Some Theoretical and Practical Aspects of Gases in Metals *

By J. H. SCAFF and E. E. SCHUMACHER

In this paper there are included a discussion of the theories pertaining to the absorption of gases by metals and descriptions of actual work illustrating them. Apparatus for the analysis and measurement of gases in metals and for melting metals in vacuum are described. Information is included, also, on commercial vacuum melting methods and the results obtained.

INTRODUCTION

SINCE Thomas Graham [1] discovered in 1866 that a piece of meteoric iron heated in vacuum yielded 2.8 times its volume of gas,[2] the solubility of gases in metals has been the subject of a large number of investigations. While these studies have not as yet afforded more than a partial understanding of the nature of the processes by which gases are dissolved in metals, they have yielded considerable knowledge of those factors which determine the extent of such solubility, and thus of the methods by which the amount of dissolved gas can be increased or diminished. At the same time they have shown the importance of dissolved gases in determining not merely the behavior of metals in casting processes, but also the magnetic, mechanical, and chemical properties of metallic materials. It is proposed to discuss, in this paper, theories of the absorption of gases by metals and to review important work on this subject.

THE EFFECT OF GASES ON THE PROPERTIES OF METALS

The importance of producing sound metals should interest every metal founder in the effects of dissolved gases. Any gas whose solubility is greater in the liquid than in the solid metal may cause the formation of blowholes. The formation of these blowholes, however, can be reduced or prevented by cooling the metal slowly enough through its freezing range to permit the escape of liberated gases. Iron saturated with hydrogen, for instance, will yield a sound ingot if cooled very slowly through its freezing point, while chill casting not only will make the metal porous but may cause an evolution of gas violent enough to throw metal from the mold. This phenome-

---

[1] Thomas Graham, *Proc. Roy. Soc.*, 15, 502 (1866).
[2] All gas volumes given in this paper are at N.T.P.

non is known as "spitting" and is a common occurrence when casting iron, copper, cobalt, and platinum saturated with hydrogen, and silver saturated with oxygen.

The magnetic properties of iron and its alloys are known to be greatly affected by gases. Cioffi,[3] of Bell Telephone Laboratories, has shown that the permeability of iron can be increased to 190,000 by heat treating it in hydrogen at 1500° C. This effect is attributed to the removal of carbon, oxygen, nitrogen, and sulphur. In this field, also, Yensen has done interesting work, details of which are contained in his publications.[4] The permeability of iron can be greatly increased, also, by vacuum melting. Here again the gaseous impurities and those which react to form gaseous products are removed by the treatment.

The influence of oxygen on the carburization of steel is not clearly understood, but its importance has been emphasized by many writers. Grossmann[5] believes that steel absorbs oxygen along with carbon during pack carburization and that this favors a solubility of cementite in alpha iron. By this mechanism, he accounts for the phenomenon of split cementite. Guthrie and Wozasek[6] found that the presence of oxygen speeds up the process of gas carburizing, which indicates that oxygen must affect the solubility and rate of solution of carbon in austenite.

The influence of nitrogen on the properties of steel is of commercial importance. It was learned first that nitrogen in steel formed nitrides which were dispersed in the metal and which caused brittleness. Later, nascent nitrogen, obtained from the thermal dissociation of ammonia, was found to react with certain constituents in steel to form an exceedingly hard case. From this discovery, the modern commercial nitriding process has been developed.

Pfeil, Lea, and others have observed that small quantities of hydrogen absorbed by iron during electrolytic pickling appreciably affect its mechanical properties. Pfeil[7] found that the tensile strength of mild steel rods is decreased from 18.34 tons per square inch to 16.69 tons and that the elongation in one inch falls from 62.5 per cent to 10.6 per cent. Normal properties are restored if the steel is allowed to stand for sometime in the air. Lea,[8] also studying mild steel, confirmed Pfeil's elongation data but found only a slight effect on

[3] Cioffi, *Phys. Rev.*, *39*, 363 (1932).
[4] Yensen, *Metal Progress*, June, 1932, p. 28; *A. I. M. M. E. Tech. Pub.* No. 185.
[5] Grossmann, *Trans. A. S. S. T.*, *16*, 1 (1929); *18*, 601 (1930).
[6] Guthrie and Wozasek, *Trans. A. S. S. T.*, *12*, 853 (1927).
[7] Pfeil, *Proc. Roy. Soc.* London, *112*, 182 (1926).
[8] Lea, *Proc. Roy. Soc.* London, *123*, 171 (1929).

tensile strength. Lea claimed, also, that the hydrogen had only a slight effect on the resistance of mild steel to impact and repeated stresses. The fracture produced by repeated stresses, however, was abnormal.

The amount of hydrogen in electrodeposited metals is believed to affect their properties. Schneidewind [9] showed that the hardness of electrodeposited chromium decreases when the metal is heated to approximately 300° C. This decrease could not be caused by re-crystallization of the deposit, for its grain size was not appreciably changed by heating even at 850° C.; nor was the decrease caused by the solution of some constituent which had caused precipitation hardening at room temperature, since quenching and aging did not restore the original hardness. Schneidewind believed that the initial hardness was due to the presence of some volatile constituent, probably hydrogen.

