temperature it was held for three or four hours. Under these conditions uranium oxide is converted to a greenish, coarse crystalline mass, which absorbs moisture only slowly. At

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[10] U. S. Patent 1,085,098.
[11] Ann. Chim. Phys. (8) **5**, 127 (1905).
[12] Ann. Chim. Phys. (8) **12**, 59 (1908).
[13] *Loc. cit.*

500° C., the UCl_4 did not melt nor sublime, but remained in the boats in the form of a compact mass of coarse crystals. It still contained some oxide, and for this reason required sublimation.

SUBLIMATION OF THE UCl_4.

An easy and convenient method of carrying out this sublimation was found to be as follows: A large hard glass tube, about 4 cm. (1.6 in.) in diam. was bent as shown in Fig. 1. The tube was filled with Cl which was bubbled through S_2Cl_2 to make sure it was dry. The UCl_4 was emptied from the bottles, in which it had been sealed, directly into the tube, so as to avoid exposure to the air, and shaken down into the lower end of the bend.

The outlet end was closed by a stopper carrying a small tube. The part of the tube containing the UCl_4 was heated to a bright red heat, with a moderate current of Cl passing through it. The UCl_4 sublimed in the form of dark red vapors, which deposited close to the hot zone in the form of a mass of coarse, greenish crystals. Besides this product, there was formed a considerable amount of a fluffy, golden-yellow, crystalline substance that deposited in the cooler part of the tube. This was apparently an addition product of UCl_4 with S_2Cl_2, for on replacing the Cl with dry N, and heating the tube containing these crystals, they were decomposed into UCl_4 and S_2Cl_2. The UCl_4 thus sublimed was poured directly into a bottle containing dry N, and sealed until it was used for reduction.

REDUCTION.

The sodium used for reduction was all sublimed in vacuum in an apparatus similar to that suggested by Lely and Hamburger.[14] This was arranged so that the cylinder containing the sodium was heated in vacuum with the same heating arrangement as used later for heating the reduction bomb. See Fig. 2.

The resublimed sodium was cut up into small pieces under redistilled benzol, which had stood over sodium for weeks. It was dried in a vacuum, and opened up under an atmosphere of dry nitrogen. About 25 per cent excess Na was used for the reduction. The UCl_4 was broken up into small lumps in an atmosphere of dry nitrogen, and this was mixed with the sodium by shaking in a bottle filled with dry N.

[14] *Loc. cit.*

The reduction was carried out in a steel bomb in vacuum. The simplest manner of accomplishing this was to use a steel cylinder closed at one end, with a steel cap screwed in the other end, using a fine thread. A copper gasket was used under the cap, and the cap was screwed down by hand. This arrangement allowed the gas in the bomb to escape, while little or no sodium was lost during the reduction. The bomb was exhausted at the same time as the chamber in which it was heated. The arrangement for carrying out the reduction is shown in Fig. 2.

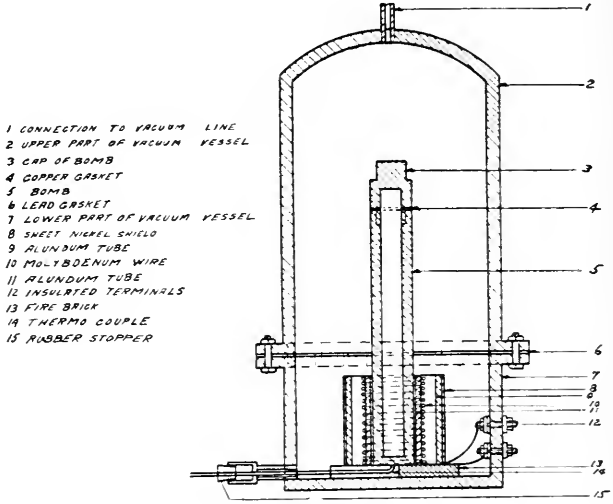

FIG. 2

The bomb was first filled with dry nitrogen, and the UCl_4 sodium mixture poured in and pressed down. The space above the charge was filled with dry nitrogen, the bomb closed up and placed inside the heater in the reduction chamber. This was exhausted to about 25 microns, and the bomb gradually heated until a sudden rise of temperature was shown by the pyrometer. The bomb was then cooled under vacuum and the vacuum broken with dry nitrogen.

EXTRACTION OF THE METAL.

The product of the reduction was a sintered grayish mass. It contained U, NaCl, Na, with possibly some small amounts of

UCl_4 and uranium oxide. The excess sodium was removed with absolute alcohol, the NaCl completely washed out with water, and then the heavy brownish residue washed with dilute (2 per cent) acetic acid. The acid was washed out completely with water and the residue washed with acetone and dried in vacuum. This washing was carried out as rapidly as possible to avoid oxidation of the wet metal. It was found necessary to break the vacuum after the metal was dry, with dry nitrogen, for the finer portions of the metal were very pyrophoric. This was true to such an extent that the metal could not be transferred from one container to another without handling it entirely in an inert atmosphere, such as nitrogen.

The resulting metal was a very heavy, brownish powder, containing a considerable proportion of small round sintered balls. The yield was usually above 90 per cent. The coarser portions of the metal (remaining on 80-mesh screen) were quite pure, analyzing as high as 99.8 per cent uranium. The finer portions were, of course, more affected by oxidation during the washing, and for this reason were not so pure.

FUSION OF THE METAL.

Since uranium reacts with almost all gases at high temperatures, and alloys readily with most metals, such as W, Mo, Fe, Ni, etc., the problem of melting or working the powdered metal into solid form offers considerable difficulty. This was finally accomplished by fusing the metal on a water-cooled table with an arc in an atmosphere of argon at a pressure of 50 to 100 microns. The apparatus used for this purpose is shown in Fig. 3.

Pellets or discs of two sizes (about 2.5 cm. and 3.75 cm. diam. and 0.5 cm. thick) were made by pressing the powdered metal in a mold using a hydraulic press. In order to prevent spontaneous ignition of the metal, the mold was filled with N and the metal powder poured into the mold through a stream of N. After pressing, the metal no longer took fire, but the discs were preserved in an atmosphere of dry N to prevent oxidation.

The large discs were clamped in the upper electrode, in the apparatus shown, and the smaller placed on the water-cooled table; usually two discs were used, placed one on top of the other. The large discs were first sintered by placing on the table and passing an arc over them.

After the air had been exhausted from the globe to 0.5 micron, the globe was washed out by passing in argon to a pressure of a few mm. and again exhausted. Then the globe was filled with argon at a pressure of about 75 to 100 microns, an arc started by in contact with the discs on the table, and then the arc was moved pushing down on the upper electrode to bring the disc of uranium around over the surface of the discs by manipulating the upper electrode. In the course of one or two minutes the surface of the discs could be all brought to fusion. The discs were then cooled, turned over on the table, and the other side fused as before. By using care not to keep the arc on too long, the whole pellet could be melted, provided too much oxide was not present. In most cases, there was sufficient oxide present to prevent complete fusion; the oxide appeared to be very difficult to fuse.

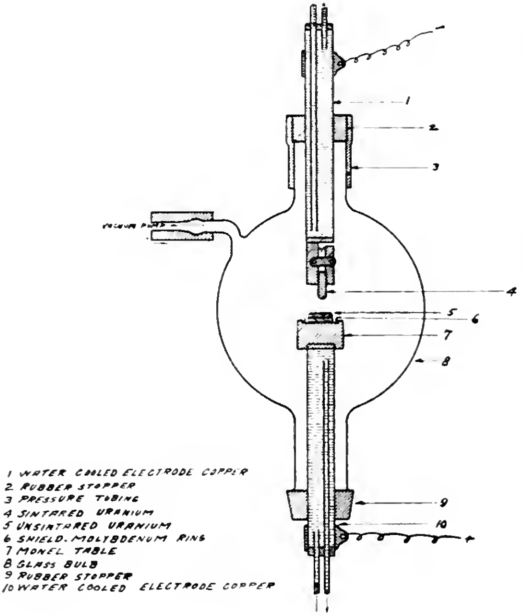

Fig. 3.

In order to obtain metal nearly free from oxide, a depression was cut in the water-cooled table, the metal discs were placed on the edge of this, and the melted uranium caused to run out of the unfused portion of the discs into the depression by tilting the table slightly. If the table were made thin and kept well cooled, the melted uranium solidified immediately in the depression without attacking the metal of the table, which was made of iron or monel metal. The small pigs of metal formed in this way were at times remelted on a smooth table to form flat smooth buttons.

PROPERTIES OF METALLIC URANIUM.

The metal thus formed had about the appearance of polished iron. It oxidized quite readily; a brightly polished piece became tarnished quite brown when exposed to air for two or three days. The metal was very ductile; some buttons formed as above were rolled cold from a thickness of about 5 mm. to small sheets about 0.375 mm. (0.015 in.) thick.

DISCUSSION.

CHAS. A. DOREMUS[1]: I desire to call the attention of the Society to the fact that Fig. 3 is substantially Robert Hare's electric furnace, invented in 1842, and which was described to this Society some years ago, and later by Edgar F. Smith in his book on "Chemistry in America."

In Hare's furnace, the top electrode was movable. He made a great many interesting experiments. It was unquestionably the first electric furnace in this country, if not in the world.

J. W. MARDEN and H. C. RENTSCHLER[2]: This paper is of great interest to us, since we are interested in the preparation and properties of certain rare metals. This discussion is intended to bring out some additional questions and difficulties which are found during the preparation of the extremely active element uranium.

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[1] New York City.

[2] Research Lab., Westinghouse Lamp Co., Bloomfield, N. J.

We have many samples of uranium powder by practically all of the methods now given in the literature, and we are thoroughly familiar with the process used by Mr. Moore.

We do not agree that the reduction of the chloride with metallic sodium is the method which gives the best results for the preparation of uranium or indeed of some other metals, such as thorium, zirconium, etc. Burger,[3] for example, in 1908 describes the reduction of uranium oxide with calcium, in which he claims a high degree of purity. This is the same method which was used in 1904 by Huppertz[4] for other rare metals. The advantage of using uranium oxide in place of uranium chloride if it can be satisfactorily reduced is obvious, since the difficulty of the preparation of the pure dry chloride is costly, tedious and difficult. The chloride must be distilled at high temperatures, and even under the most exacting of conditions it seems almost impossible to avoid traces of oxy-chlorides and also contamination from silica.

In the reduction of the chloride with sodium, if there is any trace whatever of moisture of oxy-chloride where oxide can be formed, the sodium will not reduce the oxide. It is therefore next to impossible to get 100 per cent uranium, that is, as metallic uranium free from uranium oxide in this way.

Mr. Moore states in his paper that his uranium powder was brown. We all know that molybdenum powder or tungsten powder or other metal powders when in reasonably coarse condition as Mr. Moore's probably was, are gray and not brown. The brown color indicates the presence of considerable amounts of oxide. It is possible to have a sample of uranium powder which will analyze a high percentage of total uranium, but which will also, if figured in terms of oxide, show a considerable amount of uranium oxide present, or a much lower percentage of free metallic uranium than of total uranium. This is due, of course, to the high atomic weight of uranium and the low atomic weight of oxygen. We should like to ask, therefore, if Mr. Moore actually determined the percentage of oxygen or uranium oxide in this sample. Our experience indicates to us that a sample of uranium, of the coarseness indicated by Mr. Moore, would have a consid-

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[3] Burger; Dissertation, Basel (1908).

[4] Huppertz, Chem. Cent. 1, 1383 (1904).

erable percentage of oxide if it had much of a brown color, perhaps 10 or 20 per cent of oxide figured as U_3O_8, or a much larger percentage figured as a lower oxide. We have made many samples of this kind.

We should also like to inquire whether the percentage of iron has been determined. Mr. Moore has given no data in his paper with regard to the iron content of his uranium sample, which we understand was made in an iron bomb. Fisher and Rideal[5] and others have found that with the chloride method of reduction, the uranium thus produced contains a considerable amount, say from 0.5 to 2 per cent of iron. We should like to know if the iron has been actually determined, since this has important bearing on the methods of determining the purity of uranium and its apparent melting point. If there is much iron present, and the percentage or uranium metal is determined by simply burning to oxide and getting the increased weight, the larger increase due to the presence of a small amount of iron would make up for the presence of a considerable amount of uranium oxide in the sample.

Furthermore, we should like to know the melting point of the buttons which Mr. Moore has prepared by arc-melting on pieces of monel metal. We infer from his paper that the melting point of the beads is fairly low, and should like to point out that when the reduction is carried out in an iron bomb, there is no difficulty in getting a powder which consists, partly at least, of little beads of apparently fused metal. This is not the case if the presence of iron is excluded.

It is hoped that a paper can soon be published describing methods by which uranium powder is now being produced in the Research Laboratory of the Westinghouse Lamp Company, which, as has been stated, is not brown but has the appearance and the fine pressing quality of a good sample of molybdenum powder. This kind of uranium powder can be pressed into any desired shape, and with proper precautions against oxidation and spontaneous combustion in the air can be sintered, treated into bars or into solid buttons of any desired shape suitable for example for X-ray targets or other commercial purposes.

In conclusion, the present writers have worked with the method

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[5] Z. anorg. Chem. 81, 170, (1913).

described by Mr. Moore, but were not able to obtain samples of uranium powder by any means free of oxide. It is characteristic of uranium, if it contains even very small quantities of almost any kind of metallic impurities, that when heated in a vacuum or in an inert environment beads of low melting point metal separate and run away from the remainder of the mass. We experienced considerable trouble in finding a suitable substance upon which to support uranium during its heat treatment. Uranium alloys with most metals, (even tungsten) under proper conditions, and interacts with such refractories as lime, magnesia, etc. We have devised a method for making pure thorium oxide crucibles, which, when properly heat treated, have served excellently for this purpose.

R. W. MOORE (*Communicated*): In reply to the point raised by Dr. Doremus, I would say that there was no intention of even suggesting that this type of furnace is new. Similar furnaces have been used for various purposes in the past. The present paper simply shows the application of this type to this particular problem, with some details modified to fit this case. The method of separating the metal from the oxide and obtaining a small pig of pure cast metal is believed to be new.

Messrs. Marden and Rentschler bring out several points on which there may be differences of opinion. As regards the relative values of the methods of reduction by calcium and sodium, much may be said. It would seem that the reduction products from the sodium reduction, namely NaCl, excess Na, and possibly undecomposed UCl_4, should be much more easily extracted from the uranium metal than the CaO and possibly undecomposed uranium oxide produced during the reduction by calcium. In the case of thorium, with which we tried both methods, the sodium reduction gave the best results.

In regard to the difficulty of preparing the UCl_4, I do not agree with Messrs. Marden and Rentschler. It is not particularly costly, nor tedious, and certainly not difficult. It does require care. The sublimation does not require high temperature; it is readily carried out in a hard glass tube.

Messrs. Marden and Rentschler state that the brown color of the powdered uranium metal indicates the presence of considerable amounts of oxide. Unquestionably, the color indicates oxidation of the surface of the particles. Uranium is quite easily oxidized; as mentioned in the paper, even rolled and worked metal pieces, when polished bright will turn quite brown in a few hours in the air. Naturally, during the process of washing out the NaCl, Na, etc., from the reduction mass, the metal is constantly subject to oxidation, and the particles tarnish, but probably only on the surface, since the particles are dense, and the oxygen probably does not penetrate to any appreciable depth. Since our analyses show a percentage of uranium as high as 99.8 per cent this would seem to be the case. Of course, the 0.2 per cent oxygen (assuming the difference to be all oxygen) may mean several per cent of oxide. The fact that there was some oxidation of the particles was the reason for the process described in the paper of melting the metal away from the oxide coating. The fact that the metal so obtained was very ductile would seem to indicate that it was quite well freed from oxide.

It would seem that any process of reduction would be subject to this difficulty of oxidation of the metal during extraction of the reduction products. If Messrs. Marden and Rentschler have found some method of avoiding this I shall be interested to learn what it is.

In regard to the possible content of iron in the uranium, I would refer to the paper by Messrs. Lely and Hamburger,[6] in which they state that if the uranium chloride (and also thorium chloride) is kept dry, there is no trace of iron in the metal produced in the steel bomb. We did not analyze our metal for iron, there being no reason to expect contamination from this source. After many reductions, the bomb used showed no sign of any attack by the reduction materials. Furthermore, in cases where a small amount of iron had alloyed with the melted metal during fusion of the pellets in the furnace described, the resulting alloy was very brittle. The metal we obtained was very ductile. This would indicate the absence of any considerable amount of iron. Although

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[6] Z. anorg. Chem., 87, 209.

we have no positive evidence that traces of iron may not have been present, the indications are that it was probably not present. Amounts such as suggested by Messrs. Marden and Rentschler are entirely out of the question.

The melting point of the metal produced by the method described in the foregoing paper has not as yet been definitely determined.

A paper presented at the Forty-third General Meeting of the American Electrochemical Society held in New York City, May 5, 1923, Dr. F. M. Becket in the Chair.

EXPERIMENTS RELATIVE TO THE DETERMINATION OF URANIUM BY MEANS OF CUPFERRON.[1]

By Jas. A. Holladay and Thos. R. Cunningham.[2]

Abstract.

A description is given of experimental work concerning the determination of uranium by precipitation with cupferron. Data are cited to prove that quadrivalent uranium can be quantitatively precipitated by cupferron from solutions containing from 4 to 8 per cent of H_2SO_4 (sp. gr. 1.84), that aluminum, calcium, magnesium and phosphorus remain in solution and can be completely separated from the uranium by filtration, and that the precipitate of $U(C_6H_5N_2O_2)_4$ can be quantitatively converted to U_3O_8 by ignition.

PRELIMINARY REMARKS.

Recent years have witnessed a marked increase in interest concerning uranium, and in experimental work looking to the discovery of new uses for its compounds and alloys. Coincident with and resulting directly from this activity there has arisen a need for more satisfactory analytical methods for the determination of the element. Without going into an exhaustive discussion of the present state of the art, it may be stated that although several of the commonly used methods are capable of yielding accurate results, the necessary separations are accomplished by reactions requiring numerous time-consuming and laborious re-precipitations, particularly the separation of uranium from vanadium and of uranium from aluminum. The experimental work described in this paper had for its object the development of a procedure

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[1] Manuscript received January 11, 1923.

[2] Union Carbide and Carbon Research Labs., Inc., Long Island City, N. Y.

free from these objections, *i. e.*, one based on sharp, clean-cut reactions.

It has been shown by W. A. Turner[3] that vanadium can be quantitatively separated from uranium, phosphorus, and arsenic by precipitation with cupferron in a 10 per cent sulfuric acid solution. Under these conditions aluminum, calcium, magnesium and phosphorus, impurities usually found in carnotite, pass quantitatively into the filtrate, while iron (titanium and zirconium) is completely precipitated with the vanadium. The reliability of these separations has been confirmed in this laboratory. Recently V. Auger[4] has gone on record to the effect that quadrivalent uranium can be quantitatively precipitated from an acid solution by cupferron as a brown, flocculent precipitate having the formula $U(C_6H_5N_2O_2)_4$. However, this article makes no mention of the necessary acidity nor of the behavior of aluminum, calcium, magnesium, zinc and phosphorus. Believing that these reactions might prove to be better suited to the separation and determination of uranium and vanadium than any previously proposed, experiments were carried out to obtain information on the following points.

1. To confirm Auger's statement that quadrivalent uranium is precipitated by cupferron in acid solutions, and to find out whether uranium is also precipitated when present in a still lower state of oxidation than U^{IV}.
2. To determine within what limits of acidity the precipitation is complete.
3. To learn whether the uranium precipitate, $U(C_6H_5N_2O_2)_4$, can be quantitatively converted to U_3O_8 by ignition.
4. To ascertain whether aluminum, calcium, magnesium, phosphorus, and zinc can be quantitatively separated from uranium by proper regulation of the acidity.

