

Quartz-fayalite-iron and quartz-fayalite-magnetite equilibria and the free energy of formation of fayalite (Fe₂SiO₄) and magnetite (Fe₃O₄)

HUGH ST. C. O'NEILL*

Research School of Earth Sciences, Australian National University, Canberra, 2601, A.C.T., Australia

ABSTRACT

The quartz-fayalite-iron and quartz-fayalite-magnetite equilibria have been studied in the temperature range 1000–1400 and 1050–1300 K, respectively, using an electrochemical technique. The results are in excellent agreement with the calorimetric data on fayalite (Robie et al., 1982). For magnetite, the results demonstrate conclusively that there is no zero-point entropy and that the earlier heat-content measurements of Coughlin et al. (1951) should be preferred to the measurements by differential scanning calorimetry of Gronvold and Sveen (1974) above the Curie point.

For quartz-fayalite-iron,

$$\begin{aligned}\mu_{\text{O}_2} (\pm 140) &= -542\,941 - 33.182T + 22.4460T \ln T \quad (900 < T < 1042) \\ &= -562\,377 + 103.384T + 5.4771T \ln T \quad (1042 < T < 1184) \\ &= -602\,739 + 369.704T - 27.3443T \ln T \quad (1184 < T < 1420)\end{aligned}$$

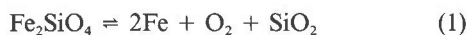
and, for quartz-fayalite-magnetite,

$$\begin{aligned}\mu_{\text{O}_2} (\pm 200) &= -587\,474 + 1584.427T - 203.3164T \ln T \\ &\quad + 0.092\,710T^2 \quad (900 < T < 1420).\end{aligned}$$

(The units for μ_{O_2} are joules per mole and T is in kelvins; the reference pressure is 10^5 Pa (1 bar); and the quoted uncertainties are one standard deviation.)

INTRODUCTION

The stability field of fayalite, Fe₂SiO₄, is bounded at low chemical potentials of oxygen (μ_{O_2}) by the reaction



and at high μ_{O_2} by



The solid assemblages, when the silica is in the form of quartz, are often known, respectively, as the quartz-fayalite-iron (QFI) and quartz-fayalite-magnetite (QFM) oxygen buffers.

Both Reactions 1 and 2 are petrologically important. Reaction 1 is the essence of the equilibrium between olivine and metal, knowledge of which is necessary for understanding the origin and evolution of planetary cores and many metal-containing meteorites. Reaction 2 is the basis of the olivine-orthopyroxene-spinel geosensor (O'Neill and Wall, in prep.), which may be used to deduce the oxygen fugacity of the Earth's upper mantle. Reaction 2 also places an important constraint on the oxygen fu-

gacity at which many igneous and metamorphic rocks have formed. Both reactions have been extensively used as oxygen buffers in the double-capsule technique (Eugster, 1957) in hydrothermal experiments, and therefore their accurate calibration has a fundamental bearing on a large body of other experimental work. Fayalite has also been used as a reference compound in oxide-melt solution calorimetry (Chatillon-Colinet et al., 1983), the simple oxide "FeO" being unsuitable for this purpose on account of its variable composition. Lastly, as fayalite shows very small deviations from ideal stoichiometry over the range of μ_{O_2} defined by Reactions 1 and 2 (Nakamura and Schmalzried, 1983), the combination of these reactions gives the free energy of formation of magnetite through the reaction



which can only be studied directly below 833 K, the decomposition temperature of wüstite, and which therefore may be used to resolve the conflicting thermodynamic data on this key substance.

Given their importance, it is not surprising that a fair number of previous studies of both reactions, using a variety of techniques, are available in the literature. A list is given in Table 1. For both reactions, agreement among

* Present address: C.R.A. Research, P.O. Box 42, Boolaroo, N.S.W. 2284, Australia.

Table 1. Previous experimental studies on the equilibria $\text{Fe}_2\text{SiO}_4\text{-Fe-SiO}_2$ and $\text{Fe}_2\text{SiO}_4\text{-Fe}_3\text{O}_4\text{-SiO}_2$ (since 1960)

Reference	T (K) range	Form of SiO_2^*	Method
		(a) $\text{Fe}_2\text{S-O}_4\text{-Fe-SiO}_2$	
Lebedev and Levitskii (1962)	1123–1423	?	CO-CO ₂ gas mixing
Taylor and Schmalzried (1964)	1173–1373	?	emf
Berliner and Shapovalova (1966)	1033–1403	Q	H ₂ -H ₂ O circulation
Schwerdtfeger and Muan (1966)	1273–1423	?	CO-CO ₂ gas mixing with thermogravimetry
Kitayama and Katsura (1968)	1402–1447	?	CO ₂ -H ₂ gas mixing
Nafziger and Muan (1967)	1423	?	CO ₂ -H ₂ gas mixing
Levitskii and Ratiani (1970)	1100–1270	Q	emf (La_2O_3 -doped ThO ₂) vs. Fe-FeO
Williams (1971)	1198, 1451	C	CO ₂ -H ₂ gas mixing
Schwab and Söhnlein (1977)	1233–1428	C	emf (CSZ) vs. Fe-FeO
Schwab and Küstner (1981)	1099–1414	C	emf (CSZ) vs. air
Rög and Kozinski (1983)	870–1200	?	emf (Fe^{2+} -doped β -alumina) vs. Fe-FeO
Myers and Eugster (1983)	1233–1413	Q	Gas mixing with thermogravimetry
		(b) $\text{Fe}_2\text{SiO}_4\text{-Fe}_3\text{O}_4\text{-SiO}_2$	
Schwerdtfeger and Muan (1966)	1373	?	Co-CO ₂ gas mixing with thermogravimetry
Wones and Gilbert (1969)	873–1073	Q	H ₂ membrane: $P = 0.8$ to 2.0 kbar
Chou (1978)	873–1073	Q	H ₂ sensor: $P = 2$ and 4 kbar
Williams (quoted in Chou, 1978)	1395	?	Gas mixing
Schwab and Söhnlein (1977)	1303–1403	C	emf (CSZ) vs. Fe-FeO and vs. air
Hewitt (1978)	923–1123	Q	H ₂ membrane: $P = 1.0$ kbar
Schwab and Küstner (1981)	1000–1400	C	emf (CSZ) vs. air
Myers and Eugster (1983)	927–1038, and 1391–1406	Q	Gas mixing with thermogravimetry and H ₂ membrane $P = 1.0$ kbar

* Q = quartz, C = cristobalite, ? = not given.

the various studies can only be described as moderate, at best. Moreover Robie et al. (1982) have recently redetermined the entropy of fayalite, which places a constraint on both reactions that most of the existing data fail to fully satisfy. There is, therefore, still a need for accurate determination of the quartz-fayalite-iron and quartz-fayalite-magnetite equilibria. To this end, an extensive series of experiments have been undertaken using an electrochemical method with oxygen-specific calcia-stabilized zirconia (CSZ) electrolytes.

