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A Solid-State Cell Study of Oxygen Activities in the Fe–Ti–O System

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A high-temperature solid-state cell using a calcia-stabilized zirconia electrolyte and iron–wustite reference electrode is described. The partial molal free energy of oxygen is reported for the phase systems iron–ilmenite–rutile (pseudobrookite) (1306–1484 K) and iron–ilmenite–ulvöspinel (1246–1455 K). Quenching experiments are described which confirm the phase systems studied in the cell. A statistical method of analysis of cell potential vs temperature data is used to show that the phase boundary between the iron–ilmenite–rutile and iron–ilmenite–pseudobrookite systems lies at 1427 ± 6 K. Factors contributing to the precision and accuracy of solid-state cell data are considered in detail.

Introduction

The Fe–Ti–O system has been extensively studied, but a complete set of thermodynamic data is not yet available. Such data are of use in understanding the formation of ferrotitanate ores both on earth and moon and in controlling oxidation–reduction processes currently in use for the treatment of these ores. This paper reports the use of a solid-state galvanic cell to measure equilibrium oxygen activities for important areas of this system.

There have been a number of phase equilibrium studies (*1–10*) of the system, the results of which are summarized in the diagrammatic isothermal sections at 1273 and 1473 K (Fig. 1). The exact location of the phase boundaries may be in doubt, but the general situation is clear. The present work involved the two three-phase regions iron–ilmenite–spinel and iron–ilmenite–rutile in which oxygen activity should be independent of composition. However, Lindsley (*6*) has shown by quenching experiments that the latter region transforms to iron–ilmenite–pseudobrookite above 1413 ± 10 K. Confirmation of this phase boundary by a steady-state technique was required.

Previous thermodynamic studies have concentrated on the first two three-phase regions mentioned above. Several studies of equilibration in gas buffer mixtures for both regions (*1*, *3*, *9–14*) have served to broadly define the system but have lacked sensitivity. Solid-state cell studies have also been reported for both regions (*15*, *16*). All the information is compared in Fig. 2 on the basis of $\overline{\Delta G}(O_2)$, the partial molal Gibbs energy of oxygen.

Several inconsistencies are apparent in the published data. The change of phase system from iron–ilmenite–rutile to iron–ilmenite–pseudobrookite should be marked by a change in $d\overline{\Delta G}(O_2)/dT$. Two sets of data (*11*, *14*) extend above and below the expected phase boundary temperature, 1413 K, but no change of slope is apparent.

For both the iron–ilmenite–rutile and iron–ilmenite–spinel systems there is a considerable spread in $\overline{\Delta G}(O_2)$ at a given temperature. This is undesirable in view of the quite small differences in $\overline{\Delta G}(O_2)$ between neighboring systems. Also, there are considerable differences in $d\overline{\Delta G}(O_2)/dT$, even between sets of data measured with the same technique, as with the cell studies of Taylor and Schmalzried (*15*) and Levitskii et al. (*16*).

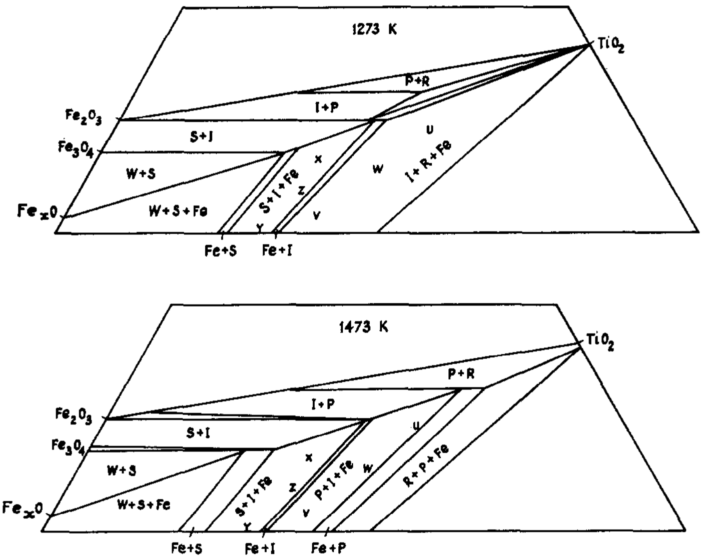

FIG. 1. Isothermal sections of Fe–Ti–O phase diagram at 1273 K (upper) and 1473 K (lower). Constructed from data in Refs. *1–10*. Phases are: W = wustite; S = spinel; I = ilmenite; P = pseudobrookite; R = rutile.

