[Contribution from U. S. Steel Corporation, Research Laboratory, Kearny, New Jersey]

The System Iron–Oxygen. I. The Wüstite Field and Related Equilibria

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This investigation was undertaken because of gaps and discrepancies in the available data, particularly at temperatures above 1000°, relating to the boundaries of the wüstite field and to the activity of the components in wüstite. These discrepancies are probably to be ascribed principally to the following facts: (1) the equilibrium state of the solid phases involved is very sensitive to change in effective pressure of oxygen in the gas phase; (2) a very small amount of impurity may seriously affect the experimental determination of the phase boundaries; (3) a quench sufficiently drastic to preserve the structure (as revealed by X-ray) is extremely difficult; indeed it is doubtful whether a method depending upon such a quench has ever revealed correctly the high temperature boundaries of the wüstite field. In order to overcome these difficulties, the method finally adopted was to equilibrate pairs of purified solid phases at temperature with a controlled partial pressure of oxygen which was varied by a factor of 10^7. Specifically, the procedure was to pass an adjusted constant gas mixture (usually CO_2–CO) through a heated tube, in which was placed either (A) a strip of oxide or of iron lightly oxidized (held in a fixed temperature gradient), the final temperature at the boundary between phases being noted; or (B) iron or iron oxides of composition on either side of the equilibrium (held at fixed temperature), the final product being chemically analyzed. Series of such measurements, when carried out with proper precautions, enabled us to determine the CO_2/CO ratio in equilibrium with (A) iron and wüstite at temperatures 1038–1365°, (B) wüstite and magnetite at temperatures 1096–1388°, and (C) wüstites of various compositions between these boundaries, and from these data to derive the phase boundaries and the activities sought. The consistency of the several measurements with one another and with related data was checked by thermodynamic calculation, which yielded values of the heat of formation of magnetite in excellent agreement with the best thermochemical data.

A brief treatment of thermal diffusion which, if not taken properly into account, may cause large errors in measurements of the type made use of in this investigation, is given in an appendix; from this it appears, moreover, that the error from this source is much smaller if the gas mixture flows upward through a vertical reaction zone than if it flows downward.

CO_2/CO Ratio in Equilibrium with Metallic Iron and Wüstite

Experimental.—The method adopted for the determination of the CO_2/CO ratio in the equilibrium with iron and wüstite at a given temperature is similar to that of Chipman and Marshall[1] for the equilibrium of H_2–H_2O with iron and wüstite, but differed in that advantage was taken of the thermal gradient of the furnace; the time of treatment was longer, and visual examination rather than gain or loss of weight was used as the criterion of equilibrium.

A known constant mixture of two gases was passed upward through the inner porcelain tube of a cylindrical furnace in which the specimen of lightly oxidized iron was suspended so that it extended from the thermal center of the furnace well into the gradient, both above and below. After suitable preliminary adjustment of gas composition and temperature, the specimen was heavily oxidized on its center but completely reduced at its ends; the position of the boundary between oxidized and reduced zones indicates the temperature of equilibrium between iron, wüstite and the particular gas mixture. This temperature was measured, after removal of the specimen, by inserting a platinum–platinrhodium thermocouple in the furnace at the level of the boundary. The error occasioned by reading temperature in a thermal gradient was minimized by preliminary adjustment of gas composition and temperature so that the gradient at the measured temperature was small; in the determinations reported, this temperature was not more than 20° lower than at the furnace center, a difference which corresponds to only 1% in the equilibrium ratio CO_2/CO.

The electrolytic iron contained these impurities: C, 0.012%; Mn, < 0.01%; P, 0.004%; S, 0.003%; Cu, 0.045%; Si, 0.007%; Ni, 0.02%; Pb, 0.04%; no other elements were detected spectrographically (sensitivity 0.001%). The specimens measured approximately 8 × 0.3 × 0.015 cm.; they were pickled in hydrochloric acid, then rinsed with water, acetone, and ether, respectively, immediately before use. A film of oxide was imparted by drawing the specimen from the hot furnace into air. The specimen was suspended directly on a heavy platinum wire, entering the furnace through a short rubber tube (30 cm. above the furnace) and held by a pinch clamp; there was a centering device so that the specimen did not touch the side walls. The controlled atmosphere was introduced through a mercury seal at the bottom and vented through a long glass tube at the top.

The furnace was of the platinum-wound tubular type, vertically mounted; it was 30 cm. long and the inner porcelain tube had a diameter of approximately 1.3 cm. The temperature controller was similar to that in use in the Geophysical Laboratory;[2] the furnace winding acts as a resistance thermometer and constitutes one arm of a Wheatstone bridge. By this means the temperature of the furnace at any point was maintained within 1° for extended periods. The temperature distribution in the furnace was such that the relation between temperature and vertical distance from the center was very nearly parabolic: a central zone about 2 cm. long was uniform within 1°.

Preparation of Controlled Atmospheres.—Commercial carbon dioxide was purified by passing it over copper gauze at 600°, then drying with activated alumina. The copper always became appreciably oxidized, so that the initial gas contained more than sufficient oxygen to oxidize any hydrogen or hydrocarbons present. Less than 0.1% of the

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(1) Chipman and Marshall, This Journal, **62**, 209 (1940).

(2) H. S. Roberts, "Temperature, its Measurement and Control in Science and Industry," Reinhold Pub. Corp., New York, N. Y., 1941, p. 684.

purified CO_2 was unabsorbed by caustic. Carbon monoxide was prepared by passing this purified carbon dioxide over granular Acheson graphite contained in a porcelain tube heated to 1200° by a platinum-wound furnace. A 500-cc. Pyrex bulb at the top served as a reservoir for the graphite, so that one charge lasted several weeks. Conversion was about 99% efficient;—the residual carbon dioxide was absorbed by caustic (Ascarite) and the carbon monoxide was dried with activated alumina. Analysis indicated that about 0.2% of the carbon monoxide thus purified was not absorbed by cuprous chloride solution.

A gas mixer, a modification of that described by Johnston and Walker,[3] was especially designed to supply continuously mixtures of these two gases in definite constant proportion; it is shown schematically in Fig. 1. The fundamental principle is to hold constant the pressure drop through each of two capillary flow meters F_1, F_2 by means of three bleeder tubes held in appropriate fixed positions in a water tank. The length of 0.5 mm. tube in F_1 and F_2 is 23 cm. and 300 cm., respectively; the manometers are 5 mm. diameter, with butyl phthalate as fluid. The third flow meter F_3 measures the rate of delivery of the mixed gas; the linear rate of flow to the furnace was kept close to 0.9 cm./sec. for reasons which are discussed later. Before being sealed together each gage was calibrated by the displacement of oil previously saturated with the gas; the reproducibility of flow rate for given settings of the two manometers (and bleeder tubes) was about 0.2%. After assembly the calibration was checked frequently by analysis of the mixture. In this analysis mercury was the confining fluid in a calibrated gas buret, and a 33% solution of potassium hydroxide was used to absorb carbon dioxide; a stronger solution was found to decompose carbon monoxide at a measurable rate, whereas a weaker solution necessitates a larger correction for the partial pressure of water vapor. This correction for the solution used was determined by use of dry nitrogen treated exactly as the mixtures to be analyzed. The CO_2/CO ratio as determined by analysis invariably checked that calculated from the gage calibrations within a few tenths of a per cent. up to a ratio of 4 to 1. The outlet gas from the furnace was also frequently analyzed; within the analytical error its stoichiometric composition did not differ from that of the inlet gas.

Procedure.—The experiments were carried out as follows: the specimen of oxidized electrolytic iron strip was suspended in the cool top of the furnace tube. A predetermined constant mixture of carbon dioxide and carbon monoxide furnished by the gas mixer was conducted through the tube in the furnace, and the controller was set so that the center of the furnace would be at a temperature estimated to be near that of the oxidation–reduction equilibrium for this mixture. After sufficient time for flushing the tube, the specimen was lowered until it was approximately centered in the furnace, care being exercised that it did not touch the porcelain; it remained there usually about an hour, and was then raised into the cool zone by drawing the platinum wire through the pinched rubber tubing in such a manner that no air entered. When cool, it was removed and examined with the naked eye or low power lens. If this preliminary sample was either oxidized all over or completely reduced, or if the boundaries between bright metal and oxidized surface were not within a distance corresponding to a few degrees from the thermal center of the furnace, the furnace temperature was readjusted, and the experiment repeated as many times as was necessary to bring the phase boundaries near the thermal center. In the final experiment with a given gas mixture, the iron strip was rather heavily oxidized in a zone 3 or 4 cm. long which had been at the highest temperature, and on either side of this was bounded by bright metal where the initial temper film had been reduced; the lower boundary line was sharp and horizontal, and its position could usually be measured to the nearest millimeter. After measuring the position of both boundaries, the specimen was reinserted in the same position in the furnace, gas composition and temperature also being the same; then after a period again removed and examined, and the positions of both boundaries again measured. If the lower line had not moved, the temperature at the two corresponding levels in the furnace was measured (with a thermocouple); that of the lower line was taken as the temperature of equilibrium between iron and wüstite in the CO_2–CO mixture used. Most samples were again reinserted and left overnight; some then oxidized through in the central portion, yet the position of the lower boundary remained unchanged.

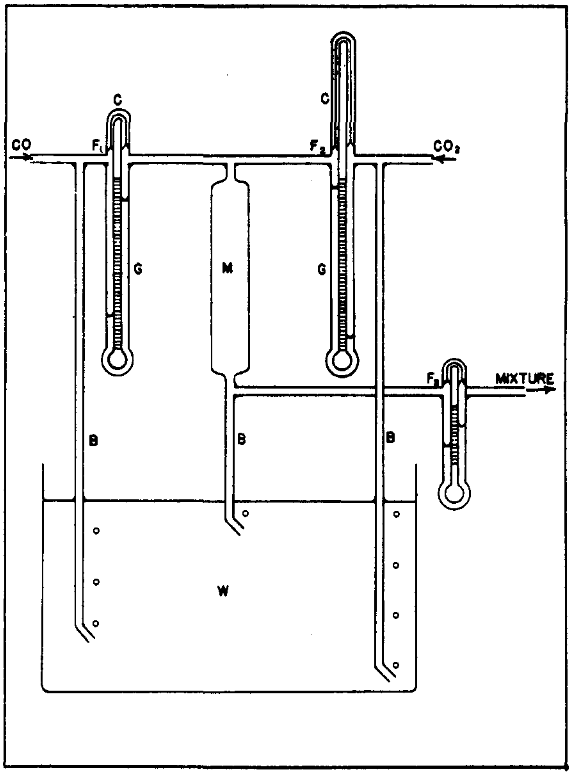

Fig. 1.—Schematic diagram of gas mixing apparatus. Each purified incoming gas passes through a flowmeter F_1, F_2 consisting of capillary C and manometer G containing butyl phthalate; the pressure drop through each flowmeter is maintained constant by bleeder tubes B at set levels below the surface of water W. The gases from F_1 and F_2 are mixed in M which contains glass beads; part of the mixture escapes through the center bleeder tube, and the rest is supplied to the furnace at a rate measured by F_3.