EXPERIMENTAL DETAILS

The theory of using oxygen concentration cells for thermodynamic measurements is well known, and some excellent reviews are available (Steele, 1968; Goto and Pluschkell, 1972; Worrell, 1977; Ramanarayan, 1980).

Such cells in essence consist of two electrodes, A and B, each defining chemical potentials of oxygen, $\mu_{\text{O}_2}^{\text{A}}$ and $\mu_{\text{O}_2}^{\text{B}}$, separated by an oxygen-conducting electrolyte such as calcia-stabilized zirconia (CSZ). The emf (E) developed by such a cell is related to the difference in the chemical potential of oxygen at the two electrodes by the equation

$$4FE = \int_{\mu_{\text{O}_2}^{\text{B}}}^{\mu_{\text{O}_2}^{\text{A}}} t_{\text{ion}} d\mu_{\text{O}_2}, \quad (4)$$

where F is the Faraday constant ($96484.56 \text{ C} \cdot \text{mol}^{-1}$) and t_{ion} is the ionic transference number, which is given by the ratio of the ionic conductivity (σ_{ion}) to the total (ionic plus electronic) conductivity:

$$t_{\text{ion}} = \sigma_{\text{ion}} / (\sigma_{\text{ion}} + \sigma_{\text{el}}). \quad (5)$$

Many studies have shown (see reviews referenced above) that for CSZ or the related electrolyte yttria-stabilized zirconia (YSZ), t_{ion} is virtually unity (>0.99) over a wide range of temperatures and for μ_{O_2} values ranging from more oxidizing than air to less

than that defined by the iron-wüstite (Fe-“FeO”) equilibrium. Under these conditions, Equation 4 reduces to

$$4FE = \mu_{\text{O}_2}^{\text{B}} - \mu_{\text{O}_2}^{\text{A}}. \quad (6)$$

Since the method measures the difference in μ_{O_2} between the two electrodes, one, with known μ_{O_2} , must be chosen as a reference. In this study, simple metal + metal oxide mixtures (e.g., Cu + Cu₂O, Fe + “FeO,” and Mo + MoO₂) have been used as reference electrodes.

Experimental design

The design of the electrochemical cells used in this study is shown schematically in Figure 1. The heart of the cell is the electrolyte, which, in all runs but one, was a flat-bottomed, calcia-stabilized zirconia (CSZ) tube supplied by the Nippon Chemical Ceramic Co. About 200 mg of the sample was pressed into a pellet of a suitable diameter to fit the inside of the CSZ tube after it had been cleaned by scraping gently on fine-grained silicon carbide paper to remove the outermost rind of material that may have been contaminated in the pellet-press; there seems little possibility of introducing SiC, as the pellets are very soft and friable at this stage. This pellet was spring-loaded against the bottom of the CSZ tube via a closed-ended alumina tube that also acted as a sheath to contain the thermocouple, which thus sits directly over the sample. The CSZ tube was inserted into an outer alumina tube containing the reference electrode pellet, made from 500 mg of the appropriate metal + metal oxide, which was spring-loaded against the bottom of the CSZ tube via an alumina rod. The tops and bottoms of the tubes were sealed with epoxy into brass heads that allowed the independent evacuation of both tubes followed by filling with highly purified argon. For accurate work, it cannot be emphasized enough how important it is to ensure that both electrode compartments are as gas-tight as possible to prevent leaks from the air. Platinum lead wires to the electrodes were run down the outside of both the alumina push rods and were kept isolated from the CSZ or

outer alumina tubes by threading them through a half section of thermocouple tubing, fixed to the push rods with high-temperature cement.

The brass heads holding the tubes were so designed that the cells could be accurately and reproducibly (to the nearest millimeter) positioned along the vertical axis, and in the constant-temperature zone, of a high-temperature vertical tube furnace (Deltech model DT-31-VT), which was heated by six MoSi₂ hairpin elements arranged in a symmetric, noninductive configuration. The position of the constant-temperature zone of the furnace was initially taken from the work reported in Holmes et al. (1986).

For some of the QFI runs with (Fe + "FeO") or (Mo + MoO₂) reference electrodes, additional pellets (~1 mm thick) made from yttria-doped thoria (YDT) with 15 mol% yttria were placed between the electrodes and the CSZ tube. The purpose of this was to see if YDT, which retains negligible electronic conductivity down to much lower oxygen potentials than CSZ, could eliminate some of the oxygen transference that was obviously occurring at higher temperatures (>1200 K). However, no difference to the properties of the cell could be detected.

For one run with QFI against (Mo + MoO₂) a SIRO₂ tube, made from an yttria-stabilized zirconia pellet eutectically welded into an alumina tube, was used in place of the CSZ tube. For this run a slight improvement in performance at high temperatures (>1300 K) was observed, which may be related to either a possible superior purity of the YSZ, or simply to the greater thickness of the YSZ electrolyte separating the two electrodes.

The emf of the cell was fed to a high-impedance (10¹⁵ Ω), very low bias current (<0.5 pA) amplifier with a nominal gain of unity, from which it was continuously monitored on a chart-recorder. This is extremely useful for accurate work, as it would allow changes of as little as ±0.2 mV in the cell emf to be observed over, say, a 24-h period. The actual emf measurements were made, via the amplifier, on a Hewlett-Packard 3450A digital multifunction meter. For each measurement, the zero reading of the amplifier was checked, as this was found to vary slightly with laboratory temperature. The measuring arrangement was calibrated against a standard Weston cell and cross-calibrated against other potentiometers; emf measurements are believed to be accurate to ±0.1 mV, and were recorded to ±0.01 mV.

