BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 3043—3046 (1971)

# The Phase Equilibria in the $FeO$-$Fe_2O_3$-$V_2O_3$ System at 1500°K

Masataka WAKIHARA and Takashi KATSURA
*Department of Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo*

(Received May 7, 1971)

The phase equilibria in the $FeO$–$Fe_2O_3$–$V_2O_3$ system have been determined at 1500°K by varying the oxygen partial pressure. The following three oxide phases have been stable in equilibrium: a sesquioxide solid solution with a corundum-type structure (approximate composition $Fe_2O_3$–$V_2O_3$), a ternary solid solution with a spinel-type structure (approximate composition $FeO\cdot Fe_2O_3$–$FeO\cdot V_2O_3$), and a ternary wüstite solid solution with a periclase-type structure which dissolves vanadium ions up to about 10 mol per cent. The extent of the solid-solution areas and the location of the oxygen isobars have been determined. The spinel phase coexisted partly with metallic iron and partly with the wüstite solid solution, corresponding to lower and higher iron contents respectively. The standard free energies of the $Fe+V_2O_3+{}^1/_2O_2=FeV_2O_4$ and $0.05\ Fe+V_2O_3+Fe_{0.95}O=FeV_2O_4$ reactions to produce $FeV_2O_4$ have been calculated to be $-45500\pm200$ cal and $-5800\pm400$ cal respectively at 1500°K on the basis of the equilibrium oxygen partial pressure.

The Fe–V–O system is of a great deal of interest to metallurgists as well as to ceramists and geochemists. The accurate phase equilibria, however, have not yet been presented, particularly at high temperatures. Binary systems of Fe–O and V–O have been studied by Darken and Gurry[1] and many other investigators.[2–9] Vanadium is a minor element in the earth's crust, and it is often found in magnetite ($Fe_3O_4$) upon the replacement of iron ions. Burdese[10] studied the phase equilibria of the Fe–V–O system and synthesized $FeV_2O_6$, $FeV_2O_4$, and $FeVO_4$. Vorob'ev *et al.*[11] investigated $Fe_3O_4$–$FeV_2O_4$ and wüstite solid solutions at 1000°K.

---

[1] L. S. Darken and R. W. Gurry, *J. Amer. Chem. Soc.*, **67**, 1398 (1945); *ibid.*, **68**, 798 (1946).

[2] W. Klemm and L. Grimm, *Z. anorg. u. allgem. Chem.*, **250**, 42 (1942).

[3] E. Hoschek and W. Klemm, *ibid.*, **242**, 63 (1939).

[4] G. Andersson, *Acta Chem. Scand.*, **8**, 1559 (1954); *ibid.*, **10**, 623 (1956).

[5] S. Andersson, *ibid.*, **14**, 1161 (1960).

[6] K. Kosuge, *J. Phys. Chem. Solids*, **28**, 1613 (1967).

[7] T. Katsura and M. Hasegawa, This Bulletin, **40**, 561 (1967).

[8] M. Wakihara and T. Katsura, *Met. Trans.*, **1**, 363 (1970).

[9] J. S. Anderson and A. S. Khan, *J. Less Common Metals*, **22**, 209 (1970).

[10] A. Burdese, *Ann. Chim.* (Rome), **47**, 785 (1957).

[11] Yu. P. Vorob'ev, V. N. Bogoslovskii, E. G. Bogachova, and G. I. Chufarov, *Dokl. Akad. Nauk, S.S.S.R.*, **166**, 664 (1966).

