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A THERMODYNAMIC STUDY OF THE WÜSTITE PHASE

by

R. J. Ackermann and R. W. Sandford, Jr.

RELEASED FOR ANNOUNCEMENT
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ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60439

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THE WÜSTITE PHASE

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R. J. Ackermann and R. W. Sandford, Jr.*

Chemistry Division

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September 1966

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*On temporary leave from Carleton College,
Northfield, Minnesota. Present address:
Dept. of Chemistry, The University of
Kansas, Lawrence.

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A THERMODYNAMIC STUDY OF THE WÜSTITE PHASE

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I. INTRODUCTION

In high-temperature chemistry, a most extensively studied problem has been the characterization of the vaporization behavior of refractory metal-oxygen systems. The characterization of the vaporization behavior involves not only the identification of the various vapor species over a condensed phase, but also the determination of the change in the free energy, enthalpy, and entropy that accompany vaporization. From the measured change in these quantities and known values for the condensed phase, the standard free energies, enthalpies, and entropies of formation of the vapor species may be evaluated, and hence, the bonding trends in metal oxides may be elucidated.

The problem that has complicated the thermodynamic analysis of almost every vaporization study of a refractory material is the uncertainty over the composition of the condensed phase due to its deviation from known stoichiometry at the high temperatures necessary to produce measurable vaporization. The phenomenon of nonstoichiometry enters into the characterization of the vaporization behavior of refractory materials, including nuclear fuels, because the concentration of a particular vapor species in many cases depends markedly on the composition of the condensed phase. The uranium-oxygen¹⁻³ and plutonium-oxygen⁴ systems are illustrative.

Since most of the thermodynamic, especially calorimetric, data in the literature involve nearly stoichiometric compounds, and since in most cases at high temperatures the condensed phase may be grossly nonstoichiometric (e.g., UO_{2+x} and PuO_{2-x}), the free energies of formation for the vapor species cannot be evaluated accurately unless the free energy of the condensed phase is known as a function of composition. This study is intended to extend a conventional equilibration method by a more precise knowledge of the experimental variables in order to determine the thermodynamic properties of any composition of a metal oxide from partial molar free energies of oxygen, the Gibbs-Duhem equation, and the calorimetrically determined value of the standard free energy of formation for a known composition of the phase.

In this investigation, it was desirable to choose a metal-oxygen system for which some thermodynamic data are available but which need

further amplification in order to clarify many existing discrepancies. Iron, which is a transition metal, possesses more than one valence state and, hence, forms nonstoichiometric oxides, the most studied of which is wüstite (FeO_{1+x}). Actually, the compound should be expressed as Fe_{1-x}O , since it appears that the metal atoms are deficient.⁵ However, in this work the usual convention of considering one mole of iron in the formula has been adopted. Many investigators have studied the iron-oxygen system, particularly the FeO_{1+x} region. Nevertheless, a clear understanding of the system demands yet further study, especially at temperatures less than 1000°C , because of numerous discrepancies in previous studies and because of the current use of an iron-wüstite electrode as a standard for the high-temperature, solid-galvanic-cell determinations of the partial molar free energy of oxygen in nonstoichiometric metal oxides.⁶

By applying the phase rule,

$$F + P = C + 2, \quad (1)$$

to the homogeneous FeO_{1+x} phase, one concludes that this phase possesses two degrees of freedom ($F = 2$). This follows from the fact that C , the number of components (Fe and O_2), and P , the number of phases (wüstite and vapor), are both two. Since, for any macroscopic chemical system, the three possible variables are pressure, temperature, and composition, the application of the phase rule to the FeO_{1+x} phase necessitates the control of two of the three possible variables in order to fix all properties of the system.

Phases of variable composition such as wüstite possess distinct upper and lower phase boundaries. It is generally agreed that the wüstite phase never has the ideal stoichiometric composition FeO , but is, in fact, superstoichiometric even at the lower phase boundary. This behavior is attributed to random vacancies in the iron sublattice of the rock-salt structure. Offroy and Aubry⁷ and Barbi⁸ compared previous results concerning the phase limits of the field of stability. The results in general indicated a greater dependence of the upper phase boundary on the temperature. The relatively insensitive dependence, or lack of dependence, of the lower phase boundary on the temperature enhances the usefulness of the iron-wüstite electrode as a standard. Unfortunately, however, previous investigators do not agree concerning the location of the phase boundaries and the critical temperature below which the wüstite phase is unstable and disproportionates to iron metal and magnetite (Fe_3O_4).

The work of Darken and Gurry⁹ is generally accepted as the most conclusive study of the iron-oxygen system. Darken and Gurry experimentally determined the dependence of the composition and the partial pressure of oxygen of the upper and lower phase boundaries of the FeO_{1+x} phase on the temperature. They determined the oxygen pressures in

equilibrium with the upper and lower phase boundaries by heating a strip of iron in a controlled CO-CO₂ atmosphere in a fixed temperature gradient. The strip oxidized, and a sharp visual boundary appeared between the two coexisting phases that formed. Darken and Gurry determined the final temperatures at the phase boundaries by visual examination of the position of the boundaries in this subsequently measured temperature gradient. The study of the FeO_{1+x} phase involved the determination of the composition after the samples were quenched from various temperatures and CO-CO₂ gas mixtures.

The principal inadequacy of Darken and Gurry's study is the deduction of the behavior of the wüstite phase at lower temperatures from measurements carried out at 1050 to 1400°C. In the extrapolation of the phase boundaries to lower temperatures, the quantity $\log p_{\text{CO}_2}/p_{\text{CO}}$ was assumed to be a linear function of $1/T$. We have proved this assumption to be incorrect.

Darken and Gurry may also have encountered some difficulty, as they have discussed, in visually determining the location of the phase boundaries in the temperature gradient. In doing so, they quenched the sample, and subsequently found on some occasions that some FeO_{1+x} converted to Fe₃O₄. Also, Darken and Gurry noted that platinum may have had a solvent effect on iron by reducing the activity of iron at temperatures above 1100°C. Since our sample container was platinum, we remained aware of this possible difficulty even though all measurements were carried out below 1100°C.

Ariya *et al.*¹⁰ also determined the composition of the FeO_{1+x} phase as a function of the oxygen pressure and the temperature. To establish the pressure of oxygen, they also used CO-CO₂ gas mixtures. Their results are inadequate for two reasons. First, the ratio of $p_{\text{CO}_2}/p_{\text{CO}}$ was obtained from absorption of the CO₂ by alkali and from absorption of the CO in an ammoniacal solution of Cu₂Cl₂. Since this process would appear to be rather time-consuming, Ariya *et al.* measured only ten experimental points (ten different $p_{\text{CO}_2}/p_{\text{CO}}$ ratios); hence, they failed to fully characterize each isotherm, especially the precise position of the phase boundaries. Second, data are given at only two temperatures, 1182 and 1104°K, which are not widely separated. These investigators also used a plot of the compositions of the upper and lower phase boundaries (mole percent CO₂ gas at the phase boundaries) vs temperature to try to determine the temperature at which wüstite disproportionates to iron and magnetite (Fe₃O₄). At the minimum temperature of stability, the compositions of the upper and lower phase boundaries become equal. However, the data are inadequate because they consist of only two sets of values of the phase boundaries, both at temperatures widely separated from the transition temperature. Ariya *et al.* also assumed the phase boundaries are linear functions of the temperature. Previous studies, as well as the present one, demonstrate that such an assumption is not warranted.

Barbi⁸ investigated the stability of wüstite below 1000°C by means of emf measurements with solid galvanic cells. He determined the values of the upper and lower phase boundaries are from 569 to 1000°C. Barbi compared the emf values found experimentally with values calculated by assuming a random athermal mixing of neutral iron atoms and octahedral holes in the magnetic structure. Unfortunately, he did not convert the emf data to partial molar quantities; he was therefore unable to make a direct comparison with the previous results.

Racchah and Vallet¹¹ measured the partial pressures of oxygen in equilibrium with wüstite in the range of 820 to 1250°C. At 920 to 1250°C, they found close agreement between their values and those reported by Darken and Gurry.⁹ Racchah and Vallet expressed the partial pressure of oxygen in equilibrium with wüstite by equations of the form, $\log p = Mx + N$, in which x is the atom ratio of oxygen to iron, and M and N depend only on the temperature and have been expressed by linear functions of reciprocal temperature.¹² However, at 820-920°C, Racchah and Vallet¹¹ reported two different sets of M and N values, depending on whether the composition of the sample in the range $O/Fe = 1.068$ to 1.106 was approached from a lower or a higher composition. That is, the dependence of $\log p_{O_2}$ on the composition within the so-called wüstite field is described by two linear segments. Racchah and Vallet¹¹ interpreted these findings to demonstrate the existence of two varieties of wüstite, the one being somewhat richer in oxygen than the other. Vallet and Racchah¹³ subsequently enlarged their interpretation to include a third variety of wüstite. Therefore, these investigators suggested that the so-called wüstite field is not a single homogeneous phase below 900°C, but rather a mixture of three.

The results of Barbi⁸ on the contrary, show no nonhomogeneity within the wüstite field, since the partial molar free energy of oxygen, which is calculated from the measured emf's of the cell, shows a linear dependence with composition at 700, 800, and 900°C.

Therefore, it appears necessary to conduct a comprehensive examination and redetermination of the thermodynamic properties of wüstite in order to gain further insight into the behavior of this phase, and thereby to contribute a critical analysis of the accuracy of the previous efforts. The successful correlation of thermodynamic properties with the microstructural aspects of many transition-metal oxides is yet a future conquest for high-temperature chemistry.

The immediate goals of the present study are to determine: (1) the precise location of the wüstite phase boundaries, (2) the precise dependence of the partial pressure of oxygen on the temperature and composition of the solid phase, and (3) the concentration of effort in a range of 950 to 1300°K, where the behavior appears most interesting, as was suggested by the work of Vallet and Racchah.¹¹⁻¹³ The present investigation has been initiated with the confidence that the simultaneous determination of the variables temperature, pressure, and composition is superior to those of previous studies.

