

## GASES IN METALS: II. THE DETERMINATION OF OXYGEN AND HYDROGEN IN METALS BY FUSION IN VACUUM

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### ABSTRACT

Nearly all metals contain small amounts of oxygen, hydrogen, and nitrogen, frequently spoken of as "gases in metals," whether or not they exist as oxides, hydrides, and nitrides or in some other form. Many differences in quality of metals not readily attributed to differences in composition, as determined by the usual chemical analyses, or to different physical treatments are supposed to be due to the presence of "gases" in the metals.

Satisfactory and generally applicable methods for determining oxygen in metals have not been available. Experimental studies were made of methods of fusion employed in previous vacuum fusion methods. Direct fusion of low-carbon iron alloys in refractory-oxide crucibles, or fusion with antimony tin in similar crucibles, does not determine all of the oxygen present in the metal. In the first case there is the additional difficulty of reduction of the refractory oxides by the carbon in the steel. In the fusion of high-carbon iron alloys this reaction between refractory oxides and carbon of the metal is very pronounced in direct fusion of the metal and is sufficient, even in fusion with antimony tin, to give values for oxygen in excess of the true oxygen content of the metal. Fusion of the metal sample in a graphite crucible permits satisfactory determination of oxygen in both low-carbon and high-carbon alloys.

A new vacuum fusion procedure for the determination of oxygen and hydrogen in metals was developed. A sample of metal of from 20 to 60 g, which may be a single solid piece thus avoiding difficulty from surface oxidation of chips, is fused in a gas-free graphite crucible in vacuum. The water vapor, carbon dioxide, carbon monoxide and hydrogen evolved during the heating and fusion of the sample are absorbed in suitable solid absorbents and determined by the increase in weight of the absorbent tubes. Total oxygen and hydrogen in the sample can then be calculated. The method does not distinguish between oxygen present in the metal as CO, CO<sub>2</sub>, oxides of nonmetallic inclusions or of metallic constituents. Under the conditions of this analysis the recovery of oxygen from the oxides of iron, manganese, silicon, aluminum, titanium, and zirconium is complete. The presence of sulphur in the iron or steel sample does not interfere with the determination of oxygen by this method. The method is applicable to the accurate determination of oxygen in pure iron, steels, cast irons, and pig irons, and also in many nonferrous metals and alloys.

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## I. INTRODUCTION

The presence of oxygen, hydrogen, and nitrogen in small amounts in most commercial metals is well known. There are many instances of differences in quality of both ferrous and nonferrous metals where the causes apparently are not differences in the mechanical or thermal treatment of the material or variations in the chemical composition judged on the basis of the elements usually reported in chemical analyses. In such cases it is often felt that differences in the "gas" content of the material are of significance. The term "gas" used in this manner indicates those substances found in metals in either combined or uncombined condition which, in their ordinary free state, exist as gases. The expression thus includes oxides, hydrides, and nitrides in metals as well as uncombined oxygen, nitrogen, hydrogen, or other gases.

## II. REVIEW OF METHODS FOR DETERMINING GASES IN METALS

The need of methods for determining gases in metals has long been recognized, but very few such methods have come into any wide use or have given data which are sufficiently complete or concordant to permit a satisfactory correlation between the gas content of metals and their qualities.

Apparently the two most frequently used methods for determining a gas in a metal have been modifications of the Ledebur method <sup>1</sup> for oxygen and of the Allen method <sup>2</sup> for nitrogen. Investigations and improvements on the method for oxygen have been reported recently by Oberhoffer and von Keil,<sup>3</sup> and by Chaudron and Blanc,<sup>4</sup> and on the solution method for combined nitrogen by Hurum and Fay <sup>5</sup> and by Jordan and Swindells.<sup>6</sup>

Cain and Pettijohn have pointed out the limitations to which the Ledebur method is subjected, namely, the extreme precautions necessary in cutting samples and in controlling the blank corrections on the apparatus; that the method can be expected to determine only oxygen present as iron oxide or the higher oxides of manganese (above MnO) and that it even fails to determine these oxides if they are combined as silicates. Cain and Adler <sup>7</sup> further state that when

<sup>1</sup> J. R. Cain and E. Pettijohn, A Critical Study of the Ledebur Method for Determining Oxygen in Iron and Steel, B. S. Tech. Paper No. 118; 1919.

<sup>2</sup> N. Tschischewski, "The occurrence and influence of nitrogen on iron and steel," Jour. Iron and Steel Inst., 92, pp. 47-90; 1915

<sup>3</sup> P. Oberhoffer and O. von Keil, "Ueber ein neues Verfahren zur Bestimmung des Sauerstoff im Eisen." Stahl und Eisen, 41, p. 1449; 1921.

<sup>4</sup> G. Chaudron and L. Blanc, "Sur le dosage de l'oxygène dans les aciers," Compt. rend., 175, pp. 885-887; 1922.

<sup>5</sup> F. Hurum and H. Fay, "The determination of nitrogen in steel," Chem. and Met. Eng., 26, pp. 218-222; 1922.

<sup>6</sup> L. Jordan and F. E. Swindells, Gases in Metals: I. The Determination of Combined Nitrogen in Iron and Steel and the Change in Form of Nitrogen by Heat Treatment, B. S. Sci. Paper No. 457; 1922.

<sup>7</sup> J. R. Cain and L. Adler, Equilibrium Conditions in the System Carbon, Iron Oxide, and Hydrogen in Relation to the Ledebur Method for Determining Oxygen in Steel, B. S. Sci. Paper No. 350; 1919.



applied to steels the influence of the carbon present is such that the Ledebur method can not determine more than 75 per cent of the oxygen present as ferrous oxide.

The Allen method for nitrogen determines principally that nitrogen which is present as nitrides of iron and manganese. Uncombined nitrogen and nitrogen present as nitrides of silicon, chromium, or some other possible alloying elements are either not at all or incompletely determined.

Methods for extracting the gases from metals by heating and melting under reduced pressures have been developed and used by many investigators. A rather complete review of such methods applied to ferrous alloys has been published by Alleman and Darlington.<sup>8</sup> They have summarized the work of Graham, Cailletet, Troost and Hautefeuille, Parry, Muller, Zyromski, Belloc, Boudouard, Baker, Austin, and Goerens and Paquet. Alleman and Darlington concluded from their study of these earlier investigations that in most cases the containing vessels were porous, especially at high temperatures; that in many cases erroneous results were caused by the diffusion of gases through the containing vessels heated by gas flames, and that the temperatures used in practically all the investigations were not high enough to expel all the gas in the metal. In addition to these sources of possible errors, it is reasonable, in many instances, to entertain considerable doubt as to the absence of reactions between metal samples and refractory crucibles, reactions causing the evolution of gas from other sources than the metal.

The work of Goerens and Paquet<sup>9</sup> is of especial interest inasmuch as it appears to have had more use than any other fusion method. It had previously been pointed out by Austin<sup>10</sup> that it is necessary to heat a metal above its melting point in order to make certain that all the gas it contains is extracted. At the temperature required to melt iron and steel, difficulty is experienced in obtaining refractory tubes which are capable of holding a vacuum. Goerens and Paquet met the requirements of a liquid metal and a gas-tight refractory by adding to the iron gas-free antimony and tin which formed with the iron an alloy melting below 1,100° C. At this temperature a fused-silica tube maintained a sufficiently high vacuum for the purposes of the determination. This method recently has been studied and applied to steels and cast irons by Oberhoffer and his coworkers.<sup>11</sup>

<sup>8</sup> G. Alleman and C. J. Darlington, "Occluded gases in ferrous alloys," *Jour. Franklin Inst.*, 185, pp. 161-198, 337-357, 461-480; 1918.

<sup>9</sup> P. Goerens and J. Paquet, "Ueber eine neue Methode zur Bestimmung der Gase im Eisen," *Ferrum* 12, pp. 57-64, 73-81; 1915.

<sup>10</sup> S. W. Austin, "Gases evolved on heating steel to its melting point in a vacuum," *Jour. Iron and Steel Inst.*, 86, II, pp. 236-240; 1912.

<sup>11</sup> P. Oberhoffer and A. Beutell, "Die Bestimmung der Gase im Eisen," *Stahl und Eisen*, 39, pp. 1584-1590; 1919. Also P. Oberhoffer, E. Piwowarsky, A. P. Schiessl, and H. Stein, "Ueber Gas und Sauerstoff-Bestimmungen im Eisen, insbesondere Gusseisen," *Ibid*, 44, pp. 113-116; 1924.

Alleman and Darlington<sup>12</sup> developed a vacuum furnace capable of service at temperatures up to approximately 1,900° C. This furnace consisted of an alundum tube wound with a molybdenum wire heating element, both tube and resistance wire being inclosed in an evacuated iron shell, as it was impossible to obtain gas-tight alundum tubes. Samples of from 3 to 7 g of steel were melted in an alundum-lined boat in this furnace and the evolved gases collected and analyzed.

While the furnace described by Alleman and Darlington is capable of developing sufficiently high temperatures and can be made to hold a vacuum, it must be, at best, a somewhat troublesome apparatus due to the porosity of the alundum tube, the tendency of the molybdenum wire to react with gases or refractory supports at high temperatures, and the necessity of using an outer vacuum jacket. The use of alundum refractories in this method is open to objections, as will be noted below under the discussion of crucible tests. Ryder<sup>13</sup> has employed a method of extracting the gases from a metal wire or strip mounted inside a glass bulb and heated by its own electrical resistance. The weight of metal sample in this method was necessarily small, and special volumetric methods for the analysis of very small amounts of gas were used. These volumetric methods involved the use of liquid air and solid carbon dioxide for the separation of the unknown gases.

The methods developed by Goerens and Paquet and by Ryder have probably been the most satisfactory procedures for extracting at high temperatures and determining the total gas in metals. The small samples of the metal employed in both of these methods yielded only small volumes of gas for collection and analysis. This restriction of the size of the sample seems to be inherent in Ryder's method, but not necessarily so in the Goerens and Paquet method. Ryder's method is, of course, limited to gases evolved below the melting point of the metal. Both methods involve the collection of the gases by means of sample-collecting mercury pumps and the volumetric determination of the constituents of the gas mixture.

Oberhoffer and Piwowarsky<sup>14</sup> have proposed a "cold decomposition" method for extracting gases from iron by means of solution of the sample in mercuric chloride or bromine. Their claim for this method is that it determines only those gases held as such in the metal by solution or occlusion, whereas the vacuum fusion methods yield gases which are in large part generated by reactions at high temperatures between carbon and oxides of iron, manganese, and silicon in the steel. A means of distinguishing between these two

<sup>12</sup> See footnote 8, p. 448.

<sup>13</sup> H. M. Ryder, "A precision method for the determination of gases in metals," *Trans. Am. Electrochem. Soc.*, 83, pp. 197-204; 1918.

<sup>14</sup> P. Oberhoffer and E. Piwowarsky, "Zur Bestimmung der Gase im Eisen," *Stahl und Eisen*, 42, pp. 801-806; 1922.



types of evolved gas is very desirable. Dissolved or included compounds of gases with iron, silicon, manganese, etc., seem, however, to be of equally great importance in any investigation of the mechanism of deoxidation or of the dependence of the qualities of metals on their nonmetallic or "gas" constituents. The "cold decomposition" method, therefore, should not be considered as displacing a vacuum fusion method, but rather as supplementing it.

Several years before the publication of the antimony-tin vacuum fusion method by Goerens, Walker and Patrick<sup>15</sup> described a vacuum fusion procedure devised by them for the determination of oxygen in iron and steel. This method depended on the fusion, in an Arsem vacuum furnace, of the metal in contact with graphite and the formation of carbon monoxide by the reduction of oxides. The carbon monoxide was determined in an aliquot part of the total gas in the furnace after dry nitrogen had been admitted to the cool furnace to bring the pressure up to that of the atmosphere. It was difficult to remove all the oxygen from the furnace at the beginning of an analysis, and blank corrections for the amounts of oxygen retained in the furnace were large at the best. Gases other than carbon monoxide were not determined, although it seems probable that a portion of the oxygen was combined as  $\text{CO}_2$  and  $\text{H}_2\text{O}$  in the gases extracted. This method seems to have had little, if any, application.

