Chemical Potential of Oxygen for Iron-Rutile-Ilmenite and Iron-Ilmenite-Ulvospinel Equilibria

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The chemical potential of oxygen corresponding to the iron-rutile-ilmenite (IRI) and iron-ilmenite-ulvospinel (IIU) equilibria has been measured employing solid-state galvanic cells,

$$\text{Pt, Fe} + \text{TiO}_2 + \text{FeTiO}_3 // (\text{Y}_2\text{O}_3)\ \text{ZrO}_2 // \text{Fe} + \text{“FeO”, Pt}$$

and

$$\text{Pt, Fe} + \text{FeTiO}_3 + \text{Fe}_2\text{TiO}_4 // (\text{Y}_2\text{O}_3)\ \text{ZrO}_2 // \text{Fe} + \text{“FeO”, Pt}$$

in the temperature range of 875 to 1275 K and 900 to 1373 K, respectively. The cells are written such that the right-hand electrodes are positive. The electromotive force (emf) of both the cells was found to be reversible and to vary linearly with temperature over the entire range of measurement. The chemical potential of oxygen for IRI equilibrium is represented by

$$\begin{aligned}\Delta\mu_{O_2}(\text{IRI}) &= -550{,}724 - 29.445T + 20.374T \ln T (\pm 210)\ \text{J mol}^{-1} \\ &\quad (875 \leq T \leq 1184\ \text{K}) \\ &= -620{,}260 + 369.593T - 27.716T \ln T (\pm 210)\ \text{J mol}^{-1} \\ &\quad (1184 \leq T \leq 1275\ \text{K})\end{aligned}$$

and that for IIU equilibrium by

$$\begin{aligned}\Delta\mu_{O_2}(\text{IIU}) &= -501{,}800 - 49.035T + 20.374T \ln T (\pm 210)\ \text{J mol}^{-1} \\ &\quad (900 \leq T \leq 1184\ \text{K}) \\ &= -571{,}336 + 350.003T - 27.716T \ln T (\pm 210)\ \text{J mol}^{-1} \\ &\quad (1184 \leq T \leq 1373\ \text{K})\end{aligned}$$

The standard Gibbs energy changes for IRI and IIU equilibria have been deduced from the measured oxygen potentials. Since ilmenite contains small amounts of Ti^{3+} ions, a correction for the activity of $FeTiO_3$ has been incorporated by assuming ideal mixing on each cation sublattice in the $FeTiO_3$-Ti_2O_3 system. Similarly, the ulvospinel contains some Fe^{3+} ions and a correction for the activity of Fe_2TiO_4 has been included by modeling the Fe_2TiO_4-Fe_3O_4 system. The third-law analysis of the results obtained for IRI equilibrium gives $\Delta H^\circ_{298} = -575\ (\pm 1.0)$ kJ mol^{-1} and for IIU equilibrium yields $\Delta H^\circ_{298} = -523.7\ (\pm 0.7)$ kJ mol^{-1}. The present results suggest that Fe^{2+} and Ti^{4+} cations mix almost ideally on the octahedral site of spinel lattice in Fe_2TiO_4, giving rise to a configurational contribution of $2R \ln 2$ (11.5256 J mol^{-1} K^{-1}) to the entropy of Fe_2TiO_4.

I. INTRODUCTION

AMONG the many minerals that contain titanium, ilmenite ($FeTiO_3$) and to a lesser extent ulvospinel (Fe_2TiO_4) are readily available. In order to extract titanium metal from these minerals, it is necessary to separate iron either by aqueous leaching or by pyrometallurgical methods. The iron-rutile-ilmenite (IRI) and iron-ilmenite-ulvospinel (IIU) equilibria are extensively used as oxygen buffers. Accurate thermodynamic data on these equilibria at elevated temperatures are necessary for the construction of a complete phase diagram for the Fe-Ti-O system. The diagram is useful from both pyrometallurgical and petrological points of view. There have been a number of investigations on IRI and IIU equilibria employing different techniques, but the agreement between the results of various groups of investigators has not been entirely satisfactory.

The Gibbs energy change for IRI equilibrium has been determined by Schmahl *et al.*[1] (1173 to 1323 K) and Levitskii *et al.*[2] (1173 to 1373 K) using the CO/CO_2 gas equilibrium method. Taylor *et al.*[3] (1123 to 1323 K) used a $CO_2 + H_2 + N_2$ gas mixture to measure the oxygen potential. El Goresy and Woermann[4] (1150 to 1340 K) employed both the $CO_2 + H_2$ gas equilibrium technique and the solid-state galvanic cell. Borowiec and Rosenqvist[5] (973 to 1373 K), Taylor and Schmalzried[6] (1073 to 1473 K), Merritt and Turnbull[7] (1306 to 1477 K), and recently, O'Neill *et al.*[8] (990 to 1320 K)

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employed the electromotive force (emf) technique incorporating calcia-stabilized zirconia as the solid electrolyte. Levitskii *et al.*[9] (1213 to 1373 K) used $(La_2O_3)ThO_2$ as the solid oxygen ion conductor in their emf measurements.

The Gibbs energy change for IIU equilibrium has been determined experimentally by Schmahl *et al.*[1] (1073 to 1323 K) and Taylor *et al.*[3] (1123 to 1483 K) using the gas equilibrium method. The chemical potential of oxygen for the IIU equilibrium has been measured by Borowiec and Rosenqvist[5] (973 to 1373 K), Taylor and Schmalzried[6] (1073 to 1473 K), Merritt and Turnbull[7] (1246 to 1409 K), and recently, by O'Neill *et al.*[8] (1050 to 1355 K) employing the emf technique. Among the earlier investigators of IRI and IIU equilibria, only O'Neill *et al.*[8] have attempted to correct for the effect of reduced activity of $FeTiO_3$ and Fe_2TiO_4 on the standard Gibbs energy of formation.

