EQUILIBRIA IN THE SYSTEMS IRON : CARBON : OXYGEN AND IRON : HYDROGEN : OXYGEN, AND THE FREE ENERGIES OF THE OXIDES OF IRON[1]

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A review of the published researches on the gas-solid equilibria in the above important systems, and of the literature concerning the oxides of iron reveals a surprising degree of confusion. The results of different investigators are not always in satisfactory agreement and are often difficult of interpretation. Some of the more recent experiments, however, indicate a few of the causes of difficulty, and remove certain phases of the subject from the realm of hypothesis. While exact knowledge of these systems must remain incomplete until further work has been done, it appears that an adequate basis exists for the determination of equilibrium constants and free energies with a certainty and accuracy sufficient for many scientific and technical purposes. In the following the numerical results of such determinations will be presented, preceded by a critical discussion and summary of the experimental data upon which they rest.

One and Two Component Systems

The polymorphism of elementary iron has been ignored throughout the following work, as the equilibrium data are in no case of enough accuracy to require a distinction between the different forms which are stable in the various temperature ranges.

The equilibria in which solid carbon appears are perhaps slightly influenced by the form in which this substance occurs. Such variations are in general small[3] and will be neglected here. Graphite is the stable phase into which "amorphous" forms in these equilibria are slowly changing, and to which the final free energy calculations are referred.

In the system iron: carbon the compound Fe_3C and solutions of it or of carbon in iron are known in the solid state. Owing to the difficulties of experimental investigation the solubility limits and temperatures and even the qualitative nature of the iron-carbon diagram are rather uncertain. Fe_3C does not appear in the equilibrium diagram of the "stable system" given in the Landolt-Börnstein "Tabellen." In the "unstable system" it does occur as a separate phase, but below 700° is represented

[3] See for example, the discussion of Falcke's work below.

as not soluble in iron. The instability of cementite is further indicated by the thermochemical datum of Ruff and Gersten,[4] who find an absorption of 15,000 cal. per mol in its formation from the elements. It has been assumed in the following that Fe_3C is not one of the phases which must be considered in the study of stable equilibria, though iron-carbon solutions may be present.

The equilibrium of hydrogen with iron has been studied by Sieverts.[5] No separate hydride phase is formed, and the solubility of hydrogen is so small that the activity of solid iron cannot be appreciably affected by it. It is, therefore, not a factor in the iron: hydrogen: oxygen system.

The compounds Fe_2O_3 and Fe_3O_4 seem to be sufficiently well established as chemical individuals. Polymorphism is found[6] in the case of each of these oxides. Of especial interest are the magnetic inversions in hematite at about 678° and in magnetite, variously given as between 525° and 581°.

The dissociation pressures of the compound Fe_2O_3 have been experimentally studied by Sosman and Hostetter.[7] They directly determined the pressure-composition curves between Fe_2O_3 and Fe_3O_4 at 1100° and 1200°. These curves are shown in Fig. 1. Their form indicates a continuous series of solid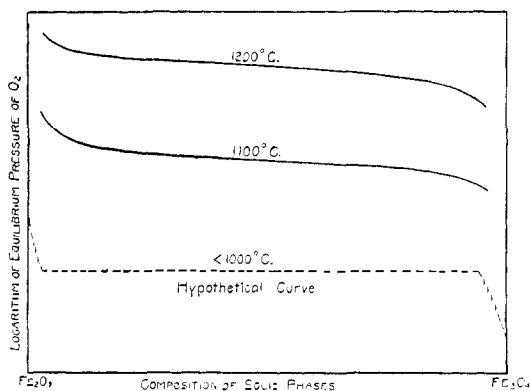 solutions of the oxides in each other at both temperatures. Smits and Bijvoet[8] have questioned (in the opinion of the writer without sufficient reason) this interpretation of the curves, claiming their continuous character to be due to slow reaction or "occlusion" of oxygen by the pure solid phases. It is seen that the experimental curve at 1200° slopes more and shows less tendency to discontinuity than that at 1100°.

Fig. 1.—Equilibrium pressures in the system Fe: O.

This would not be the case, it is believed, if the explanation of Smits and Bijvoet were correct, but would be expected if the oxides were soluble in all proportions. Sosman and Hostetter actually prepared, at 1200°, various solutions intermediate between Fe_2O_3 and Fe_3O_4 which remained homogeneous, as shown by their optical properties, even at atmospheric temperatures. The persistence of such solutions does not, however,

[4] Ruff and Gersten, Ber., 45, 63 (1912); 46, 394 (1913).
[5] Sieverts, Z. physik. Chem., 77, 591 (1911).
[6] Sosman, J. Washington Acad. Sci., 7, 55 (1917).
[7] Sosman and Hostetter, THIS JOURNAL, 38, 807, 1188 (1916).
[8] Smits and Bijvoet, Proc. Acad. Sci. Amsterdam, 21, 386 (1919).

preclude the possibility that they are unstable (supersaturated) at low temperatures. The approach of the pressure-composition curve to the two-phase type is very close even at 1100°. It seems probable, therefore, that a separation into distinct phases occurs, in the equilibrium case, at temperatures a few hundred degrees lower. This hypothetical behavior, also suggested by Smits and Bijvoet, is illustrated by the dotted curve of Fig. 1.

The methods which have been proposed in the literature for the preparation of ferrous oxide (FeO) do not give a pure product, as has been shown by Hilpert and Beyer.[9] In very careful experiments these workers failed to obtain ferrous oxide free from ferric oxide by reducing higher oxides in a stream of hydrogen and water vapor or carbon monoxide and carbon dioxide of proportions such that ferro-ferric oxide but not ferrous oxide should be reduced. They attribute their failure to the formation of solid solutions between ferrous and ferro-ferric oxides. Matsubara's experiments (vide infra), do show ferro-ferric oxide to be soluble to some extent in ferrous oxide. Hilpert's results may have been due to this, but could equally well be explained by the instability of ferrous oxide with respect to ferro-ferric oxide and iron below some definite temperature. This behavior was anticipated as a possible cause of difficulty by Sosman[7] and by Smits and Bijvoet.[8] It is apparent from the form of the equilibrium curve of Fig. 3 below, and has recently been independently verified in qualitative experiments by Chaudron.[10] When, therefore, ferrous oxide is prepared at a high temperature, on cooling it reacts in part according to the equation

$$4\ FeO = Fe_3O_4 + Fe \tag{1}$$

and the product will always show more or less ferric iron on analysis, the amount depending on the rapidity of cooling of the sample. More concerning this reaction and solid solution among the oxides will be said later.

The System Iron:Carbon:Oxygen

Braithwaite[11] was able to establish in a qualitative way the reversibility of the reaction of carbon monoxide upon ferro-ferric oxide. He also showed that carbon monoxide is nearly completely oxidized to the dioxide by ferric oxide at "low red heat."

Baur and Glaessner[12] were the first to publish quantitative results in this field. They undertook to determine the equilibrium composition of gas in the reactions

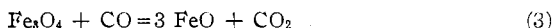[9] Hilpert and Beyer, Ber., **44**, 1608 (1911).
[10] Chaudron, Compt. rend., **172**, 152 (1921); Ann. chim., **16**, 221 (1921).
[11] Braithwaite, Chem. News, **72**, 211 (1895).
[12] Baur and Glaessner, Z. physik. Chem., **43**, 354 (1903).

$$FeO + CO = Fe + CO_2 \qquad (2)$$

and

$$Fe_3O_4 + CO = 3\ FeO + CO_2 \qquad (3)$$

In outline their methods follow.