In order to resolve these discrepancies, new measurements have now been made with a solid-state cell method of considerably improved precision over that used hitherto.

Experimental

Apparatus

The solid-state cell operated under high-vacuum conditions at temperatures up to 1500 K. A double-wall vacuum system was used, with the cell and annular space between the two walls pumped by separate vacuum systems. An earthed stainless steel shield held between the walls served for electrical isolation and temperature equalization. For temperature control a Kanthal-wound resistance furnace with a Platinel II control thermocouple was used.

The two compartments of the cell were separated by a flat-ended tube of stabilized zirconia (ZrO_2/7.5 wt% CaO, from Zirconium Corporation of America) which served as the main cell electrolyte. The lower, open end of this tube was joined to the glass vacuum system by an indium seal. Since the cell compartments joined only at the main pumping manifold there was negligible gas transport between opposite sides of the cell.

The electrode pellets were separated from the zirconia tube, to avoid contamination of the tube, by pellets of calcia-stabilized zirconia. The cell assembly was held in place by alumina clamps attached to springs in the lower, unheated region. Electrical contact with the electrode pellets was through the platinum wires of Pt/Pt 13% Rh thermocouples. High-impedance glass reed switches enabled the potential of any of the thermocouples or that of the cell to be measured. The thermocouple potential was measured to a precision of 1 μV with a potentiometer. The cell potential was switched to either an electrometer (Keithley 615) or a specially constructed high-impedance amplifier, as desired. The unity-gain outputs of these were measured to a precision of 0.02 mV with the potentiometer. The input impedance of both instruments was of the order of 10^{13} ohm, whereas the cell impedances were between 10^4 and 10^5 ohm. The electrometer gave good long-term accuracy, while the amplifier gave lower short-term noise which was useful in following small changes in cell potential.