Temperature—measurement, control, and gradients

The temperature of a cell was measured to ±0.1 K with a Pt-Pt₉₀Rh₁₀ thermocouple placed directly over the sample. The cold junction of the thermocouple was kept in an ice bath. The thermocouple emf was measured with the same Hewlett-Packard 3450A multifunction meter as were the cell emf values. Thermocouples were calibrated using this arrangement by measuring the emf at the melting point of gold (10.3343 mV at 1337.58 K, IPTS 1968). It was assumed that the percentage deviation of the emf from this standard point applied throughout the range of temperature measured, and hence the readings of the thermocouple were corrected accordingly. This assumption was confirmed for two thermocouples, with rather different calibration emf values, by measuring the melting point of NaCl; results on melting gave 1073.7 ± 0.2 K, and on cooling 1074.0 ± 0.4 K, which is in complete agreement with the accepted value of 1073.8 K. Duplicate calibrations on the same thermocouple yielded results that were always within ±0.003 mV (i.e., 0.25 K at the gold melting point). Thermocouples made from the same spools of wire generally gave identical results within this limit. Temperatures are reported to the nearest 1 K, which allows for errors in calibration and also for the unfortunate fact that some ther-

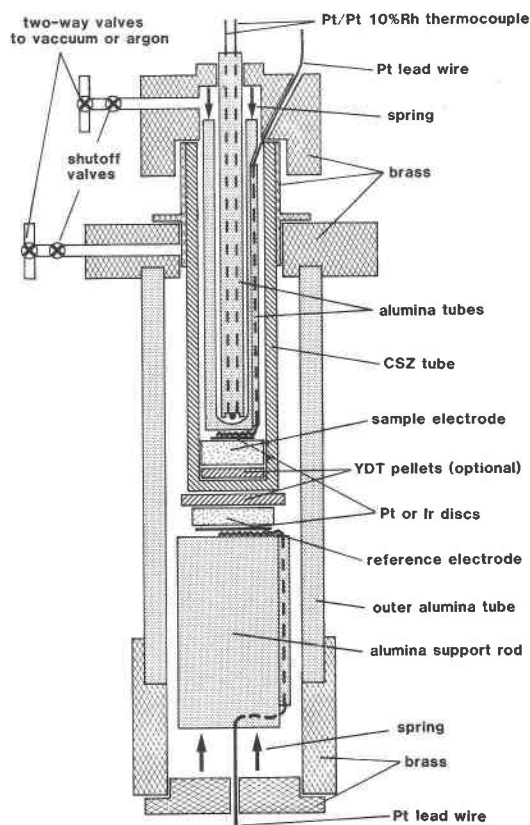


Fig. 1. Schematic diagram of the electrochemical cells (the vertical scale is greatly compressed relative to the horizontal). All joints are made with epoxy and have not been shown for reasons of clarity.

mocouples broke before they could be calibrated, in which case they were assumed to behave similarly to other thermocouples taken from the same spools of wire. It is to be noted that temperature errors of even ±2 K would have but a trivial effect on the results.

The furnace temperature controller was found to control to within ±0.2 K over a period of several hours. Longer-term stability was to within ±2 K over several weeks.

The cells were positioned as carefully as possible in the zone of constant temperature, or "hot spot," of the furnace, which is quite difficult to do, as anything put into the furnace tends to slightly alter the geometry of the temperature profile. The part of the hot spot that is within 0.5 K of the peak temperature in the furnace is only 10 mm long (Holmes et al. 1986). The cells themselves, as measured from the thermocouple bead at the top to the bottom platinum electrode (see Fig. 1), are ~6 mm in length without the YDT discs, ~8 mm with them, and ~15 mm for the cell with the SIRO₂ tube. The presence of any temperature gradient across the cell was checked for by constructing in identical fashion to the actual cells used for the experiments symmetrical cells of the type



where M + MO refers to the solid reference electrodes (i.e., Cu + Cu₂O, Fe + "FeO," Mo + MoO₂). Such cells should produce a zero emf. In fact, for the earliest experiments, involving all the runs with Cu + Cu₂O and a few of those with Fe + "FeO,"

small (<1.0 mV), reproducible emf values that changed linearly with temperature were observed. These were interpreted to be due to incorrect positioning of the cell in the constant-temperature zone, which was probably caused by the position of the latter being changed by heat conduction through the cell assembly itself. Since, to a first approximation, such thermoelectric emf values are expected to be independent of the composition of the sample, they were subtracted from the final readings obtained with these assemblies. Later attempts with an experimental design that was adjusted to compensate for the apparent change in the position of the constant-temperature zone produced negligible emf values in the symmetrical cells (<0.2 mV). These symmetrical cells also served to confirm that the experimental arrangement effectively eliminated any leakage of oxygen from the atmosphere into either electrode compartment.

There are two advantages that solid metal-metal oxide mixtures have as reference electrodes over the more commonly used gas mixture such as air, CO₂-CO or CO₂-H₂: (1) There is no flowing gas that may cool parts of the assembly, introducing complexities to the geometry of the temperature profile, reducing the length of the constant-temperature zone and making its exact location extremely difficult. (2) Since the μ_{O_2} vs. T slopes of most solid oxygen buffers are quite similar, any absolute error in temperature measurement translates into a relatively small error in the μ_{O_2} of the unknown.

Demonstration of equilibrium

Various trials showed that the emf of a satisfactorily operating cell at constant temperature remained stable (to within ± 0.3 mV) for at least several days at temperatures below ~ 1150 K. Although this is a powerful indication that both electrodes have achieved equilibrium, it is not conclusive, as was shown, for example, by several attempts to measure QFM at low temperatures (<1050 K), which also gave stable but obviously quite erroneous emf values.

Equilibrium may be demonstrated by (1) obtaining data at different temperatures both by increasing and decreasing the temperature of the cell; (2) passing a small current through the cell, which titrates O₂ from one electrode to the other (if the cell is reversible, the emf should then return to the original value); and (3) evacuating one or other of the electrode compartments and refilling with an oxidizing or reducing gas such as air or Ar-CH₄, Ar-H₂, or CO, which may then either be left in until the next reading is taken, or, if less drastic action is deemed appropriate, left for a few minutes before again evacuating and filling with purified argon. This procedure can be done independently for either the sample or the reference electrode.

It should be noted that especially toward the lower limit of temperature at which the cell is found to operate, the cell often does not return to equilibrium after options 1 or 2, which were therefore used sparingly.

In addition, duplicate runs were performed for all types of cell so as to confirm the precision of the measurements.

Materials

The fayalite used was kindly donated by V. J. Wall of Monash University. It had been made by sintering a mixture of Fe, Fe₂O₃, and amorphous SiO₂ in an evacuated silica tube for seven days at 1050°C. It was greenish yellow in color, and no unreacted material could be detected by X-ray diffraction; optical examination under a high-power microscope with refractive index oils indicated better than 99% purity, with just the occasional very small grain of low-birefringent material, which may possibly be

cristobalite or tridymite. No magnetic material could be detected with a magnet. Iron metal (>99.5%) was supplied by Merck, Fe₃O₄ ("specpure") by May and Baker. The accuracy of some previous determinations of Reactions 1 and 2 is slightly compromised by the form of SiO₂ not being explicitly identified; in this study quartz, obtained from a large, colorless, natural single crystal of gem quality was used. No tridymite or cristobalite could be detected, by either X-ray diffraction or optical examination, at the end of any experimental run.