Two g. of a mixture of ferro-ferric oxide (79.06%) and ferrous oxide (20.94%), prepared by reducing pure ferric oxide in a stream of hydrogen and treating the resulting iron with carbon dioxide at 600°, was placed in a porcelain boat in an electrically heated glazed porcelain tube which was connected to a mercury buret and a pump. After evacuation, the tube was filled either with carbon monoxide or dioxide and maintained at constant temperature, measured by a thermocouple in the tube near the boat, for periods varying mainly from 12 to 24 hours. The gas was then withdrawn and analyzed for carbon monoxide and dioxide. The ferrous oxide-iron mixtures were obtained by repeated treatment of the above preparation with carbon monoxide at 800°, the procedure being otherwise the same. The time of each run appears to have been more or less arbitrary, the degree of concordance of results approaching equilibrium from both sides being relied upon to determine whether reaction had been completed in the time allowed.

An inspection of the points representing their work, in Fig. 3, leaves little doubt that at the higher temperatures equilibrium was really attained. At 600° and below, the observations in the ferrous oxide-iron system deviate widely from the general mean, due in part perhaps to extreme slowness of reaction at these temperatures.

Schenck, Semiller, and Falcke[13] have published data relating to systems in which in addition to iron and ferrous oxide, solid carbon was present.

The solid phases were prepared by reduction of ferrous oxalate in a stream of hydrogen at 650° and passing carbon monoxide over the reduced metal for 4 hours at 600°. About 10 g. of the mixture so obtained, probably containing considerable quantities of each of the phases, iron, ferrous oxide, carbon, was used in each experiment. The mixture being studied was contained in a porcelain bulb kept at constant temperature, measured by a calibrated Le Chatelier thermocouple near the bulb in the furnace, and the progress of the reaction followed by observing the total pressure. When the pressure became constant, equilibrium was assumed to have been established and a sample of gas was then withdrawn and analyzed.

The composition of gas fixed by such a procedure should be the same in the presence of solid carbon as without it, provided that iron and ferrous oxide phases are present and active in establishing equilibrium. The latter condition appears to have been fulfilled in the first series of experiments and the points representing their results in Fig. 3 in general agree with those of other observers. In addition to these values Schenck, Semiller and Falcke give data concerning systems the solid phases of which they assumed to consist of iron, ferrous oxide, graphite; iron carbide (Fe_3C), ferrous oxide, carbon (amorphous); and ferro-ferric oxide, ferrous oxide, carbon (amorphous), and Schenck and Heller[14] for iron, ferrous oxide, with various forms of carbon. For reasons which will appear later

[13] Schenck, Semiller and Falcke, *Ber.*, **40**, 1704 (1907).
[14] Schenck and Heller, *ibid.*, **38**, 2132, 2139 (1905).

these data and the theoretical treatment of carbide formation founded
upon them are valueless.

Levin, in Nernst's Festschrift,[15] gives smoothed curves representing
results by Koster in the iron: ferrous oxide and ferrous oxide: ferro-ferric
oxide systems and by Van Royen in the iron: ferrous oxide system. The
dotted curves of Fig. 3 are constructed from them. Experimental details
have not been available to the writer and this work cannot, therefore, be
criticized here. Falcke,[27] however, in his fourth paper (referred to below)
gives a table of Van Royen's[16] individual results and states that they were
obtained using iron treated in a stream of carbon monoxide at 600°.
These experiments, therefore, parallel portions of Falcke's own work, and
they are in general agreement with it.

Falcke[17] continuing researches begun with Schenck, experimentally
proves most of the earlier work of Schenck and his co-workers to have
been vitiated by the use of incompletely decomposed ferrous oxalate
as a source of ferrous oxide. This preparation is indefinite, and when
heated at constant temperature until gas ceases to come off, resumes
evolution of carbon monoxide and dioxide upon elevation of the tempera-
ture. It was undoubtedly this partial and undefined "decomposition
pressure" which was being measured by Schenck and Heller in their ex-
periments with graphite, diamond, etc., as solid phases, since Falcke shows
that under the conditions they used, no appreciable reaction is obtained
with ferrous oxide and carbon. The objectionable ferrous oxalate prepa-
ration was also used in the iron—ferrous oxide—graphite, and ferro-ferric
oxide—ferrous oxide—carbon experiments of Schenck, Semiller and Falcke.

The reaction between iron and carbon monoxide in the neighborhood
of 600° is also studied by Falcke. He finds that carbon appears as a sepa-
rate phase only when the iron is treated for a long time in a stream of the
gas, as shown by the carbon residue which remains when the solid prod-
ucts of reaction are treated with hydrochloric acid. The products of
reaction in a closed tube dissolve without residue in hydrochloric acid;
in both cases hydrocarbons are formed by the treatment with acid.

Hilpert and Dieckmann[18] have also studied the reduction of iron oxide
in a stream of carbon monoxide. Results were not very reproducible,
but are generalized as follows. The products of reduction never contained
oxygen. Titration with permanganate showed 99.8% of iron when

[15] Halle, 1912, 252.

[16] Van Royen, *Dissertation*, Bonn, 1911.

[17] Falcke, *Ber.*, **46**, 743 (1913).

[18] Hilpert and Dieckmann, *ibid.*, **48**, 1281 (1915). Other experiments on the re-
action of Fe with CO are described by Gautier and Clausman, *Compt. rend.*, **151**, 16,
355 (1911) and Carpenter and Smith, *J. Iron Steel Institute*, Sept., **1918**. These last,
for example, worked at 650° and report that the solid products contain both oxygen and
carbon, and the formation of Fe_3C is indicated.

reduction occurred at 950°. At 850° the product always contained carbon and between 720° and 800° deposition of carbon by the decomposition of carbon monoxide was very greatly catalyzed. By treatment of the reduced iron with acid it was found that free carbon was not left as residue until the product attained a composition of 6% of carbon (Fe₃C = 6.6% C). Products containing 4–6% of carbon were easily obtained, as were those containing more than 10% of total carbon. Percentages (total carbon) between 7 and 10 were not readily obtained. The Curie point in the solid masses which catalyzed the decomposition of carbon monoxide was found to be somewhat lower than that for iron carbide (Fe_3C), which is known to be much lower than for pure iron. The authors for this reason assume unstable carbides of the type Fe_2C or FeC to have been present, and that the catalysis was due to their formation.

The results of Falcke and of Hilpert and Dieckmann make it appear certain at least that in the systems of Schenck and Heller, and Schenck, Semiller and Falcke, obtained by reaction of carbon monoxide on iron in a closed tube, carbon as a separate phase was not present, as they assumed it to be, and that if iron carbide (Fe_3C) was ever present in large amount it should have been in the first series of experiments of Schenck, Semiller and Falcke described above.

Falcke[19] in another paper describes experiments with purified amorphous carbon prepared in various ways and with several varieties of purified natural graphite, compressed with iron and ferrous oxide and heated in an evacuated tube. No appreciable reaction was found to occur in any instance below 650°. Above this the different samples reacted with very different speeds. The amorphous carbon reacted very slowly and in no instance was the final equilibrium pressure observed. The graphite samples exhibited different reactivities also; pressure was developed slowly at first, then with increasing speed to a definite final value which was approximately the same in all cases. The total pressure-temperature curves fell only a little below those obtained by Schenck and Falcke and others with iron treated with carbon monoxide. Some gas analyses are also given though doubt is expressed that they necessarily represent equilibrium conditions. In only one case in all the experiments tried was there any evidence of carbide formation with the iron (i. e., of hydrocarbons in the gas formed by reaction of residues with hydrochloric acid).