The present investigation aims at the redetermination of Gibbs energy change for IRI and IIU equilibria employing the solid-state galvanic cells,

$$\text{Pt, Fe} + TiO_2 + FeTiO_3//(Y_2O_3)\,ZrO_2//\text{Fe} + \text{“FeO”, Pt} \qquad [I]$$

and

$$\text{Pt, Fe} + FeTiO_3 + Fe_2TiO_4//(Y_2O_3)\,ZrO_2//\text{Fe} + \text{“FeO”, Pt} \qquad [II]$$

in the temperature ranges 875 to 1275 K and 900 to 1373 K, respectively. Yttria-stabilized zirconia is preferred over calcia-stabilized zirconia because of its stability in the temperature range of measurements. The calcia-stabilized zirconia is metastable, and the cubic phase is known to undergo a phase transformation on prolonged exposure, giving rise to instabilities.

II. EXPERIMENTAL

A. *Materials*

Puratronic grade Fe, Fe_2O_3, and TiO_2 powders were obtained from Johnson and Matthey Chemicals (Royston, United Kingdom). Ilmenite ($FeTiO_3$) was prepared by intimately mixing the powders of Fe, Fe_2O_3, and TiO_2 in the appropriate molar ratio and reacting the compacted mixture at 1373 K for 3 days. The pellet was contained in an alumina crucible which was sealed inside an evacuated quartz capsule. The pellet was ground, pelletized, and sintered again under identical conditions for a period of 3 days. After each heat treatment, a thin layer of the pellet in contact with the alumina crucible was removed by grinding to minimize possible contamination by alumina. The X-ray diffraction analysis indicated single-phase $FeTiO_3$. Similarly, ulvospinel (Fe_2TiO_4) was prepared by intimately mixing the powders of Fe, Fe_2O_3, and TiO_2 in the appropriate molar ratio. The cycle of mixing, pelletizing, and firing was repeated three times. The final product was found to be mostly Fe_2TiO_4 by X-ray diffraction analysis with a very small amount of unreacted Fe and $FeTiO_3$. There was no sign of TiO_2 in the X-ray diffraction pattern.

The three-phase electrode of cell-I was prepared by pelletizing an equimolar mixture of Fe + TiO_2 + $FeTiO_3$ and sintering at 1373 K for 2 days in an alumina crucible inside a quartz capsule sealed under vacuum. The three-phase electrode used in cell-II was prepared by a similar procedure. The flat surfaces of the three-phase electrode pellets were polished before use in the cell for emf measurements. The biphasic Fe + "FeO" reference electrode was prepared from an intimate mixture of Fe and Fe_2O_3 in the appropriate molar ratio compacted inside a yttria-stabilized zirconia tube and sintered *in situ* at 1400 K under prepurified argon gas, with a platinum lead embedded in the mixture. High-density $(Y_2O_3)ZrO_2$ tube was obtained from Zirconium Corporation of America (Cleveland, OH).

B. *Apparatus and Procedure*

A schematic diagram of the apparatus for emf measurement is shown in Figure 1. The Fe + "FeO" reference electrode is taken inside the electrolyte tube. The three-phase electrode pellet was spring-loaded against the bottom of the electrolyte tube by means of a supporting system of alumina slabs and rods. A platinum wire gauze was placed between the three-phase electrode and the supporting alumina slab. A platinum lead was spot-welded

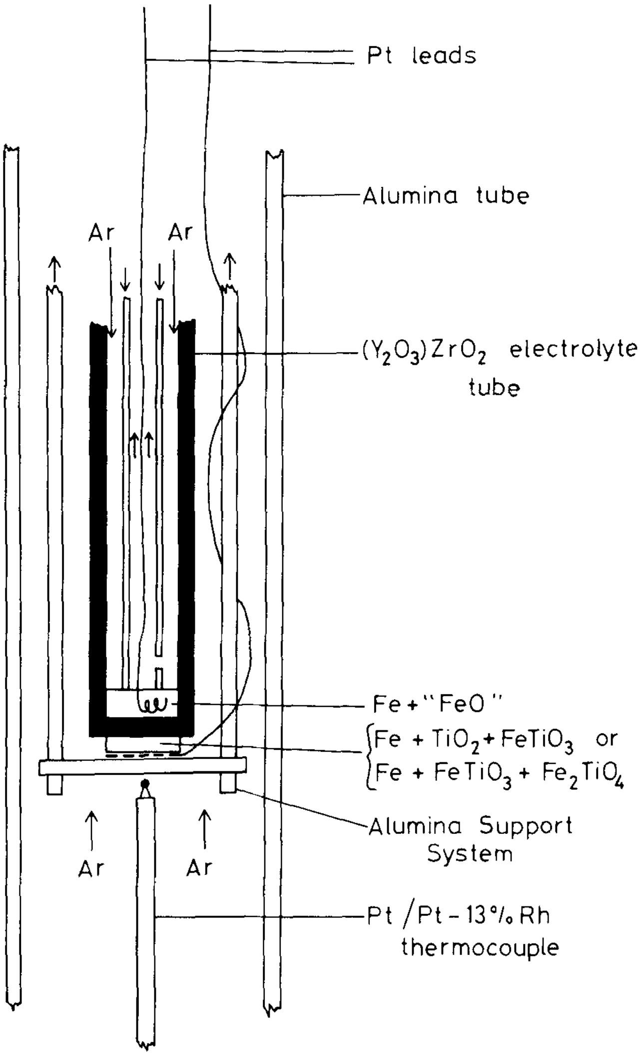

Fig. 1—Schematic diagram of the solid-state galvanic cell.

to the gauze. The electrical contact to the reference electrode was made by a platinum lead embedded in it. Both the electrodes were flushed by separate streams of argon gas. Argon gas was dried over anhydrous phosphorous pentoxide and deoxidized by passing over copper wool at 723 K and titanium granules maintained at 1123 K prior to being introduced into the emf apparatus. The temperature of the cell was measured by a Pt/Pt-13 pct Rh thermocouple placed adjacent to the three-phase electrode.

