

Thermodynamics of FeO–TiO₂ melts saturated with iron at 1475°C

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Synopsis

The activities of FeO in the system FeO–TiO₂ have been measured at 1475°C by equilibration of the melts with iron crucibles and at a controlled oxygen potential. The results obtained can be expressed in the form

$$a_{\text{FeO}} = -0.636 + 0.253 N_{\text{FeO}} - 0.630 N_{\text{FeO}}^2$$

The data are discussed in terms of ionic fractions and the best model is found to be that based on a regular solution model for the cations.

There are few published data on the thermodynamics of liquid oxide systems containing TiO₂. Industrial slags containing TiO₂ are now produced more often, and knowledge of the effects of TiO₂ on the activities of their components is becoming more important. The Sorel slags are titania-rich FeO–TiO₂ slags, and slags produced in the Elkin and Highveldt processes and in some iron smelting processes also contain appreciable amounts of titania. In iron smelting slags the presence of TiO₂ has been considered by some operators to lead to viscous slags, but the evidence for this is by no means generally accepted—indeed, viscosity measurements suggest the opposite. The reasons are probably concerned with reducing conditions leading to lower oxides of titanium and to titanium carbide formation. There appears to be no published work on the thermodynamics of the binary system FeO–TiO₂; hence, the present work concerned itself with a study of the activity of ferrous oxide in the system FeO–TiO₂ as a first step towards a study of more complex systems.

Two equilibrium diagrams for the system FeO–TiO₂ have been published.^{1,2} The first was that of Grieve and White,¹ who made DTA measurements with molybdenum crucibles to contain their melts and in an inert atmosphere. They proposed a phase diagram showing two interoxide compounds, 2FeO.TiO₂ (pseudo-brookite) and FeO.TiO₂ (ilmenite). Both compounds were considered to melt congruently and to have melting points of approximately 1470°C. MacChesney and Muan² redetermined the phase diagram with melts in iron crucibles under a nitrogen atmosphere or enclosed in silica capsules with an iron–wustite buffer to control the oxygen potential. Their diagram (Fig. 1) shows three congruently melting compounds FeO.TiO₂ (ilmenite), 2FeO.TiO₂ and FeO.2TiO₂. They suggested that 2FeO.TiO₂ had been named wrongly by Grieve and White, and they called it ulvospinel; the compound FeO.2TiO₂ was named pseudo-brookite. Ulvospinel was found to melt at 1395°C, ilmenite at 1400°C and pseudo-brookite at 1494°C.

MacChesney and Muan indicated a considerable range of solid solution in wustite, ulvospinel and pseudo-brookite. Attempts were made in the course of the present work to establish the limit of solubility of TiO₂ in FeO at 1475°C. Slags of varying TiO₂ content held in iron crucibles in an argon atmosphere were heated to 1475°C for 2 h. It was found that only slags with less than 62 per cent TiO₂ were completely molten at this temperature. MacChesney and Muan's diagram

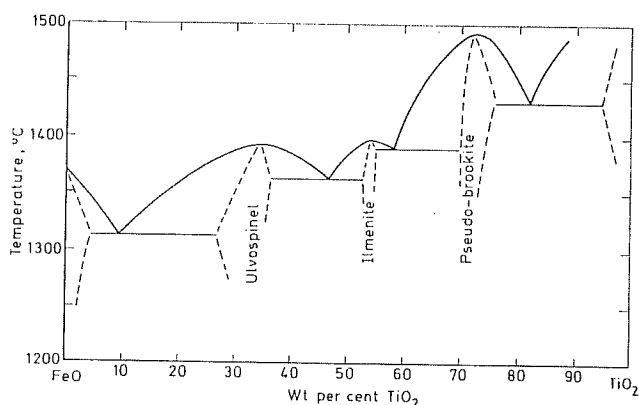


Fig. 1 Phase diagram FeO–TiO₂

suggests that slags in the range 79–85 per cent TiO₂ would melt at 1475°C, but attempts to melt them failed. This work would suggest that saturation with TiO₂ is attained at 62 per cent TiO₂ and that the primary phase formed is TiO₂.