In a third research Falcke[20] obtained equilibrium data in numerous experiments involving reactions between carbon monoxide and pure iron, and iron which had been treated in a stream of carbon monoxide at 600°, (referred to as "carbonized iron") and iron, graphite and ferrous oxide.

[19] Falcke, Z. Elektrochem., 21, 37 (1915).

[20] Falcke, ibid., 22, 121 (1916).

The ferrous oxide was a pure preparation heated until gas was no longer evolved. It contained some higher oxides. A typical mixture as used by Falcke is 1 g. of iron, 3 g. of ferrous oxide and 0.8 g. of graphite. When iron alone was used the amount was about 3 g. The mixtures were placed in porcelain bulbs, four of which enclosed in a copper sheath could be heated simultaneously. Temperatures within the sheath were measured with a thermocouple. Because results with identical preparations deviated by amounts corresponding to 20°, Falcke corrected the temperatures measured with the thermocouple by utilizing the temperature coefficient of the reaction of CO upon iron. This procedure is of questionable value in the opinion of the writer. The course of reactions in which the solid phases were allowed to evolve gas starting in vacuum, or in which gas was absorbed from an initial pressure of an atmosphere, was followed by observing the total pressure. When this became constant, the gas mixtures were analyzed. Comparatively large amounts of indifferent gases were always found, and are corrected for in the final results.

The value of the equilibrium constant of Reaction 2 does not differ significantly among the different preparations in any of the experiments.

The results relating to total pressures indicate that at all temperatures the equilibrium pressure and therefore also the constant $K = (CO)^2/(CO_2)$ of the reaction

$$CO_2 + C = 2\ CO \qquad (4)$$

are higher for the pure iron reacting with carbon monoxide in a closed tube, than for the "carbonized" iron. When the latter preparation was heated for half an hour at 900°, however, new equilibrium values of the pressure were obtained at the lower temperature (without change in composition of the gas) which were close to those for pure iron. The pressures in the experiments with graphite and ferrous oxide were slightly less than with the iron treated with carbon monoxide. With graphite and ferrous oxide prepared by oxidation of iron in a stream of carbon monoxide mixed with the dioxide the pressures were still lower. The equilibrium constants of Reaction 4 as obtained from Falcke's corrected curves in the several cases are compared in Table I with those calculated from the free energies of carbon monoxide and dioxide, (referred to graphite) given by Lewis and Randall.[21]

TABLE I

EQUILIBRIUM CONSTANTS, $(CO)^2/(CO_2)$

Temperature	600	700°
"Pure iron"	0.230 atm.	1.57
"Carbonized iron"	0.146	1.27
Graphite and pure comm. FeO	0.115	1.18
Graphite and FeO from Fe	...	0.87
From free energies	0.080	0.965

The divergence of the results in the "pure iron" and "carbonized iron" experiments from each other and from those calculated from the free energies is seen to be larger at the lower temperature. Falcke believes

[21] Lewis and Randall, THIS JOURNAL, **37**, 458 (1915).

the differences at each temperature and the approach to equality at higher temperatures to represent real effects, and suggests the formation of unstable carbides to account for them. From the analytical evidence the conclusion appears safe that carbide was present in both series, with little or no free carbon in the former, but large amounts in the latter. Just how the presence of carbide explains all the equilibrium effects is not clear to the writer. The maximum difference among the constants in Table I corresponds to about 20° in temperature, an amount which seems to be no larger than the uncertainties in the measurement and control of temperatures in the experiments. Nevertheless, Falcke later (see below) obtained similar results upon repetition of the experiments. Whatever the cause of these effects, if real, it seems assured that ferrous oxide and moderately pure iron were present as separate phases in the "carbonized iron" experiments. Whether this is true also of the "pure iron" runs cannot be said. Considerable amounts of carbon monoxide were often absorbed while the tubes were connected to the gas supply; an oxide phase may therefore have resulted. On the other hand, the ratio of carbon monoxide to iron and the side of approach do not appear to have been varied sufficiently in Falcke's experiments or those of his predecessors to prove the equilibrium to be divariant in this case. Evidence given later is strong that with small amounts of carbon monoxide trivariant systems result. Because of this uncertainty as to the phases, no results with pure iron are finally used.

Schenck[22] continuing discussion of points raised by Falcke compares values of various observers of equilibrium constants of Reaction 4 in the presence and absence of iron and believes the results to be in sufficient agreement to prove the presence of carbon as a separate phase in the iron experiments. He also states that some free carbon may be observed in many cases where iron absorbs carbon monoxide, the amount depending on the duration of heating. He believes that a stable carbide is formed in part directly with carbon monoxide and in part by reaction of free carbon with iron on long heating. Discussion of the conditions for the existence of such a carbide leads him to assign the approximate formula Fe_7C.

Terres and Pongracz[23] have worked in the ferrous oxide: iron system and have studied the reaction of carbon dioxide upon iron.

In the equilibrium measurements, 22 g. of "Ferrum Limatum" was placed in a porcelain bulb of 146.7 cc. capacity connected with a manometer, pump and gas supply and enclosed in an electric-tube furnace. The temperature was then maintained at 950°, as measured by a thermocouple outside the bulb in the furnace, the bulb evacuated and carbon dioxide at 1 atmosphere pressure introduced. At the end of 7 hours a sample of gas was withdrawn and analyzed, the pressure being restored to 1 atmosphere by

[22] Schenck, Z. Elektrochem., 24, 248 (1918).
[23] Terres and Pongracz, ibid., 25, 386 (1919).

addition of more carbon dioxide. The reaction was then allowed to proceed for 16 hours longer, when a sample was again taken. The furnace was then regulated at a lower temperature, the pressure of carbon dioxide in the bulb adjusted and samples were taken after the same time intervals as before. This procedure was repeated 6 times, the temperature of the last experiments being 550°. The iron which had been used in all these runs was then treated at 800° with carbon dioxide, in the closed bulb, the gas being renewed about 40 times. The same plan was then followed with this preparation as with the iron alone, except that carbon monoxide was now used instead of the dioxide.

From the results of the gas analyses in the two series of 16-hour runs the points shown in Fig. 3 have been derived. Terres and Pongracz believed that equilibrium was actually established at 825° and above in this series because the two curves closely approach each other. (They actually cross at 900°.) They believed the larger amount of iron used to be responsible for the deviation of their results •from those of other investigators and undertook to test this point.

In experiments at 550° in which powdered iron or iron wire was treated with carbon dioxide for 12 hours or a mixture of iron and iron oxide with the monoxide, it was found that increasing the weight of iron used increased the ratio of carbon monoxide to the dioxide at the end of the experiment. Since the reactions were far from completion these results do not prove anything. The same thing is true of similar experiments in which the solid phases were analyzed. Some oxide higher than ferrous was always found to be present, which the authors interpret as necessitating the assumption of solid solution of ferrous oxide and ferro-ferric oxide in one another.

In other experiments it is apparently definitely established that there is a decrease in volume when carbon dioxide reacts with iron in a closed tube. This diminution is most rapid at the beginning of the reaction and gradually falls off to zero as the reaction proceeds. If carbon monoxide and oxides of iron were the only products of the reaction this obviously would not be the case. Carbon dioxide therefore reacts directly with iron, giving carbon in some form as well as oxygen in the solid product. Apparently owing to changing "temperature coefficients of solubility" of the gases in iron, when iron is heated in a closed bulb with carbon dioxide the pressure increases as the temperature is slowly raised from 600° to 820°, decreases up to 900°, and above this increases steadily again. In a final series of experiments at 550° in which iron was treated with carbon dioxide for 12 hours, the solid and gas phases were both analyzed and a "balance" of the oxygen exchanged between them attempted. Results were not conclusive but might be interpreted as indicating a greater absorption of carbon dioxide than of the monoxide by the iron, *i. e.*, that the iron phase contained more oxygen than carbon. Criticism of the work of Terres and Pongracz will be returned to later.