The emf was measured with a high impedance ($>10^{12}\ \Omega$) digital voltmeter. The reversibility of each cell was confirmed by microcoulometric titration ($\sim 50\ \mu A$ for 300 seconds) of oxygen in both directions. In each case, the emf was found to return to its original value before the titration. The absence of a thermal gradient was ensured by measuring the emf of a symmetric cell with Fe + "FeO" as the electrodes. The emf of such a cell was found to be ±0.1 mV at all temperatures of measurement between 875 and 1373 K. The emf was found to be independent of the flowrate of argon over the electrodes in the range of 1 to 4 ml s^{-1}. The emf of each cell was reproducible during heating and cooling cycles. At the end of each experiment, the electrodes were examined by X-ray diffraction. There was no evidence of change in the phase assemblage of the electrodes during the experiment. The steady-state emf was obtained in 2 to 8 ks, depending on the temperature of measurement. The slower response at lower temperatures was caused by the sluggish reaction involving three condensed phases.

III. RESULTS

The reversible emf of cell-I is plotted as a function of temperature in Figure 2. The corresponding plot for cell-II is shown in Figure 3. The numbers on the plot indicate the sequence of measurement. The emfs of both the cells vary linearly with temperature over the entire range of measurement. The least-squares regression analysis of the emf of cell-I gives

$$E_I = 123.74 - 0.0175T(\pm 0.12)\ \text{mV}$$

$$(875 \leq T \leq 1275\ \text{K}) \qquad [1]$$

According to Borowiec and Rosenqvist,[5] the phase combination of iron and ulvospinel converts to wustite + ilmenite below 953 K. The emf of cell-I was reproducible on temperature cycling up to 900 K. This suggests that either the IRI equilibrium is stable or persists metastably up to 900 K. For cell-II, the temperature dependence of the emf is represented by

$$E_{II} = -3.00 + 0.0333T(\pm 0.25)\ \text{mV}$$

$$(900 \leq T \leq 1373\ \text{K}) \qquad [2]$$

The uncertainty limits correspond to twice the standard deviation. The response of cell-II was more sluggish compared to that of cell-I. It was difficult to measure the emf of cell-II below 900 K. The increase in the solubility (~6 mol pct) of Fe_3O_4 in Fe_2TiO_4 with decreasing temperature at the oxygen potentials prevailing over the three-phase electrode may be responsible for the lack of reproducibility of emf below 900 K.

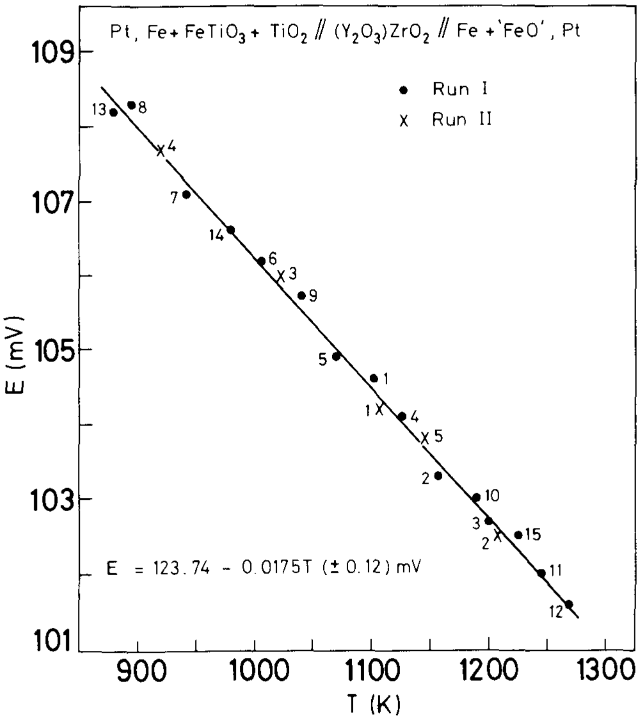

Fig. 2—Temperature dependence of the emf of cell-I.

A. *Standard Gibbs Energy Change for IRI Equilibrium*

The half-cell reactions occuring at the right-hand and the left-hand electrode of cell-I are, respectively,

$$Fe_{0.953}O(s) + 2e^- \rightarrow 0.953\ Fe(s) + O^{2-} \qquad [3]$$

and

$$TiO_2(rut) + Fe(s) + O^{2-} \rightarrow FeTiO_3(il) + 2e^- \qquad [4]$$

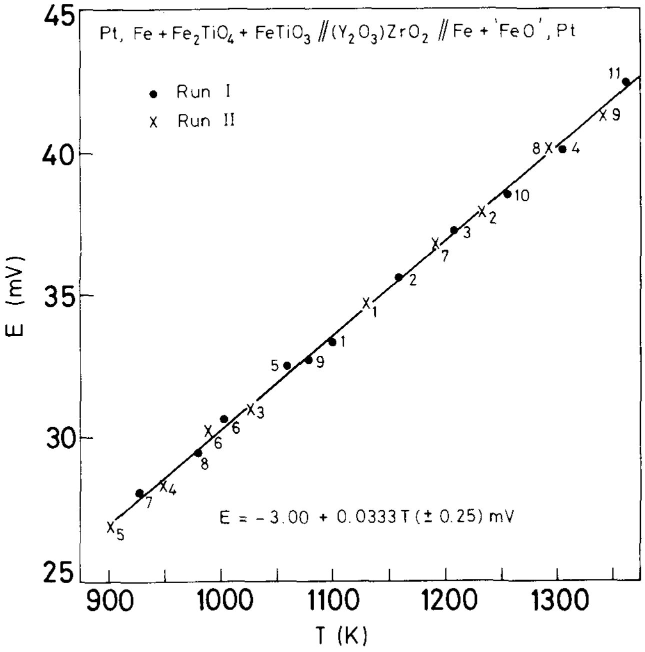

Fig. 3—Variation of the emf of cell-II with temperature.