### III. DEVELOPMENT OF THE RECOMMENDED PROCEDURE FOR VACUUM FUSION OF METALS AND DETERMINATION OF EVOLVED GASES

It seemed desirable to develop a method for the extraction of gases from metals at high temperatures which would avoid the use of sample-collecting vacuum pumps and volumetric methods of analysis and at the same time permit the use of a large sample. The method was originally desired for the analysis of gases evolved from iron and steel. These gases were known from the data of previous investigations to be, for the most part, carbon monoxide, carbon dioxide, hydrogen, nitrogen, and occasionally hydrocarbons in very small amounts. Since these gases are evolved from most other metals, besides iron and steel, under similar heating, the same method would, with little or no modification, be applicable to these metals.

#### 1. GRAVIMETRIC DETERMINATION OF GASES AT LOW PRESSURES

If the usual analytical absorbents for water and carbon dioxide function in a rather highly evacuated system as satisfactorily as under ordinary conditions of pressure, it should be possible to determine the gases evolved from a metal heated in vacuum by con-

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<sup>15</sup> W. M. Walker and W. A. Patrick, "Determination of oxygen in iron and steel by reduction in an electric vacuum furnace," Original Com., 8th Internat. Cong. of Applied Chem., 21, pp. 139-148; 1912.

necting one end of a suitable absorption train with a simple mechanical vacuum pump and the other end of the train with the evacuated furnace in which the sample is fused. The first step in the development of such a vacuum fusion method was, therefore, the determination of the efficiency of absorbents under rather low pressures.

(a) TRAIN OF ABSORBENTS

The absorption train as assembled for efficiency tests is shown in Figure 1. In the preliminary work, ordinary U tubes fitted with well-ground stopcocks and special ground-glass connections sealed to the side tubes (fig. 2) were used for holding the absorbents. A form of absorption tube (fig. 3), which is more conveniently filled and cleaned and is more robust than the U tube first used, was designed in the course of the investigation. This tube, made of

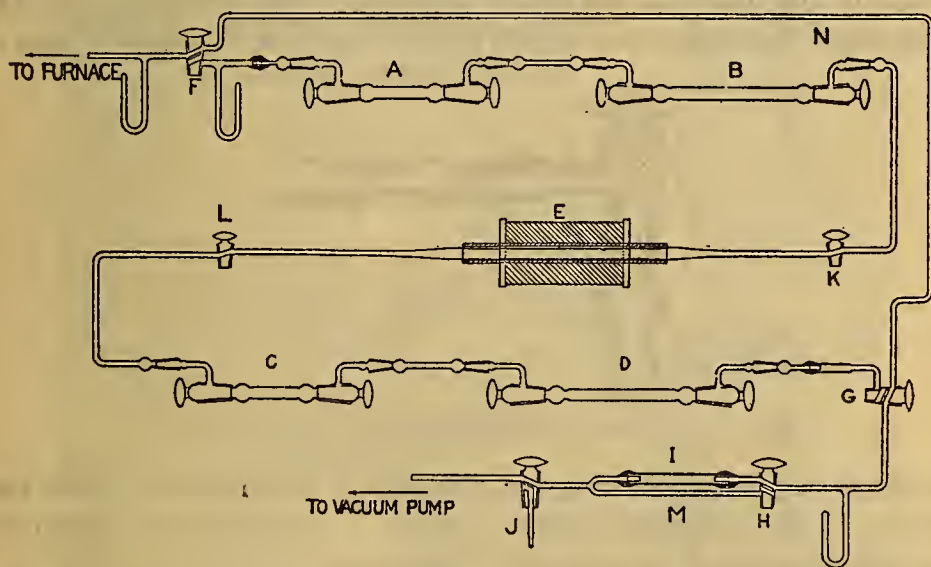


FIG. 1.—Train for the absorption of oxygen and hydrogen evolved from metals fused in vacuum

Pyrex glass throughout, has been used in the present work, except in a few of the earlier determinations. The dimension *B* is 4 cm for phosphorus pentoxide tubes and 9 cm for ascarite tubes. Tubes *A* and *C* (fig. 1) are filled with phosphorus pentoxide for the absorption of water evolved as such from the furnace containing the sample and that formed by the oxidation of hydrogen in the copper-oxide furnace *E*, respectively. Tubes *B* and *D* are filled with ascarite, a granular sodium hydroxide-asbestos absorbent, used for the absorption of carbon dioxide in the direct-combustion method for carbon in steel. This absorbent proved more efficient and more easily handled in the present work than soda lime or freshly ground potassium hydroxide. A short layer of phosphorus pentoxide is added in each end of the



tube in order to prevent the escape from the tube of moisture in the ascarite. The drying agent is required in each end of the tube, since the moisture from the ascarite will diffuse in both directions in the train when the pressure is low. The ascarite tubes serve for the absorption of carbon dioxide drawn from the furnace as such and also for that formed by the oxidation of carbon monoxide in the copper oxide furnace. The hard glass tube in *E* contains an 8-inch column of cupric oxide (10 to 20 mesh) heated to 300° C. by a chromel or nichrome wound resistance furnace. The train is arranged to function in the following order: Absorption of water vapor (*A*) and of carbon dioxide (*B*) from the furnace, oxidation of hydrogen and carbon monoxide (*E*), and absorption of water (*C*) and carbon dioxide (*D*) thus formed.

The vacuum furnace for the fusion of the sample (fig. 4) is connected to this train at the left of stopcock *F* (fig. 1) and a suitable mechanical vacuum pump at the left of stopcock *J*. Both *F* and *G*

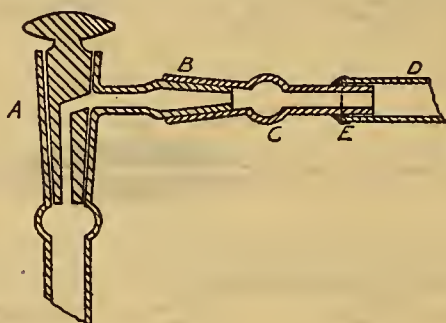


FIG. 2.—Method of sealing absorption tubes in train

are three-way stopcocks connected in such a manner as to allow the furnace to be evacuated either directly to the vacuum pump or through the train of absorbents to the pump.

A complete assembly of the apparatus is shown in Figure 5; the furnace is at the left and the vacuum pump with its motor at the extreme right.

The ground glass and de Khotinsky wax joint, shown in detail in Figure 2, was used for connecting the absorption tubes throughout the train with satisfactory results. *D* shows a rigidly fixed portion of the glass line and *E* a seal of de Khotinsky wax which can be softened by warming, so as to allow the sliding of the short tube *C* into *D*, thus separating the ground-glass connection at *B*. With a little care in the use of lubricant at *B*, the absorption tubes can be wiped entirely free from lubricant when they are removed for weighing.

As based on the amounts of water and carbon dioxide collected by the absorption tubes *A*, *B*, *C*, and *D* (fig. 1) in the fusion of metals containing carbon or of samples in graphite crucibles, conclusions



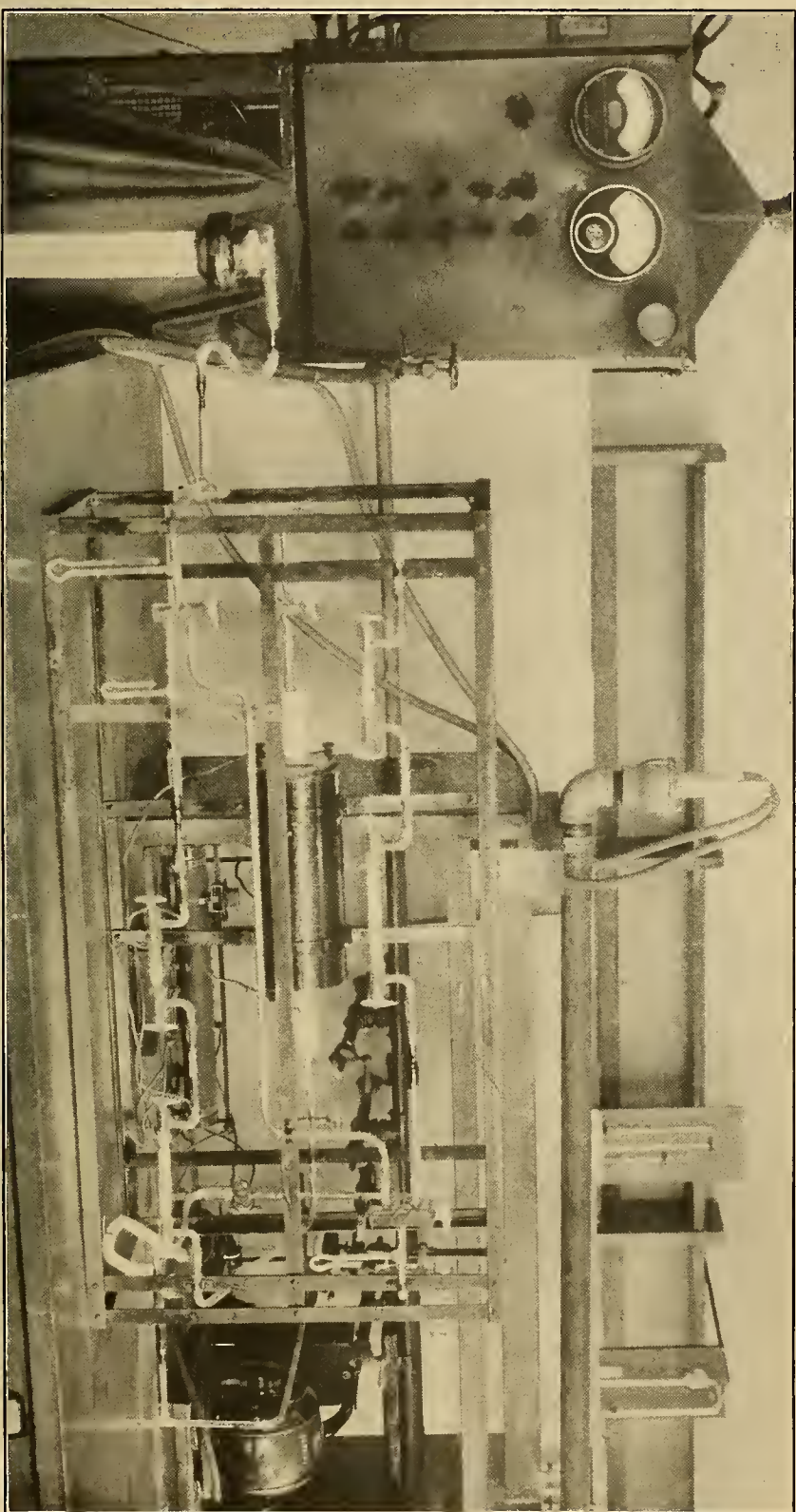


FIG. 5.—Complete assembly of apparatus for the determination of oxygen and hydrogen in metals by fusion in vacuum

regarding the gases originally present in the metal are limited to the calculation of the equivalent oxygen and hydrogen. No distinction can be made between the oxygen of metallic oxides and of oxides of carbon or between carbon monoxide and carbon dioxide. Duplicate analyses of steels made under conditions where the rates of heating differ yield carbon monoxide and carbon dioxide in widely varying ratios, yet give check results on the total amounts of oxygen and hydrogen evolved. Some distinction between oxygen present as metallic oxides and that present as CO and CO<sub>2</sub> may be possible in the case of carbon-free metals. In such a case the excess of oxygen obtained by melting in graphite over that obtained by melting in a refractory oxide should represent oxides in the metal reduced by carbon.