Chaudron[10] gives equilibrium measurements obtained as follows.

Two g. of ferric oxide contained in a boat in a porcelain tube and maintained at constant temperature in a resistance furnace was treated with successive known volumes of carbon monoxide. The gas was passed in a cycle through the apparatus and over the solid oxide. The progress of the reaction was followed by means of an interferometer arranged to observe the density of the gas mixture in the system. From the known compositions of gas and the volumes used the compositions of the solid could be determined. Measurements of equilibrium composition of gas, obtained partly on reduction and partly by oxidation of the solid, were made at various temperatures. In the principal series of runs, the solid may be calculated to have consisted of approximately 50 and 75 mol % respectively of ferrous oxide with ferro-ferric oxide, and 33 and 67 mol % of iron with ferrous oxide. The results of these series, together with a few measurements in which the solid phases were prepared by oxidation of iron with carbon dioxide, are shown in Fig. 3. One point at 1050° in the ferro-ferric oxide: ferrous oxide system falls off the field of the diagram, and one of the ferrous oxide: iron points at 670° which falls very close to the curve could not be shown without obliterating several points by other observers. The temperature at which the three curves meet is given by Chaudron as 580° in his first paper and 570° in the final one.

Little criticism can be made of Chaudron's methods. The gas analyses might have been subject to minor errors due to the presence of gases other than carbon monoxide or dioxide. Other observers have often reported 2–4% of nitrogen, for example. The partial decomposition of carbon monoxide into the dioxide and carbon in the cooler zones of the furnace might also introduce uncertainties. It was found necessary to place the thermocouple outside the porcelain tube in the furnace. It is stated, however, that differences were always less than 5° in comparison tests with another couple inside the tube, after the furnace temperature had remained constant for 15 minutes. The time required for attainment of practically constant composition of gas was about 6 hours below 550° and 4 hours above. A complete circuit of the apparatus was made by the gas in about 3 hours.

Matsubara[24] also describes equilibrium measurements in this system.

A weighed amount of ferric oxide, prepared by ignition of purified hydroxide at a rather low temperature in a current of oxygen, was placed in a magnesia boat at the middle of a furnace in a glazed porcelain test-tube. Both ends of this tube projected beyond the furnace, the open end being connected to the vacuum, gas supply, manometer, etc. With the furnace regulated at constant temperature, a measured amount of carbon monoxide was introduced and allowed to react until equilibrium was established. The time required for this was about 2 hours at 1100° and 14 to 20 hours at 850°. (How this was determined is not stated.) The gas was then withdrawn and analyzed for carbon monoxide, carbon dioxide and nitrogen. The results of the analyses were used to calculate the composition of the solid phase. This procedure was repeated until reduction was nearly complete. The composition of the solid was checked in some instances by weighing the boat at the conclusion of an experiment and also by analysis. The compositions determined in these ways were in essential agreement. A platinum platin-rhodium thermocouple was used for temperature measurement. The thermo-junction was outside of the porcelain tube at the center of the furnace. With both ends of the

        [24] Matsubara, *Trans. Am. Inst. Mining Met. Eng.*, preprint No. 1051, issued with *Mining and Metallurgy*, February, 1921.

reaction tube projecting from the furnace the thermocouple could scarcely have measured accurately the temperature at any point inside the tube. Matsubara states: "correction of temperature in the furnace was made by repeating Boudouard's experiment[25] and by determining the composition of the gaseous phase in equilibrium with amorphous carbon at various temperatures, at nearly one atmosphere, and then determining the average temperatures in the furnace by the result of Boudouard." The magnitude of these "corrections" is not stated.

Fairly complete diagrams of equilibrium composition of gas *vs.* composition of solid phase were obtained at 1175°, 1070° and 863° respectively. That reproduced in Fig. 2 is typical. In addition, experiments were made
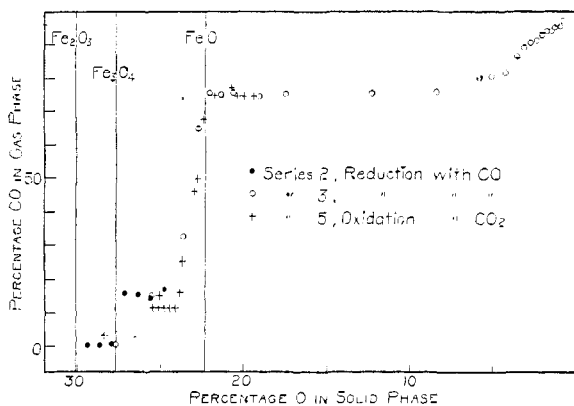

Fig. 2.—Matsubara, composition diagram at 1175° in the system Fe:C:O.

with mixtures of composition corresponding to the horizontal portions of this curve at a number of other temperatures. These results and the preceding are shown in Fig. 3. The remaining experiments and discussion in Matsubara's paper deal with the "carburization" of iron and will not be included here except to cite the results of a series of experiments at 965°.

Starting initially with about 7 g. of reduced iron containing 2.01% of oxygen, equilibrium was obtained with successive portions of carbon monoxide. In going from 2.01 to 1.43% of oxygen in the solid the equilibrium composition of gas changed from 70.72 to 75.20% of carbon monoxide and there was always an initial decrease in pressure which was then slowly regained. After this the pressure always remained lower than the initial value, the percentage of oxygen in the solid going to 0.57 and of carbon monoxide in the gas to about 91.1. Further treatment did not change the composition of the gas very much. Examination of the solid phase showed "strong carburization" but no soot deposition.

It is stated that in the last experiments of this series iron carbide or some other substance rich in carbon appeared as a separate phase, but the evidence on which this statement is based is not given. In fact the experimental evidence as to the nature of the solid phases present in this

[25] Boudouard, *Ann. chim. phys.*, **7**, 24 (1901).

case, where Matsubara gives them as ferrous oxide dissolved in iron and iron carbide (Fe_3C), and in other experiments in which he thinks that iron and iron carbide have been present, is very incomplete. The writer inclines to the belief that the equilibria under discussion are trivariant. However, the point is not an important one from the present standpoint.

From the data shown in Fig. 2 it may be calculated that at 1175° the phases which are present in the two equilibria are ferro-ferric oxide containing not more than 25 mol % of ferrous oxide, and ferrous oxide with about 12% of ferro-ferric oxide, and nearly pure ferrous oxide with iron containing about 25 mol % of dissolved ferrous oxide. This high percentage of oxygen in the iron phase is rather surprising. The points in this portion of the curve were all obtained by the action of carbon monoxide, and it is not mentioned that any special attempt was made to be sure that equilibrium had actually been reached. Further, it is possible that ferrous oxide might partly dissolve in the magnesia of the boat, which would result in curves of similar form. This behavior would have been eaily observed had it occurred, but no mention of it is made. The only evidence of an experimental nature which might be brought against the solubility of ferrous oxide in iron is the claim of Schenck and Falcke that their results with carbon monoxide acting on pure iron in a closed tube could be reversed to give the same final value of equilibrium constant, together with similar experiments in the hydrogen system. This could scarcely be the case had the ferrous oxide not been present as a separate phase. Examination of these experiments does not convince the writer, however, that conditions have been varied sufficiently to prove the reactions mentioned to represent definite divariant equilibria. On the other hand the disagreement in the equilibrium constants obtained by other observers when, for example, the relative amounts of iron and gas were varied, is perhaps good evidence that Matsubara's work is correct. Pending further experiments, the writer therefore accepts the result of Matsubara that iron dissolves ferrous oxide to the extent of 20 mol % or more at the temperatures in question. This conclusion is a very important one. For example, it makes it necessary to exclude from final consideration the values of Schenck and of Falcke determined with iron and carbon monoxide in a closed tube, and of Terres and Pongracz with iron and carbon dioxide. It may be calculated from the volume of the apparatus of the last named authors that their treatment of iron with carbon dioxide did not produce enough ferrous oxide for saturation, so that even in their experiments starting with carbon monoxide, there could have been no separate ferrous oxide phase present at equilibrium. It is perhaps interesting to note that in a trivariant equilibrium of this kind, increasing the weight of iron or decreasing the volume of the gas space, other things being equal, operate in a way to make the equilibrium constant used here numerically smaller. Terres

and Pongracz were partially correct, therefore, if their reactions were completed in the time allowed, in their explanation of the lower percentages of carbon dioxide as due to the considerable weight of iron present.