PREPARATION OF STANDARD SOLUTIONS.

In order to carry out the proposed study of the reactions, the following standard solutions were prepared:

1. *Uranyl Sulfate, $UO_2(SO_4)_2$, Solution.* Prepared by dissolving 1.2 grams of the C. P. salt in water and making the solu-

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[3] Am. J. Sci. **42**, 109-10 (1916).

[4] Compt. Rend., 170, 995-6 (1920).

tion up to 500 cc. in an accurately calibrated 500 cc. volumetric flask. If the uranyl sulfate, $UO_2(SO_4)_2$, had been pure, 100 cc. of the solution should have contained 0.1237 g. of uranium. The actual uranium content was determined by the following three methods:

(a) Precipitation as $(NH_4)_2U_2O_7$ and Weighing as U_3O_8. The uranium in a 50 cc. aliquot part of the solution was precipitated with ammonium hydroxide[5] and ignited to U_3O_8. The weight of the precipitate of U_3O_8 was 0.0750 g., corresponding to 0.1272 g. U in 100 cc. of the solution.

(b) Precipitation as $(NH_4)_2UO_3V_2O_5 . H_2O$ and Weighing as $2UO_3 . V_2O_5$. The uranium in a 25 cc. aliquot part of the solution was precipitated as ammonium uranyl vanadate, and ignited and weighed as $2UO_3 . V_2O_5$ according to Blair.[6] The result obtained by this method was 0.1276 g. of U in 100 cc. of the solution.

(c) Reduction with Zinc and Titration with 0.1 *N* $KMnO_4$. A 50 cc. aliquot part of the solution was acidified with 6 cc. of H_2SO_4 (sp. gr. 1.84), diluted to 100 cc. cooled to room temperature, and passed through a Jones reductor having a zinc column about 25 cm. (10 in.) long. The uranium was completely removed from the reductor by the use of 125 cc. of water. Approximately six minutes were consumed in passing the solution and washings through the reductor. When the amount of uranium to be reduced exceeds about 0.3 g., a preliminary reduction in the beaker with 5 g. of zinc is necessary. The solution was vigorously stirred for 1.5 minutes to re-oxidize the small amount of uranium reduced below the uranous $(U(SO_4)_2)$ state, and titrated with 0.1 *N* $KMnO_4$ that had been standardized against Bureau of Standard's sodium oxalate. By this procedure the result 0.0631 U in 50 cc., or 0.1262 in 100 cc., was obtained.

A resume of the results obtained by the three methods follows:

	Grams U in 100 cc.
Amount theoretically present	0.1237
Amount found by weighing U_3O_8	0.1272
Amount found by weighing $2UO_3.V_2O_5$	0.1276
Amount found by zinc reduction	0.1262
Average	0.1270

[5] C. A. Pierle, J. Ind. and Eng. Chem., 12, 1, 60.

[6] "Chemical Analysis of Iron," p. 210.

2. *Sodium Vanadate Solution.* Prepared by covering 2 g. of pure V_2O_5 with hot water, and adding Na_2O_2 in small amounts until the V_2O_5 had dissolved. The resulting solution was boiled, filtered, and made up to 500 cc. in a volumetric flask. If the V_2O_5 had been pure the vanadium value of 100 cc. of the solution should have been 0.2240 g. A determination made of a 25 cc. aliquot part of the solution by reduction with H_2O_2 in concentrated sulfuric acid solution, followed by titration with 0.1 *N* $KMnO_4$ (Cain and Hostetter's method) yielded the result 0.2020 g., while another determination made by passing a 25 cc. aliquot portion, acidified with 6 cc. of H_2SO_4 (sp. gr. 1.84) and diluted to 100 cc., through a Jones reductor into ferric phosphate solution and titrating with 0.05 *N* $KMnO_4$, gave an identical result.

3. *Phosphorus Solution.* Prepared by dissolving 0.1065 g. of ammonium phosphate, $(NH_4)_2HPO_4$, in 250 cc. of water in a volumetric flask. The phosphorus content of a 25 cc. aliquot part of this solution was determined by precipitating with "molybdate solution" and filtering and washing the ammonium phosphomolybdate. The "yellow precipitate" was subsequently dissolved in NH_4OH, acidified with H_2SO_4, and the resulting solution passed through a Jones reductor into ferric phosphate solution and titrated with a solution of $KMnO_4$ (1 cc. = 0.0000431 g. P) that had been standardized against Bureau of Standards sodium oxalate. The actual phosphorus value of the solution was found to be 0.000114 g. per cc. as against the theoretical of 0.0001 g.

4. *Aluminum Solution.* Prepared by dissolving 8.9 g. of $Al_2Cl_6 . 12H_2O$ in water, adding H_2SO_4, evaporating until all free H_2SO_4 had been expelled, dissolving in water, and filtering and making up to 500 cc. in a volumetric flask. One hundred cc. of the solution was found to contain 0.2014 g. of aluminum.

5. *Calcium and Magnesium Sulfates.* In the experiments where known amounts of calcium and magnesium were added weighed amounts were employed of the c. p. salts, $CaSO_4 . 2H_2O$ and $MgSO_4 . 7H_2O$.

GENERAL DESCRIPTION OF EXPERIMENTS.

"Synthetic" solutions containing known amounts of one or more of the elements under consideration—uranium, vanadium, aluminum, calcium, magnesium, phosphorus and zinc—were prepared by measuring with accurately calibrated pipettes aliquot portions of the standard solutions or in a few instances (calcium and magnesium) by weighing the salts. When vanadium was present, the "synthetic" solution (volume 100 cc.) was acidified with 12 cc. of H_2SO_4 (sp. gr. 1.84), treated with enough $KMnO_4$ (approximately 0.1 *N*) to give a permanent pink color, and cooled to 10° C. The vanadium was precipitated by addition of an excess of a cold 6 per cent solution of cupferron and the precipitate (mixed with paper pulp) was filtered and washed with cold 10 per cent H_2SO_4 containing 1.5 g. of cupferron per L.

If the determination of vanadium was a part of the program, the paper holding the cupferron precipitate was dropped into an Erlenmeyer flask, and treated with 30 cc. of H_2SO_4 (sp. gr. 1.84) and 10 cc. of HNO_3 (sp. gr. 1.42) and evaporated to fumes. After several successive evaporations with 10 cc. portions of HNO_3 to destroy carbonaceous matter and one evaporation with 10 cc. of water to expel every trace of HNO_3, the vanadium was reduced with H_2O_2 and titrated with 0.05 *N* $KMnO_4$ (Cain and Hostetter's method). The filtrate from the cupferron precipitate was evaporated to a volume of about 50 cc., 20 cc., of HNO_3 (sp. gr. 1.42) were added, and the evaporation was continued until clouds of sulfur trioxide were evolved. A second evaporation with HNO_3 was made to destroy all organic matter, and the solution was finally evaporated with 10 cc. of water to remove all HNO_3. The solution was then diluted with the volume of water necessary to give the desired acidity—for example, 137 cc. of water if 8 per cent acidity was desired—cooled to room temperature, and passed through a Jones reductor in the manner previously described, the reductor then being washed with 100 cc. of the same strength (8 per cent in the example cited) sulfuric acid. The quadrivalent uranium solution was finally cooled to 5°-10° C. and treated with an excess of a freshly prepared 6 per cent solution of cupferron.

The precipitate does not begin to form until from 5 to 10 cc. of cupferron have been added. Some ashless paper pulp was introduced and the brown precipitate was filtered on an 11 cm. paper. The precipitate of $U(C_6H_5N_2O_2)_4$ was washed with cold 5 per cent H_2SO_4, containing 1.5 g. of cupferron per L., and ignited in a weighed platinum crucible, first at a low temperature and then at 1000-1050° C. in an electric muffle furnace into which a current of oxygen was passed. The crucible and precipitate were then cooled and weighed and the amount of uranium was calculated from the weight of U_3O_8. As a check on the gravimetric method the precipitate was fused with $K_2S_2O_7$, dissolved in 100 cc. of 6 per cent H_2SO_4, and the uranium determined by passing the cold solution through a Jones reductor and titrating with 0.1 *N* $KMnO_4$ as previously outlined.

Experience indicated that high uranium results are always obtained when uranium oxide (or ammonium di-uranate) is dissolved in HNO_3, and evaporated to fumes with H_2SO_4, preliminary to reduction with zinc and titration with $KMnO_4$. Addition of water and evaporation to fumes a second time does not eliminate the error, which is apparently due to obstinate retention of nitric acid by the uranium compound and subsequent reduction of the nitrate to hydroxylamine, NH_2OH, which is oxidized by $KMnO_4$. Uranium compounds should therefore be dissolved in H_2SO_4, or fused with $K_2S_2O_7$ and dissolved in H_2SO_4, rather than dissolved in HNO_3 and evaporated with H_2SO_4, as a preliminary to passage through the Jones reductor.

When elements such as aluminum, phosphorus, etc., were present in the "synthetic" solutions, the filtrate from the $U(C_6H_5N_2O_2)_4$ was evaporated with HNO_3 as already described, and the elements in question were determined by the usual methods.

1. *Experiments to Determine Whether Uranium in the Quadrivalent Form or in a Still Lower State of Oxidation is Quantitatively Precipitated by Cupferron.*

The factors that were kept constant in these experiments were:

1. The amount of uranium present, 0.0842 g. in each case.

2. The volume and acidity. In each experiment 100 cc. of the solution containing 6 cc. of H_2SO_4 (sp. gr. 1.84) were passed through the reductor, which was then washed with 100 cc. of 6 per cent H_2SO_4. The uranium was therefore precipitated from a solution having a volume of 200 cc. and containing 12 cc. of H_2SO_4 (sp. gr. 1.84).

3. Time of passage of solution and washings through reductor, about six minutes.

The conditions that were varied were:

1. The temperature of the solution passed through the reductor. In Experiments Nos. 1 and 2 the solutions were at room temperature, while in No. 3 the solution was heated to boiling previous to reduction to increase the amount of uranium reduced below the quadrivalent form.

2. In Experiment No. 2 the solution was given a preliminary reduction with 2 g. of zinc before being put through the reductor, the object being to reduce as much uranium as possible to a lower state of oxidation than the quadrivalent form. Similarly, in Experiment No. 1 the reduced solution was vigorously stirred for three minutes before precipitating the uranium with cupferron, while in Experiments 2 and 3 the uranium was precipitated immediately after the reduction.

Expt. No.	Acidity Per Cent.	Weight of U Used g.	Weight of U Found by Weighing the U_3O_8 g.	Weight of U Found by Zn Reduction and $KMnO_4$ Titration g.
1	6	0.0842	0.0843	0.0842
2	6	0.0842	0.0840	0.0835
3	6	0.0842	0.0844	0.0837

These results constitute reasonably conclusive evidence that:

1. Auger's statement that quadrivalent uranium can be quantitatively precipitated with cupferron is correct.

2. That uranium present in a lower state of oxidation than the quadrivalent form is also precipitated.

3. That the precipitation can be made in a solution containing 6 cc. of H_2SO_4 (sp. gr. 1.84) per 100 cc.

4. That when the precipitation is made from a solution containing 6 cc. of H_2SO_4 (sp. gr. 1.84) per 100 cc. the presence of zinc sulfate does not lead to any contamination of the $U(C_6H_5N_2O_2)_4$.

5. That the precipitate of $U(C_6H_5N_2O_2)_4$ can be quantitatively converted to U_3O_8.

The following two additional experiments furnish further confirmation of the above statements and also illustrate the separation of uranium from vanadium:

Expt. No.	Acidity Per Cent.	Weight of U Used g.	Weight of U Found by Weighing the U_3O_8 g.	Weight of U Found by Zn Reduction and $KMnO_4$ Titration g.	Weight of V Used g.	Weight of V Found g.
4	6	0.0127	0.0124	0.0123	0.1300	0.1295
5	6	0.1270	0.1264	0.1262	0.0260	0.0260

2. *Experiments to Determine Within What Limits of Acidity the Precipitation is Complete.*

The experiments already cited under (1) show that complete precipitation is obtained from a solution containing 6 cc. of H_2SO_4 (sp. gr. 1.84) per 100 cc. and the results of experiments shown under (4) prove that an acidity as high as 8 per cent can be successfully employed. Qualitative tests showed that when the concentration of H_2SO_4 was increased much above 8 per cent the uranium is not completely precipitated. Inasmuch as the results of the experiments shown under (4) prove that sharp separations from the accompanying impurities can be obtained in a 6 per cent H_2SO_4 solution, there is no reason for using higher concentrations than 6 per cent or 7 per cent.

3. *Experiments to Determine Whether the Uranium Precipitate, $U(C_6H_5N_2O_2)_4$, Can be Quantitatively Converted to U_3O_8 by Ignition.*

The results of numerous experiments tabulated under 1, 2 and 4 prove that the precipitate can be quantitatively ignited to U_3O_8.

4. *Experiments to Determine Whether Aluminum, Phosphorus, Calcium and Magnesium can be Quantitatively Separated from Uranium by Proper Regulation of the Acidity.*

(See Table on next page.)

Experiments 6 and 7 show that if the acidity is reduced as low as 2 per cent or 3 per cent the uranium precipitate drags down aluminum and probably phosphorus, while Experiment 8 proves that a sharp separation of uranium from aluminum and phosphorus is obtained with an acidity of 4 per cent. Experiments 9 and 10 show that uranium can be quantitatively precipitated from a 6 per cent H_2SO_4 solution, and that aluminum is not carried down, while Experiments 11 to 14 inclusive illustrate the separation from aluminum, calcium, magnesium, and phosphorus under similar conditions. Experiments 15 and 16 prove that the precipitation of uranium is complete with an acidity of 8 per cent.

Expt. No.	Acidity Per Cent	Uranium			Vanadium		Phosphorus		Wt. of Al_2O_3 Added g.
		Added g.	Found as U_3O_8 g.	Found with Zn and $KMnO_4$ g.	Added g.	Found g.	Added g.	Found g.	
6	2	0.2105	0.2188	0.2108	.....	.....	0.00057	......	0.1140
7	3	0.2105	0.2137	0.2097	.....	.....	0.00057	......	0.1140
8	4	0.1684	0.1679	0.1675	.....	.....	0.00114	0.00114	0.1980
9	6	0.0318	0.0316	0.0314	0.0260	0.0260	......	......	0.0760
10	6	0.0635	0.0628	0.0622	0.1300	.....	......	......	0.1885
11*	6	0.0635	0.0625	0.0624	0.1010	0.1022	0.00114	0.00112	0.1885
12*	6	0.0635	0.0636	0.0628	0.0202	0.0203	0.00342	0.00340	0.1885
13*	6	0.4210	0.4210	0.4194	.....	.....	0.00285	0.00284	0.1885
14*	6	0.2105	0.2103	0.2100	.....	.....	0.00285	0.00288	0.1885
15*	8	0.4210	0.4208	0.4200	.....	.....	0.00285	0.00285	0.0580
16	8	0.1684	0.1688	0.1681	.....	.....	0.00114	0.00116	0.1980

* In experiments 11 to 15 inclusive there were present in addition to the elements shown in the tabulation 0.05 g. CaO and 0.05 g. MgO. Zinc sulphate was of course present in all of the experiments.

Experiments 11 and 12 also illustrate the accuracy of the separation of vanadium from uranium, aluminum, calcium, magnesium, and phosphorus.

The following tabulations show the averages of the uranium and vanadium results obtained in the entire series of experiments excepting Nos. 6 and 7.

Uranium

Average weight used	0.1431 g.
Average weight found by weighing the U_3O_8	0.1429 g.
Average weight found by Zn reduction and $KMnO_4$ titration	0.1424 g.

Vanadium

Average weight used	0.0606 g.
Average weight found	0.0608 g.

CONCLUSIONS.

Study of the results of these experiments leads to the following conclusions:

1. Quadrivalent uranium, or uranium in a lower state of oxidation than the quadrivalent form, can be completely precipitated with a freshly prepared solution of cupferron from solutions containing from 2 to 8 cc. of H_2SO_4 (sp. gr. 1.84) in 100 cc.

2. The precipitate can be quantitatively converted to U_3O_8 by ignition.

3. If the amount of sulfuric acid in the solution is less than 4 cc. per 100 cc., aluminum, and probably phosphorus, will be carried down with the uranium, while if the acidity exceeds 8 cc. the uranium will not be completely precipitated. If the acidity be maintained between 4 and 8 per cent (preferably at about 6 per cent) a sharp separation of uranium from aluminum, zinc, calcium, magnesium, and phosphorus can be obtained by a single precipitation.

A large amount of convincing data has been presented to prove that uranium and vanadium can be separated and determined with a satisfactory degree of accuracy in the presence of widely varying amounts of iron, aluminum, calcium, magnesium and phosphorus, by a process involving the following steps:

1. Precipitation of the vanadium and iron from a 12 per cent H_2SO_4 solution in which the uranium, vanadium, and iron are present in the higher states of oxidation, *viz.*, in the sexivalent, pentavalent and trivalent forms. Uranium, aluminum, calcium (unless present in amount sufficient to precipitate out as the difficultly soluble $CaSO_4$), magnesium, and phosphorus pass quantitatively into the filtrate when the solution is filtered. Vanadium can be determined in this precipitate by any of the usual methods.

2. Destruction of the cupferron by evaporation of the filtrate with nitric acid.

3. Reduction of the uranium by passage of the solution through a Jones reductor. The zinc sulphate introduced into the solution does not interfere with the subsequent reactions.

4. Precipitation of the uranium from a 6 per cent H_2SO_4 solution with cupferron, followed by filtration and washing to remove aluminum, zinc, calcium, magnesium and phosphorus.

5. Ignition of the uranium precipitate to U_3O_8. After having weighed the U_3O_8, its uranium content may be checked by fusing it with $K_2S_2O_7$, dissolving the fusion in H_2SO_4, and passing the solution through a Jones reductor and titrating it with 0.1 *N* $KMnO_4$.

The reactions upon which this method is based are more sharp cut and dependable than any other with which the writers are familiar. The procedure has been applied to the analysis of uranium and vanadium ores and alloys with excellent results.

A paper presented at the Forty-third General Meeting of the American Electrochemical Society held in New York City, May 4, 1923, President Schluederberg in the Chair.

COBALT—ITS PRODUCTION AND USES.[1]

By C. W. Drury.[2]

Abstract.

In the preparation of the following paper dealing with the production and uses of the metal cobalt, an attempt has been made to review only the essential points. An extensive study of the occurrences, metallurgy, uses, and alloys of the metal cobalt was published recently,[3] and the reader is referred to that report for any detailed information.

In Table I is given the production of cobalt ores in the various countries. The figures in the table are interesting since they show the history of the mining of cobalt. The deposits of cobalt were small and often the metal was obtained as a by-product. Austria was the first large producer, followed by Germany, Norway and Sweden, Spain, Germany, New Caledonia and Canada. The consumption of cobalt compounds has gradually increased from that sufficient to supply the pottery industries of Europe, which would perhaps be approximately 10 tons in 1860, to a world's supply of 400 tons in 1920. The use of cobalt compounds for coloring glass has been known by the Chinese for perhaps 60 or 75 years. No record is available of the production, but it must have been small. At present the Chinese import cobalt supplies from America. A few remarks summarizing the metallurgy of cobalt have been incorporated in the paper.

In Table II a list of the commercial compounds of cobalt, showing the range in cobalt content, has been prepared.

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[1] Manuscript received February 24, 1923.