The reference electrodes were made from mixtures of metal and metal oxide in the molar ratio 3 to 1. "FeO," Cu₂O, and MoO₂ were prepared from Fe and Fe₂O₃, Cu and CuO, Mo and MoO₃, mixed in the appropriate ratio but with a slight excess of metal, and sintered at 1000°C under a flowing stream of highly purified argon for ~ 16 h. All reagents were stated to be of >99.5% purity. The argon used in this and for filling the spaces in the electrode compartments was purified by passing successively over activated charcoal, phosphorous pentoxide, and titanium chips at 800°C.

RELIABILITY OF THE METHOD

The experimental arrangement described here has been extensively tested by doing series of experiments on combinations of the simple metal-metal oxide oxygen buffers (Cu + Cu₂O), (Ni + NiO), (Co + CoO), and (Fe + "FeO") in both the sample- and reference-electrode positions. The results, which will be reported elsewhere, show that (1) the internal precision is better than ± 100 J per mole of O₂, (2) there is complete agreement with the literature calorimetric data, within the latter's limits of accuracy, and (3) there is excellent agreement with the recent work of Holmes et al. (1986), who measured all four buffers independently using air as the reference electrode.

There was no evidence for any side reaction between the sample or reference electrodes and the CSZ or YDT electrolytes in either these runs or the ones reported in this paper. In particular, it is worth noting that since runs with YDT discs produce identical results to those without, there is no evidence for reaction of the CaO or ZrO₂ with SiO₂. Also in some runs, Ir discs were used to separate the platinum lead wires from the sample or reference electrodes; again no difference was detected.

RESULTS

The experimental results for Reactions 1 and 2 are given in Tables 2 and 3. The chemical potentials of oxygen defined by the metal-metal oxide reference electrodes have been taken to be (in J·mol⁻¹):

$$\begin{aligned} \mu_{\text{O}_2}^{\text{Fe-FeO}}(\pm 90) &= -605812 + 1366.718T - 182.7955T \ln T \\ &\quad + 0.103592T^2 \quad (833 < T < 1042) \\ &= -519357 + 59.427T \\ &\quad + 8.9276T \ln T \quad (1042 < T < 1184) \\ &= -551159 + 269.404T \\ &\quad - 16.9484T \ln T \quad (1184 < T < 1450) \\ \mu_{\text{O}_2}^{\text{Cu-Cu}_2\text{O}}(\pm 40) &= -347705 + 246.096T \\ &\quad - 12.9053T \ln T \quad (750 < T < 1330) \\ \mu_{\text{O}_2}^{\text{Mo-MoO}_2}(\pm 140) &= -603268 + 337.460T \\ &\quad - 20.6892T \ln T \quad (1000 < T < 1450). \end{aligned}$$

Table 2. Results for the cells Pt, Fe₂SiO₄ + Fe + SiO₂(qz)|CSZ|Fe + FeO or Mo + MoO₂, Pt

T (K)	emf (mV)	$\Delta H_{r,298}$ (kJ·mol ⁻¹)	T (K)	emf (mV)	$\Delta H_{r,298}$ (kJ·mol ⁻¹)
Run 1 (Fe + FeO)					
1106	55.0	-566.53	1081	56.0	-566.50
971	60.0	.29	1114	54.0	.27
1000	59.7	.63	1224	50.3	.62
1028	58.5	.61	1268	47.8	.35
1054	57.3	.58			
Run 2 (Fe + FeO)					
1017	58.7	-566.51	1138	53.2	-566.36
1022	58.7	.59	1196	50.9	.41
1036	58.0	.55	1208	50.5	.44
1088	55.4	.38	1220	50.1	.48
1101	55.0	.44	1232	49.6	.48
1114	54.3	.39	1244	49.1	.48
1126	53.9	.43	1255	48.5	.42
Run 3 (Fe + FeO)					
1061	56.4	-566.32	1162	52.8	-566.59
1074	56.0	.38	1174	52.1	.51
1087	55.6	.45	1086	55.6	.43
1100	55.2	.51	1072	56.0	.35
1112	54.9	.59	1125	54.2	.53
1125	54.4	.61	1149	53.2	.54
1138	54.0	.67	1137	53.5	.46
1149	53.5	.65	1198	51.0	.48
Run 4 (Fe + FeO)					
1052	56.7	-566.31	1191	50.9	-566.32
1065	56.3	.35	1203	50.7	.44
1079	55.5	.27	1214	50.1	.39
1092	55.0	.30	1226	49.6	.38
1105	54.5	.32	1237	48.9	.29
1118	54.0	.34	1155	52.8	.48
1131	53.7	.44	1131	54.0	.56
1143	53.5	.55	1105	54.6	.36
1154	53.1	.58	1118	54.2	.42
1167	52.6	.59	1130	53.6	.38
1179	51.6	.40	1143	53.0	.36
Run 5 (Mo + MoO ₂)					
1274	49.0	-566.39	1317	51.8	-566.52
1296	50.7	.56	1338	52.8	.44
Run 6 (Mo + MoO ₂)					
1097	39.1	-566.59	1219	45.8	-566.36
1110	39.2	.31	1231	46.7	.44
1123	40.1	.34	1242	47.4	.47
1135	41.2	.48	1253	47.5	.27
1148	41.7	.37	1265	48.3	.32
1159	42.1	.26	1275	49.1	.41
1171	42.9	.29	1286	50.0	.51
1183	43.7	.32	1309	51.5	.58
1196	44.4	.32	1328	52.4	.51
1207	45.2	.39			
Run 7 (Mo + MoO ₂) SiRO ₂ electrolyte (YSZ)					
1119	39.8	-566.33	1358	53.9	-566.42
1132	41.0	.48	1378	54.9	.36
1145	42.0	.55	1398	56.1	.37
1156	42.9	.64	1388	55.3	.29
1169	43.8	.69	1294	50.0	.34
1181	44.6	.71	1338	52.5	.33
1192	45.1	.67	1181	43.8	.41
1204	45.1	.41	1295	50.3	.43
1251	47.5	.32	1317	51.6	.45
1295	50.1	.35	1357	54.0	.48
1337	52.7	.43			

Note: The order is that in which the measurements were made.

