

# Thermodynamic Properties of Wustite ( $\text{FeO}_{1+y}$ )

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(Received September 29, 1969)

E.m.f. measurements of the cell,  $\text{Pt/FeO}_{1+y}/\text{ZrO}_2(\text{CaO})/\text{Ni-NiO/Pt}$ , have been carried out to investigate the thermodynamic characteristics of wustite ( $\text{FeO}_{1+y}$ ). From these results, the relationship between temperature, oxygen pressure and composition of wustite and the phase boundaries of wustite phase in the binary system Fe-O were obtained and compared with those given by Darken and Gurry.

The thermodynamic quantities such as activities of iron and oxygen in wustite, partial molar enthalpies and entropies of solution of oxygen in wustite and free energy of formation of magnetite were also evaluated.

The defect structure of wustite was discussed in relation with the  $P_{\text{O}_2}$  dependence of cation vacancy concentration of wustite.

## 1. Introduction

The construction of phase diagrams showing the relationship between temperature, oxygen pressure and composition of wustite ( $\text{FeO}_{1+y}$ ) phase in the system Fe-O was proposed to obtain the thermodynamic properties and defect structure of wustite, known as a defect-type semiconductor, containing an excess of oxygen over the stoichiometric composition FeO.

The previous method was to pass a gas mixture of constant known composition over the condensed phase, maintained at one of a series of constant temperatures, until equilibrium was attained, then to quench the ferrous oxide and determine its composition by means of chemical analysis made by Darken and Gurry<sup>1)</sup>, by means of lattice constant measurements effected by Jette<sup>2)</sup> and by means of thermogravimetry made by Bransky<sup>3)</sup>.

The purpose of this study is the direct measurement of partial oxygen pressure of wustite sample of known composition, maintained at a given temperature, by the method of e.m.f. measurement using zirconia solid electrolyte. The results

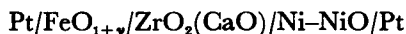
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were presented in the relationship between temperature, oxygen pressure and composition of wustite region and its thermodynamic data were deduced and discussed.

## 2. Experimental

The oxygen partial pressures of wustite were obtained from the following solid state electrochemical cell



where  $FeO_{1+y}$  indicates the wustite phase of various compositions containing the wustite in equilibrium with metallic iron and magnetite and Ni-NiO the reference reversible electrode. The zirconia electrolyte  $ZrO_2(CaO)$  contained 15 mol % CaO and was in form of a tube supplied by Nihon Kagakutogyo, Osaka.

According to the phase rule, the number of degrees of freedom for wustite is 2, indicating that the oxygen pressure is uniquely given when the temperature and the composition of wustite were fixed. On the other hand, the variance of the Ni-NiO mixture is 1, indicating that a constant oxygen pressure is given when the mixture is maintained at a constant temperature.

The e.m.f. of the cell is related to the oxygen pressure of wustite  $P'_{O_2}$  and of Ni-NiO mixture  $P_{O_2}$  by

$$E = -\frac{RT}{4F} \ln P_{O_2}/P'_{O_2} \quad (1)$$

where  $R$  is the gas constant,  $T$  the absolute temperature and  $F$  the Faraday constant, providing the transport number of oxygen ion in zirconia electrolyte is unity<sup>4)</sup>. The oxygen partial pressure of wustite is obtained by this relation replacing  $P_{O_2}$  with the values calculated from the free energy of formation of NiO, previously given<sup>5)</sup>

$$F_{NiO_2}^0 = 42.01 T - 102,40 (\pm 200) \text{ cal/mol } O_2 \quad (2)$$

and  $E$  with measured values.