[2] Professor of Metallurgical Research, Queen's University, Kingston, Ont.

[3] Report of Ontario Bureau of Mines, XXVII, Part 3, 1918.

ORES.

The mining of cobalt ores has been carried on in Europe for a considerable time but no records of production are available previous to 1856. With the discovery of the cobalt deposits in Canada in 1903, the mining of cobalt ores in Europe and New Caledonia practically ceased. The mining of cobalt ore flourished best previous to 1860, in Austria, in Germany between 1872-1876 and 1889-1893, in Norway from 1877 to 1893, in Sweden 1876-1893, and in New Caledonia between 1893 and 1908.

Cobalt ores are usually associated with nickel, iron, copper, and silver minerals. Bismuth, antimony, arsenic, sulfur, manganese and lead are also often present.

The ore of New Caledonia is a hydrated oxide of manganese, cobalt and nickel, high in iron. The ores of West Australia are practically free from nickel. In Africa at the Union Miniere du Haut Katanga, cobalt is associated with copper. In the United States at Fredericktown, Missouri, nickel, copper and lead are the chief metallic constituents of the cobalt ore. The ores of Cobalt, Canada, contain chiefly arsenic, antimony, iron, and copper, and in addition, lead and bismuth.

The world's consumption of cobalt amounts to approximately 400 tons. The chief source of supply is Cobalt, Canada, but a small quantity (80 to 150 tons)[4] has been obtained within the last two years from Queensland, West Australia. The shipments from Australia have been made in the form of a concentrate containing from 20 to 33 per cent cobalt. The consumption is distributed between cobalt metal, oxide, and salts in about the following proportion: metal 175, oxide 200, salts 25 tons.

The tons of cobalt ore mined in the United States are not given separately, but the production of cobalt oxide has been recorded. Between 1870 and 1902, the quantity of cobalt oxide produced in the United States varied from 5,000 to 10,000 lb. per annum. In 1903 and 1908, the production increased to 120,000 and 100,000 lb. respectively. No further production has been reported until 1920 when 102,000 lb. was produced. These large recoveries were due to the operation of the Missouri mines and smelter.

The ores of Ontario continue to supply practically the world's

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[4] Mining Magazine, 26, 97 (1922).

requirements of cobalt. A few years ago, it was thought that the deposits of Belgian Congo would produce sufficient cobalt to satisfy the demands of Europe and Asia, but so far little, if any, has been recovered, and it is doubtful whether the recovery of cobalt from the copper ores would prove a commercial operation.

Several reports concerning the deposits of West Australia have appeared in the technical journals. In 1922 a crushing and concentrating plant at a cost of $200,000 was constructed. To concentrate at a profit an ore for the cobalt content alone presents a difficult problem. It is true the ores of Cobalt, Canada, are concentrated, but the silver recovered is charged with the costs of operation. Unless the costs of mining, milling and refining the ores of West Australia are low, there will no doubt, be many difficulties to overcome before the deposits are fully developed.

TABLE I.

Tons of Cobalt Ore Mined.

Year	Germany	Austria	Norway	Sweden	New Caledonia	Spain	Canada
1856	6	136	...	...	....	...	....
1861	1	...	...	...	....	...	....
1871	18	...	25	...	....	4	....
1881	33	40	80	556	....	102	....
1891	576	...	187	244	....	60	....
1901	36	...	...	...	3.123	...	....
1904	41	...	...	...	8.964	...	16*
1909	...	...	...	...	979	...	1,533
1911	...	...	...	...	....	...	852
1916	...	...	...	...	....	...	400
1917	...	...	...	...	....	...	337
1918	...	...	...	...	....	...	380
1919	...	...	...	...	....	...	298
1920	...	...	...	...	....	...	283
1921	...	...	...	...	....	...	127
1922	...	...	...	...	....	...	221

* Figures for Canadian production are given in tons of cobalt metal.
For complete Table see report of Ontario Bureau of Mines XXVII, Part 3, 1918.

METALLURGY.

The common methods employed to treat cobalt ores are either chemical or smelting. The chemical method is employed more for the fairly pure ores, and consists generally in dissolving the metallic constituents of the ore in acid, followed by precipitations to remove the various metals and impurities. The smelting process which is used almost entirely on the ores of Cobalt, Canada, produces first a speiss. The speiss contains approximately 35 to 40 per cent cobalt and nickel, 15 per cent iron, 35 per cent arsenic, and 1100 oz. of silver per ton, in addition to lead and copper.

The separation of the several metals in speiss from the cobalt presents numerous difficulties. These are due mainly to the similar properties of the three metals, iron, nickel, and cobalt. It is impossible in a commercial operation to separate the previously mentioned metals by fire methods, by depending on the different degrees of oxidation or reduction. Therefore, in the standard process for treating speiss, all the constituents are dissolved in acid, sulfuric being commonly employed. The necessity of adding acid to dissolve all other metals in addition to the cobalt adds greatly to the cost. The similarity of the properties of the three metals still exists after being rendered soluble. Alkaline hydrates or carbonates, the cheapest precipitants, precipitate under ordinary conditions hydrates or carbonates of the three metals. The large quantities of iron, arsenic, and acid which must be removed retain considerable quantities of cobalt solutions, and are a source of heavy losses. For the foregoing reasons, it is necessary to operate on dilute solutions to effect anything approaching efficiency in the various precipitations.

The following figures show the extent of the removal of the impurities in the metallurgy of cobalt.

Analysis	Co	Ni	Fe	As	S	Cu	SiO_2
Ore	5	4	10	14	7	1	20
Oxide	70.5	1.0	0.25	trace	0.1	0.03	0.2

The corrosive effect of solutions obtained at the different stages in the metallurgy of cobalt is serious. The handling of large tonnages containing sulfuric acid, copper and ferric sulfates presents a problem most difficult to solve. Practically every metal or alloy on the market has been tested in the solutions, but so far nothing has been found which will withstand the corrosion and abrasion. It may be of interest to the members of this Society to know in the production of 1 lb. of cobalt it is necessary to handle 3000 lb. of solution.

After the sulfur, iron, arsenic and copper have been removed, the separation of the cobalt from nickel is the next operation. The cobalt is precipitated as cobaltic hydrate $Co(OH)_3$ by hypochlorite solutions. To get a pure product the oxide is dissolved and reprecipitated. In the precipitation of cobalt, chlorine is evolved, which is hard on the workmen, and the moist chlorine gas is very corrosive on exhaust fans and pipe lines.

The metallurgy of cobalt presents some interesting problems, to those engaged in the study of finding a suitable material to resist the combined corrosive effect of acid solutions of copper and ferric sulfates.

Recently a patent[5] was granted covering the treatment of cobalt ores with chlorine gas. It is planned to operate the process at the plant of the Coniagas Reduction Co., Thorold, Ont. Little is known at present of the details of the process, but it is understood that the arsenic and iron are volatilized as chlorides at certain temperatures.

USES.

Cobalt metal is used chiefly in the manufacture of stellite, and as one of the main constituents of permanent magnets. The superiority of stellite as a cutting tool has been definitely established. The addition of cobalt permits magnets[6] to be made of less than half the weight of those made of ordinary tungsten magnet steel.

The oxide is used mainly for coloring in the ceramic and enamel industries and in the preparation of cobalt salts. Cobalt salts are used as driers in paints and varnishes, as catalytic agents in the hydrogenation of oils, in the preparation of certain printing inks, and in stains in the ceramic industries. Cobalt silicate possesses a rich blue color and is used extensively in the china trade. In enamels, cobalt is used to neutralize the yellow tinge due to iron oxide.

The salts of cobalt which are at our disposal in commercial quantities are all of the cobaltous or divalent type. It has been found that although they can be readily used in the manufacture of driers, and worked like the various compounds of manganese,

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[5] E. W. Westcott, U. S. Patent No. 1,406,595.

[6] Honda and Saite, K. S. Magnet Steel, Electrician, 85, 705, (1920); Steels for Permanent Magnets, Electrician, 86, 327, (1921); Kayser, Electrician, 88, 421 (1922).

lead, zinc, calcium, aluminum, etc., the organic compounds formed, which are the basis of the so-called driers, are not efficient while in the cobaltous state. The formation of trivalent cobalt compounds is sought in the making of driers. The value of cobalt compounds depends not on their power to dry linseed oil, but on their ability to make the lower priced semi-drying oils act like linseed oil.

TABLE II.

Composition of Commercial Cobalt Compounds.

	Formula	Theoretical Per Cent Cobalt	Per Cent Cobalt in Commercial Product
Cobalt	Co	....	97.5
Cobaltous Oxide	CoO	78.65	75.0
Cobaltous Cobaltic Oxide	Co_3O_4	73.43	70.5
Cobaltic Oxide	Co_2O_3	71.00	...
Cobalt Acetate	$Co(C_2H_3O_2)_2 . 4H_2O$	23.70	23.0
Cobalt Borate	$2CoO . 2B_2O_3 . 4H_2O$	32.60	30.0
Cobalt Carbonate	$CoCO_3$	49.58	43.5
Cobalt Chloride	$CoCl_2 . 6H_2O$	24.80	24.0
Cobalt Hydrate:			
Black	$Co(OH)_3$	53.64	50.+
Pink	$Co(OH)_2$	63.44	57-62
Cobalt Nitrate	$Co(NO_3)_2 . 6H_2O$	20.27	20
Cobalt Linoleate:			
Solid	$Co(C_{18}H_{31}O_2)_2$	9.56	7.-7.5
Liquid	....	....	5.0
Cobalt Phosphate	$Co_3(PO_4)_2 . 2H_2O$	43.92	41.0
Cobalt Resinate	$Co(C_{44}H_{62}O_4)_2$	4.31	1.5 (fused)
Cobalt Sulfate	$CoSO_4 . 7H_2O$	20.90	20-21
Cobalt Ammonium Sulfate	$CoSO_4 . (NH_4)_2SO_4 . 6H_2O$	14.93	14.5
Cobalt Tungate stereoisomer of linoleate	....	9.56	...

In conclusion it may be added that unless some extensive cobalt deposits are found, the source of cobalt is limited. The cobalt content of the present ores is gradually decreasing and the impurities are increasing, which has a tendency to raise the cost of production. The superiority of cobalt and its compounds in the stellite, magnet steel, ceramic, paint and varnish industries has been established. The properties of cobalt and its compounds are remarkable, varying from imparting great hardness and strength in stellite, high magnetic retentivity in permanent magnets, beautiful blue color in china and enamels, to its action as a catalytic agent in the oxidation or hydrogenation of oils. The demand for cobalt or its compounds is becoming greater, but its use will no doubt, be confined to those industries in which the price of the raw material is small in comparison with the results achieved or savings effected.

DISCUSSION.

KENNETH S. GUITERMAN[1] (*Communicated*): I have read this paper with exceeding interest. Having in mind the fact that the cobalt industry as such would undoubtedly be materially benefited through a better understanding of the metallurgy, I venture to emphasize some of the salient features which have apparently escaped the attention of Prof. Drury.

As is undoubtedly well appreciated, the primary cause of the high cost of producing cobalt has, in the past, been a consequence of the cumbersome and highly unsatisfactory method of separating it from its constituent, nickel. This has almost universally been accomplished through the medium of sodium or calcium hypochlorite. Through the addition of this oxidizing agent to an essentially neutral solution containing both cobalt and nickel, it was possible to precipitate a hydrated oxide of cobalt. Unfortunately, the precipitation was extremely imperfect, in that the precipitant likewise reacted with nickel. The net result of this was that the separation had to be carried out through numerous fractionizations, each product thereof containing varying proportions of cobalt and nickel. Hence, it is obvious that an operating plant became burdened with large quantities of intermediary by-products, none of which were suitable for the market and all of which necessitated re-treatment.

In 1914 and 1915 the Research Department of the American Smelting and Refining Company, under my direction, undertook the development of a new and more efficient process for the separation of cobalt and nickel. This work was largely a conse-

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[1] New York City.

quence of the Smelting Company having in its possession large tonnages of cobalt-nickel speiss. This speiss, of course, locked up an appreciable amount of both gold and silver. Hence, it was primarily with a view to recovering these precious metals that the process was devised.

After some months of laborious and pains-taking work, a method of electrochemical separation was devised, whereby it became possible to separate cobalt from nickel electrolytically and without the formation of by-products, under conditions of operating efficiency in excess of 98 per cent. The process, as patented by myself, consisted briefly of sulfating the speiss, followed by a solution thereof in water. After the preliminary removal of iron, arsenic, copper, etc., the resultant cobalt-nickel sulfate solution was evaporated to a high degree of concentration. Salt was added slightly in excess of the theoretical quantity necessary to produce nascent sodium hypochlorite. The solution was then electrolyzed in soapstone hopper-bottom tanks, under conditions of great velocity of circulation and high current density. Copper cathodes and graphite anodes were employed. The solution was maintained faintly acid at all times through the addition of a solution of sodium carbonate of approximately $N/1$ normal. In order to preclude the formation of insoluble carbonates, the addition of the sodium carbonate was made in the form of a cloud over the reservoir containing the circulating sulfate solution. Regulation of the acidity was maintained throughout the entire process by frequent electrotitrometric determinations, litmus and other indicators being worthless, because of the intense green color of the solution.

The current efficiency of the process was excellent, and as I have stated above, the separation of the cobalt from nickel was all that could be desired. The end-point of the reaction was manifest through the practical absence of cobalt in solution. As soon as this moment was reached, the entire solution was filter-pressed, thereby removing the hydrated oxide of cobalt from suspension. This was washed in the usual method with water and possibly dilute sulfuric acid. The filter-pressed cakes after discharge were then calcined, so as to produce the gray or black oxide of cobalt as might be desired.

Throughout the entire operation of the plant, the process functioned without difficulty, and the most high-grade product was put on the market. Insofar as costs were concerned, I may say that they were low, and would have permitted of the active competition of cobalt versus nickel, without appreciable danger to the former.

The above briefly described method is, in my judgment, eminently superior to the others which have so far been devised, including that of treatment with chlorine gas. The objection to all of these is that by-products either form or are so liable to formation as to render the process hazardous. No such condition presents itself in the electrolytic method.

E. O. BENJAMIN[2]: A use was devised for cobalt by I. H. Levin, as an oxygen electrode in electrolytic cells, claiming a higher efficiency or lowering of the oxygen over-voltage. But since the time of the appearance of that patent[3], as well as the description, I have made some experiments which do not seem to confirm that claim. I have found the efficiency of a cobalt electrode is somewhat lower than that of a nickel electrode.

COLIN G. FINK[4]: May I ask Mr. Benjamin if a cobalt-plated iron electrode was used?

E. O. BENJAMIN: Yes.

COLIN G. FINK: Our tests have shown that a cobalt-plated iron electrode is decidedly better as an oxygen electrode than a nickel-plated iron electrode. Perhaps you did not get enough cobalt on your electrode.

O. C. RALSTON[5]: I am a little surprised to hear the present commercial methods of separating nickel and cobalt accused of being so inefficient. It recalls a little piece of work done by M. J. Udy and myself some years ago on separating these two metals from each other. Chlorine was used to oxidize the cobalt to the higher stage of oxidation in the presence of finely divided calcium carbonate to cause its hydrolysis to the black oxide. As long as the solution was kept cold only the cobalt precipitated and the

[2] Consulting Engr. and Chemist, Newark, N. J.

[3] U. S. Pat. 1,214,934.

[4] Consulting Metallurgist, New York City.

[5] U. S. Bureau of Mines, Berkeley, Calif.

separation was practically quantitative. In fact, Mr. Udy, who did most of the experimental work, told me that he found he could use it also as an analytical method and that it seemed to be more sensitive than the dimethyl glyoxime separation.

COLIN G. FINK: I may add to Mr. Ralston's remark that Prof. Edgar F. Smith and Prof. H. S. Lukens, of the University of Pennsylvania, have worked out an analytical method for the separation of cobalt from nickel[6]. Cobalt is deposited as an oxide at the anode, and nickel as metal at the cathode.

R. B. MOORE[7]: The price of cobalt oxide for a good many years was from $1.00 to about $1.50 a pound, and then it went up to $4.50. We tried to investigate why that was, but without success, unless it was that at that time the principal cobalt property in this country was absorbed by foreign interests. However, the question that is obvious is, how long would a $3.00 price last if other companies got into the game? There are a number of small cobalt deposits in this country, and naturally if there were a chance of their succeeding we would like to see them do something. But under such conditions, would the price of $3.00 a pound suddenly drop?

C. W. DRURY (*Communicated*): Mr. K. S. Guiterman emphasizes the electrochemical method of precipitating cobalt compared with that employing hypochlorite solutions. In the electrochemical method, it appears that the salt is electrolyzed, giving chlorine and caustic. These two products unite in the cell, giving what Mr. Guiterman calls "nascent hypochlorite."

To produce cobalt as cobaltic hydrate, a certain quantity of hypochlorite is necessary. The standard, as well as the Guiterman method, requires hypochlorite, and the whole question under discussion appears to be whether hypochlorite can be prepared more cheaply from calcium bleach, liquid chlorine and soda, or by electrolyzing the salt solution as in the Guiterman method. Special attention has been given to the development of cells to produce chlorine efficiently, *e. g.*, Nelson, Allen Moore, and Townsend, and even in the best an energy efficiency of 60 per cent is high.

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[6] Trans. Am. Electrochem. Soc., 27, 31 (1915).

[7] c/o The Dorr Co., New York City.

A paper presented at the Forty-third General Meeting of the American Electrochemical Society held in New York City, May 4, 1923, President Schluederberg in the Chair.

CHROMIZING.[1]

By F. C. Kelley.[2]

Abstract.

It is the purpose of this paper to give a brief summary of the work which has been done to date upon the diffusion of metals in the solid state, and to describe in detail the process of chromizing, and its effects upon the physical and chemical properties of iron. The practical application of this process is also considered.

There are many other metals which diffuse in the same manner when brought into contact with each other at temperatures below their melting points. This field may be the subject of a future paper.

SUMMARY OF LITERATURE.

It has long been known that solid bodies are capable of diffusing into one another. The old cementation processes are based upon this fact, but it is only within comparatively recent years that any practical use has been made of this knowledge.

Faraday and Stodard in 1820 while experimenting on the alloys of iron observed that steel and platinum wires when tied together in bundles could be welded at a temperature considerably below that at which either of the metals melted. Upon etching the welded mass with acid, the iron appeared to be alloyed with the platinum.

Chernoff in 1877 discovered that if two surfaces of iron are

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[1] Manuscript received February 1, 1923.

[2] Research Laboratory. General Electric Co., Schenectady, N. Y.

heated to 650° C. in intimate contact with each other they will unite.

Spring in 1882 discovered that alloys might be produced by compression of their constituent metals in a fine state of division.

Hallock in 1888 showed that similar results to those of Spring could be obtained at higher temperatures without pressure.

Roberts-Austen in 1896 published results of experiments on diffusion of gold in solid lead at various temperatures, and in 1900 published additional data on the same work in the Proceedings of The Royal Society.

C. E. Van Ostrand and F. P. Dewey of the U. S. Geological Survey in 1915 checked up Roberts-Austen's work.

Tycho Van Aller of the General Electric Company patented in 1911 a process (calorizing), which depends upon the diffusion of aluminum into metals below its melting point.

E. G. Gilson, of the General Electric Company, patented in 1914 another process of calorizing metals, in which greater penetration of aluminum is obtained by operating at higher temperatures, and in an atmosphere which protects the aluminum from oxidation. Hydrogen is the usual atmosphere used.

Cowper-Coles, in June, 1902, and in August, 1906, received patents on coating iron with zinc to protect it from corrosion. The zinc forms an alloy with the iron at a temperature below the melting point of zinc, and the surface of the coated metal is nearly pure zinc, which resists corrosion.