Experimental Precautions.—The most significant, though least obvious, source of error in the determination of equilibrium between a gas mixture and a condensed phase at high temperature arises from the phenomenon of thermal diffusion.[4] When a uniform gas mixture is in a temperature gradient, thermal diffusion tends to make the mixture non-uniform; in general, the heavier molecules tend to move toward the cool zones, the lighter toward the hot zones.

In order to ascertain how fast the CO_2–CO

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[3] Johnston and Walker, THIS JOURNAL, **47**, 1807 (1925).

[4] The investigation of thermal diffusion was conducted by L. S. Darken and R. P. Smith; the following discussion and the appendix are contributed by them.

mixture must flow through our apparatus to make the effect of thermal diffusion negligible, we made special experiments at different rates of gas flow, under conditions believed to be typical. In these, the temperature at the center of the furnace was 1100°; the inlet gas, which contained about 26% CO_2, was introduced by a capillary gooseneck through a mercury seal about 25 cm. below the bottom of the furnace, and escaped through a capillary an equal distance above the top. To determine composition at the bottom, a capillary, introduced through the mercury seal, was connected to a micro-buret from which mercury was forced to the tip of the capillary; the gas mixture was then allowed to flow through the furnace (in which there was then no iron or iron oxide) for about eighteen hours, when a sample (0.5–1 cc.) was withdrawn and analyzed by absorption of the carbon dioxide in potash. Inlet and outlet gas were analyzed likewise; the precision was about 0.1%, and the agreement with analysis by an Orsat apparatus and with the calibration of the flow meter settings was also about 0.1%. To determine the composition of the gas at the center of the furnace, that of the gas entering the furnace was adjusted until that at the center was in equilibrium with iron and wüstite, as previously described; the composition at the center was then read from the final chart (Fig. 2) representing the equilibrium measurements finally made at a rate of flow at which the effect of thermal diffusion was negligible. The results are given in Table I, in which the first column is the linear rate of flow (f_0) at room temperature (the rate inside the furnace is faster in proportion to the absolute temperature); the second is the difference (Δ) in % CO between the inlet gas and that at the bottom, or center, respectively, of the furnace; the third shows that the product $f_0\Delta$ is in each case substantially constant. That these results are in general accord with theoretical considerations is shown in an appendix, which is added because it brings out in the figure the considerable difference in gas composition through the system according as it flows upward (which proves to be far preferable) or downward.

TABLE I

SEPARATION BY THERMAL DIFFUSION OF A 74% CO–26% CO_2 MIXTURE IN A VERTICAL TUBE (INSIDE DIAMETER 1.3 CM.); HOTTEST ZONE 1100°

Position in furnace	Rate of flow at room temp., cm./sec., f_0	Thermal separation: %CO at stated position minus %CO in inlet gas[a] Δ	$f_0\Delta$
Bottom	0.05	−2.40	−0.12
	.20	−0.70	− .14
	.22	− .65	− .14
	.60	− .20	− .12
Center	.025	+1.50	+ .038
	.07	+0.55	+ .038
	.16	+ .23	+ .037
	.16	+ .24	+ .039
	.16	+ .28	+ .045
	.32	+ .10	+ .032

[a] Gas compositions at the inlet, outlet and furnace bottom were determined by direct analyses; those at the center were determined indirectly from Fig. 2 as described in the text.

From the constancy of the product $f_0\Delta$ it was concluded that if f_0 is greater than 0.6 cm./sec., the error from this source would be less than 0.05% CO, corresponding to 0.25% in the ratio CO_2/CO. On the other hand, it was found that a rate of about 1.2 cm./sec. introduced an uncertainty of over 1° in the temperature measurement. Accordingly a rate of about 0.9 cm./sec. was maintained in all the definitive measurements which alone are reported here. Although the error due to thermal diffusion is somewhat greater for CO_2–H_2 mixtures the following result, based on experimental data to be reported in a later paper, shows it to be still inappreciable. The composition of liquid iron oxide in contact with a given CO_2–H_2 mixture at a temperature about 1600°, where the effect of thermal diffusion should be more pronounced, was identical within experimental error (corresponding to 1% in the ratio CO_2/CO) whether the rate of flow was 1.7 or 0.5 cm./sec.

As a second precaution, the zone of reaction was kept near the thermal center, not only that the temperature of the boundaries might be determined more precisely but also that the gas composition should not change appreciably. Below the center the gas column moves upward with minimum convection, hence the gas composition at the lower line is but little influenced by any reaction in the zone above. (Considerably longer time was required for precise measurement when the gas flow was reversed.) The upper boundary was less distinct since the gas composition at that level has been altered slightly by the reaction, especially at short times. At temperatures below 1000° the atmospheres used were mildly carburizing (at equilibrium at 1000° the iron phase contains about 0.03% C); for this reason the specimen could not extend far into the gradient without absorbing some carbon, hence changing the atmosphere. Several analyses of the outlet gas indicated no measurable difference between incoming and outgoing gas composition after the sample had been in the furnace for an hour.

In the third place, it was found that considerable care was needed to avoid contamination of the sample by siliceous material, a minute amount of which results in the formation of a very thin spreading film of a ferrous silicate. Sanded specimens developed spots under conditions where pickled specimens remained bright, even though care was taken to remove all traces of the abrasive. Pickled specimens occasionally developed such spots, presumably from siliceous dust; such samples were discarded. At the higher temperatures volatilization of silica from the porcelain tube was noticeable. Specimens held at 1350° under conditions such that the original oxide film was reduced in ten to fifteen minutes developed in ten to twenty hours a slight tarnish (not sufficient to produce temper colors) undoubtedly caused by volatilization of silica, yet the boundary between the thick oxide layer and this thin film was still sharp and easily discernible. The reality of such volatilization of silica (or possibly some other silicon compound) into iron was demonstrated by suspending a specimen of electrolytic iron (0.007% Si) in a porcelain tube in a current of dry hydrogen at 1000°; after twenty hours analysis showed 0.25% Si in the iron. In the CO–CO_2 mixtures used, the pickup of silicon by the specimen was however negligible. Since the position of the boundary did not change with time despite the appearance of the presumably siliceous film at high temperatures and long times, it is concluded that traces of silica have negligible effect on the equilibrium investigated—*i. e.*, that the solid solubility of silica in wüstite is negligible, hence that the traces present exist as a separate phase (fayalite or liquid silicate) and do not alter the activity of iron or oxygen in wüstite. On the other hand, silica is soluble in *liquid* iron oxide, and measurement of the equilibrium iron–liquid oxide is noticeably affected by volatilization of silica from the porcelain tube; this effect will be discussed in a later paper.

Results.—The final results on the CO_2/CO ratio in equilibrium with iron and wüstite at a series of temperatures (1038–1365°) are given in Table II, and graphically in Fig. 2 as a plot of log p_{CO_2}/p_{CO} against $10^4/T$ which covers the range (910–1370°) in which wüstite and γ-iron are both stable. Figure 2 includes the experimental results of Schenck and co-workers,[5] also points based on those selected as "best" by Chipman and Marshall,[1] and on data of Emmett and Schultz[6] as calculated from their measured H_2O/H_2 ratio by use of the water gas equilibrium.[7]

TABLE II

DEFINITIVE MEASURED VALUES OF RATIO p_{CO_2}/p_{CO} IN EQUILIBRIUM WITH IRON AND WÜSTITE

Temp., °C.	p_{CO_2}/p_{CO}
1038	0.377
1092	.357
1177	.331
1224	.315
1303	.297
1357	.285
1363	.281
1365	.281

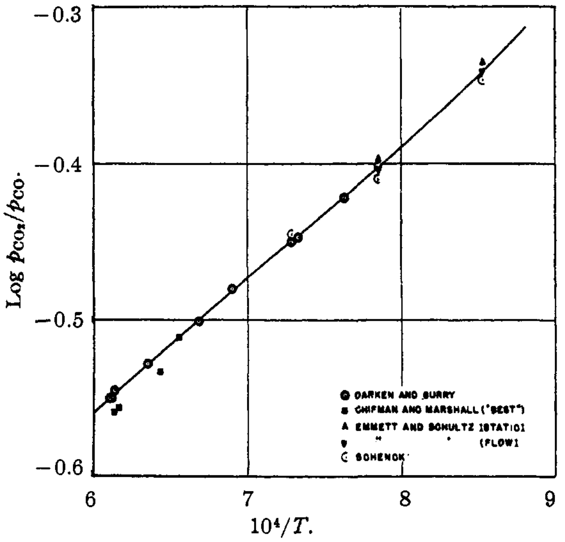

Fig. 2.—CO_2/CO ratio in equilibrium with iron and wüstite as a function of temperature.

The curve is very nearly linear; values interpolated from it at even temperatures are given in Table IV.

CO_2/CO Ratio in Equilibrium with Wüstite and Magnetite

This equilibrium was measured by essentially the same method. A longer time was required for the iron to be oxidized uniformly throughout its thickness. In preliminary experiments the

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(5) R. Schenck, Dingmann, Kirscht and Wesselkock, *Z. anorg. allgem. Chem.*, **182**, 97 (1929).

(6) Emmett and Schultz, THIS JOURNAL, **52**, 4268 (1930); **55**, 1376 (1933).

(7) The values of the equilibrium constant $p_{CO}p_{H_2O}/p_{CO_2}p_{H_2}$, given by L. S. Kassel [*ibid.*, **56**, 1838 (1934)] were corrected to conform to the new value of ΔH_0^0 given by F. D. Rossini [*J. Research Nat. Bur. Standards*, **22**, 407 (1939)]. The corrected values at 1000, 1100, 1200, 1300 and 1400° are 1.68, 2.08, 2.49, 2.90$_5$ and 3.32, respectively. Wagman, Kilpatrick, Taylor, Pitzer and Rossini [*ibid.*, **34**, 143 (1945)] have just published values of various equilibrium constants as calculated anew on the basis of a statistical interpretation of spectroscopic data. It is a rather disconcerting to find that these new values for the water gas equilibrium constant differ by 3 to 4% from those listed above and used in our calculations. A comparison of these new calculated values with those obtained experimentally, compiled by Emmett and Schultz,[6] does not lead to confidence in these calculated values. A tabular comparison at 800°, the highest temperature at which experimental data from all sources listed are available, follows:

Type of experiment or calculation, and author		$p_{CO}p_{H_2O}/p_{CO_2}p_{H_2}$ at 800°
Direct determination	Hahn	0.906
	Neumann and Kohler	.93
Equilibrium with Fe–wüstite	—Emmett and Schultz	.919
Equilibrium with FeO–Fe_3O_4	—Emmett and Schultz	.918
Equilibrium with Sn–SnO_2	—Emmett and Schultz and Eastman and Robinson	.918
	—Emmett and Schultz and Meyers and Scheffer	.893
Spectroscopic—Kassel (corrected for new ΔH_0^0		.938
Spectroscopic—Bur. of Stds., 1945		.962

The new value is higher than any experimental value and is 4% higher than the mean of the direct experimental results.