The net cell reaction can be written as

$$0.047\ \mathrm{Fe(s)} + \mathrm{Fe_{0.953}O(s)} + \mathrm{TiO_2(rut)} \rightarrow \mathrm{FeTiO_3(il)} \qquad [5]$$

The Gibbs energy change for Reaction [5] is directly related to the measured emf of cell-I:

$$\Delta G_5 = -n\mathrm{F}E_{\mathrm{I}} \qquad [6]$$

where $n = 2$ is the number of electrons participating in the electrode reactions, $\mathrm{F} = 96{,}500\ \mathrm{J\ V^{-1}}$ is the Faraday constant, and E_{I} is the measured emf of cell-I in V. The oxygen potential corresponding to the IRI equilibrium,

$$2\mathrm{Fe(s)} + 2\mathrm{TiO_2(rut)} + \mathrm{O_2(g)} \rightarrow 2\mathrm{FeTiO_3(il)} \qquad [7]$$

is obtained by combining the free energy change for Reaction [5] and the chemical potential of oxygen for the coexistence of Fe + $\mathrm{Fe_{0.953}O}$ from Sjoden *et al.*[10] The Gibbs energy change for IRI equilibrium is given by the following equations:

$$\begin{aligned}\Delta\mu_{\mathrm{O_2}}(\mathrm{IRI}) = \Delta G_7 &= -550{,}724 - 29.445T \\ &\quad + 20.374T \ln T(\pm 210)\ \mathrm{J\ mol^{-1}} \\ &\quad (875 \leq T \leq 1184\ \mathrm{K}) && [8] \\ &= -620{,}260 + 369.593T \\ &\quad - 27.716T \ln T(\pm 210)\ \mathrm{J\ mol^{-1}} \\ &\quad (1184 \leq T \leq 1275\ \mathrm{K}) && [9]\end{aligned}$$

For a rigorous analysis, the possibility of dissolution of small amounts of $\mathrm{Ti_2O_3}$ and $\mathrm{Fe_2O_3}$ in $\mathrm{FeTiO_3}$ needs to be explored. These two sesquioxides can readily form solid solutions with ilmenite.[5] The activity of $\mathrm{Ti_2O_3}$ in ilmenite in equilibrium with iron and rutile can be obtained from the thermodynamic data for Reactions [10] and [11]:

$$2\mathrm{TiO_2(rut)} \rightarrow \mathrm{Ti_2O_3(s)} + 1/2\mathrm{O_2(g)} \qquad [10]$$

$$\ln a_{\mathrm{Ti_2O_3}} = \left(\frac{-\Delta G^{\circ}_{10}}{\mathrm{R}T}\right) - 1/2 \ln p_{\mathrm{O_2}} \qquad [11]$$

Using the value of oxygen potential along the IRI boundary and the standard Gibbs energy of formation of $\mathrm{TiO_2}$ and $\mathrm{Ti_2O_3}$ from the JANAF tables,[11] the activity of $\mathrm{Ti_2O_3}$ in ilmenite is obtained as 1.3×10^{-5} at 900 K and 6.0×10^{-3} at 1300 K. Similarly, the activity of $\mathrm{Fe_2O_3}$ in ilmenite in equilibrium with iron and rutile can be obtained from the standard Gibbs energy change for Reaction [12]

$$2\mathrm{Fe(s)} + \frac{3}{2}\mathrm{O_2(g)} \rightarrow \mathrm{Fe_2O_3(s)} \qquad [12]$$

$$\ln a_{\mathrm{Fe_2O_3}} = \left(\frac{-\Delta G^{\circ}_{12}}{\mathrm{R}T}\right) + \frac{3}{2} \ln p_{\mathrm{O_2}} \qquad [13]$$

Using the measured oxygen potential for the IRI equilibrium and the standard Gibbs energy of formation of $\mathrm{Fe_2O_3}$ from the JANAF tables,[11] the activity of $\mathrm{Fe_2O_3}$ in ilmenite is computed as 4.5×10^{-6} at 900 K and 3.9×10^{-5} at 1300 K. The values of activity of $\mathrm{Fe_2O_3}$ are negligible, whereas those of $\mathrm{Ti_2O_3}$ are not. Therefore, the composition of the solid solution $\mathrm{Ti_2O_3}$-$\mathrm{FeTiO_3}$ and the activity of $\mathrm{FeTiO_3}$ must be determined in order to calculate the standard Gibbs energy change for the IRI equilibrium. It is known[12] that iron and titanium exists in di- and tetravalent states in $\mathrm{FeTiO_3}$. In $\mathrm{Ti_2O_3}$, the titanium is in a trivalent state.[13] Since the mixing in $\mathrm{Ti_2O_3}$-$\mathrm{FeTiO_3}$ solid solution occurs on two cationic sites, the activity of $\mathrm{Ti_2O_3}$ is given by the expression

$$a_{\mathrm{Ti_2O_3}} = X^2_{\mathrm{Ti_2O_3}} \qquad [14]$$

when ideal mixing is assumed on each sublattice. Based on the activity of $\mathrm{Ti_2O_3}$ calculated from Eq. [11] along the oxygen potential boundary for IRI equilibrium and using Eq. [14], the composition of $\mathrm{Ti_2O_3}$-$\mathrm{FeTiO_3}$ solid solution is computed at different temperatures. The activity of $\mathrm{FeTiO_3}$ is obtained from the relation

$$a_{\mathrm{FeTiO_3}} = X^2_{\mathrm{FeTiO_3}} \qquad [15]$$

at various temperatures. The activities of $\mathrm{Ti_2O_3}$ and $\mathrm{FeTiO_3}$ between 900 and 1300 K calculated from Eqs. [14] and [15] are given in Table I.