Regarding Matsubara's equilibrium constants, in spite of the objectionable temperature measurement, the points lie within the limits of error upon straight lines, and appear to agree well with the average of the other determinations. They have, therefore, been given much weight in drawing the final curves.

In a fourth paper upon the subject of the reaction between ferrous oxide and carbon and between carbon dioxide and iron, Falcke[26] reviews the earlier work and replies to Schenck. In the review he tabulates results by Nippert[27] (which have not been available to the writer) in systems obtained by allowing iron to absorb carbon monoxide. He also gives results of repetitions of his own previous experiments in this system and that obtained by treatment of iron in a stream of carbon monoxide. These were accompanied by experiments in which nickel was used as catalyst in Reaction 4. The constant $(CO)^2/(CO)_2$ of this reaction is again found to be higher at all temperatures for the "pure iron" than for the carbonized, and the latter to be higher than in the nickel experiments, which are taken to be the true constants of Reaction 4. The constants of Reaction 2, $(CO_2)/(CO)$ as obtained with iron treated in a stream of carbon monoxide, are included in Fig. 3 but not distinguished from his former work. These constants again agree fairly well with those of the "pure iron" experiments, but on account of the uncertainty as to the presence of a ferrous oxide phase, neither Falcke's nor Nippert's results in this series are shown in Fig. 3. Falcke still believes that both series represent definite monovariant equilibria, and that the carbides which are present constitute the active carbon phase rather than free carbon.

Equilibrium Constants in the System Iron : Carbon : Oxygen

In Fig. 3 the common logarithms of the equilibrium constants assumed by the different observers to correspond to the reactions

$$FeO + CO = Fe + CO_2 \qquad\qquad (2)$$

and

$$Fe_3O_4 + CO = 3 FeO + CO_2 \qquad\qquad (3)$$
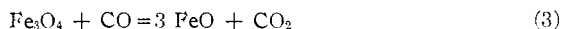
are plotted against the reciprocal of the absolute temperature. This procedure is adopted because of the approximately linear relationship which should hold when the variables are so chosen. Representing the partial pressures of the gases by their formulas in brackets, the equilibrium constant here used is, for each reaction, $K = (CO_2)/(CO)$.

The only data which have been found that are not shown in Fig. 3 are

[26] Falcke, Z. Elektrochem., **27**, 268 (1921).

[27] Nippert, Dissertation, Breslau, **1913**.

those of Schenck and Heller, Schenck, Semiller and Falcke, Nippert, and Falcke in which unreduced ferrous oxalate was used, or which were obtained by the reaction of carbon monoxide upon pure iron, and the 7-hour runs of Terres and Pongracz. The 16-hour runs of the last mentioned observers are shown for comparison only; reasons have already been pointed out for rejecting them from final consideration. For all of the other points shown there is good evidence that separate, definite solid phases were present in large amounts, and the very general agreement which is found is further support of this. The points due to Falcke and to Schenck, Semiller and Falcke belong to systems in which carbon was present, obtained by deposition from carbon monoxide, or as various kinds
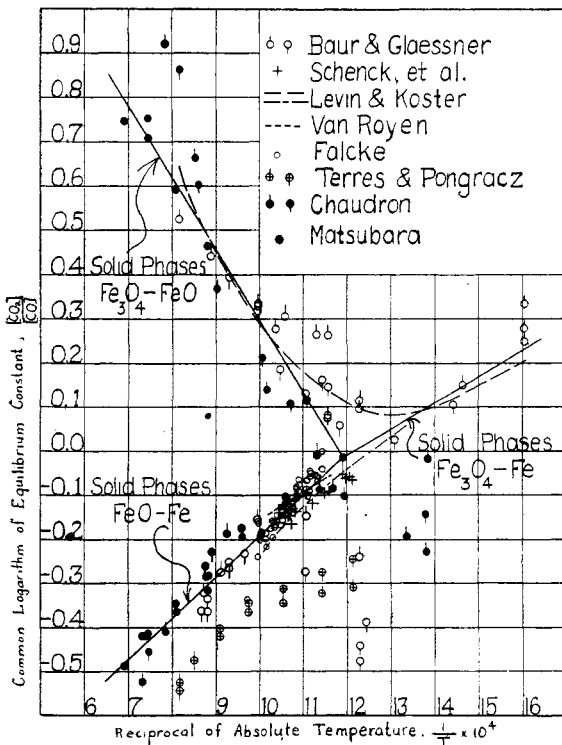

Fig. 3.—Equilibrium constants and temperature in the system Fe: C: O.

of graphite in some of Falcke's work. The points of Baer and Glaessner, Terres and Pongracz, and Chaudron are marked with a stroke pointing downward to denote that approach to equilibrium in the experiment was from the carbon dioxide side, upward for carbon monoxide.

The solid lines in Fig. 3 have been drawn as best representing all of the experiments. They conform qualitatively to the behavior required if

ferrous oxide is unstable with respect to ferro-ferric oxide and iron below 565°, the temperature at which the iron-ferrous oxide and ferro-ferric oxide—ferrous oxide curves intersect in the diagram. It is seen that the former curve is quite sharply defined: agreement in the latter case is not so good, but the general course of the curve is undoubtedly correct. At 500° and below, the points are too few and too divergent to fix the ferro-ferric oxide curve accurately, and at temperatures over 1000° some tendency to diverge is seen in the other systems also. For these reasons numerical calculations have been confined to the temperature range 600–1000°. In Table II, below, are found the values of the equilibrium constants K_2 and K_3 of Reactions 2 and 3, respectively, as taken from the average curves of Fig. 3.

TABLE II

EQUILIBRIUM CONSTANTS, $(CO_2)/(CO)$

| Temperature °C.	Fe: FeO System K_2	FeO: Fe$_3$O$_4$ System K_3
600	0.871	1.15
700	0.678	1.77
800	0.552	2.54
900	0.466	3.43
1000	0.403	4.42

The constants in Table II refer to systems in which the solid phases are in general not quite pure. Thus in the Fe:FeO system, while the ferrous oxide phase at equilibrium is nearly pure, the iron phase probably contains considerable amounts of ferrous oxide in solid solutions, and some dissolved carbon. The fugacity of the iron in this equilibrium is, therefore, probably somewhat smaller than that of pure iron at the same temperature. The effect of this should be to make the equilibrium constant numerically larger than that for pure iron—how much larger cannot be said. The deviations of these solutions from the behavior of a perfect solution are so large and of such a character, however, that it may safely be assumed that the fugacity of the iron in these cases is essentially that of pure iron, and that the equilibrium constants, K_2, do not lie much above the true ones. In the ferro-ferric oxide: ferrous oxide system each solid phase is apparently somewhat contaminated by the other. Here the effects on the constant are partly compensating, and probably not large.