In order to obtain sound castings of copper, it is necessary, in the usual fire refining process, to stop the operation before the oxygen is entirely removed. If the operation is continued further the copper would take up gases from the furnace and unsound castings would invariably be the result. Copper in the tough pitch condition, therefore, contains a nominal quantity of oxygen (0.04 per cent). Although for ordinary uses this product is perfectly satisfactory, when exposed to reducing gases at elevated temperatures, the contained oxygen combines with them to form products which cause embrittle-ment. For use at high temperatures with reducing gases, therefore, copper must be deoxidized. In the past, metallic deoxidizers were added to the copper during the casting operations, but, in order to assure complete deoxidation, an excess had to be added which reduced the electrical conductivity of the finished product.

Recently, a brand of copper [10] has been placed on the market which is said to be kept free from oxygen during melting and therefore needs no deoxidation. This material can be heated in reducing gases without embrittlement, has electrical conductivity comparable to that of electrolytic copper, and is claimed to be tougher and more ductile than fire refined copper and to have better working properties.

The studies of Tullis [11] and Rosenhain [12] on the gas removal and grain refinement of aluminum have yielded results which may have

[9] Schneidewind, *Trans. A. S. S. T.*, *19*, 115 (1931).
[10] Oxygen Free High Conductivity Copper, produced by the United States Metals Refining Co.
[11] Tullis, *Jour. Inst. Metals*, *40*, 55 (1928); *Metal Ind.* (London), *34*, 339 (1929); *Metal Ind.* (London), *34*, 371 (1929).
[12] Rosenhain, *Jour. Inst. Metals*, *44*, 305 (1931), No. 2.

great commercial importance. Tullis has found that the treatment of molten aluminum with gaseous chlorine completely removes the dissolved gases. Subsequent treatment with boron trichloride causes the formation of small grains in the castings. Rosenhain [12] has reported that both gas removal and grain refinement can be effected in one operation by the use of volatile chlorides such as titanium tetrachloride. Both of these methods are being tested on a commercial scale in England. It is claimed that secondary aluminum, treated in this way, gives strong castings as free from pinholes as does virgin metal. If the cost is sufficiently low and if the industrial hazards attending its use can be controlled satisfactorily, this method of gas treatment should have a wide applicability to refining secondary aluminum.

The descriptions, given above, of the effect of gases on the properties of metals should indicate how important these effects are and how small a quantity of gas may suffice to produce them. It seems necessary, therefore, to consider gaseous impurities along with others in metallurgical studies.

THEORY

The Effect of Temperature on the Solubility of Gases in Metals

Metal founders of early times had great difficulty making castings which did not contain blowholes. Knowing that the solubility of gases in aqueous liquids decreased with increasing temperature, they tried to remove the gases from molten metal by heating to a higher temperature before casting. They found, however, that their product was less sound than before. This suggested to later workers a difference between the action of gases in aqueous liquids and in molten metals and several systematic investigations were begun.

Sieverts, one of the first men to study this problem, found that, in general, the solubility of gases in metals increases with increasing temperature.[13] He found, for instance, that one volume of copper absorbs 0.006 volume of hydrogen at 400° C., and 0.19 volume just below its melting point. As the copper melts, the quantity of gas absorbed increases to 0.54 volume, while at 1550° C. 1.25 volumes are absorbed. The amount of hydrogen absorbed by iron increases from 1.05 volumes for the solid to 2.10 volumes for the liquid at the same temperature.

Some known exceptions to the general rule that absorption of gas increases with increasing temperature are the solubility of hydrogen

---

[12] Loc. cit.

[13] Sieverts published a useful résumé of his work, with references to the original articles in *Zeit. für Metallkunde, 21,* 37 (1929).

in palladium, cerium, thallium, zirconium, titanium, tantulum, and vanadium. The solubility changes of hydrogen in palladium are particularly interesting. One volume of this metal absorbs 670 to 800 volumes of hydrogen at 20° C., 50.6 volumes at 138° C., and in the liquid state at 1600° C. only 4.3 volumes.[13]

Since the solubility of gases in aqueous liquids decreases with increasing temperature, and since these data form the bulk of the total available, some workers have suggested that the increase in solubility of gases in metals with increasing temperature is anomalous. No anomaly appears, however, when the solubility relationship is considered in the light of van't Hoff's law of mobile equilibrium. This law states that when the temperature of a system in equilibrium is raised only that reaction can occur which is accompanied by an absorption of heat, that is, an endothermal reaction. The increasing solubility of gases in metals with increasing temperature, therefore, should be taken as evidence of an endothermic reaction rather than as an anomaly.

Data are available which show that increasing solubility of gases with increasing temperature is not limited to gas-metal systems. Just[14] has shown that the solubility of hydrogen, carbon monoxide, and nitrogen in carbon disulphide, nitrobenzene, acetone, and other organic solvents increases with increasing temperature. Lannung[15] has reported data showing that the solubility of argon, neon, and helium in methyl alcohol, and acetone increases with increasing temperature. In this respect the gas-metal systems seem to be similar to some of the gas-organic liquid systems.