II. EXPERIMENTAL PROCEDURE

To determine the partial pressure of oxygen over a known composition of wüstite at a given temperature, a system was devised for controlling and determining the three experimental variables of the macroscopic system (the pressure of oxygen, the temperature, and the composition of the solid phase). As was shown above by the use of the phase rule, the wüstite phase has two degrees of freedom. Thus when any two of the three variables are controlled, the third is fixed. The experiment was designed in the conventional manner to control the pressure of oxygen and the temperature, and to determine the composition of FeO_{1+x} as a function of these controlled variables.

A. Pressure of Oxygen

At 900-1300°K, the pressure of oxygen over FeO_{1+x} is very small, of the order of 10^{-13} to 10^{-22} atm, which precludes the possibility of controlling the pressure of oxygen directly. Therefore, the equilibrium between CO and CO_2 has been utilized to control indirectly the oxygen pressure in the system and can be expressed as

The expression

$$P_{\text{O}_2} = \left(\frac{P_{\text{CO}_2}}{P_{\text{CO}}} \cdot \frac{1}{K_2} \right)^2 \quad (3)$$

shows the dependence of the oxygen pressure on the ratio $P_{\text{CO}_2}/P_{\text{CO}}$ and on the equilibrium constant K_2 . From the tables of thermodynamic constants in JANAF,¹⁴ K_2 was determined from the equation

$$\log K_2 = \log K_f^\circ(\text{CO}_2)_g - \log K_f^\circ(\text{CO})_g \quad (4)$$

as a function of temperature from a least-squares plot of $\log K_2$ vs $10^4/T$ (T in °K). The result is given by Eq. I-1 in Table I.

The ratio $P_{\text{CO}_2}/P_{\text{CO}}$ was controlled by a system of gas flowmeters, which independently measured the flowrates of the CO_2 and CO gases and then mixed the gases in the same ratio as the ratio of their individual flowrates, as shown by the relationship,

$$\frac{P_{\text{CO}_2}}{P_{\text{CO}}} = \frac{\text{flowrate CO}_2}{\text{flowrate CO}} \quad (5)$$

TABLE I. Least-squares Equations* and Errors Pertinent to the Measurement of Weight, Temperature, and Gas Composition

$$\text{Log } K_2 = -4.4567 + 1.4607 \left(\frac{10^4}{T} \right) + 7.2032 \times 10^{-4} \left(\frac{10^4}{T} \right)^2 \quad (\text{I-1})$$

$$\frac{V}{T} (\text{CO}) = 8.5927(\Delta h) - 0.060625(\Delta h)^2 \text{ (cm}^3/\text{min)} \quad (\text{I-2})$$

$$\frac{V}{T} (\text{CO}_2) = 5.1779(\Delta h) - 0.012746(\Delta h)^2 \text{ (cm}^3/\text{min)} \quad (\text{I-3})$$

$$\Delta(\text{millivolts from absolute}) = (8.861 - 2.386 \text{ mV}_{\text{meas.}}) 10^{-3} \quad (\text{I-4})$$

$$\Delta W = 32.581(\Delta \ell) + 0.012669(\Delta \ell)^2 \text{ (mg)} \quad (\text{I-5})$$

Variable	Standard Deviation	Variable	Standard Deviation
$P_{\text{CO}_2}/P_{\text{CO}}$	$<\pm 0.01$	$T, ^\circ\text{K}$	± 1.0
O/Fe	± 0.002	$\Delta \bar{G}_{\text{O}_2}, \text{kcal}$	± 0.020

*Since these least-squares equations (as well as all other least-squares equations in this report) were used for further calculations, significant figures are not adhered to in the coefficients. Instead, all quantities calculated from these equations were ultimately rounded off to the proper number of significant figures.

Figure 1 is a diagram of the gas meter system. The commercial analytical-grade gas ($>99.5\%$ pure) enters through a Hoke needle valve, is

Fig. 1. Gas Flowmeter for $p_{\text{CO}_2}/p_{\text{CO}}$ Determination

dried in a column of magnesium perchlorate, and flows through a capillary, thereby creating a pressure differential across the manometer. A bubbler immersed in oil allows excess gas to escape; this minimizes fluctuations in the gas differential. After passing through the respective capillaries, the gases flow into a mixing tube filled with glass beads, and the mixture then flows through a final meter, which measures the total flow of mixed gases.

The gas meters were calibrated by determining, for a given capillary, the gas flowrate vs the differential (Δh) of the liquid levels in the manometer. The rates of gas flow were measured for various values of Δh ; then a least-squares equation as calculated for each capillary (Table I, Eqs. I-2 and I-3) so that for any Δh , the gas flowrate and hence the $p_{\text{CO}_2}/p_{\text{CO}}$ ratio could be calculated.

Two methods were needed for calibrating the meters and capillary tubes, depending upon the magnitude of the gas flow. For very small flowrates, a soap-bubble method proved best. A soap bubble was introduced into a horizontally positioned burette, which was attached to the outlet end of the flowmeter. The gas flow forced the bubble through the burette thereby sweeping out a measured volume of the burette in a known time, which was conveniently measured with a stopwatch. For flowrates greater than 20 cc/min, a wet-test flowmeter, manufactured by the Precision Scientific Co., was used.

The first flowmeter was calibrated using CO gas. Since CO_2 is highly soluble in water, and both calibration methods involved the use of water, CO_2 could not be used to calibrate the second flowmeter. Instead, this meter was calibrated with CO, and the flowrates were corrected to that of CO_2 by the use of Poisseuilles' law,

$$\frac{dV}{dt} = \frac{(P_1^2 - P_2^2) R^4}{16\ell\eta P_0}, \quad (7)$$

in which dV/dt is the flowrate, η is the viscosity, and $(P_1^2 - P_2^2) R^4/16\ell P_0$ are terms related to the geometry and pressure differential of the capillary. Since the geometry factor is the same for all gases, one obtains for a given pressure differential the relationship

$$\frac{\left(\frac{dV}{dt}\right)_1}{\left(\frac{dV}{dt}\right)_2} = \frac{\eta_2}{\eta_1}, \quad (8)$$

which relates the flowrates of the two gases to the ratio of their viscosities. As a check on the applicability of Poisseuilles' law to this system, argon and nitrogen were also used as calibration gases. The flowrates of argon and

nitrogen that were corrected by Eq. 8 to give the flowrate of CO, agreed within a very small experimental error ($\pm 0.2\%$) with the actual measured flowrate of CO.

As an independent check on the calibration of the flowmeters, and also on the consistency of the mixing and the purity of the gases, many samples of various CO-CO₂ mixtures and several pure samples were collected and subsequently analyzed with a mass spectrometer. The agreement between our calibration results and the mass-spectrometric results was $\leq \pm 1\%$. The major gas contaminants (water vapor, nitrogen, and oxygen) were quite insignificant.

The great advantage to this gas meter system was that the pressure of one gas could be varied independently of the other. Thus, any gas ratio, as well as any total flow desired (within the range of the capillaries), could be obtained by adjustment of the two Hoke valves at the inlet of the meters.

Once obtained, the gas mixture (pressure slightly greater than atmospheric) was flowed through the Morganite (dense recrystallized Al₂O₃)

Fig. 2. Schematic Diagram of Furnace and Quartz Helix Balance

tube in which the container and sample were suspended from a quartz helix balance and were heated to a constant temperature. A schematic diagram of the furnace and balance is shown in Fig. 2. Before the introduction of the sample, all parts of the gas flow system were out-gassed, and all joints were sealed to prevent contamination of the CO-CO₂ mixture by air.

A potential problem in relation to the flow of mixed gases through the heated Morganite tube is thermal segregation of the components in a temperature gradient due to their different molecular weights. In general, the heavier gas tends to move toward the cooler region and the lighter gas toward the warmer region of a thermal gradient such

as occurs over the entire length of the Morganite tube. This means that the CO should collect preferentially near the hotter middle of the tube, and the CO₂ near the cooler ends. Thus, the gas ratio actually influencing the sample may not be the same as that determined by the meters at constant room temperature.

To eliminate thermal segregation, two precautions were taken. First, the flow of gas through the small volume (less than 1 liter) of the Morganite tube was maintained in excess of 5 liters/hr.

Fig. 3. Schematic Diagram of Furnace

To determine the composition of the gas after it had passed over the sample, and as a check against both thermal segregation and possible impurities in the system, gas samples were collected at the outlet port just below the condenser. In all cases the composition of the outlet gas was within $\pm 1\%$ of that of the inlet gas. In addition, no new impurities were discovered. Thus, thermal segregation and outgassing do not seem to have presented any problems.

B. Temperature

It was desirable to control the temperature of the sample to within $\pm 1^\circ$ of a chosen temperature between 900 and 1300°K. Since the container and the sample were to be suspended vertically from a helical balance, the vertical position of the container and sample would change with variation in the sample composition in accordance with the gain or loss of weight.

Secondly, a device for promoting additional turbulence was positioned into the inlet end of the Morganite tube shown in Fig. 3. This device, a series of platinum disks, approximately 1/2 in. apart, separated by small Morganite sections, extended to just below the sample. Since the gas was forced to take a restricted annular path around the disks through the lower column, the gas had a much greater overall velocity at the restrictions. Consequently the flow of gas was sufficient to create a noticeable oscillation of the sample in the balance.

Hence a convenient control of the temperature of the sample required the maintenance of a constant temperature not only for an indefinite time but also over a finite vertical distance. Very large changes in weight were compensated for by raising or lowering the adjustable balance support shown in Fig. 2.