Experimental technique

The present work was aimed at equilibrating FeO–TiO₂ melts in iron containers with a gas mixture of controlled oxygen potential. One of the sources of error in work of this type is the difficulty of keeping an accurate control of the gas mixture throughout the equilibration. To avoid this problem it was decided to premix the gases in a cylinder under pressure. This gave a simple method of controlling the gas composition and also allowed accurate analysis of the equilibrium gas. The method of gas analysis used was based on the MS10 spectrometer. It was hoped that this could be used in the form of a continuous gas analyser in which a portion of the gas flow was admitted through a porous leak, but the accuracy of this method was not considered to be sufficiently high for the present work. Because of this a method by which batch samples were employed was developed. The relative sensitivity of the instrument was determined by use of the pure component gases. The gas mixture employed in this work was a H₂–CO₂–A mixture, this being chosen because of its suitability for analysis on the mass spectrometer. The relative sensitivity of the instrument and the mass spectra of these gases were determined each week during the

work—in this way an accuracy of 2 per cent of the component concentration could be maintained in the analysis. At least five samples of the mixed gas were analysed to obtain the composition.

The gas mixtures were prepared from cylinders of high-purity hydrogen, argon and carbon dioxide. These were admitted into an evacuated cylinder to give a total mixed gas pressure of 800 lb/in². The gases were allowed to mix for about three days and then checked for homogeneity by analysis. The mixture was analysed after each experimental measurement.

All the experimental measurements were made at 1475°C, as it was found that this was the maximum temperature at which Armco iron crucibles could be used. Most of the equilibration runs were performed in a horizontal furnace. This furnace was wound over 16 in with platinum wire and its temperature was controlled with a Smith's temperature controller. The furnace had a hot zone of 3 in, over which the temperature variation was within $\pm 2^\circ\text{C}$. The temperature was measured by a thermocouple placed just outside the mullite reaction tube, and this thermocouple was calibrated against a thermocouple placed inside the reaction tube during a blank experiment. The emf from the thermocouples was measured by a potentiometer. Calibrations of this type were repeated frequently. The geometry of this furnace allowed five iron crucibles of about 1.2-cm diameter and 0.5-cm height to be located in a row within the hot zone during an equilibration experiment.

Some difficulty was encountered with certain slags due to creeping, and in some cases the crucible almost emptied during equilibration. Creeping was found to be most severe in slags with compositions close to ilmenite and caused some trouble in the measurements. MacChesney and Muan² had also encountered creeping in FeO–TiO₂ slags and had resorted to a sealed tube containing the slag and also a buffer of wustite–iron; the tube being placed in the furnace in such a way that a temperature gradient was set up in the tube with the buffer at a slightly lower temperature ($\sim 20^\circ\text{C}$); the oxygen pressure was then slightly lower than that for the Fe–FeO equilibrium at the temperature of the slag.

Several different designs of the shallow crucibles were tried to minimize creeping, but these were not successful and for slags which were prone to creeping tall crucibles 1.2 cm in diameter and 1.7 cm high were used. These charges were equilibrated in a vertical tube furnace similar in size and characteristics to the horizontal furnace.

Ferrous oxide was prepared by decomposition of ferrous oxalate at 1050°C. After slowly heating to this temperature in an iron tube and holding for about one hour, the tube was sealed and then quenched in water. Titanium dioxide was the purest laboratory reagent available; it was dried before use.

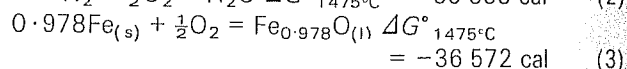
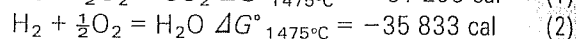
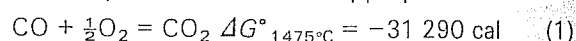
The mixtures used for the experimental melts were prepared by weighing accurately the appropriate amounts of FeO and TiO₂ and mixing thoroughly in a mortar. The charge was made up to contain about

5 per cent FeO less than that estimated for equilibrium with the gas mixture being used. The charge to each crucible was about 1 g, which, when melted, almost filled the crucible.