The absorption train, as here described, does not provide for the determination of the nitrogen present in the mixture of gases given off from most metals or for the determination of methane which may be present in small amounts in isolated cases.<sup>16</sup>

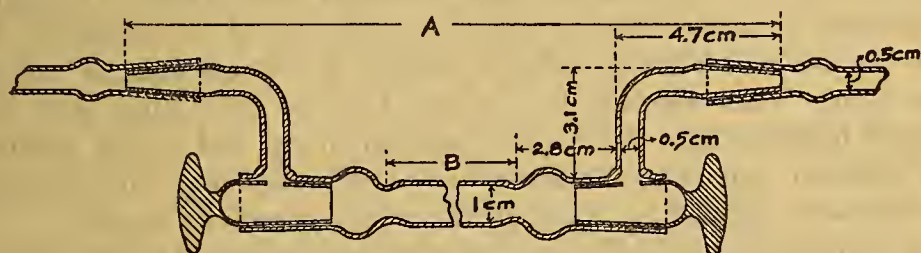


FIG. 3.—Designs of Pyrex glass absorption tubes

The determination of nitrogen in the gases evolved from metals fused in vacuum can be effected by the use in the absorption train of an evacuated tube containing metallic calcium heated to 700 to 800° C. Under such conditions free nitrogen and the calcium vapors form calcium nitride very readily. The contents of the calcium-containing tube may then be dissolved in dilute hydrochloric acid and the nitrogen in the solution determined by distillation from an alkaline solution and subsequent titration. The details of such a method for nitrogen will be described in a later paper.

Methane present in gases passing through the absorption train would not be oxidized by copper oxide at 300° C., and its hydrogen would therefore escape determination. If the determination of methane in the gas mixture resulting from fusion in vacuum of any special sample is desired, it can be effected in one of two ways—either by determining the gases first by the method as outlined above and then making a second determination on another sample, but with

<sup>16</sup> H. M. Ryder, "The relation between gases and steel," *Elec. Jour.*, **17**, pp. 161-165; 1920.



the copper oxide furnace operated at 800° C., a temperature at which the methane will be oxidized to water and carbon dioxide,<sup>17</sup> or by placing in the train following tube *D* (fig. 1), a second copper oxide furnace, operated at the higher temperature, and a tube containing phosphorus pentoxide, whereby the hydrogen of the evolved methane is determined from the water absorbed.

#### (b) BLANK CORRECTIONS IN TRAIN

In order to determine the effectiveness of the ground-glass connections in the train, and what, if any, corrections might be necessary in the weights of the various absorption tubes due to leaks, moisture absorbed in the train when standing with absorption tubes removed, moisture or other volatile matter from the copper oxide tube, or other sources of blank corrections, a number of runs of one hour each were made with all tubes in the train, the copper oxide at 300° C., and the vacuum pump running, but with stopcock *F* closed, thus shutting off the vacuum tube of the induction furnace. In no case did tube *A*, *B*, or *C* show any gain in weight greater than 0.1 mg per hour and in most cases no gain whatever could be detected. In the first series of blanks tube *D* showed a uniform gain of 0.8 mg per hour. This was due to the fact that no protecting tube was placed between tube *D* and the vacuum pump and it was possible for gases or vapors to diffuse from the oil pump into tube *D* when there was no flow of gas through the train toward the pump.

A similar series of blanks was run after a guard tube *I* of phosphorus pentoxide had been inserted in the line between tube *D* and the vacuum pump. Under these conditions the gain in weight in tube *D* was between 0.1 and 0.2 mg per hour. That this gain in weight was due to something other than moisture was indicated by the fact that no gain in weight was obtained when a phosphorus pentoxide tube was substituted in the train in the position usually occupied by tube *D*, a soda-lime tube.

The practice of weighing the absorption tubes to 0.1 mg was justified by the results of these blank tests for the train. No corrections for blanks on the train were used in the tests of the efficiency of the train with known mixtures of gases. In the application of the method any blank due to the train is included in the total blank determined for the furnace and train combined. This blank will be discussed later.

#### (c) EFFICIENCY OF ABSORBENTS WITH KNOWN GASES

A series of tests with pure gases and mixtures of gases of known composition was carried out in order to determine the efficiency of the absorbents in the above train under the low pressures maintained

<sup>17</sup> G. O. Burrell and G. G. Oberfell, "The use of copper oxide for fractionation combustion of hydrogen and carbon monoxide in gas mixtures," *Jour. Ind. and Eng. Chem.*, 8, pp. 228-231; 1916.

by the continuous pumping of gases from the furnace and train during the heating of the specimen. The same tests also determined the efficiency of the copper-oxide tube in oxidizing hydrogen and carbon monoxide at low pressures.

The purity of the gases used in these tests and the composition of the mixtures of hydrogen and carbon monoxide were determined accurately by standard methods of gas analysis.<sup>18</sup> The analysis of the hydrogen was made by the gas interferometer method,<sup>19</sup> and that of the carbon monoxide and the mixture of hydrogen and carbon monoxide by means of a modified Orsat apparatus.<sup>20</sup> The known gas or gas mixture was drawn into a gas buret connected to the train of absorbents in place of the vacuum induction furnace at the left of stopcock *F* (fig. 1) and a measured volume of the gas admitted to the train. This gas was in most tests admitted quite slowly, so that the pressure of the gas on its entrance into the train was not greater than 10 to 15 mm of mercury, often much less. Some tests were made in which the gas was admitted very rapidly to simulate any sudden liberation of large amounts of gas from a metal sample. Practically all the gas admitted to the train was absorbed in the various tubes regardless of the rate of its admission.

The data from a few typical runs with carbon monoxide, hydrogen, and mixtures of the two are given in Tables 1, 2, and 3. The average percentage recovery of carbon monoxide indicated by the data in Table 1 is 99.5. The recovery of hydrogen shown in Table 2 averages 100.0 per cent. The values for the hydrogen and carbon monoxide in mixtures of the two gases averaged slightly higher than the values given by standard gas analysis methods. The average value for hydrogen in Table 3 is only 0.1 per cent higher than the value given by the interferometer method and for carbon monoxide 0.4 per cent higher than by the standard method. These results indicate complete oxidation of carbon monoxide and hydrogen and absorption of water vapor and carbon dioxide by the train of absorbents described above and under conditions closely approximating those existing during an actual absorption of gases evolved from heated and fused metals.

<sup>18</sup> The authors are indebted to S. F. Pickering and P. G. Ledig, of the Bureau of Standards, for determining the purity of the hydrogen and the composition of the carbon monoxide-hydrogen mixture.

<sup>19</sup> J. D. Edwards, Application of the Interferometer to Gas Analysis, B. S. Tech. Paper No. 131; 1919.

<sup>20</sup> E. R. Weaver and P. G. Ledig, "New forms of combustion apparatus for use in gas analysis," Jour. Ind. and Eng. Chem., 12, p. 268; 1920.



TABLE 1.—Oxidation of carbon monoxide to carbon dioxide by cupric oxide at low pressures

[Purity of carbon monoxide, 99.9 per cent]

Test number	Volume of carbon monoxide taken	Weight of carbon dioxide recovered	Equivalent volume of carbon monoxide	Recovery of carbon monoxide <sup>1</sup>
	<i>cm</i> <sup>3</sup>	<i>g</i>	<i>cm</i> <sup>3</sup>	<i>Per cent</i>
1	27.22	0.0536	27.27	100.3
2	21.44	.0419	21.32	99.5
3	25.39	.0489	24.88	98.1
4	27.05	.0535	27.22	100.7
5	16.29	.0317	16.13	99.1
Average				99.5

<sup>1</sup> The value for per cent recovery takes into consideration the purity of the carbon monoxide used; that is, volume of carbon monoxide actually present in the gas used is 99.9 per cent of the volume given in the second column.

TABLE 2.—Oxidation of hydrogen to water by cupric oxide at low pressures

[Purity of hydrogen, 99.3 per cent]

Test number	Volume of hydrogen taken	Weight of water recovered	Equivalent volume of hydrogen	Recovery of hydrogen <sup>1</sup>
	<i>cm</i> <sup>3</sup>	<i>g</i>	<i>cm</i> <sup>3</sup>	<i>Per cent</i>
1	28.85	0.0230	28.66	100.0
2	27.71	.0219	27.29	99.2
3	35.54	.0284	35.38	100.3
4	36.64	.0293	36.51	100.3
5	39.54	.0316	39.38	100.3
Average				100.0

<sup>1</sup> The value for per cent recovery takes into consideration the purity of the hydrogen used; that is, volume of hydrogen actually present in the gas used is 99.3 per cent of the volume given in the second column.

TABLE 3.—Oxidation by cupric oxide and recovery of hydrogen and carbon monoxide from a mixture of the two gases at low pressures

[Mixture contained hydrogen=61.7 per cent; carbon monoxide=37.0 per cent]

Test number	Volume of mixture taken	Weight of water recovered	Weight of carbon dioxide recovered	Equivalent volume of hydrogen recovered	Equivalent volume of carbon monoxide recovered	Hydrogen	Carbon monoxide
	<i>cm</i> <sup>3</sup>	<i>g</i>	<i>g</i>	<i>cm</i> <sup>3</sup>	<i>cm</i> <sup>3</sup>	<i>Per cent</i>	<i>Per cent</i>
1	34.15	0.0170	0.0251	21.19	12.77	62.0	37.4
2	37.75	.0187	.0278	23.30	14.14	61.8	37.5
3	29.36	.0145	.0215	18.07	10.94	61.5	37.3
4	39.04	.0194	.0286	24.18	14.55	61.9	37.3
Average						61.8	37.4

## 2. METHOD OF HEATING METAL SAMPLES

In the preliminary work on methods for extracting gases from metals in vacuum the use of platinum-wound resistance furnaces for melting ferrous metals in gas-free graphite boats or crucibles and of small Arsem furnaces for melting metal samples contained in crucibles within refractory (alundum or impervite porcelain) tubes proved unsatisfactory.

With the development of the high-frequency induction furnace<sup>21</sup> by E. F. Northrup, many of the difficulties previously attendant on the production of high temperature under a vacuum were obviated. This method of heating was at once recognized as particularly adapted for use in the study of gases in metals, both for the extraction and determination of gases present in metals and for the determination of the solubility of gases in solid and liquid metals.

#### HIGH-FREQUENCY INDUCTION VACUUM FURNACE

The fundamental theories of inductive heating by means of high-frequency currents have been discussed by Northrup.<sup>22</sup> The high-frequency induction furnace consists, essentially, of a water-cooled inductor coil of copper tubing (*D*, fig. 4) whose terminals are connected to a source of supply of high-voltage, high-frequency current. Such current is usually supplied from electrostatic condensers charged by 60-cycle current at 6,600 volts and discharging through a spark gap and inductor coil, producing a current of a frequency of 10,000 cycles or over. Any electrically conducting material placed centrally within the coil of copper tube, but thermally and electrically insulated from the coil, is rapidly heated by induced eddy currents.

With proper design of the inductor coil and efficient heat insulation the temperature attainable in a sample of metal is limited only by the boiling point of the metal and the melting point of the refractory surrounding the metal. Fairly accurate and rapid control of the temperature of the metal is possible by regulation of the power input of the furnace, and with careful regulation a rather constant temperature can be maintained over a considerable length of time.

High temperatures are more readily attained and temperature control is just as rapid and easy when the heating is carried out in vacuum. In order to heat in a vacuum, it is only necessary to place the metal to be heated in a crucible within a closed-end fused silica tube, which fits closely inside the water-cooled inductor coil. With proper heat insulation between the metal and the walls of the tube, the latter, aided by the water-cooling from the inductor coil, stay cold enough to maintain a vacuum when the metal sample is heated to 2,000° C. and higher.

The inductor coil and the tube used in the present investigation for the heating or melting of metals in vacuum is shown in Figure 4. Within the inductor coil *D* is placed the fused silica tube *C* ( $2\frac{1}{4}$  inches inside diameter and 24 inches long), which is fitted with a cap, either as shown at *A* or with a simple hard glass cap with a side tube, for the vacuum connection. For most work the latter type of cap is entirely satisfactory. The cap of either type is sealed to the silica

<sup>21</sup> Anon., "Northrup-Ajax high-frequency induction furnace," Chem. and Met. Eng., 19, p. 155; 1918.

<sup>22</sup> E. F. Northrup, "Principles of induction heating with high-frequency currents," Trans. Am. Electrochem. Soc., 35, pp. 69-153; 1919.



tube with de Khotinsky wax. The upper part of the metal cap *A*, water-cooled through the channel *H*, is threaded and screwed down on the lower part of the cap. The joint between the two parts of the cap is made vacuum tight by means of a lead, fiber, or rubber gasket. A glass window in the top of the cap allows observation of the contents of the silica tube and temperature readings with an optical pyrometer. The absorption train described above (fig. 1) is connected to the furnace at *B*. The crucible *G*, of electrically fused magnesium oxide or other suitable refractory, serves as a radiation screen and heat insulator and contains an inner crucible *F* of graphite. The cylindrical block *E* of the same material as the heat insulator *G* is sometimes necessary in order to center the graphite crucible with respect to the inductor coil.