Table 3. Results for cells Pt, Fe₂SiO₄ + Fe₃O₄ + SiO₂(qz)|CSZ|Cu + Cu₂O, Pt

T (K)	emf (mV)	$\Delta H_{r,298}$ (kJ·mol ⁻¹)	T (K)	emf (mV)	$\Delta H_{r,298}$ (kJ·mol ⁻¹)
Run 1					
1218	311.0	-531.61	1110	317.1	-531.84
1266	308.6	.72	1135	315.5	.69
1256	309.0	.66	1160	314.1	.63
1244	309.9	.74	1196	312.8	.85
1233	310.6	.77	1209	311.1	.46
1198	311.7	.46	1221	310.3	.40
1186	312.4	.49	1233	309.5	.35
1174	313.0	.48	1278	308.1	.80
1149	314.5	.58	1289	308.2	.71
1123	316.3	.78	1300	305.9	.47
			1311	304.6	.23
Run 2 (with 1% by weight KOH added)					
1144	315.2	-531.75	1117	315.3	-531.28
1118	315.6	.41	1130	314.9	.37
1091	316.5	.26	1142	314.5	.44
1064	318.1	.39	1155	314.0	.50
1049	319.1	.51	1167	313.4	.50
1063	317.9	.30	1180	312.9	.56
1077	316.9	.16	1193	312.2	.56
1090	316.3	.17	1205	311.5	.53
1104	315.7	.19			

electrochemical cells with air as the reference. They are slight modifications of the results of Holmes et al. (1986). The Mo-MoO₂ values are from O'Neill (1986) and were obtained using the experimental technique described in this paper with Fe-“FeO” as the reference electrode. As an extra check on internal consistency, Cu-Cu₂O was measured in like manner against Fe-“FeO” with completely satisfactory results (i.e., agreement to better than ± 100 J·mol⁻¹).

For the QFI equilibrium, few problems were encountered. At the start of a run, the emf came smoothly to a steady value within about 24 h. Thereafter, the emf generally changed almost instantaneously to the new equilibrium value on increasing the temperature, and within a few hours on decreasing the temperature. It was found that below about 1000 K, equilibrium could not be reliably established, the recorded emf becoming somewhat irregular, fluctuating slowly (typically within limits of approximately ± 0.5 mV) over a period of hours. No improvement occurred even when the run was left for several days. Above a certain temperature, generally in the range 1200–1250 K, the emf began to decrease slowly but inexorably shortly after the run had reached temperature. This is undoubtedly due to the increasing electronic conductivity of the electrolyte with increasing temperature, causing small amounts of oxygen transfer between the sample and reference electrodes. The solution to this problem was to record data at these higher temperatures as quickly as possible. When any untoward decrease of emf was noted, the run temperature was either lowered or the run abandoned. Thus the method should be most reliable in the range 1100–1250 K. The list of experimental results given in Table 2 does not include certain data recorded below about 1000 K, or at higher temper-

The reference pressure for oxygen is 1 bar (10⁵ Pa), and the uncertainty given in parentheses, both here and subsequently, is one standard deviation. The values for Fe-“FeO” and Cu-Cu₂O are from O'Neill (in prep.) using

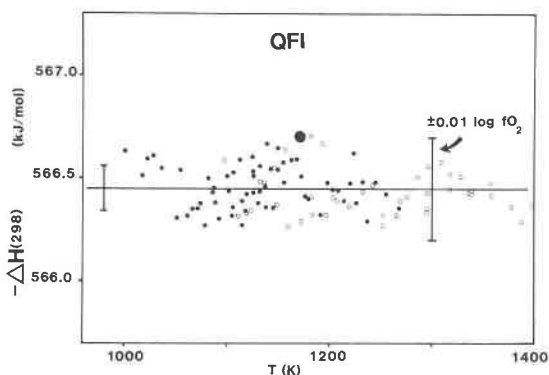


Fig. 2. Standard enthalpy ($\Delta H_{r(298,15K)}$) for the reaction $\text{Fe}_2\text{SiO}_4 \rightarrow 2\text{Fe} + \text{SiO}_2(\text{qz}) + \text{O}_2$ calculated for each datum using the calorimetric data of Table 4 and plotted against the temperature of the datum. If the calorimetric data are correct, such a plot should yield a horizontal line. ●, obtained with the Fe + "FeO" reference electrode; ○, with Mo + MoO₂. Error bar on the left-hand side represents ± 1 standard deviation in the enthalpy of reaction and includes the errors for the reference electrodes, but not those for calorimetric data. For comparison, an error bar of $\pm 0.01 \log f_{\text{O}_2}$ at 1300 K has also been drawn.

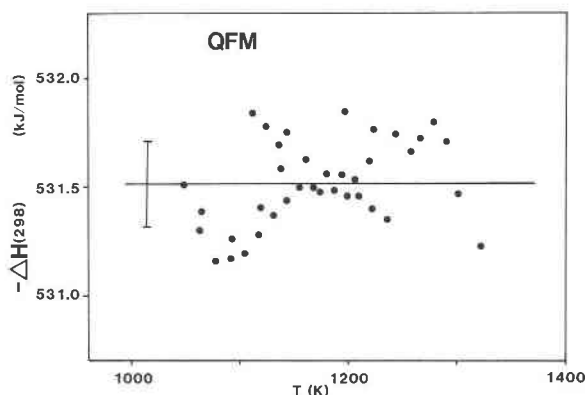


Fig. 3. Standard enthalpy vs. temperature for the data on the reaction $3\text{Fe}_2\text{SiO}_4 + \text{O}_2 \rightarrow 2\text{Fe}_3\text{O}_4 + 3\text{SiO}_2(\text{qz})$.

give the standard enthalpy of reaction at 298.15 K by the third-law method:

$$\Delta_r H_{m,298.15}^0 = \Delta_r G_{m,T}^0 - \int_{298.15}^T \Delta_r C_{p,m}^0 dT + T \left(\Delta_r S_{m,298.15}^0 + \int_{298.15}^T \Delta_r C_{p,m}^0 / T dT \right).$$

atures following any observable emf decrease, for these reasons.

The QFM equilibrium proved considerably less tractable. At the start of a run, the initial emf was over 100 mV off from the equilibrium value in the sense that the QFM electrode was too reduced. The emf then decayed toward the equilibrium value extremely slowly, so slowly that it would not have been feasible to attempt to obtain data below about 1100 K. However, a successful run was also performed in which about 1% by weight of KOH was added to the QFM mixture; results for this run were obtained down to 1050 K and are in complete agreement with the other run at higher temperatures. The sample pellet from this run was firmly welded to the bottom of the tube and unfortunately could not be retrieved for examination. The inevitable decrease of the emf due to oxygen leakages seemed to occur above about 1250–1300 K. Since much longer times are necessary to reach equilibrium using QFM than using QFI, no data are presented from higher temperatures.