Kunnmann *et al.*[12] synthesized some transition metal oxides in the temperature range from 1073° to 1380°K and calculated the standard free energy of $FeV_2O_4$. Recently, Schmahl and Dillenburg[13] studied the phase equilibria of the Fe–V–O system at 900°C and calculated the activities for the $Fe_3O_4$–$FeV_2O_4$ solid-solution series and the standard free energy of $FeV_2O_4$. Also, they recognized that the $Fe_2O_3$–$V_2O_3$ solid solution has an immiscible region in the range of 78—93 mol per cent $V_2O_3$ at 900°C. In this solid-solution series, Cox *et al.*[14] also found an immiscibility gap in the range of 80—90 mol per cent $V_2O_3$ on the basis of their magnetic data collected at 1000°C. Wakihara *et al.*[15] synthesized the $Fe_3O_4$–$FeV_2O_4$ spinel solid solution at 1500°K and measured the magnetic properties. They proposed these cation distributions: $Fe^{3+}(Fe^{2+}Fe^{3+}_{\mu}V^{3+}_{1-\mu})O_4$ $(0 \leqq \mu \leqq 1)$ for the $Fe_3O_4$–$Fe_2VO_4$ series, and $Fe^{3+}_{\lambda}$-$Fe^{2+}_{1-\lambda}(Fe^{2+}_{\lambda}V^{3+}_{2-\lambda})O_4$ $(0 \leqq \lambda \leqq 1)$ for the $Fe_2VO_4$–$FeV_2O_4$ series.

In the present study, accurate phase equilibria of the $FeO$–$Fe_2O_3$–$V_2O_3$ system has been determined at 1500°K by varying the oxygen partial pressure. The standard free energy of the reaction to produce $FeV_2O_4$ has been calculated at 1500°K on the basis of the equilibrium oxygen partial pressure.

## Experimental

*1) General Procedure.* Different experimental methods were used in the present study; the quenching and thermogravimetric methods have previously been described by Katsura and Muan[16] and by Katsura and Kimura.[17]

In the quenching method, oxide samples were heated at 1500°K and at a chosen oxygen partial pressure until equilibrium was attained among the gas and condensed phases. The samples were then quenched rapidly to the temperature of cold water and the phases present were determined by the X-ray diffraction method. The total compositions were determined by means of the gravimetric weight-gain method.

In the thermogravimetric method, a pellet of an oxide mixture was suspended in a vertical tube-quenching furnace by means of a thin platinum wire stretched from the bottom of the quick weighing balance. The weight changes were recorded as a function of the oxygen partial pressure at 1500°K.

The furnace temperatures were kept constant to approximately ±3°K throughout this investigation.

*2) Materials.* The $V_2O_5$ was obtained by the decomposition of the reagent grade of ammonium meta vanadate at 450°C in air for 12 hr. Analytical-grade $Fe_2O_3$ was fired at 700°C in air for 12 hr. Mixtures of the desired ratios of the above two oxides were then prepared. The mixture was loosely pressed into a small-size platinum crucible, and then heated at 650°C in a mixed gas of $CO_2/H_2=1$ for 20 min. The griding, pressing, and heating were repeated to obtain an uniform mixture. An error in the atomic ratio of V/Fe in the mixture was estimated to be within ±0.1 per cent. The prepared sample was a mixture of reduced forms of vanadium and iron oxides. The pellet of the oxide sample was suspended in a furnace tube; here it was heated at 1500°K in a desired $CO_2$–$H_2$ gas mixture for 10—18 hr until equilibrium was attained among the gas and the solid phases. The details of the procedure have been described by Katsura and Kimura.[17]

*3) Analysis of Total Compositions.* The total compositions of the quenched samples were determined by the gravimetric weight-gain method. About 1 g of the quenched sample was accurately weighed. Then, the sample was completely oxidized to the mixture of $V_2O_5$ and $Fe_2O_3$ at 800°C in air for 24—48 hr, and then again it was weighed. As the $Fe_2O_3/V_2O_5$ mol ratio of starting materials was known, the total compositions of the quenched sample were evaluated by means of the difference in weight between before and after the oxidation. The vaporization of $V_2O_5$ was insignificant during heating within the present limits of accuracy. The error in the total compositions was estimated to be within ±0.2 per cent.