The values of $\mathrm{R}T \ln a_{\mathrm{FeTiO_3}}$ from Table I are used to obtain the standard Gibbs energy change for Reaction [7]:

$$\begin{aligned}\Delta G^{\circ}_7 &= \Delta G_7 - 2\mathrm{R}T \ln a_{\mathrm{FeTiO_3}} && [16] \\ &= -519{,}274 - 303.943T \\ &\quad + 55.656T \ln T(+225)\ \mathrm{J\ mol^{-1}} \\ &\quad (875 \leq T \leq 1184\ \mathrm{K}) && [17] \\ &= -588{,}810 + 95.095T \\ &\quad + 7.566T \ln T(\pm 225)\ \mathrm{J\ mol^{-1}} \\ &\quad (1184 \leq T \leq 1275\ \mathrm{K}) && [18]\end{aligned}$$

B. *Standard Gibbs Energy Change for IIU Equilibrium*

The half-cell reactions taking place at the right-hand and the left-hand electrodes of cell-II are, respectively,

$$\mathrm{Fe_{0.953}O(s)} + 2e^{-} \rightarrow 0.953\ \mathrm{Fe(s)} + \mathrm{O^{2-}} \qquad [19]$$

and

$$\mathrm{FeTiO_3(il)} + \mathrm{Fe(s)} + \mathrm{O^{2-}} \rightarrow \mathrm{Fe_2TiO_4(usp)} + 2e^{-} \qquad [20]$$

The net cell reaction is

$$0.047\mathrm{Fe(s)} + \mathrm{Fe_{0.953}O(s)} + \mathrm{FeTiO_3(il)} \rightarrow \mathrm{Fe_2TiO_4(usp)} \qquad [21]$$

Table I. Activity of $\mathrm{Ti_2O_3}$ in $\mathrm{FeTiO_3}$ in Equilibrium with Metallic Fe and $\mathrm{TiO_2}$ along the Oxygen Potential Boundary for IRI Equilibrium

T (K)	$a_{\mathrm{Ti_2O_3}}$	$X_{\mathrm{Ti_2O_3}}$	$a_{\mathrm{FeTiO_3}}$	$\mathrm{R}T \ln a_{\mathrm{FeTiO_3}}$ ($\mathrm{J\ mol^{-1}}$)
900	1.345×10^{-5}	0.0116	0.9769	− 174.6
1000	4.615×10^{-4}	0.0215	0.9575	− 361.4
1100	1.27×10^{-3}	0.0356	0.9299	− 664.9
1200	2.943×10^{-3}	0.0542	0.8945	−1111.9
1300	5.876×10^{-3}	0.0766	0.8527	−1722.7

The Gibbs energy change for Reaction [21] is directly obtained from the measured emf of cell-II. The Gibbs energy change for the IIU equilibrium,

$$2\mathrm{Fe(s)} + 2\mathrm{FeTiO_3(il)} + \mathrm{O_2(g)} \rightarrow 2\mathrm{Fe_2TiO_4(usp)} \qquad [22]$$

is obtained by combining the free energy change for Reaction [21] and the chemical potential of oxygen for the coexistence of Fe + $Fe_{0.953}O$ reported by Sjoden *et al.*[10] The Gibbs energy change for IIU equilibrium is given by the following equations:

$$\Delta G_{22} = \Delta\mu O_2(\mathrm{IIU}) = -501{,}800 - 49.0345T + 20.374T \ln T (\pm 210)\ \mathrm{J\ mol^{-1}} \quad (900 \leq T \leq 1184\ \mathrm{K}) \qquad [23]$$

$$= -571{,}336 + 350.0035T - 27.716T \ln T (\pm 210)\ \mathrm{J\ mol^{-1}} \quad (1184 \leq T \leq 1373\ \mathrm{K}) \qquad [24]$$

At the oxygen potentials existing over the three-phase electrode of cell-II, there is a possibility of formation of Fe_3O_4-Fe_2TiO_4 solid solution. Magnetite forms a continuous solid solution with Fe_2TiO_4 at high temperatures.[5] The activity of Fe_3O_4 in Fe_2TiO_4 can be computed from the thermodynamic data for Reaction [25]:

$$3\mathrm{Fe(s)} + 2\mathrm{O_2(g)} \rightarrow \mathrm{Fe_3O_4(sp)} \qquad [25]$$

$$\ln a_{\mathrm{Fe_3O_4}} = \left(\frac{-\Delta G^\circ_{25}}{RT}\right) + 2 \ln p_{\mathrm{O_2}} \qquad [26]$$