A Marshall furnace equipped with a platinum-10% rhodium winding (as shown in Fig. 3) was used. The furnace itself consists of a Morganite tube around which the heating wire is wound. The tube and wire are surrounded by alumina powder and enclosed in a stainless-steel case. The furnace winding is separated into nine independently controlled segments by means of isolation transformers. The primary of each transformer is connected to a variac so that by adjustment of the variacs, and hence the current in the secondary to the nine parts of the heating element, a constant temperature ($\leq \pm 1.0^\circ\text{K}$) could be maintained over a 4-in. vertical distance in the middle of the furnace.

To maintain the temperature at a constant value indefinitely, a Wheelco Magnetic Modulator Current Type Controller, combined with a Wheelco Saturable Power Reactor, Galvanometer, and Pilot Amplifier, was used. This control system works as follows: For each temperature, the bucking-voltage supply on the controller is set at the emf that is produced at a desired temperature by a platinum-platinum 10% rhodium thermocouple positioned at the center of the furnace. When the temperature of the furnace is such that the emf of the thermocouple just equals the bucking emf of the controller, there is no change in the net flow of current through the furnace winding. When an imbalance between the thermocouple and the bucking emf occurs, the controller adjusts the current flow to the variacs and, hence, into the furnace, to compensate for this imbalance.

Three auxiliary controls (the proportional band, rate time, and reset) regulate the efficiency and the cycling characteristics of the controller. The rate time and reset together determine the number of times per minute the controller senses or "looks for" an error signal. The more times per minute the controller checks this error signal, the less is the chance for a wide deviation from a constant temperature. If the controller checks for an error current too often, however, cycling will occur because the controller will sense a small error current, overcompensate for it, and hence cause an error current in the opposite direction. Thus, the rate time and reset must be set at the values that give the maximum number of controller checks with a minimum amount of cycling.

The third auxiliary control, the proportional band, determines the capacity with which the controller responds to compensate for an error current and hence temperature change. In effect, the proportional band is a voltage divider. Thus, when set too high, the proportional band allows the controller to sense only a part of the error current, and the controller's

response is slow. When the proportional band is set too low, the controller senses nearly all the error current and responds much more quickly.

With the proper adjustment of these three controls (the rate-time, reset, and proportional band), a constant temperature could be obtained to within $\pm 0.5^\circ\text{K}$. The combination of the controller with the system of isolation transformers and variacs made it possible to maintain this constant temperature with a gradient $\leq 1.0^\circ$ up to a 4-in. vertical distance in the central section of the furnace.

The most fundamental aspect of temperature measurement is the exact determination of the absolute temperature. A Sargent Model TR recorder, a potentiometer, and two calibrated thermocouples were used for this purpose. Two platinum-platinum 10% rhodium thermocouples were placed $1\frac{1}{2}$ in. apart, each $\frac{3}{4}$ in. from the center of the constant-temperature region, on the outside of the Morganite tube in which the sample was suspended. The position of the sample container was adjusted so that it was always suspended between the thermocouples, and hence, always in the center of the constant-temperature region. The thermocouples were calibrated at the freezing points of Pb, Sn, Zn, Al, Ag, and Cu. A correction curve was constructed, and a least-squares equation used to correct the measured emf's (see Eq. I-4, Table I). The two thermocouples were constructed from the same material, and the maximum correction was 2° at the copper point. The recorder was used only to monitor the constancy of temperature with time and to determine quickly any difference between the two thermocouples. The emf's were measured with a Leeds and Northrup No. 8662 potentiometer, and the appropriate corrections applied.

One problem in the exact determination of the temperature is whether the temperature measured by the thermocouples on the outside of the Morganite tube is the same as the temperature on the inside of the tube where the sample is located, and also where there is a flow of gas that could cool the inside of the tube relative to the outside. Because of the thinness of the Morganite tube (approximately 3 mm), there appears to be no significant temperature gradient between the inside and the outside of the tube. Also, the flow of gas presents no real problem because the width of the constant-temperature region ensures that the gas is already heated to the temperature of the sample region before the gas reaches the sample.

C. Composition of the Iron Oxide

As has been stated from the phase rule, the exact composition of the oxide is a function of both the temperature of the oxide and the partial pressure of oxygen over the oxide. In this experiment, the composition of the oxide was fixed by controlling the temperature and the CO-CO₂ mixture. The remaining problem then becomes one of determining the exact composition of the oxide. For this purpose two quantities were needed: first, the

change in weight of the oxide as the temperature and/or the partial pressure of the oxide are changed; second, the initial composition and weight of the oxide.

To determine the change in weight of the oxide, the quartz helical balance shown in Fig. 2 was used. The balance has a maximum capacity of 650 mg. The balance was fastened to a movable brass rod, so that it could be raised or lowered to position the sample near the center of the constant-temperature zone. To minimize changes in sensitivity, the balance was kept at constant temperature ($16^{\circ}\text{C} \pm 1^{\circ}$) throughout the calibration process and the experiment by flowing tap water through the surrounding condenser.

The balance was calibrated by determining the change in length of the helix by means of a cathetometer focused on the balance pointer (located just below the helix) as various class S weights were placed on a small quartz pan attached to the helix by means of a quartz rod. A least-squares equation of the form $\Delta W = B(\Delta \ell) + C(\Delta \ell)^2$ (where ΔW = change in weight and $\Delta \ell$ = change in length) was obtained for the weight on the balance vs the extension of the balance. The numerical form of the equation is given in Table I by Eq. I-5.

The starting material used to prepare the wüstite samples was analytical grade Fe_2O_3 , which had been heated in air in a platinum crucible at $980 \pm 10^{\circ}\text{C}$ for at least 18 hr and then stored in a desiccator. Once prepared, part of the sample was finely ground, loaded into a platinum container, connected to the balance by means of a 0.002-in.-diam platinum 10% rhodium support wire, and lowered into the Morganite tube inside the Marshall furnace. The initial weight of the sample was determined on a Mettler semi-micro balance. Because the maximum load capacity of the spring balance was 650 mg, approximately 550 mg of sample were contained in a platinum container constructed from 0.0001-in.-thick platinum foil folded into the form of an open-end, right-cylindrical capsule, approximately 8 x 25 mm. The folded seams were spot-welded. The weight of the container and the support wire was approximately 80 mg.

The initial composition of the sample was determined by reduction of the remaining prepared oxide to pure iron in a platinum crucible in a stream of dry hydrogen at approximately 900°C for approximately 24 hr (sufficient time to guarantee a constant weight). From the initial weight of oxide in the platinum crucible, the final weight of iron after reduction, and the assumption that all the weight loss in the reduction process is oxygen, the initial composition of the oxide could be calculated. The accuracy of this assumption is confirmed by the analysis of the iron metal for trace amounts of oxygen by a sensitive fusion method.¹⁵ Only a few parts per million of oxygen were detected. In all cases, the composition of the starting material was $\text{Fe}_2\text{O}_3 \pm 0.003$.

Equilibration of the sample with a given partial pressure of oxygen at a known temperature resulted in a weight loss, since the initial oxide was Fe_2O_3 and the final oxide was FeO_{1+x} . The entire measured weight loss was attributed to loss of oxygen from the sample since the volatility of Fe(s) at the temperatures of interest was quite insignificant as calculated from available thermodynamic data.¹⁴

Hence, from the initial composition and weight of the sample $W_{\text{Fe}_2\text{O}_3}$ and the change in the weight of the sample ΔW , the exact composition of FeO_{1+x} could be determined from the following equations:

$$\frac{\Delta W \text{ (Eq. I-5)}}{W_{\text{Fe}_2\text{O}_3}} = \frac{[3 - 2(1+x)] 15.999}{159.691}; \quad (10)$$

$$1 + x = 1.500 - 4.991 \Delta W / W_{\text{Fe}_2\text{O}_3}. \quad (11)$$

Some relatively minor, but yet important aspects of the apparatus should be mentioned. The Morganite tube and balance-condenser assembly were securely fastened to a massive vertical steel beam in the laboratory to minimize movement and vibration, and thereby ensure that any change in length of the balance was due to a change in weight of the sample. To eliminate any errors in the balance measurements due to the movement of the cathetometer, the position of the cathetometer was periodically checked relative to a reference point on the beam. Also, to detect any movement that may have occurred in the balance-condenser assembly when the furnace was heated or its temperature changed, a reference point was established on the condenser near the point of the balance suspension. All initial reference points were corrected for any subsequent movement of the condenser and/or the cathetometer. The Morganite tube was cooled directly above the furnace by the air blast, preventing the passage of hot gases through the balance and the condenser. There were two gas outlets, one in the brass connector between the condenser and the Morganite tube, the other at the very top of the brass tube supporting the balance. The lower outlet was used only for collecting outlet gas samples; the upper outlet was used at all other times. By using the upper outlet, the flow of gas through the entire system minimized the accumulation of air inside the condenser, which could diffuse down the Morganite tube and possibly affect the pressure of oxygen over the sample. At the inlet end of the Morganite tube, a needle valve controlled the flow of gas through the tube. Because of the bouyancy and oscillation of the platinum bucket in the gas stream, the flow of gas had to be stopped momentarily while measurements were taken on the balance. Finally, in the positioning of the sample and bucket in the Morganite tube, the bucket had to be in the middle of the constant temperature zone, and the bucket had to be

hanging freely in the center of the tube, not touching the walls. This was checked visually before sealing the tower of platinum plates into the bottom of the tube, and was checked during the experiment by observing the free oscillation of the balance as the gas flow was quickly turned on and off. Thus the three variables necessary to characterize the wüstite phase were evaluated and controlled.