*4) Control of Atmosphere.* A desired partial pressure of oxygen was provided by using a gas mixture of $CO_2$ and $H_2$ or $CO_2$ and $O_2$. The mixed gas was prepared by a gas mixer similar to that used by Darken and Gurry.[1] The actual oxygen partial pressure was measured by means of a solid electrolyte cell composed of stabilized zirconia, $(ZrO_2)_{0.85}(CaO)_{0.15}$. The principles and procedure have been described previously.[7,8]

*5) Thermogravimetry.* The rate of the approach to equilibrium was observed thermogravimetrically. Also, the method was used to determine the ranges of the oxygen partial pressure and the composition in which both spinel and wüstite solid solutions exist in equilibrium. The technique was described in detail in previous papers.[7,8,17]

*6) Identification of Phases.* The phases present in the quenched samples were identified by an X-ray diffraction method using $FeK_{\alpha}$ radiation.

The presence of metallic iron in the phase assemblages was evidenced by the liberation of hydrogen gas when samples were dipped in hydrochloric acid. This test is sensitive enough to detect iron in amounts as small as 0.2 per cent, as has been described in a previous study.[17]

## Results and Discussion

*1) Phase Equilibria.* The equilibrium data obtained at 1500°K are summarized in Table 1 and are illustrated graphically in Fig. 1.

Three solid solution phases are stable under the present expremental conditions: the sesquioxide solid solution, the spinel solid solution, and the wüstite solid solution. The compositions of the sesquioxide phase were stoichiometric within the limits of experimental error and were well represented by the formula $(Fe \cdot V)_2O_3$. Sesquioxides of 80—90 mol per cent $Fe_2O_3$ were prepared by using a gas mixture of $CO_2$ and $O_2$. Each phase of the sesquioxide solid solution was identified by the X-ray diffraction method.

The spinel phase is a ternary solid solution with a stable existence at 1500°K within the composition area, $Fe_3O_4$–$FeV_2O_4$–$Fe_2O_3$. The range of oxygen partial pressure in which the spinel solid solution exists in equilibrium is shown in Fig. 2. The figure illustrates

---

[12] W. Kunnmann, D. B. Rogers, and A. Wold, *J. Phys. Chem. Solids*, **24**, 1535 (1963).

[13] G. Schmahl and H. Dillenburg, *Z. Phys. Chem.*, **65**, 119 (1969).

[14] D. E. Cox, W. J. Takei, R. C. Miller, and G. Shirane, *J. Phys. Chem. Solids*, **23**, 863 (1962).

[15] M. Wakihara, Y. Shimizu, and T. Katsura, *J. Solid State Chem.*, (In Press).

[16] T. Katsura and A. Muan, *Trans. A.I.M.E.*, 230, 77 (1964).

[17] T. Katsura and S. Kimura, This Bulletin, **38**, 1664 (1965).

Table 1. Results of equilibration experiments at 1500°K at various oxygen partial pressures
mol % $x$: FeO $y$: $Fe_2O_3$ $z$: $V_2O_3$ ses: sesquioxide solid solution
sp: spinel solid solution wü: wüstite solid solution