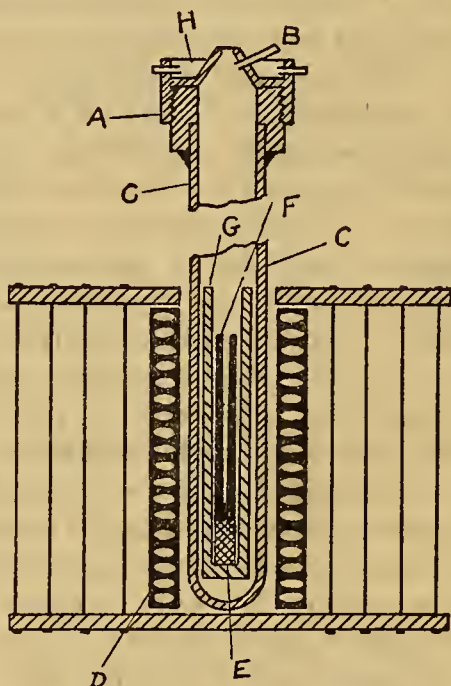


FIG. 4.—High-frequency vacuum furnace for melting metal samples

The above arrangement of the vacuum furnace will accommodate a 200 g sample, if necessary, and is employed when it is desired to heat a very large metal sample in contact with carbon, as, for example, a sample in which the gas content is very low or there is segregation of the gas-forming substances. However, in most cases of heating the sample in contact with carbon and in heating the sample directly in nonconducting refractory crucibles, the furnace, as shown in Figure 4, is slightly modified. In these cases a smaller silica tube is used ( $1\frac{1}{2}$  inches inside diameter by 24 inches long), with a correspondingly smaller inductor coil, magnesia insulator, and graphite crucible. Such a graphite crucible will hold 50 to 60 g of metal. With this smaller diameter tube a hard glass, tubulated cap with no

water cooling, sealed to the silica tube with de Khotinsky wax, serves just as well as the more complicated water-cooled metal cap, which may be required with shorter or larger diameter vacuum tubes. In the case where the sample is heated directly in nonconducting refractory crucibles, *F* (fig. 4) represents the metal sample contained in the nonconducting refractory oxide crucible *G*, which serves both as crucible and as heat insulator.

### 3. FUSION OF IRON AND STEEL IN REFRACTORY OXIDE CRUCIBLES

A review of the work of earlier investigators suggested the trial, in the present work, of three methods of fusing the metal samples in the high-frequency vacuum furnace, namely, fusion of the metal (*a*) in a refractory oxide crucible,<sup>23</sup> the heating taking place by direct induction in the metal sample; (*b*) with antimony tin in an oxide or silicate crucible,<sup>24</sup> heating by induction in both metal sample and antimony-tin alloy; and (*c*) in a gas-free graphite crucible,<sup>25</sup> heating chiefly by induction in the graphite. The first of these three methods may, for convenience, be designated as the "direct-fusion" method. In the present investigation each of these three methods was tested, using both carbon steels and pure electrolytic iron.

#### (a) REDUCTION OF CRUCIBLE MATERIAL BY CARBON AND IRON-CARBON ALLOYS

The first method of melting studied was the direct fusion of the metal in refractory oxide crucibles. Many refractory oxides dissociate appreciably or are readily reduced by carbon under low pressures at the high temperatures required for the fusion of iron and steels.<sup>26</sup> Difficulty is therefore to be anticipated in finding a refractory oxide which can hold molten steel in a vacuum without any reaction between the oxide of the crucible and the carbon of the steel.

1. **MAGNESIA.**—Magnesia crucibles have been used by Goerens and Paquet and by Oberhoffer and Beutell in their method for gas extraction. Similar crucibles have been used at the Bureau of Standards in melting electrolytic iron and iron-carbon alloys in Arsem furnaces. In this latter work it has been found that the magnesia is reduced by contact with iron-carbon alloys at temperatures, about 1,600° C., reached in fusing pure iron. The products of such reduction, magnesium and carbon monoxide, seem to undergo the reverse reaction and to deposit as magnesia and finely divided

<sup>23</sup> See footnote 8, p. 448.

<sup>24</sup> See footnote 9, p. 448.

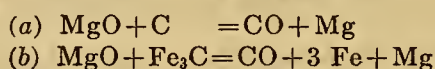
<sup>25</sup> See footnote 15, p. 450.

<sup>26</sup> R. E. Slade, "Reducibility of magnesium oxide by carbon," *Jour. Chem. Soc.*, 93, p. 327 T; 1908. H. C. Greenwood, "Reduction of refractory oxides by carbon." *Ibid*, 93, p. 1483 T; 1908. E. Tiede and E. Birnbrauer, "Spezielle Arbeitsmethoden zur Erzeugung hoher Temperaturen im Vakuum und das Verhalten einige Metalle, Oxyde und Carbide bei denselben," *Zeit. anorg. Chem.*, 87, p. 129-168; 1914.



carbon in the cooler parts of the furnace. Watts<sup>27</sup> reported such a reaction between carbon and magnesia, and also made the statement that magnesia is more readily reduced by carbides of iron, nickel, and chromium than by pure carbon.

Such behavior would produce erroneous results in the use of magnesia crucibles for containing molten steel in the determination of evolved gases, in that, as long as carbon remained in the steel, carbon monoxide would be formed according to one of the following reactions:



Except in the rather improbable case of complete reversal of these reactions in the much cooler zones of the vacuum furnace, the evolution of carbon monoxide would continue until decarburization of the steel was complete and a portion of the oxygen determined under such conditions would have had its origin in the crucible refractory rather than in the metal sample.

Crucibles of electrically fused magnesia, containing 15 per cent zirconium silicate as a binding agent, have good mechanical strength and are easily prepared. The first crucibles tested for the present work were of this type. These crucibles are prepared from a mixture of magnesia and zirconium silicate, ground to pass an 80-mesh screen and moistened with just sufficient water to permit packing firmly around a mandrel in a graphite mold. After tamping in the crucible material the mandrel is removed and the crucible and mold together are dried in an oven at about 130° C. and then heated to 1,600 to 1,700° C. in an Arsem vacuum furnace. This higher heating makes the magnesia-zirconium silicate crucible dense and mechanically strong and produces enough shrinkage to allow the crucible readily to be removed from the mold. The walls of the finished crucible have a thickness of  $\frac{1}{4}$  to  $\frac{3}{8}$  inch; they serve also as heat insulation between the molten metal and the silica tube (fig. 4). These crucibles are about 5 inches deep and taper slightly both inside and outside.

This type of crucible was first tested for its resistance to reduction by hot graphite in a vacuum. A cylinder of graphite was placed inside the crucible and the annular space between the crucible walls and the cylinder tightly packed with graphite powder. The crucible was then placed in the vacuum furnace and heated for one hour while evolved gases were pumped out and discarded. This was for the purpose of eliminating any gases occluded in the graphite or crucible. Stopcocks *F* and *G* (fig. 1) were then turned to connect the vacuum pump to the furnace through the train of absorbents and the heating continued for 15 minutes. This procedure was

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<sup>27</sup> O. P. Watts, "The action of carbon on magnesia at high temperatures," *Trans. Am. Electrochem. Soc.*, 11, pp. 279-289; 1907. See also footnote 26, p. 459.

carried out while heating the graphite at three different temperatures, approximately 1,480, 1,590, and 1,690° C. No carbon monoxide was evolved during the 15 minutes' heating at either of the two lower temperatures. At 1,690° C. the beginning of reduction of the crucible was evidenced by the absorption of 0.5 mg of carbon monoxide in absorption tube *D*. This result corresponds closely with the temperature of 1,700° C. found by Slade<sup>28</sup> for the reduction of magnesia by carbon. It would thus appear that, with respect to reduction by free carbon, magnesia-zirconium silicate crucibles may safely be used up to temperatures of 1,600° C.

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<sup>28</sup> See footnote 26, p. 459.



TABLE 4.—Tests of refractory oxide crucibles for melting carbon steel

Crucible test number	Composition of crucibles; parts by weight	Composi- tion of steel before fusion <sup>1</sup>	Weight of sample	Time molten	Approximate temperature of melt	Maxi- mum pres- sure	Weight of gases evolved				Per cent by weight of gases evolved		Composi- tion of steel after fusion <sup>1</sup>	Loss in carbon
							H <sub>2</sub> O	CO <sub>2</sub>	H <sub>2</sub> (weigh- ed as H <sub>2</sub> O)	CO (weigh- ed as CO <sub>2</sub> )	Total carbon	Total hydro- gen	Total oxygen	
				<i>Min.</i>	<i>° C.</i>	<i>mm Hg</i>	<i>g</i>	<i>g</i>	<i>g</i>	<i>g</i>				<i>Per cent</i>
1	85 electrically fused magnesia; 15 zirconium silicate	<i>Per cent</i> C=0.53 C=0.53 C=0.25 Si=0.02	61.4	170	1,550-1,600	35	0.0006	0.0129	0.0041	0.0438	0.04	0.0088	0.057	C=0.10
2	do	C=0.53 C=0.25 Si=0.02	53.2	180	1,550-1,600	50	0.0006	0.0224	0.0019	0.0417	0.03	0.0034	0.045	C=0.06
3	Electrically fused magnesia	C=0.25 Si=0.02	100.9	17	1,550	57	0.0018	0.0035	0.0007	0.0604	0.03	0.0009	0.038	C=0.20
4	Pure magnesia (silicon-free)	C=0.25 Si=0.02	97.1	20	1,525	90	0.0017	0.0030	0.0006	0.0641	0.03	0.0008	0.042	C=0.10
5	Alumina (sodium-silicate binder)	C=0.25 Si=0.02	95.4	7	1,600	>100	0.0123	0.0063	0.0057	0.0585	0.03	0.0074	0.051	C=0.19
6	95 alumina; 5 silica	C=0.25 Si=0.02	100.1	7	1,535	>95	Nil.	0.0016	0.0008	0.0137	0.01	0.0008	0.009	C=0.21
7	80 alundum; 20 zirconium silicate	C=0.25 Si=0.02	100.6	10	1,600	>95	Nil.	0.0034	0.0010	0.0147	0.01	0.0010	0.011	Si=0.09
8	90 zirconia; 10 alumina	C=0.25 Si=0.02	98.2	60	1,560-1,600	41	0.0027	0.0027	0.0027	0.0217	0.01	0.0030	0.017	C=0.14
9	do	C=0.25 Si=0.02	98.5	45	1,560-1,700	29	0.0082	0.0052	0.0083	0.0107	0.01	0.0043	0.017	Si=0.18
10	do	C=0.25 Si=0.02	97.2	170	1,540-1,570	65	0.0107	0.0039	0.0033	0.0120	0.01	0.0046	0.020	C=0.22
11	Zirconium silicate	C=0.53	90.7	30	1,600	110	Nil.	0.0047	0.0030	0.1527	0.07	0.0033	0.100	C=0.25
12	90 zirconia; 10 alumina	C=0.76	90.4	80	1,540-1,590	95	0.0136	0.0033	0.0035	0.0398	0.02	0.0055	0.041	C=0.28
13	do	C=0.74	85.5	110	1,540-1,590	40	0.0204	0.0078	0.0030	0.0144	0.01	0.0062	0.037	C=0.63
14	do	C=0.72	88.9	260	1,540-1,590	>100	0.0064	0.0181	0.0029	0.0164	0.01	0.0041	0.032	C=0.53

<sup>1</sup> The authors are indebted to H. A. Bright and W. C. Fedde, of the chemistry division, for the determinations of carbon, silicon, sulphur, and manganese in iron and steel samples reported here and elsewhere throughout this paper.