along the IIU equilibrium. Based on the measured oxygen potential for the IIU equilibrium and the standard free energy of formation of Fe_3O_4 given in the JANAF tables,[11] the activity of Fe_3O_4 in Fe_2TiO_4 has been calculated as 2.8×10^{-2} at 900 K and 1.0×10^{-2} at 1300 K. Since the values are not negligible, the composition of the spinel solid solution and the activity of Fe_2TiO_4 need to be evaluated. For this purpose, the activity-composition relationship for the Fe_3O_4-Fe_2TiO_4 system was calculated using a simple cation distribution model.[14] The octahedral site preference energy (OSPE) for Fe^{2+} and Fe^{3+} has been taken from Dunitz and Orgel.[15] The value for Ti^{4+} has been calculated from the high-temperature cation distribution in Fe_2TiO_4 reported by Forster and Hall.[16] The OSPEs of the cations used in the computation of cation distribution in Fe_3O_4-Fe_2TiO_4 spinel solid solution are given in Table II. Based on these values and the simple cation distribution model,[14] the activity of component spinels in the Fe_3O_4-Fe_2TiO_4 solid solution has been calculated as a function of composition between 600 and 800 K.

Table II. Octahedral Site Preference Energies of Cations Used in the Computation of Cation Distribution

Cation	OSPE (J mol^{-1})	Reference
Fe^{2+}	−16,740	13
Fe^{3+}	0	13
Ti^{4+}	−40,890	16*

*OSPE calculated based on the high-temperature cation distribution in Fe_2TiO_4 reported by Forster and Hall.[16]

From these activity-composition relationships, the ideal free energy of mixing is obtained for the spinel solid solution as a function of temperature. The excess free energy of mixing for Fe_3O_4-Fe_2TiO_4 spinel solid solution is estimated by modeling the subsolidus phase diagram of the system Fe_3O_4-Fe_2TiO_4 reported by Vincent *et al.*,[17] assuming symmetric enthalpy of mixing. The regular solution parameter that gave the best fit to the subsolidus phase diagram of Vincent *et al.* is 33 kJ mol^{-1}. Using this value and the ideal free energy of mixing calculated from the cation distribution in Fe_3O_4-Fe_2TiO_4 spinel solid solution as a function of temperature, the activity-composition relationship in the spinel solution is computed between 900 and 1300 K. The composition of the spinel solid solution and the activity of Fe_2TiO_4 along the oxygen potential boundary of IIU equilibrium have been obtained from the activity of Fe_3O_4 calculated using Eq. [26] and the activity-composition relationship computed for the spinel solid solution at different temperatures. The activity of Fe_2O_3 in $FeTiO_3$-Fe_2O_3 solid solution along the oxygen potential boundary of IIU equilibrium is calculated using Eq. [13], adopting the same procedure as that employed for the IRI equilibrium. The calculations yield the activity of Fe_2O_3 equal to 2.4×10^{-3} at 900 K and 1.0×10^{-3} at 1300 K. Using these values of activity of Fe_2O_3 in Fe_2O_3-$FeTiO_3$ solid solution obtained along the oxygen potential boundary of IIU equilibrium, the activity of $FeTiO_3$ is calculated assuming ideal mixing on each site. The values of the activity of component oxides in Fe_3O_4-Fe_2TiO_4 and Fe_2O_3-$FeTiO_3$ solid solutions between 900 and 1300 K along the oxygen potential boundary of IIU equilibrium are summarized in Table III. The standard Gibbs energy change

Table III. Activity of Fe_2O_3 in $FeTiO_3$ and Fe_3O_4 in Fe_2TiO_4 in Equilibrium with Metallic Iron along the IIU Boundary

T (K)	$a_{\mathrm{Fe_2O_3}}$	$X_{\mathrm{Fe_2O_3}}$	$a_{\mathrm{FeTiO_3}}$	$a_{\mathrm{Fe_3O_4}}$	$X_{\mathrm{Fe_3O_4}}$	$a_{\mathrm{Fe_2TiO_4}}$	$RT \ln \frac{a_{\mathrm{Fe_2TiO_4}}}{a_{\mathrm{FeTiO_3}}}$ (J mol^{-1})
900	2.35×10^{-3}	0.0485	0.9053	0.0281	0.025	0.94	281.0
1000	1.65×10^{-3}	0.0406	0.9204	0.0177	0.02	0.96	349.8
1100	1.27×10^{-3}	0.0356	0.9301	0.0127	0.015	0.97	384.5
1200	1.06×10^{-3}	0.0326	0.9359	0.0103	0.01	0.98	459.7
1300	1.02×10^{-3}	0.0319	0.9372	0.0101	0.01	0.98	482.4

for Reaction [22] is obtained by incorporating the following estimated activities:

$$\Delta G^\circ_{22} = \Delta G_{22} - 2RT\ln(a_{\mathrm{Fe_2TiO_4}}/a_{\mathrm{FeTiO_3}}) \quad [27]$$

$$= -501{,}455 - 50.060T + 20.374T\ln T(\pm 225)\ \mathrm{J\ mol^{-1}} \quad (900 \leq T \leq 1184\ \mathrm{K}) \quad [28]$$

$$= -570{,}991 + 348.978T - 27.716T\ln T(\pm 225)\ \mathrm{J\ mol^{-1}} \quad (1184 \leq T \leq 1373\ \mathrm{K}) \quad [29]$$

IV. DISCUSSION

A. *The IRI Equilibrium*

The chemical potential of oxygen for IRI equilibrium obtained in the present investigation is compared with the earlier measurements reported in the literature in Figure 4. There is a change in slope at 1184 K corresponding to the α-γ transition in iron. It can be seen from Figure 4 that the present results are in excellent agreement with the CO/CO_2 gas equilibrium measurements of Levitskii *et al.*[2] at 1200 K. The gas equilibrium measurements of Schmahl *et al.*[1] are in good agreement, whereas the data of El Goresy and Woermann[4] are significantly more positive than the present results. The results of emf measurements of O'Neill *et al.*[8] and Levitskii *et al.*[9] are in good agreement. The emf results of Merritt and Turnbull[7] agree exactly at 1200 K when extrapolated linearly to lower temperatures but have a slightly steeper slope than that obtained in this study. The $\Delta\mu_{O_2}$(IRI) values obtained by Taylor and Schmalzried[6] employing an emf method agree reasonably well at higher temperatures but are more negative by approximately 5 kJ mol^{-1} at 1073 K. The data of Borowiec and Rosenqvist[5] are significantly more positive. The results of a gas equilibrium study by Taylor *et al.*[3] are in complete disagreement with the results of this study and those reported in the literature.