| $-\log P_{O_2}$ $\pm 0.05$ | $x$ | $y$ | $z$ | phases present | $-\log P_{O_2}$ $\pm 0.05$ | $x$ | $y$ | $z$ | phases present |
|---|---|---|---|---|---|---|---|---|---|
| 13.13 | 50.3 | 0 | 49.7 | ses+sp | | 78.7 | 15.3 | 6.0 | sp+wü |
| 11.71 | 9.8 | 4.5 | 85.7 | ses+sp | | 82.2 | 13.4 | 4.4 | sp+wü |
| | 27.1 | 3.7 | 69.2 | ses+sp | | 85.5 | 11.6 | 2.8 | wü |
| | 41.2 | 3.2 | 55.6 | ses+sp | | 89.3 | 10.7 | 0 | wü |
| | 45.8 | 2.8 | 51.4 | ses+sp | 9.75 | 49.5 | 35.4 | 15.1 | sp |
| 11.61 | 49.6 | 16.5 | 33.8 | sp | | 61.4 | 28.2 | 10.4 | sp+wü |
| | 57.9 | 13.7 | 28.4 | sp+wü | | 71.9 | 21.8 | 6.4 | sp+wü |
| 11.48 | 51.1 | 19.1 | 29.8 | sp+wü | | 81.4 | 15.6 | 3.0 | sp+wü |
| | 66.0 | 13.9 | 20.1 | sp+wü | 9.01 | 49.6 | 40.9 | 9.4 | sp |
| | 72.7 | 11.4 | 15.9 | sp+wü | | 49.6 | 42.8 | 7.5 | sp |
| | 78.4 | 9.4 | 12.2 | sp+wü | | 49.7 | 44.7 | 5.6 | sp |
| | 84.0 | 7.2 | 8.7 | sp+wü | | 61.4 | 35.1 | 3.5 | sp+wü |
| | 88.7 | 5.8 | 5.6 | wü | | 82.6 | 17.4 | 0 | wü |
| | 92.0 | 5.3 | 2.7 | wü | 8.59 | 0 | 20.0 | 80.0 | ses |
| 11.36 | 50.2 | 19.8 | 30.0 | sp+wü | | 12.1 | 17.4 | 70.4 | ses+sp |
| | 59.4 | 17.1 | 23.4 | sp+wü | | 23.4 | 14.8 | 61.8 | ses+sp |
| | 63.8 | 15.8 | 20.4 | sp+wü | | 30.1 | 13.3 | 56.6 | ses+sp |
| | 70.8 | 13.0 | 16.2 | sp+wü | | 41.9 | 10.6 | 47.5 | ses+sp |
| | 76.9 | 10.8 | 12.3 | sp+wü | | 48.9 | 13.3 | 37.8 | sp |
| | 82.5 | 8.7 | 8.8 | sp+wü | | 49.2 | 16.9 | 34.0 | sp |
| | 87.4 | 6.9 | 5.6 | sp+wü | | 49.5 | 35.4 | 15.0 | sp |
| | 91.5 | 5.8 | 2.7 | wü | | 49.3 | 43.2 | 7.5 | sp |
| 10.94 | 5.3 | 6.9 | 16.2 | ses+sp | | 49.5 | 46.7 | 3.8 | sp |
| | 24.7 | 5.3 | 70.0 | ses+sp | 7.61 | 2.0 | 28.8 | 69.3 | ses+sp |
| | 39.4 | 4.3 | 56.3 | ses+sp | | 13.4 | 24.4 | 62.1 | ses+sp |
| | 44.4 | 3.8 | 51.8 | ses+sp | | 29.4 | 19.5 | 51.1 | ses+sp |
| | 48.6 | 4.1 | 47.3 | ses+sp | | 39.1 | 16.6 | 44.3 | ses+sp |
| | 48.8 | 5.9 | 45.4 | sp | 6.30 | 11.6 | 36.6 | 51.8 | ses+sp |
| | 49.7 | 20.3 | 30.0 | sp | | 25.7 | 30.7 | 43.6 | ses+sp |
| | 52.6 | 22.9 | 24.5 | sp+wü | | 35.9 | 27.2 | 37.0 | ses+sp |
| | 57.9 | 20.8 | 21.3 | sp+wü | | 46.9 | 22.5 | 30.6 | sp |
| | 65.3 | 17.8 | 16.9 | sp+wü | | 47.0 | 30.0 | 23.0 | sp |
| | 73.0 | 14.3 | 12.7 | sp+wü | 4.41 | 3.0 | 52.6 | 44.4 | ses+sp |
| | 79.2 | 11.8 | 9.1 | sp+wü | | 20.2 | 43.9 | 36.0 | ses+sp |
| | 85.4 | 8.9 | 5.7 | sp+wü | | 35.1 | 37.4 | 27.5 | ses+sp |
| | 90.1 | 7.1 | 2.8 | wü | | 42.2 | 34.2 | 23.6 | ses+sp |
| | 93.5 | 6.5 | 0 | wü | 2.94 | 8.8 | 72.1 | 19.1 | ses+sp |
| 10.04 | 50.3 | 30.9 | 18.7 | sp+wü | | 24.7 | 62.2 | 13.1 | ses+sp |
| | 61.5 | 24.7 | 13.8 | sp+wü | | 39.7 | 52.4 | 8.0 | ses+sp |
| | 71.0 | 19.4 | 9.6 | sp+wü | | | | | |