The values we have used may be regarded as an extrapolation (based on spectroscopic measurements) of the best experimental data. The new values given by the Bureau of Standards cannot be so regarded. Hence we have not seen fit to reperform all calculations using these new values. If the new values are used to convert Chipman and Marshall's data from p_{H_2O}/p_{H_2} to p_{CO_2}/p_{CO}, their measurements collate less well with the present measurements than they do when the older values of the water gas constant are used.

phase boundary was determined with the aid of a weakly magnetized iron wire; the final determination was made by microscopic examination of a polished longitudinal section. The specimen was cooled by being rapidly lifted to the cool top of the furnace tube, yet this was not sufficiently rapid to prevent decomposition of some wüstite. In fact, it was found impossible completely to prevent partial decomposition of wüstite near equilibrium with magnetite even by dropping it into mercury with a platinum weight attached to ensure immersion. Thus the zone which at the high temperature had been homogeneous wüstite appeared as a two-phase region (wüstite grains surrounded by magnetite) under the microscope: the zone which had been homogeneous magnetite remained so. Before the final microscopic examination the specimen was held at temperature at least eighteen hours after magnetic inspection had indicated that the phase boundary had ceased moving.

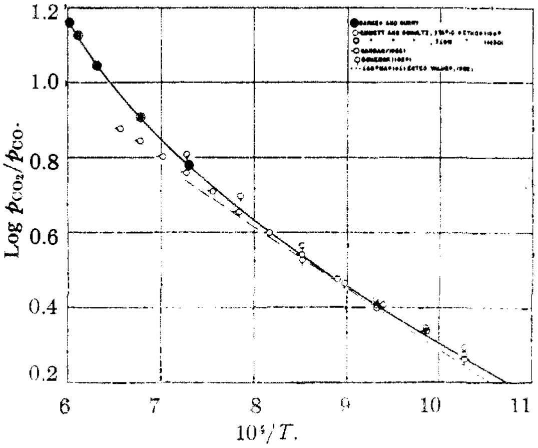

Fig. 3.—CO_2/CO ratio in equilibrium with wüstite and magnetite as a function of temperature.

The results are given in Table III. The first three were made with gas mixtures initially CO_2 and H_2 as delivered by the mixer; the initial gas composition as recorded was obtained from the setting of the flow meters, and this was checked by analysis to within 0.05% (0.5% in the ratio); from it the corresponding ratio p_{CO_2}/p_{CO} was calculated by aid of the water gas equilibrium.[8] The last two determinations were made with CO_2–CO mixtures, the recorded ratios being determined by analysis; the ratios in inlet and outlet gas were identical to the three significant figures recorded.

Table III

Definitive Measured Values of Ratio p_{CO_2}/p_{H_2} or p_{CO_2}/p_{CO} in Equilibrium with Wüstite and Magnetite

Temp., °C.	p_{CO_2}/p_{H_2}	Water gas constant[a]	p_{CO_2}/p_{CO}
1096	6.525	2.07	6.04
1203	8.65	2.51	8.08
1312	11.82	2.96	11.18
1365	....	..	13.5
1388	..	..	14.6

[a] See footnote 7.

The foregoing data are plotted in Fig. 3 along with those of Emmett and Schultz,[6] Garran,[9] and Schenck and Dingmann[10]; also included is a line representing older values as selected by Eastman.[11] It will be noticed that Garran's data at the higher temperatures are roughly linear, yet the facts (mentioned later) that the heat of formation of magnetite in this range is sensibly constant, and that the oxygen content of the high-oxygen boundary of the wüstite field increases with temperature, require that the graph curve upwards as in Fig. 3.

For the convenience of the reader we tabulate in Table IV values of the CO_2/CO ratio in equilibrium with (A) iron–wüstite (B) wüstite–magnetite at a number of round temperatures, interpolated from large plots of Figures 2 and 3; together with calculated values of the ratio p_{H_2O}/p_{H_2} and of p_{O_2}.[12] These correspond to two of the lines bounding the wüstite field in the phase diagram.

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(8) If a mixture initially CO_2 and H_2 reacts according to the equation $CO_2 + H_2 \rightarrow CO + H_2O$, then from the conservation of matter we may write the following relation between the initial partial pressures (subscripted i) and the equilibrium partial pressures (unsubscripted)

$$\frac{p_{CO_2(i)}}{p_{H_2(i)}} = \frac{p_{CO_2} + p_{CO}}{p_{H_2} + p_{H_2O}} = \frac{p_{CO}}{p_{H_2O}} \frac{(1 + p_{CO_2}/p_{CO})}{(1 + p_{H_2}/p_{H_2O})}$$

Since the initial mixture contained only CO_2 and H_2 it follows from the chemical equation above that $p_{CO} = p_{H_2O}$, hence

$$\frac{p_{CO_2(i)}}{p_{H_2(i)}} = \frac{1 + (p_{CO_2}/p_{CO})}{1 + (p_{H_2}/p_{H_2O})}$$

If the mixture equilibrates according to the above chemical equation then we may also write the equilibrium constant (water gas constant)

$$K = \left(\frac{p_{CO}}{p_{CO_2}}\right)\left(\frac{p_{H_2O}}{p_{H_2}}\right)$$

The ratio p_{H_2}/p_{H_2O} may now be eliminated between these two equations.

$$\frac{p_{CO_2(i)}}{p_{H_2(i)}} = \frac{p_{CO_2}}{p_{CO}} \left(\frac{1 + p_{CO_2}/p_{CO}}{1/K + p_{CO_2}/p_{CO}}\right)$$

As the expression on the left side and K are known the only unknown is the ratio p_{CO_2}/p_{CO} for which the equation may be solved either by successive approximations or by throwing the equation into standard quadratic form.

It will be noted from the above equation that if the value taken for K is in error by a small percentage Δ then the corresponding per cent. error in p_{CO_2}/p_{CO} as calculated is approximately $\Delta/(1 + Kp_{CO_2}/p_{CO})$, an appreciably smaller per cent. particularly when p_{CO_2}/p_{CO} is large.

(9) R. P. Garran, *Trans. Faraday Soc.*, **24**, 201 (1928).

(10) Schenck and Dingmann, *Z. anorg. allgem. Chem.*, **166**, 113 (1927).

(11) E. D. Eastman, This Journal, **44**, 975 (1922).

(12) The water gas constant used to calculate p_{H_2O}/p_{H_2} was obtained as previously described; p_{O_2} was obtained from p_{CO_2}/p_{CO} and values of the equilibrium constant for the reaction $2CO_2 = 2CO + O_2$. Values of $(E_0^0 - F^0)/T$ for CO_2, CO, and O_2 are given by L. S. Kassel [*ibid.*, **56**, 1838 (1934)], Clayton and Giauque [*ibid.*, **55**, 5071 (1933)], and Johnston and Walker [*ibid.*, **57**, 682 (1935)], respectively. These were combined with the value of ΔH_0^0 given by F. D. Rossini [*J. Research, Nat. Bur. Standards*, **22**, 407 (1939)] to yield values of the equilibrium constant. The values thus determined for 1000, 1100, 1200, 1300 and 1400° are 8.28×10^{-15}, 3.98×10^{-13}, 1.122×10^{-11}, 2.06×10^{-10} and 2.65×10^{-9}, respectively.

TABLE IV

INTERPOLATED VALUES AT ROUND TEMPERATURES OF GAS COMPOSITION IN EQUILIBRIUM WITH:

T, °C.	A. Iron–Wüstite			B. Wüstite–Magnetite		
	p_{CO_2}/p_{CO}	p_{H_2O}/p_{H_2}	p_{O_2}, atm.	p_{CO_2}/p_{CO}	p_{H_2O}/p_{H_2}	p_{O_2}, atm.
1100	0.355	0.738	5.01×10^{-14}	6.12	12.7	1.49×10^{-11}
1200	.322	.802	1.16×10^{-12}	8.02	20.0	7.21×10^{-10}
1300	.297	.861	1.81×10^{-11}	10.79	31.3	2.40×10^{-8}
1350	.285	.888	6.25×10^{-11}			
1400				15.03	49.9	6.00×10^{-7}

Equilibria within the Wüstite Field

The equilibrium between gas phase and solid oxides within the wüstite field was determined by heating the charge in a controlled atmosphere at fixed temperature until equilibrium was established. Riedel and de Haen's ferric oxide ("titrimetric standard") was used as starting substance in the major part of the work; spectrographic analysis indicated the following impurities: Cu, 0.04%; Ni, 0.02%; Mn, 0.01%; Cr, <0.005%; Co, <0.01%; Al, Sn and Pt group metals were not detected. A small amount of very pure iron oxide prepared by Cleaves and Thompson[13] was available; this oxide contained 0.01% Si as major impurity, with traces of Ca, Al, Mg and Cu totalling less than 0.001%; no other impurities were detected. To approach equilibrium from the low oxygen side, electrolytic iron (previously described) or a partially reduced specimen of one of the above oxides was used.

Experimental Procedure.—The furnace and controller were the same as previously described. The same gas mixer was used; in some cases mixtures of CO_2 and H_2 rather than CO_2 and CO were employed. The runs using the 1 to 1 mixture of CO–CO_2 were made before the gas mixer was constructed; this atmosphere was generated by the action of sulfuric acid on oxalic acid, then dried. Its analysis seldom varied from the stated ratio by more than 1%.

The charge, consisting of about 0.5 g. of Fe_2O_3 or lower oxide, was placed in a 1-ml. platinum crucible, which was suspended on a platinum wire; some of the charges were paired—*i. e.*, two crucibles, one containing Fe_2O_3, the other a wüstite of lower oxygen content than the equilibrated product, were suspended side by side. Occasionally it was a coil of thin strip of electrolytic iron; this was attached to the platinum wire by means of a "coupon" about 2 cm. long which was discarded before analysis. When temperature and gas mixture were properly controlled, the charge was lowered to the thermal center of the furnace. The time required for equilibration was estimated from previous experience and finally prolonged until the composition of the pair of samples (one on either side of the equilibrium) became the same. The sample was brought to room temperature either by quenching in mercury or simply by raising it into the cool head of the furnace tube; samples quenched in mercury were heated to 180° in vacuum for thirty minutes to remove traces of mercury prior to chemical analysis. After removal of the sample, the atmosphere was displaced with air and the temperature measured by insertion of a thermocouple in the position previously occupied by the charge.

The final composition of all samples was determined by chemical analysis. The usual procedure was to dissolve the sample in hot hydrochloric acid solution under an atmosphere of carbon dioxide, air being rigorously excluded. Manganous phosphate and phosphoric acid were added to the cooled solution which was then titrated for ferrous iron with permanganate solution. The solution was reduced by passing through a Jones reductor and again titrated with the same permanganate solution for total iron. The permanganate was standardized against sodium oxalate and the small blank and end-point corrections were frequently checked against samples of electrolytic iron. The ratio (r) of ferrous plus ferric iron to ferrous iron (*i. e.*, the ratio of the two corrected amounts of permanganate solution required) was regarded as the primary analysis of the sample; compositions expressed in any other way were calculated from this ratio. Duplicate analyses were frequently made and found to check within 1 or 2 parts per thousand in the ratio. The liter of the permanganate solution was used only as a check on the analysis; the sum of the FeO and Fe_2O_3 nearly always added to 100.0 ± 0.2%.