Collins and Capp, of the General Electric Company, patented a process of sherardizing in January, 1916, in which they describe an improved sherardizing process, in which the zinc content of the sherardizing mixture and the temperature are correlated in a new way.

Calorizing and sherardizing are two commercial processes which depend upon the alloying of metals at temperatures below their melting points. In the case of calorizing I refer to the Van Aller process.

Chromizing, the subject with which this paper is chiefly concerned, is another patented process which depends upon this same property of diffusion of metals at temperatures below their melting points.

THE METHOD.

The process consists of packing the material to be treated into a powdered mixture of alumina and chromium. The amount of each material used in the mixture is 45 per cent of alumina and 55 per cent of chromium by weight. The material is usually packed into a tube of iron, and then heated at 1300 to 1400° C. in hydrogen, in vacuum or in some neutral atmosphere, for lengths of time depending upon the penetration and concentration of chromium desired.

Where a protective atmosphere like hydrogen is used it is absolutely necessary that it should be free from all oxygen and water vapor, for at the high temperatures at which this work is carried on the chromium powder would be rapidly consumed by oxidation. In fact as soon as a film of oxide is formed on the surface of the fine particles they refuse to react with the metal to be chromized. This purification is accomplished by first passing the hydrogen through a sulfuric acid tower, to remove most of the water. The gas is then passed over a copper gauze, heated to about 600° C., to get rid of any oxygen present by combining the oxygen with the hydrogen, the copper acting as a catalyzer. The water formed in the copper furnace is then taken out by passing the gas through additional sulfuric acid towers, after which it is passed over potassium hydroxide to take out any sulfuric acid vapors. Finally it is passed over phosphorus pentoxide to remove the last traces of moisture. This gas then goes directly to the chromizing furnace.

The furnaces used for this work consist of alundum tubes wound with molybdenum wire as a heating unit. These tubes are placed in a suitable furnace casing and surrounded with alumina powder, which acts as a heat insulating material.

The hydrogen atmosphere of this furnace serves a double purpose. It not only prevents the burning up of the chromium, but it also protects the molybdenum from oxidation, and thus enables us to attain with ease the high temperatures at which we operate.

In order to indicate the size of the furnace of this type which may be used to advantage, I may say that we have operated two furnaces, which were each made of four alundum tubes, 60 cm.

long, 20 cm. inside diameter and 13 mm. walls, placed end to end in a metal casing, and held in line by means of a strip of sheet molybdenum 25 mm. wide and 0.63 mm. thick bound around the tubes at the joints. The tubes at the joints were supported in the furnace casing by fire brick cut to fit the tubes. The molybdenum band also serves to keep the alumina from falling into the furnace through the joints formed at the ends of the tubes.

The winding for these tubes was molybdenum wire 1.91 mm. diameter, and there were two windings on each tube. Each winding consisted of 22 turns 12.7 mm. apart, with the exception of the two end windings, which were wound 8.5 mm. apart to compensate for radiation at the ends of the furnace. The furnace casing was 2.74 meters long and 53.3 cm. square. The inside was lined with a single row of fire brick, and the space between the brick and furnace tube was filled with alumina.

The furnace was operated directly from a 1000-volt a. c. generator, by means of a resistance in the field of the machine. Two large transformers, connected in parallel, were used to step the voltage down from 1000 to as low as 12 volts. The windings of the furnace were all connected in parallel.

These furnaces will carry without trouble a charge weighing 136 kg. (300 lb.) distributed over 1.83 m. (6 ft.) of its length at 1350° C.

The chief use for these furnaces was in chromizing turbine buckets, which have been installed in various turbines throughout the country, in order to test them for corrosion under actual operating conditions.

MATERIALS REQUIRED.

In chromizing it is necessary to have powdered chromium of at least 95 per cent purity, for chromizing iron which is intended to withstand corrosion. Powdered Al_2O_3 is necessary as a diluting agent, and to prevent excess sintering of the powdered material at high temperatures. It is also necessary to have pure hydrogen, free from moisture and oxygen. And last of all it is necessary to have a furnace which will operate at a temperature of 1300° C. or higher, and in an atmosphere of hydrogen.

STRUCTURE.

Chromized iron, with which I am going to deal chiefly, when examined under the microscope, has a structure which seems to be characteristic of all metallic coatings obtained by diffusion. This chromium-iron alloy, which is a solid solution of chromium in iron, is made up of an area of elongated grains, with their longer axes perpendicular to the surface chromized, and the line of penetration is generally very sharp. Sometimes there seems to be a cylinder of grains arranged in this manner on the surface of a chromized iron rod. Then again there seems to be two or more such bands or cylinders, which contain varying amounts of chromium, for each band etches up differently. The one with the highest chromium content etches up the slowest.

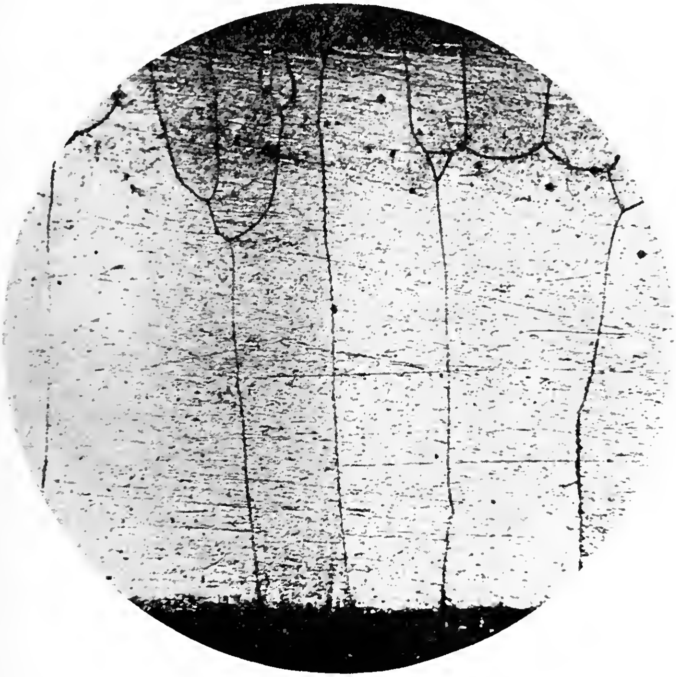

FIG. 1.
Chromized iron heated at 1,350° C. for 4 hr. x 70.

Fig. 1 illustrates the chromized iron surface, consisting of a layer of elongated grains. The longer axis of each grain is at right angles to the surface chromized. Fig. 2 illustrates a piece of chromized iron, showing two distinct bands on the surface. If we were to analyze samples from each band, we would find that the inner band had a lower chromium content than the outer band.

FIG. 2

Chromized iron showing banded structure of the chromized section.

Fig. 3 also shows three distinct bands outside of the iron core. The outer band, which is very narrow, seems to be made up of almost pure chromium, sintered together and alloyed to the chromium-iron band just underneath. This is a cross section of a sample fired in pure chromium at 1350° C. for 3 hr.

If we chromized a sample at the same temperature as the sample shown in Fig. 1, but for twice the length of time (8 hr.) we would get no sharp line of penetration, and the large elongated grains we would find had broken into somewhat smaller grains, as is shown in Fig. 4. If we analyzed the surface coatings of samples shown in Fig. 1 and 4, we would find that the sample of Fig. 1 would show the higher per cent of chromium. The chromium content of the other sample would be reduced, due to greater diffusion for it has been fired twice as long.

Fig. 3.
Chromized iron heated in pure chromium powder at 1,350° C. for 3 hr. x 57.

CONTACT PROCESS.

In chromizing, even at these high temperatures, the vapor pressure of chromium is very low, and all of the chromium which is taken up by the iron must be in contact with it. If it is desired to increase the chromium content of a surface coating, it is necessary to give the sample a second treatment. This fact is illustrated by examination of the somewhat sintered chromizing mixture where it has been in contact with the iron treated. The surface of the sintered mixture is white, showing that all of the chromium has been taken up by the iron surface in contact with these finely divided particles, leaving only the white Al_2O_3 behind. If this sintered piece of mixture is broken at right angles to the surface examined, chromium particles will be found just under the Al_2O_3 surface.

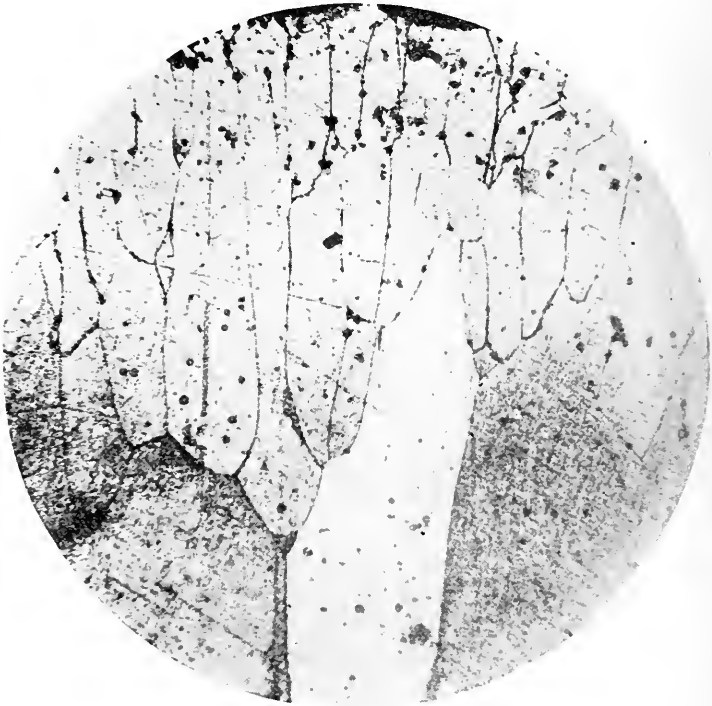

FIG. 4
Chromized iron heated at 1,350° C. for 8 hr. x 42.

THE EFFECT OF CARBON.

In order to get the best chromizing results it is necessary to use an iron or steel of low carbon content, for iron of high carbon content does not chromize well. The carbon seems to retard the penetration of the chromium. It is possible to chromize it if it is first decarbonized by firing in hydrogen. Another essential point is to have the samples to be chromized well cleaned and free from oxide or rust.

THE DIFFICULTIES.

The Al_2O_3 if new should first be fired before using, in order to drive out any moisture which it may have taken up. Then it may be mixed with chromium powder and kept in closed cans. This mixture may be used over and over again, and chromium added at intervals to maintain the chromium content.

The determination of the amount of free chromium metal present is one of the worst troubles with which we had to contend. We were not able to determine the amount of chromium present exclusive of the oxides of chromium. The only way that we could check up our mixture was to put test samples in each run and compare these samples with others which we considered good.

It is almost impossible to run a furnace of the type which I have described without getting some oxidation, because the Al_2O_3 used as the furnace insulation and also as a part of the chromizing mixture is active towards moisture. But where the furnace and mixture are being constantly used, there is little chance to take up moisture, and under these conditions we get the best results. The oxidation of the chromium mixture always took place to some extent at the open end of the containing vessel, and this powder at the end was always discarded, so as not to contaminate the rest of the mixture when used again.

CHROMIZING DATA.

In order to give an idea of the amount of chromium taken up by a sample and the penetration I shall give the data shown in Table I. These samples were about 1.27 cm. x 1.27 cm. x 1.27 to 1.59 cm. (½ x ½ x ½ to ⅝ in.) Three samples were used and one sample was taken out after each chromizing run at 1300° C. for 3 hr.

Table II contains the data on samples heated at 1200° C., 1350° C. and 1400° C. for 3 hr. periods.

Fig. 5 shows the effect of time upon the penetration of chromium at 1300° C. The samples were rechromized into a new mixture after each run of 3 hr.

Fig. 6 shows the effect of temperature upon the penetration, where the time of heating at each temperature is maintained constant for 3 hr.

We must remember that in firing a sample of iron in a chromizing mixture and in a hydrogen furnace, that a sample which is fired at 1400° C. must be brought up through the range of temperatures between 1200-1400° C., and that chromizing and diffusion are taking place during the time that the sample is being heated through this range. It is almost impossible to put a chromizing charge into a hydrogen furnace at 1200-1400° C. without having the entire charge blown out of the containing tube due to the sudden expansion of gases. Even if this were possible it

TABLE I.

Chromizing Data.

Sample No.	Weight before chromizing g.	Weight after first chromizing g.	Difference in weight in grams and per cent	Weight after second chromizing g.
2.1	19.7518	19.8861	0.67 per cent 0.1343 g.	
2.2	21.9863	22.1382	0.69 per cent 0.1519 g.	22.2325
2.3	23.1170	23.2802	0.706 per cent 0.1632 g.	23.3780

	Difference in weight in per cent and grams.	Weight after 3rd chromizing g.	Difference in weight in grams and per cent	Average penetration of chromium mm.
2.1	....	....	....	0.178
2.2	1.12 per cent 0.2462 g.	....	....	0.343
2.3	1.13 per cent 0.2610 g.	23.3275	1.77 per cent 0.4105 g.	0.558

TABLE II.

Sample No.	Weight before chromizing g.	Weight after chromizing g.	Difference in weight in per cent and grams	Temperature in °C.	Average Penetration mm.
H.1.12	16.5594	16.5776	0.11 per cent 0.0182 g.	1200	0.076
H.1.135	20.7165	20.8590	0.69 per cent 0.1425 g.	1350	0.457
H.1.14	21.9600	22.220	1.18 per cent 0.2600 g.	1400	1.09

would be hard to judge just when the samples within this heat insulating mixture came up to any given temperature. These figures then must be taken as the average obtained in standard practice.

It is almost impossible to chromize a steel of high carbon content, such as drill rod, until after the carbon content has been greatly reduced by decarbonization, as by firing in hydrogen. If a sample of drill rod is chromized at 1300° C. in the regular way, we notice that it has lost in weight, but, upon examination, we find that some chromium has been taken up by the iron. When we polish a cross section of the sample, and examine it under the microscope, we find that the penetration is very irregular and varies so much that it is not possible to state even the average penetration for such a sample. There seem to be shiny needle-

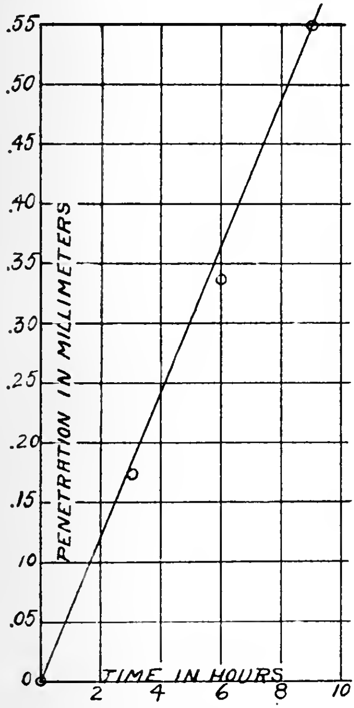

FIG. 5.
Curve showing the change in penetration of chromium with the time.

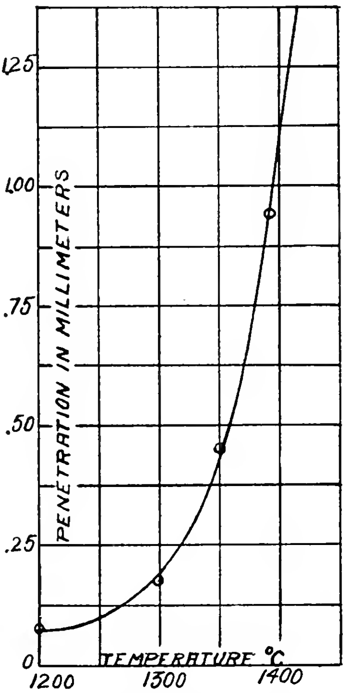

FIG. 6.
Curve showing the effect of temperature upon the penetration of chromium.

like projections from the well-defined chromized ring at the edge, which is about 0.05 to 0.076 mm. (0.002-0.003 in.) in width. Upon refining a sample a second and still a third time, we notice that the sample begins to increase in weight, because the carbon is nearly all taken out of the sample by the hydrogen. The chromized ring takes on a much more regular shape or has a more uniform penetration, and with each firing takes up an increasing amount of chromium.

The data given in Table III are obtained by firing three drill rod samples of about 0.8 per cent carbon in chromizing mixture at 1300° C. for 3-hr. periods, removing one sample after each firing.

TABLE III.

Chromizing Drill Rods

Sample No.	Weight before chromizing g.	Weight after first chromizing g.	Difference in weight in g. and per cent	Weight after second chromizing g.	Difference in weight in g. and per cent	Weight after third chromizing g.	Difference in weight in grams and per cent	Average penetration of Cr mm.
3.1	19.6248	19.6152	0.05 per cent —0.01 g.	Removed	....	....	....	0.076
3.2	20.6339	20.6256	0.04 per cent —0.008 g.	20.6958	0.34 per cent +0.07 g.	Removed	....	0.127
3.3	19.7910	19.7890	0.01 per cent —0.002 g.	19.8630	0.37 per cent +0.074 g.	19.9783	0.957 per cent +0.1893 g.	0.420

In order to show the effect of diffusion at 1350° C., I took eight especially turned sample rods and chromized them all at 1350° C. for 3 hr. I took out sample No. 1 and had the chromized surface turned off to the depth of penetration of the chromium. The remaining seven samples were then fired in hydrogen for an equal length of time at 1350° C. and sample No. 2 was taken out and the chromized surface turned off. This was repeated until we had chromized four times and reheated in hydrogen four times. The samples were taken out as above, one by one in their order. After each treatment the turnings were analyzed for chromium content. The results are given in Table IV.

TABLE IV.

Sample No.	Time chromized hr.	Time heated in H_2 hr.	Temperature of chromizing and heating °C.	Per cent of chromium
1	3	..	1350	10.42
2	3	3	1350	6.97
3	6	3	1350	12.15
4	6	6	1350	8.70
5	9	6	1350	15.50
6	9	9	1350	9.62
7	12	9	1350	14.39
8	12	12	1350	9.77

We must remember that this analysis represents the average chromium content of the layer turned off. The chromium content of this layer near the surface of the sample is much higher than the average shown by analysis. The fact that the percentage of chromium content decreases each time after firing in hydrogen is due to increased penetration of the chromium into the chromized layer. Since the surface is not in contact with chromium when reheated in hydrogen, it is not able to take up additional chromium. The diffusion of the chromium, gained by chromizing, through a greater volume of the sample by means of firing in hydrogen decreases the percentage of chromium content.

We notice that with each additional chromizing treatment the tendency of the chromized layer is to increase in percentage of chromium content above that of the previous chromizing, in spite of the fact that between each chromizing the chromium content of this layer has been reduced by diffusion. That is, the chromium content of the layer is reduced on the average by hydrogen firing 4.24 per cent, and for every time it is rechromized it increases on the average of 5.4 per cent, so the net result is a continual percentage increase of the chromium with each chromizing.

Fig. 7 is a photograph about actual size taken of samples which have been alternately chromized and heated at 1350° C. The first sample shown at the left is chromized, and from left to right they are alternately chromized and heated so that the last sample has been chromized four times and heated four times. The penetration is quite sharp in each sample with the exception of sample No. 2, which has been heated in hydrogen for 3 hr. after the first chromizing. The diffusion of the chromium has decreased the distinctness of the chromized layer.