The crucibles were charged to the furnace on an alumina tray and, after the furnace ends were sealed, nitrogen was passed through for about 5 min to flush the air from the furnace. The gas mixture was then turned on at a flow rate of 200 ml min⁻¹ and the temperature was raised over a period of 3 h to 1475°C. The gas flow rate was then increased to 450 ml min⁻¹ and the molten slag was held at this temperature for 2 h. Initial experiments had shown that this time was sufficient to establish equilibrium in the system. The gas mixture was then replaced by a flow of high-purity nitrogen and the slags were cooled to room temperature. The slag was separated from the crucible by squeezing the wall and crushed to -150 mesh. The slags were analysed for total iron and, in some cases, for titanium. It had been intended to analyse for ferric and ferrous iron, but this proved impossible because of the extreme difficulty encountered in dissolving these slags. Fusion with potassium bisulphate had to be resorted to, and this precluded any possibility of analysing for ferrous iron. After fusion the iron content was determined by solution in sulphuric acid, stannous chloride reduction and titration with potassium dichromate solution.

In most cases the titania content was obtained by difference, but occasional checks were made with X-ray fluorescence on the solution. The values obtained by this method agreed, within experimental error, in all cases with those obtained by difference. The experimental data are presented in Table 1. All analyses are the mean of two determinations which agreed within better than ± 0.5 per cent, and all data are the result of two separate equilibrations for each gas mixture.

The activities of ferrous oxide were calculated from the thermodynamic data for the appropriate reactions.³



The standard state for the activity of ferrous oxide was 'FeO' in equilibrium with solid delta-iron at 1475°C. From the iron–oxygen phase⁴ system this oxide has the formula Fe_{0.978}O; it is distinguished from stoichiometric ferrous oxide in the subsequent discussion by being denoted 'FeO'. All the data obtained in the present investigation are plotted in Fig. 2, giving the activity of 'FeO' as a function of composition. The curve drawn through the points can be represented by the equation $a_{\text{FeO}} = -0.636 + 0.253 N_{\text{FeO}} - 0.630 N_{\text{FeO}}^2$ (4)

which is valid in the range N_{FeO} unity to 0.46 at 1475°C. The data indicate a negative deviation from ideality throughout the range of composition liquid at 1475°C.

In order to calculate activity data for TiO₂ in the melts by the Gibbs–Duhem integration a reference point for the titania activity is necessary. Two different solubilities

Table

Gas mixture
% CO₂

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Table 1 Results of experimental measurements

Gas mixture		% A	a_{FeO}	Slag analysis		N_{FeO}	γ_{FeO}	Remarks
% CO ₂	% H ₂			FeO wt %	TiO ₂			
18.15	35.91	45.89	0.90	91.0 91.1	9.0 8.9	0.918	0.98	Horizontal furnace
17.6	36.8	45.58	0.84	88.0 87.8	12.0 12.2	0.891	0.93	Horizontal furnace
15.14	37.86	46.99	0.67	69.5 69.5	30.5 30.5	0.717	0.935	Horizontal furnace
15.34	37.95	46.7	0.67	70.8 70.8	29.2 29.2	0.730	0.92	Vertical furnace
15.19	38.06	46.74	0.66	67.6 68.3	32.3 31.7	0.703	0.94	Vertical furnace
13.6	38.1	48.3	0.58	61.5 61.5	38.5 38.5	0.64	0.91	Horizontal furnace
12.03	38.1	49.87	0.50	59.0 59.1	41.0 40.9	0.615	0.815	Horizontal furnace
11.47	38.52	50.02	0.47	57.5 57.4	42.5 42.6	0.601	0.78	Horizontal furnace
13.67	45.06	41.26	0.46	55.7 56.3	44.3 43.7	0.586	0.79	Vertical furnace
10.67	37.3	52.05	0.44	53.9 53.8	46.1 46.2	0.559	0.79	Horizontal furnace
12.46	50.31	37.22	0.37	49.0 49.2	51.0 50.8	0.516	0.716	Vertical furnace
8.70	38.69	52.61	0.32	46.0 45.7	54.0 54.3	0.485	0.66	Vertical furnace
9.9	42.29	47.8	0.30	45.7 46.0	54.3 54.0	0.487	0.615	Vertical furnace