In these experiments the platinum crucibles took up a considerable amount of iron. If the solubility of platinum in wüstite is small, the iron content of the platinum has negligible influence on the gas–wüstite equilibrium once the equilibrium between gas, wüstite and platinum is established. (No platinum was found in the wüstites by chemical analysis.) However, it was necessary to consider the possibility that the platinum removed iron from the wüstite faster than the corresponding amount of oxygen was carried away by the gas, causing the wüstite to have a higher oxygen content than the true equilibrium amount. Since the charges sintered fairly rapidly and shrank away from the crucible side, leaving only the bottom in direct contact, any such error would be more pronounced at the bottom than at the top. Therefore several samples resulting from single charges of Fe_2O_3 in an atmosphere which yielded wüstite near the iron side of the field (the optimum condition for the effect under consideration) were split horizontally, and the top and bottom portions analyzed separately. The ratio of ferrous plus ferric iron to ferrous iron seldom differed by more than 1 or 2 parts per thousand between the two halves (see Table V). It will be noted that errors introduced by lack of sufficient time for equilibration of gas and wüstite would be of the same sign (in the case of an Fe_2O_3 charge) as that caused by platinum, since access to gas is at the top of crucible. A further check on the possible effect of platinum was provided by experiments in which coiled electrolytic iron was used as charge and no portion of the sample analyzed had been in contact with platinum; the results were in accord with those obtained in the usual way.

Results.—The experimental results thus obtained on the composition of wüstite in equilibrium with various atmospheres at various temperatures are given in Table V.

A direct plot, Fig. 4, of these values of r shows that all points for any one gas composition lie very close to a smooth curve which is linear except for the lowest CO_2/CO ratio; the maximum departure (Δr) from the curve of the observed ratio (r) is, except for a single case, about 0.003.

In our earlier attempts to investigate the composition of the low oxygen boundary of the wüstite field, a small iron crucible was used to hold

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[13] Cleaves and Thompson, *J. Research. Nat. Bur. Standards*, **18**, 595 (1937).

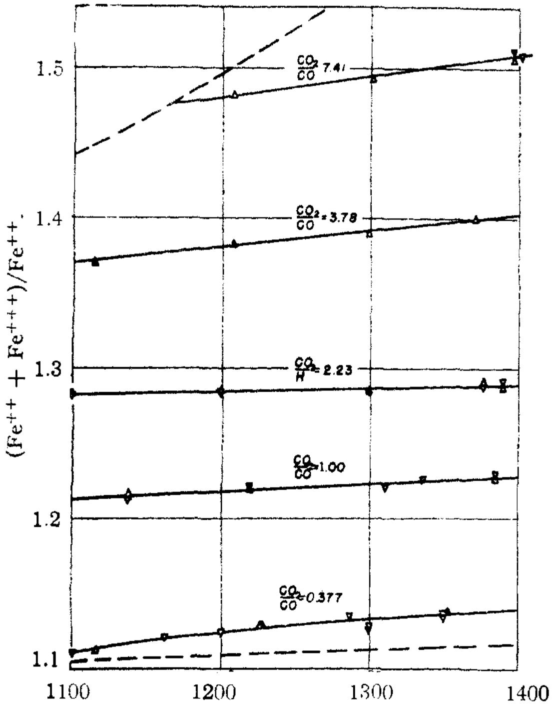

Fig. 4.—Variation of wüstite composition with temperature at fixed gas compositions. Broken lines indicate boundaries of the wüstite field. (In the case of the H_2–CO_2 mixture the molecular composition of the equilibrated gas, *e. g.*, p_{CO_2}/p_{CO}, is clearly a function of temperature.)

Table V

Experimental Results on Equilibrium of Wüstite with Several Gas Mixtures at Various Temperatures

Starting material[a]	Temp., °C.	Time, hr.	$(Fe^{++} + Fe^{+++})/Fe^{++}$ top	γ	bottom
A. CO_2/CO = 0.377					
Fe_2O_3 B. of S.	1101	17	1.112		
Fe electrolytic	1116	96	1.112		1.112
Fe_2O_3 from electrolytic Fe	1162	72	1.120		1.122
Fe_2O_3 B. of S.	1200	7	1.125		1.126
Fe_2O_3 B. of S.	1200	18	1.124		1.127
Fe_2O_3 de Haen's	1200	18	1.125		
Fe electrolytic	1226	16	1.128		1.130
Fe electrolytic	1228	38	1.130		
Fe_2O_3 de Haen's	1287	16	1.136		1.137
Fe_2O_3 B. of S.	1300	6	1.128		1.129
Fe_2O_3 B. of S.	1300	18	1.124		1.129
Fe_2O_3 B. of S.	1300	26	1.123		1.133
Fe_2O_3 B. of S.	1350	7	1.137		
Fe_2O_3 B. of S.	1350	8	1.132		1.138
Fe electrolytic	1353	24	1.138		1.139
B. CO_2/CO = 1.00					
{ Fe_2O_3 de Haen's	1138	18		1.214	
{ Fe_2O_3 de Haen's reduced				1.216	
{ Fe_2O_3 de Haen's	1220	18		1.222	
{ Fe_2O_3 de Haen's reduced				1.220	
Fe_2O_3 de Haen's	1311	5		1.222	
Fe_2O_3 de Haen's	1336	5.5		1.227	
{ Fe_2O_3 de Haen's	1387	18		1.229	
{ Fe_2O_3 de Haen's reduced				1.227	
C. CO_2/H_2 = 2.23[b]					
{ Fe_2O_3 de Haen's	1100	18		1.284	
{ Fe_2O_3 de Haen's reduced				1.284	
{ Fe_2O_3 de Haen's	1200	5		1.286	
{ Fe_2O_3 de Haen's reduced				1.286	
{ Fe_2O_3 de Haen's	1299	18		1.286	
{ Fe_2O_3 de Haen's reduced				1.286	
{ Fe_2O_3 de Haen's	1377	18		1.290	
{ Fe_2O_3 de Haen's reduced				1.291	
{ Fe_2O_3 de Haen's	1390	18		1.292	
{ Fe_2O_3 de Haen's reduced				1.288	
D. CO_2/CO = 3.78					
Fe electrolytic	1115	18		1.370	
Fe electrolytic	1208	15		1.383	
Fe electrolytic	1302	18		1.390	
Fe electrolytic	1372	18		1.400	
E. CO_2/CO = 7.41					
Fe electrolytic	1208	18		1.483	
Fe electrolytic	1302	18		1.494	
Fe electrolytic	1398	5.5		1.507	
Fe_2O_3 B. of S.	1398	40	1.513		1.512
Fe_2O_3 de Haen's	1404	23	1.510		1.511
Fe_2O_3 de Haen's	1409	5	1.522		1.521

[a] The paired values refer to paired samples run simultaneously in separate crucibles, and approaching equilibrium from opposite sides. [b] Constancy of this initial ratio means that the CO_2/CO ratio is not the same at all temperatures; this is discussed in the text.

the charge (the top was closed by bending the walls together); it was suspended in an atmosphere of nitrogen which was purified by passing through purified iron powder at 900° and drying so that it produced no (or very slight) temper film on the outside of the crucible. About 100 experiments of this type were performed with iron from several sources as container, and oxide from different sources as charge. However, no satisfactory reproducibility was ever obtained. For example, Bureau of Standards oxide in an electrolytic iron crucible held at 1200° for eighteen hours had a final ratio of ferrous plus ferric to ferrous iron ranging from 1.09 to 1.11. Since this difference is ten times that observed in equilibration of charges with a gaseous atmosphere, this method was abandoned, and the data are not presented. Instead, an indirect method was employed to determine the composition of wüstite in equilibrium with iron; at each of the four temperatures, 1100, 1200, 1300, 1350°, oxide samples were equilibrated with a series of gas mixtures just slightly more oxidizing than that previously found to be in equilibrium with iron and wüstite. The results are given in Table VI.

It was found that in this region the result is very sensitive to the purity of the initial oxide. This point is brought out in Table VIB and in the pair of 1200° isotherms, one for each oxide, in Fig. 5; the results with both samples of Fe_2O_3 are in agreement at a fair distance from the iron boundary of the wüstite field, but not in the immediate vicinity of this boundary. The reason for this discrepancy becomes apparent when we consider the effect of a small amount of a metallic oxide more readily reducible than iron oxide. Any such oxide will be completely reduced in the atmospheres used here and will tend to form a metallic solid solution which immediately acts as a "sink" for iron, whose activity is nearly unity

TABLE VI

EXPERIMENTAL RESULTS ON EQUILIBRIUM OF WÜSTITE WITH CO-CO_2 MIXTURES NEAR THE LOW OXYGEN BOUNDARY AT SEVERAL TEMPERATURES

Starting material	CO_2/CO	Time, hr.	$(Fe^{++} + Fe^{+++})/Fe^{++}$ top	r	bottom
	A.	1100°			
Fe_2O_3 B. of S.	0.385	6		1.114	
Fe_2O_3 B. of S.	.376	17		1.112	
Fe_2O_3 B. of S.	.368	7		1.109	
Fe_2O_3 B. of S.	.360	4		1.109	
Fe_2O_3 B. of S.	.359	18		1.108	
Fe_2O_3 B. of S.	.353	8	1.044		1.104
	B.	1200°			
Fe_2O_3 B. of S.	.382	18		1.125	
Fe_2O_3 B. of S.	.342	18		1.114	
Fe_2O_3 B. of S.	.341	3		1.115	
Fe_2O_3 B. of S.	.334	3		1.112	
Fe_2O_3 B. of S,	.327	8		1.109	
Fe_2O_3 B. of S.	.321	8	1.093		1.105
Fe_2O_3 de Haen's	.361	18		1.120	
Fe_2O_3 de Haen's	.360	18	1.117		1.112
Fe_2O_3 de Haen's	.351	6	1.109		1.112
Fe_2O_3 de Haen's	.346	18	1.107		1.108
Fe_2O_3 de Haen's	.342	18		1.106	
Fe_2O_3 de Haen's	.341	2		1.105	
Fe_2O_3 de Haen's	.339	9	1.104		1.101
Fe_2O_3 de Haen's	.337	18	1.103		1.107
Fe_2O_3 de Haen's	.337	4	1.098		1.099
Fe_2O_3 de Haen's	.336	18		1.093	
Fe_2O_3 de Haen's	.334	18	1.091		1.096
Fe_2O_3 de Haen's	.333	6		1.095	
	C.	1300°			
Fe_2O_3 B. of S.	.337	3	1.123		1.125
Fe_2O_3 B. of S.	.336	18	1.116		1.125
Fe_2O_3 B. of S.	.309	5		1.119	
Fe_2O_3 B. of S.	.307	43	1.116		1.111
Fe_2O_3 B. of S.	.299	7	1.111		1.113
Fe_2O_3 B. of S.	.293	7	1.103		1.096
	D.	1350°			
Fe_2O_3 B. of S.	.339	18	1.127		1.134
Fe_2O_3 B. of S.	.313	22	1.122		1.117
Fe_2O_3 B. of S.	.292	18	1.119		1.120
Fe_2O_3 B. of S.	.286	40	1.116		1.116
Fe_2O_3 B. of S.	.283	23	1.106		1.107