Another fairly well known influence of temperature on the quantity of gas absorbed by a metal is due to an allotropic change in the structure. That the amount of gas absorbed by a metal changes abruptly when the allotropic form changes, is illustrated by the iron-nitrogen system. One hundred grams of iron heated to 878° C. absorbs only 1.6 milligrams of nitrogen, but at 930° C., in the gamma modification, it takes up 21.6 milligrams.[13]

The Effect of Pressure on the Solubility of Gases in Metals

The effect of changes in pressure on the solubility of gases in metals has been studied intensively by Sieverts. He made the discovery that the quantity of gas dissolved in a metal at constant temperature

[13] Loc. cit.
[14] Just, *Zeit. Phys. Chem.*, 37, 342 (1901).
[15] Lannung, *Jour. Am. Chem., Soc.*, 52, 73 (1930).

is proportional to the square root of its partial pressure.[13] This square root relationship (which may well be called Sieverts' law) emphasizes the difference between the solution phenomena of gases in metals and gases in aqueous liquids, since, in the latter, solubility is proportional to the partial pressure of the gas (Henry's law). There are, however, some gas-metal systems in which solubility does not follow Sieverts' law. It is well known that the solubility of hydrogen in palladium is not proportional to the square root of the gas pressure and this is true also of hydrogen in cerium, thallium, zirconium, titanium, tantalum, and vanadium. These exceptions are the same as those mentioned in the section above on the effect of temperature. These metals are noteworthy for their comparatively great absorption of hydrogen and for their compound formation with it.

Sieverts' law is usually explained by application of the Nernst distribution law, which states that there is a constant ratio between the concentrations of a given molecular species distributed between two phases of a system in equilibrium. Considering, first, molecular oxygen dissolved in a liquid, let P_{O_2} denote its partial pressure in the gas phase and C_{O_2} its concentration in the liquid. The distribution law is then

$$P_{O_2} = kC_{O_2}. \tag{1}$$

The concentration here is directly proportional to the partial pressure, a fulfillment of Henry's law which is a special case of the distribution law. This adequately describes the solubility of most gases in aqueous liquids.

Considering, now, the solubility of gases in metals, and assuming that molecular gas is dissociated into atoms at the surface of the metal before it is dissolved, let P_{O_2} denote the partial pressure of molecular oxygen, P_0 the concentration of atomic gas at the metal surface, and C_0 the concentration of atomic gas in the metal. Then, according to the law of mass action,

$$P_{O_2} = k_1(P_0)^2. \tag{2}$$

Applying the distribution law to the equilibrium between atomic oxygen at the metal surface and atomic oxygen dissolved gives

$$P_0 = k_2 C_0. \tag{3}$$

Combining equations (2) and (3) gives

$$P_{O_2} = k_1(k_2 C_0)^2 = KC_0^2. \tag{4}$$

[13] Loc. cit.

This shows that the square root relationship found by Sieverts can be explained by assuming a dissociation of the molecules of gas somewhere in the process of solution.

Donnan and Shaw [16] applied this type of analysis to the solubility of oxygen in silver and have shown that the solubility is proportional to the square root of the gas pressure not only if dissociated gas is dissolved as described above, but also if this dissolved gas reacts with the silver to form a compound containing one atom of gas per molecule, in this instance, Ag_2O. This conclusion can be reached easily by extending the analysis in the preceding paragraph to include an application of the law of mass action to the reaction between the dissolved atomic gas and the metal. If this is done, it is found that the concentration of compound is directly proportional to the concentration of atomic gas, which has been shown to be proportional to the square root of the gas pressure. Hence the concentration of compound is proportional also to the square root of the gas pressure.

It is apparent from this discussion that data showing the effect of pressure on gas solubility do not show whether gases are dissolved in metals as atoms or as compounds. In order to learn the state in which gases exist in metals, Sieverts [13] studied the solubility of sulphur dioxide in copper. He expected that changes in the pressure would affect the solubility of this triatomic gas differently from that of a diatomic gas. He was surprised, therefore, to find that for this system also the solubility was proportional to the square root of the gas pressure. In this instance, adherence to the square root law could not be explained by assuming dissociation of the gas molecules into atoms.

In this field, Stubbs [17] made some interesting contributions after those of Sieverts. He showed that the freezing point of copper saturated with sulphur dioxide was depressed 2.54 times as much from that of pure copper as should be expected from van't Hoff's freezing point formula if the gas remained molecular in solution. If there were complete reaction between the gas in solution and the metal, the freezing point depression should be three times that for the existence of molecules only, and the amount of gas absorbed should vary as the cube root of the pressure. Stubbs took the discrepancy in these figures to indicate that about 70 per cent of the dissolved sulphur dioxide reacted with the copper according to the equation,

$$SO_2 + 6Cu = Cu_2S + 2Cu_2O.$$
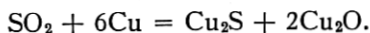
[16] Donnan and Shaw, *Jour. Soc. Chem. Ind.*, 29, 987 (1910).
[13] Loc. cit.
[17] Stubbs, *Jour. Chem. Soc.*, 103, 1445 (1913).

Stubbs also believed that Sieverts' data showed that the solubility of sulphur dioxide in copper varied as some higher root of the pressure (2.4 root) than the square root and that it supported his theory of partial reaction of the gas with the copper.

Because very little is known of the state in which dissolved gases exist in metals, certain data reported by Franzini [18] are interesting. Franzini believed that, if ionized gas existed in metals, it could be displaced by the action of an electric field. His data on the variation in electrical resistance, caused by application of an electrical field to iron and nickel wires which previously had been saturated with hydrogen, show that the absorbed gas can be displaced toward the negative pole. Thus, evidence of the presence of ionized gas in a metal was obtained.

ILLUSTRATIVE EXAMPLES OF GAS-METAL ABSORPTION STUDIES

The Solubility of Oxygen in Silver

Steacie and Johnson's [19] careful experiments on the solubility of oxygen in silver form a good illustration of the problems involved in this type of study. Since their work yielded some of the best data available on any gas-metal system, it is reviewed here in some detail.