A cell design as shown in Fig. 1 was used. The various parts of the cell, solid electrolyte, electrodes, platinum contact leads, chromel-alumel thermocouple, etc., were contained in the closed and high alumina tube and maintained in a purified argon atmosphere. The electrolyte was zirconia stabilized by 15 mol % CaO and in form of close flat end tube (16 mm $\phi$   $\times$  500 mm). The wustite pellet was placed close to the outside bottom and the Ni-NiO mixture pellet to the inside bottom of the zirconia tube. The two pellets were pushed tightly with the platinum

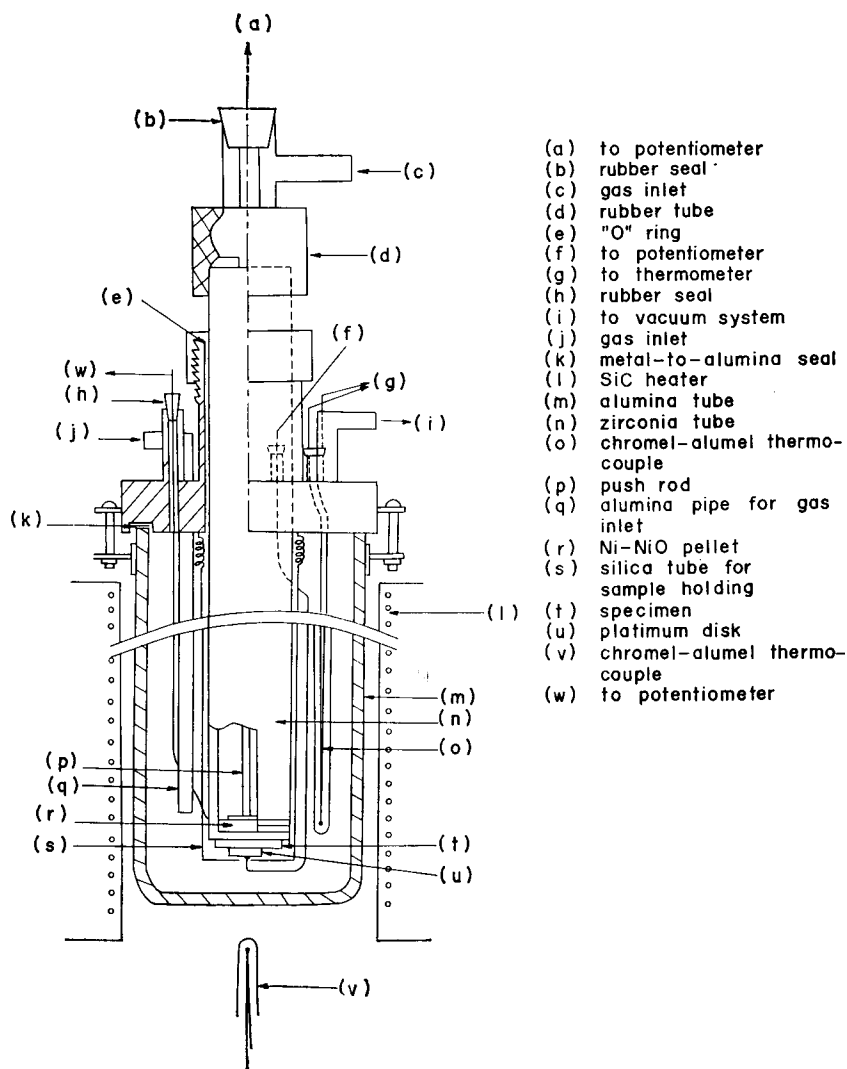


Fig. 1. Cell design.

disks connected by platinum leads capable of measuring e.m.f. of the cell on a potentiometer (Shimazu Seisakusho Type K-2).

The  $\text{Fe-FeO}_{1+y}$  mixture may be used as reference electrode for determining the partial oxygen pressure of wustite in view of the definition that the wustite in equilibrium with metallic iron is chosen as the standard of activity expression. However, in this investigation, the Ni-NiO mixture was chosen as reference electrode of the reasons of;

1. obtaining relative high electromotive force,

2. obtaining stable electromotive force for a long period of time in the heating stage and avoiding the contamination with zirconia electrolyte.

### 3. Sample preparations

#### 1. Ni-NiO electrode

Ni-NiO pellets were made by mixing the reagent grade Ni and NiO powders in 1/1 weight proportion, compressing the powders at  $4 \text{ tons} \cdot \text{cm}^{-2}$  into pellets 10 mm diam. and 1.5 mm thick, heating the pellets in vacuum at  $200^\circ\text{C}$  to dehydrate, sintering for 10 hrs at  $900^\circ\text{C}$  and cooling in water.