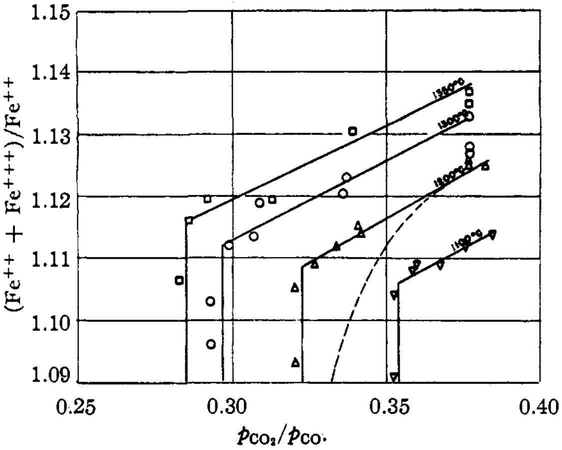

Fig. 5.—Determination of composition of wüstite at the iron-wüstite boundary by extrapolation of gas-oxide equilibrium data (Tables V and VI) near the boundary to the gas composition at the boundary as given in Table IV. This figure represents on a very open scale the extreme lower left-hand corner of Figure 6. Bureau of Standards oxide was used as starting substance for all points shown; the effect of a small percentage of impurity as contained by de Haen's oxide is shown for 1200° by the dashed curve.

in these experiments; hence a considerable quantity of iron may be reduced to the metallic state by this means. For example, consider the effect of the 0.02% nickel present in the de Haen's oxide. The activity of iron in this region is approximately equal to $(p^0_{CO_2}/p^0_{CO})(p_{CO}/p_{CO_2})$, where the first term is the CO_2/CO ratio in equilibrium with iron and wüstite, and the second the reciprocal of the CO_2/CO ratio in which the impure oxide is treated. If it is approximated that the activity of iron is equal to its atom fraction (N_{Fe}) in the alloy formed, then N_{Fe} is equal to the above expression, and the atomic ratio of iron to nickel is $N_{Fe}/(1 - N_{Fe})$. In the last experiment cited in Table VIB, p_{CO_2}/p_{CO} is 0.333, $p^0_{CO_2}/p^0_{CO}$ equals 0.323 at 1200°, hence N_{Fe} is 0.97 and the atomic ratio of iron to nickel is 32. Thus the amount of metallic iron may be expected to be 0.64% (*i. e.*, 32 times 0.02%) of the initial weight of Fe_2O_3 or 0.91% of the total iron present. Since every per cent. of metallic iron present introduces an error of 1 to 3% in the analytical ratio (*r*) (depending on whether the metallic iron reduces ferric iron or merely liberates hydrogen on solution in acid), it would be expected on this basis that the ratio *r* given in the last line of Table VIB would be in error by about 2%. Comparison of this with the corresponding ratio obtained using Bureau of Standards oxide for the same atmosphere shows such an error. The presence of 0.04% copper might be expected to cause a similar error, though the limited miscibility in the iron-copper system would probably diminish the error in this case. Hence the purer Bureau of Standards iron oxide was used in all subsequent experiments in the vicinity of the iron boundary.

The composition of wüstite in equilibrium with iron was then derived by a short extrapolation of a linear plot of these data to the gas composition (from Table IV) corresponding to equilibrium at each temperature, as shown in Fig. 5. It will be noted that the ratio $p^0_{CO_2}/p^0_{CO}$ (iron-wüstite equilibrium) as determined previously is verified by the data of Table VI. The break in composition occurs at the predicted position. The composition, thus determined, of the iron boundary of the wüstite field is given later in Table VIII.

The composition of the magnetite boundary of the wüstite field was determined in a similar way. Since a much more oxidizing atmosphere is in equilibrium with wüstite and magnetite at higher temperature, additional data were needed in the vicinity of 1400°; these are given in Table VII.

Table VII

Experimental Results on Equilibrium of Wüstite with CO_2/CO Mixtures at 1400° near the High Oxygen Boundary

Starting material	CO_2/CO	Time, hr.	$(Fe^{++} + Fe^{+++})/Fe^{++}$ r
Fe_3O_4, oxidized Fe, electrolytic	13.44	18	1.624
Fe_2O_3, de Haen's	14.03	70	1.637
Fe, electrolytic	14.03	40	1.632
Fe, electrolytic	14.03	20	1.634
Fe_2O_3 B. of S.	14.03	40	1.632
Fe_2O_3 de Haen's	14.55	48	1.638
Wüstite, reduced Fe_2O_3, de Haen's	14.55	72	1.640

The data of Tables V and VI were plotted on a large scale, and the composition was read at the round temperatures 1100, 1200, 1300 and 1400°, a short extrapolation being sometimes necessary.

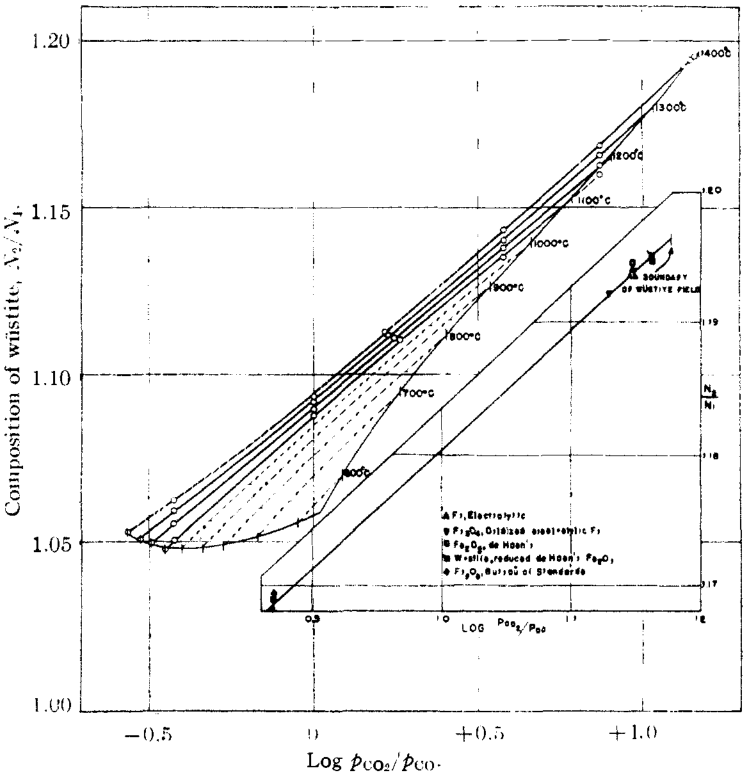

Fig. 6.—Variation of wüstite composition with gas composition at round temperatures, and determination of composition of wüstite in equilibrium with magnetite by extrapolation of curves based on data in Tables V and VI to the equilibrium gas composition as given in Table IV. The isotherms below 1100° were obtained by extrapolation on a plot of log CO_2/CO *vs.* $1/T$ at constant wüstite composition; the field boundaries so determined appear in Fig. 9. Since the field covers a more extended range of gas composition at higher temperature, additional data were obtained at 1400° (Table VII); these are shown in the inset.

The isothermal relationships between the composition of wüstite and of gas are shown in Fig. 6, the ordinate N_2/N_1 (the atomic ratio of oxygen to iron; N_2 and N_1 being the atom fractions of oxygen and iron, respectively; $N_2/N_1 = (3r - 1)/2r$), and the abscissa log (p_{CO_2}/p_{CO}) being chosen because they are required for an integration which is discussed later.

The compositions of the magnetite side of the wüstite field, as found by extrapolation of these nearly straight curves to the gas compositions given in Table IV (rounded values from Fig. 3), are given in Table VIII. The lower isotherms in Fig. 6 will be discussed later; they result from extrapolation of the experimental data (1100–1400°) within the wüstite field and, when combined with data on gas composition at the boundaries, give the oxide composition at these boundaries as shown in Table XII and in Fig. 9.

Table VIII

Values of Composition of Wüstite at Rounded Temperatures in Equilibrium with

	A. Iron		B. Magnetite	
T, °C.	$(Fe^{++} + Fe^{+++})/Fe^{++}$ r	Wt. % oxygen	$(Fe^{++} + Fe^{+++})/Fe^{++}$ r	Wt. % oxygen
1100	1.106	23.09	1.440	24.83
1200	1.109	23.11	1.495	25.03
1300	1.112	23.13	1.561	25.26
1350	1.115	23.15		
1400			1.648	25.53

Thermodynamic Calculations

The partial molal heat of solution of oxygen in wüstite ($\overline{H}_2$) is obtained readily from the temperature coefficient of the oxygen pressure at constant composition. The partial molal heat of transfer of oxygen from a CO_2–CO mixture to wüstite of fixed composition ($\overline{H}_2'$) is found from the data of Fig. 6. $\overline{H}'_2$ differs from $\overline{H}_2$ by the heat of formation of CO_2 from CO and O_2. Values of log (p_{CO_2}/p_{CO}) at round compositions were read from Fig. 6 and plotted against $1/T$; the resulting curves are essentially straight over the temperature range covered. Their slope multiplied by 4.575 gives $\overline{H}'_2$ which is shown as a function of composition in Fig. 7.

The activity of iron in wüstite (a_1) is obtained from the Gibbs–Duhem equation

$$\log a_1 = -\int \frac{N_2}{N_1} d \log a_2$$

TABLE IX

GAS COMPOSITION IN EQUILIBRIUM WITH WÜSTITE AND ACTIVITY OF Fe AND FeO IN WÜSTITE

	1100°			1200°			1300°			1400°		
N_2/N_1	$\log \frac{p_{CO_2}}{p_{CO}}$	$-\log a_{Fe}$	$-\log a_{FeO}$	$\log \frac{p_{CO_2}}{p_{CO}}$	$-\log a_{Fe}$	$-\log a_{FeO}$	$\log \frac{p_{CO_2}}{p_{CO}}$	$-\log a_{Fe}$	$-\log a_{FeO}$	$\log \frac{p_{CO_2}}{p_{CO}}$	$-\log a_{Fe}$	$-\log a_{FeO}$
1.0477	−0.450	0	− 0									
1.0495	.....	...	....	−0.492	0	0						
1.0506	.....	...	....	.....	...	....	−0.528	0	0			
1.0528	.....	...	....	.....	...	....	.....	...	....	−0.562	0	0
1.055	− .369	.085	.0042	− .423	.073	.0036	− .474	.057	.0028	− .529	.035	.0018
1.07	− .199	.266	.0148	− .238	.269	.0151	− .276	.267	.0151	− .311	.266	.0154
1.09	+ .034	.517	.0334	+ .004	.530	.0344	− .023	.540	.0353	− .051	.547	.0362
1.11	+ .273	.780	.0573	+ .246	.797	.0586	+ .221	.809	.0597	+ .193	.816	.0606
1.14	+ .634	1.186	.1025	+ .602	1.197	.1031	+ .572	1.203	.1035	+ .543	1.209	.1043
1.1528	+ .787	1.362	.1249	.....	...	....	.....	...	....	.....	...	....
1.16	(+ .874)[a]	(1.462)[a]	(0.1385)[a]	+ .839	1.470	.1386	+ .802	1.468	.1379	+ .772	1.473	.1387
1.1656				+ .904	1.545	.1492	.....	...	....	.....	...	....
1.1797							+1.033	1.738	.1771	.....	...	....
1.1965										+1.177	1.950	.2109

[a] Values outside the range for stable wüstite, included for purpose of interpolation.