III. RESULTS

Isotherms of the ratio $p_{\text{CO}_2}/p_{\text{CO}}$ vs the composition of the FeO_{1+x} phase were constructed in the following manner: Initially, the Fe_2O_3 sample was placed in the proper position of the furnace, and all the reference points (cathetometer, condenser, and initial balance reading) were recorded. The sample was then heated to the desired temperature in air, and when the temperature was controlled and constant, the CO-CO_2 gas flow was begun. When the sample reached a constant weight, which is indicative of equilibrium between the sample and the pressure of oxygen determined by the $p_{\text{CO}_2}/p_{\text{CO}}$ ratio at that temperature, the composition of the sample was calculated by Eq. 11. Then the $p_{\text{CO}_2}/p_{\text{CO}}$ ratio was changed, and another equilibrium point determined. Once an isotherm had been thoroughly characterized and the phase boundaries well determined, the temperature was changed and another isotherm similarly constructed.

To minimize systematic errors and ensure that the experimental points were truly at equilibrium, the sample was randomly oxidized and reduced. That is, for a particular $p_{\text{CO}_2}/p_{\text{CO}}$ ratio, the equilibrium composition was approached both from a composition greater than (by reduction), and from a composition less than (by oxidation), the equilibrium composition. The results coincided, within experimental error.

The data for the isotherms taken at 1277, 1182, 1075, 1023, and 972°K are given in Tables II-VI, respectively. The quantities $p_{\text{CO}_2}/p_{\text{CO}}$, p_{O_2} , and O/Fe were calculated from Eqs. I-2, I-3, 3, and 11. The partial molar free energies of oxygen, $\Delta\bar{G}_{\text{O}_2}$, are given in the last column of each table. The standard deviations associated with each experimental quantity are summarized in Table I.

In the study of the 1182°K isotherm, the sample was completely reduced to iron when the CO_2 gas was inadvertently turned off overnight. This sample was subsequently reoxidized, and equilibrium points taken thereafter agree with those taken before the reduction. After the study of this isotherm, when samples had to be changed because the support wire broke, some of the iron had diffused through the wall of the platinum container during the reduction. However, the effect of the platinum on the activity of the dissolved iron must have been insignificant, since the points taken before and after the complete reduction to iron do agree.

A minor problem encountered in the study of every isotherm was caused by the sintering of the sample after its prolonged heating and use. This problem did not affect the results, but increased the time necessary to achieve equilibrium. The sintering problem could be alleviated if the sample was occasionally oxidized to the heterogeneous $\text{FeO-Fe}_3\text{O}_4$ system and subsequently reduced. Apparently the change in specific volume upon oxidation was sufficiently great to break up the sample and increase its surface area.

TABLE II. Experimental Data for Wüstite at 1277°K

M*	No.	$\frac{PCO_2}{PCO}$	PO_2 , atm	Δl , cm	O/Fe	O_2/Fe	$\Delta \bar{G}_{O_2}$, kcal
2	9	4.789	2.0361E-13	1.175	1.1396	.5698	-74.158
2	9	4.671	1.9367E-13	1.185	1.1365	.5682	-74.285
2	8	4.445	1.7537E-13	1.190	1.1350	.5675	-74.537
2	7	4.348	1.6785E-13	1.195	1.1335	.5667	-74.649
2	6	4.237	1.5940E-13	1.200	1.1319	.5659	-74.780
2	5	4.082	1.4795E-13	1.205	1.1304	.5652	-74.969
2	30	3.821	1.2964E-13	1.210	1.1289	.5644	-75.304
2	4	3.896	1.3478E-13	1.210	1.1289	.5644	-75.205
2	33	3.557	1.1229E-13	1.220	1.1258	.5629	-75.669
1	34	3.309	9.7203E-14	1.230	1.1227	.5613	-76.035
2	3	2.973	7.8461E-14	1.240	1.1197	.5598	-76.578
2	2	2.459	5.3687E-14	1.265	1.1120	.5560	-77.541
2	1	1.936	3.3294E-14	1.290	1.1043	.5521	-78.754
1	19	1.630	2.3593E-14	1.310	1.0982	.5491	-79.628
1	20	1.434	1.8263E-14	1.325	1.0936	.5468	-80.278
1	21	1.224	1.3299E-14	1.340	1.0890	.5445	-81.083
1	22	1.071	1.0195E-14	1.355	1.0844	.5422	-81.757
1	23	.878	6.8571E-15	1.380	1.0767	.5383	-82.764
1	24	.785	5.4774E-15	1.392	1.0729	.5364	-83.334
1	25	.713	4.5204E-15	1.400	1.0706	.5353	-83.821
1	26	.646	3.7134E-15	1.415	1.0680	.5330	-84.320
1	27	.495	2.1762E-15	1.445	1.0568	.5284	-85.676
1	28	.474	1.9942E-15	1.450	1.0553	.5276	-85.898
1	29	.439	1.7128E-15	1.460	1.0522	.5261	-86.284
1	31	.428	1.6298E-15	1.470	1.0491	.5245	-86.410
1	32	.422	1.5819E-15	1.475	1.0476	.5238	-86.486

*Method by which the point was obtained: 1 = reduction; 2 = oxidation.

**Plotted as one point in Fig. 6.

TABLE III. Experimental Data for Wüstite at 1182°K

M*	No.	$\frac{PCO_2}{PCO}$	PO_2 , atm	Δl , cm	O/Fe	O_2/Fe	$\Delta \bar{G}_{O_2}$, kcal
1	33	3.632	1.6415E-15	1.030	1.1912	.5956	-79.965
2	28	3.612	1.6231E-15	1.225	1.1327	.5663	-79.991
2	24	3.476	1.5029E-15	1.230	1.1312	.5656	-80.172
2	27	3.552	1.5696E-15	1.230	1.1312	.5656	-80.070
2	35	3.484	1.5099E-15	1.230	1.1312	.5656	-80.161
2	34	3.399	1.4373E-15	1.235	1.1297	.5648	-80.277
2	17	3.312	1.3651E-15	1.240	1.1282	.5641	-80.398
2	23	3.311	1.3639E-15	1.240	1.1282	.5641	-80.400
2	16	3.133	1.2213E-15	1.250	1.1252	.5626	-80.659
1	22	3.037	1.1475E-15	1.255	1.1237	.5618	-80.806
2	15	2.913	1.0555E-15	1.265	1.1207	.5603	-81.002
2	6	2.584	8.3099E-16	1.270	1.1192	.5596	-81.564
1	5	2.329	6.7476E-16	1.290	1.1132	.5566	-82.053
1	25	1.784	3.9610E-16	1.315	1.1057	.5528	-83.304
2	3	1.829	4.1647E-16	1.315	1.1057	.5528	-83.187
2	2	1.560	3.0282E-16	1.335	1.0997	.5498	-83.935
3	1	1.029	1.3175E-16	1.395	1.0817	.5408	-85.890
1	7	.676	5.6886E-17	1.440	1.0682	.5341	-87.863
2	14	.620	4.7856E-17	1.450	1.0652	.5326	-88.269
1	8	.571	4.0598E-17	1.460	1.0622	.5311	-88.655
1	9	.513	3.2803E-17	1.475	1.0577	.5288	-89.156
1	10	.480	2.8692E-17	1.490	1.0532	.5266	-89.470
2	13	.471	2.7604E-17	1.600	1.0202	.5101	-89.561

*Method by which the point was obtained: 1 = reduction; 2 = oxidation.

TABLE IV. Experimental Data for Wüstite at 1075°K

M*	No.	$\frac{PCO_2}{PCO}$	PO_2 , atm	Δl , cm	O/Fe	O_2/Fe	$\Delta \bar{G}_{O_2}$, kcal
1	39	2.942	3.5528E-18	1.240	1.1279	.5639	-85.834
1	40	2.890	3.4284E-18	1.270	1.1189	.5594	-85.910
2	28	2.667	2.9208E-18	1.275	1.1174	.5587	-86.252
2	27	2.528	2.6234E-18	1.280	1.1159	.5579	-86.481
1	41	2.427	2.4183E-18	1.285	1.1144	.5572	-86.655
2	22	2.508	2.5816E-18	1.285	1.1144	.5572	-86.516
2	26	2.466	2.4969E-18	1.285	1.1144	.5572	-86.587
2	20	2.084	1.7832E-18	1.298	1.1105	.5552	-87.306
2	19	1.869	1.4342E-18	1.315	1.1054	.5527	-87.772
2	18	1.675	1.1520E-18	1.330	1.1003	.5504	-88.239
1	42	1.479	8.9788E-19	1.340	1.0979	.5489	-88.772
2	33	1.263	6.5462E-19	1.355	1.0934	.5467	-89.447
2	17	1.236	6.2726E-19	1.360	1.0919	.5459	-89.538
1	10	1.122	5.1748E-19	1.365	1.0904	.5452	-89.949
1	30	1.046	4.4915E-19	1.380	1.0853	.5429	-90.252
1	11	.820	2.7636E-19	1.415	1.0754	.5377	-91.289
1	32	.817	2.7416E-19	1.415	1.0754	.5377	-91.306
1	12	.727	2.1738E-19	1.435	1.0694	.5347	-91.802
1	13	.645	1.7115E-19	1.455	1.0634	.5317	-92.313
1	14	.604	1.5015E-19	1.465	1.0604	.5302	-92.593
1	15	.535	1.1783E-19	1.490	1.0529	.5264	-93.110
1	37	.512	1.0777E-19	1.505	1.0484	.5242	-93.301

*Method by which the point was obtained: 1 = reduction; 2 = oxidation.