The principle of their method of determining solubility is a variation of the method ordinarily used. A known weight of silver, contained in a silica bulb, is heated to a given temperature. All traces of gas are removed by evacuation of the apparatus, and then a known amount of purified oxygen is admitted to the silica bulb. After equilibrium between the oxygen and the silver is reached, the pressure of the gas is measured by a permanently connected manometer. The theoretical pressure of oxygen in the system, assuming none is absorbed by the silver, is calculated from the quantity of gas introduced, its temperature, and the volume of that part of the apparatus it occupies. The difference between calculated and observed pressures is a measure of the amount of gas absorbed by the metal.

In order to determine the solubility of gases in metals accurately, sufficient time must be allowed for equilibrium to be reached. Although equilibrium was reached very quickly at the highest temperature (800° C.) used by Steacie and Johnson, several days were required at the lowest temperature (200° C.). It is obvious that this long time greatly increases the possibility of errors from leakage of gas into the apparatus. Since Steacie and Johnson were especially interested in solubility at low temperatures, to be certain that no errors were

---

[18] Franzini's work was reviewed in *Nature*, March 12, 1932, p. 404.
[19] Steacie and Johnson, *Proc. Roy. Soc.* London, *112*, 542 (1926).

introduced by leakage, they pumped the gas out of the silica bulb and the silver at the end of each experiment, collected it, and determined its quantity.   If the amount of gas collected after an experiment was not substantially the same as the amount introduced originally, the experiment was discarded.

Data relative to the solubility of oxygen in silver are given in Table I.   The solubility can be seen to be proportional to the square root of the oxygen pressure, except for pressures below 10 cms. when the temperature is below 600° C.   Here a marked divergence from the square root law appears, which might be explained by assuming that these measurements were made before equilibrium was established.
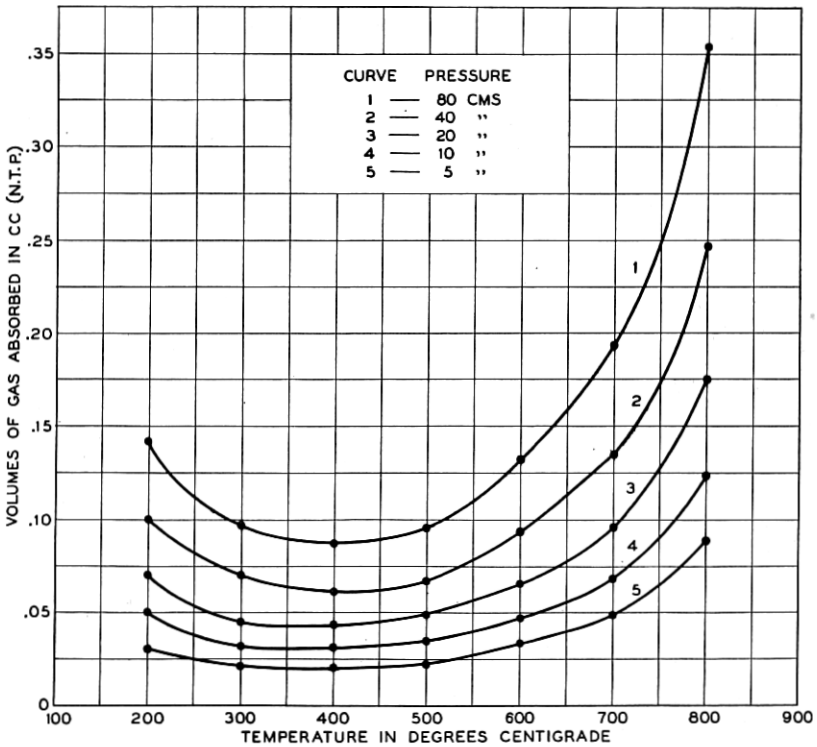

Fig. 1—Solubility of oxygen in silver as a function of temperature with pressure as a parameter (Steacie and Johnson).

These data are plotted, in Fig. 1, to show the variation of solubility with temperature, giving pressure as a parameter.

The curves of Fig. 1 differ from those for other systems in that a minimum point occurs at about 400° C.   It would be logical to explain this minimum as an adsorption effect, but Steacie and Johnson

TABLE I

SOLUBILITY OF OXYGEN IN SILVER AT VARIOUS PRESSURES AND TEMPERATURES *

Pressure (cms.)	$T_1 = 200°$ C.		$T_2 = 300°$ C.		$T_3 = 400°$ C.		$T_4 = 500°$ C.		$T_5 = 600°$ C.		$T_6 = 700°$ C.		$T_7 = 800°$ C.	
	Volumes Absorbed (c.c., n.t.p.)	Constant	Volumes Absorbed (c.c., n.t.p.)	Constant	Volumes Absorbed (c.c., n.t.p.)	Constant	Volumes Absorbed (c.c., n.t.p.)	Constant	Volumes Absorbed (c.c., n.t.p.)	Constant	Volumes Absorbed (c.c., n.t.p.)	Constant	Volumes Absorbed (c.c., n.t.p.)	Constant
P	Q	$\sqrt{P}/Q$	Q	$\sqrt{P}/Q$	Q	$\sqrt{P}/Q$	Q	$\sqrt{P}/Q$	Q	$\sqrt{P}/Q$	Q	$\sqrt{P}/Q$	Q	$\sqrt{P}/Q$
5	0.030	74.5	0.021	106.5	0.020	112.0	0.022	102.0	0.033	68.0	0.048	46.7	0.088	25.5
10	0.050	63.4	0.032	90.8	0.031	102.3	0.034	93.2	0.047	67.5	0.068	46.6	0.124	25.6
20	0.071	63.3	0.045	91.0	0.044	102.3	0.048	93.4	0.066	67.9	0.096	46.7	0.175	25.6
40	0.100	63.5	0.070	90.5	0.061	103.9	0.067	94.5	0.093	68.1	0.134	46.3	0.247	25.7
80	0.142	63.2	0.097	91.7	0.087	103.0	0.095	94.3	0.132	67.9	0.193	46.5	0.354	25.3