the relationship between the oxygen partial pressure and the compositional parameter, $x$, for the general formula of the spinel: $Fe_{1+2x}V_{2-2x}O_4$ $(0 \leq x \leq 1)$. The solid lines in the range indicate the values of the atomic ratio of $4(Fe+V)/O$. No spinel with a greater metal-to-oxygen ratio than 3:4 was found in the present study. These situations are quite similar to the case of the other spinel solid solutions, $Fe_2TiO_4$–$Fe_3O_4$[18] and $FeCr_2O_4$–$Fe_3O_4$[16].

The wüstite phase has a extensive homogeneous range with some $V^{3+}$ ions in the structure. The extent of these compositional ranges is shown in Fig. 1.

The results in the present study at 1500°K on the binary FeO–$Fe_2O_3$ system are consistent with those obtained by Darken and Gurry[1] within the limits of experimental error.

Schmahl and Dillenburg[13] and Cox *et al.*[14] reported an immiscible gap of the sesquioxide phase with a rhombohedral (corundum-type) structure in the range about from 80 to 90 mol per cent $V_2O_3$ at 900°C and 1000°C respectively. The gap, however, was not found in the present study throughout the $Fe_2O_3$–$V_2O_3$ system at 1500°K, within our limits of experimental error.

The phase equilibria of the FeO–$Fe_2O_3$–$V_2O_3$ system were similar to those of the FeO–$Fe_2O_3$–$Cr_2O_3$ system previously investigated.[16] Some characteristic differences were these: no deviation of the oxygen-to-cation ratio below the stoichiometric 3:2 ratio in the sesquioxide phase was found in the present study, and the

---

[18] R. W. Taylor, *Amer. Mineral.*, **49**, 1016 (1964).

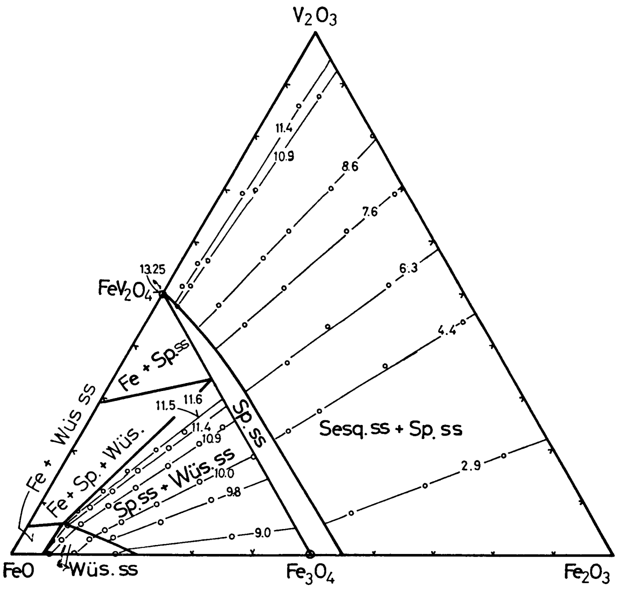

Fig. 1. Graphical representation of equilibrium data obtained for the $FeO$–$Fe_2O_3$–$V_2O_3$ system at 1500°K (mol per cent). Lines in the composition triangle indicate oxygen isobar and numbers on the lines are values of $-\log P_{O_2}$.