For both equilibria, each datum has been analyzed to

The calorimetric data used in this analysis are given in Table 4. The data for magnetite will be discussed later. The calculated values of $\Delta_r H_{m,298.15}^0$ are listed in Tables 2 and 3 and illustrated in Figures 2 and 3, where they are plotted against the temperature of the experimental datum. Such plots should yield a horizontal line: for QFI, linear regression of $\Delta_r H_{m,298.15}^0$ vs. T actually gives a slope of $+0.13 \pm 0.12 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, and for QFM a slope of $-1.02 \pm 0.43 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. Thus for both reactions, agreement of the emf data with the calorimetric data is extraordinarily good. In view of the possibility of small systematic errors at the extremes of the temperature range of measurement, these slopes have been assumed to be effectively zero, and therefore for QFI,

$$\Delta_r H_{m,298.15}^0 = -566.45 \pm 0.14 \text{ kJ},$$

and for QFM,

$$\Delta_r H_{m,298.15}^0 = -531.52 \pm 0.20 \text{ kJ}$$

Table 4. Calorimetric data used in calculating $\Delta H_{r,298.15}$

Substance	Ref.	T range (K)	Ref. T (K)	S_T ($\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)	$H_T - H_{298.15}$ ($\text{J} \cdot \text{mol}^{-1}$)	C_p ($\text{in } \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$) = $A + BT + CT^2 + DT^{-0.5} + ET^{-2}$				
						A	B ($\times 10^3$)	C ($\times 10^6$)	D	E ($\times 10^{-6}$)
Fe*	Barin et al. (1977)	800–1000	900	61.62	9564	-263.454	255.810	—	—	61.923
		1000–1042	1000	66.71	24400	-641.905	696.339	—	—	—
		1042–1060	1042	69.54	27300	1946.255	-1787.497	—	—	—
		1060–1184	1100	72.50	30469	-561.932	334.143	—	—	291.211
		1184–1665	1200	76.91	35543	23.991	8.360	—	—	—
Fe ₃ O ₄	Robie et al. (1978)	848–1800	1000	390.24	147986	96.823	52.733	—	—	56.413
SiO ₂	Richet et al. (1982)	847–1676	1000	116.26	45579	65.277	5.5288	—	—	1.8463
Fe ₂ SiO ₄	Robie et al. (1982)	298–1450	1000	349.23	118432	176.02	-8.808	2.471	—	-3.889
O ₂	Barin et al. (1977)	298–1800	1000	243.58	22694	48.318	-0.69132	—	-420.66	0.49923

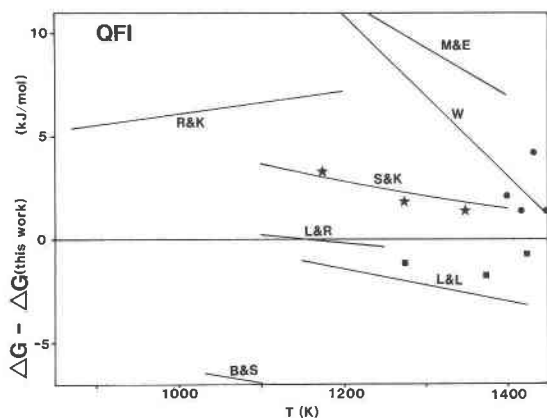


Fig. 4. Comparison showing the difference between various experimental determinations of the free energy of the reaction $\text{Fe}_2\text{SiO}_4 \rightarrow 2\text{Fe} + \text{SiO}_2(\text{qz}) + \text{O}_2$ and that of this work. L & L, Lebedev and Levitskii (1962); B & S, Berliner and Shapovalova (1966); L & R, Levitskii and Ratiani (1970); W, Williams (1971); S & K, Schwab and Küstner (1981); R & K, Róg and Kozinski (1983); M & E, Myers and Eugster (1983). ●, Kitayama and Katsura (1968); ■, Schwerdtfeger and Muan (1966); ★, Taylor and Schmalzried (1964). Where SiO_2 is known to be in the cristobalite form, I have corrected for this using the data in Richet et al. (1982), but assuming an equilibrium temperature of transition between quartz and cristobalite of 1300 K.

(the uncertainties given are one standard deviation and include those given for the reference electrodes).

With the accepted value of the standard enthalpy of formation of quartz [$-910.7 \pm 1.0 \text{ kJ}\cdot\text{mol}^{-1}$, Robie et al. (1978)], this gives a standard enthalpy of formation of fayalite of $-1477.15 \pm 1.0 \text{ kJ}\cdot\text{mol}^{-1}$, which compare quite favorably with the calorimetric determination of $-1479.4 \pm 2.5 \text{ kJ}\cdot\text{mol}^{-1}$ of King (1952), as later modified by Hemingway and Robie (1977) to take into account an improved value for the heat of solution of quartz and also revised values for the enthalpies of some subsidiary reactions in the calorimetric scheme.

For both equilibria, the above values for the standard enthalpy of reaction were combined with the calorimetric data to calculate values for the free energy of reaction between 900 and 1420 K at 20 K intervals, which were then used to obtain the following chemical potentials (in $\text{J}\cdot\text{mol}^{-1}$) by the least-squares method:

$$\begin{aligned} \mu_{\text{O}_2}^{\text{QFI}}(\pm 140) &= -542941 - 33.182T \\ &\quad + 22.4460T \ln T \quad (900 < T < 1042) \\ &= -562377 + 103.384T \\ &\quad + 5.4771T \ln T \quad (1042 < T < 1184) \\ &= -602739 + 369.740T \\ &\quad - 27.3443T \ln T \quad (1184 < T < 1420) \\ \mu_{\text{O}_2}^{\text{QFM}}(\pm 200) &= -587474 + 1584.427T - 203.3164T \ln T \\ &\quad + 0.092710T^2 \quad (900 < T < 1420). \end{aligned}$$

(Values in terms of $\log f_{\text{O}_2}$ may be obtained from the

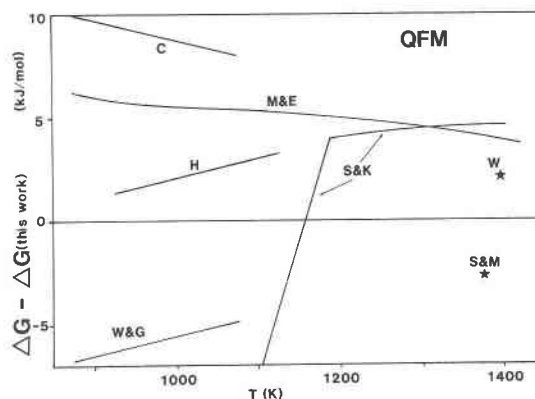


Fig. 5. Comparison showing the difference between various experimental determinations of the free energy of the reaction $2\text{Fe}_3\text{O}_4 + 3\text{SiO}_2(\text{qz}) \rightarrow 3\text{Fe}_2\text{SiO}_4 + \text{O}_2$ and that of this work. S & M, Schwerdtfeger and Muan (1966); W & G, Wones and Gilbert (1969); C, Chou (1978); W, Williams (quoted in Chou, 1978); H, Hewitt (1978); S & K, Schwab and Küstner (1981); M & E, Myers and Eugster (1983).

above by dividing by $RT \ln 10$, where $R = 8.31441 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.)