#### 2. Wustite electrode

Wustite pellets were prepared by the firing of calculated proportions of iron or ferric oxide and wustite obtained by thermal decomposition of ferrous oxalate. The preparation schedule was carried out as follows.

The reagent grade ferrous oxalate was dehydrated in vacuum at  $200^\circ\text{C}$ , and then decomposed in vacuum to produce ferrous oxide in alumina boats at  $900^\circ\text{C}$ , it was then allowed to cool in water. The ferrous oxide powders were then mixed with iron or ferric oxide powders in calculated proportions, compressed at  $5 \text{ tons} \cdot \text{cm}^{-2}$  into pellets 10 mm diam. and 1.5 mm thick, fired in vacuum for 48 hrs at  $900^\circ\text{C}$  in silica tube and then quenched in water. All the pellets obtained were ground together and mixed again. After compressing these powders at  $8 \text{ tons} \cdot \text{cm}^{-2}$  into pellets ( $10 \text{ mm}\phi \times 1.5 \text{ mm}$ ), they were fired during 72 hrs at  $900^\circ\text{C}$  in vacuum and then quenched in water.

The wustite pellets prepared by the above procedure were all divided into two parts; one was used for e.m.f. measurements and the other was reserved for the identification of phase and the determination of composition.

#### 3. Determination of compositions

The thermogravimetric method and X-ray method were employed for the determination of compositions. The thermogravimetric method was to heat a suitable weight of samples for 21 hrs at  $1000^\circ\text{C}$  in air to form stoichiometric  $Fe_2O_3$ , weigh the gain of mass in accuracy of  $10^{-3}$  mg and determine the initial oxygen content of wustite.

The experimental determinations of the lattice constants for wustite composition range and for the wustite phase in small adjoining parts of the two phase regions are plotted in Fig. 2.

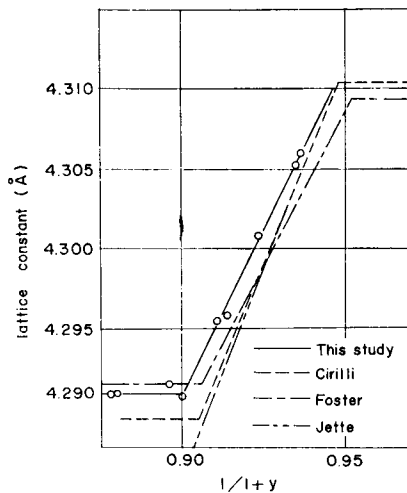


Fig. 2. Lattice constant data for wustite composition range and for wustite phase in small adjoining parts of the two-phase regions.

Table 1. Compositions of wustite used and linear relation between e.m.f. and temperature.

Specimen Number	Compositions	$E(mV) = AT(^{\circ}K) + B$
a	Fe-FeO <sub>1+y</sub>	$E = 0.119T + 132.8$
b	FeO <sub>1.068</sub>	$E = 0.100T + 148.7$
c	FeO <sub>1.083</sub>	$E = 0.087T + 142.9$
d	FeO <sub>1.094</sub>	$E = 0.070T + 146.4$
e	FeO <sub>1.111</sub>	$E = 0.040T + 158.1$
f	FeO <sub>1.137</sub>	$E = -0.015T + 188.6$
g	FeO <sub>1+y</sub> -Fe <sub>3</sub> O <sub>4</sub>	$E = -0.156T + 359.4$