of TiO₂ in these melts were given by Grieve and White¹ and MacChesney and Muan.² The former authors suggested a solubility of 85 mole per cent TiO₂, whereas the latter indicated a solubility of 62 mole per cent TiO₂ in equilibrium with pseudo-brookite. The work of MacChesney and Muan is to be preferred, since they took care to establish the system under a controlled oxygen potential, but the liquidus above 50 mole per cent TiO₂ was established with extremely few melts and could be in error by several per cent titania. Examination of the melts made in the course of the present work suggests that the liquidus composition at 1475°C was somewhat less than that reported by MacChesney and Muan, and melts containing above about 58 mole per cent TiO₂ did not completely melt at 1475°C. There are no free energy data for pseudo-brookite, but there are some for ulvospinel and ilmenite.^{3,5} For ilmenite two sets of data are available, one of which yields a free energy for the formation of liquid ilmenite of -4410 ± 500 cal at 1475°C. The other, when the heats of fusion of ilmenite and ferrous oxide are taken into account, yields a free energy of formation of -2820 ± 500 cal. Combined with the present data for 'FeO' activities, these give values for the activity of TiO₂ in liquid ilmenite of 0.86 ± 0.02 and 1.34 ± 0.03, respectively. The latter value is impossible, and, indeed,

in order to obtain a reasonable value for the activity of TiO₂ with a free energy of -2820 cal, a positive deviation from ideality would be required for 'FeO'.

The activity curve for TiO₂ in Fig. 2 has been derived by use of an activity of TiO₂ of 0.86 in the liquid composition $N_{\text{TiO}_2} = 0.5$ and a Gibbs-Duhem integration. The Gibbs-Duhem integration would suggest that saturation with solid TiO₂ was reached at 55 mole per cent TiO₂. This is of the same order as the liquidus composition at 1475°C indicated in the present work, but not in agreement with the phase diagram.² If the free energy of formation of ilmenite was 500 cal more negative, saturation with TiO₂ would be reached at approximately 60 mole per cent TiO₂.

Activities of 'FeO' in the system 'FeO'-SiO₂ have been measured in several investigations.^{6,7} The data for 1600°C on the same standard state as the present data are compared with those for 'FeO'-TiO₂ in Fig. 3. Unlike the 'FeO'-TiO₂ system, where the deviations from ideality are negative throughout, the activities of 'FeO' in the 'FeO'-SiO₂ system show positive deviations from ideality above 75 mole per cent 'FeO'. The integral free energy of mixing curves for the two systems is compared in Fig. 4.

A consideration of ionic models for systems containing FeO is complicated by the non-stoichiometry of