The differences in the free energy of reaction for Reaction 1 (QFI) between this work and previous experimental studies are illustrated in Figure 4, and for Reaction 2 (QFM) in Figure 5. For QFI, it may be observed that there is a sort of consensus in that many of the studies fall within $\pm 4.0 \text{ kJ}\cdot\text{mol}^{-1}$ (i.e., $\sim 0.2 \log f_{\text{O}_2}$ at 1100 K) of the present one, some exceptions being two of the more recent, those of Myers and Eugster (1983) and Róg and Kozinski (1983). The emf study of Levitskii and Ratiani (1970) is almost in exact agreement. It should be noted that since the present study is in essentially perfect accord with the calorimetrically determined entropy of reaction, any deviation from a horizontal line in Figure 4 correspondingly implies disagreement.

For QFM, the present data almost agree with those of Hewitt (1978) within the latter's stated limits of accuracy ($\pm 0.1 \log f_{\text{O}_2}$), the maximum discrepancy being $0.15 \log f_{\text{O}_2}$ at 1123 K.

Apart from being in disagreement with the calorimetric data, especially with regard to the μ_{O_2} vs. T slopes of the various reactions, which are very tightly constrained by these data, the recent work of Myers and Eugster (1983) on oxygen buffers in the system Fe-Si-O is also internally inconsistent. Thus the (metastable) Fe- Fe_3O_4 equilibrium, obtained from the combination of the QFI and QFM equilibria, should intersect in μ_{O_2} vs. T space with the Fe-"FeO" and "FeO"- Fe_3O_4 equilibria at the isobarically invariant point at 833 K (or nearby, to allow for some curvature outside the temperature range of the measurements). This the data of Myers and Eugster fails to do, by several hundreds of degrees. The apparent kink in the curve for QFM reported by Schwab and Küstner (1981) at 1187 K would, if real, correspond to a phase transition in either Fe_3O_4 with an enthalpy of $\sim 74 \text{ kJ}\cdot\text{mol}^{-1}$, or in

SiO₂ with 49 kJ·mol⁻¹, and would therefore seem to be inherently unlikely.

FREE ENERGY OF FORMATION OF MAGNETITE (Fe₃O₄)

Combination of the standard enthalpies of reaction for the QFI and QFM equilibria gives the standard enthalpy of formation of magnetite:

$$\Delta_f H_m^0(298.15 \text{ K})(\text{Fe}_3\text{O}_4) = \frac{1}{2}(3\Delta_f H_m^0(298.15 \text{ K})(\text{QFI}) + \Delta_f H_m^0(298.15 \text{ K})(\text{QFM}))$$

which is found to be $-1115.43 \pm 0.30 \text{ kJ}\cdot\text{mol}^{-1}$, in excellent agreement with the value obtained by the author (O'Neill, 1986, in prep.) for the Fe₃O₄ + Fe equilibrium (Reaction 3) measured against air in the temperature range 750–830 K ($-1115.39 \pm 0.19 \text{ kJ}\cdot\text{mol}^{-1}$) and also with the results of Rau (1972) obtained by equilibration with H₂-H₂O in the range 573–839 K. This consistency has implications for two important details pertaining to the calorimetric data on magnetite. First, there has long been a controversy, since the idea was first proposed by Anderson (1956), as to whether Fe₃O₄ has a zero-point entropy ($3.36 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ according to Anderson). The present results are sufficiently accurate and, when combined with the low-temperature results mentioned above, cover a wide enough temperature range to demonstrate conclusively that there is no such zero-point entropy.

The second point concerns the entropy of magnetite above the Curie point, which occurs at $\sim 848 \text{ K}$. The heat capacity of magnetite has been measured directly up to 1050 K by Gronvold and Sveen (1974) using adiabatic calorimetry and has also been derived from heat-content measurements up to 1800 K by Coughlin et al. (1951). The two determinations are in good agreement up to the Curie point; thus from Gronvold and Sveen, $S_{800} - S_{298.15} = 191.99 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, compared to $191.50 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ from Coughlin et al. However, there is increasing disagreement with increasing temperature above the Curie point: for example, $S_{1000} - S_{298.15} = 246.16 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ according to Gronvold and Sveen, but $243.67 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ according to Coughlin et al. Moreover, the heat capacities measured by Gronvold and Sveen near the temperature limit of their work are $\sim 6\%$ greater than those of Coughlin et al. Although Gronvold and Sveen ascribed the discrepancy across the Curie point in the heat-content measurements to the "magnetic transition being partially suppressed by rapid cooling, with spins temporarily locked in various positions," this cannot explain the discrepancy in C_p observed above the transition. The present study uses the representation of the calorimetric data for Fe₃O₄ given by Robie et al. (1978), which is a compromise between the two sets of data, being closer to Gronvold and Sveen at temperatures below the Curie point and to Coughlin et al. above. The present results thus, in effect, support the earlier work of Coughlin et al. at higher temperatures.

ACKNOWLEDGMENTS

I would like to thank Richard Holmes and Richard Arculus for much encouragement and discussion of the experimental techniques of using solid electrolytes; Richard Holmes furthermore contributed much to the discussion on the heat-capacity data for magnetite. I would also like to thank Paul Willis and Bill Hibbertson for machining the brass heads. Gene Ulmer, David Hewitt, Don Lindsley, and Dick Arculus contributed helpful reviews.