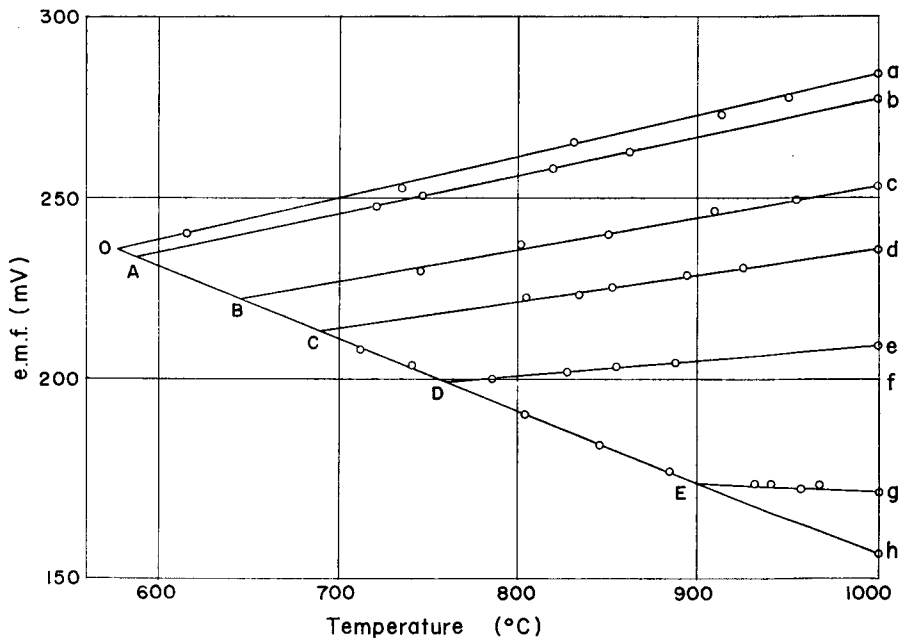


Fig. 3. E.m.f.-temperature plots for cell: Pt/FeO<sub>1+y</sub>/ZrO<sub>2</sub>(CaO)/Ni-NiO/Pt.

#### 4. Experimental results

E.m.f. measurements on the above cell were recorded for wustite in equilibrium with metallic iron and magnetite between 600° and 1000°C. In addition e.m.f. data were obtained for five compositions shown in Table 1 together with e.m.f. values. Fig. 3 includes the e.m.f.-temperature plots for wustite of various compositions.

The above cell was cycled over the full temperature range, usually 600°–1000°C for a period of several days. The observed e.m.f. vs. temperature plots were linear within experimental certainty for each wustite region, which may be represented by the equation

$$E = AT + B \quad (3)$$

In Fig. 3, the points A, B, C, D and E correspond to the change from the two phase region containing  $FeO_{1+y}$  and  $Fe_3O_4$  to the single phase wustite.

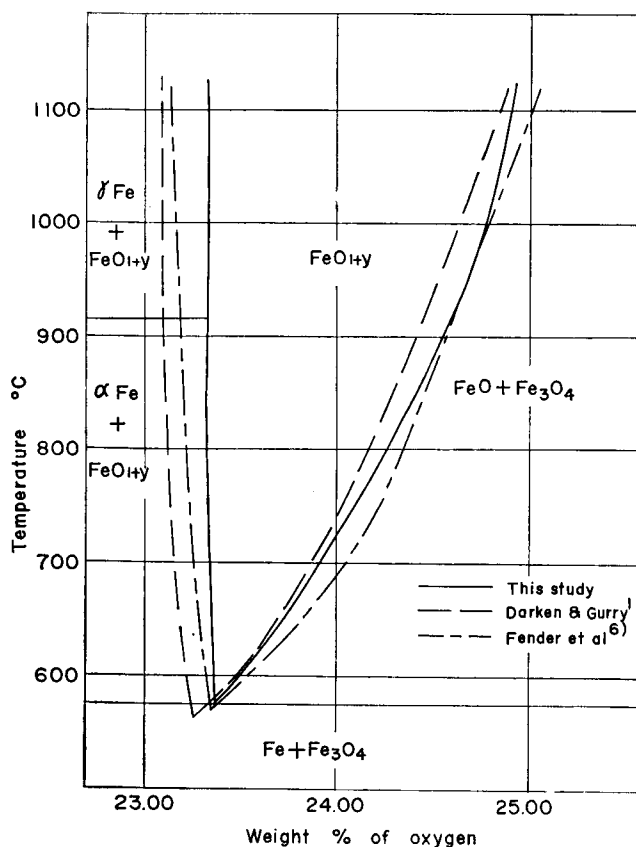


Fig. 4. The temperature-composition phase diagram of wustite region.

The composition analysis of wustite samples were effected before and after the e.m.f. measurement to check if the composition was changed during heating period, and no measurable oxygen loss and uptake was observed.