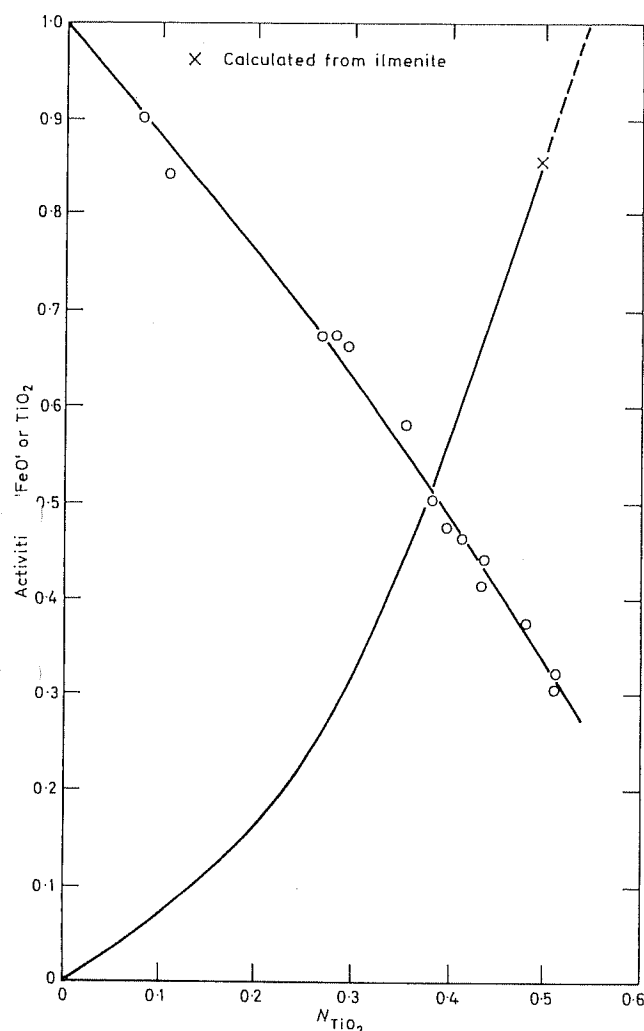


Fig. 2 Experimental data for wustite activities and derived data for titania activities

ferrous oxide. As was mentioned earlier, it was found possible to obtain reliable analytical data for the Fe_2O_3 content of the melts in this investigation, owing to difficulties in dissolving the slags in acid. But it appears from other investigations² that the Fe_2O_3 contents will be similar to those in 'FeO'- SiO_2 melts at equilibrium with iron at similar oxygen potentials, and this assumption has been made in the subsequent discussion. The actual Fe_2O_3 contents will be small and any errors involved in this assumption will be very small in comparison with the assumptions made in the various ionic models.

To compare the data in ionic terms the activity must be expressed with reference to a hypothetical stoichiometric FeO, and there are several assumptions which can be made to do this. The simplest is that the activity of FeO in the reference state 'FeO' is equal to the simple ionic fraction of Fe^{2+} ions, i.e.

$$a_{\text{FeO}} = \frac{N_{\text{Fe}^{2+}}}{N_{\text{Fe}^{2+}} + N_{\text{Fe}^{3+}}} = N_{\text{Fe}^{2+}} \quad (5)$$

This gives an activity of stoichiometric FeO in the reference standard state of 0.96.

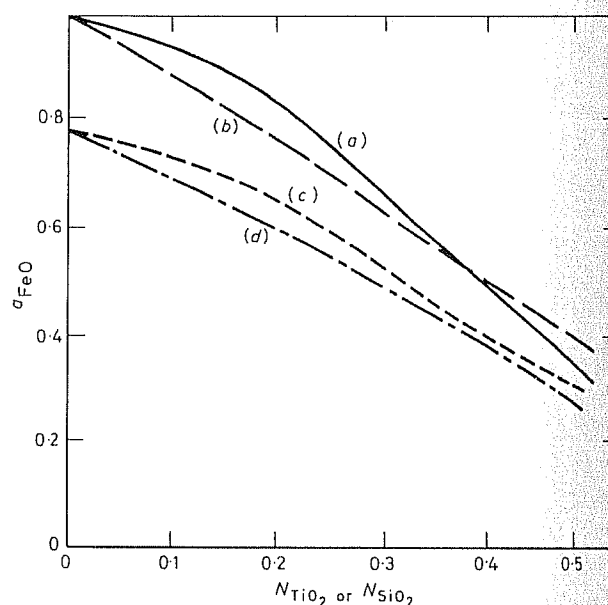


Fig. 3 Comparison of activities in FeO-TiO_2 and FeO-SiO_2 systems on different reference states. (a) FeO-SiO_2 system, reference state wustite in equilibrium with solid iron at 1475°C ; (b) FeO-TiO_2 system on same reference state as (a); (c) FeO-TiO_2 system, reference state equation 10; (d) FeO-TiO_2 system, reference state equation 10