The solid curves on the diagram of Fig. 3 have been drawn for the ferrous oxide: iron and ferro-ferric oxide: ferrous oxide systems, considering only the experimental points. The intersection of these two curves together with the direct experimental points were then used to determine the ferro-ferric oxide — iron curve. In a system of this kind, however, there is a necessary connection of the three curves. Thus it can be shown that the ratio of carbon dioxide to the monoxide in the ferro-ferric oxide: iron system must be equal to $K_2^{3/4} \times K_3^{1/4}$. Projecting the curve

representing the latter constant linearly it is found that at $1/T = 0.00148\overline{5}$, log $(CO_2)/(CO)$ should be 0.065 on the ferro-ferric oxide—iron curve. The experimental curve at this point gives 0.158. Of the three the ferrous oxide-iron curve is best defined. If this kind of criterion may be used, the discrepancy of 25% represented in the above figures is due mainly to error in the ferro-ferric oxide—ferrous oxide and ferro-ferric oxide—iron curves, especially the latter, since the data relating to it are few and the experimental difficulties are greater than at higher temperatures.

The System Iron:Hydrogen:Oxygen

In this system the very early work of Deville[28] is the model for all later investigations. His method of experiment was to measure the total pressure developed when water vapor from a reservoir of liquid water kept at constant temperature was allowed to react with metallic iron at a series of temperatures between $150°$ and $1600°$. As the pressure of water vapor was its vapor pressure, it was always fixed and known, and from it and the total pressure, the pressure of hydrogen could be found. Equilibrium was regarded as established when the pressure became constant. Deville varied the weight of iron used in the different experiments, approached equilibrium from the side of increasing and decreasing pressure and, in one set of experiments, allowed hydrogen to react with large amounts of iron oxide prepared by the action of water on iron at $800°$. The temperature measurement in these experiments was approximate only. Deville assumed his reactions to correspond to the equation

$$3 \text{ Fe} + 4 \text{ H}_2\text{O} = \text{Fe}_3\text{O}_4 + 4 \text{ H}_2 \tag{5}$$
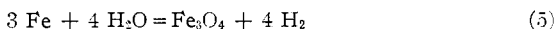
As has been pointed out, it is possible that in the temperature range below $500°$, ferro-ferric oxide actually is the oxide in equilibrium with iron. Deville, however, had no adequate experimental ground for this assumption, and it is undoubtedly incorrect at the higher temperature.

The numerical results obtained are shown in Fig. 4 with the exception of a few at very high and very low temperatures which fall off the field of the diagram. It is seen that they are not at all concordant among themselves. Except for minor errors in the temperature scale and rather imperfect control of the water temperatures, no reason is apparent why Deville's work should not be as reliable as that of later investigators. His conditions of approach to equilibrium were more varied than in most later work, and his results probably substantiate the ideas concerning solid solution developed in the preceding, and indicate that water vapor reacting on iron in a closed tube does not produce a separate oxide phase under ordinary conditions.

[28] Deville, *Compt. rend.*, **70**, 1105, 1201 (1870); **71**, 30 (1871).

Preuner[29] in his work adopted in principle the method of Deville and also accepted without question his equation for the reaction.

In Preuner's experiments iron foil of 25 sq. cm. surface was wrapped about the porcelain thermocouple tube, and protected from it and the narrow glazed porcelain containing tube by platinum foil. The water vapor and hydrogen formed were forced back and forth through the tube between two reservoirs of water. Beginning with no hydrogen the reaction was allowed to proceed until pressure became constant. At the temperatures used, 900, 1038, and 1150°, the reaction was fast and constancy in pressure was always attained in less than 30 minutes. To get the reverse reaction, the tube was connected to the pump while being heated. This in effect subjected the iron to the action of a stream of water vapor. This treatment was carried on for 10 minutes, after which hydrogen was introduced at a pressure about twice the anticipated equilibrium pressure, and the pressure decrease observed.

The pressure-time curves so obtained from the two sides often intersected each other. This behavior Preuner attributed to the fact that the water reservoirs were often saturated with hydrogen at a pressure higher than the equilibrium value. This hydrogen would then be given off slowly, causing a gradual increase in pressure after the real equilibrium between water vapor and iron had been reached. He considers the failure of the excess hydrogen to react with oxide to restore equilibrium to be due to the very small amount of oxide and consequent slowness of reaction. When precautions were taken to exclude excess hydrogen from the water reservoirs the curves no longer crossed. The average of the values obtained beginning with water and with hydrogen were used to determine the equilibrium constant. The averages of all such determinations at the three temperatures are shown in Fig. 4. The divergence of different results at one temperature from each other is between 3 and 7%.

It is not possible to estimate independently the value of Preuner's results. In spite of his explanation of the crossing of the curves approaching equilibrium from opposite sides, this behavior casts some doubt on the validity of his results. Again, it cannot be known definitely whether or not more than one solid phase was ever present. On the other hand, his results are in good agreement with the most reliable ones which have yet appeared. The objections to his work may, therefore, be more apparent than real.

Chaudron[30] also uses the principle of Deville.

Two g. of iron or a mixture of 1 g. of iron and 1 g. of ferrous oxide was placed in a boat, in a porcelain tube in a resistance furnace. Temperatures of the solids were measured by a thermocouple in the tube over the boat. A few cc. only of water was used in the reservoirs at each end of the tube to establish the vapor pressure, avoiding Preuner's difficulty. Artificial circulation of gas was not used, but with the arrangement employed convection should have been vigorous. Experiments were also made in which 2 g. of

[29] Preuner, Z. physik. Chem., **47,** 385 (1904).

[30] Chaudron, Compt. rend., **159,** 237 (1914); Ann. chim., **16,** 221 (1921).

ferrous oxide or a mixture of 1 g. of ferrous oxide with 1 g. of ferro-ferric oxide was used. The statement is made that final results were the same starting with iron or ferrous oxide alone as with the mixtures respectively. Above 400° equilibrium was attained in a few hours.

The points for the two series are shown in Fig. 4, the system in which they were obtained, but not the side of approach to equilibrium being indicated. Chaudron's curve for ferrous oxide—ferro-ferric oxide does not appear to intersect the iron—ferrous oxide curve. This undoubtedly indicates error in at least some of the points. Errors of measurement were estimated to be between 4 and 7%. Those determinations in which the mixtures of equal weights of the two solid phases were used could not well have been subject to errors due to solid solution.

Wöhler[31] again uses the Deville method. Like Preuner, he uses an artificial circulation of the reacting gases.

A roll of iron foil of 125 sq. cm. surface (in one case 5–10 g. of iron powder in a perforated crucible) was suspended in a vertical porcelain tube in a regulated resistance furnace. A thermocouple was inside the tube close to the iron. After establishing equilibrium by circulating the water vapor and hydrogen developed from it over the iron, the tube was evacuated, "a large amount—up to 120 cc." of hydrogen introduced and equilibrium determined with falling pressure.

The time-pressure curves obtained from the opposite sides never crossed and in some cases apparently reached almost identical values. This would ordinarily indicate a perfectly definite divariant system. It is questionable, however, whether the conditions were sufficiently varied to be assured of this in the face of the considerations previously discussed.

Schreiner and Grimnes[32] used the same principle as the previous investigators. They dispensed with artificial circulation of the gases and confirm their conclusion that it is unnecessary by a comparison of the times required to reach equilibrium in their experiments with those of other workers.