In Fig. 4 the results at e.m.f. vs. temperature plots at all compositions are summarised in a phase diagram. The magnetite side of the wustite phase limits was obtained from intersections between extrapolated e.m.f.-temperature plots and e.m.f.-temperature plots from wustite in equilibrium with magnetite, and the metallic iron side was obtained from intersections between extrapolated e.m.f.-composition plots and e.m.f.'s obtained from wustite in equilibrium with iron. The limits of  $\text{FeO}_{1+y}$  phase are in reasonable agreement with those proposed by Darken and Gurry<sup>1)</sup> by the method described earlier and by Fender<sup>6)</sup> by e.m.f. method using zirconia electrolyte cell with Fe- $\text{FeO}_{1+y}$  reference electrode.

Fig. 5 shows e.m.f.-wustite composition plots for various temperatures. E.m.f. of the cell being related to oxygen partial pressure of wustite by the equation

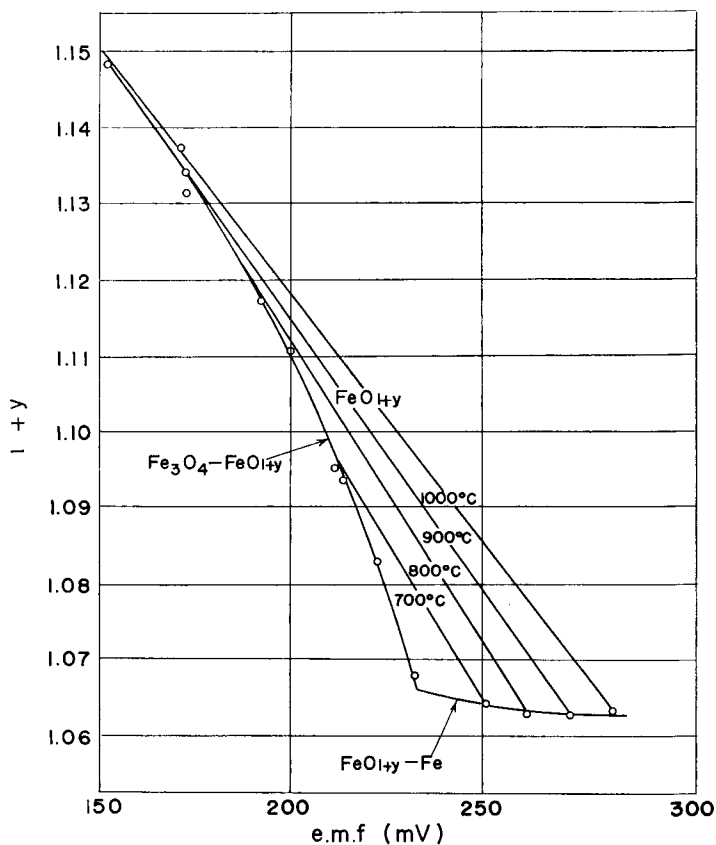


Fig. 5. Relations between e.m.f. and composition of wustite, expressed as  $\text{FeO}_{1+y}$ .

$$\Delta F_{\text{oxygen}} = RT \log P_{\text{O}_2}^{1/2} = \Delta F_{\text{NiO}}^0 - 2FE \quad (4)$$

where  $\Delta F_{\text{oxygen}}$  is the partial molar free energy of solution of oxygen in  $\text{FeO}_{1+y}$ , one obtains the relationship between temperature, oxygen pressure and composition of wustite as shown in Fig. 6. Fig. 6 is the isobaric representation of the relation between logarithm of compositions and oxygen pressures; the curves a and b indicate the phase limits of wustite corresponding to iron and magnetite side respectively.