* Steacie and Johnson.

found that, below 400° C., the solubility of oxygen in two samples of silver with different ratios of surface to volume was the same. If an appreciable part of the gas had been adsorbed on the surface of the metal instead of being in solution, a difference in apparent solubility should have been observed. They suggested, then, that the minimum point might indicate a change in the silver from one allotropic form to another. This explanation was found unsatisfactory later, because experiments showed that the solubility of hydrogen in silver passes through no minimum as does that of oxygen.

Mechanism of Solution of Oxygen in Silver

Following Langmuir's conception of the mechanism of adsorption Steacie and Johnson [20] proposed an explanation of the mechanism of solution of oxygen in silver in which the solubility minimum is attributed to a change in the form of the oxygen in solution. While a detailed criticism of this explanation would require more space than is available here, it seems unsatisfactory to the present authors, who wish to suggest the following alternative explanation.

Suppose that dissolved gas is held within the interior of the metal, and that it is in equilibrium with that adsorbed on the surface. Now the concentration in the interior which will be in equilibrium with a given surface concentration increases with increasing temperature. The surface concentration, however, which is due to adsorption, will itself decrease with increasing temperature. Hence the final equilibrium depends on two factors which vary with temperature in opposite directions. Below 400° C. surface concentration may be the controlling factor. Thus, as the temperature rises towards 400° C., the surface concentration decreases faster than the dissolved gas in equilibrium with it increases. Hence the solubility decreases with increasing temperature. Above 400° C., the amount of dissolved gas in equilibrium with the adsorbed surface gas increases faster with increasing temperature than the surface concentration decreases, and the amount of gas dissolved increases with increasing temperature. Theoretically, this explanation applies equally well to other gas-metal systems and would lead one to expect solubility minima in them. These minima, however, in some systems may be at temperatures below the range subject to investigation.

The Rate of Solution of Oxygen in Silver

In addition to their determination of solubility of oxygen in silver, Steacie and Johnson made very careful measurements of its rate of

[20] Steacie and Johnson, *Proc. Roy. Soc.* London, *117*, 662 (1928).

solution.[20]   These data support their assumption that the process of solution consists first of saturation of a surface layer of the silver with oxygen and then diffusion into the metal.   If diffusion is the limiting factor in rate of solution, the data obtained should be expressed by the equation:

$$K = \frac{1}{t} \log \frac{s}{s - x},$$ (5)

where K is a constant, t is time, s is the concentration of a saturated solution of gas in the metal, and x is the average concentration of gas dissolved in the metal at time t.   Steacie and Johnson found that their data did fit this equation, if the first few points were neglected, and they plotted curves showing the change in rate of solution with temperature.

THE ANALYSIS AND MEASUREMENT OF GASES IN METALS

Theory

The most obvious method of determining the quantity and composition of gases in metals consists of melting a sample in vacuum and collecting, measuring, and analyzing the liberated gases.   The experimental procedure is difficult, however, and the inherent errors are of such magnitude that most results are at best only qualitative.

One of the principal sources of error in these experiments is the evolution of gases from furnace walls and hot refractories.   When the metal is heated by induced high frequency electric currents, however, this error can be reduced, and it can be minimized further by maintaining a large metal to refractory ratio.   Another source of error, of equal importance, is introduced when metal vapor condenses on the comparatively cool parts of the apparatus and reabsorbs some of the gas previously liberated.   Although this effect results usually from heating the metal in a high vacuum to too high a temperature, it is not easy to eliminate, because, when the temperature is reduced, the evolution of gas becomes too slow and the recovery of gas incomplete.   Errors also are introduced by gaseous products often formed by reactions between impurities in the metal melted and the refractory oxides of the crucible.   This occurs, for instance, when melting steel in a refractory oxide crucible.   The carbon reacts with the oxides to form carbon monoxide, carbon dioxide, or both.

Apparatus and Method

Despite difficulties and errors in the determination of gases evolved from metals melted in vacuum, some special vacuum melting pro-

[20] Loc. cit.

cedures have been devised which can be used satisfactorily for certain gases. A method of determining oxygen, nitrogen, and hydrogen in ferrous alloys, developed by Jordan [21] and his co-workers, and by Oberhoffer,[22] is now widely used.

In the method of Jordan, the samples to be analyzed are melted in vacuum in a gas-free Acheson graphite crucible. The liberated gases consist of carbon monoxide, nitrogen, and hydrogen. The carbon monoxide is formed by interaction of oxygen (or oxides) from the metal with carbon from the crucible. The nitrogen, which may originate from dissociation of nitrides, is evolved from the metal without chemical reaction with the crucible. The form in which hydrogen exists in the metal is unknown. These gases are pumped away from the melting compartment and collected for analysis. The carbon monoxide and hydrogen are oxidized to carbon dioxide and water, respectively, by passing them over heated copper oxide, and their quantities are determined by absorption in suitable absorbents. The residual gas, nitrogen, is determined by a volumetric method.