Since at any fixed temperature the activity of oxygen (a_2) is directly proportional to p_{CO_2}/p_{CO}, the activity of iron at any temperature and any composition is obtained by integration of the appropriate isotherm in Fig. 6, from the composition in equilibrium with metallic iron to the composition under consideration. Similarly the **activity of FeO,** which is proportional to the product a_1a_2, is found from the relation

$$\log a_{FeO} = \log a_1 + \log a_2 = -\int\left(\frac{N_2}{N_1} - 1\right) \mathrm{d} \log a_2$$

the integral to be taken between the same limits. This may be obtained with considerably greater accuracy than $\log a_{Fe}$ since it is smaller numerically and is much less sensitive to error in the ratio p_{CO_2}/p_{CO} in equilibrium with iron and wüstite. The integrations were carried out analytically.

Values of $\log a_{Fe}$ and $\log a_{FeO}$ are given in Table IX; the activity of oxygen, or of any iron–oxygen complex can be found by suitable combination of these values, the result obtained always being relative to the value in wüstite in equilibrium with iron. The activity of FeO is taken arbitrarily as unity for the wüstite in equilibrium with iron (at each temperature), as indicated in Table IX. The odd compositions at the end correspond to wüstites in equilibrium with magnetite. The precision of the tabulated values of $\log a_{FeO}$ may be estimated from Fig. 6. There are only two departures of as much as 0.01 log unit (in $\log p_{CO_2}/p_{CO}$) from a smooth curve but there are several departures of as much as 0.004 log unit (*i. e.*, 1% in p_{CO_2}/p_{CO} or 0.03% in N_2/N_1). A systematic error of this amount corresponds to only $[(N_2/N_1) - 1]$ times as much, or 0.0002 to 0.0008, in $\log a_{FeO}$ and N_2/N_1 times as much or 0.004 in $\log a_{Fe}$. The "probable error" may be estimated as about one-half as great or ±0.0001 to ±0.0004 for $\log a_{FeO}$ and ±0.002 for $\log a_{Fe}$.

The partial molal heat of solution ($\overline{H}_1$) of metallic iron in wüstite of a definite composition is obtained from a plot of $\log a_{Fe}$ against $1/T$ by multiplying the slope of the line by 4.575. $\overline{H}_1$ is also calculable from the thermodynamic relation

$$\overline{H}_1 = -\int \frac{N_2}{N_1}\, \mathrm{d}\overline{H}_2 + \text{constant}$$

The constant can be evaluated only by comparison of the above integral with $\overline{H}_1$ derived by the other method; its average value is 1430 cal. $\overline{H}_1$ from both methods is shown as a function of composition in the lower curve of Fig. 7. Based on a value of −66,980 cal. for the heat of reaction $CO + {}^1/_2O_2 = CO_2$ (the value at 1250° calculated from Rossini's value of ΔH^0_0 and heat contents from the spectroscopic data previously mentioned) values of the following heats are recorded in Table X at various compositions: $\overline{H}_2$, $\overline{H}_1$, $\overline{H}_1 + \overline{H}_2$ (the heat of addition of one gram-atom of metallic Fe and one-half gram-mole of O_2 to

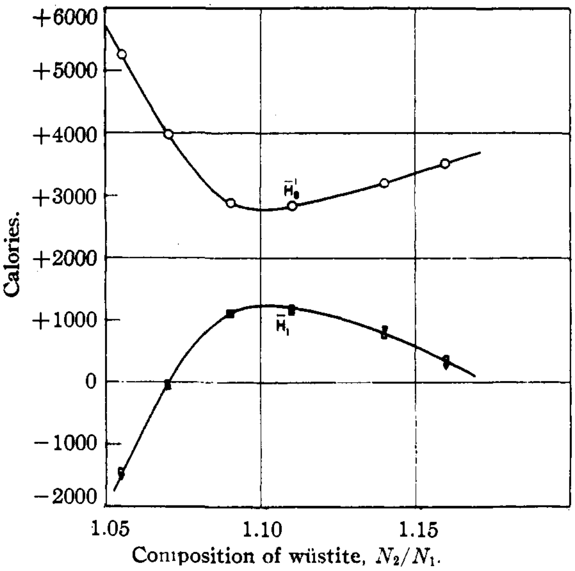

Fig. 7.—Partial molal heat of addition of iron, H_1, and of oxygen (relative to CO_2–CO mixtures) H_2', to wüstite of various compositions. $\overline{H}_1$ from activities of iron is denoted by triangles, that from $\overline{H}_2'$ by squares.

Table X

Heat of Formation of Wüstite at 1250°

N_2/N_1	1.055	1.07	1.09	1.11	1.14	1.16
$\bar{H}_2$	−61,720	−63,000	−64,100	−64,140	−63,780	−63,460
$\bar{H}_1$	− 1,430	− 70	+ 1,110	+ 1,160	+ 750	+ 380
$\bar{H}_1 + \bar{H}_2$	−63,150	−63,070	−62,990	−62,980	−63,030	−63,080
ΔH_W	−32,380	−32,600	−32,900	−33,190	−33,630	−33,900
$\Delta H_W/N_2$	−63,080	−63,070	−63,080	−63,090	−63,120	−63,130
$\Delta H_W/N_1$	−66,550	−67,480	−68,750	−70,040	−71,960	−73,220

wüstite), ΔH_W $(=N_1\bar{H}_1 + N_2\bar{H}_2)$, $\Delta H_W/N_2$ (the heat of formation of Fe_xO, where $x = N_1/N_2$) and $\Delta H_W/N_1$ (the heat of formation of FeO_y, where $y = N_2/N_1$). It is interesting to note that the heat of formation of wüstite per atom of oxygen is very nearly independent of composition. It is even more remarkable that, to a rough approximation, the total heat of formation is the partial molal heat of addition of oxygen.

It may be shown thermodynamically that at equilibrium with iron 4.575 d log a_2/d $1/T$ = $\Delta H_W/N_2$; this serves as a check on the values of $\Delta H_W/N_2$, since, as seen from Table X, this quantity is very nearly independent of composition. From Fig. 2, d log (p_{CO_2}/p_{CO})/d $1/T$ = +860 (1250°); hence $\Delta H_W/N_2$ = −66,980 + (860) (4.575) = −63,050, in satisfactory agreement with the values given in Table X (at the lower values of N_2/N_1).

The precision of the various quantities listed in Table X is rather difficult to state. An error of 1% in p_{CO_2}/p_{CO} at 1400°, uncompensated by a similar error at 1100°, corresponds to an error of 150 cal. in $\bar{H}_1$ and a similar amount in $\bar{H}_2$. Due to cancellation of errors, values of the other functions tabulated are rather insensitive to experimental error in the center of the wüstite field and depend mainly on the values of Table II; the consistency here is of the order of 0.3% in p_{CO_2}/p_{CO} corresponding to a precision of ±50 cal. in $\Delta H_W/N_2$, etc. Unknown systematic errors would lessen the accuracy.

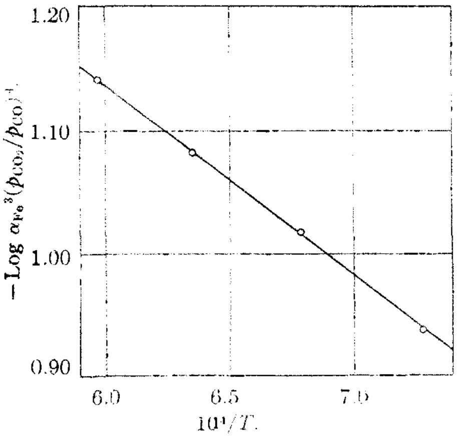

Fig. 8.—Plot of wüstite–magnetite equilibrium leading to the heat of formation of magnetite.

Heat of Formation of Magnetite.—Since the composition of wüstite in equilibrium with magnetite is by no means independent of temperature, the heat of formation of magnetite from wüstite cannot be calculated in the usual simple manner from the partial pressure of oxygen in equilibrium with magnetite and wüstite. However, since the composition of magnetite in equilibrium with wüstite is independent of temperature (as will be shown in another paper), its heat of formation from the elements may be expressed in a fairly simple manner. For the chemical reaction

$$3Fe(\gamma) + 2O_2\ (gas) = Fe_3O_4\ (magnetite)$$
$$1/K_M = a^3_{Fe}\,(p_{O_2}{}^{1/2})^4$$

and

$$\Delta H_M = -4.575\,\frac{d\log K_M}{d\,1/T}$$

Also the heat of reaction $CO + {}^1/_2O_2 = CO_2$ may be expressed

$$\Delta H_{CO_2} = -4.575\,\frac{d}{d\,1/T}\left[\log\left(\frac{p_{CO_2}}{p_{CO}}\right)\frac{1}{p_{O_2}{}^{1/2}}\right]$$

Hence

$$\Delta H_M = 4.575\,\frac{d}{d\,1/T}\left[\log a^3_{Fe}\left(\frac{p_{CO_2}}{p_{CO}}\right)^4\right] + 4\Delta H_{CO_2}$$

ΔH_M can be evaluated directly from this expression using the values of a_{Fe} and p_{CO_2}/p_{CO} in equilibrium with magnetite given in Tables IX and IV. The plot of the quantity in brackets against 1/T is shown in Fig. 8. The slope of this line corresponds to a heat of 7,050 cal., or ΔH_M = −260,870.