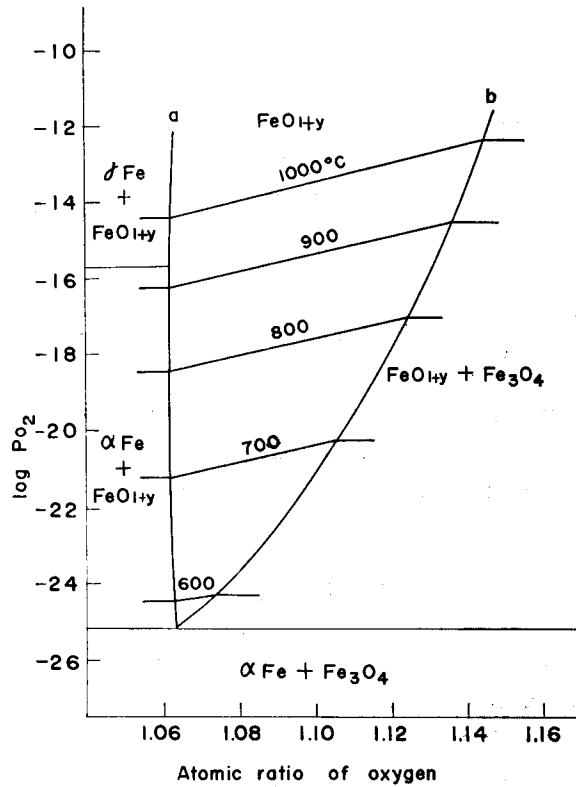


Fig. 6. Relations between  $\log P_{\text{O}_2}$  and compositions of wustite.

From a fundamental theorem of partial derivatives and usual expression for  $\Delta \bar{S}_{\text{oxygen}}$  and  $\Delta \bar{H}_{\text{oxygen}}$  in terms of partial molar free energy of solution of oxygen it follows that

$$\Delta \bar{S}_{\text{oxygen}} = -\left(\frac{\partial \Delta F_{\text{oxygen}}}{\partial T}\right) \quad (5)$$



$$\Delta H_{\text{oxygen}} = \frac{\partial \left( \frac{\Delta F_{\text{oxygen}}}{T} \right)}{\partial \left( \frac{1}{T} \right)} \quad (6)$$

Using Eq. (2), (3) and (4), the relations,

$$\Delta \bar{S}_{\text{oxygen}} = -21.00 - 2AF \text{ (cal/deg} \cdot \frac{1}{2} \text{ mol O}_2\text{)} \quad (7)$$

and 
$$\Delta \bar{H}_{\text{oxygen}} = -57,000 - 2BF \text{ (cal/} \frac{1}{2} \text{ mol O}_2\text{)} \quad (8)$$

are deduced and the calculated results are recorded in Table 2.

Table 2. Partial molar entropies and enthalpies of solution of oxygen.

Compositions FeO <sub>1+y</sub> 1+y	$-\Delta S_{1/2\text{O}_2}$ (cal. deg <sup>-1</sup> ·mole <sup>-1</sup> )	$-\Delta H_{1/2\text{O}_2}$ (cal. mole <sup>-1</sup> )
1.068	16.3 (±0.2)	63,850 (±200)
1.083	17.0	63,530
1.094	17.7	63,700
1.111	19.1	64,250
1.137	21.7	65,750

The activity of oxygen in wustite at temperature  $T$  is derived in terms of oxygen pressure if the standard state of oxygen and iron in wustite is selected as oxygen and iron in wustite in equilibrium with metallic iron, which in this case reduces to

$$\alpha_{\text{O}} = \left( \frac{P'_{\text{O}_2}(T)}{P''_{\text{O}_2}(T)} \right)^{1/2} \quad (9)$$

where  $P'_{\text{O}_2}(T)$  is oxygen pressure of wustite at  $T^\circ K$  and  $P''_{\text{O}_2}(T)$  oxygen pressure of wustite in equilibrium with metallic iron at  $T^\circ K$ .

For the activity of iron, from Eq. (1) and (9)

$$d \log \alpha_{\text{O}} = -\frac{2F}{RT} dE \quad (10)$$

One has in view of the Gibbs-Duhem equation,

$$d \log \alpha_{\text{Fe}} = -\frac{N_{\text{O}}}{N_{\text{Fe}}} d \log \alpha_{\text{O}} \quad (11)$$

where  $N_{\text{O}}$  and  $N_{\text{Fe}}$  are atomic fraction of oxygen and iron in wustite respectively. Integration of Eq. (11) from the oxygen composition of wustite in equilibrium with iron to the composition  $1+y$  yields

$$\log \alpha_{Fe} = \int_{N_{Fe}/FeO_{1+y}}^{N_{FeO_{1+y}}} -\frac{N_O}{N_{Fe}} d \log \alpha_O \quad (12)$$