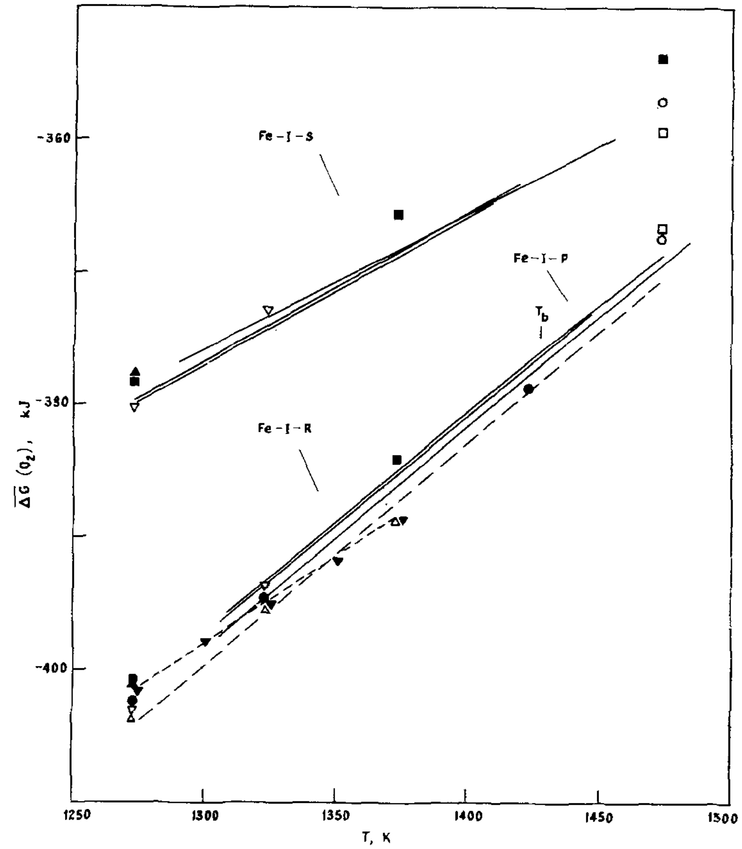

FIG. 2. Partial molal Gibbs energy of oxygen vs temperature: iron–ilmenite–tutile (Fe–I–R); iron–ilmenite–pseudobrookite (Fe–I–P); iron–ilmenite–spinel (Fe–I–S). (○) Ref. *1*, (□) Ref. *3*, (▽) Ref. *9*, (▲) Ref *10*, (— —) Ref. *11*, (△) Ref. *12*, (▼) Ref. *13*, (●) Ref. *14*, (■) Ref. *15*, (----) Ref. *16*, (——) Present work.

Procedure

At the start of an experiment the cell was evacuated to ~10^{-5} N m^{-2} and then slowly heated to 1370 K while maintaining the pressure below 10^{-4} N m^{-2}. The position of the furnace was then adjusted to give a temperature gradient across the cell of <1 K. The temperature was changed in steps, starting from the highest temperature to be studied, and the cell potential measured as a function of time at each temperature. Although the temperature stabilized within ±0.5 K after 30 min, the cell potential was still changing at a measurable rate after 12 hr. Measurements of potential made when the drift rate had fallen to <0.1 mV hr^{-1} (usually 0.03 mV hr^{-1}) were found to give sufficient precision.

A split reference electrode was used, and, except in cases of poor electrical contact, the potential was independent of which half of the pellet was used as reference. The potential was measured with the furnace on, since checks had shown the change of potential on switching the furnace off was only 0.02 mV.

Materials

The powder for the electrolyte pellets was prepared by dissolving Analytical Reagent calcium carbonate and high purity zirconium oxychloride in nitric acid, evaporating to dryness, and calcining at 920 K for 12 hr. After analysis to check the CaO content (7.5 wt %), the powder was pressed into pellets at 10 ton in^{-2} and then sintered at 1920 K for

14 hr. Examination by X-ray diffraction showed the presence of only the cubic solid solution.

The reference pellets were prepared from Koch–Light iron powder and Fisher Certified Reagent ferric oxide mixed in a molar ratio of 4:1. The mixture was lightly pressed into pellets and then sintered in vacuum at 1270 K.

The sample pellets were prepared from iron powder, rutile and ferric oxide, or ilmenite mixed in the desired proportions, lightly pressed, and sintered in vacuum at 1270 K. The ilmenite was synthesized by reducing a mixture of Fisher Certified Reagent titanium dioxide (anatase) and ferric oxide with either a gas buffer or metallic iron. Both sample and electrolyte pellets were rubbed smooth and flat on No. 600 carborundum paper, further polishing being unnecessary.

A two-step analysis was performed on the mixed powders, the sintered pellets and the sample pellets after use. The weight gain was measured on oxidation in air at 1070 K, and the oxidized product was analysed for iron and titanium by the methods of Tittle (*17*). The pellets were also examined before and after use by X-ray diffraction after slow cooling.

Quenching

In order to check the phases present in the sample electrodes at operating temperatures, quenching experiments were performed. Pellets with compositions similar to those of the electrode pellets were placed in a platinum boat and sealed in a quartz tube under a pressure of $<10^{-3}$ N m^{-2} ($\sim 10^{-5}$ Torr). After holding at a chosen temperature between 1120 and 1420 K for at least 20 hr, the tube was quenched in liquid nitrogen. The phases present in the quenched pellet were determined by X-ray diffraction.

Results

To test the operation on a well-known system, a two-phase wustite–magnetite sample was first investigated. In the temperature range covered, 1070–1370 K, the measured potentials agreed with data reported for a similar cell study (*18*) within ±3 mV. The best fit (*19*) of all available results for oxygen pressures at the wustite–magnetite phase boundary had a mean deviation of ±0.15 log p_{O_2} units. The present results fell well within these limits.

Preliminary experiments on the iron–ilmenite–rutile (pseudobrookite) system showed the following important facts.