TABLE V. Experimental Data for Wüstite at 1023°K

M*	No.	$\frac{P_{CO_2}}{P_{CO}}$	P_{O_2} , atm	Δl , cm	O/Fe	O ₂ /Fe	$\Delta \bar{G}_{O_2}$, kcal
2	6	2.035	6.8560E-20	1.275	1.1088	.5544	-89.707
1	10	1.898	5.9654E-20	1.275	1.1088	.5544	-89.990
2	7	2.322	8.9258E-20	1.250	1.1164	.5582	-89.171
2	14	2.279	8.5974E-20	1.260	1.1134	.5567	-89.247
2	16	2.203	8.0354E-20	1.265	1.1113	.5559	-89.385
1	18	2.269	8.5214E-20	1.265	1.1118	.5559	-89.265
2	13	1.851	5.6718E-20	1.280	1.1072	.5536	-90.093
1	11	1.556	4.0099E-20	1.298	1.1017	.5508	-90.798
1	43	.899	1.3396E-20	1.375	1.0781	.5390	-93.027
2	5	1.638	4.4444E-20	1.300	1.1011	.5505	-90.589
2	3	1.443	3.4496E-20	1.310	1.0980	.5490	-91.104
1	4	1.134	2.1298E-20	1.340	1.0888	.5444	-92.084
1	12	1.010	1.6890E-20	1.360	1.0827	.5413	-92.556
1	1	.817	1.1059E-20	1.385	1.0750	.5375	-93.416
1	44	.754	9.4210E-21	1.395	1.0719	.5359	-93.742
1	2	.669	7.4238E-21	1.415	1.0658	.5329	-94.227
1	45	.674	7.5316E-21	1.420	1.0642	.5321	-94.197
1	46	.595	5.8761E-21	1.435	1.0596	.5298	-94.702
2	19	.559	5.1788E-21	1.445	1.0566	.5283	-94.959

*Method by which the point was obtained: 1 = reduction; 2 = oxidation.

TABLE VI. Experimental Data for Wüstite at 972°K

M*	No.	$\frac{PCO_2}{PCO}$	PO_2 , atm	Δl , cm	O/Fe	O_2/Fe	$\Delta \bar{G}_{O_2}$, kcal
2	11	1.837	1.7145E-21	1.325	1.1011	.5505	-92.360
2	23	1.808	1.6598E-21	1.335	1.0981	.5490	-92.423
1	24	1.787	1.6219E-21	1.345	1.0951	.5475	-92.467
2	6	1.672	1.4197E-21	1.345	1.0951	.5475	-92.724
2	7	1.770	1.5914E-21	1.345	1.0951	.5475	-92.504
2	5	1.535	1.1974E-21	1.350	1.0935	.5467	-93.053
2	4	1.401	9.9774E-22	1.355	1.0920	.5460	-93.406
1	10	1.297	8.5478E-22	1.365	1.0890	.5445	-93.705
1	12	1.284	8.3774E-22	1.368	1.0881	.5440	-93.743
2	3	1.256	8.0112E-22	1.370	1.0875	.5437	-93.830
2	2	1.157	6.8044E-22	1.380	1.0845	.5422	-94.145
1	13	1.081	5.9334E-22	1.388	1.0821	.5410	-94.410
2	18	1.007	5.1510E-22	1.405	1.0770	.5385	-94.683
1	1	1.004	5.1215E-22	1.405	1.0770	.5385	-94.694
2	22	.906	4.1724E-22	1.420	1.0725	.5362	-95.090
1	14	.943	4.5175E-22	1.420	1.0725	.5362	-94.936
1	15	.902	4.1324E-22	1.420	1.0725	.5362	-95.108
1	16	.791	3.1789E-22	1.440	1.0664	.5332	-95.615
1	17	.759	2.9267E-22	1.445	1.0649	.5324	-95.775
1	19	.697	2.4703E-22	1.465	1.0589	.5294	-96.102
1	20	.667	2.2627E-22	1.480	1.0544	.5272	-96.272
1	25	.660	2.2116E-22	1.495	1.0499	.5249	-96.316
1	21	.642	2.0987E-22	1.520	1.0423	.5211	-96.417
1	21	.637	2.0603E-22	1.550	1.0333	.5166	-96.453

**

*Method by which the point was obtained: 1 = reduction; 2 = oxidation.

**Plotted as one point in Fig. 10.

The lowest temperature employed in this study is 972°K because of practical complications produced by the reaction

As determined from the thermodynamic data in JANAF,¹⁴ the change in free energy for Reaction 12 is

$$\Delta G_{12}^\circ = 41,158 - 42.20T + RT \ln \frac{p_{\text{CO}}^2}{p_{\text{CO}_2}} \quad (13)$$

Equation 13 states that for a given temperature, there is a minimum $p_{\text{CO}_2}/p_{\text{CO}}$ ratio, below which $\text{C}(\text{s})$ will be precipitated. This will occur when $\Delta G_{12}^\circ \geq 0$. By fixing the total gas pressure at 1 atm, the minimum ratio $p_{\text{CO}_2}/p_{\text{CO}}$ that would prevent carbon precipitation was calculated as a function of temperature. The result is plotted in Fig. 4.

Fig. 4. Plot of Minimum Usable Ratio of $p_{\text{CO}_2}/p_{\text{CO}}$ vs Temperature

Reaction 12 explains the observations encountered in a series of measurements when the temperature was lowered below 972°K. Very soon thereafter, the sample would gain weight continuously even though it was in a reducing atmosphere and was expected to lose weight. This behavior can be explained by Fig. 4. Since the temperature was below 972°K and was, in fact, 900°K, and the $p_{\text{CO}_2}/p_{\text{CO}}$ ratio was less than two, carbon was being precipitated on the sample and its container.

This hypothesis was verified subsequently by placing the sample and container in hot aqua regia. After the sample was dissolved and the solution cooled, tiny carbon particles were floating on the liquid surface. Hence the use of a $\text{CO}-\text{CO}_2$ gas mixture for fixing the oxygen pressure is limited by the temperature and gas ratios permitted by Reaction 12.

The precise determination of the phase boundaries was the most time-consuming part of the experiment. The manner in which the exact position of the boundaries was determined is as follows: For $p_{\text{CO}_2}/p_{\text{CO}}$ ratios within the homogeneous FeO_{1+x} phase, the composition is

time-invariant once equilibrium is reached. However, for ratios above the upper, and below the lower, phase boundaries the composition is not time-invariant, but continues to change continuously due to the formation of either magnetite or iron at the upper or lower phase boundary, respectively. The boundaries were located then by a process of trial and error by finding the particular $p_{\text{CO}_2}/p_{\text{CO}}$ ratio that would result in an invariant behavior, but which if infinitesimally changed in the proper direction would cause the transformation of the sample to a heterogeneous system. The results for the phase boundaries are presented in Table VII and Fig. 5.

TABLE VII. Compositions and Thermodynamic Properties of the Upper and Lower Phase Boundaries of Wüstite

T, °K	O/Fe	O ₂ /Fe	$\Delta\bar{G}_{\text{O}_2}$	$\Delta\bar{G}_{\text{Fe}}$	$\Delta\bar{G}_f^\circ$
A. Upper Phase Boundary					
972	1.096	0.548	-92.643	-28.035	-50.906
1023	1.113	0.556 ₅	-89.289	-28.520	-50.247
1075	1.120	0.560	-85.800	-29.029	-49.408
1182	1.132	0.566	-79.937	-29.308	-47.607
1277	1.137	0.568 ₅	-74.092	-29.863	-45.894
B. Lower Phase Boundary					
972	1.054	0.527	-96.251	-26.088	-50.303
1023	1.056	0.528	-94.960	-25.438	-49.461
1072	1.052	0.526	-93.168	-25.011	-48.504
1182	1.054	0.527	-89.539	-24.061	-46.659
1277	1.052	0.526	-86.365	-23.147	-44.938

Fig. 5. Plot of Upper and Lower Phase Boundaries of Wüstite; Temperature vs Composition

In general, the lower phase boundary was located more rapidly than the upper phase boundary. Points near the lower phase boundary either equilibrated or reduced rapidly, so that in a short time (less than 1 hr) one could determine whether the lower phase boundary had been exceeded by a given $p_{\text{CO}_2}/p_{\text{CO}}$ ratio. On the other hand, the position of the upper phase boundary could be determined more precisely from the increasing slope of the isotherm; i.e., a given change in gas ratio produced a relatively small change in composition. For this reason, the upper phase boundary would appear to be the easier one to locate. Such was not the case, however, because of the relatively slow kinetics of oxidation. For some points, the sample took up to 18 hr either to achieve certainty of equilibration or continue to oxidize at noticeable

rate. Thus the trial-and-error process for locating the $p_{\text{CO}_2}/p_{\text{CO}}$ ratio for the upper phase boundary was somewhat tedious.

The slow rate of oxidation at the upper phase boundary relative to the rate of reduction at the lower phase boundary, may be explained qualitatively as follows: At the lower phase boundary, the outer surface of each particle is reduced first to iron. Since iron is much more dense than FeO_{1+x} (7.86 g/cc, compared to 5.7 g/cc),¹⁶ iron has a smaller specific volume. Thus the reduction process effectively opens the sample and allows the oxygen to leave by means of CO_2 by continually decreasing the volume of the sample surface. At the upper phase boundary, the FeO_{1+x} sample (again most likely on the outer surface of each particle) is oxidized to Fe_3O_4 . The Fe_3O_4 , being less dense (5.18 g/cc, compared to 5.7 g/cc)¹⁶ and thus having a greater specific volume than the FeO_{1+x} , effectively "covers" the outer surface of the sample and impedes the rate of gas flow into the sample.

IV. THERMODYNAMIC TREATMENT OF THE DATA

Once the isotherms have been thoroughly determined, the data must be interpreted thermodynamically to be of fundamental as well as practical value. That is, from the pressure of oxygen, the temperature, and the composition, the thermodynamic quantities including the free energy, enthalpy, and entropy are obtained.

The equilibrium pressure of oxygen over various FeO_{1+x} compositions is related to the partial molar free energy of oxygen, $\Delta\bar{G}_{\text{O}_2}$, by the equation

$$\Delta\bar{G}_{\text{O}_2} = 2.303 RT \log p_{\text{O}_2}. \quad (14)$$

Values of the partial molar free energies of oxygen for the experimental points are given in the last columns of Tables II-VI. In addition, Figs. 6-10 are isothermal plots of the partial molar free energy of oxygen vs composition in terms of the ratio O_2/Fe . Least-squares equations for $\Delta\bar{G}_{\text{O}_2}$ as a function of O_2/Fe are given in Table VIII, and for O_2/Fe as a function of $\Delta\bar{G}_{\text{O}_2}$ in Table IX. The errors in the coefficients are standard deviations.