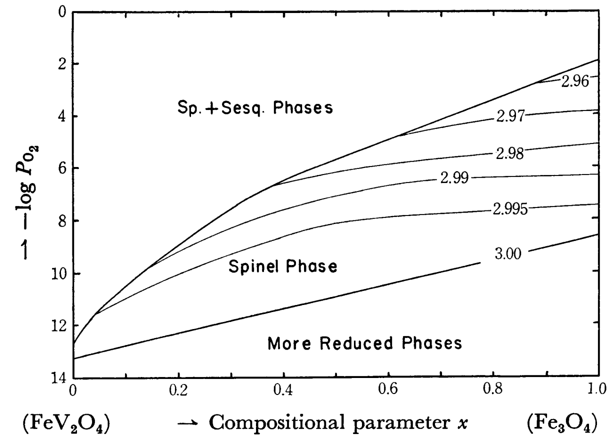

Fig. 2. Relationship between $\log P_{O_2}$ and compositional parameter $x$ for $Fe_{1+2x}V_{2-2x}O_4$ at 1500°K; here, lines in the spinel phase region indicate the value of mole ratio, $4(Fe+V)/O$.

spinel-phase region in equilibrium with metallic iron (almost from $FeV_2O_4$ to $Fe_2VO_4$) was larger than those of the magnetite–iron chromite solid solution series.[16] The latter result may be partly due to the difference in the experimental temperature between the present and previous studies.[16]

*2) Thermodynamic Calculations.* The oxygen partial pressure at which metallic iron, $FeV_2O_4$, and $V_2O_3$ coexist in equilibrium was determined in this investigation ($\log P_{O_2} = -13.25 \pm 0.05$). This value was obtained thermogravimetrically, as is shown in Fig. 2. Therefore, the standard free energy of the reaction to produce $FeV_2O_4$ from metallic iron and sesquioxide components at 1500°K may be calculated as follows:

$$Fe + V_2O_3 + 1/2O_2 = FeV_2O_4 \qquad \text{(A)}$$

The standard free energy of Reaction (A) is given by the following equations:

$$\Delta G^\circ(\text{A}) = -\boldsymbol{R}T\ln\frac{a_{FeV_2O_4}}{a_{Fe}\cdot a_{V_2O_3}\cdot P_{O_2}{}^{1/2}} = 1.152\boldsymbol{R}T\log P_{O_2} \qquad \text{(A')}$$

$$= -45500 \pm 200 \text{ cal}$$

where the $a_{Fe}$, $a_{V_2O_3}$, and $a_{FeV_2O_4}$ activities are equal to unity because these components are pure compounds at the oxygen partial pressure of $\log P_{O_2}(\text{A}) = -13.25$.

The standard free energy of Reaction (A) was determined by Kunnmann *et al.*[12] over the temperature range from 1073° to 1380°K by varying the oxygen partial pressure using $CO_2/CO$ gas mixtures. The standard free energy resulting from the present investigation at 1500°K was reasonably consistent with the extrapolated value of their data. According to the data of Darken and Gurry,[1] the oxygen partial pressure at which metallic iron and wüstite phases are stable in equilibrium was logarithmically estimated to be $\log P_{O_2} = -11.58 \pm 0.05$ at 1500°K. Thus, the standard free energy of the formation of wüstite from metallic iron can be readily calculated:

$$0.95Fe + 1/2O_2 = Fe_{0.95}O \qquad \text{(B)}$$

$$\Delta G^\circ(\text{B}) = -\boldsymbol{R}T\ln\frac{a_{Fe_{0.95}O}}{a_{Fe}{}^{0.95}\cdot P_{O_2}{}^{1/2}} = 2.303/2\boldsymbol{R}T\log P_{O_2}(\text{B}) \qquad \text{(B')}$$

$$= -39700 \pm 200 \text{ cal}$$

where $\log P_{O_2}(\text{B}) = -11.58 \pm 0.05$, and where the $a_{Fe}$ and $a_{Fe_{0.95}O}$ activities are unity.

The substraction of Eq. (B) from Eq. (A) gives the following equation:

$$0.05Fe + V_2O_3 + Fe_{0.95}O = FeV_2O_4 \qquad \text{(C)}$$

while the standard free energy of Reaction (C) is given by:

$$\Delta G^\circ(\text{C}) = \Delta G^\circ(\text{A}) - \Delta G^\circ(\text{B}) = \boldsymbol{R}T\ln\frac{P_{O_2}(\text{A})}{P_{O_2}(\text{B})} \qquad \text{(C')}$$

$$= -5800 \pm 400 \text{ cal}$$