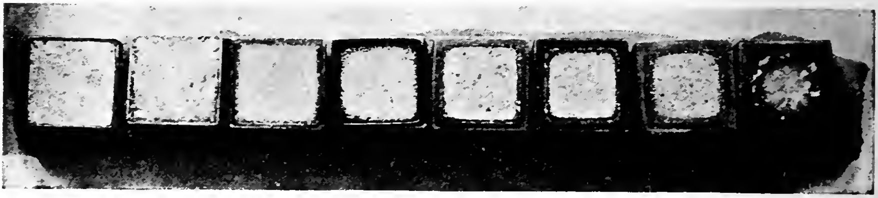

Fig. 7.
Samples of chromized iron showing the effect of alternate chromizing and heating. x 1.

The effect of concentration of chromium powder is shown when we pack the samples to be chromized into pure chromium powder, for the penetration at any given temperature for a given length of time is greatly increased. This is shown in Table V.

Table V.

Sample No.	Weight before chromizing g.	Weight after chromizing g.	gain in weight g.	Per cent gain in weight	Time of chromizing hr.	Temperature of chromizing °C.	Penetration mm.
1	43.8459	45.8186	1.9727	4.5	3	1350	0.852
2	43.7816	45.5701	1.7885	4.10	3	1350	....
3	43.7585	44.9604	1.2019	2.74	2	1350	0.533
4	43.8480	44.8967	1.0487	2.40	2	1350	....
5	43.7020	44.7787	1.0767	2.46	1	1350	0.406
6	43.7895	44.7177	0.9282	2.12	1	1350	....

The percentage gain in weight is much greater where pure chromium is used, for the pure chromium particles are fused to the surface in a much closer arrangement, and the rate of diffusion being so much greater also helps to account for the increase in weight.

In order to get some of the physical characteristics of chromized iron, I fired some iron wire in vacuum at 1300° to 1400° C. for 1.5 hr. and obtained the results recorded in Table VI.

TABLE VI.

Physical Characteristics of Chromized Iron.

Temperature of chromizing °C.	Time chromized hr.	Weight before chromizing g.	Weight after chromizing g.	Per cent increase in weight	Diameter before chromizing mm.	Diameter after chromizing mm.
1300-1400	1.5	2.2673	2.568	11.7	0.89	1.0
1400	2	2.2666	2.7705	22.6	...	...

Temperature of chromizing °C.	Per cent increase in diameter	Resistance before chromizing in microhms per cc.	Resistance after chromizing in michrohms per cc.	Specific gravity before chromizing	Specific gravity after chromizing
1300-1400	12.9	...	...	...	...
1400	..	11.53	86.2	8.11	7.62

This wire had a large grain structure, but was not brittle. It was surprisingly soft for the amount of chromium which it had taken up. The chromium had diffused entirely through the wire. It was heated in the open air by passing a current through it at 1050° C. for 200 hr. without burning out, thus showing the protective value of chromium as far as oxidation is concerned.

RESISTANCE TO CORROSION.

In testing samples of chromized iron, we ran them in salt spray along with blanks and found that after a month the blank sample, 3 mm. (0.125 in.) thick, was about half corroded away, while a chromized sample had here and there slight signs of attack.

Chromized samples tested along with sherardized iron samples in salt spray after six weeks showed only slight attack and held up under test just as well as the sherardized samples.

The samples under test showed up so well that we made additional tests upon turbine buckets. These chromized nickel steel buckets showed up so well that the Turbine Department decided

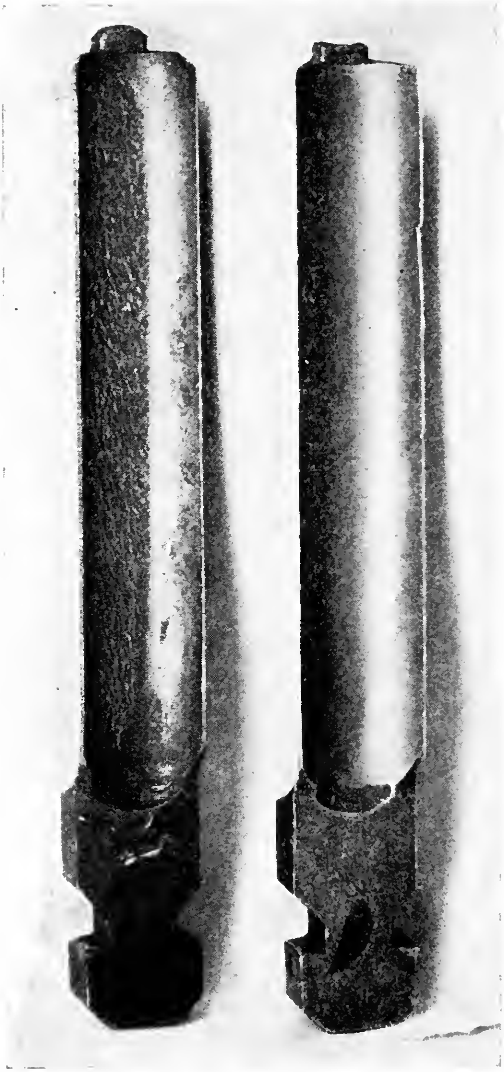

FIG. 8.

Chromized and unchromized nickel steel turbine buckets after one year of actual service.

to put them into various turbines throughout the country, and into some of the turbines of ocean-going vessels. The best comparison of resistance to corrosion of chromized and unchromized turbine buckets under service conditions is illustrated in Fig. 8 of this paper. These buckets were run side by side in the same wheel of a turbine for one year. The unchromized nickel steel bucket at the left has its edge entirely corroded and eroded away, and in addition the face of the bucket is badly corroded. The chromized bucket on the right is in perfect condition, showing no signs of corrosion.

EFFECT OF HEAT TREATMENT.

In cases where the material chromized must stand high tension and fatigue stresses, the high temperature of chromizing lowers the resistance of the material to these stresses, but by proper heat treatment the original properties may be almost completely restored.

EFFECT OF CARBONIZING.

Carbonizing of chromized iron lowers its resistance to corrosion, and polished samples of chromized iron which have been case hardened will show numerous globules of water if allowed to stand in the open air for only a short time.

Chromized iron itself is quite soft and ductile, but by case hardening and heat treatment it may be made very hard.

RESISTANCE TO ACIDS.

Chromized iron samples were tested in 10 per cent HCl, HNO_3 and H_2SO_4. They stood up for five months in the 10 per cent HNO_3 without discoloring the solution or showing any signs of attack, but they broke down almost immediately in the other two acids.

ADDITIONAL PROPERTIES.

In addition to these characteristics, chromized iron has a silver color, it takes a high polish, and the most remarkable thing about it is its softness even where large percentages of chromium are present.

OTHER CHROMIZED METALS.

There are other metals which may be chromized besides iron, but under somewhat different temperature conditions. Nickel may be chromized if the temperature used does not exceed 1300° C. If a higher temperature is used the eutectic alloy of (Cr-Ni) is formed and the whole mass melts. The composition of this alloy is (42 per cent Ni, 58 per cent Cr) and it melts just under 1300° C. There does not seem to be much trouble with fusion when chromizing at 1300° C., because the rate of diffusion of chromium into nickel is slow at this temperature.

Molybdenum and tungsten may also be chromized, but in order to get any penetration a temperature of 1600° C. is necessary, which is above the critical point of crystallization, and the wire obtained is of large grain structure and very brittle.

ANOTHER APPLICATION.

Chromizing may be used for another purpose than protection from corrosion. It may be used to prevent the flow of a metal like copper on iron at a temperature above the melting point of copper. In a case like this it is better to oxidize the chromized metal first before attempting to use it. If the chromized metal, say iron, is used to prevent copper from wetting it in hydrogen at above 1200° C., it will if fired for long enough time eventually alloy with the copper, due to the lowering of the concentration of chromium at the surface, due to diffusion. But it will resist alloying for a limited length of time even at this high temperature.

This is an interesting field of research, and there are indications that there may be future developments and applications for metals treated by diffusion processes.

DISCUSSION.

Colin G. Fink[1]: Mr. Kelley states that hydrogen performs two functions. One is to keep the chromium in reduced condition, and the other is to prevent the molybdenum resistor from oxidizing. Without the hydrogen, the alloying between chromium and iron would probably not take place. Hydrogen is the only efficient "flux" that I know of commercially for this case.

L. O. Hart[2]: Mr. Kelley's paper opens up a new field. There seems to be, from a manufacturing standpoint, some objections to

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[1] Consulting Metallurgist, New York City.

[2] Driver-Harris Co., Harrison, N. J.

this process. The requirements of temperature and purity of hydrogen mean that the process of chromizing necessarily must be an expensive one. It requires expert supervision and expensive apparatus, and it seems to me that a number of the results might be obtained more cheaply by making the articles of a chrome-iron alloy rather than chromizing a steel or a nickel steel.

If the process were capable of operation at a cost comparable with sherardizing, I think that chromizing would have a much wider application than it has now.

H. K. Richardson[3]: We have three things to say about this process. At present we are using a process in an experimental way, of chromium plating nickel-steel wire. This wire is heated in its final stage of preparation to about 1,100° C., and for less than half a minute. The process is continuous, whereby a strictly adherent coating of ductile chromium is made upon an undercoating of nickel steel.

I would like to speak about one or two of our observations. Mr. Kelley's curve on page 361, regarding the penetration in time, does not seem to be borne out in its lower regions by our experience. We have a penetration of about 0.01 mm. in a half minute or less.

Regarding the amount of chromium, we put 8 per cent or thereabouts upon a wire, and that coating after passing through the process at 1,100° C. can be drawn, under the right conditions, from 25 mils to 10 mils, with little cracking on the surface.

Now some friends have taken this coating and have submitted it to X-ray analysis. The resulting spectrogram shows that the chromium has inter-penetrated the nickel-steel lattice and as such has made a much more dense alloy than Mr. Kelley shows here. There is no indication at 250 magnifications of any crystals whatsoever on the coating. Sometimes the coating can not be seen at 250 magnifications. The only way that we can find out that we have a coating is by special etches. That is, when things have been done rightly. We do not always get the result, for sometimes, due to faulty cleaning, we have a line of demarcation between the chromium coating and the nickel-steel under-body.

In our own work we can not use any nickel-iron-chromium alloy, because it would have too high a resistance, and it would

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[3] Westinghouse Lamp Co., Bloomfield, New Jersey.

have a wrong coefficient of expansion. So we are limited to an under-body which has the right coefficient of expansion. The chromium serves only the purpose of making the contact between the glass and the right coefficient under-body.

F. C. KELLEY: In answer to Dr. Fink's statement, that hydrogen is acting as a flux in this process, and is the essential thing which makes it work, you may call hydrogen a flux, or whatever you will. It is not essential to the operation of the process, but it is the most convenient way of preventing oxidation and of carrying on the process. It can be done in a lamp exhausted down to very low pressures. I will go so far as to say that from my experience and knowledge of the facts, an iron wire can be chromized inside of a lamp where the pressure is extremely low, as low as the best vacuum we know.

I have treated cold-rolled iron in this same way and at these same temperatures in vacuum, and produced the same results. I should say that good, clean contact surfaces between the powdered chromium and iron, and an atmosphere where oxidation can not take place, or a vacuum, are the essential conditions under which this temperature treatment should take place.

In regard to the wire to which Mr. Richardson has referred, he is dealing with a nickel-iron alloy wire, I assume, with a high nickel content. Nickel and chromium form a eutectic alloy, which melts below 1,300° C., and in his case a ternary alloy is probably formed. It is an entirely different material from cold-rolled iron which my data cover. As to the nickel-steel buckets, to which I referred in my paper, I wish to make clear that the data given in this paper do not deal with the rate of penetration of chromium in nickel steel, but only in cold-rolled iron. I have no accurate data on the diffusion of chromium into nickel steel or nickel-iron alloys of high nickel content at 1,100° C., but I do know that it is possible to chromize pure nickel in this same way and at lower temperatures, and that chromized nickel steel resists corrosion to a marked degree.

You can chromize many other metals. In fact, this diffusion of metals at high temperatures and below their melting points occurs generally. This is a wide field for investigation and little is known about what is really going on outside of the fact that diffusion takes place.

A paper presented at the Forty-thira General Meeting of the American Electrochemical Society held in New York City, May 5, 1923, Dr. F. M. Becket in the Chair.

THE PREPARATION OF PLATINUM AND OF PLATINUM-RHODIUM ALLOY FOR THERMOCOUPLES.[1]

By Robert P. Neville.[2]

Abstract.

The Bureau of Standards has prepared in its laboratories thermo-element platinum and platinum-rhodium alloy for standard thermo-couples, to determine what performance might justly be required of such instruments. Melting of the pure metal and of the alloy was carried out in an Ajax-Northrup high frequency induction furnace, in crucibles of lime or thoria. Platinum and platinum-rhodium alloy, superior in quality to the best material of this kind formerly in the possession of the Bureau, was prepared.

I. INTRODUCTION.

One of the essential properties of thermocouples is constancy of calibration. Deficiencies in this property may be due to several causes, chief among which are inhomogeneity in the alloy wire and contamination of either the pure metal or the alloy. Deterioration may be due either to introduction of impurities during use, which is especially true of rare-metal couples, or to impurities in the metal and alloy from which the thermocouple was made. Lack of constancy in calibration caused by contamination during use may be prevented by proper precautions, but a solution of the problem when the deterioration is due to a lack of sufficient purity in the original metals is less easily attained.

As a part of its general investigation of the metals of the platinum group the Bureau of Standards was desirous of making

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[1] Published by the permission of the Acting Director of the Bureau of Standards of the U. S. Department of Commerce. Manuscript received February 2, 1923.

[2] Associate chemist, Bureau of Standards, Washington, D. C.

up in its own laboratories standard rare-metal thermocouples to determine what performance might justly be required in such instruments.

II. MELTING TECHNIQUE.

1. *Requisites*: Platinum melting is usually done with an oxy-hydrogen or oxy-gas flame on a fire-clay or lime refractory. When extreme purity of the fused metal is of utmost importance, the method of heating and the composition of the crucible must be considered with respect to other conditions than simply refractoriness and sufficiently high temperature. In addition to possessing the usual necesssary refractory qualities, the container in which pure platinum is melted should be a material free from all substances which might alloy with the metal, either directly or after reduction by the molten platinum. It also must be a material which does not appreciably dissociate when heated to very high temperatures under vacuum.

The first essential of a method of heating is the attainment of the temperature at which platinum melts, but in addition to this the method also must be such as not to promote decomposition of the refractory. Calcium oxide is sufficiently reduced by an oxy-hydrogen flame, especially if the flame is deficient in oxygen, for calcium to be detected in the platinum thus melted. Other oxides behave in a similar manner. The method of heating, therefore, must be such as not to favor the reduction of the refractory.

2. *Furnace*: The Ajax-Northrup high frequency induction furnace is particularly well adapted to the melting of pure platinum, and the preparation of platinum metal alloys. A description of the furnace and a mathematical explanation of the theory of its method of heating may be found in a paper by Dr. Northrup.[3] A small inductor coil especially adapted to melting small amounts of platinum was made for this work. It differed from the usual coils only in size, the inside diameter being 3 cm., and the length 10 cm. A 25 kva. converter supplied the high frequency current.

3. *Refractories*: Molded crucibles of the necessary size, shape and composition were not available. Hand tamped crucibles,

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[3] E. F. Northrup, Trans. Am. Electrochem. Soc. 35, 69-158 (1919).

usually either of lime or thoria, were made from materials prepared in the Bureau's laboratories for this purpose.

Calcium oxide has the advantage of being the least expensive and the most easily purified of the refractory materials tried. Its use is advantageous for small melts where solidification of the metal is allowed to take place in the container. The crucibles are less troublesome to make, the resulting ingots may be easily cleaned with hydrochloric acid, and the quality of the metal produced compares favorably with the best. The special purification of the material employed at the beginning of the work was later found unnecessary. The oxide obtained by igniting "c. p." calcium carbonate at about 1000° C. in an electric muffle furnace was found just as satisfactory.

The thoria used was prepared from the "c. p." nitrate of commerce by successive precipitations as $Th(OH)_4$ and finally as the oxalate, and ignition in an electric muffle furnace at about 1000° C. Calcination at a higher temperature would have been desirable, but means of obtaining a higher temperature without danger of contamination were not available. It was necessary to use thoria whenever large quantities of the purest metal attainable were desired, or whenever the melt was to be poured. Crucibles of thoria have a high density, and unusual mechanical strength for an unsintered material. Their very low thermal conductivity makes them more suitable than lime for large melts, where the heat capacity is much greater. Ingots melted in thoria, however, are very troublesome to clean. Several fusions in potassium pyrosulfate are necessary to dissolve the refractory still remaining after all possible has been removed by mechanical means.

The best lot of platinum that has been prepared up to the present time was melted in thoria. It was found to be 10 microvolts thermoelectrically negative at 1200° C. to the Bureau's standard, known as "K." This standard, K, was a melt made in lime and was 45 microvolts negative at 1200° C. to the best Heraeus thermo-element wire formerly used as a standard. This later melt in thoria then superseded K as a standard.

Zirconium oxide, if pure, would probably serve as well as thoria. A few melts were made in zirconium oxide prepared by igniting Kahlbaum's zirconium nitrate in an electric muffle furnace. Platinum melted in crucibles of this oxide was about 30 microvolts positive to the standard then used, or 40 microvolts positive to the present standard. The number of these melts was insufficient to justify definite conclusion as to its suitability.

The same general method of making crucibles was used for the different refractory materials. The procedure was that of tamping the refractory in a cylindrical crucible of alundum of very thin walls. Thoria, in the dry powdered form, is sufficiently coherent when slight pressure is applied for crucibles to be made without moistening. Calcium oxide packs less easily, so this material was moistened with petroleum ether. The hydration of calcium oxide necessitated the use of petroleum ether, but it was also used with thoria or zirconia if moistening was necessary, because of its rapid evaporation and the consequently quick drying of the crucible. The mandrel was removed after tamping, and if the material was thoria, the crucible was ready to use. Lime crucibles were dried and lightly calcined.

4. *Melting*: A number of experiments were made to determine the best method of heating, and to work out details of melting and crucible making. The melting of previously fused platinum in the induction furnace was a simple matter so far as ability to obtain the necessary temperature was concerned. The melting of sponge, however, was found to be more difficult. Sponge could be quickly heated to about 1500° or 1600° C., but it was very difficult to continue heating from this point up to the melting point of platinum. If the sponge was compressed it would then heat as readily as the solid platinum. The method tried first was to melt a small piece of the compressed sponge and then to add to this the remainder of the platinum as uncompressed sponge. The time required for the addition of this uncompressed sponge allowed excessive shrinkage of the refractory, and thereby frequently caused failure and loss of the melt. For this reason it was found more satisfactory to compress all the sponge into pellets.

The compression block used for this purpose was a steel cylinder of uniform diameter, highly polished and "glass" hard on the inner surface, closed with a tightly fitting plug at one end and a removable plunger at the other. With the plug in place the block was filled with sponge and the plunger inserted. Pressure was applied to the plunger until the sponge was compressed into a compact mass, after which the plug was released and the pressure reapplied which forced out the plug followed by the pellet of platinum. The cylindrical pellets made in this manner were 1 cm. in diameter and about 1.5 or 2 cm. long. They had the bright metallic appearance of fused metal and possessed sufficient mechanical strength so that no particular care was necessary in handling them.