The iron was placed in an alundum boat in a porcelain tube connected at one end to the water container and at the other to the manometer. The thermocouple was inside the tube near the boat. The procedure was to allow the pressure to become constant starting with water vapor only. The temperature was then raised about 50°, under which condition hydrogen was used up and a constant pressure thus approached from the other side. The tube was then evacuated and equilibrium established at the last temperature beginning again with pure water vapor, and so on.

It is seen that in this research also there is no assurance at all that more than one solid phase was present. The results are again shown in Fig. 4. They are in general agreement with Wöhler but not with Chaudron, Preuner, or Deville. Of the possible reasons which the authors advance to explain this poor agreement, they seem to favor solid solution between ferrous oxide and iron.

31 Wöhler, Z. Elektrochem., **23**, 199 (1917).
32 Schreiner and Grimnes, Z. anorg. Chem., **110**, 311 (1920).

In his latest paper Chaudron[33] describes measurements intended to supplant his earlier results in the hydrogen system. He implies that with the method first used the attainment of approximate constancy of pressure is not proof of close approach to equilibrium, particularly at lower temperatures, on account of slow diffusion in the gas. Forced circulation of gas through a saturator and over the boat in the furnace was therefore resorted to in the new experiments. The solid phases were prepared in the apparatus by partial reduction of 1 g. of ferric oxide with electrolytic hydrogen. The volume of hydrogen oxidized in each preparation is given and from it the composition of the solid mixture may be calculated. In one series of measurements this corresponded to 75 mol % of ferrous oxide with 25% of ferro-ferric oxide, in another to 17 mol % of iron with 83% of ferrous oxide, and in a third to 83 mol % of iron with 17% of ferrous oxide. The last composition falls within the region where Matsubara found solid solutions. The results in this series are nevertheless in agreement with the second.

These final results of Chaudron's fall in the upper temperature range upon two curves intersecting at 570°, which is the same as the intersection point of his carbon monoxide-dioxide curves. Below 570° the points lie upon a single curve. The points shown in Fig. 4 indicate the side of approach to equilibrium, but not the particular series to which they belong. Agreement among the points is good and there is no apparent objection to the experimental work. It does not, however, agree with his earlier work. It seems unlikely that the discrepancy is due to slow gas diffusion in the first measurements, especially in view of Schreiner and Grimnes' conclusion on this point. Further, the ferrous oxide-iron curves of the first and final measurements above 600° cross at a considerable angle, rather than approach each other at the higher temperatures, as they should do if diffusion were alone responsible for the divergence.

From the values of the equilibrium constants of Reactions 2 and 6 Chaudron calculates the equilibrium constant of the water gas reaction. At 686° the constant so obtained differs from that of Haber by 40%; at 786° by 1%; at 886° by 7%; and at 986° by 5%.

Equilibrium Constants in the System Iron:Hydrogen:Oxygen

An inspection of Fig. 4 shows the futility of any attempt to draw a curve which shall be representative of the results in the iron : ferrous oxide system. For reasons which have been discussed, there appears to be no work which can be accepted without question. That of Chaudron seems by far the most reliable, and it is possible that the average of his results will eventually be substantially verified. But until further experimental work can be done it seems that the best values of the constants in these

[33] Chaudron, *Ann. chim.*, 16, 221 (1921).

systems can be obtained from the carbon system. For the sake of the comparison these have been calculated, using the free energies of the iron
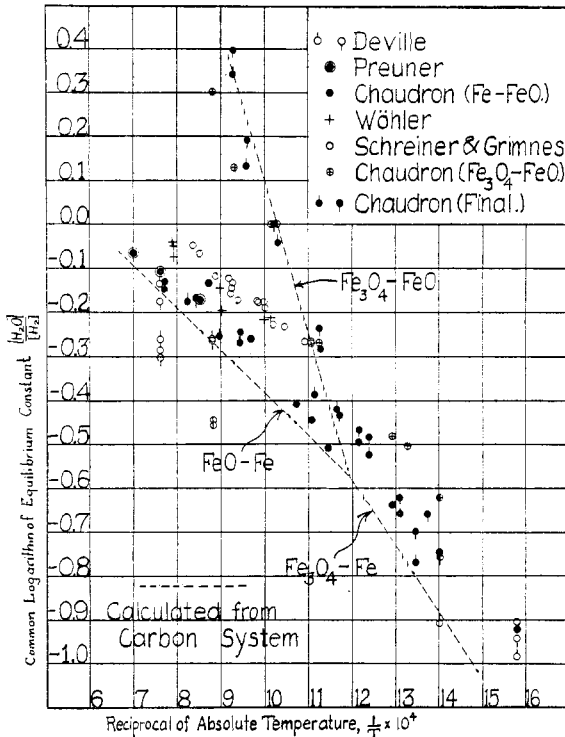

Fig. 4.—Equilibrium constants and temperature in the system Fe: H: O.

oxides as obtained from the carbon system, and the free energies of water vapor of Lewis and Randall,[34] and are contained in Table III below. The constants, $(H_2O)/(H_2)$ are given for the reactions

$$FeO + H_2 = Fe + H_2O \tag{6}$$

and

$$Fe_3O_4 + H_2 = 3 FeO + H_2O \tag{7}$$

and are designated K_6 and K_7.

TABLE III

CALCULATED EQUILIBRIUM CONSTANTS IN THE HYDROGEN SYSTEM

Temperature °C.	Fe: FeO System K_6	FeO: Fe$_3$O$_4$ System K_7
600	0.298	0.393
700	0.398	1.04
800	0.493	2.25
900	0.585	4.27
1000	0.662	7.2

[34] Lewis and Randall, THIS JOURNAL, 36, 1969 (1914).

The dotted curves of Fig. 4 represent these calculated values. With the exception of Deville's, the results of all observers lie above the calculated iron—ferrous oxide curve. Of the others the points of Preuner and Chaudron are fairly close to the curve. Deville in some cases and Chaudron in nearly all definitely had large amounts of both phases present in their determinations. Preuner may possibly have obtained a separate oxide phase in some of his experiments, though this is doubtful. These facts are perhaps of significance in connection with the better agreement with the carbon system of the points due to their work. If a separate oxide phase is not produced by water vapor acting on iron in a closed tube, the equilibrium constants obtained by the reaction should be smaller the greater the weight of iron used and the smaller the gas volume. The volume of Preuner's apparatus was undoubtedly smaller than that of any of the others, and Deville used much greater amounts of iron than the others, which may account in part for the position of their points relative to the others. It is also true that under the condition just stated the equilibrium constants with a single phase consisting of Fe with dissolved ferrous oxide should be smaller than the definitely fixed ones in the presence of a separate FeO phase. Assuming the carbon system data to be essentially correct the question then arises as to the cause of higher values generally obtained in the hydrogen system. This question cannot at present be answered. The suggestion occurs, however, that under the conditions prevailing in most of the experiments the iron surface soon gains an adherent and relatively impervious coating of oxide, the outer layers of which consist mainly of ferro-ferric oxide. Real equilibrium could then be established only by the slow diffusion of oxygen through the solid phases, which might occur extraordinarily slowly.

The Free Energies of the Oxides of Iron

The equilibrium constants of Reaction 2, given in Table II, have been used to calculate the standard free energy changes of this reaction by means of the equation[35]

$$\Delta F = -RT \ln K$$

From the values of ΔF and Lewis and Randall's[34] free energies of carbon monoxide and dioxide the free energies of ferrous oxide have been calculated at 100° intervals between 600° and 1000°, and are tabulated below. Using the equilibrium constants of Equation 3 (Table II) and the ferrous oxide free energies in Table IV the free energies of ferro-ferric oxide have been obtained, and are given in the table. No attempt has been made to determine theoretical equations showing free energies as functions of the temperature, as the required data do not in general exist at present. No

[35] The notation and conventions are those of Lewis, THIS JOURNAL, **35**, 1 (1913).

data were found in the literature which would permit the calculation of the free energy of ferric oxide.