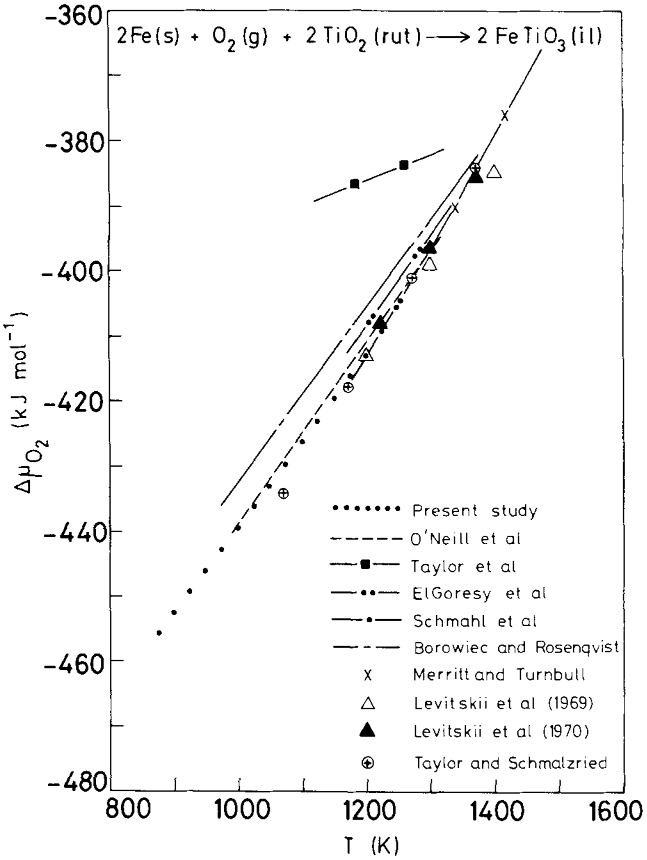

Fig. 4 — Comparison of the oxygen potential for IRI equilibrium with the data reported in the literature.

The third-law analysis is an accurate indicator of temperature-dependent errors in emf measurements. The standard enthalpy change (ΔH°_{298}) for Reaction [7] can be calculated from the standard Gibbs energy change at each temperature using the following expression:

$$\Delta H^\circ_{298} = \Delta G^\circ_T - T\Delta\Phi \quad [30]$$

where

$$\Phi = \frac{G^\circ_T - H^\circ_{298}}{T} = -S^\circ_{298} - \int_{298}^{T}\frac{C^\circ_p}{T}\,dT + \frac{1}{T}\int_{298}^{T} C^\circ_p\,dT \quad [31]$$

If the calorimetric data for all species involved in the reaction and the experimental measurements are correct, the values of ΔH°_{298} must be independent of temperature. The thermal functions for Fe, TiO_2, and O_2 are taken from the JANAF tables[11] and that for $FeTiO_3$ has been calculated from the S°_{298} and $C^\circ_p(T)$ reported by Anovitz *et al.*[18] Using these thermal functions, the ΔH°_{298} corresponding to Reaction [7] has been calculated. It can be seen from Figure 5 that the value of ΔH°_{298} for Reaction [7] shows a small temperature dependence, with an average value of -575 (± 1) kJ mol^{-1} between 875 and 1200 K. Part of the temperature dependence of ΔH°_{298} may arise from the assumption of ideal mixing used in modeling the solid solution. It may also reflect small errors in the values for S°_{298} for reactants and products used in the analysis. The recent results of O'Neill *et al.*[8] give ΔH°_{298} for Reaction [7] which shows significantly larger temperature dependence.

B. *The IIU Equilibrium*

The chemical potential of oxygen for IIU equilibrium obtained in the present study is compared with the data reported in the literature in Figure 6. The values of $\Delta\mu_{O_2}$(IIU) calculated from Eqs. [23] and [24] are in excellent agreement with those obtained by Taylor and Schmalzried.[6] The recent emf measurements of O'Neill *et al.*[8] and the gas equilibrium measurements of Schmahl *et al.*[1] are in reasonable agreement with the present results. The results of Merritt and Turnbull[7] are more negative by about 2 kJ mol^{-1}. The data of Borowiec and Rosenqvist[5] agree well at higher temperature but are more positive by about 5 kJ mol^{-1} at 1000 K. The gas equilibrium measurements of Taylor *et al.*[3] are more positive by about 12 kJ mol^{-1} at 1150 K and by about 2 kJ mol^{-1} at 1373 K.