The above tests do not, however, give any indication as to the tendency to reduction of this refractory by metal carbides. Accordingly, analyses for evolved gases were made on two samples of a 0.53 per cent carbon steel (crucible tests 1 and 2, Table 4). Each of the two samples was melted four successive times, each time in a fresh magnesia-zirconium silicate crucible, before it was possible to reduce the pressure in the furnace to 5 mm of mercury or less with the metal sample still liquid. During every melting the temperature of the metal was maintained at between 1,550 and 1,600° C. The total time each sample was held molten was approximately three hours. The carbon content of the samples after this treatment was 0.10 and 0.06 per cent, respectively. The carbon lost from the metal was thus 0.43 and 0.47 per cent, while the carbon recovered as CO and CO<sub>2</sub> evolved was equivalent to only 0.04 and 0.03 per cent. Inasmuch as the evolution of CO and CO<sub>2</sub> did not cease until the steel was practically completely decarbonized and only a small portion of the carbon lost from the steel was evolved as oxides of carbon, it is to be concluded that this type of crucible is reduced by carbon dissolved in iron and that the reverse reaction between CO and metallic magnesium vapor is only partially complete. This type of crucible is therefore not suitable for use in the direct melting of steels for the determination of evolved oxygen.

While the use of 15 per cent of zirconium silicate in the above type of crucible as a binder gave crucibles of better mechanical strength than was the case when magnesia alone was used, there was the possibility that the silicate was causing some of the difficulty. Accordingly crucibles made of magnesia alone were employed in two test analyses on a low-carbon steel. This steel contained 0.25 per cent carbon and 0.02 per cent silicon.

The magnesia crucibles, as well as all other refractory oxide crucibles used in this investigation, were molded and burned in a manner similar to that described above for the magnesia-zirconium silicate crucibles. The first magnesia crucible was of electrically fused material, which normally contains from a few tenths up to 1.0 per cent of silica. A second magnesia crucible was prepared from specially purified oxide which was practically free from silica.<sup>29</sup>

A sample of the 0.25 per cent carbon steel was held molten for 17 minutes in the electrically fused magnesia crucible (3, Table 4). The temperature reached shortly after the metal melted was 1,550° C. A dense smoke soon began to come from the crucible, and further temperature readings could not be taken. The pressure within the furnace rose steadily to 57 mm of mercury and was still increasing when the heating was stopped. The fused sample contained 0.20

<sup>29</sup> R. P. Neville and J. R. Cain, *The Preparation and Properties of Pure Iron Alloys: I. Effects of Carbon and Manganese on the Mechanical Properties of Iron*, B. S. Sci. Paper No. 453; 1922.



per cent carbon and 0.05 per cent silicon as compared with the original 0.25 per cent carbon and 0.02 per cent silicon.

A similar test with another sample of the same steel was made with the silica-free magnesia crucible (4, Table 4). This crucible behaved in a manner similar to the fused magnesia crucible. The metal sample was held molten for 20 minutes; the same evolution of smoke, probably a cloud of  $\text{MgO}$  formed by the reduction of carbon monoxide by metallic magnesium vapor, was observed shortly after melting and when the temperature was approximately  $1,525^{\circ}\text{C.}$ ; the pressure at the end of the heating was 90 mm of mercury and was still rising. The carbon remaining in the fused sample was 0.10 per cent and the silicon 0.02 per cent. There is thus a loss in carbon, but no increase in silicon.

These two tests show clearly that neither zirconium silicate nor silica is responsible for the formation of the oxides of carbon and the decarburization of the metal during the fusion of a carbon steel; that pure magnesia does rapidly oxidize the carbon in molten steel at temperatures below that at which it begins to oxidize free graphite; and that magnesia crucibles are not suitable for use in the direct fusion of carbon steels in vacuum for the determination of evolved oxygen.

2. ALUMINA.—Crucibles of alumina were next tested (5 to 7, Table 4). To one crucible a very slight amount of sodium silicate was added as a binder and to another 5 per cent of silica. A third crucible was made of 80 parts of alundum and 20 parts of zirconium silicate. Samples of the same low-carbon steel were run in all crucibles. Large amounts of gas were evolved when the metal was melted, and the pressure in the furnace in each case increased within a few minutes to over 100 mm of mercury, pressures greater than those developed when melting in magnesia refractories.

The melt from each crucible was appreciably decarburized as well as being higher in silicon than the original steel. The increase in silicon was especially marked in the metal from the alundum-zirconium silicate crucible. Aluminum oxide refractories of the compositions tested were, therefore, even less satisfactory than magnesia for use in melting carbon steels in vacuum without the generation of oxides of carbon from the interactions of melt and refractory. In this connection it has already been pointed out that the use of alundum refractories by Alleman and Darlington may be open to serious objection.

3. ZIRCONIA.—Crucibles of zirconium oxide were then prepared for test. Since several crucibles made without the addition of any binding agent lacked suitable mechanical strength, it was found after a trial of several binding agents that a mixture of 90 parts of calcined  $\text{ZrO}_2$  and 10 parts of  $\text{Al}_2\text{O}_3$  produced a fairly strong refrac-

tory after heating in an Arsem furnace to 1,600 to 1,700° C. The objection might naturally be made, in view of preceding tests, that alumina is an undesirable addition. The results with these crucibles on low-carbon steels do not sustain such an objection. This may possibly be due to the fact that the small amount of alumina at the surface of such crucibles was eliminated or converted to carbide during the calcination of the crucible. It had been observed that the outside of zirconia-alumina crucibles was very noticeably changed by heating in the graphite mold in an Arsem furnace. It was thought that some formation of carbide took place and accordingly the zirconia-alumina crucibles were filled with powdered graphite during their calcination to promote the formation of carbide on the inner surface.

Three tests of zirconia-alumina crucibles were made, using samples of the low-carbon steel employed in the previous tests (8, 9, and 10, Table 4). These tests were very satisfactory. The maximum pressure in the furnace from the evolution of gas was 30 to 60 mm of mercury and was reached shortly after the sample melted. Thereafter the pressure decreased steadily until the still molten sample was practically gas free at the expiration of 50 to 60 minutes. The carbon remaining in the fused metal was very nearly the same as in the original steel, namely, 0.22, 0.22, and 0.23 per cent for the three tests, as compared with 0.25 per cent before fusion. In run 10, Table 4, the steel sample was kept molten for nearly three hours, the same length of time that sufficed for the nearly complete decarburization of a 0.53 per cent carbon steel in magnesia-zirconium silicate crucibles. This longer heating caused no greater loss of carbon from the steel than the 45 and 60 minute heatings in runs 8 and 9, Table 4.

The failure of the magnesia-zirconium silicate crucibles to resist reduction by carbon steels had been shown not to be due to the zirconium silicate content of the refractory. In view of the promising behavior of zirconia-alumina crucibles, a test run (11, Table 4) was made, using a crucible of zirconium silicate, as the latter refractory is more easily obtained and made into crucibles. A sample of the 0.53 per cent carbon steel was held molten in this crucible in two runs of 15 minutes each, or 30 minutes in all. Very large volumes of gas were evolved, largely carbon monoxide, and the pressure within the furnace rose to a maximum of 110 mm of mercury. This sample was not held molten until free from gas, as it was evident from the rapid evolution of gas that reaction with the crucible was taking place. That such was the case is further indicated by the loss in carbon from the fused samples, namely, 0.25 per cent.



The three tests with zirconia-alumina crucibles on low-carbon steel (8, 9, and 10, Table 4) led to the conclusion that this refractory was satisfactory for the use desired. Somewhat later results from the analysis of certain steels for oxygen and hydrogen raised a question as to the suitability of this refractory for higher carbon steels. Tests were, therefore, made with samples of rail steel, containing about 0.7 per cent carbon (12 to 14, Table 4). It was found in these tests that there was a considerable decarburization of the melt by the zirconia-alumina crucible, that greater pressures were developed within the furnace, and that it was not possible, even in a four-hour heating period, to obtain a lower pressure indicating a melt free from gases.

The data from all of the above tests on magnesia, alumina, and zirconia refractories for the direct melting of carbon steels in vacuum (assembled in Table 4) indicate that the zirconia-alumina crucibles were the only ones sufficiently resistant to reduction by molten carbon steels to give any promise of being suitable for the service desired in the case of steels containing 0.3 per cent carbon or less. This refractory was, however, found not suitable for use in melting higher carbon steels; for example, a 0.7 per cent carbon steel.

The values given in Table 4 for the oxygen and hydrogen content of the steels used are not corrected by any blank due to furnace and train. They are calculated as per cent by weight from the total amount of gas evolved from the fused steel, including any gases formed by reactions with the crucible. On this basis they are simply comparable among themselves to indicate the suitability of the various types of crucibles. In order to secure corrected values for oxygen and hydrogen determined by direct fusion of the steel, the blank on the apparatus must be taken into account.

#### (b) BLANK CORRECTIONS

It has already been shown that the absorption train introduces little, if any, blank correction. The furnace proper, consisting of the evacuated silica tube and the refractory crucible, does, however, necessitate a considerable blank correction. In order to determine the value of the total blank in determinations in which zirconia-alumina crucibles were used, the gas-free melts of the low-carbon steel from runs 8, 9, and 10, Table 4, were remelted in fresh zirconia-alumina crucibles under conditions exactly duplicating the original determinations. Appreciably higher values for the oxygen and hydrogen blank were obtained when the zirconia-alumina crucibles were allowed to stand for any appreciable time in the air than when used immediately after making gas free or kept in a desiccator until used. All crucibles used in gas determinations have been those giving the lower blank, which averaged 0.0096 g for oxygen and 0.0028 g for hydrogen (Table 5).

Similar blanks were determined for the direct fusion of electrolytic iron in the zirconium silicate crucibles. The results are given in Table 6. The average value for this blank was 0.0096 g oxygen and 0.0011 g hydrogen.

TABLE 5.—Gases from low-carbon steel (0.25 per cent C) fused in vacuum

Test number	Method of fusion	Weight of sample	Per cent by weight of gas evolved		Typical crucible blanks	
			Oxygen	Hydrogen	Oxygen	Hydrogen
8.....	Solid samples in 90 per cent zirconia and 10 per cent alumina crucibles.	<i>g</i>			<i>g</i>	<i>g</i>
9.....		98.2	0.0084	0.0006		
10.....		98.5	.0086	.0018	0.0087	0.0024
		97.2	.0108	.0021	.0105	.0032
Average.....			.0093	.0015	.0096	.0028
17.....	Solid samples with gas-free antimony-tin alloy in magnesia crucibles.	37.2	.0075	.0007		
18.....		32.5	.0185	.0009	.0047	.0008
19.....		29.2	.0100	.0013	.0049	.0007
20.....		33.9	.0062	Lost.		
Average.....			.0105	.0010	.0048	.0008
21.....	Solid samples in graphite crucibles.	25.0	.0160	.0015		
22.....		29.0	.0277	.0016	.0039	.0004
23.....		25.0	.0178	.0015	.0039	.0003
Average.....			.0205	.0015	.0039	.0004
16.....	Finely milled sample with gas-free antimony-tin alloy in magnesia crucible	33.0	.0400	.0032	( <sup>1</sup> )	( <sup>1</sup> )
24.....	Finely milled sample in graphite crucible	33.0	.0412	.0037	( <sup>2</sup> )	( <sup>2</sup> )

<sup>1</sup> As in tests 18 and 19.<sup>2</sup> As in tests 22 and 23.