TABLE IV

FREE ENERGIES OF OXIDES OF IRON

T. °C.	FeO cal.	Fe₃O₄ cal.
600	−49700	−198320
700	−48075	−190425
800	−46445	−182550
900	−44840	−174735
1000	−43255	−166980

Without an independent check upon the results, such as would be afforded by the data in the hydrogen system if they were in agreement among themselves, the accuracy of the figures in Table IV cannot well be estimated. It is believed that the free energies of ferro-ferric oxide and ferrous oxide there given are, however, essentially correct, the latter probably to within two or three hundred calories at all temperatures.

The equilibrium constants of Table II may also be used to calculate the heat effects in Reactions 2 and 3 by means of the van't Hoff equation. Thus calculated, Reaction 2 evolves 4260 cal. and Reaction 3 absorbs 7440 cal., the temperature being the average over which the data extend, $i.\ e.$, about 800°. As a test of the consistency of the equilibrium data of the two reactions the heat content (heat absorbed in formation from elements) of ferrous oxide has been calculated, using the calculated heats of reactions above and the experimental heat contents of the other substances in the equations. The average of five determinations in the literature of the heat content of ferro-ferric oxide is −270200 cal. at ordinary temperatures. At 800° this becomes about −264600 cal., using specific heats of ferro-ferric oxide, iron, and oxygen as 38.9 (Regnault), 5.9 and 7.0 cal. per mol per degree and assuming them constant. From Lewis and Randall's equations the heat contents of carbon monoxide and dioxide at 800° are −26278 and −94272 respectively. Calculated from Equation 2, the heat content of ferrous oxide at 800° is then −63730 cal. and from Equation 3, −63055 cal. The difference between these results is within that which might be attributed to error in the experimental heat content of ferro-ferric oxide. Measured values of the heat content of ferrous oxide at ordinary temperatures are recorded by Le Chatelier and by Mixter of −65700 and −64300 cal., respectively.

Summary

The present paper brings together and attempts to appraise and interpret the widely scattered and often discordant data relating to the oxides of iron and equilibria in which they are involved. The essential details of the more important researches are given. The conclusions which have

been reached in the course of this study are summarized, and the calculations which have been made are listed in the following paragraphs.

1. Ferric oxide and ferro-ferric oxide at 1100° and above form a continuous series of solid solutions, though the indications are that at temperatures much below 1000° they may not be soluble in each other in all proportions. Ferro-ferric oxide and ferrous oxide up to 1100°, at least, definitely do not form a continuous series of solutions, though they do dissolve to a limited extent in each other. Ferrous oxide appears to be soluble in iron to the extent of 20–25 mol % (6–8% oxygen) though metallic iron is not appreciably soluble in the oxide.

2. Ferrous oxide is unstable with respect to ferro-ferric oxide and iron below about 565°. Interestingly, ferro-ferric oxide shows an inversion in the same region.

3. When pure carbon monoxide reacts upon pure iron in a closed tube above 500° carbon is not ordinarily deposited as a separate phase. At temperatures above 800° a trivariant equilibrium with iron containing dissolved carbon or carbide as the solid phase may be established, or one in which the solid phase contains dissolved oxygen as well as carbon, and the gas is richer in carbon dioxide than in the former case. It is possible that stable divariant equilibria corresponding to these, with a separate dissolved carbon or carbide phase, may also be established on repeated treatment, but this does not appear to be proved. Whether monovariant systems are ever obtained, and if so what the active solid phases are, also remains to be proved.

4. With a stream of carbon monoxide acting on iron in the vicinity of 650° separate phases consisting of carbon, ferrous oxide, and iron containing dissolved oxygen and carbon (or carbide) are probably formed. At higher temperatures the oxide and separate carbon phases do not appear, and the amount of dissolved carbon decreases.

5. Carbon dioxide acting upon iron in a closed tube probably produces again a trivariant system. At temperatures in the neighborhood of 600° and lower, carbon is present in the solid phase, decreasing in amount as the temperature is increased.

6. Numerous investigators have studied univariant and divariant equilibria involving iron or ferrous oxide, ferrous oxide or ferro-ferric oxide, carbon monoxide, carbon dioxide and carbon under conditions such that the presence of separate and definite solid phases (not always quite pure) in large amounts was assured. The individual results of such investigations are graphically compared and are in sufficient agreement to permit the use of equilibrium constants and free energies based on them. These constants have been tabulated at 100° intervals between 600° and 1000° inc. Certain thermal calculations employed as checks of the equilibrium data are described.

7. Supposedly divariant equilibria involving iron or ferrous oxide, ferrous oxide or ferro-ferric oxide, water and hydrogen have been studied by only one method which in the hands of different observers yields different results. Possible reasons for these variations are discussed. It is decided that in the present state of the hydrogen system the equilibrium data cannot be used and that more reliable results may be obtained by calculation from the carbon system. Equilibrium constants so calculated are tabulated and compared graphically with the experimental ones.
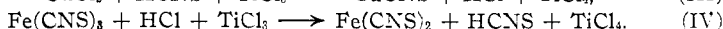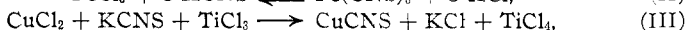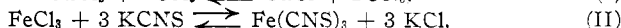
BERKELEY, CALIFORNIA

TRIVALENT TITANIUM. II. THE ESTIMATION OF COPPER AND IRON IN THE PRESENCE OF EACH OTHER

By WILLIAM M. THORNTON, JR.

Introduction

The volumetric estimation of copper through the agency of a standard solution of titanous chloride was first made known by Rhead.[1] The copper salt is titrated in the presence of an excess of potassium thiocyanate and a sufficient quantity of iron (all of which must be in the ferrous condition) until the red color of ferric thiocyanate just disappears. The following equations will serve to make the matter clear.

$$CuCl_2 + FeCl_2 \rightleftarrows CuCl + FeCl_3, \qquad (I)$$
$$FeCl_3 + 3 KCNS \rightleftarrows Fe(CNS)_3 + 3 KCl, \qquad (II)$$
$$CuCl_2 + KCNS + TiCl_3 \longrightarrow CuCNS + KCl + TiCl_4, \qquad (III)$$
$$Fe(CNS)_3 + HCl + TiCl_3 \longrightarrow Fe(CNS)_2 + HCNS + TiCl_4. \qquad (IV)$$

Moser,[2] in turn, has studied this determination and has found it possible to dispense with all indicators, relying solely upon the color of the cupric salt itself. Monnier,[3] however, employs certain dyestuffs, viz., safranine or indulin, as indicators. Mach and Lederle[4] have in like manner investigated the subject. Finally, Knecht and Hibbert,[5] besides giving Rhead's procedure, make use of the alternate plan of adding a measured amount of standard ferric ammonium sulfate and subsequently deducting its equivalent in terms of the titanous chloride solution, the titer thus corrected being proportional to the copper only.

Regarding the determination of copper when accompanied by iron, Rhead[1] dismisses the case by saying that the iron may be removed as

[1] Rhead, J. Chem. Soc., **89**, 1491 (1906).

[2] Moser, Chem.-Ztg., **36**, 1126 (1912).

[3] Monnier, Ann. chim. anal., **21**, 109 (1916).

[4] Mach and Lederle, Landw. Vers. Sta., **90**, 191 (1917).

[5] Knecht and Hibbert, "New Reduction Methods in Volumetric Analysis," Longmans, Green and Co., **1918**, pp. 13 and 55.