From the knowledge of a partial molar thermodynamic quantity of one component of a two-component system and the Gibbs-Duhem equation,

Fig. 6. Plot of Partial Molar Free Energies of Oxygen and Iron vs Composition at 1277°K

Fig. 7. Plot of Partial Molar Free Energies of Oxygen and Iron vs Composition at 1182°K

Fig. 8. Plot of Partial Molar Free Energies of Oxygen and Iron vs Composition at 1075°K

Fig. 9. Plot of Partial Molar Free Energies of Oxygen and Iron vs Composition at 1023°K

Fig. 10

Plot of Partial Molar Free Energies of Oxygen and Iron vs Composition at 972°K

TABLE VIII. Least-squares Equations for Relative Partial Molar Free Energy of Oxygen

T, °K	$\Delta \bar{G}_{O_2} = A + B(O_2/Fe) + C(O_2/Fe)^2$ (kcal/mole)		
	A	B	C
972	1186.81 ± 296.06	-4941.27 ± 1099.51	4756.39 ± 1020.72
1023	328.269 ± 112.157	-1750.90 ± 412.98	1797.97 ± 380.06
1075	550.087 ± 72.017	-2575.15 ± 264.64	2570.78 ± 243.04
1182	-219.295 ± 1.240	246.215 ± 2.242	0
1277	-238.263 ± 0.660	288.778 ± 1.199	0

TABLE IX. Least-squares Equations for O_2/Fe Ratio

T, °K	$O_2/Fe = A + B(\Delta\bar{G}_{O_2}) + C(\Delta\bar{G}_{O_2})^2$		
	A	B	C
972	-6.51063 ± 0.90937	$-(1.54818 \pm 0.19286) \times 10^{-1}$	$-(8.48750 \pm 1.02242) \times 10^{-4}$
1023	-0.939984 ± 0.338183	$-(3.71887 \pm 0.73565) \times 10^{-2}$	$-(2.28811 \pm 0.39990) \times 10^{-4}$
1075	-0.974101 ± 0.198241	$-(3.84622 \pm 0.44400) \times 10^{-2}$	$-(2.39937 \pm 0.24846) \times 10^{-4}$
1182	0.890132 ± 0.003075	$(4.05509 \pm 0.03692) \times 10^{-3}$	0
1277	0.824974 ± 0.001140	$(3.46161 \pm 0.01437) \times 10^{-3}$	0

$$d\bar{Y}_1 = -\frac{N_2}{N_1} d\bar{Y}_2, \quad (15)$$

where $\bar{Y}_i$ = a partial molar thermodynamic quantity, and N_2/N_1 = mole ratio of the two components, the partial molar thermodynamic quantity of the other component can be calculated. In particular, for a given composition FeO_{1+x} ,

$$\Delta\bar{G}_{Fe}(O_2/Fe) - \Delta\bar{G}_{Fe}(LPB) = - \int_{\Delta\bar{G}_{O_2}(LPB)}^{\Delta\bar{G}_{O_2}(O_2/Fe)} \frac{N_{O_2}}{N_{Fe}} d\Delta\bar{G}_{O_2}. \quad (16)$$

The value of $\Delta\bar{G}_{Fe}$ for the FeO_{1+x} composition of the lower phase boundary (LPB) is needed in Eq. 16 because the Gibbs-Duhem equation is only capable of giving relative changes in the partial molar free energy of iron for compositions within the FeO_{1+x} phase. The $\Delta\bar{G}_{Fe}(LPB)$ term accounts for the change in the free energy of the iron in going from pure iron at its vapor pressure to iron at its partial pressure at the lower phase boundary of the FeO_{1+x} phase at a given temperature.

To calculate the value of $\Delta\bar{G}_{Fe}$ for any composition FeO_{1+x} , one must know the value at the lower phase boundary at the temperatures of interest. This quantity is given by

$$\Delta\bar{G}_{Fe}(LPB) = \frac{\Delta G_f^\circ(LPB) - N_{O_2} \Delta\bar{G}_{O_2}(LPB)}{N_{Fe}}, \quad (17)$$

where $\Delta G_f^\circ(LPB)$ is the calorimetrically measured standard free energy of formation of wüstite at its lower phase boundary (namely, $FeO_{1.054}$), which is sufficiently constant at all temperatures of measurement. The quantity, $\Delta\bar{G}_{O_2}(LPB)$, is the experimentally determined value given in Table VII, and N_{O_2} and N_{Fe} are the mole fractions of O_2 and Fe in $FeO_{1.054}$ (0.345 and 0.655, respectively). Values of $\Delta G_f^\circ(LPB)$ are given by the equation

$$\Delta G_f^\circ(\text{FeO}_{1.054}) = -65.3192 + 0.0139(T) + 1.6000 \times 10^{-6} (T)^2 \text{ (kcal)}, \quad (18)$$

which resulted from a least-squares fit of the data from 800 to 1300°K compiled by Wicks and Block.¹⁷

From the calculated values of $\Delta \bar{G}_{\text{Fe}}(\text{LPB})$, and the least-squares equations in Table IX expressing O_2/Fe as a function of the partial molar free energy of oxygen, Eq. 16 can be solved and the partial molar free energy of iron as a function of composition for each isotherm can be calculated. The numerical values are given in Tables X-XIV, and the results are shown in Figs. 6-10. The least-squares equations for $\Delta \bar{G}_{\text{Fe}}$ as a function of O_2/Fe are given in Table XV.

The functional forms of the least-squares equations for the partial molar free energies of oxygen and iron, $\Delta \bar{G}_{\text{O}_2}$ and $\Delta \bar{G}_{\text{Fe}}$, as functions of composition, are strictly empirical. A sufficiently complete model, which will accurately predict the observed nonlinearity of $\Delta \bar{G}_i$ vs composition, remains for future study.

The standard free energy of formation of one mole of FeO_{1+x} is given by

$$\Delta G_f^\circ(\text{O}_2/\text{Fe}) = N_{\text{O}_2} \Delta \bar{G}_{\text{O}_2} + N_{\text{Fe}} \Delta \bar{G}_{\text{Fe}}. \quad (19)$$

The results for various compositions for each isotherm are given in Tables X-XIV, and are represented by the least-squares equations in Tables XV, XVI, and XVII.

The temperature dependences of the partial molar free energies of O_2 and Fe for a series of constant compositions in the wüstite phase are given by the least-squares equations in Tables XVIII and XIX. The standard deviations of the respective coefficients indicate that the nonlinearity of temperature dependence appears to be real. The families of equations for oxygen and iron are plotted in Figs. 11 and 12, respectively.

The partial molar enthalpies and entropies can be evaluated from the equations in Tables XVIII and XIX by the partial derivatives,

$$\left[\frac{\partial \Delta \bar{G}}{\partial T} \right]_{\text{P, O}_2/\text{Fe}} = -\Delta \bar{S} \quad (20)$$

and

$$\left[\frac{\partial \Delta \bar{G}/T}{\partial (1/T)} \right]_{\text{P, O}_2/\text{Fe}} = \Delta \bar{H}. \quad (21)$$

TABLE X. Derived Thermodynamic Quantities
(kcal/mole) for Wüstite at 1277°K

O/Fe	O ₂ /Fe	$\Delta\bar{G}_{O_2}$	$\Delta\bar{G}_{Fe}$	ΔG_f° (FeO _{1+x})
1.0520	.5260	-86.365	-23.147	-44.938
1.0560	.5280	-85.788	-23.451	-44.991
1.0600	.5300	-85.210	-23.757	-45.044
1.0640	.5320	-84.633	-24.063	-45.096
1.0680	.5340	-84.055	-24.371	-45.148
1.0720	.5360	-83.478	-24.680	-45.198
1.0760	.5380	-82.900	-24.990	-45.247
1.0800	.5400	-82.322	-25.302	-45.296
1.0840	.5420	-81.745	-25.614	-45.343
1.0880	.5440	-81.167	-25.928	-45.390
1.0920	.5460	-80.590	-26.242	-45.436
1.0960	.5480	-80.012	-26.558	-45.481
1.1000	.5500	-79.435	-26.875	-45.525
1.1040	.5520	-78.857	-27.194	-45.569
1.1080	.5540	-78.279	-27.513	-45.611
1.1120	.5560	-77.702	-27.834	-45.653
1.1160	.5580	-77.124	-28.155	-45.694
1.1200	.5600	-76.547	-28.478	-45.734
1.1240	.5620	-75.969	-28.802	-45.773
1.1280	.5640	-75.392	-29.127	-45.811
1.1320	.5660	-74.814	-29.454	-45.848
1.1360	.5680	-74.237	-29.781	-45.885
1.1370	.5685	-74.092	-29.863	-45.894

TABLE XI. Derived Thermodynamic Quantities
(kcal/mole) for Wüstite at 1182°K

O/Fe	O ₂ /Fe	$\Delta\bar{G}_{O_2}$	$\Delta\bar{G}_{Fe}$	ΔG_f° (FeO _{1+x})
1.0540	.5270	-89.539	-24.061	-46.659
1.0560	.5280	-89.293	-24.191	-46.687
1.0600	.5300	-88.801	-24.451	-46.742
1.0640	.5320	-88.308	-24.713	-46.797
1.0680	.5340	-87.816	-24.975	-46.850
1.0720	.5360	-87.323	-25.239	-46.903
1.0760	.5380	-86.831	-25.503	-46.956
1.0800	.5400	-86.338	-25.768	-47.007
1.0840	.5420	-85.846	-26.035	-47.058
1.0880	.5440	-85.354	-26.302	-47.108
1.0920	.5460	-84.861	-26.571	-47.157
1.0960	.5480	-84.369	-26.840	-47.205
1.1000	.5500	-83.876	-27.110	-47.253
1.1040	.5520	-83.384	-27.382	-47.300
1.1080	.5540	-82.891	-27.654	-47.346
1.1120	.5560	-82.399	-27.927	-47.391
1.1160	.5580	-81.907	-28.202	-47.436
1.1200	.5600	-81.414	-28.477	-47.480
1.1240	.5620	-80.922	-28.753	-47.523
1.1280	.5640	-80.429	-29.030	-47.565
1.1320	.5660	-79.937	-29.308	-47.607