The Jordan apparatus with some modifications,[23] as shown in Figs. 2 and 3 is used at Bell Telephone Laboratories. The most important change is in the method of determining the weights of carbon dioxide and water formed during the analysis. In Jordan's apparatus, the absorbents for carbon dioxide and water are contained in weighing tubes which must be weighed along with the absorbent and the absorbed gas. In most experiments, the weight of gas absorbed is only a few milligrams and an elaborate technique is required, therefore, to weigh this small quantity when contained in a tube whose weight is relatively large. In the new modification, in order to minimize errors in the measurement of weight, and to simplify the technique required, a quartz spring balance has been substituted for the weighing tube. The absorbent for the gas is contained in a light glass basket attached to a quartz spring. The extension of the spring is measured with a cathetometer and the weight of gas absorbed determined from calibrations. Springs are made in various sizes so that one can always be found to fit the range of weights it is necessary to measure.

[21] Jordan and Eckman, U. S. Bureau of Standards *Scientific Paper No.* 514 (1925). Jordan and Vacher, U. S. Bureau of Standards, *Jour. of Research*, 7, 375 (1931).

[22] Oberhoffer, *Archiv für das Eisenhüttenwesen*, p. 583, March, 1928.

[23] These modifications were developed by Mr. E. S. Greiner who will describe them in the near future in a paper giving the complete details, together with a critical study of the method.
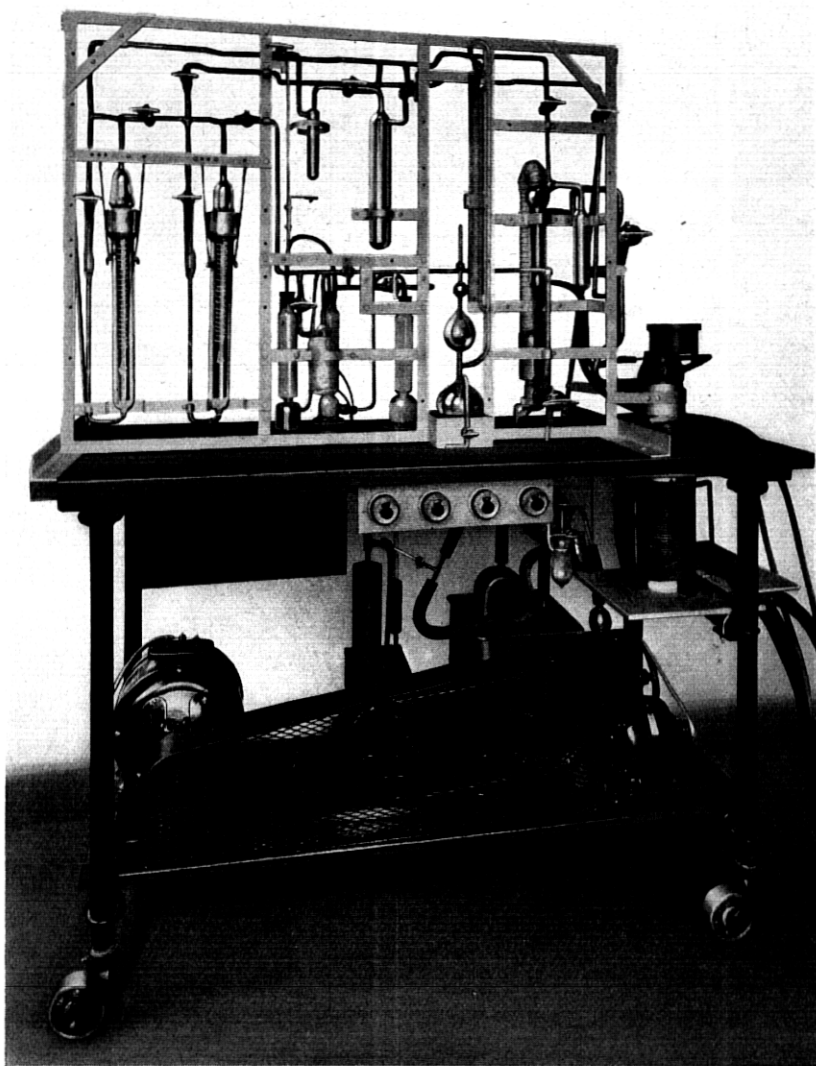
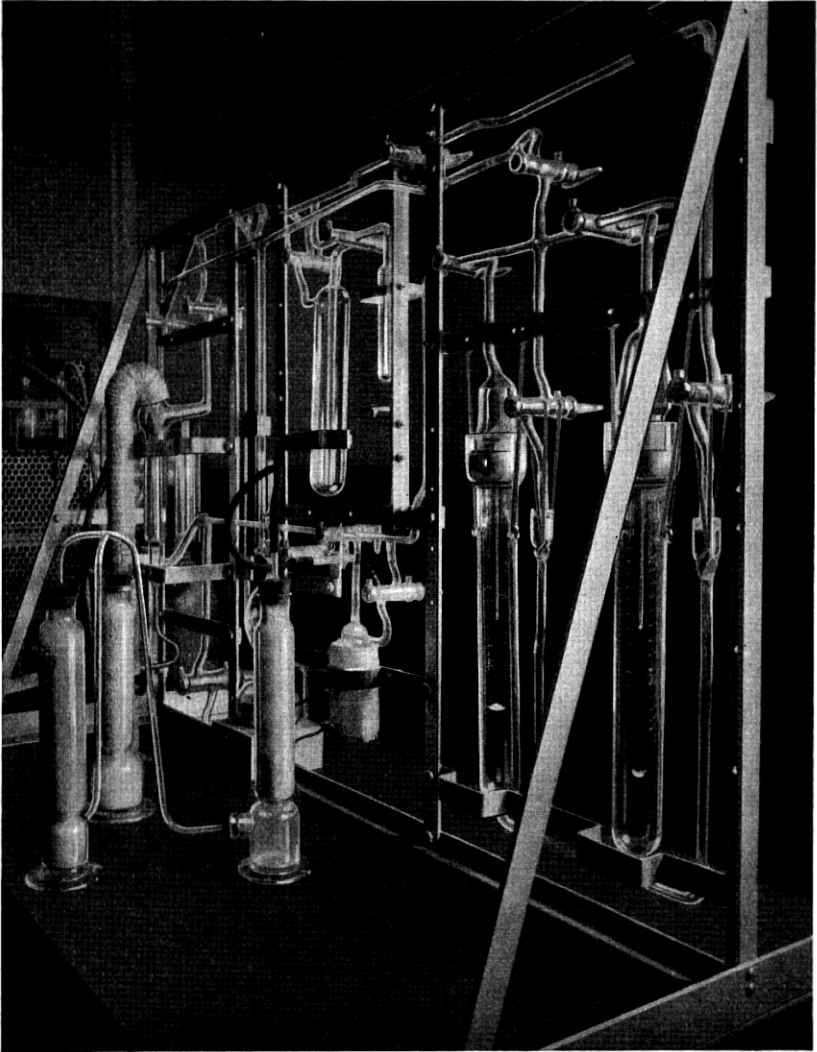Fig. 2—Modified Jordan apparatus for the determination of oxygen, nitrogen, and hydrogen in ferrous alloys.