There is an alternative method for calculating ΔH_M as follows. The total derivatives in the foregoing equation are replaced by partial derivatives

$$\Delta H_M = 4.575\left[3\left(\frac{\partial\log a_{Fe}}{\partial\,1/T}\right)_N + 3\left(\frac{\partial\log a_{Fe}}{\partial N}\right)_T\frac{dN}{d\,1/T} + 4\left(\frac{\partial\log p_{CO_2}/p_{CO}}{\partial\,1/T}\right)_N + 4\left(\frac{\partial\log p_{CO_2}/p_{CO}}{\partial N}\right)_T\frac{dN}{d\,1/T}\right] + 4\,\Delta H_{CO_2}$$

where the composition variable N refers to the wüstite field. Substituting

$$\bar{H}_1 = 4.575\left(\frac{\partial\log a_{Fe}}{\partial\,1/T}\right)_N$$

$$\bar{H}_2{}' = 4.575\left(\frac{\partial\log p_{CO_2}/p_{CO}}{\partial\,1/T}\right)_N,\quad\text{and}$$

$$\left(\frac{\partial\log a_{Fe}}{\partial N}\right)_T = -\frac{N_2}{N_1}\left(\frac{\partial\log\frac{p_{CO_2}}{p_{CO}}}{\partial N}\right)_T$$

$$\Delta H_M = 3\bar{H}_1 + 3\frac{N_2}{N_1}\bar{H}_2' + 4.575\left(4 - \frac{3N_2}{N_1}\right)$$
$$\left[\left(\frac{\partial \log p_{CO_2}/p_{CO}}{\partial N}\right)_T \frac{dN}{d\,1/T} + \left(\frac{\partial \log p_{CO_2}/p_{CO}}{\partial\,1/T}\right)_N\right] + 4\,\Delta H_{CO_2}$$

Replacing the term in brackets by the corresponding total derivative and the first two terms by $3\,\Delta H_W/N_1 - 3\,\frac{N_2}{N_1}\,\Delta H_{CO_2}$

$$\Delta H_M = \frac{3\,\Delta H_W}{N_1} + \left(4 - 3\,\frac{N_2}{N_1}\right)\left[4.575\,\frac{d \log p_{CO_2}/p_{CO}}{d\,1/T} + \Delta H_{CO_2}\right]$$

Although the use of this equation requires the graphical determination of slopes, the total contribution of the slope term is only 5000 to 8000 cal. Using again the value of −66,980 cal. for ΔH_{CO_2}, values of $\Delta H_W/N_1$ obtained from the identity[14]

$$\frac{\Delta H_W}{N_1} = \frac{\Delta H_W}{N_2}\left(\frac{N_2}{N_1}\right)$$

and values of 4.575 [d log p_{CO_2}/p_{CO}]/d $1/T$ obtained graphically from Fig. 3 and given in the second column of Table XI, the heats of formation of magnetite given in the third column are obtained.

TABLE XI

HEAT OF FORMATION OF MAGNETITE

Temp., °C.	$-\frac{4.575\ d \log p_{CO_2}/p_{CO}}{d\ 1/T}$	$-\Delta H_M$ (using const. value of ΔH_{CO_2})	$-\Delta H_M$
1100	10,070	260,010	260,730
1200	11,900	260,430	260,670
1300	15,170	261,330	261,090
1400	19,100	262,020	261,240

The variation in ΔH_M in the third column is due in part to the difficulty of measuring the slopes, in part to the fact that ΔH_{CO_2} changes with temperature (although here considered constant) and in part to the fact that ΔH_M is also a function of temperature. If the variable value of ΔH_{CO_2} is used in the foregoing equation (including its use in the evaluation of ΔH_W), the more uniform values of ΔH_M in the fourth column are obtained. Its mean value is −260,930 cal., and the average departure of the several values from this is ±230 cal., comparable to the *a priori* estimate of probable error from the experimental error of the data in Tables II and III. It is worthy of note that the heat of formation of magnetite per atom of oxygen is −65,230 cal., a value very close to the heat of formation of wüstite per atom of oxygen, which as shown in Table X varies only from −63,070 to −63,130 cal. over the entire field.

ΔH_M at 25° was calculated from the value −260,930 cal. at 1250° by using the following data: heat contents of iron,[15] magnetite,[16] and CO and CO_2 (from sources already mentioned); the heat of the reaction $CO + {}^1/_2\,O_2 = CO_2$ at 25° (Rossini) and at 1250° (−66,980 cal.); whence it is −267,200 cal. This may be compared with the latest room temperature calorimetric values −266,760 and −265,700 cal. obtained by Roth and Wienert[17] by the acid solution and bomb calorimetric methods, respectively, and the value −266,900 cal. selected by Bichowsky and Rossini.[18] Uncertainties in the heat contents used are more than sufficient to explain the difference of 440 cal. between our result and the acid solution value.

All the foregoing calculations involve no assumption as to the molecular constitution of wüstite. One approach to interpretation of the data in terms of structure is to determine whether the solid solution behaves ideally with respect to any arbitrarily chosen components; if ideal, a plot of activity against mole fraction for each component will be linear. Such calculations were made not only with $FeO–Fe_2O_3$ and $FeO–Fe_3O_4$ as components, but also with several other complexes of fractional ratio of oxygen to iron; in every case a large departure from Raoult's (and Henry's) law was found. Similar choices of components for a pseudo-ternary solution gave the same result. This approach, therefore, did not appear fruitful and the results are not presented.

Temperature–Composition Diagram of Wüstite Field

Although this diagram is but a small part of the present investigation, it merits consideration since it is of general interest and because there is a wide disagreement between previous investigators. The various determinations have been the subject of numerous reviews,[19] hence will not be discussed again in detail here.

The diagram of Jette and Foote (see Fig. 9), perhaps the most widely accepted in this country, is based on X-ray investigation of quenched samples; although the X-ray has been called "that ultimate arbiter" of numerous questions, it obviously can give results no better than the samples analyzed. Their diagram is in such serious discord with the present determination that, if it were correct, nearly half of our points of Table V would be in the two-phase field, wüstite–magnetite; but actually they lie on such smooth curves for the single phase wüstite field that the

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(14) As shown in Table X, $\Delta H_W/N_2$ varies but little with composition and may be graphically extrapolated to higher values of N_2/N_1 with greater precision.

(15) J. Chipman, "Basic Open Hearth Steelmaking," AIME, 1944, Chap. XVI.

(16) Esser, Averdieck and Grass, *Archiv. Eisenhuttenwesen*, **6**, 289 (1932/33).

(17) Roth and Wienert, *ibid.*, **7**, 455 (1933/34).

(18) Bichowsky and Rossini, "Thermochemistry of Chemical Substances," Reinhold Pub. Corp., New York, N. Y., 1936.

(19) Pfeil and Winterbottom, "Review of Oxidation and Scaling of Heated Solid Metals," H. M. Stationery Office, London, 1935, p. 18; Jette and Foote, *Trans. American Institute of Mining & Metallurgical Engineers, Iron and Steel Division*, **105**, 276 (1933); O. C. Ralston, "Iron Oxide Reduction Equilibria," Bureau of Mines Bulletin 296 (1929).

Table XII

The Wüstite Field

	Fe-wüstite boundary p_{CO_2}/p_{CO}					Wüstite-magnetite boundary p_{CO_2}/p_{CO}				
T, °C.	Emmett and Schultz	Schenck	Fig. 2	Selected value	% O	Emmett and Schultz	Schenck	Fig. 3	Selected value	% O
600	...	0.895	...	0.895	23.22	1.198	1.228	...	1.23	23.47
700	0.670	.664–0.620	...	.667	23.15	1.875	1.831	1.840	1.84	23.88
800	.530	.534	...	.532	23.11	2.52	2.636	2.56	2.56	24.16
900	.460	.445– .466	0.460	.460	23.10	...	3.67	3.47	3.47	24.40
1000	...	....	.396	.396	23.09	...	...	4.62	4.62	24.62
1100	...	....	.355	.355	23.10	...	...	6.12	6.12	24.83

authors are constrained to believe that the Jette and Foote points are in serious error, at least in the range 1100–1425°. The source of this error lies most likely in the fact that a wüstite may easily be quenched so as to preserve its gross chemical composition (the only requirement of the quench for the present investigation) but not in such manner as to preserve its structure as revealed by X-ray (the requirement of Jette and Foote's method).

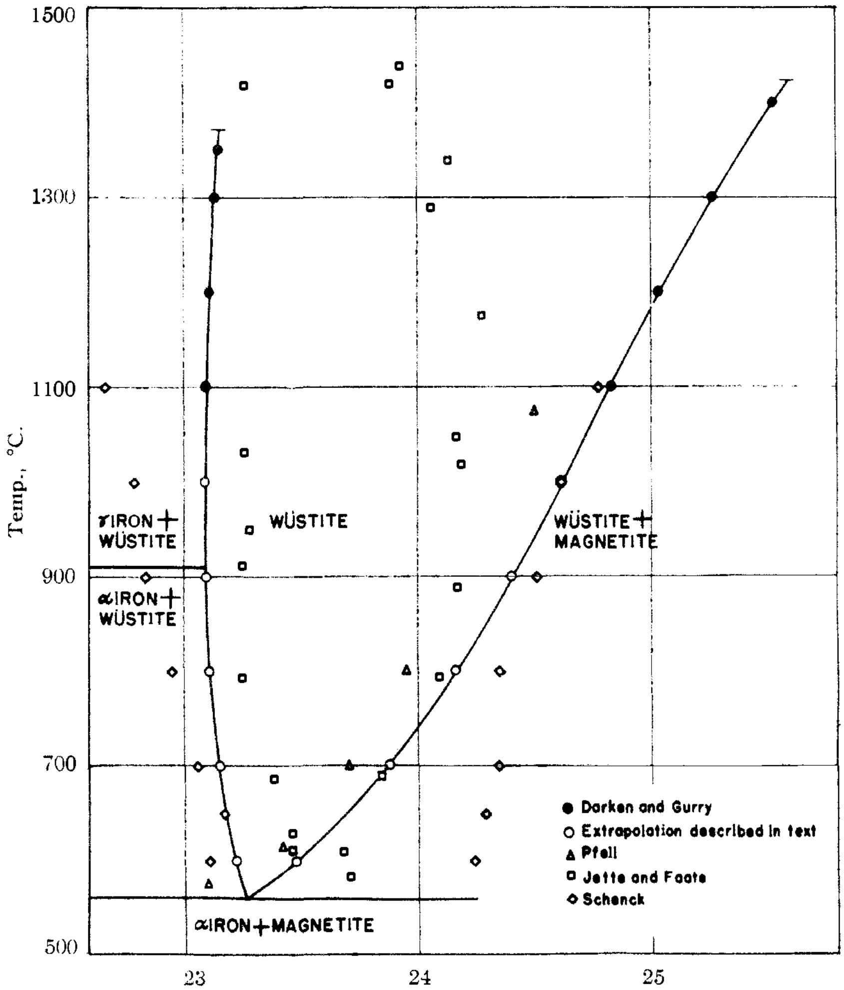

Fig. 9.—The range of stability of wüstite. Circles below 1100° result from extrapolation and are taken from Fig. 6.

The diagram of Pfeil[20] (see Fig. 9), also widely accepted, is in better agreement than any other previous diagram with the results of this paper. He indicates a slightly narrower wüstite field than the present work; this slight discrepancy may arise from the fact that his method depends on preservation of microstructure by quench.