1. An initial heating of the cell to above 1450 K was necessary, to give potentials in agreement with previously reported data (*10–16*).
2. To obtain reversibility between heating and cooling at temperatures above 1420 K, three or four cycles between 1470 and 1360 K were needed.
3. Samples which used ilmenite in their preparation equilibrated more rapidly than those which used ferric oxide.
4. The value of dE/dT was slightly smaller above 1420 K than below this temperature.

Preliminary experiments on the iron–ilmenite–spinel system showed an insignificant difference between equilibration rates for samples prepared using ilmenite or ferric oxide. The value of dE/dT showed no change in the temperature range 1250–1450 K.

Using the techniques suggested by the preliminary work, six experiments were performed: U, V, and W for compositions in the iron–ilmenite–rutile (pseudobrookite) phase region (Fig. 1) and X, Y, and Z for compositions in the iron–ilmenite–spinel phase region. Compositions calculated from reagent weights are given in the second column of Table I and the analysed compositions in the following columns. For every sample, the ratio Fe/(Fe + Ti) was lower than for an identically prepared but unused pellet. This was undoubtedly caused by evaporation of iron during the experiment.

The measured temperature gradient across the cell had a maximum value of 2 K. The cell potential was referred to the mean temperature and the correction for the differences in dE/dT between sample and reference electrodes had a maximum value of 1 mV.

For experiments U and W a distinct change of slope was seen in plots of cell potential vs temperature. For experiment V this was

TABLE I

CHEMICAL AND PHASE COMPOSITION OF SAMPLES

Expt.	Weighed powder r[a]	x_O[a]	Mixed powder r	x_O	Unused pellet r	x_O	Sample pellet r	x_O	Phases present[b]
U	0.400	0.592	—	—	—	—	0.388	0.604	Fe–R–I[c]
V	0.601	0.516	0.600	0.520	0.605	0.522	0.583	0.533	Fe–R–I
W	0.500	0.556	0.507	0.557	0.509	0.557	0.491	0.566	Fe–R–I
X	0.604	0.566	0.603	0.571	0.603	0.569	0.594	0.575	Fe–I–S
Y	0.684	0.500	0.688	0.508	0.690	0.503	0.679	0.512	Fe–I–S
Z	0.625	0.539	0.633	0.543	0.634	0.541	0.615	0.552	Fe–I–S

[a] $r = \mathrm{Fe}/(\mathrm{Fe}+\mathrm{Ti})$ atom ratio; $x_O = \mathrm{O}/(\mathrm{Fe}+\mathrm{Ti}+\mathrm{O})$ atom ratio.

[b] Sample slow-cooled after use.

[c] R = rutile; I = ilmenite; S = ulvöspinel.

less obvious due to increased scatter caused by noise pick-up in the measuring circuit. In view of the small change in slope, a computer program was developed to find the best value of the phase boundary temperature, T_b. Each set of E vs T data was arranged in ascending order of T, and a series of pairs of straight lines was fitted by the method of least squares. For each pair of lines, the variances of the slopes were used in the Student t

TABLE II

STATISTICAL SUMMARY OF RESULTS

Expt	No. of data points Heating	Cooling	Cell potential E (mV)	SD in E (mV)	Phase boundary T_b (K)
U	17	15	$E = 0.1017T - 231.68$, $1306 \leqslant T \leqslant 1425$ $E = 0.0918T - 217.52$, $1425 \leqslant T \leqslant 1484$	0.16 0.19	1425 ± 16
V	14	13	$E = 0.0944T - 219.02$, $1306 \leqslant T \leqslant 1477$	0.44	—
W	7	7	$E = 0.0970T - 222.43$, $1306 \leqslant T \leqslant 1429$ $E = 0.0701T - 183.93$, $1429 \leqslant T \leqslant 1477$	0.21 0.40	1429 ± 20
X	15	16	$E = -0.0714T + 51.92$, $1290 \leqslant T \leqslant 1455$	0.37	—
Y	2	16	$E = -0.0483T + 19.54$, $1273 \leqslant T \leqslant 1420$	0.25	—
Z	2	11	$E = -0.0452T + 14.77$, $1246 \leqslant T \leqslant 1409$	0.17	—

test (20) to find the probability that the slopes were different. Also, the variances about the lines were used to find which pair of lines gave the best combined fit to the data. The pair of lines showing the highest probability of a change of slope and the best combined fit was selected and the intersection taken as T_b.