Fig. 3—View of gas analysis apparatus showing quartz spring balances.

Vacuum Melting

Apparatus and Method

In order simply to prepare metals as gas-free as possible, at Bell Telephone Laboratories a special vacuum furnace was devised and constructed which has been extremely satisfactory and helpful in studying the effects of gases on the properties of metals. A schematic diagram of this furnace is shown in Fig. 4. The metal to be melted
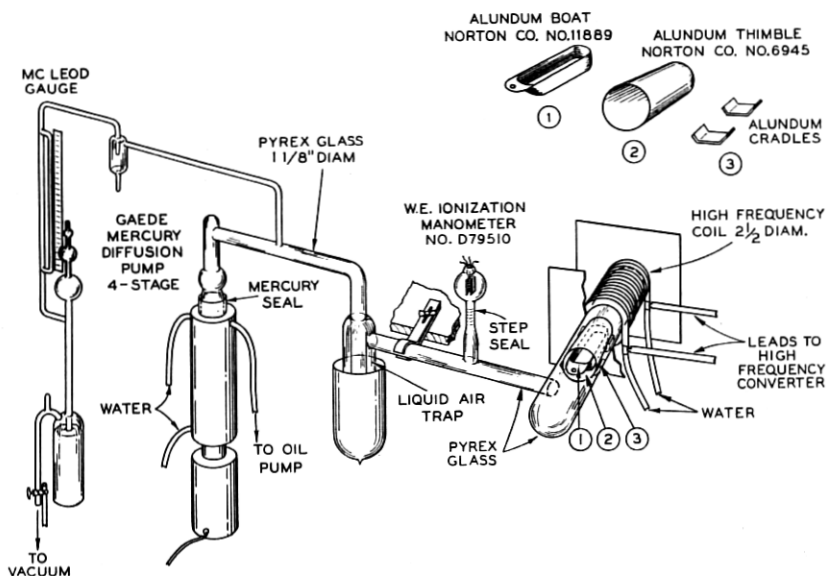

Fig. 4—Furnace for melting metals in high vacuum.

is contained in an alundum boat which is placed horizontally in an alundum thimble. The alundum thimble acts as a radiation shield and is supported concentrically on alundum cradles in a horizontal pyrex glass tube. The metal is heated inductively by high frequency currents supplied by a 35 KVA Ajax Northrup converter.

After the furnace is charged, the pyrex tube is sealed off with an oxygen hand torch, and is baked out at 450° C. by a nichrome wound furnace, the position of which is interchangeable with that of the high frequency induction coil. The pyrex tube is baked out for several hours so that subsequent heating by radiation from the melted metal causes no appreciable evolution of gas.

The gases given up by the liquid metal are pumped out of the system by a four stage Gaede mercury diffusion pump backed by an oil pump. A liquid air trap prevents mercury vapor from entering

the furnace tube and increases the efficiency of the pumping system by removing water vapor and carbon dioxide from the gases to be pumped out. Rough measurements of gas pressure are made with a McLeod gauge on the pump side of the liquid air trap, but measurements of low pressures are made with an ionization manometer on the furnace side.

With this furnace, and using clean alundum parts, metals can be melted with very little contamination of any kind. Copper and iron have been melted under a pressure never rising above 1×10^{-2} mm. Hg and having a final value of 1×10^{-5} to 1×10^{-6} mm. Hg. Even lower pressures can no doubt be obtained by cooling the pyrex furnace tube more effectively, as by use of a water jacket, and by using gas absorbing chemicals such as activated charcoal.