From Eq. (11) and (12) it follows that

$$\log \alpha_{Fe} = \frac{2F}{RT} \int_{N_{Fe}/FeO_{1+y}}^{N_{FeO_{1+y}}} \frac{N_O}{N_{Fe}} dE \quad (13)$$

For the activity of wustite  $\alpha_{FeO}$ , according to the relation

$$\alpha_{FeO_{1+y}} = \alpha_{Fe} \times \alpha_O \quad (14)$$

it follows, upon substitution of Eq. (10) and (13) in Eq. (14), that

$$\log \alpha_{FeO_{1+y}} = \frac{2F}{RT} \int_{N_{Fe}/FeO_{1+y}}^{N_{FeO_{1+y}}} \left( \frac{N_O}{N_{Fe}} - 1 \right) dE \quad (15)$$

If values of  $\log \alpha_{Fe}$ , corresponding to the area below each line in Fig. 5, are available from the relations between temperature, composition and e.f.m. as given in Table 1,  $\log \alpha_{FeO_{1+y}}$  may be evaluated, using Eq. (14), from the values of  $\log \alpha_{Fe}$  and  $\log \alpha_O$ . The evaluated  $\log \alpha_O$ ,  $\log \alpha_{Fe}$  and  $\log \alpha_{FeO_{1+y}}$  are plotted in function of composition in the case of 1000°C (Fig. 7).

The partial molar enthalpies of solution of iron in wustite may be derived

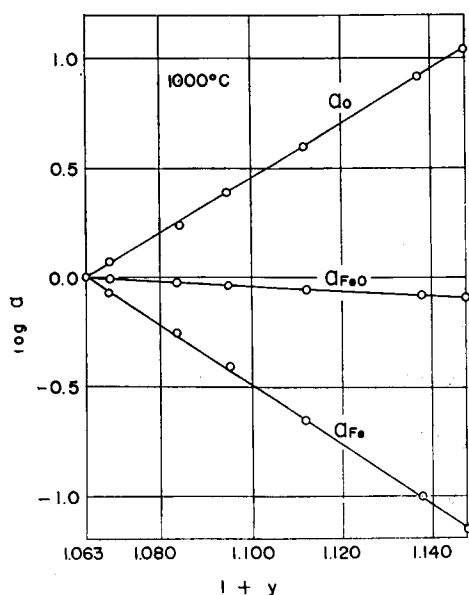


Fig. 7. Activities of iron, oxygen and wustite evaluated at 1000°C.

Table 3. Partial molar enthalpies of solution of iron.

Composition $FeO_{1+y}$	$\Delta H_{Fe}$ (cal/mol)
1.068	359 ( $\pm 50$ )
1.083	74
1.094	242
1.111	844
1.137	2356

from the values of  $\log \bar{G}_{\text{Fe}}$  at a given composition using Fig. 7 and the following relationship

$$\left( \frac{\partial \ln \bar{G}_{\text{Fe}}}{\partial \left( \frac{1}{T} \right)} \right)_{1+y=\text{const.}} = \frac{\Delta H_{\text{Fe}}}{R} \quad (16)$$

and are shown in Table 3.

The free energy change for the reaction



is given in the form

$$\Delta F^0 = -RT \log \frac{\bar{G}_{\text{Fe}_3\text{O}_4}}{\bar{G}_{\text{Fe}}^3 \bar{P}_{\text{O}_2}^2} \quad (18)$$

where  $\bar{G}_{\text{Fe}_3\text{O}_4}$  is unity when the equilibrium reaction between magnetite, iron and oxygen on the magnetite side of the phase limits of wustite is considered, and  $\bar{G}_{\text{Fe}}$  and  $P_{\text{O}_2}$  are replaced by the activity of iron and oxygen pressure of wustite in equilibrium with magnetite respectively. Thus, the enthalpy of formation of magnetite may be calculated from the following expression.

$$\Delta H_{\text{Fe}_3\text{O}_4}^0 = \frac{d(F^0/T)}{d\left(\frac{1}{T}\right)} = R \left( \frac{d \log \bar{G}_{\text{Fe}_3\text{O}_4}^3 P_{\text{O}_2}}{d\left(\frac{1}{T}\right)} \right) \quad (19)$$