The use of equivalent ion fractions would lead to a value of 0.94, where

$$a_{\text{FeO}} = \frac{2n_{\text{Fe}^{2+}}}{2n_{\text{Fe}^{2+}} + 3n_{\text{Fe}^{3+}}} = N'_{\text{Fe}^{2+}} \quad (6)$$

Lumsden⁸ examined the thermodynamic data for the $\text{FeO-Fe}_2\text{O}_3$ system and came to the conclusion that it was not a simple ionic solution but that there were interactions between Fe^{2+} and Fe^{3+} ions which he expressed in the relations

$$\text{FeO}(\text{FeO}_{1.5}:1): RT \ln \gamma = -4460 N_{\text{Fe}^{3+}}^2 \quad (7)$$

$$\text{FeO}_{1.5}(\text{FeO}:1): RT \ln \gamma = -4460 N_{\text{Fe}^{2+}}^2 \quad (8)$$

But in order to fit the expressions to the experimental data at low concentration of Fe_2O_3 an assumption of disproportionation of ferrous ions to ferric ions, and free electrons was made, i.e.

$$\text{Fe}^{2+}(\text{O}^{2-}:1) = (\text{Fe}^{3+} + e^-)(\text{O}^{2-}:1) \quad (9)$$

for which Lumsden calculated the disproportionation constant 0.0123 at 1475°C . These assumptions lead to a free energy equation for the formation of an 'ideal stoichiometric FeO' of

$$\text{Fe}_{(s)} + \frac{1}{2}\text{O}_2 = \text{FeO}_{(l)} \quad (\Delta G^\circ = -54\,585 + 10\,867 \text{ cal}) \quad (10)$$

On this model the activity of FeO in the wustite reference state would be 0.78. Neither the model based on simple ionic fractions nor that based on equivalent ion fractions agrees with the present experimental data. The comparisons are shown in Fig. 5, which illustrates