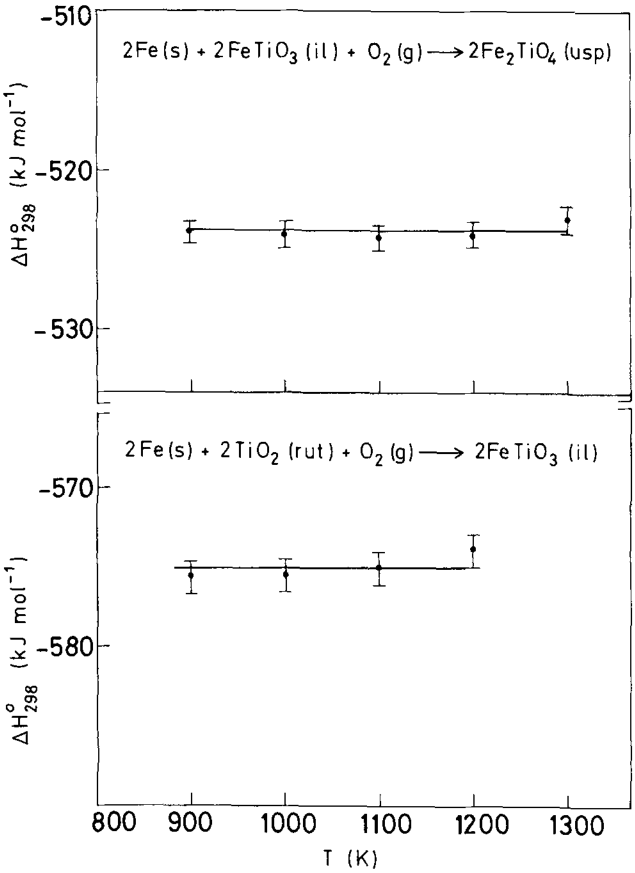

Fig. 5—Third-law values of ΔH°_{298} for IRI and IIU equilibria calculated from the results of this study.

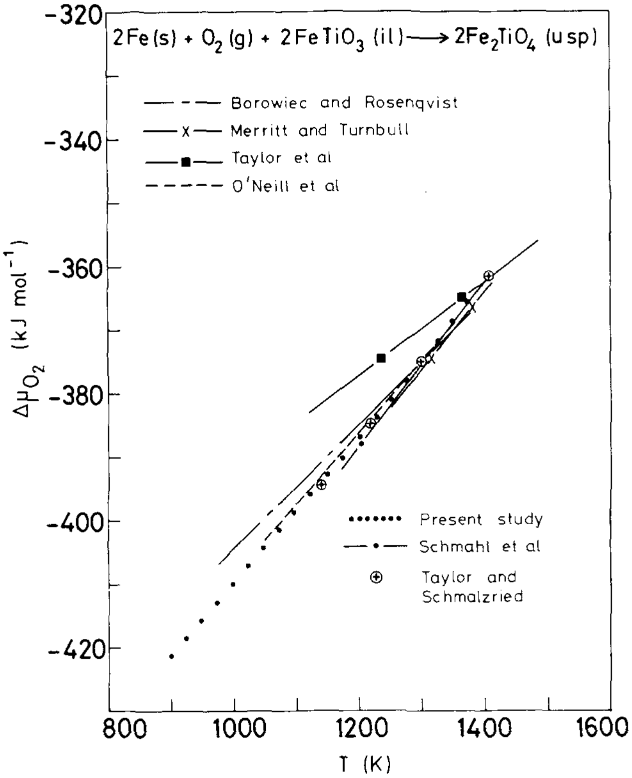

Fig. 6—Comparison of the chemical potential of oxygen for IIU equilibrium with the measurements reported in the literature.

The third-law analysis of the present results for IIU equilibrium has been carried out using the thermal functions for Fe and O_2 from the JANAF tables,[11] for $FeTiO_3$ from Anovitz *et al.*,[18] and for Fe_2TiO_4 from Robie *et al.*[19] with addition of a configurational contribution. At low temperature, Fe_2TiO_4 has a spinel structure with almost an inverse cation distribution. Hence, all of the Ti^{4+} and half of the Fe^{2+} ions mix on the octahedral site of the spinel structure. This gives rise to a possibility of a zero point entropy which cannot be measured calorimetrically. Assuming that the cations mix randomly on the octahedral site, a value of $2R \ln 2$ has been added to S°_{298} for the Fe_2TiO_4 reported by Robie *et al.*[19] It can be seen from Figure 5 that the third-law analysis of present results gives a value of -523.7 (± 0.7) kJ mol^{-1} for ΔH°_{298}, almost independent of temperature between 900 and 1250 K.

The data obtained in this study for IIU equilibrium can be combined with the earlier measurement[20] on iron-quartz-fayalite (IQF) equilibrium to compute the invariant temperature for an equilibrium between five condensed phases, iron + fayalite + ulvospine + quartz + ilmenite. Since the oxygen potential for both IIU and IQF[20] is measured by the solid oxide galvanic cell technique with Fe + "FeO" as the reference electrode, the invariant temperature is that which corresponds to the same value of emf for both cells.

The calculated invariant temperature is 1410 (± 10) K. This analysis assumes that no titanate dissolves in silicate and no silica dissolves in titanate phases. El Goresy and Woermann[4] evaluated this temperature based on the data of Taylor *et al.*[3] as 1328 (± 5) K. As seen from Figure 6, the oxygen potential reported by Taylor *et al.*[3] differs substantially from the results of other investigations. The value of 1410 (± 10) K obtained in this study therefore appears to be a better estimate of the invariant temperature in the Fe-Ti-Si-O system.

V. SUMMARY

The oxygen potential for IRI and IIU equilibria has been measured over a range of temperatures using a solid oxide galvanic cell technique. Unlike most previous measurements, the third-law analysis of the present results yields temperature-independent values of ΔH°_{298} for IRI equilibrium equal to -575 (± 1) kJ mol^{-1} and for IIU equilibrium equal to -523.7 (± 0.7) kJ mol^{-1}. The present results for IIU equilibrium suggest that there is a configurational contribution of $2R \ln 2$ to the entropy of $FeTi_2O_4$ because of the mixing of cations on the octahedral site.

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