It has been found with this furnace that, even when melting iron, the temperature of the glass furnace tube never rises above 150° C. Since pyrex glass does not soften below 500° C., it should be possible to melt metals with higher melting points than that of iron.

In this furnace, a horizontal boat rather than a crucible is used to hold the sample for two reasons: First, the surface area of metal is greater and the pressure head of metal less so that the melt is degasified more rapidly than it would be in a vertical crucible. Second, very much smaller and less troublesome pipes form in horizontal ingots than in vertical ones.

Commercial Vacuum Melting

Vacuum melting on a commercial scale was developed in Germany during the war because of the need for a method by which the composition of alloys could be accurately controlled. The scarcity of platinum, for instance, necessitated the commercial production of substitute alloys for thermocouples which could be used, without calibration, in direct reading instruments. From the small furnaces used for this work, vacuum furnaces capable of handling up to four tons have been developed.

A brief description of one of these furnaces and of the obstacles encountered in their development has been given by Rohn in his publications.[24] The furnace described by Rohn operates by high frequency induction. It has a horizontal, ring-shaped melting chamber surrounded by the primary induction coils and an iron core. The whole is enclosed in an air-tight casing arranged so that it can be tilted about a horizontal axis. Two molds are fastened on opposite sides of the casing through air-tight connectors. When the charge is

[24] Rohn, *Zeit. für Metallkunde, 21*, 12 (1929). *Engineering*, Oct. 18, p. 512 (1929).

molten and degassed, the ingots are poured by tilting the entire furnace first to one side and then to the other.

Rohn claims that by dividing the iron core into several parts, a homogeneous field is obtained while there is only a small induction effect in the metal casing. The primary coil, also, is composed of four separate units which can be connected in series or energized separately. Energizing only one unit of the primary, it is claimed, causes vigorous stirring of the molten charge, thus facilitating the degasification. When the units are energized in series, the uniform field obtained causes but little stirring.

One of the chief obstacles it was necessary to overcome during the development of these large furnaces was lack of a satisfactory vacuum casting procedure. Rohn and his co-workers found that, if a normal casting procedure were followed after all the gases were removed from a charge of metal, ingots were obtained with such large shrinkage cavities that working them was impossible. When using iron or sand molds the formation of these cavities could not be prevented. A vertical water-cooled, copper mold was developed, however, that was satisfactory when the melt was poured slowly.

Another obstacle encountered was in obtaining a satisfactory lining for the vacuum furnaces. A moistened material, tamped into place, could not be used because of the difficulty in removing water vapor. The method adopted consisted of packing the regular refractory, as a dry powder, between the outside furnace wall and a template made of the same metal as the charge to be melted. The temperature of the charge was then so controlled that the refractory powder sintered before the template melted.

The Advantages of Vacuum Melting

In addition to freedom from blowholes in castings, one of the main improvements effected by using vacuum furnaces for melting metals is the degree of quality and composition control which can be attained. With this method, no gas can interact with constituents of the melt to cause composition changes, and the melt can therefore be kept liquid for long intervals of time. This allows the suspended particles of slag and oxides to rise to the surface, and results in ingots freer from inclusions. Furthermore, the usual deoxidation methods can be dispensed with. For instance, the iron oxide in molten steel is completely eliminated by reaction with carbon, and therefore, no deoxidation is necessary. Likewise, for non-ferrous metals, no deoxidizers are needed, for during vacuum melting no oxidation of the melt can occur. Thus, inclusions from these sources also are avoided.

In a recent publication [25] Rohn states that iron, nickel, and copper may be freed of oxygen by dissociation of their oxides during vacuum melting. According to our experiments, however, when tough pitch copper is melted under a pressure even as low as 1×10^{-5} mm. approximately, the oxygen is not removed. After this treatment the material is still embrittled by annealing in hydrogen. This failure of the oxide to dissociate may be reasonably ascribed to a reduction in dissociation pressure caused by solution of the oxide in molten copper. This explanation is supported by the thermodynamical calculations of many workers.[26] Furthermore, as the oxide solution in liquid copper becomes less concentrated, its dissociation pressure is lowered so that removal of the last traces of oxygen by dissociation becomes exceedingly difficult.

Rohn [25] has reported that magnetic materials, thermocouple metals, metals for vacuum tube parts, metals for sealing through glass, and nickel-chromium alloys for heating elements are being produced advantageously by vacuum melting. He claims, also, that all of the working properties of the nickel-chromium series of alloys are improved by vacuum melting and that alloys containing up to 33 per cent chromium can be worked satisfactorily.

Concerning the economy of vacuum melting, Rohn points out that production by this method is more costly than production by standard methods. He states that vacuum melting increases the cost of metals ten cents a pound when using a four ton furnace and starting with a cold charge. This can be reduced to one or two cents a pound if the vacuum furnace is used only for the final refining treatment of molten charges. This extra cost should be balanced, in many instances, by the improved quality of metal obtained. Rohn's expectations, which seem to be justified, are that alloys can be made by this process for highly important parts such as turbine blades, tubing for superheaters, and aeroplane parts.

[25] Rohn, *A. I. M. M. E.—Tech. Publication* No. 470.
[26] Ellis, *A. I. M. M. E.—Tech. Publication* No. 478. Allen, Inst. of Metals, Advance Copy No. 604 (1932).