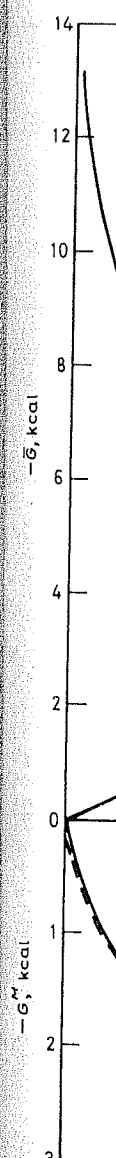


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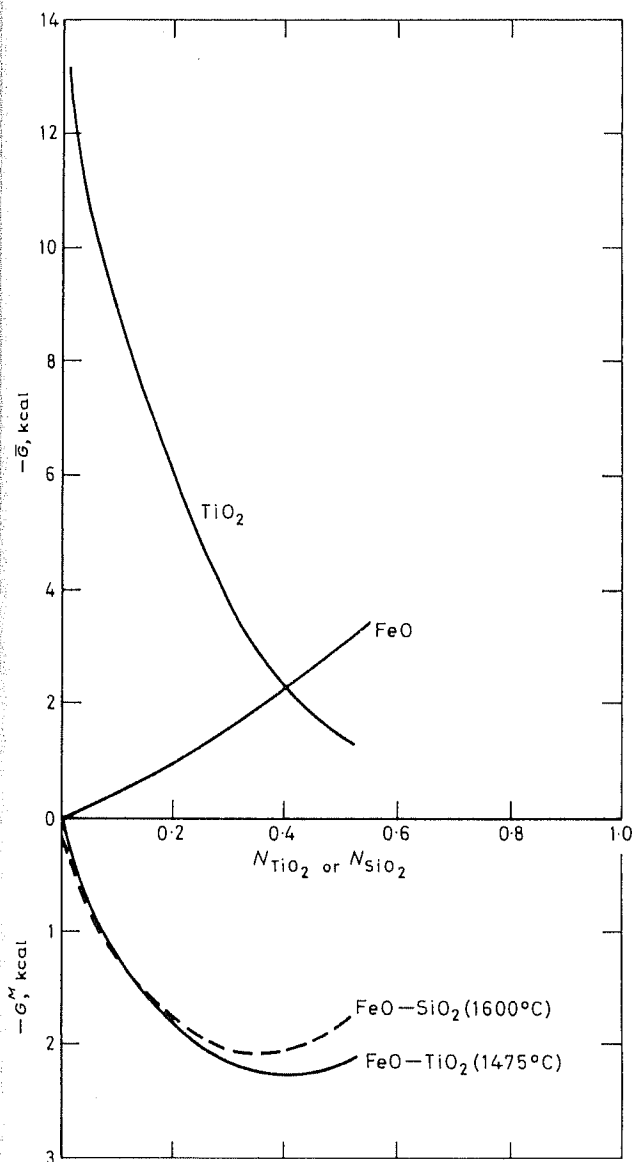


Fig. 4 Partial molar and integral free energies of mixing for the systems FeO-TiO₂ and FeO-SiO₂

that simple ionic fractions lead to higher activities of FeO than those measured, whereas that based on equivalent ion fractions leads to lower activities for titania concentrations below 40 mole per cent.

Lumsden's regular solution model would lead to an expression for the activity coefficient of FeO in these melts of the form

$$RT \ln \gamma = -4460N_{Fe^{3+}}^2 + k_2N_{Ti^{4+}}^2 + k_3N_{Fe^{3+}}N_{Ti^{4+}} \quad (11)$$

where k_2 is the interaction constant for the system FeO-TiO₂ and k_3 is the sum of the interaction constants for the systems FeO-Fe₂O₃ and FeO-TiO₂ less that for the system Fe₂O₃-TiO₂.

Activities of FeO referred to equation 10 for the systems 'FeO'-SiO₂ and 'FeO'-TiO₂ shown in Fig. 3 are, within experimental error, almost the same for TiO₂ and SiO₂ contents above 30 mole per cent. At these levels the concentrations of ferric ion in the melts are very

small, and, hence, the interaction constants on Lumsden's model will be almost the same for FeO-SiO₂ and FeO-TiO₂. The deviations between 'FeO'-SiO₂ and 'FeO'-TiO₂ at lower concentrations of TiO₂ and SiO₂ must then be ascribed to differences in the interaction constants for Fe³⁺ and Ti⁴⁺ and Si⁴⁺. This would

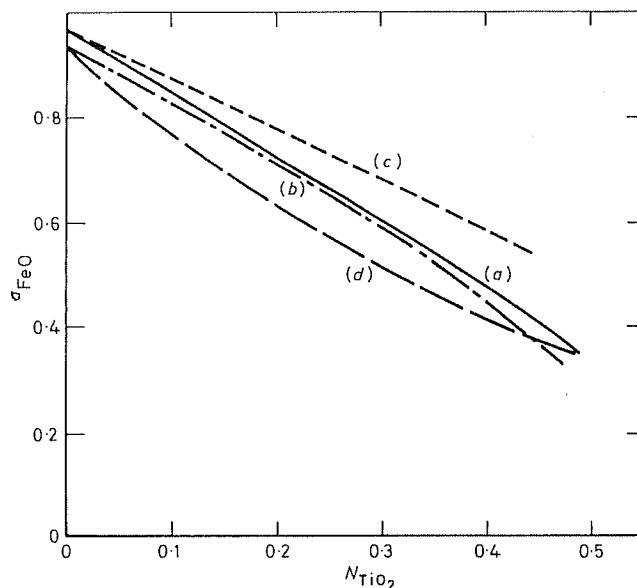


Fig. 5 Comparison of activities calculated by use of ionic fractions. (a) Data of Fig. 2, reference state a_{FeO} in wustite of 0.97; (b) data of Fig. 2, reference state a_{FeO} in wustite of 0.94; (c) $a_{FeO} = N_{Fe^{2+}}N_{O^{2-}}$; (d) $a_{FeO} = N'_{Fe^{2+}}N'_{O^{2-}}$