Experiments were carried out varying the rate of heating, the temperature of the melt, length of time the melt was kept molten, and the number of repeated meltings. In these experiments the metal was allowed in every instance to solidify in the crucible in which it was made. Superheating to any extent was found not only to be of no advantage but undesirable, and to subject the melt to danger of loss through shrinking and cracking of the refractory. Excessive heating increased liability of contamination. The method found to produce the best results consisted in a rapid heating to a temperature just below the melting point, followed by a much slower heating to fusion. After dropping the temperature so as to permit partial solidification, and remelting two or three times with alternate scant solidification, the metal was allowed to cool slowly to below the freezing point. The slower rate of heating just before fusion kept the temperature from suddenly running up too high when the metal melted. Likewise there was more certainty that the metal was not being heated to an excessive temperature when, instead of being kept continuously molten, it was remelted several times with alternate scant solidification. If the temperature was allowed to run too high, or the metal kept molten an excessively long time, shrinkage took place in the refractory (especially if it was thoria), which allowed cracks to develop into which the metal would run, and cause the ingot to have an irregular shape and uneven surface. A calcination of the refractory at a higher temperature would have been a means of preventing this, if calcination could have been accomplished without contamination. A method of calcining thoria crucibles under vacuum in a tungsten shell will be discussed below.

Several experimental melts were carried out in which attempts were made to control shrinkage cavities by regulating the method of solidification, so as to obtain progressive freezing of the ingot from the bottom toward the top. In this manner the diminution in the volume of the metal upon transition from the liquid to the solid phase could be localized at the top of the ingot. The method of controlling the order of freezing consisted in cooling through the solidification temperature, by gradually lowering the crucible down through the furnace inductor coil without any change in the power input of the furnace. This progressive freezing of the melt was obtained by lowering the crucible through the inductor coil by means of a screw in the crucible support, the power input remaining unchanged during the process. The bottom thus began to cool first, and solidification was progressive from the bottom to the top of the ingot. Thus since the direction of freezing was entirely lengthwise in the crucible, the shrinkage was localized at the top, and any cavity was at the top rather than in the interior or on the side of the ingot. The method was not entirely successful, because the longer time required for solidification in this manner often caused the failure of the refractory and consequent loss of the melt.

5. *Casting*: The preparation of platinum alloys introduces a difficulty which does not accompany the melting of pure platinum, namely, inhomogeneity in composition, resulting from selective freezing upon solidification. Selective freezing may be prevented by extremely slow cooling with stirring, or by so sudden a transition from the liquid to the solid phase that segregation can not take place. Casting the melt in a chill mold is the obvious solution, hence the first requirement is a crucible of sufficient mechanical strength to permit pouring. This mechanical strength was not present in the crucibles used for melting pure platinum, where solidification took place in the crucible. This again brought up the question of a feasible method of calcining crucibles.

The preparation of hard-burned crucibles from compressed refractory powders, without the calcination of the crucibles before their removal from the shells in which they were molded, was practically impossible. Tungsten seemed to be the only practical material in which this calcination could be carried out without detriment to the quality of the crucible. Graphite so used caused the formation of carbide in the refractory. Recent work[4] had shown that thoria is slightly reduced by tungsten at temperatures below 2300° C., but apparently not enough to interfere with its utilization for the present purpose.

Crucibles were made by tamping thoria, previously calcined at 1800° C., in cylinders of sheet tungsten. The thoria lined tungsten shells were calcined in an electric vacuum furnace to about 1800° C. The resulting sintered crucibles were very hard and possessed good mechanical strength, but as a precaution they were not used without the reinforcement of an outer crucible of alundum. Any space intervening between the thoria crucible and the alundum shell was filled in carefully with finely ground thoria. Castings were in a few instances made from uncalcined crucibles, but the fragility of the thoria was a source of annoyance.

The melting procedure for casting was the same as usual except that, instead of allowing the melt to solidify in the furnace, the crucible was removed from the coil and the melt poured into a graphite mold, made by drilling out the desired ingot shape in a large block of Acheson graphite.

A melt to be poured must be superheated somewhat more than one permitted to solidify in the crucible, or solidification will take place before pouring is possible, particularly when the melting has been done in a sintered crucible whose thermal conductivity is greater. The pouring temperature was kept as near the freezing point as possible, as high casting temperatures were found to cause unsoundness in the ingot. The amount of gas dissolved by the molten metal, especially the platinum-rhodium alloy, apparently increased as the temperature of heating was raised, which seemed to cause more blow holes on freezing. However, if the melt was held for a short time at the lowest temperature permitting pouring without premature freezing, little gas was evolved on solidification in the mold, and chances for a sound ingot were greater.

III. MECHANICAL WORKING.

1. *Rolling*: The ingots were rolled through 5 cm. (2 in.) diamond grooved hard steel rolls. The grooves were graduated

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[4] C. J. Smithells, Reduction of Thorium Oxide by Metallic Tungsten, Jour. Chem. Soc. (Lon.), **122**, 2236 (1922).

in size from 19 mm. (3/4 in.) square for the first to 2 mm. (5/64 in.) for the last, which had slightly rounded corners. In order to prevent contamination during mechanical working particular care was taken to keep the roll surfaces in the best possible condition. Spectrographic analysis revealed no trace of iron in pure platinum after rolling.

2. *Drawing*: Sapphire dies were used for drawing the wire from the 5/64-inch rod. Before drawing, the wire was cleaned by rubbing between filter paper saturated with alcohol to remove grease and any adhering flakes of metal. The reductions in the dies were 0.0076 mm. (0.003 in.) at each draft at the start. The last few drafts were slightly less. The final diameter of the wire was 0.63 mm. (0.0246 in.)

Platinum is so malleable that unevenness of the ingot and many other defects may be rolled out and obscured. Such flaws possibly may be cold-welded so that they are as sound as any portion of the metal, but since there was some uncertainty, discards were always made from both ends of the drawn wire. The wire was cleaned after drawing in the same manner as after rolling.

IV. THERMO-ELEMENT PLATINUM.

1. *Sponge*: The separation of the metals and the purification of the sponge will not constitute a part of this paper. It is assumed here that the materials melted were in every case of the highest degree of purity attainable. Preparatory to melting the sponge was pressed into small cylinders of sufficient density to permit heating by direct induction.

2. *Melting*: Several different lots of platinum were melted with slight variations in method. This description will follow in detail the method of melting the best of the large ingots made.

The melting was done in a thoria crucible made in an outer crucible of alundum as described above. Its inside diameter was slightly greater than that of the cylinders of compressed sponge. The cylinders of sponge were placed in the crucible, one on top of the other, until the crucible was full, and the whole set in the coil of the furnace ready for melting. The graphite mold was set a few inches away from the furnace, and the remainder of the compressed cylinders for the charge placed conveniently for quick addition after fusion had begun. The furnace was started at a power input of 5 kw. and reduced to about 4 kw. before fusion had begun, which usually occurred in about a minute. Quick adjustment of power input permitted ready control of the temperature of the melt. As the first part of the charge melted and sank the remaining cylinders were added. As soon as the mass was thoroughly liquid after all the sponge had been added, it was allowed to cool to superficial solidification and again melted.

Two or three successive remeltings with alternate superficial solidification were a means of preventing unintentional superheating, and at the same time assured that the time the melt was molten was long enough for the volatilization of any remaining salt or other foreign matter in the sponge. Upon melting the last time the temperature was carried on up until judged high enough for the metal to remain liquid until it could be poured. The power was cut off, the crucible removed with tongs and the melt poured as quickly as possible. Solidification was almost instantaneous.

The main body of the ingot was about 1 cm. in diameter and 6 cm. long. The top part of the mold was of a larger diameter so as to provide for a head which would solidify last and confine the shrinkage cavity to the top. The ingot (124 g. in weight) was sound, of smooth surface, and with no sign of a defect. The shrinkage cavity on solidification was localized at the top of the head, which was cut off before the ingot was rolled.

3. Wire: Since this ingot was cast, no cleaning was necessary before rolling as was the case when the melt was allowed to solidify in the furnace. Pure platinum is so ductile that rolling and drawing are simple matters. A slight contamination of very pure platinum noticeably increases the hardening resulting from the cold working during drawing. After rolling and drawing to 0.63 mm. (0.0246 in.) wire, without any annealing during the process, the pure platinum wire was still soft. After cleaning and making discards from the ends, the wire was ready for testing and cutting into convenient lengths for thermocouples.

Spectrographic analysis failed to reveal the presence of any impurity. Results of thermo-electric comparisons and service tests are discussed below.

V. THERMO-ELEMENT ALLOY.

1. *Materials and Melting*: The platinum sponge used in making the 90 per cent platinum-10 per cent rhodium alloy was the same as that used for the platinum element, and was handled in the same way. The rhodium, however, was not added as sponge but in the form of a fused ingot. The rhodium sponge, approximating in weight a tenth of the total weight of alloy to be made, was compressed into a cylinder and fused under vacuum. This preliminary vacuum fusion eliminated any gaseous and volatile matter in the sponge and facilitated the addition of a definite amount of rhodium to the melt.

The melting procedure for the rhodium differed little from the melting of pure platinum. The crucible was of powdered calcium oxide pressed into a shell of alundum. This crucible, containing the compressed rhodium sponge, was placed in the bottom of a closed-end hard glass tube and set in the coil of the induction furnace. The rhodium was fused under vacuum, held molten a few minutes, and allowed to cool in the crucible while the vacuum was maintained.

The charge was then accurately calculated on the basis of the weight of the cleaned rhodium ingot, the platinum weight being nine times the weight of rhodium. In melting the alloy the procedure was the same as described above for melting pure platinum. The rhodium ingot was dropped in while the platinum was molten so it would dissolve quickly and not be exposed to the air long while at a high temperature. The method of pouring the alloy differed from that of pure platinum only in that more care had to be taken that the alloy was not too hot when poured; otherwise an unsound ingot resulted.

2. *Wire*: The alloy was rolled and drawn to 0.63 mm. (0.0246 in.) wire in the same manner as the pure platinum, except for annealing, which was unnecessary with the latter. The alloy hardens more with deformation than pure platinum, so it was annealed at frequent intervals during the mechanical working. The finished wire was as smooth and uniform as the pure platinum wire.

The alloy was tested spectrographically for contamination, with negative results. No difficulty was experienced in preparing alloys of the desired composition by direct synthesis. Complete homogeneity, however, was the doubtful point, so thermo-electric tests were made to detect any inhomogeneity in composition. Careful thermo-electric comparisons made at frequent intervals along the entire length of the wire indicated a maximum difference in composition corresponding to less than 1° at 1200° C. In lengths suitable for thermocouples there was no significant difference in e.m.f. between the opposite ends.

VI. SERVICE TEST.

One of the thermocouples made as described and designated as C1 was subjected to continuous heating. After a flash annealing, which consisted in heating the cold-drawn wire to about 1500° C. by the momentary passage of an electric current, the couple was compared with the standard couple. It was then heated for 25 hours at about 1600° C. by passing an electric current through the wire suspended in air, and again compared with the standard. The platinum and alloy were found to have dropped 5.5 and 14.5 microvolts, respectively, at 1200° C., the equivalent of less than 1° C., which is about the usual drop noticed upon annealing preparatory to calibration.

Life tests made at the Bureau on thermocouples of commercial manufacture have shown that the usual change in calibration resulting from 18 to 24 hours heating at 1500° to 1600° C. subsequent to preliminary annealing is from 3° to 10° C.

Upon calibrating C1, subsequently to the treatment mentioned above, its calibration curve was found to be almost identical with the standard temperature-e.m.f. curve for platinum-platinum-rhodium thermocouples as given by the Geophysical Laboratory of the Carnegie Institution.[5]

VII. SUMMARY.

1. As part of its general investigation of the platinum metals now in progress, the Bureau of Standards desired to prepare in its own laboratories standard rare-metal thermocouples in order to determine what performance might justly be required of such instruments.

[5] Adams, Bull, A. I. M. M. E., 159, 2111 (1919).

2. A method of melting was developed which consisted in fusing the sponge in crucibles of pure thoria or lime by means of an Ajax-Northrup high frequency induction furnace. The crucibles were made by tamping the powdered material around a mandrel in an outer crucible of alundum or tungsten. The melts of alloy were cast in a chill mold and those of pure platinum were usually allowed to solidify in the furnace.

3. Platinum and platinum-rhodium alloy superior in quality to the best material of this kind formerly in the possession of the Bureau were prepared. Thermocouples were made from this material which dropped off on 25 hours heating at about 1600° C. the equivalent of about 1° C.

The author wishes to make several acknowledgments. The preparation of the platinum and rhodium sponges was done by E. Wichers, chemist; the spectrographic analyses were made by W. F. Meggers, physicist; the thermocouple service test was made by W. F. Roeser, laboratory assistant; the entire work was conducted under the supervision of E. Wichers and Louis Jordan, chemist.

Other papers dealing with the investigation of platinum metals by the Bureau of Standards are as follows:

G. K. Burgess and P. D. Sale. A Study of the Quality of Platinum Ware, Bureau of Standards Sci. Papers, No. 254.

G. K. Burgess and R. G. Waltenberg, Further Experiments on the Volatilization of Platinum, Bureau of Standards Sci. Papers, No. 280.

L. J. Gurevich and E. Wichers, Comparative Tests of Palau and Rhotanium Ware as Substitutes for Platinum Laboratory Utensils, Ind. Eng. Chem. **11**, 570 (1919).

E. Wichers, The Preparation of Pure Platinum, J. Am. Chem. Soc. **43**, 1268 (1921).

E. Wichers and L. Jordan, Investigations on Platinum Metals at the Bureau of Standards, Trans. Am. Electrochem. Soc. This volume.

DISCUSSION.

H. K. Richardson[1]: The author says that the preparation of hard-burned crucibles from compressed refractory powders, without calcination of the crucibles before their removal from the shells in which molded, is practically impossible. We have been using thoria crucibles the last year or so, which were made by

[1] Westinghouse Lamp Works, Bloomfield, New Jersey.

practically standard methods of the ceramic art, *i. e.*, by casting and also by pressing methods. In both cases we have, by suitable calcination and burning, obtained a crucible which has a perfectly smooth surface, and to which we have found, in one or two cases, that platinum scrap when melted does not adhere.

So far we have not been able to make a crucible larger than 2 inches in diameter by 6 inches long. These crucibles, when made in a furnace of the carbon-plate resistance type, are not satisfactory for use in induction furnaces, because they take up carbon from the atmosphere of the furnace and do not make a satisfactory container at 2,200 to 2,500° C., due to conducting the current and breaking down.

These crucibles were made up for uranium research. One crucible has been carried to approximately 2,500° C. at least seven times. Molten material at this temperature has dropped into the crucible without cracking same, showing in a practical way their low coefficient of expansion. Under this condition of use they do not soften or lose shape.

In the manufacture of the crucible, the thoria is very sensitive to taking up various materials; but after once being made, except for metallic iron in an oxidizing atmosphere, the metals do not seem to react much with the crucibles.

H. T. Reeve[2]: Has Dr. Jordan ever tried working down a bar of sintered platinum to wire. Melting seems unnecessary when it requires such troublesome methods to prevent contamination.

F. E. Carter[3]: What does Dr. Jordan mean by the inhomogeneity of the wire? Does he mean that one end of a thermoelement wire has a different composition from the other, or that there is coring of the crystals?

Also, on page 372, it is stated that "the container in which pure platinum is melted should be a material free from all substances which might alloy with the metal, either directly or after reduction by the molten platinum." Actually, if you use the oxyhydrogen flame, and under oxidizing conditions, the purity of the lime crucible does not seem to be of much importance. The impurities are taken out of the platinum by the lime rather than the impurities of the lime by the platinum. I have found, for

[2] Western Electric Co., New York City.

[3] Metallurgist, Baker & Co. Inc., Newark, N. J.

instance, I could get a purer platinum by melting in a lime crucible with oxy-hydrogen flame, making sure it is thoroughly oxidizing, than by using the high-frequency induction furnace.

When the metal is cast into a graphite mould, has the author ever had any indication of the platinum being attacked by the carbon? Is a carbide formed under these conditions? I notice the author used a closed end, hard-glass tube when working with a vacuum in the high-frequency furnace. I have found it more convenient to work the other way around, *i. e.,* to use the ordinary vitreosil insulator closed by a disc of transparent quartz at the top, and evacuate at the bottom.

Louis Jordan[4]: In regard to making the crucibles, Mr. Richardson calls attention to the statement that it is practically impossible to make them by ordinary methods. Since the preparation of Mr. Neville's paper, work with methods of casting the crucibles has been in progress.

With regard to reaction with tungsten, there is a reference at the bottom of page 377 to the reduction of thorium oxide by metallic tungsten. The work cited was at a somewhat higher temperature than that employed for the platinum melting, and at 1,800° C. we did not notice any reaction between the tungsten and the thoria. This was a thoria-lined tungsten shell, rather than a tungsten-lined thoria. It was calcined in an Arsem furnace, but we found no decrease in the purity of the platinum melted in such crucibles, and no apparent change in the crucible indicating contamination by carbon.

It is, of course, not necessary actually to melt the compressed platinum sponge. That is an European practice, I believe. It was not difficult to melt the compressed platinum sponge. A considerable charge of platinum sponge was melted in a high-frequency induction furnace in a few minutes, and it was as easy to melt completely as to sinter and hammer the metal sponge.

We did not find any trouble in casting the pure metal or its alloys in Acheson graphite moulds. The mould was a chilled mould for the amount of metal we used, and freezing took place instantly and without, as far as we could see, any reaction with the carbon.

[4] Bureau of Standards, Washington, D. C.

A paper presented at the Forty-third General Meeting of the American Electrochemical Society held in New York City, May 5, 1923, Dr. F. M. Becket in the Chair.

INVESTIGATIONS ON PLATINUM METALS AT THE BUREAU OF STANDARDS.[1]

By Edward Wichers[2] and Louis Jordan.[2]

Abstract.

The Bureau of Standards has undertaken a comprehensive investigation of the platinum metals, involving the purification of all metals of the platinum group, critical studies of analytical separation of the platinum metals, the melting and mechanical working of the pure metals and their alloys, the study of selected alloys with respect to their suitability for platinum ware, and the determination of a variety of physical properties of such metals and alloys. The first three phases of this investigation are actively in progress; the last two phases are to be undertaken in the immediate future.

I. INTRODUCTION.

A considerable amount of work on platinum and platinum group metals has been carried out or is in progress in various divisions of the Bureau of Standards. It is believed that it will be of interest to give a brief account of this research, and call to the attention of those interested the activities of the Bureau of Standards in this field. It is the Bureau's desire to assist both users and the manufacturers in improving the standards of quality and performance of platinum and platinum alloy products.

The importance of platinum and platinum metals for chemical laboratory ware, catalysts, resistance thermometers, thermoelectric pyrometers, electrical contacts, dental alloys, standards of mass and length, as well as their wide use in jewelry and in

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[1] Published by permission of the Acting Director, Bureau of Standards, Department of Commerce. Manuscript received February 2, 1923.

[2] Chemists, Bureau of Standards.

numerous other miscellaneous but important applications, are all too well known to require more than mention.

1. *Beginning of Platinum Work at the Bureau of Standards.*

In 1910 the American Chemical Society formed a committee on quality of platinum laboratory utensils, with Dr. W. F. Hillebrand, chief of the division of chemistry of the Bureau of Standards, as chairman. This committee made two reports, the first in 1911[3] and a supplementary one in 1914.[4] In the first report were summarized the principal difficulties experienced with laboratory ware at that time, namely, (1) undue loss of weight on ignition; (2) undue loss of weight on acid treatment, especially after ignition; (3) discoloration, crystallization, or frosted appearance of the surface after ignition; (4) adherence of crucibles to platinum triangles after ignition; (5) alkalinity of surface after ignition; (6) blistering; (7) development of cracks after continued heating.