TABLE 6.—Gases from electrolytic iron fused in vacuum

Test number	Method of fusion	Weight of sample	Per cent by weight of gas evolved		Typical crucible blanks	
			Oxygen	Hydrogen	Oxygen	Hydrogen
25 <sup>1</sup> .....	Solid sample in zirconium silicate crucible.	<i>g</i>			<i>g</i>	<i>g</i>
26 <sup>1</sup> .....		102.8	0.0097	0.0013	0.0095	0.0011
		98.2	.0086	.0012	.0097	.0011
Average.....			.0092	.0013	.0096	.0011
27.....	Solid sample with gas-free antimony-tin alloy in zirconium silicate crucible.	33.7	.0083	.0017	.0041	.0005
28.....		36.5	.0093	.0017	.0039	.0005
Average.....			.0088	.0017	.0040	.0005
29.....	Solid sample in graphite crucible.	29.7	.0162	.0010	.0051	.0003
30.....		28.3	.0163	.0011	.0049	.0003
					.0047	.0003
Average.....			<sup>2</sup> .0163	<sup>2</sup> .0011	.0049	.0003
31.....	Solid sample in graphite crucible.	39.9	.0185	.0018	.0039	.0004
32.....		34.5	.0183	.0018	.0039	.0003
					.0037	.0004
Average.....			<sup>2</sup> .0184	<sup>2</sup> .0018	.0038	.0004

<sup>1</sup> The composition before fusion of the electrolytic iron used in tests 25 and 26 was C, 0.034; Mn, trace; Si, 0.033; S, 0.003; P, 0.007. After fusion for the determination of gases the sample from run 25 contained C, 0.010; Si, 0.016; S, 0.004; and P, 0.009. The sample from run 26 contained C, 0.014; Si, 0.022; S, 0.008; and P, 0.007.

<sup>2</sup> Test numbers 25 to 30, inclusive, represent one lot of electrolytic iron; test numbers 31 and 32 represent another lot.



(c) OXYGEN AND HYDROGEN FROM IRON AND STEEL FUSED IN ZIRCONIA  
REFRACTORIES

The corrected values for oxygen and hydrogen in the 0.25 per cent carbon steel melted in zirconia-alumina crucibles are given in Table 5. The average values are 0.0093 per cent oxygen and 0.0015 per cent hydrogen in the steel. The loss of carbon from the steels during these tests (8, 9, and 10, Table 4) was as high as 0.03 per cent. If this loss represents carbon oxidized to CO by the refractory, then the amount of oxygen taken from the crucible during the determination is greater than the apparent oxygen content of the steel as shown in Table 5. Such a condition, therefore, means that even the zirconia-alumina crucibles, the best of the refractory oxide crucibles tested, give results open to considerable doubt for the oxygen content of low-carbon steels.

Tests were made to determine whether or not fusing electrolytic iron, containing not more than 0.02 or 0.03 per cent carbon, in zirconium-silicate crucibles would give as satisfactory results as in the zirconia-alumina refractory. The loss of carbon from the pure iron fused in this manner was again about 0.02 per cent (Table 6), while the apparent oxygen content of the pure iron was 0.0092 per cent, nearly the same as in the low-carbon steel. These results, therefore, are open to the same doubt as in the case of the low-carbon steel.

4. FUSION OF IRON AND STEELS WITH ANTIMONY-TIN ALLOY

Analyses for oxygen and hydrogen in this same low-carbon steel and in electrolytic iron were next made by the Goerens antimony-tin alloy method.

(a) SUITABILITY OF MAGNESIA CRUCIBLES

While the tests with magnesia crucibles, described above, proved this refractory unsuitable for what has been designated as "direct melting" of carbon steels, it does not follow that such crucibles have caused fictitious results for carbon monoxide or oxygen when they have been used in the Goerens method for the determination of gases. In this method a gas-free alloy of antimony and tin is melted with the iron or steel. The resulting molten alloy of iron-antimony-tin does not dissolve carbon; that is, the carbon in a steel is thrown out of solution as the steel dissolves in the liquid antimony tin. It has been shown above that free carbon has no reducing action on magnesia refractories below temperatures of 1,600° C. As a further factor of safety the melting point of the iron-antimony-tin alloy is not over 1,100° C. Magnesia crucibles might, therefore, be expected to serve satisfactorily in the extracting of gases from steels by the Goerens alloy method.

## (b) PREPARATION OF ANTIMONY-TIN ALLOY

The antimony-tin alloy was prepared by melting together in a graphite crucible in a vacuum furnace equal weights of tin and antimony. Some graphite powder was added with the charge; this powder formed a layer over the surface of the alloy which was kept molten in vacuum until there was no further evolution of gas. For the gas determination by this method 2 g of the 50-50 antimony-tin alloy were used for each gram of the steel sample.

## (c) BLANK CORRECTION

The blank correction for this fusion method was determined by heating in a fresh crucible a gas-free melt of steel-antimony-tin alloy. Blanks were determined for both magnesia crucibles (18 and 19, Table 5) and zirconium silicate crucibles (27, Table 6). The average blank for the magnesia crucibles was 0.0048 g oxygen and 0.0008 g hydrogen and for the zirconium silicate crucibles 0.0040 g oxygen and 0.0005 g hydrogen. These blanks are appreciably lower than those for the direct fusion of the metal in zirconia-alumina or zirconium silicate crucibles.

## (d) OXYGEN AND HYDROGEN FROM IRON AND STEEL FUSED WITH ANTIMONY TIN

In the first determination by the antimony-tin method (16, Table 5) the steel sample was cut under oil on a milling machine to give very fine chips, as directed by Oberhoffer and Beutell.<sup>30</sup> The milled sample was washed free from oil and dried in accordance with the usual methods employed in preparing samples for the Ledebur oxygen determination. The clean chips were then mixed with an equal weight of crushed antimony-tin alloy poured into a magnesia crucible and a second equal portion of alloy in larger pieces placed on top of the charge.

In runs 17 to 20 (Table 5) the steel samples were each a single piece of metal. The crucible was charged first with a portion of antimony-tin alloy, then the steel sample, and finally the remainder of the alloy. It had been found that by heating in the high-frequency induction furnace no trouble was experienced in getting such a single piece of steel, 40 g in weight, to dissolve completely in the molten antimony tin if the carbon content of the steel was about 0.3 per cent or lower. Rail steels (0.7 per cent carbon) and malleable cast irons (2 to 2.5 per cent carbon) dissolved completely only with considerable difficulty. The metal from the surface of such samples dissolved readily in the antimony tin, but at the same time the liberated carbon collected at the interface between the molten alloy and the undissolved steel or cast iron until it formed a film so thick and continuous as to hold the antimony-tin alloy entirely out of contact

<sup>30</sup> See footnote 11, p. 448.



with the undissolved portion of the sample. Superheating, accompanied by the vigorous stirring characteristic of the high-frequency induction furnace, usually overcame this difficulty.

The average value for the oxygen content of the 0.25 per cent carbon steel by the antimony-tin fusion procedure, using solid samples of the steel, was 0.0105 per cent and for hydrogen 0.0010 per cent. Nearly four times as much oxygen, 0.0400 per cent, was obtained on fine millings of the same steel (16, Table 5). Similarly, higher results were obtained by the fusion of millings in graphite crucibles (21 to 23, and 24, Table 5).

The higher values with millings are to be attributed to chips not having been thoroughly cleaned or having become somewhat oxidized during the cutting of the sample. These results are not to be taken as meaning that it is impossible to obtain correct results from samples of chips or millings but simply that, even with the exercise of numerous precautions in cutting, washing, and drying a finely milled sample, the liability to error due to the chips not being thoroughly cleaned or having slightly oxidized surfaces is very great. The cutting of chips under oil according to the procedure described in the reference cited<sup>31</sup> is a troublesome and time-consuming operation, and is preferably to be avoided if possible.

Accepting as more nearly correct the results obtained with solid samples, the average values for both oxygen and hydrogen by the Goerens method on low-carbon steels are very nearly the same as those obtained by direct fusion of the steel in an inert refractory oxide crucible. Solid samples of vacuum-fused electrolytic iron also gave results by the antimony-tin method which were nearly the same as were obtained on the same material by direct fusion (27 and 28, Table 6).

## 5. FUSION OF IRON AND STEEL IN GRAPHITE CRUCIBLES

Analyses for oxygen and hydrogen in the low-carbon steel and in electrolytic iron were made by melting the samples in crucibles machined from Acheson graphite. The 1½-inch vacuum tube was used as described above. The heat insulator (*G*, fig. 4) inclosing the graphite crucible may, in this case, safely be of magnesia or magnesia-zirconium silicate, as it has been shown that graphite alone does not reduce such material at temperatures below 1,600° C.

The heat insulator containing the empty graphite crucible is placed inside the vacuum tube, the Pyrex glass cap sealed on the open end of the silica tube, and the empty crucible heated at 1,600° C (with the tube connected to the vacuum pump through the by-pass *N*, fig. 1) until no further evolution of gas from the crucible and heat insulator is shown when stopcock *F* is closed. The crucible is then

<sup>31</sup> See footnote 11, p. 448.

allowed to cool completely in vacuum, the vacuum tube opened, the crucible removed, charged with the metal sample, and returned to the vacuum tube as rapidly as possible. The cap is again sealed on and the furnace evacuated. The fusion and absorption of gases then follows, as in either of the other methods of fusion. The graphite crucible has the advantage of allowing several successive meltings and freezings of the metal without any danger of cracking the crucible as in the case of direct fusion and, to a lesser extent, in fusion with antimony tin. The metal sample is kept molten until all the gases are evolved and the residual pressure in the vacuum tube is less than 1 mm of mercury.

(a) BLANK ON FURNACE AND TRAIN

The blank correction for a graphite crucible, used with a magnesia heat insulator, is determined by removing the gas-free graphite crucible from the vacuum tube for as long a time as would, in an actual determination, allow inserting the specimen, returning the empty graphite crucible to the vacuum tube, and proceeding from that point just as in melting a steel sample. The average values for the blank on a large graphite crucible, such as was used earlier in this investigation, were found to be 0.0049 g oxygen (0.0051, 0.0049, and 0.0047 check determinations) and 0.0003 g hydrogen (0.0003, 0.0003, and 0.0003 check determinations) and on a small graphite crucible 0.0038 g oxygen (0.0039, 0.0039, and 0.0037 check determinations) and 0.0004 g hydrogen (0.0004, 0.0003, and 0.0004 check determinations).

This blank seems to be due chiefly to the air absorbed by the gas-free crucible when removed from the vacuum tube for the insertion of the metal sample. The crucible should be held with tongs at this time, as handling with the fingers often will result in an appreciably higher blank. It is obvious that a clean, dry surface should be available if it is desired to set the crucible down during the loading of the sample.

(b) REDUCTION OF OXIDES

Walker and Patrick <sup>32</sup> state that, in their method of fusing the metal in contact with graphite in an Arsem vacuum furnace, nearly all of the oxygen of  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{SiO}_2$  was determined, and that other easily reducible oxides, such as manganese and copper, will introduce no difficulty.

Tests on the reduction of  $\text{Fe}_2\text{O}_3$ ,  $\text{SiO}_2$ , and  $\text{Al}_2\text{O}_3$  were repeated in the present investigation and, in addition, tests were made with manganous carbonate, titanium oxide, and zirconium oxide. Table 7 gives the data from these tests. A known amount of the carefully dried oxide was placed in the gas-free graphite crucible with about

<sup>32</sup> See footnote 15, p. 450.



30 g of gas-free iron-carbon alloy from a previous determination of oxygen. The run was made in the usual manner, and the completeness of the reduction of the oxides was calculated from the total oxygen evolved in excess of the blank.

The recovery of oxygen from ferric oxide, silica, alumina, and manganese carbonate (used as a convenient substitute for manganous oxide) was from 93 to over 100 per cent of the calculated oxygen content of the oxides, thus indicating the complete reduction of these oxides by this method of analysis.

Some difficulty was encountered in the first tests with  $\text{TiO}_2$  and  $\text{ZrO}_2$ . In test 16, Table 7, the zirconia was placed in a small hole drilled in the end of a steel rod of known oxygen content. After the melt was completed it was found that the zirconia had sintered in the form of a small cylinder which apparently was reduced to carbide on the surface only. This carbide apparently was not soluble in the molten iron-carbon alloy, and the major portion of the  $\text{ZrO}_2$  was thus not reduced. In tests 17 to 20, Table 7, the oxide powder was placed loose in the bottom of the graphite crucible and under the gas-free iron-carbon alloy. The recovery of oxygen in these tests left little doubt that  $\text{ZrO}_2$  was reduced under the conditions of vacuum fusion. Complete reduction was secured by using smaller samples of oxide (tests 19 and 20). The tests with titanium oxide also showed complete recovery of oxygen when a small sample was used.