suggest an interaction constant for Fe₂O₃-TiO₂ of about 4200 (3200 for the Fe₂O₃-SiO₂ system). By use of Lumsden's model the present data fit an expression of the form

$$FeO (FeO_{1.5}, TiO_2 : l) \\ RT \ln \gamma = -4460N_{Fe^{3+}}^2 - 10\,000N_{Ti^{4+}}^2 - 18\,660N_{Ti^{4+}}N_{Fe^{3+}} \quad (12)$$

It must be emphasized that this expression has been derived on the basis of data from iron-saturated slags, and the range of Fe₂O₃ contents is therefore very limited.

These models should also be applicable to the calculation of TiO₂ activities in the same way as FeO activities, but the comparison must be made with reference to liquid TiO₂ as standard state. The heat of fusion³ of TiO₂ is 15.5 ± 1.5 kcal; hence

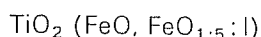
$$TiO_{2(s)} = TiO_{2(l)} (\Delta G^\circ = 15\,500 - 7.47T) \quad (13)$$

The activities of TiO₂ calculated by the simple ionic fraction model yield activities much higher than those derived from the Gibbs-Duhem integration recalculated to a standard state of liquid TiO₂.

By use of equivalent ion fractions the activity of titania in the melts would be given by

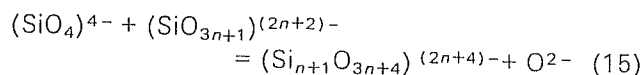
$$a_{TiO_2} = (N'_{Ti^{4+}})^2$$

This expression yields values which are much closer to those derived by the Gibbs–Duhem integration, and, bearing in mind the uncertainty in the heat of fusion of TiO_2 and the reference point for the integration, could represent the data. But since the model does not represent the FeO activities with sufficient precision it cannot be considered applicable to this system in its simple form. The regular solution model would lead to an expression



$$RT \ln \gamma = -10\,000N_{\text{Fe}^{2+}}^2 + 4200N_{\text{Fe}^{3+}}^2 - 1340N_{\text{Fe}^{3+}}N_{\text{Fe}^{2+}} \quad (14)$$

This expression leads to activity values of TiO_2 somewhat lower than those in Fig. 2, but if the uncertainty in the reference point for the TiO_2 activities and in the heat of fusion of TiO_2 is taken into account, the data could be reconciled. Masson and co-workers⁹ proposed a model for silica-containing melts based on polymer theory and polycondensation equilibrium of the type



Although this approach may be valid for melts containing silica, it is unlikely to be a suitable model for TiO_2 containing melts since (a) titanium in solid TiO_2 has a sixfold coordination, and this is unlikely to change to a fourfold in FeO-TiO_2 melts; (b) the phase diagram¹⁰ for $\text{TiO}_2\text{-SiO}_2$ shows an extensive region of liquid immiscibility, suggesting that liquid SiO_2 and TiO_2 have different liquid structures; and (c) observations show liquid TiO_2 and titania-rich melts in the systems CaO-TiO_2 and MgO-TiO_2 to be very fluid—unlike silica-rich melts. It appears more realistic to consider the melts examined in the present investigation as ionic melts of Ti^{4+} , Fe^{2+} , Fe^{3+} and O^{2-} , as has been

done above. On this basis the model which best fits the experimental data is that based on simple ion fractions, but taking into account ionic interactions. The main drawback to this approach is the necessity for an assumption of disproportionation of ferrous ions.

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