Following the suggestions of this committee as to points requiring investigation, Burgess and Sale,[5] of the Bureau of Standards, determined losses on ignition and on treatment with acid for a number of platinum utensils. In order to show the relation of these losses to the composition of the platinum ware, they developed a thermoelectric test for purity, a test which did not injure the article tested, and which furnished data which made it possible to classify the metal in terms of its content of iridium, at that time the most common impurity or alloying element.

This method consists in clamping or arc soldering two pure platinum wires to opposite sides of a platinum dish or crucible and connecting these wires with a millivoltmeter. With one junction at room temperature or cooled in an air jet, the other junction was heated in a small blast flame to a definite temperature, say 1,100° C., and the thermoelectromotive force of the impure platinum of the crucible against the pure platinum wire was read. From a chart of isothermal curves of electromotive force in millivolts against the percentage of iridium alloyed with platinum, the amount of impurity in the crucible was found in

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[3] J. Ind. Eng. Chem., 3, 686-91 (1911).

[4] J. Ind. Eng. Chem., 6, 512-13 (1914).

[5] B. S. Scientific Papers No 2.54; 1915.

terms of the equivalent iridium content. The crucibles tested for losses on ignition and acid treatment were then classified according to their iridium content or in one or two instances according to their rhodium content, when this was known to be the alloying and hardening element.

Burgess and Waltenberg[6] carried out further tests on the volatilization of platinum, working over a range of temperatures from 700 to 1,200° C. In testing for volatilization losses the ware was heated in an electric resistance furnace, but always with a stream of air passing through the heated chamber, since losses in weight of platinum on ignition seem to be influenced by the presence of oxygen. The data obtained from these experiments indicated that above 900° C. the volatilization of platinum containing iridium was greater than that of pure platinum, and increased with the iridium content and with temperature; the loss of platinum containing rhodium was less than for pure platinum at all temperatures.

2. *Present Need for Research on Platinum Metals.*

It was not possible for the platinum committee to obtain reliable information as to the composition of platinum ware further than that given by the thermoelectric test. That is to say, qualitative information as to the nature of the impurity could not be obtained, and little could be done in correlating composition with quality of service in the absence of definite knowledge of the nature of the impurities.

The committee in their supplementary report outlined in the following sentences the procedure which seemed to them desirable in continuing work on the quality of platinum ware. "This information . . . can be gained only by carrying out an elaborate investigation involving the preparation of the pure metals and some of their alloys, and also by the careful analysis of commercial ware. It is hoped that in time the Bureau of Standards may be able to take up such an investigation. . . . The investigation should not be restricted to a study of the subject from the point of view of the chemist alone, but should be made comprehensive as to the physical behavior of the metals and their alloys so that all users of platinum might benefit."

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[6] B. S. Scientific Papers No. 280; 1916.

II. CURRENT INVESTIGATION OF PLATINUM METALS.

The Bureau of Standards has recently been able to commence this comprehensive investigation of platinum metals. The major phases of this work are the preparation of all the platinum metals in a state of very high purity; the development and critical examination of methods of analysis, not only chemical, but also spectrographic and thermoelectric methods; the development of the technique of melting and mechanical working of metals and alloys of extreme purity; the preparation and testing for quality of platinum laboratory ware of accurately controlled composition, the determination of selected physical properties of metals and alloys of composition identical with the ware, and the correlation of composition, physical properties, and quality of service; the determination of the most important physical constants and the physical and chemical behavior of all available platinum metals and alloys in so far as the facilities of the Bureau permit.

1. *Purification of Metals.*

It is obvious that the first essential in an investigation such as was just outlined is the preparation of each of the platinum metals in the highest possible degree of purity. This important feature has been neglected too often in the past, and to this neglect are undoubtedly due many of the questionable data on physical properties found in the literature. This work of purification has already progressed to a stage where quantities of each metal, except ruthenium, sufficient for our immediate needs have been prepared. Ruthenium has been omitted thus far because its scarcity probably will prevent any extensive application.

The purification of platinum and palladium has been reduced to a routine procedure. A preliminary paper on pure platinum has been published, this paper dealing particularly with the contamination of platinum with calcium when the metal is melted in lime crucibles under unfavorable conditions.[7] The preparation of pure osmium, involving a new method for converting osmium tetroxide to quadrivalent osmium chloride, will be published shortly in connection with the re-determination of the atomic weight of osmium, the latter work having been done at The Johns Hopkins University.

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[7] E. Wichers, J. Am. Chem. Soc., **43**, 1268 (1921).

The study of methods of purification has developed considerable material suitable for publication, but which will first be supplemented with additional work. It may be stated that the simple process of repeated precipitation with ammonium chloride is an entirely feasible method of purifying platinum. The existing literature contains but little useful information on the purification of most of the platinum metals, especially iridium and rhodium.

It was realized from the first that the presence of very small quantities of impurities in the metals prepared would have to be detected by other than chemical methods. For this purpose spectrographic analysis, and the comparison of thermoelectric force, and the coefficient of electrical resistance, have been used with much success. Spectographic examination has been applied to all of the metals, but the other two methods have been applicable only in the case of palladium and platinum, the two metals which can be readily drawn into wire.

Thermoelectric comparison has been found to be particularly useful in controlling the purification of platinum. Observations are made at an approximately fixed temperature (1,200° C.) against an arbitrary standard. Readings can be completed in a few minutes, and the sensitiveness is far in excess of the requirements. The e. m. f. can be measured to tenths of microvolts without difficulty, and differences of 10 or even 15 microvolts can hardly be interpreted in terms of a definite impurity even by means of the spectroscope. All evidence indicates, however, that the purest samples (as prepared from the usual sources) are the most negative. The best samples of platinum thus far prepared gave an e. m. f. of about 30 microvolts negative to the best material (consisting of a single sample) to which the Bureau had had access previously. One of these best samples is now used as the standard for thermoelectric comparison, and all platinum prepared is required to give an e. m. f. of not more than 15 microvolts positive to this sample at 1,200° C.

A series of alloys of rhodium in platinum and one of iridium in platinum, both from 1 per cent down to 0.001 per cent, were prepared to determine the thermoelectric behavior of dilute alloys toward pure platinum. It was found that in these two series the variation in e. m. f. was directly proportional to composition; that is, the isothermal curve of e. m. f. plotted against composition was practically a straight line. for alloys up to 1 per cent.[8] Thermoelectric comparison has been applied in a similar way to palladium, particularly to the metal which is being used to determine the palladium melting point on the optical scale of temperature.

Less use has been made of the determination of the coefficient of electrical resistance. This method is far less sensitive than the thermoelectric comparison, takes more time, and so far as it has been used has not given much additional information. It is generally accepted that the coefficient of resistance increases with increasing purity. The thermo element platinum purchased by the Bureau in the past few years has usually had a coefficient (between 0° and 100°) of about 0.003910, while one of a group of three samples, which were of a foreign manufacture, gave a value of 0.003917. A sample of American manufacture, recently received, gave a value of 0.003906 as received, and 0.003917 after heating at 1,500° for several hours. Samples of platinum prepared at the Bureau have given a coefficient up to 0.003917 as drawn and up to 0.003922 after a period of heating such as that just described.

This method as well as the thermoelectric comparison fails to give any information as to the nature of the impurity or impurities which are present. For this purpose the method of spectrographic analysis is used. The application of this to platinum has been described by Meggers, Kiess and Stimson.[9] The sensitiveness of the method to the most persistent impurities was determined by examining series of progressively diluted alloys, down to 0.001 per cent. It is believed that the presence of 0.001 per cent of any of the usual impurities in the platinum metals can be detected in the spectrogram. The aim in routine purification is to prepare material which shows no lines of any impurities, except in some cases the faintest lines of the elements in the refractories used for melting. Sometimes even these can be eliminated.

Table I will serve as an illustration of the way in which spectrographic analysis and the thermoelectric comparison were

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[8] C. O. Fairchild. Communication to the Philosophical Society of Washington, Feb. 11, 1922.

[9] B. S. Scientific Papers No. 444, "Practical Spectrographic Analysis;" 1922.

used in the control of the process of purification. No. 94 is a sample taken from a 500-g. lot of sponge of commercial purity purchased from an American refiner. No. 95 is metal from the first precipitation of ammonium chloroplatinate. No. 96 is from the second and No. 105 is from the third and last precipitation. All were melted in pure lime in the induction furnace, as will be described in a subsequent part of the paper.

The values for e. m. f. are those found against our standard at 1,200° C. The values are given in microvolts and all are positive. The figures given in the spectrographic analysis are intensities estimated relative to those of platinum lines, the faintest of which are designated as 1 and the strongest as 10. These values are not interpreted in absolute proportions present, except that the "trace" of rhodium in No. 96 is estimated as less than 0.001 per cent.

TABLE I.

Results Obtained in Purifying Platinum.

Thermoelectric Comparison.

	No. 94	No. 95	No. 96	No. 105
e. m. f.	442	57	24	8
Spectrographic Analysis. Figures indicate estimated relative intensities.				
Palladium	3	2	1 —	0
Rhodium	1	1 —	trace	0
Copper	1	trace	0	0
Iridium	0	0	0	0
Ruthenium	0	0	0	0
Iron	0	0	0	0
Tin	0	0	0	0
Lead	0	0	0	0
Calcium	trace	trace	trace	trace

It is interesting to note that the original source of this platinum was probably platiniferous copper or nickel ore, rather than alluvial platinum deposits. This is indicated by the predominance of palladium among the impurities and the absence of iridium.

2. *Analytical Methods.*

With a quantity of each of the pure metals (except ruthenium as noted) at hand, it became possible to undertake some of the studies contemplated when the work was begun. A critical investigation of analytical separations and methods of determination seemed to be of prime importance, both as a means of providing adequate control of the composition of alloys used in other phases of the general research, and because of the lack of accepted standard methods for the analysis of various articles of commerce containing one or more of the platinum metals. The evaluation of crude platinum metals, ore concentrates, catalytic masses, manufacturers' scrap and sweeps, and the control of composition of alloys for electrical work, jewelry and dental work, are matters of every-day necessity in the platinum industry.

The Bureau's study of analytical methods is at present directed mainly toward two problems. The first is the accurate determination of iridium in platinum alloys, and the second an accurate and reasonably rapid method for the partial or complete analysis of crude platinum concentrates or native grain platinum. The work on the latter has been begun only recently, and may be said to show promise. The principal novel feature of the method is the avoidance of the separation of the concentrates into two fractions, respectively soluble and insoluble in *aqua regia*. If this is successful it will permit of the determination of total iridium, rather than the portion which is insoluble in *aqua regia*. The high relative cost of iridium makes the proper evaluation of the native platinum important.

The work on the determination of iridium in platinum alloys will be published shortly. No new method is proposed, but the old method of Deville and Stas is brought up to date, and made to conform to modern laboratory methods. The procedure consists of fusing the alloy with ten or more parts of lead, and parting the resulting lead ingot first with nitric acid and then with dilute *aqua regia*. The factors of temperature of the lead fusion, time of fusion, proportion of lead, and concentration of *aqua regia* used in the second parting, as well as the influence of the presence of iron, ruthenium, and rhodium have been carefully studied. The method was found to be capable of giving results of great accuracy, except that slightly low results for the iridium content are obtained in alloys containing about 15 to 20 per cent, corresponding to contact point metal. This error can be corrected by a second separation of iridium. It is proposed to submit this method to commercial laboratories for comment before it is published.

3. *Technique of Melting and Working.*

(a) Refractories. The first method employed for melting the pure platinum sponge was the usual one of fusion on lime in an oxyhydrogen blast flame. Calcium was always detected in metal melted in this manner. Contamination by calcium was serious whenever the blast was allowed to become deficient in oxygen while the metal was molten.[10] Platinum melted in lime in the Ajax-Northrup high-frequency induction furnace, with free access of air and without excessive superheating, was of satisfactory purity as determined by the thermoelectric tests, although spectrographic evidence of calcium usually was found.

Small quantities of platinum melted on pure magnesia in the oxy-hydrogen flame with an excess of oxygen were of high purity. Melts of platinum in magnesia in the induction furnace were seriously contaminated with magnesium when a graphite or tungsten shell was used outside the refractory liner. The reduction of the refractory may have been caused by the carbon or carbon monoxide or by the metallic tungsten. However, a consideration of the qualities required in a refractory for general use in melting the metals of the platinum group and their alloys, led to the belief that thorium or zirconium oxide should be more satisfactory than lime or magnesia, and tests with magnesia in the induction furnace were discontinued.

Thorium oxide has an exceedingly high heat of formation, a high fusion point, low thermal conductivity, and can readily be made into refractory shapes of good mechanical strength without the use of any additional substance as a binder. It therefore gave promise of being suitable for crucibles for melting all of the platinum metals, and of being little liable to dissociation at high temperatures and reduced pressures. These latter characteristics are required, because it is desirable to carry out the fusion of certain platinum metals in a vacuum, as in the case of palladium and rhodium. Thoria has been used as the refractory in all melts, both in air and in vacuum, when the highest purity was required.

Very pure zirconium oxide is difficult to obtain. The best

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[10] See footnote 7.

oxide available, prepared by ignition of Kahlbaum's zirconium nitrate, was used as the refractory in a few melts of platinum. The quality of the resulting metal as judged by the thermoelectric test was not as good as that of metal fused on lime or thoria.

(b) Furnace. The high-frequency induction furnace proved to be a convenient and satisfactory means of melting platinum metals with the minimum contamination. The range of temperatures available is sufficient for melting the most refractory of the metals. Temperature control and the control of the atmosphere over the molten metal or melting under vacuum are easily accomplished. Homogeneous alloys are readily made; small melts can be cast in chill molds; the location of shrinkage cavities can be controlled; and a very accurate synthesis of alloys is possible.

(c) Working of Platinum Metals. The mechanical working of the pure metals and alloys presents no particular difficulty in so far as contamination during rolling and drawing are concerned. Careful attention to the condition of the surface of steel rolls, and the use of jewel (sapphire and diamond) dies for wire drawing, allow satisfactory working. More complete details of the technique of melting and working as involved in the preparation of the Bureau's standard thermocouples are given in a paper by R. P. Neville to be presented at this meeting.

4. Quality of Platinum Laboratory Ware.

The results of the first three major phases of the general investigation of the platinum metals, namely the purification of metals, methods of analysis, and melting and working technique, are rapidly becoming available. It is thus possible to undertake the study of platinum alloys with reference to their suitability for platinum laboratory ware.

In the Bureau's experience, based on the small portion of its platinum laboratory ware purchased from commercial sources and on the few samples of ware submitted from other laboratories for tests of quality, some of the difficulties mentioned in the platinum committee's first report are no longer so frequently encountered. The most serious point of failure in platinum ware at present seems to be the tendency to develop cracks after continued heating. The causes of this failure and methods for its prevention are apparently unknown.

The present plan for this portion of the general investigation is to determine mechanical and certain other physical properties of test specimens and crucibles made from selected platinum metal alloys, to make accelerated service tests, and to attempt to correlate the two series of data.

5. *Physical Properties of Platinum Metals.*

The preparation of the pure platinum metals and their alloys for the purposes of the several phases of the general investigation thus far outlined, provides an opportunity for the measurement of a variety of physical properties of such materials. The platinum metals have properties of unusual interest, and are in constant use in the prosecution of scientific investigations. Some of the data already reported in the literature are contradictory, and many more are doubtless incorrect or very inaccurate, both because of faulty measurements and because the degree of purity of the materials studied has frequently been ignored.

In so far as the nature of the samples available from the preceding phases of this work and the facilities of the Bureau of Standards will permit, the more important electrical, thermal, optical, mechanical and various other miscellaneous physical properties of the pure metals and selected alloys of the platinum group will be determined.

It is believed that the results obtained from the investigations outlined will be of interest and value to all users and manufacturers of platinum. Manufacturers of platinum have already expressed their interest in this investigation. Detailed reports on the various phases of the research will be made as rapidly as the progress of the work warrants. The Bureau will welcome correspondence or conference with both manufacturers and users of platinum, with a view to establishing closer contact with the outstanding problems of the industry.

DISCUSSION.

F. E. CARTER[1]: I have just two remarks to make. I do not altogether agree with the authors that the thermoelectric test is

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[1] Metallurgist, Baker & Co., Inc., Newark, N. J.

better than the coefficient of electrical resistance. I think that the figures given in the same paragraph show that you readily distinguish between the purity of platinum by the latter test. I would be interested to learn whether the Bureau is working out electrolytic methods of separation of the platinum metals, for I think the future lies along that line. Getting only partial separation and having to repeat the precipitation is a great nuisance in chemical separations. As an example of what I mean, Dr. Jordan states that the method for determining iridium in platinum was found capable of giving results of great accuracy except that slightly low results for the iridium content are obtained in alloys containing about 15 to 20 per cent, where actually greatest accuracy is required.

The manufacturer does not take into account whether there is half per cent or one-third per cent of iridium in platinum; in such cases he pays for platinum only. But if appreciable quantities are present it is different; he pays for the iridium, the amount of which he must know accurately, because the difference in price between iridium and platinum is great.

I quite agree with the statement that in platinum ware the tendency to develop cracks upon continued heating is serious. This cracking appears to take place most frequently when determining, say, volatile matter in coal or in other materials. I think it has something to do with the formation of carbides.

A paper presented at the Forty-third General Meeting of the American Electrochemical Society held in New York City, May 5, 1923, Dr. F. M. Becket in the Chair.

SOME NOTES ON THE METALS OF THE PLATINUM GROUP.[1]

By Fred E. Carter.[2]

Abstract.

Some general remarks on metals of the group are given, particular mention being made of the liability to gas absorption and of the consequent difficulties of melting. Results are given to show that the addition of iridium to platinum raises considerably the temperature required for annealing. Some alloys of the platinum metals among themselves are discussed, particularly those of platinum and iridium.

When the comparative rarity of the platinum metals is taken into consideration, it is quite remarkable that so much attention has been given to them; this statement applies, however, more accurately to the chemical rather than to the physical side, because, although large numbers of complex salts, etc., of the platinum metals have been prepared and investigated, the physical properties of the metals of the group and their alloys have not been nearly so exhaustively examined. The average analyst has felt that there is something uncanny about the platinum metals; he has found that it is practically impossible to get complete quantitative separation by a simple laboratory operation and that to make such separations complete precipitations, etc., must be carried out many times in succession. He ordinarily considers, for example, platinum ammonium chloride as an insoluble salt, particularly in the presence of alcohol, yet actually there are many salts which may be present in the solution, and in which the precipitated salt may be appreciably soluble. The author prefers therefore to

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[1] Manuscript received February 9, 1923.

[2] Baker and Co., Inc., Newark, N. J.

avoid in this paper the chemistry of the platinum metals, and to write down some facts on the subject from the physical and metallurgical standpoint.

It is necessary, first of all, to emphasize the fact that much that has been published on the physical properties of the platinum metals is quite erroneous, because the metals used in the tests have been by no means pure, although this difficulty is not at all peculiar to the group in question, but applies generally to data on the metallic elements and their alloys. The platinum metals further add to our troubles by their susceptibility to gases. It is not intended in this paper to present precise measurements of physical standards, but rather to give, as is indicated by the title, some random notes on the platinum metals and to point out certain facts which may be of general interest.

The platinum group of metals is composed of platinum, iridium, osmium, palladium, rhodium, and ruthenium. They occur practically always in the elemental state, so that their metallurgy is comparatively simple and need not be discussed here. All the platinum metals are white in color; most writers differentiate between their appearance, platinum being called tin-white, rhodium aluminum-white, osmium bluish, etc., but actually it is difficult to distinguish the group members by appearance only. The author would hesitate to say that there is any difference in color between platinum, palladium, and rhodium; iridium might be conceded a more brilliant white appearance and ruthenium is whiter still; osmium certainly has a bluish tinge. Such differences as are noted here might easily be due to surface oxide films or to variable crystal grain sizes, rather than to inherent different shades of color.