The complete data sets from experiments U and W gave 99% probabilities of phase boundaries and T_b values in good agreement (Table II). A mean T_b value of 1427 ± 18 K was obtained by separate treatment of heating and cooling cycles from these two experiments. Run V gave a low probability of a phase boundary due to excessive scatter, reflected in a doubling of the standard deviation in E. Thus, only a single best-fit line through the whole data set is reported. For experiments X, Y, and Z the probabilities of a slope change were also low, although the scatter was similar to that of experiments U and V. This was expected for the phase system involved and this provided a check that the method did not produce spurious phase boundaries.

Discussion

Thermodynamic data

The previously published phase equilibrium data (1–10), confirmed by the present quenching experiments, show that the overall cell reactions were as follows:

$$(1-x)\mathrm{Fe} + \underset{\text{wustite}}{\mathrm{Fe}_x\mathrm{O}} + \underset{\text{rutile}}{(\mathrm{TiO}_2)} \rightarrow \underset{\text{ilmenite}}{(\mathrm{FeTiO}_3)} \qquad (1)$$

$$(1-x)\mathrm{Fe} + \underset{\text{wustite}}{\mathrm{Fe}_x\mathrm{O}} + \underset{\text{pseudobrookite}}{(\mathrm{FeTi}_2\mathrm{O}_5)} \rightarrow \underset{\text{ilmenite}}{2(\mathrm{FeTiO}_3)} \qquad (2)$$

$$(1-x)\mathrm{Fe} + \underset{\text{wustite}}{\mathrm{Fe}_x\mathrm{O}} + \underset{\text{ilmenite}}{(\mathrm{FeTiO}_3)} \rightarrow \underset{\text{ulvöspinel}}{(\mathrm{Fe}_2\mathrm{TiO}_4)} \qquad (3)$$

For wustite, $\mathrm{Fe}_x\mathrm{O}$, the value of x varies from 0.9511 at 1273 K to 0.9524 at 1473 K (19). The iron titanates do not have the ideal compositions given above, but have small solid-solution ranges as suggested in Fig. 1. There is no general agreement on the nature or extent of these solid-solution regions (1–3, 8–10). The present data are thus reported as $\overline{\Delta G}(\mathrm{O}_2)$ for known Fe–Ti–O compositions corresponding to known phase systems, derived from the relation:

$$\overline{\Delta G}(\mathrm{O}_2) = 4 \times 96{,}487 \times E + 2 \times \Delta G_f(\mathrm{w}) \qquad (4)$$

where E is the cell potential and $\Delta G_f(\mathrm{w})$ is the standard Gibbs energy of formation of wustite (21). For comparison with previous work (Fig. 2) using equilibration with H_2–$\mathrm{H}_2\mathrm{O}$, CO–CO_2, or H_2–CO_2 gas mixtures, thermodynamic data for these gases (22) were used to calculate $\overline{\Delta G}(\mathrm{O}_2)$.

For the iron–ilmenite–rutile (pseudobrookite) systems, all the data agree within their combined uncertainties in the range 1273–1323 K. The present work agrees closely over the whole range, 1306–1484 K, with the previous cell study of Taylor and Schmalzried (15) and with five studies using CO–CO_2 equilibration (1, 3, 9, 11, 14). However, the work of Levitskii et al. with a solid-state cell (16) and with CO–CO_2 equilibration (12) and the H_2–$\mathrm{H}_2\mathrm{O}$ equilibration work of Shomate et al. (13) show a significantly lower slope than the remainder. Extrapolation to 1473 K would show a considerable divergence between the two sets of results. In comparing the two previous cell studies, Levitskii et al. (16) suggested that the sample used by Taylor and Schmalzried (15) contained pseudobrookite, since it was prepared at 1473 K. This is not supported by the present work, which showed a change in dE/dT corresponding to a change of phase system on first cooling from 1470 K.