TABLE 7.—*Reducibility of oxides in iron by vacuum fusion in graphite*

Test number	Oxide	Weight of oxide used	Weight of oxygen calculated	Weight of oxygen found	Recovery
		g	g	g	Per cent
1	$\text{Fe}_2\text{O}_3$	0.0423	0.0127	0.0130	102
2	do	.0432	.0130	.0130	100
3	do	.0269	.0081	.0074	92
4	do	.0210	.0063	.0064	102
5	$\text{SiO}_2$	.0253	.0135	.0132	98
6	do	.0255	.0136	.0137	101
7	$\text{Al}_2\text{O}_3$	.0070	.0033	.0032	97
8	do	.0339	.0159	.0146	92
9	$\text{MnCO}_3$	.0429	.0179	.0181	101
10	do	.0404	.0169	.0153	91
11	$\text{TiO}_2$	.0386	.0154	.0101	66
12	do	.0297	.0119	.0129	108
13	do	.0318	.0127	.0107	84
14	do	.0269	.0107	.0098	92
15	do	.0048	.0019	.0019	100
16	$\text{ZrO}_2$	.0762	.0199	.0030	15
17	do. <sup>1</sup>	.0679	.0185	.0100	54
18	do	.0857	.0233	.0128	55
19	do	.0112	.0030	.0031	103
20	do	.0176	.0048	.0048	100

<sup>1</sup> The zirconia used in tests 17 to 20 contained approximately 4 per cent silica. The calculated values in the fourth column are, therefore, slightly higher than would be the case if the oxide used had been pure  $\text{ZrO}_2$ .

Oxide inclusions originally present in ferrous alloys should be even more readily reduced in so far as they are more finely divided and thoroughly dispersed throughout the metal than any artificial additions of oxides as used in the above tests. The method of vacuum fusion in graphite for the determination of gases in metals should, therefore, give the total oxygen in ferrous alloys, including oxygen combined with iron, manganese, silicon, aluminum, titanium, and zirconium.

#### (c) OXYGEN AND HYDROGEN IN METAL SAMPLES

Twenty-five to thirty gram samples of the 0.25 per cent carbon steel were used in test 21 to 23, Table 5. The average values from three determinations in graphite were 0.0205 per cent oxygen and 0.0015 per cent hydrogen. The result for hydrogen is practically the same as by the other two methods of fusion. The result for oxygen is, however, distinctly higher than by either the direct fusion or the antimony-tin method.

In Table 6 test numbers 29 and 30 are duplicate determinations of oxygen and hydrogen in the same electrolytic iron as was used in the other two methods of melting, test numbers 25 to 28. It will be noted that the oxygen by the graphite fusion method is nearly twice as much as by either of the other two methods.

#### (d) NONINTERFERENCE OF SULPHUR IN IRON AND STEEL

The question arose as to the possible evolution of sulphur gases from irons and steels fused in vacuum in graphite crucibles. The presence of  $H_2S$  or  $SO_2$  in the gases drawn through the absorption tubes would lead to error in the determination of oxygen, since such gases would be absorbed in tube *B* (fig. 1), and thus be mistaken for carbon dioxide.

That such interference of sulphur did not exist was indicated by the fact that in the analysis for oxygen of a series of steels of increasing sulphur content (to a maximum of 0.17 per cent sulphur) the gain in weight of tube *B* gave no indication of increasing with increasing sulphur. Further evidence in support of this point was furnished by gravimetric determinations of sulphur in the carbon-saturated melts of low, medium, and high sulphur steels after they had been fused in the regular manner for the determination of oxygen. If no sulphur is lost from the steel by vacuum fusion, the sulphur content of the carbon-saturated metal after fusion should be only slightly lower than in the original steel on account of the solution of from 4.5 to 5.0 per cent carbon from the graphite crucible. Taking into account this change in composition of the steel after fusion, the determination of sulphur showed no loss of sulphur by fusion in vacuum in graphite crucibles.



TABLE 8.—*Effect of vacuum fusion on the sulphur content of steels*

Sulphur in original steel	Calculated sulphur in vacuum fused alloy	Sulphur by analyses of vacuum fused alloy
<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>
0.028	0.027	0.024
.058	.055	.056
.179	.17	.17

An attempt was also made to detect traces of  $\text{H}_2\text{S}$  or  $\text{SO}_2$  in the gases evolved from a sample of the 0.179 per cent sulphur steel when fused in the regular manner for a determination of oxygen. For this purpose tube *B* of the absorption train was filled with lead dioxide;<sup>33</sup> a small amount of phosphorus pentoxide was placed in each end of the tube. Preliminary tests were made by allowing mixtures of air-hydrogen sulphide and of air-sulphur dioxide to pass through similar absorbent tubes under reduced pressures and at room temperatures. No  $\text{H}_2\text{S}$  or  $\text{SO}_2$  could be detected at the exit end of the absorbent tube. No gain in weight in excess of the blank was shown in the lead dioxide tube when included in the absorption train during a regular vacuum fusion analysis of the high sulphur steel.

It appears certain that sulphur in steel does not interfere in any way in the method for determining oxygen by fusion of the steel in graphite and under a vacuum.

## 6. COMPARISON OF THE THREE VACUUM FUSION METHODS

The average values of Tables 5 and 6 for oxygen and hydrogen obtained by the three methods of vacuum fusion on electrolytic iron and the 0.25 per cent carbon steel are given in Table 9. In addition there are given values by the same three methods for a 0.72 per cent carbon steel.

TABLE 9.—*Comparison of the three methods of vacuum fusion analysis*

Method of analysis	Electrolytic iron		Low-carbon steel, 0.25 per cent C		High-carbon steel, 0.72 per cent C	
	Oxygen	Hydrogen	Oxygen	Hydrogen	Oxygen	Hydrogen
	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>
Fusion in zirconia-alumina.....	0.0092	0.0013	0.0093	0.0015	<sup>a</sup> 0.021	<sup>a</sup> 0.0009
Fusion with Sb-Sn in magnesia.....	.0088	.0017	.0105	.0010	.042	.0018
Fusion in graphite.....	.0163	.0011	.0205	.0015	.0027	.0003

<sup>a</sup> The extraction of gas was not carried to completion in this test, as the very high pressure developed in the vacuum furnace indicated rapid reaction between the molten steel and the oxides of the crucible.

<sup>33</sup> Dr. E. T. Allen of the geophysical laboratory of the Carnegie Institution, Washington, D. C., kindly suggested this absorbent and advised us on its preparation and use.

## (a) VALUES FOR OXYGEN

In the case of the electrolytic iron and low-carbon steel, graphite fusion determines the total oxygen more completely than the other two methods. In the direct fusion of low-carbon metal there is not present sufficient carbon to bring about the reduction of oxides of manganese, silicon, aluminum, etc., which are reduced by fusion in graphite in the presence of iron. On the other hand, even with low-carbon steels and electrolytic iron containing a few hundredths of 1 per cent carbon, an appreciable decarburization is caused by fusing the metal in refractory oxides. This decarburization is accompanied by the production of carbon monoxide representing oxygen from the crucible refractory rather than from the metal.

This same reaction with the crucible refractory is especially marked in the direct fusion of high-carbon steel. Even an incomplete analysis by direct fusion indicated an oxygen content of a high-carbon steel as 0.021 per cent (Table 9), while fusion of the same steel in graphite showed only 0.0027 per cent oxygen as actually present in the steel.

Direct fusion in refractory oxide containers is, therefore, not satisfactory for the determination of oxygen in either low-carbon or high-carbon ferrous alloys.

Fusion of electrolytic iron, low-carbon, and high-carbon steels with antimony tin gives results practically the same as those given by direct fusion and for the same reasons. For pure iron and low-carbon steel the results are lower than the true values given by fusion in graphite because of the lack of sufficient carbon to reduce the oxides in the metal, while for high-carbon steel the oxygen is higher than the correct value due to reactions with the crucible refractory.

## (b) VALUES FOR HYDROGEN

Practically the same value for hydrogen is given by all three methods with pure iron and low-carbon steel. Fusion of the high-carbon steel with antimony tin did not give quite the same value for hydrogen as fusion in graphite. There is, however, no obvious choice of methods based on the values obtained for hydrogen.

## (c) SELECTION AND MELTING OF SAMPLES

Fusion in graphite is the most convenient of the three methods of melting the samples in vacuum by high-frequency induction and allows the widest range in the amount and the form of the sample. The heating takes place in the graphite crucible and is uniform and easily controlled regardless of the size, shape, or closeness of packing of the metal sample, three factors which necessarily must often vary and introduce difficulties in the uniform heating and complete fusion of metal samples by direct induction in the metal, as is required in "direct fusion" or fusion with antimony tin.



#### IV. DETAILED PROCEDURE ADOPTED FOR THE DETERMINATION OF OXYGEN AND HYDROGEN BY VACUUM FUSION IN GRAPHITE

Fusion in graphite by high-frequency induction is the most accurate and convenient of the three methods studied for the determination of oxygen and hydrogen in both low-carbon and high-carbon ferrous alloys. The details of procedure and manipulation for a typical determination of oxygen and hydrogen in a metal by fusion in a graphite crucible in vacuum are as follows:

##### 1. SAMPLE AND CRUCIBLE

There is a wide range in the form and size of the metal sample that can be used in this determination. A sample weighing as much as 200 g may be employed. The sample may be in the form of chips of any fineness, strips, wire, or one or more sections of a rod or bar. This method of vacuum fusion in the analysis of gases is therefore not at all restricted as to the form of the metal sample, permits the use of solid rods or bars of metal, and avoids loss of occluded gas on cutting up a mass of solid metal or errors due to the surface oxidation of fine chips. On the other hand, the use of metal powder or sponge, wires or sheets is possible when information as to the gas content, including surface oxides of such material, is desired.

The crucibles are prepared from rods of Acheson graphite 1 inch in diameter and about  $3\frac{1}{2}$  inches long. These rods are turned on a lathe to  $\frac{13}{16}$  inch outside diameter and bored out with a cutting tool to  $\frac{9}{16}$  inch inside diameter and to a depth of  $2\frac{3}{4}$  inches. About  $\frac{1}{2}$  inch is cut off the solid end of the graphite, leaving the outside depth of the crucible about 3 inches and the thickness of the bottom about  $\frac{1}{4}$  inch. The magnesia heat insulators for the graphite crucibles are  $4\frac{1}{2}$  inches high,  $\frac{7}{8}$ -inch inside diameter and  $1\frac{5}{8}$  inches outside diameter. They are prepared from electrically fused magnesia, ground to pass an 80-mesh screen, and moistened with just enough water to permit packing around a mandrel (preferably of brass) in a graphite mold. After the insulator material is tamped into the mold the mandrel is removed and the slightly moist insulator left in the mold and dried over night in an oven at about 130° C. The insulator and the mold are then heated to 1,600 or 1,700° C. in an Arsem vacuum furnace. This heating gives considerable mechanical strength to the crucible and causes enough shrinkage to allow the insulator to be removed readily from the mold. Such an insulator can be used for several determinations.

## 2. FREEING GRAPHITE CRUCIBLE FROM GASES

The magnesia insulator containing the graphite crucible is slid to the bottom of the silica tube (*C*, fig. 4). The silica tube is placed in such a position that the crucible is centrally located within the induction coil. The Pyrex glass cap is sealed on with de Khotinsky wax. The tube is evacuated through the by-pass (*N*, fig. 1) to a pressure of about 0.5 mm of mercury and then the heating is started with the vacuum pump still running. The crucible is heated to about 1,450° C. and held at that temperature until no increase in pressure is noted on the furnace manometer, when stopcock *F* (fig. 1) is closed for five minutes. At this point the heating is stopped and the evacuating of the tube continued until the crucible has cooled to a dull red. Stopcock *F* is then closed and the silica tube and its contents allowed to cool.

## 3. PREPARATION OF ABSORPTION TUBES

The empty absorption tubes (fig. 3) are washed with water and dried with alcohol and ether. The phosphorus pentoxide tubes (*A* and *C*, fig. 1) are filled by clamping the tube with both stopcocks removed, in a vertical position, and lowering the tube over a metal rod until the top end of this rod is even with the lower end of the constriction, indicated in Figure 3 by the dimension *B*. A plug of glass wool is first packed tightly against this constriction and the end of the metal rod, followed by phosphorus pentoxide, introduced through a wide-stemmed funnel in an amount sufficient to form a column about 0.5 to 1.0 cm long when pressed firmly down under a second plug of glass wool. After the shells of both stopcocks are carefully cleaned the stopcock plugs are lubricated,<sup>34</sup> inserted, and the tube weighed against a counterpoise after standing for at least 15 minutes in or close to the balance case. The ground-glass tips of the side tubes are then lubricated and the tube is ready for insertion in the train, with the constriction, against which the absorbent is packed, always placed nearest the vacuum pump to prevent the shifting of the absorbent and plugs.