REFERENCES

- Anderson, P.W. (1956) Ordering and antiferromagnetism in ferrites. *Physical Review*, 102, 1008–1013.
- Barin, I., Knacke, O., and Kubaschewski, I. (1977) Thermochemical properties of inorganic substances (Supplement). Springer-Verlag, Berlin.
- Berliner, L.D., and Shapovalova, R.D. (1966) Thermodynamics of the equilibrium of fayalite (iron orthosilicate) with hydrogen. *Russian Journal of Physical Chemistry*, 40, 1561–1563.
- Chatillon-Colinet, C., Kleppa, O.J., Newton, R.C., and Perkins, D., III. (1983) Enthalpy of formation of Fe₃Al₂Si₃O₁₂ (almandine) by high temperature alkali borate solution calorimetry. *Geochimica et Cosmochimica Acta*, 47, 439–444.
- Chou, I-Ming. (1978) Calibration of oxygen buffers at elevated P and T using the hydrogen fugacity sensor. *American Mineralogist*, 63, 690–703.
- Coughlin, J.P., King, E.G., and Bonnicksen, K.R. (1951) High temperature heat contents of ferrous oxide, magnetite and ferric oxide. *American Chemical Society Journal*, 73, 3891–3893.
- Eugster, H.P. (1957) Heterogeneous reactions involving oxidation and reduction at high pressures and temperatures. *Journal of Chemical Physics*, 26, 1760–1761.
- Goto, K.S., and Pluschkell, W. (1972) Oxygen concentration cells. In J. Hladik, Ed. *Physics of electrolytes*, vol. 2, p. 540–622. Academic Press, London.
- Gronvold, F., and Sveen, A. (1974) Heat capacity and thermodynamic properties of synthetic magnetite (Fe₃O₄) from 300 to 1050 K: Ferrimagnetic transition and zero-point entropy. *Journal of Chemical Thermodynamics*, 6, 859–872.
- Hemingway, B.S., and Robie, R.A. (1977) Enthalpies of formation of low albite (NaAlSi₃O₈) and NaAlO₂: Revised values for ΔH_f^0 and ΔG_f^0 of aluminosilicates. *U.S. Geological Survey Journal of Research*, 5, 413–429.
- Hewitt, D.A. (1978) A redetermination of the fayalite-magnetite-quartz equilibrium between 650 and 850°C. *American Journal of Science*, 278, 715–724.
- Holmes, R.D., O'Neill, H.St.C., and Arculus, R.J. (1986) Standard Gibbs free energy of formation for Cu₂O, NiO, CoO and Fe_xO: High resolution electrochemical measurements using zirconia solid electrolytes from 900–1400 K. *Geochimica et Cosmochimica Acta*, 50, 2439–2452.
- King, E.G. (1952) Heats of formation of manganese metasilicate (rhodonite) and ferrous orthosilicate (fayalite). *American Chemical Society Journal*, 74, 4446–4448.
- Kitayama, K., and Katsura, T. (1968) Composition of fayalite and its standard free energy of formation. *Japanese Journal of Physical Chemistry*, 41, 525–528.
- Lebedev, B.G., and Levitskii, V.A. (1962) Equilibrium in the reduction of iron orthosilicate with carbon monoxide between 850 and 1150°C. *Russian Journal of Physical Chemistry*, 36, 329–331.
- Levitskii, V.A., and Ratiani, D.D. (1970) Thermodynamic properties of fayalite (Fe₂SiO₄). *Russian Metallurgy*, 45–51.
- Myers, J., and Eugster, H.P. (1983) The system Fe-Si-O: Oxygen buffer calibrations to 1500 K. *Contributions to Mineralogy and Petrology*, 82, 75–90.
- Nafziger, R.H., and Muan, A. (1967) Equilibrium phase com-

- position and thermodynamic properties of olivines and pyroxenes in the system MgO-“FeO”-SiO₂. *American Mineralogist*, 52, 1364-1385.
- Nakamura, A., and Schmalzried, H. (1983) On the nonstoichiometry and point defects of olivine. *Physics and Chemistry of Minerals*, 10, 27-37.
- O'Neill, H.St.C. (1986) Mo-MoO₂ (MOM) oxygen buffer and the free energy of formation of MoO₂. *American Mineralogist*, 71, 1007-1010.
- Ramanarayan, T.A. (1980) Limiting factors in measurements using solid electrolytes. In E.C. Subbarao, Ed. *Solid electrolytes and their applications*, p. 81-98. Plenum Press, New York.
- Rau, H. (1972) Thermodynamics of the reduction of iron oxide powders with hydrogen. *Journal of Chemical Thermodynamics*, 4, 57-64.
- Richet, P., Bottinga, Y., Denielou, L., Petit, J.P., and Tequi, C. (1982) Thermodynamic properties of quartz, cristobalite and amorphous SiO₂: Drop calorimetry measurements between 1000 and 1800 K and a review from 0 to 2000 K. *Geochimica et Cosmochimica Acta*, 46, 2639-2658.
- Robie, R.A., Hemingway, B.S., and Fisher, J.R. (1978) Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10⁵ pascals) pressure and at higher temperatures. U.S. Geological Survey Bulletin 1452.
- Robie, R.A., Finch, C.B., and Hemingway, B.S. (1982) Heat capacity and entropy of fayalite (Fe₂SiO₄) between 5.1 and 383 K: Comparison of calorimetric and equilibrium values for the QFM buffer reaction. *American Mineralogist*, 67, 463-469.
- Róg, G., and Kozinski, S. (1983) Thermodynamics of iron orthosilicate. *Journal of Chemical Thermodynamics*, 15, 111-113.
- Schwab, R.G., and Küstner, D. (1981) Die Gleichgewichtsfugazitäten technologisch und petrologisch wichtiger Sauerstoffpuffer. *Neues Jahrbuch für Mineralogie Abhandlungen*, 140, 111-142.
- Schwab, R.G., and Söhnlein, G. (1977) Homogene und heterogene Redoxgleichgewichte des Fayalits. *Neues Jahrbuch für Mineralogie Abhandlungen*, 129, 15-31.
- Schwerdtfeger, K., and Muan, A. (1966) Activities in olivine and pyroxenoid solid solutions of the system Fe-Mn-Si-O at 1150°C. *Metallurgical Society of the AIME Transactions*, 236, 201-210.
- Steele, B.C.H. (1968) High-temperature thermodynamic measurements involving solid electrolyte systems. In C.B. Alcock, Ed. *Electromotive force measurements in high temperature systems*, p. 3-27. Institute of Mining and Metallurgy, London.
- Taylor, R.W., and Schmalzried, H. (1964) The free energy of formation of some titanates, silicates and magnesium aluminate from measurements made with galvanic cells involving solid electrolytes. *Journal of Physical Chemistry*, 68, 2444-2449.
- Williams, R.J. (1971) Reaction constants in the system Fe-MgO-SiO₂-O₂ at 1 atm between 900 and 1300°C: Experimental results. *American Journal of Science*, 270, 334-360.
- Wones, D.R., and Gilbert, M.C. (1969) The fayalite-magnetite-quartz assemblage between 600 and 800°C. *American Journal of Science*, 267-A, 480-488.
- Worrell, W.L. (1977) Oxide solid electrolytes. In S. Geller, Ed. *Solid electrolytes*, p. 143-168. Springer-Verlag, Berlin.

MANUSCRIPT RECEIVED AUGUST 30, 1985

MANUSCRIPT ACCEPTED SEPTEMBER 2, 1986