The phase boundary temperature of 1427 ± 18 K given by the steady-state cell method is not significantly different from the previous value of 1413 ± 10 obtained by quenching (6). A lower phase boundary temperature could be accounted for by the presence of

Mg(II) or Fe(III) impurities which are known to stabilize pseudobrookite to lower temperatures (*7*, *23*). Fetisov et al. (*14*) determined equilibrium for the iron–ilmenite–pseudobrookite system at 1423 K, but the accuracy of their temperature is not quoted. Lenev and Novokhatskii (*11*) used CO–CO_2 equilibration over the range 1173–1473 K, but it is now evident that this method is not sensitive enough to reveal the change of phase system.

The quenching experiments showed the presence of iron–ilmenite–rutile below 1350 K and iron–ilmenite–pseudobrookite above 1440 K. The 90 K intermediate range where all four phases were present contravenes the phase rule and is attributed to low equilibration rates. This is consistent with the preheating to 1473 K and temperature cycling needed to attain reversibility in the cell.

For the iron–ilmenite–spinel system the present work agrees with the previous cell study of Taylor and Schmalzried (*15*) within the rather large uncertainty of the latter. There is also good agreement with the results of four gas equilibration studies using both H_2–H_2O (*10*) and CO–CO_2 (*1*, *3*, *9*). The quenching experiments showing the presence of only iron, ilmenite and spinel in the range 1120–1400 K, together with the absence of a slope change in the cell data in the range 1246–1455 K, confirm previous phase equilibrium data.

Precision and Accuracy

The precision of measurement represents a considerable improvement over earlier work on this system. For a single measurement the cell potential resolution was ±0.02 mV, the temperature resolution was ±0.2 K, and the temperature stability was ±0.5 K. Thus the overall uncertainty of a single measurement was ±0.08 mV. The long-term stability of the cell and the good reversibility between heating and cooling were reflected in the small scatter of results. The mean standard deviation for a single experiment was 0.20 mV (Table II) or three times the uncertainty of a single measurement. A factor contributing to this scatter was the still measurable drift of potential at the time the data were measured. This drift was small enough not to have seriously affected the precision of measurement. A reasonable supposition is that the drift resulted from slow composition changes of the solid-solution phases after a change of temperature. In comparison, gas equilibrium studies commonly have achieved a precision of ±0.01 log units in oxygen activity, equivalent to ±0.7 mV at 1373 K in a cell study. Clearly, gas equilibration would not have sufficient precision to detect the change of phase system discussed here.

The overall accuracy in $\overline{\Delta G}(O_2)$ was estimated from a consideration of the following factors. The thermocouples were calibrated *in situ* against melting silver and gold to an accuracy of ±1 K. The effect of variations in temperature of the ice water reference was kept below ±0.2 K by air stirring. Errors resulting from iron contamination of the thermocouples were considered to be small, since no systematic change in potential was observed over a 2- to 3-wk experiment. The overall uncertainty in temperature, ±1.9 K, was equivalent to ±0.17 mV in potential. The quoted accuracy of the electrometer was ±0.3 mV, and room temperature changes caused an additional uncertainty of ±0.75 mV. The high-impedance amplifier used to measure the data reported here showed differences from the electrometer of up to ±0.5 mV. The overall uncertainty due to temperature and potential measurement was thus ±1.75 mV.

As seen in Table II, the spread of results between different samples was ±3 mV for both systems studied. The uncertainties in composition of the samples, ±1% in r and in x_0 (Table I), and the loss of iron from the samples by evaporating, should not have affected the cell potential provided the phase mixtures remained the same. It is likely, therefore, that there were additional small sources of error such as contact potentials between electrodes and electrolyte or electrodes and potential leads. A final source of error was the uncertainty in the thermodynamic data for the iron–wustite reference, ±0.84 kJ mol^{-1} (*21*). The overall accuracy of the $\overline{\Delta G}(O_2)$ data was thus estimated to be ±1.5 kJ. This was quite comparable with the accuracy of other techniques used to study this system.

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