The ascarite tubes (*B* and *D*, fig. 1) are filled in the same manner with layers of absorbent and packing in the following order: A glass-wool-plug, 1 to 2 cm of phosphorus pentoxide, 3 to 4 cm of ascarite, 1 to 2 cm of phosphorus pentoxide, and a plug of glass wool.

Tube *B* is connected at its right-hand side to the copper oxide tube *E* (fig. 1) by means of a fixed ground-glass joint and on the left to the tube *A* by means of a single section of glass tubing having a ground connection at each end. Tube *A* is then connected on its left to

<sup>34</sup> The lubricant used throughout the absorption train is a rather hard stopcock grease, which remains in place better and is therefore more efficient in vacuum work than grease of thinner consistency. It contains approximately 60 parts of Para rubber, 40 parts of vaseline, and 6 to 8 parts of paraffin.



stopcock *F* by means of an adjustable ground-glass joint (*C*, fig. 2), which slides to its proper position inside the tube *D* (fig. 2) and is finally sealed with de Khotinsky cement. Tubes *C* and *D* (fig. 1) are then placed in the train in the same manner at the other side of the copper oxide furnace *E*, making the connections in the reverse order from left to right, with the de Khotinsky seal next to stopcock *G*.

#### 4. CHARGING THE VACUUM FURNACE

After the absorption tubes have been connected the silica tube (*C*, fig. 4), now cool after having been evacuated and heated to free the graphite crucible and magnesia insulator from gas, is relieved of its vacuum by admitting air through the open end of stopcock *J*, the phosphorus pentoxide tube *I*, by-pass *N*, and stopcock *F*. The cap is then removed from the furnace tube and the gas-free crucible taken out. The metal sample is placed in the crucible as quickly as possible, the latter returned to position in the tube, the cap replaced and resealed with de Khotinsky cement, and the side tube of the cap sealed to the absorption train. Stopcocks *F* and *G* are turned so that the silica tube is evacuated through by-pass *N* until the pressure is about 0.5 mm of mercury. Stopcock *F* is then closed.

#### 5. EVACUATING THE ABSORPTION TRAIN

With stopcocks *L* and *K* closed, *G* is turned to connect *D* with the pump. The stopcocks of tubes *C* and *D* are then opened and the evacuation of the train started. The train from *L* to *K* is always kept evacuated and the copper oxide hot. With *F* closed, the stopcocks of tubes *A* and *B* are opened. *K* is then opened very slowly in order that the air may not rush into *E* so rapidly as to compress the column of absorbents in tubes *A* and *B*. By this time the train from the pump to *L* has been partially evacuated and *L* is now turned slowly to connect *C* and *E*. Thus far the pump has been connected to the train through *M*. When the pressure in the train is reduced to a few millimeters, stopcock *H* is turned to connect pump and train through the phosphorus pentoxide by-pass *I*. The evacuation of the train is continued until the manometer between stopcock *F* and tube *A* shows only 0.5 mm pressure.

#### 6. HEATING THE SAMPLE

The heating of the sample is then started. The power is gradually increased, so that in about 10 minutes the sample starts to melt. As soon as the pressure in the furnace has become greater than that in the absorption train stopcock *F* is opened and the gases allowed to pass into the train. With careful adjustment of the power input and frequent readings of the temperature of the metal with an

optical pyrometer, the sample is held at 1,450° C. or slightly higher for one hour. In nearly every case at the end of one hour's heating the pressure in the furnace has dropped to about 0.5 to 1.0 mm and the heating is stopped. If, by any chance, the pumping is slow or the volume of evolved gas is unusually large, the heating can be continued longer without introducing any errors.

After the heating is completed the pumping of the furnace and train is continued until the sample has cooled below a visible heat. The stopcock (not shown in fig. 1) between the furnace and stopcock *F* is then closed. Stopcock *F* also is closed and the train pumped for about 10 minutes longer. The stopcocks of the absorption tubes and copper oxide tube are then closed.

#### 7. FINAL WEIGHING OF ABSORPTION TUBES

Before removing tubes *A* and *B* the vacuum between stopcock *F* and tube *A* is relieved with dry air, which has first been admitted to the space between the furnace stopcock and stopcock *F* through stopcock *J*, phosphorus pentoxide tube *I*, and by-pass *N*. The vacuum between stopcock *G* and tube *D* is relieved with air dried in the same way.

The absorption tubes are then removed from the train in the reverse order of that in which they were connected. They are then filled with air admitted through a tube containing  $P_2O_5$  and ascarite to remove moisture and carbon dioxide and the tips of their side tubes wiped free of lubricant with a cloth moistened with ether. Care should be taken to remove any small amounts of lubricant which may have worked into the open ends of the side tubes. The final weighing of each tube is made after it has hung in or close to the balance case for 15 minutes with its counterpoise.

#### 8. REFILLING ABSORPTION TUBES

With the type of absorption tubes described it has been found desirable to use freshly filled tubes for every determination. While the efficiency of the absorbent may be but slightly diminished after one run, yet the rate at which gas can be pumped through the tube is often very seriously decreased, and attempts to use an absorption tube a second time without refilling frequently necessitate a longer period of pumping, after the heating of the sample is completed, before all the evolved gases can be removed from the silica tube.

#### 9. DISCUSSION OF BLANKS

Blanks on the entire apparatus are run in the same manner as has just been described for the actual fusion of a metal sample, except that no sample is used. If the blank is determined with a gas-free



melt in the graphite crucible the same result as with an empty crucible is obtained.

Insulators prepared from the same lot of fused magnesia and used with the same furnace and train give blanks which check within 0.2 or 0.3 mg of oxygen. If, however, different lots of magnesia are used or if the magnesia has required special treatment for the removal of sulphur (as described below), it is advisable to make a new blank determination as the first run with each new heat insulator. Such blank determinations, moreover, serve very well as checks on the condition of the entire absorption train.

TABLE 10.—*Constancy of blanks for a given magnesia heat insulator used continuously*

Run number	Duration of heating	Oxygen	Hydrogen
	<i>Hours</i>	<i>g</i>	<i>g</i>
1-----	1	0.0046	0.0005
6-----	1	.0044	.0004
7-----	1 $\frac{3}{4}$	.0048	.0003

The blanks given in Table 10 were determined on the same magnesia heat insulator but with different graphite crucibles. It is to be noted that the sixth run gave practically the same blank as the first run. There is, therefore, no change in the value of the blank for successive runs with a given heat insulator. As has been stated above, it is sometimes necessary to heat a sample longer than one hour. In the seventh run the blank was determined for a one and three-fourths-hour heating period with practically the same result as for the usual one-hour period.

If the electrically fused magnesia contains sulphur, as is sometimes the case, the blanks are much higher than usual and are not consistent. Tests indicated that in such cases magnesium sulphide is formed during the preliminary heating of the graphite crucible. This magnesium sulphide hydrolizes through the presence of moisture in the air when the cap is removed from the furnace, forming hydrogen sulphide, which escapes, and magnesium hydroxide, which remains in the insulator. This magnesium hydroxide during the heating in the subsequent determination gives off water which may enter the absorption train either as water vapor, or as hydrogen and carbon monoxide after reaction with the hot graphite crucible. In either case high blanks result. In order to eliminate most of the sulphur and render sulphur-bearing magnesia suitable for insulators, the magnesia is heated in a graphite crucible to 1,500 to 1,600° C. in an Arsem furnace. This calcined material is ground, moistened with water, and allowed to stand in the air several hours or over

night, so that the magnesium sulphide formed may hydrolize and the hydrogen sulphide escape. This treatment may be repeated if necessary, and the material is now suitable for making finished insulators giving consistent blanks.

#### 10. AGREEMENT OF DUPLICATE ANALYSES

Table 11 shows the agreement obtained in duplicate analyses by fusion in graphite of 13 irons and steels. Check analyses do not always agree. Such lack of agreement seems to be characteristic of certain irons and steels rather than to be due to any unreliability in the method of analysis. This is not surprising when it is recalled that the samples used for analysis are single solid pieces of metal which might be expected to show any nonuniform distribution of oxygen existing in the metal. The lack of agreement in check analyses of certain steels and irons is plainly shown in samples 2, 12, and 13. The excellent agreement of check analyses is shown in samples 1, 5, 6, 9, 10, and 11.

In this table results for oxygen are given to the fourth decimal in order to show more clearly the magnitude of the usual variations in duplicate analyses. For the same reason the values for hydrogen are here given to the fourth decimal. The analytical results by this method, however, are more properly reported to not more than the third decimal or more than two significant figures for oxygen and to not more than the fourth decimal or more than one significant figure for hydrogen; values giving less than 0.001 per cent oxygen or less than 0.0001 per cent hydrogen are best reported as "less than" the values mentioned.

TABLE 11.—Agreement of duplicate analyses for different irons and steels

Sample number	Material	Oxygen	Hydrogen	Sample number	Material	Oxygen	Hydrogen
		<i>Per cent</i>	<i>Per cent</i>			<i>Per cent</i>	<i>Per cent</i>
1-----	Steel-----	{0.0096	0.0002			{0.0742	0.0005
		.0096	.0003			.0812	.0013
		.0105	.0031			.0695	.0001
2-----	do-----	.0160	.0015	8-----	Oxidized iron-----	.0700	.0003
		.0277	.0016			.0844	.0002
		.0178	.0015			.0812	.0002
3-----	Welding steel-----	.0087	.0003	9-----	Cast iron-----	.0029	.0004
		.0081	.0013			.0027	.0005
4-----	Carburizing steel-----	.0330	.0003	10-----	do-----	.0098	.0008
		.0310	.0001			.0098	.0009
5-----	Fused electrolytic iron.	.0162	.0010	11-----	do-----	.0135	.0001
		.0163	.0011			.0135	.0001
6-----	do-----	.0185	.0018			.0103	.0007
		.0183	.0018	12-----	do-----	.0043	.0009
		.1410	.0018			.0090	.0012
7-----	Oxidized iron-----	.1400	.0021			.0010	.0011
		.1270	.0015	13-----	do-----	.0079	.0004
						.0034	.0001
						.0129	.0012



## V. SUMMARY

1. A train of solid absorbents was developed suitable for the direct determination of water vapor and carbon dioxide and for the indirect determination of carbon monoxide and hydrogen when these gases were passing through the train at low pressures. By means of this train one or all of these gases present in the mixture of gases evolved from a metal sample fused in vacuum may be accurately determined.

2. The high-frequency induction furnace was used for the fusion of the metal samples. This type of furnace permits the fusion of the samples in a small silica tube and holding the metal molten at temperatures of  $1,500^{\circ}$  C. or more while the walls of the tube remain comparatively cool. Thus, no difficulty is encountered from the failure of the tube to hold a vacuum.

3. Three methods of fusion previously employed in the determination of gases in metals fused in vacuum were applied to pure iron, a low-carbon steel, and a high-carbon steel. These methods were (a) direct fusion of the metal in a refractory oxide crucible, (b) fusion in a refractory oxide crucible with the addition of antimony and tin, and (c) fusion in a gas-free graphite crucible. Neither (a) nor (b) is satisfactory for determining oxygen in ferrous alloys. Method (c) gives the most dependable values for total oxygen. The values obtained for hydrogen offer no choice between the three methods for the determination of this element.

4. Fusion of ferrous alloys in graphite determines, besides any oxygen present as such, the oxygen that may be present in the metal as CO, CO<sub>2</sub> and oxides of iron, silicon, manganese, aluminum, zirconium, and titanium. The sulphur in the iron or steel sample does not interfere with the determination of oxygen.

5. The fusion in graphite method is also applicable to the determination of oxygen and hydrogen in many nonferrous metals and alloys.

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