TABLE XII. Derived Thermodynamic Quantities
(kcal/mole) for Wüstite at 1075°K

O/Fe	O ₂ /Fe	$\Delta\bar{G}_{O_2}$	$\Delta\bar{G}_{Fe}$	ΔG_f° (FeO _{1+x})
1.0520	.5260	-93.168	-25.011	-48.504
1.0560	.5280	-92.899	-25.152	-48.562
1.0600	.5300	-92.610	-25.306	-48.620
1.0640	.5320	-92.300	-25.470	-48.677
1.0680	.5340	-91.969	-25.646	-48.734
1.0720	.5360	-91.618	-25.834	-48.790
1.0760	.5380	-91.246	-26.034	-48.845
1.0800	.5400	-90.854	-26.245	-48.900
1.0840	.5420	-90.441	-26.468	-48.954
1.0880	.5440	-90.008	-26.704	-49.008
1.0920	.5460	-89.554	-26.951	-49.060
1.0960	.5480	-89.079	-27.211	-49.113
1.1000	.5500	-88.584	-27.483	-49.164
1.1040	.5520	-88.068	-27.767	-49.214
1.1080	.5540	-87.532	-28.064	-49.264
1.1120	.5560	-86.975	-28.373	-49.313
1.1160	.5580	-86.398	-28.694	-49.361
1.1200	.5600	-85.800	-29.029	-49.408

TABLE XIII. Derived Thermodynamic Quantities
(kcal/mole) for Wüstite at 1023°K

O/Fe	O ₂ /Fe	$\Delta\bar{G}_{O_2}$	$\Delta\bar{G}_{Fe}$	ΔG_f° (FeO _{1+x})
1.0560	.5280	-94.960	-25.438	-49.461
1.0600	.5300	-94.658	-25.598	-49.520
1.0640	.5320	-94.341	-25.766	-49.579
1.0680	.5340	-94.009	-25.943	-49.637
1.0720	.5360	-93.663	-26.128	-49.695
1.0760	.5380	-93.303	-26.321	-49.752
1.0800	.5400	-92.928	-26.523	-49.808
1.0840	.5420	-92.539	-26.734	-49.864
1.0880	.5440	-92.136	-26.953	-49.919
1.0920	.5460	-91.718	-27.180	-49.973
1.0960	.5480	-91.286	-27.417	-50.027
1.1000	.5500	-90.840	-27.662	-50.080
1.1040	.5520	-90.379	-27.916	-50.132
1.1080	.5540	-89.903	-28.179	-50.184
1.1120	.5560	-89.414	-28.451	-50.234
1.1130	.5565	-89.289	-28.520	-50.247

TABLE XIV. Derived Thermodynamic Quantities
(kcal/mole) for Wüstite at 972°K

O/Fe	O ₂ /Fe	$\Delta\bar{G}_{O_2}$	$\Delta\bar{G}_{Fe}$	ΔG_f° (FeO _{1+x})
1.0540	.5270	-96.251	-26.088	-50.303
1.0560	.5280	-96.175	-26.128	-50.333
1.0600	.5300	-95.993	-25.224	-50.392
1.0640	.5320	-95.773	-26.341	-50.452
1.0680	.5340	-95.515	-26.479	-50.511
1.0720	.5360	-95.218	-26.637	-50.569
1.0760	.5380	-94.884	-26.816	-50.627
1.0800	.5400	-94.512	-27.017	-50.684
1.0840	.5420	-94.102	-27.239	-50.741
1.0880	.5440	-93.653	-27.483	-50.797
1.0920	.5460	-93.167	-27.748	-50.852
1.0960	.5480	-92.643	-28.035	-50.906

TABLE XV. Least-squares Equations for
Relative Partial Molar Free Energy of Iron

T, °K	$\Delta\bar{G}_{Fe} = A + B(O_2/Fe) + C(O_2/Fe)^2$ (kcal/mole)		
	A	B	C
972	-740.833 ± 1.757	2749.59 ± 6.54	-2643.90 ± 6.09
1023	-284.516 ± 0.730	1058.76 ± 2.69	-1075.93 ± 2.48
1075	-406.438 ± 1.208	1517.09 ± 4.45	-1505.62 ± 4.10
1182	10.1899 ± 0.0014	-0.219712 ± 0.005045	-122.908 ± 0.005
1277	16.8171 ± 0.0012	-0.0553838 ± 0.0044419	-144.338 ± 0.004

TABLE XVI. Least-squares Equations for Standard Free Energy of Formation of FeO_{1+x} vs Temperature ($^{\circ}\text{K}$)

O_2/Fe	$\Delta G_f^{\circ} = A + BT + CT^2$ (kcal/mole)		
	A	B	C
0.530	-65.432	1.390×10^{-2}	1.618×10^{-6}
0.540	-65.747	1.384×10^{-2}	1.705×10^{-6}
0.550	-65.954	1.360×10^{-2}	1.881×10^{-6}
0.560	-65.482	1.221×10^{-2}	2.548×10^{-6}
0.570	-61.819	0.537×10^{-2}	5.548×10^{-6}

$$\Delta H_f^{\circ} = A - CT^2; \quad \Delta S_f^{\circ} = -B - 2CT.$$

TABLE XVII. Least-squares Equations for Standard Free Energy of Formation of FeO_{1+x} vs Composition

T, $^{\circ}\text{K}$	$\Delta G_f^{\circ} = A + B(\text{O}_2/\text{Fe}) + C(\text{O}_2/\text{Fe})^2$ (kcal/mole)		
	A	B	C
972	- 0.867	-140.498	107.819
1023	- 5.365	-128.681	95.491
1075	- 8.985	-120.681	86.600
1182	-10.734	-116.764	82.228
1277	-14.081	-107.165	72.929

TABLE XVIII. Least-squares Equations for the Relative Partial Molar Free Energy of Oxygen vs Temperature ($^{\circ}\text{K}$)

O_2/Fe	$\Delta \bar{G}_{\text{O}_2} = A + B(T) + C(T)^2$ (kcal/mole)		
	A	B	C
0.528	-112.474 ± 13.277	$(0.30630 \pm 2.36796) \times 10^{-2}$	$(1.39790 \pm 1.05069) \times 10^{-5}$
0.534	-115.332 ± 9.062	$(0.68013 \pm 1.62238) \times 10^{-2}$	$(1.38775 \pm 0.71987) \times 10^{-5}$
0.540	-111.780 ± 10.061	$(0.02823 \pm 1.80114) \times 10^{-2}$	$(1.78761 \pm 0.79919) \times 10^{-5}$
0.544	-105.845 ± 12.061	$-(0.97702 \pm 2.15926) \times 10^{-2}$	$(2.28230 \pm 0.95809) \times 10^{-5}$
0.548	-97.0649 ± 15.1572	$-(2.43771 \pm 2.71349) \times 10^{-2}$	$(2.95904 \pm 1.20400) \times 10^{-5}$
0.556*	-70.9254 ± 26.5989	$-(6.73200 \pm 4.76180) \times 10^{-2}$	$(4.86144 \pm 2.11286) \times 10^{-5}$
0.560*	-53.5954 ± 35.5664	$-(9.56133 \pm 6.36719) \times 10^{-2}$	$(6.08553 \pm 2.82519) \times 10^{-5}$

*For these compositions, the constants A, B, and C were obtained with short extrapolations of the equations for 972 and 1023 $^{\circ}\text{K}$ in Table VIII beyond the upper phase boundary.

TABLE XIX. Least-squares Equations for the Relative Partial Molar Free Energy of Iron vs Temperature ($^{\circ}\text{K}$)

O_2/Fe	$\Delta\bar{G}_{\text{Fe}} = A + B(T) + C(T)^2 \text{ (kcal/mole)}$		
	A	B	C
0.528	-40.4994 ± 6.9395	$(1.96434 \pm 1.24233) \times 10^{-2}$	$-(4.93513 \pm 5.51237) \times 10^{-5}$
0.534	-38.9787 ± 4.7234	$(1.76529 \pm 0.84560) \times 10^{-2}$	$-(4.87877 \pm 3.75203) \times 10^{-6}$
0.540	-40.8885 ± 5.2726	$(2.11579 \pm 0.94391) \times 10^{-2}$	$-(7.02805 \pm 4.18822) \times 10^{-6}$
0.544	-44.1154 ± 6.3586	$(2.66246 \pm 1.13833) \times 10^{-2}$	$-(9.71720 \pm 5.05091) \times 10^{-6}$
0.548	-48.9092 ± 8.0409	$(3.45988 \pm 1.43951) \times 10^{-2}$	$-(1.34115 \pm 0.63873) \times 10^{-6}$
0.556*	-63.0144 ± 14.2055	$(5.77426 \pm 2.54311) \times 10^{-2}$	$-(2.36717 \pm 1.12841) \times 10^{-5}$
0.560*	-72.0825 ± 18.8558	$(7.24885 \pm 3.37562) \times 10^{-2}$	$-(3.00545 \pm 1.49780) \times 10^{-5}$

*For these compositions, the constants A, B, and C were obtained with short extrapolations of the equations for 972 and 1023 $^{\circ}\text{K}$ in Table VIII beyond the upper phase boundary.