The metals do not oxidize at ordinary temperatures, but on heating, certain of the group oxidize and volatilize. Table I, based on the contradictory literature on the subject, shows what probably happens when a hypothetical mixture of all the metals is gradually heated up.

One of the most interesting general properties of the platinum group of metals is their capacity for dissolving gases, for therein probably lies the reason for their great activity as catalytic bodies. This property is extremely disagreeable to the manufacturer; if the composition of the gas used for melting, say, platinum, is incorrect, gas may be dissolved by the molten metal and, since the solid metal is a much poorer solvent than the molten, set free on solidification, the metal then "spits" in the same manner as does solidifying silver which has been saturated with oxygen in the molten condition. Generally, however, the gas has not the opportunity to escape in this way, and is partly entrapped in the bar as small gas inclusions. These often do not appear until the bar is rolled down to thin sheet and annealed, when the surface is found covered with numerous gas blisters. A bar that is much gassed swells badly on solidifying and is remelted forthwith, but the manufacturer's trouble chiefly comes when not so much gas is trapped that swelling occurs and only shows up in the finished bar

TABLE I.

Results of Heating the Platinum Group Metals.

100° C.	OsO_4 begins to evolve (if the metal is very finely divided the vapor is observed at considerably lower temperature, but compact metal does not oxidize appreciably below a dull red heat).
450° C.	Pt oxidizes to black PtO (if metal is finely divided and oxygen is passed).
500° C.	PtO decomposes to give Pt and PtO_2.
550° C.	PtO_2 decomposes to Pt and O_2.
600° C.	Rh and Ru, if finely divided, oxidize to black Rh_2O_3 and bluish RuO_2.
	Pd begins to oxidize to PdO, giving blue and red colors.
700° C.	Pd oxidizes to PdO.
800° C.	Ir begins to oxidize to IrO_2.
900° C.	PdO is decomposed to Pd and O.
1,000° C.	Ir begins to volatilize freely as oxide.
	RuO_2 partially decomposes to Ru and O_2. If oxygen is passed, some RuO_4 is formed and evolved.
	Pd, Pt and Rh begin to volatilize appreciably in the order named, as metals.
1,150° C.	Rh_2O_3 decomposes to Rh and O.
1,550° C.	Pd melts.
1,755° C.	Pt melts.
1,950° C.	Rh melts.
2,350° C.	Ir melts.
2,450° C.	Ru melts.
2,500° C.	Rh boils.
2,520° C.	Ru boils.
2,540° C.	Pd boils.
2,550° C.	Ir boils.
2,700° C.	Os melts.
3,910° C.	Pt boils.

The temperatures given from 2350° C. upwards are questionable.

as a few blisters scattered throughout the bar. It is hoped that x-ray examination may eventually be useful in showing gas bubbles in the interior of ingots, but the usefulness of this method of examination has not yet been proved in the case of platinum.

Coal gas and oxygen or hydrogen and oxygen are generally used for melting the metals, and it is obvious that great care must be taken to have the correct proportions of gas or hydrogen and oxygen. Platinum must be melted in a distinctly oxidizing atmosphere, otherwise the blister trouble will appear; palladium, if melted by a reducing flame, is absolutely friable, the well-formed crystal grains being apparently without cohesion and easily separable by the fingers; rhodium blisters if melted under oxidizing conditions; iridium behaves like platinum; osmium and ruthenium rapidly volatilize in an oxidizing flame. It will be evident that difficulties arise when, say, alloys of platinum, iridium, and rhodium, or of platinum, palladium, and osmium have to be melted; in such cases experience has pointed out the special precautions that must be taken.

The obvious method of overcoming such difficulties is to melt *in vacuo* and by electricity, but even then the troubles are not yet avoided, because refractories which are suitable for oxy-hydrogen gas melting may react with the molten metals under such conditions. Wichers[3] has shown that platinum-calcium alloys are formed if platinum is melted in a lime crucible with a reducing atmosphere existing in the crucible. If such alloy formation is to be avoided excess oxygen in the oxy-hydrogen flame must be used. Also it was shown that if platinum is melted electrically in a magnesia crucible an alloy of platinum containing about three per cent magnesium may be produced. In parenthesis, it may be observed that such results force us to the conclusion that our ideas of stability of compounds must be modified when we get into the higher ranges of temperature.

Of course, graphite would be the ideal crucible material to use for melting *in vacuo,* but unfortunately the platinum metals are readily attacked by carbon. It is not even necessary actually to melt the metal in carbon vapor for the platinum to be rendered quite dark in appearance, to be strongly modified in its microscopic structure, and to be made absolutely brittle. One way of

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[3] J. Am. Chem. Soc., 43, 1268 (1921).

avoiding these troubles is to use the old "French method," which consists in pressing Pt sponge into a briquet and heating to about 1,000° C. In this way the grey platinum mass is gradually "metallized," and can then be worked down to thin sheets in the usual way. The finer the state of division of the original platinum, the more readily does this metallizing take place. The process, however, lacks one advantage of the ordinary melting process, namely, the refining effect (*i. e.*, removing the base metal) of the lime on the molten metal.

Some indication has been given above of how the loss of the platinum metals by volatilization takes place, which loss is of course important in crucible ware; it is necessary to decide what is the alloy which will lose least weight when heated to 1,000° or 1,200° C. for several hours. Platinum-iridium alloys, high in iridium, lose in weight considerably at these temperatures, owing to volatilization of the iridium and must be avoided; platinum-rhodium is practically eliminated by the high cost of the rhodium, chemically pure platinum is good so far as constancy in weight is concerned, but is rather soft. The Bureau of Standards[4] has therefore recommended as a compromise that a small amount of platinum metals (chiefly iridium) other than platinum may be present, suggesting that the alloy used should not show more than 1 m. v. against chemically pure platinum at 1,100° C.; this corresponds to about 0.3 per cent iridium. Crucibles, etc., made from such material are constant in weight and reasonably stiff.

The metals of the group alloy with one another in all proportions, the alloys being solid solutions, as is usual in the case of combinations amongst the closely related elements of a group. There does not appear to be any case where the melting point of the alloy is lower than either of the constituents (as, for example, occurs with gold and copper), but always the melting points of the alloys are intermediate between those of the constituent metals. Micro-photographs show that the addition of a second platinum metal to platinum itself causes a distinct refining of the crystal structure. For example, the crystal grains of a series of annealed iridio-platinum alloys show with increasing iridium a decreasing size of grain. Metallurgical examination also shows

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[4] Bureau of Standards, Sci. Paper 254.

that the alloys are homogeneous and, after adequate annealing, are practically free from any "coring" in the crystal grains.

The temperature required to render platinum dead soft is comparatively low, but this temperature is considerably raised by the addition of even a small percentage of iridium. Fig. 1 shows the large effect of traces of iridium on the annealing point of platinum. The curve marked "C. P." is for platinum of a high degree of purity (temperature coefficient of resistance, 0.00391), and that marked "Cruc." is for platinum containing 0.1 per cent iridium (0.48 m. v. against C. P. Pt), such as is used for crucible ware, etc. The furnace, a platinum-wound electric tube furnace equipped with platinum-rhodium thermocouple, was slowly brought up to temperature, and the samples of metal, 1.9 x 1.3 x 0.3 cm. (¾ x ½ x ⅛ in.) were introduced and kept in the fur-

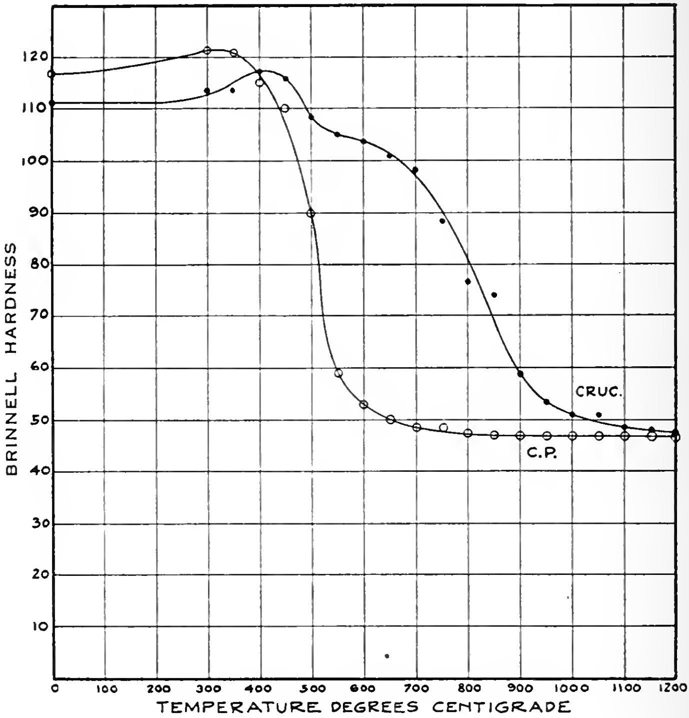

Fig. 1.

nace for 5 min. after they had reached the furnace temperature; the hardness was tested in a Brinnell machine.

It is necessary to make some further reference to Fig. 1. Rose[5] showed that traces of impurity raise the annealing temperature of gold appreciably; hydrogen was found to be especially effective in this respect, 0.002 per cent raising the temperature of annealing from 150° C. to over 300° C. Phelps[6] confirmed Rose's results. It was believed by the present author that a similar effect had been shown for platinum, although the impurity is not necessarily hydrogen. However, another factor may have been influential in the results here obtained. It is well known that an increase in the amount of cold work done on a metal previous to annealing causes a decrease in the temperature required to anneal, and it was thought possible that the two samples of platinum in Fig. 1 were not in exactly the same strained condition, in spite of the fact that both had been cold rolled from ⅜ in. to ⅛ in. Another sample of platinum, not quite so pure (it gave 0.05 m. v. positive to the platinum previously used), was rolled in the same way, and tested, and it was found that the temperature required for annealing was practically as high as that necessary for the "crucible" platinum of the figure. The same sample was then remelted and cold rolled from ⅝ in. to ⅛ in. instead of from ⅜ in. to ⅛ in. The annealing temperature now was even lower than that shown in the figure. There seems to be little doubt, therefore, that in the case of almost pure platinum the previous history of the sample has more effect on the annealing temperature than has the purity.

It will be seen from the figure that for pure platinum the required temperature is about 650° C., while for platinum with only 0.1 per cent iridium the temperature is about 1,000° C. Further additions of iridium do not raise the annealing point much. For example, platinum with ten per cent iridium requires 1,150° C. to become fully annealed in five minutes; complete crystallization of the alloys containing 20 and 25 per cent iridium may be brought about at this same temperature, but require a considerably longer time.

It is unnecessary here to do more than to draw attention to the

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[5] J. Inst. of Metals, 10, 150 (1913).

[6] J. Inst. of Metals, 12, 125 (1914).

slight increase in hardness of platinum on annealing at about 300° C. This phenomenon of a slight hardening at temperatures just below that at which softening begins seems to be a general one in commercially pure metals and in alloys. It certainly is quite pronounced in many gold alloys for which the author has drawn curves similar to Fig. 1. It is interesting, in view of some theories which have been advanced in explanation, to find this phenomenon occurring in the case of a metal of such extreme purity as the platinum used here.

PHYSICAL CHARACTERISTICS OF EACH METAL.

Platinum. Electrical resistance at 0° C. is 60.5 ohms per mil foot (10.06 microhms per cm. cube) for hard drawn platinum, and 59.8 ohms per mil foot (9.96 microhms per cm. cube) for the annealed material. The temperature coefficient of resistance is 0.00392 or even slightly higher for the extremely pure metal.[7]

The melting point is 1,755° C.,[8] apparently being the same for metal melted in air or *in vacuo*. The melting point is depressed by the presence of traces of carbon in the metal.

The Brinnell hardness is about 110 in the hard worked and 47 in the annealed condition. The Erichsen number for ductility of the annealed sheet 0.040 in. thick is 12.2 mm.

Pt wire is drawn down commercially directly to 0.0007 in., while if drawn by the Wollaston method (that is, a platinum core and a covering tube of a metal, *e. g.*, silver, which can be dissolved off later without attacking the platinum, are drawn down together) the diameter may be made one-tenth or even one-hundredth of this size.

Iridium. The melting point is about 2,350° C.[9] and possibly higher. This metal is little used except in alloy form. It is generally stated to be quite a hard metal, but actually such statements are made from tests with a very impure material. The chemically pure metal is fairly soft—about the same as 90 Pt 10 Ir. Brinnell hardness, 172 (cast). Iridium is insoluble in *aqua regia*.

Osmium. The melting point is about 2,700° C., but this figure must be considered as only an approximation. It volatilizes

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[7] Bureau of Standards.

[8] Bureau of Standards, Circular 35.

[9] *Loc. cit.*

rapidly as osmium tetroxide if heated in air, and the melting should be done *in vacuo;* even *in vacuo* osmium on heating close to its melting point volatilizes in the form of a brown vapor. Osmium is insoluble in *aqua regia.*

Palladium. The melting point is 1,550°C.;[8] as ordinarily melted the metal retains considerable quantities of gas, as is shown by the fact that if it is remelted *in vacuo* there is a violent evolution of gas just at the melting point. The metal forms different oxides which are stable only within certain narrow limits of temperature. If an ingot of palladium is allowed to cool slowly it becomes coated with thin oxide films of red, green and blue. If it is desired to have a bright finish to a bar, it is only necessary to quench it, red-hot, in water. Brinnell hardness, 49 (Cast). Palladium is soluble in concentrated nitric acid and in *aqua regia.*

Rhodium. This metal has been obtained in a high state of purity, since it is used for making the 10 per cent alloy with platinum, as the positive element in precious metal thermocouples; if the metal is even slightly impure the curve for the electromotive force against platinum at once shows discrepancies.

The melting point is 1,950° C.,[9] if melted in air the metal is coated with a blue oxide film, but *in vacuo* the metal is perfectly white. Brinnell hardness, 139 (Cast). Rhodium is insoluble in *aqua regia.*

Ruthenium. The melting point is about 2,450° C.,[9] but it is not at all certain that the metal has ever been obtained in the chemically pure state. Melted in air it is coated with a blue-black oxide; melted *in vacuo* it remains quite bright, although a black deposit settles in cooler parts of the apparatus. Brinnell hardness, 220 (Cast), but the pure metal would certainly be considerably softer than this. Ruthenium is insoluble in *aqua regia.*

ALLOYS.

The metals of the platinum group form many useful alloys with other metals outside the group, of which may be cited palladium-gold alloys for laboratory ware, etc., palladium-silver for contacts, platinum-copper alloys of remarkably high electrical resistance, etc. Discussion of these would lead too far afield, and in this paper mention will be made only of the alloys formed among the platinum metals themselves.

Platinum-iridium alloys undoubtedly constitute the most important series. "Crucible platinum" is platinum with a small quantity of iridium in it (less than 0.3 per cent.) This iridium is sufficient to stiffen the pure metal slightly and probably helps to reduce the tendency to form large crystals. Ordinary commercial platinum is by no means pure platinum; it contains from 1 to 3 per cent. iridium, which, although double the value of platinum, is not worth while extracting, owing to the chemical difficulties involved; also traces of all the other platinum metals are present, together with appreciable quantities of iron. Alloys useful to the jewelry world are platinum with 5 to 10 per cent iridium, known to the trade as "hard" platinum; here again the iridium includes all the other platinum metals in small quantity. C. P. platinum with 10 per cent C. P. iridium would be much softer than the ordinary commercial "10 per cent." The 15 and 20 per cent iridium alloys are used for electrical contacts and for hypodermic needles, and indeed in many places where a hard precious metal alloy with reasonably good working properties is required. The 25 and 30 per cent iridium alloys are considerably harder and are rather difficult to work without special precautions. They are chiefly used for hypodermic needles.

The approximate figures for Brinnell hardness of some typical commercial iridio-platinum alloys are shown in Table II. These alloys are widely used for resistance wires where a precious metal alloy is required. The approximate resistances of some of the commercial alloys are given in Table III. Alloys made from pure materials have resistances as shown in Table IV.

The addition of iridium to platinum decreases the rate at which the latter dissolves in *aqua regia;* platinum with 20 per cent iridium is very slowly dissolved, while the 25 and 30 per cent alloys are practically unattacked.

Platinum-rhodium. The only important alloy of these metals is that containing 10 per cent rhodium, used at the present time for the positive element of the well-known Pt-PtRh thermocouple; although the electromotive force developed by this couple is only about 60 per cent of that given by the corresponding Pt-PtIr couple, it is preferred on account of the low volatility of the rhodium compared with the iridium, and the consequent greater constancy of e. m. f. A great many industries require accurate

TABLE II.

Hardness of Commercial Iridio-Platinum Alloys.

Composition		Brinnell Hardness	
Pt per cent	Ir per cent	Hard Worked	Annealed
95	5	170	110
90	10	220	150
85	15	280	190
80	20	330	230
75	25	370	270
70	30	400	310

TABLE III.

Resistances of Commercial Iridio-Platinum Alloys.

Composition		Resistance	
Pt per cent	Ir per cent	Microhms per cm. cube	Ohms per mil ft.
95	5	20.0	120
90	10	26.6	160
85	15	30.8	185
80	20	33.3	200
75	25	34.9	210

TABLE IV.

Resistances of Pure Iridio-Platinum Alloys.

Composition		Resistance	
Pt per cent	Ir per cent	Microhms per cm. cube	Ohms per mil ft.
99.9	0.1	11.0	66.0
99.8	0.2	11.3	67.9
99.0	1.0	12.4	74.7
98.0	2.0	15.0	89.9
96.0	4.0	17.3	104
94.0	6.0	19.5	117

temperature control at some stage of manufacture, and it is essential to have reliable thermocouples. Pt-PtRh certainly remains the most constant in e. m. f. and, with care in manufacture, can be made to agree to the standard curve of Day and Sosman to within a degree or two. Certain other alloys, with the rhodium somewhat above or below 10 per cent are used in thermocouples, but that containing exactly 10 per cent seems the most satisfactory.

The 10 per cent rhodium alloy is much softer (Brinnell number, 90 when annealed) than the corresponding iridium alloy and also has lower electrical resistance (110 ohms per mil ft.; 18.3 microhms per cm. cube).

Platinum-palladium alloys are used to some extent in jewelry; the addition of the palladium does not harden the platinum much, and the resulting alloys are readily workable.

Platinum-osmium alloys have been made containing up to 30 per cent osmium; they are extremely hard, the osmium having about two and one-half times the hardening effect of iridium.[10] The osmium also increases the electrical resistance of platinum about two and one-half times as much as does the same amount of iridium. They are not used commercially, because annealing at even a dull red heat is sufficient to expel some of the osmium and thus alter the composition of the alloys.

Iridium-osmium alloys occur in the natural state as osmiridium; the grains are extremely hard and are used as tips for fountain pens. The alloys are now being made artificially in any desired proportions and by suitable treatment crystal grains of the proper size for pens are obtained.

Palladium-osmium alloys are easily workable, but cannot be heated without losing osmium.

There are also several ternary and quaternary alloys finding commercial application which may be mentioned. *Platinum-iridium-osmium* alloys are used for sparking points; *platinum-iridium-rhodium* alloys are used for radio tubes; *platinum-palladium-osmium* alloys were formerly used in jewelry, but the partial volatilization of the osmium as tetroxide was disagreeable and *platinum-palladium-rhodium* alloys are now preferred.

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[10] Johnson, B. P. 29723 (1910); Heraeus, G. P. 239,704 (1913); Zimmermann, U. S. P. 1,055,199 (1913).

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