The diagram of Schenck[5] (see Fig. 9) was obtained by a method somewhat similar to ours but differed in that the gas atmosphere was static and the wüstite composition was obtained not by analysis but by calculation from change in composition of the atmosphere. A re-plot of the original data indicates that his precision was not of the best (particularly at the lower temperatures) and that the divergence from our data is within the range of his experimental error.

Since reliable data are available on the CO_2–CO ratio in equilibrium with wüstite at its phase boundaries[5,6] at temperatures down to the lower stability limit of wüstite, it is possible to determine the phase diagram at these lower temperatures by extrapolating[21] our graphs of log CO_2/CO vs. $1/T$ at constant composition within the wüstite field to give isotherms of wüstite vs. gas

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(20) L. B. Pfeil, *J. Iron Steel Inst.* (London), **123**, 237 (1931).

(21) Extrapolations were linear in all cases except for N_2/N_1 = 1.055 at which composition slight curvature was required to produce a smooth family of curves.

composition, and reading from these at the appropriate gas composition as shown in Fig. 6. Although it might seem foolish to extrapolate over such a large temperature range, actually a considerable error in extrapolation causes an error in the temperature–composition diagram which is perhaps smaller than existing discrepancies. The resulting boundaries of the wüstite field at lower temperatures are given in Table XII and in Fig. 9; these points are in fairly good agreement with those of Pfeil.

The heavy lines of Fig. 9 represent our best estimate and are in accord with the points obtained by the method just described; they pass through the experimental points of the present investigation (*i. e.*, are determined by them at the higher temperatures), and fall almost midway between the points of Pfeil and those of Jette and Foote in the vicinity of the eutectoid, which is taken at 560° in accord with the careful work of Emmett and Schultz.

Appendix: The Occurrence of Thermal Diffusion

A uniform mixture of gases (*e. g.*, CO_2 and CO) flowing through any apparatus which is not at the same temperature throughout, tends to become non-uniform in composition in each temperature gradient; in general, the heavier gas tends to move toward the cooler, the light toward the hotter zones. This phenomenon of thermal diffusion was first predicted by Enskog[22] and observed in 1917 by Chapman and Dootson.[23] Emmett and Schultz[6] discussed at length its bearing on the results of measurements, by the static method, of the equilibrium H_2O–H_2–Fe–wüstite, in which case the error introduced in some reported H_2O/H_2 ratios was as great as 40%. It is interesting to compare the composition inequality due to thermal diffusion as measured by us (Table I) with that derived from theoretical considerations, particularly as the latter bring out the fact that in such work upward flow of the gas mixture (through a vertically mounted tubular furnace) is decidedly preferable to downward flow when it is desirable to minimize the composition inequality of the gas.

If the effect of convection is ignored, the steady state of a gas mixture (*e. g.*, CO_2 + CO) flowing through a (one-dimensional) thermal gradient may be mathematically formulated by equating the total mols of one species (CO) passing a unit plane per unit time to the sum of the mols transported across this plane by flow and by diffusion. Thus (after dividing through by mols per cm. of length)

$$rN_0 = rN + D\left[\left(\frac{dN}{dx}\right)_{r=0} - \frac{dN}{dx}\right]$$

where r = linear rate of flow of gas mixture
N = % CO at distance x
N_0 = % CO at inlet (and outlet)
D = diffusivity (of CO)

The composition gradient dN/dx due to thermal diffusion at zero flow at T (absolute temperature at distance x) is

$$\left(\frac{dN}{dx}\right)_{r=0} = k_T\frac{d\ln T}{dx} \quad \text{where}$$

k_T = coefficient of thermal diffusion at T

Qualitative deductions from this equation (as to position of maximum, etc.) combined with the experimental data of Table I allow a fair estimate to be made of the concentration at other points below the center of the furnace tube. Between center and top of the tube, convection appears to play the dominating role. The heavy curve of Fig. 10 represents the estimated variable composition, along the length of the furnace tube (highest temperature 1100°), of a CO_2–CO mixture flowing upwards at a rate of 0.2 cm./sec. (at room temperature and pressure). The rather unexpected form of the curve is most easily interpreted by reasoning backward from the outlet, at which, when a steady state has been attained, gas must be of the same composition as the inlet gas (provided that there is no leak or reaction). Thermal diffusion tends to heap up carbon monoxide at the center of the furnace; this tendency is opposed by convection, since the colder, heavier gas is above the lighter gas of the central zone. Below the center thermal separation is much greater since there is but little convection, the result being a marked impoverishment of carbon monoxide at the level of the furnace bottom; below this the temperature gradient is small, thermal diffusion is negligible; and ordinary diffusion is incapable of transporting an appreciable amount of gas more than a few centimeters against this rate of flow. At a very slow rate, or if the inlet capillary extends to near the bottom of the fur-

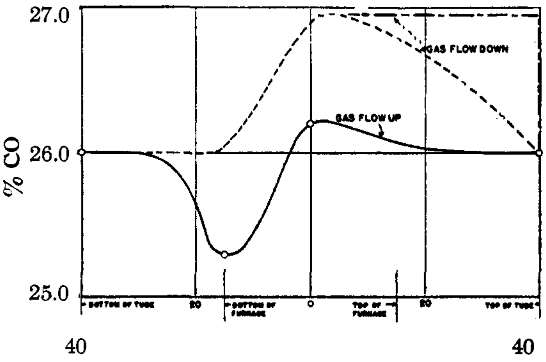

Fig. 10.—Thermal separation of CO_2–CO mixtures in vertically mounted tubular furnace; inside diameter 1.3 cm., hottest zone 1100°, linear rate of flow 0.2 cm./sec at room temperature and pressure. (The center point shown is interpolated from the data of Table I; the bottom point is taken directly from the data of that table.) When the gas is flowing up the composition is indicated by the full line; flowing down by a dashed line and for the limiting case of very rapid convection above the furnace center by the dash-dot line.

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(22) D. Enskog, "Kinetische Theorie der Vorgänge in Mässig verdünnten Gasen," Inaug. Dissertation, Upsala, 1917.

(23) Chapman and Dootson, *Phil. Mag.*, **33**, 248 (1917).

nace, the gas composition at the lower end of the furnace tube will not be identical with that delivered by the inlet.

If the flow is reversed so that the mixture flows downwards through the furnace, similar reasoning leads to a distribution shown approximately by the dashed curve of Fig. 10. A single experiment indicated that the difference between the composition at the center and at the inlet was several times as great as with the normal upward flow. The dash-dot line shows the composition under the limiting condition of very fast convection above the center of the furnace.[24]

If the temperature gradient be idealized as constant, the rate of flow be set proportional to T, and the diffusivity to T^2, the foregoing differential equation reduces to

$$\frac{\mathrm{d}N}{\mathrm{d}\ln T} = k_{\mathrm{T}} + \frac{r_0T_0}{aD_0}(N - N_0)$$

where a is the temperature gradient, T_0 is 273° K., and r_0 and D_0 are the values of r and D at 273°K. Integrating from the values of N and T at the bottom of the furnace (subscript 1) to the corresponding values at the center (subscript 2) yields the expression:

$$\frac{aD_0}{r_0T_0}\log\frac{k_{\mathrm{T}} + \dfrac{r_0T_0}{aD_0}(N_2 - N_0)}{k_{\mathrm{T}} + \dfrac{r_0T_0}{aD_0}(N_1 - N_0)} = \log\frac{T_2}{T_1}$$

At rates of flow sufficiently great that the separation is small compared to that at zero rate this expression reduces approximately to

$$k_{\mathrm{T}} = \frac{r_0T_0}{aD_0}(N_0 - N_1)$$

Setting, a = 60°/cm., D_0 = 0.14 cm.^{2}/sec. and taking r_0 $(N_0 - N_1)$ as 0.0013 cm./sec. (mean value of the product in the upper part of the third column of Table I, expressed as volume fraction of carbon monoxide instead of % as tabulated) gives k_{T} = 0.042.

Ibbs and Underwood[25] find k_{T} to have identical values for CO–CO_2 mixtures as for N_2–CO_2 mixtures between 10 and 100° (k_{T} having the value 0.010 at 25% CO_2). Ibbs and Wakeman[26] find that values of k_{T} for N_2–CO_2 mixtures increase markedly at a temperature near 145°—this increase being attributed to a change in the carbon dioxide molecules; hence k_{T} for CO–CO_2 mixtures probably behaves similarly. The value of k_{T} nearly always increases slightly with temperature so that the value 0.04 estimated from the data of Table I is not at all unreasonable as an average value between 200–900°. This rough agreement tends to substantiate the interpretation previously given that thermal separation of a gas mixture flowing in this vertical tubular furnace may be accounted for by considering only non-turbulent flow and diffusion in the bottom half of the furnace; turbulence and convection play a major role only in the top half.

Summary

By measuring the temperature corresponding to the position of the sharp boundary between phases produced by holding a strip of iron or iron oxide in a known small temperature gradient in contact with a gas of definite composition, the CO_2/CO ratio in equilibrium with iron and wüstite was obtained at temperatures from 1038 to 1365°, and that in equilibrium with wüstite and magnetite from 1096 to 1388°. Between these boundaries the composition of wüstite in equilibrium with various gas mixtures was determined, and that at the boundaries derived by short extrapolation at constant temperature to the gas compositions at these points.

From these measurements the activities of iron and FeO in wüstite have been calculated, and therefore the activity of any other iron–oxygen complex is available. The partial molal heat of solution of oxygen and of iron in wüstite, as well as the heat of formation of wüstite, is recorded at various compositions. The heat of formation of magnetite has been computed to be −260,930 cal. at 1250° and −267,200 cal. at 25°, in excellent agreement with the best calorimetric values.

Kearny, New Jersey Received April 4, 1945

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[24] This conclusion may appear rather startling at first thought, however the apparent discrepancy between this and preconceived notions about the behavior of the system may be eliminated by consideration of the following analogy: consider a tank with two inlets (delivering different materials, *e. g.*, water and alcohol) and one outlet; if the liquid in the tank is very well stirred then there will be discontinuities in the composition of the liquid at each of the two inlet mouths but there will be no such discontinuity at the outlet, and consequently it is easier to reason backward from the outlet as was done in the discussion. Now consider the cool head of the furnace as the tank; gas enters this head by (1) the inlet capillary, and (2) from the hot zone of the furnace (by convection) and leaves by one outlet which in this case is identical with inlet no. 2. If stirring (convection) is vigorous then the composition will be uniform in this zone and there will be a discontinuity in composition at the mouth of the inlet capillary. If on the other hand convection is negligibly small then the half of the dashed curve to the right of the furnace center would be nearly the mirror image of the left half. In the actual case convection is neither very vigorous nor negligibly small and the actual curve lies somewhere between these two limiting positions. The dashed curve shown represents one of the many possible ways the composition could vary at points intermediate between the thermal center of the furnace and the inlet capillary.

[25] T. L. Ibbs and L. Underwood, *Proc. Physics Soc.*, **39**, 327 (1927).

[26] T. L. Ibbs and A. C. R. Wakeman, *Proc. Roy. Soc.* (London) **A134**, 613 (1932).