Fig. 11. Plots of Partial Molar Free Energy of Oxygen vs Temperature for Various Compositions of FeO_{1+x}

Fig. 12. Plots of Partial Molar Free Energy of Iron vs Temperature for Various Compositions of FeO_{1+x}

Various isotherms of the partial molar enthalpies and entropies vs composition were plotted from Eqs. 20 and 21 and are shown in Figs. 13-16. In the construction of these equations and the corresponding figures, the values of $\Delta\bar{G}_{O_2}$ were extrapolated from Table VIII and the values of $\Delta\bar{G}_{Fe}$ from Table XV beyond the upper phase boundary for the 972 and 1023°K isotherms. These extrapolations are beneficial to the analysis because they make it possible to extend the temperature range for which the series of constant compositions can be analyzed. Figures 13-16 show that only the values of O_2/Fe from 0.527 to 0.548 are common to all temperatures, unless the results extrapolated from the 972 and 1023°K isotherms are used. The extension of the analysis to compositions near the upper phase boundary without the use of the extrapolated low-temperature results, yields rather large random errors in the derived thermodynamic quantities as a result of the restriction to the relatively short temperature range over which higher values of O_2/Fe are commonly found. Admittedly, it is debatable whether the errors incurred by the extrapolation of empirical equations are comparable to those incurred by the reduction of the useful temperature range. However, Figs. 13-16 indicate that the extrapolations do not change at least the qualitative nature of the isotherms, in that the respective minima and maxima are thoroughly characterized exclusive of the extrapolated regions of the curves.

Fig. 13. Plots of Partial Molar Enthalpy of Oxygen vs Composition for Various Temperatures

Fig. 14. Plots of Partial Molar Enthalpy of Iron vs Composition for Various Temperatures

Fig. 15. Plots of Partial Molar Entropy of Oxygen vs Composition for Various Temperatures

Fig. 16. Plots of Partial Molar Entropy of Iron vs Composition for Various Temperatures

V. DISCUSSION

The results reported by Ariya *et al.*¹⁰ are in relatively poor agreement with those of the present study. For example, the values of the oxygen pressure at 1182°K are approximately a factor of five larger than those reported here. If, however, their ratios of CO₂/CO are converted to oxygen pressure by the use of Eq. 3, the disagreement is reduced to approximately a factor of two, which is reflected as a 1- to 2-kcal error in $\Delta\bar{G}_{O_2}$ in the temperature range of this study. Therefore, a significant discrepancy exists between the sources of thermodynamic data used to derive the oxygen pressure from the equilibrium involving CO₂ and CO (Eq. 2), as well as one that exists between the experimentally measured quantities.

The results reported by Raccach and Vallet¹¹ at 1273°K can be directly compared with the results in Table X. The agreement is quite good since our values of $\Delta\bar{G}_{O_2}$ in the wüstite field are only 0.1 to 0.3 kcal less negative than the results of Raccach and Vallet. If the results of Darken and Gurry⁹ are extrapolated down to 1273°K, one obtains values of $\Delta\bar{G}_{O_2}$ that are approximately 0.5-1.0 kcal more negative than those reported here.

The most interesting aspect of the present study is the negative deviation from linearity observed for $\Delta\bar{G}_{O_2}$ vs O₂/Fe at 972, 1023, and 1075°K (see Figs. 8-10). For any composition within the wüstite phase, the numerical discrepancy between values of $\Delta\bar{G}_{O_2}$ calculated from the equations in Table XVIII and those reported by Raccach and Vallet¹¹ at 1093°K (the lowest temperature of the latter work) is less than 0.5 kcal. As stated in the Introduction, Raccach and Vallet¹¹ have interpreted their measurements in terms of linear segments of the form, $\log p_{O_2} = Mx + N$, both above and below a critical composition, which, for example, is O/Fe = 1.084 at 1093°K. In the present work, however, the precision of the measurements of $\Delta\bar{G}_{O_2}$ (or $\log p_{O_2}$ using Eq. 14) does not permit such an interpretation, but rather indicates the continuous curvature of $\Delta\bar{G}_{O_2}$ vs O₂/Fe. Hence, the present results do not suggest any macrophasic heterogeneity within the wüstite field. On the other hand, the deviation from linearity of $\Delta\bar{G}_{O_2}$ vs O₂/Fe at the lower temperatures, and the disappearance of this deviation at higher temperatures, as seen in Figs. 6-10, strongly suggest a microphase or domain ordering of the oxygen at low temperatures; the ordering is ultimately randomized by thermal energy at the higher temperatures. Note that the suggested microphase ordering involves the oxygen component, whereas the iron component, by virtue of the Gibbs-Duhem integrations, appears to exhibit a disordering effect. The effect of both composition and temperature on the ordering of the oxygen component (and the inverse effect on the iron component) is shown in Figs. 13-16. The increase of temperature appears to drive the minima in $\Delta\bar{H}_{O_2}$ (Fig. 13) and $\Delta\bar{S}_{O_2}$ (Fig. 15) from a composition near the lower phase boundary toward and beyond the upper phase boundary.

If this interpretation is correct, then some interesting microstructural changes occur within the wüstite field. Some evidence of this or a related kind of behavior was recorded by Manenc,¹⁸ who reported the existence of superstructural X-ray reflections in quenched wüstite samples. It may be profitable, then, to pursue this suggested correlation of thermodynamic properties with microstructural properties by means of a controlled-atmosphere, high-temperature X-ray diffractometer.¹⁹

The emf study of the wüstite field reported by Barbi⁸ does not yield any evidence of heterogeneity or ordering since the plots of $\Delta\bar{G}_{O_2}'$ vs composition appear to be linear at all temperatures from 600 to 1000°C. The values of the measured emf in volts, E , are converted to values of $\Delta\bar{G}_{O_2}$ by the equation

$$\Delta\bar{G}_{O_2} = 2\Delta G_f^\circ(\text{LPB}) - 92,240E, \quad (22)$$

in which the quantity $\Delta G_f^\circ(\text{LPB})$ can be evaluated from Eq. 18. Values of $\Delta\bar{G}_{O_2}$ thus obtained are 1.5 to 2 kcal less negative (depending on the temperature) than those reported here. At present, these rather large discrepancies are difficult to understand.

The field of stability or the homogeneity region of wüstite has been the subject of many studies. The values of the lower and upper phase boundaries found in the present study, as shown in Fig. 5, agree most closely with those reported by Darken and Gurry⁹ and by Gerdanian and Dode.²⁰ Many of the results of previous investigations compiled by Offroy and Aubry⁷ and by Barbi⁸ indicate that the lower phase boundary varies significantly with temperature. The present study and that of Darken and Gurry⁹ indicate that the lower boundary is relatively constant with temperature. The values $\text{FeO}_{1.048}$ to $\text{FeO}_{1.054}$ at 800°C reported by Gerdanian and Dode²⁰ confirm our findings.

The disproportionation temperature of wüstite, i.e., the temperature at which wüstite of unique composition is in equilibrium with iron metal and magnetite, can be deduced from the data in Table VII. Plots of $\log p_{O_2}$ vs reciprocal temperature yield the following empirical least-squares equations for the lower and upper phase boundaries, respectively:

$$\log p_{O_2}(\text{LPB}) = (7.163 \pm 0.171) - (28,038 \pm 186)/T, \quad (23)$$

and

$$\begin{aligned} \log p_{O_2}(\text{UPB}) = & (9.036 \pm 3.300) - (23.755 \pm 7.353) \frac{10^3}{T} \\ & - (5.115 \pm 4.062) \frac{10^6}{T^2}. \end{aligned} \quad (24)$$

At the disproportionation temperature, the phase boundaries merge and the oxygen pressure is unique. Consequently, Eqs. 23 and 24 can be equated and solved for $T = 857 \pm 20^\circ\text{K}$. Figure 5 indicates that this deduced temperature is consistent with the extrapolation of the measured phase boundaries. In general, the results of most previous investigators fall within the rectangular area. As can be seen, the coordinates for the disappearance of the wüstite phase are not extremely well known. Most of the previous investigators, including Darken and Gurry,⁹ Ariya *et al.*¹⁰ and Vallet and Raccach,¹³ deduced the disproportionation temperature by the extrapolation of linear equations of $\log p_{\text{O}_2}$ vs reciprocal temperature. A linear equation would appear to yield a reliable extrapolation for the lower phase boundary since the change in composition of the boundary does not significantly change with temperature; the only nonlinear factor neglected from the linear approximation would be a very small temperature variation of the change in heat capacity for the reaction at the lower phase boundary. However, there appears to be no compelling reason why the variation of $\log p_{\text{O}_2}$ vs reciprocal temperature for the upper phase boundary should be linear, in view of the rather striking variation of composition on temperature. In fact, the results given in Table VII indicate the nonlinear behavior shown by Eq. 24. Once again the functional form of this equation is strictly empirical, and consequently, the validity of the approximately 100° extrapolation may be questioned.

Aside from the measurements by Barbi,⁸ there have been no direct measurements of the disproportionation temperature of wüstite. The structural nature of this transformation is undoubtedly complicated and may involve a substantial temperature hysteresis that is brought about by the nucleation of domains or microphases. It is not surprising, then, that much of the previous work involving quenched samples, extrapolations of oxygen pressures of the phase boundaries, etc., does not yield a consistent temperature and composition for this transformation.

VI. SUMMARY

The thermodynamic properties of the FeO_{1+x} phase have been measured over a temperature range of 970-1280°K by determining the values of x for known pressures of oxygen. Free energies, enthalpies, and entropies, as well as their respective trends with composition and temperature, have been derived from the measured quantities, the Gibbs-Duhem equation, and calorimetric data. In addition to being more precise, the results correspond to a much lower temperature range than those reported in most of the earlier studies. The behavior of the partial molar quantities for oxygen and iron suggests the likelihood of the existence of a complicated temperature-dependent microstructure or superstructure and illustrates the need for an investigation to elucidate the structural changes that must occur as functions of temperature and composition.

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