For this purpose, the values of  $(3 \log \bar{G}_{\text{Fe}} + 4 \log P_{\text{O}_2}^{1/2})$  were plotted against the reciprocal temperature in Fig. 8. These plots show a linear relation, the tangent of which give value of  $\Delta H_{\text{Fe}_3\text{O}_4}^0$

$$\Delta H_{\text{Fe}_3\text{O}_4}^0 = -263,060 (\pm 200) \text{ cal/mol}$$

The oxygen deficiency  $v$  in a sample represented by the formula  $\text{FeO}_{1+y}$  may be written

$$v = y/1+y \quad (20)$$

$\log v$  was plotted against  $\log P_{\text{O}_2}$  at 800°C and 900°C in Fig. 9, and the relationship

$$v \propto P_{\text{O}_2}^{1/5.75} \quad (21)$$

was obtained, regarding  $\log v$ - $\log P_{\text{O}_2}$  plots were linear.

Darken and Gurry's thermodynamic studies<sup>1)</sup> to show that the deviation from stoichiometry caused by cation vacancies was proportional to the six root of the oxygen pressure. A model consistent with these findings is that oxygen can be dissolved into the lattice by,

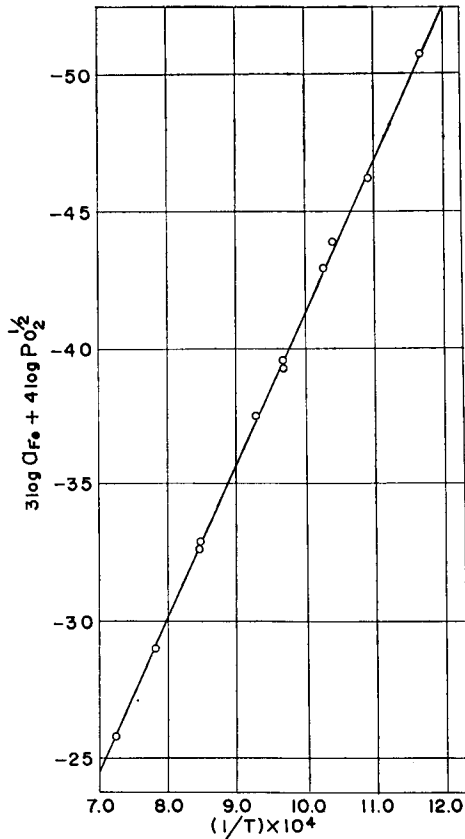


Fig. 8. Relations between  $(3 \log a_{Fe} + 4 \log P_{O_2}^{1/2})$  and the reciprocal temperature.

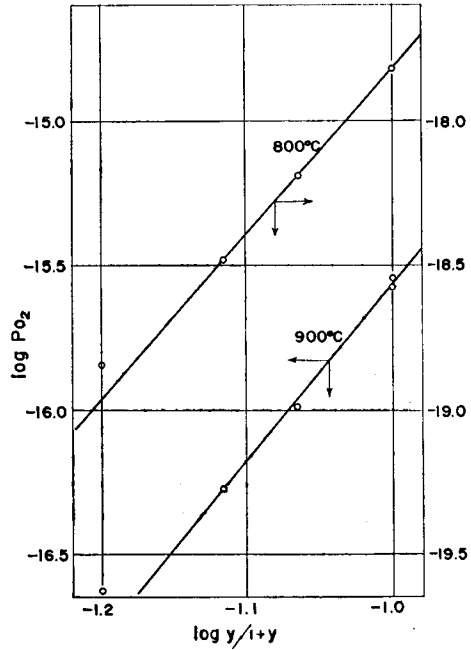
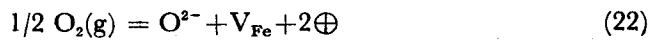


Fig. 9. Partial oxygen pressure-cation vacancy concentration relationship.



where the symbol,  $O^{2-}$ , denotes an oxygen ion in the lattice,  $V_{Fe}$  a cation vacancy and  $\oplus$  an electron hole. However, more recently, Vallet<sup>7)</sup>, Geiger<sup>8)</sup> have showed experimentally non-linear relation between  $\log v$  and  $\log P_{O_2}$ , and Fender<sup>6)</sup> confirmed the presence of three wustite regions separated by order-disorder transitions.

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