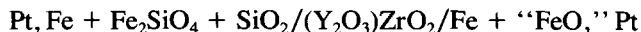# Chemical Potentials of Oxygen for Fayalite-Quartz-Iron and Fayalite-Quartz-Magnetite Equilibria
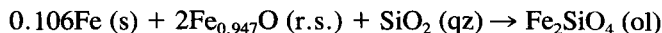
K.T. JACOB, G.M. KALE, and G.N.K. IYENGAR

The oxygen potentials corresponding to fayalite-quartz-iron (FQI) and fayalite-quartz-magnetite (FQM) equilibria have been determined using solid-state galvanic cells:

$$Pt, Fe + Fe_2SiO_4 + SiO_2/(Y_2O_3)ZrO_2/Fe + \text{``FeO,''} Pt$$

and

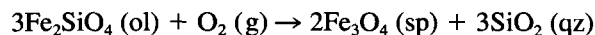$$Pt, Fe_3O_4 + Fe_2SiO_4 + SiO_2/(Y_2O_3)ZrO_2/Ni + NiO, Pt$$

in the temperature ranges 900 to 1400 K and 1080 to 1340 K, respectively. The cells are written such that the right-hand electrodes are positive. Silica used in this study had the quartz structure. The emf of both cells was found to be reversible and to vary linearly with temperature. From the emf, Gibbs energy changes were deduced for the reactions:

$$0.106Fe \text{ (s)} + 2Fe_{0.947}O \text{ (r.s.)} + SiO_2 \text{ (qz)} \rightarrow Fe_2SiO_4 \text{ (ol)}$$

$$\Delta G^\circ = -39,140 + 15.59\,T\,(\pm150) \quad J\,mol^{-1}$$

and

$$3Fe_2SiO_4 \text{ (ol)} + O_2 \text{ (g)} \rightarrow 2Fe_3O_4 \text{ (sp)} + 3SiO_2 \text{ (qz)}$$

$$\Delta G^\circ = -471,750 + 160.06\,T\,(\pm1100) \quad J\,mol^{-1}$$

The "third-law" analysis of fayalite-quartz-wustite and fayalite-quartz-magnetite equilibria gives value for ΔH°_{298} as -35.22 (±0.1) and -528.10 (±0.1) kJ mol^{-1}, respectively, independent of temperature. The Gibbs energy of formation of the spinel form of Fe_2SiO_4 is derived by combining the present results on FQI equilibrium with the high-pressure data on olivine to spinel transformation of Fe_2SiO_4.

I. INTRODUCTION

AS part of a larger research program on silicates and their solid-solutions,[1,2] electrochemical measurements have been undertaken to determine the thermodynamic stability of fayalite at high temperature. Accurate information on solid phases is useful for the evaluation of data on liquid silicates and for the computation of phase diagrams. At high pressures, fayalite (Fe_2SiO_4) transforms from the olivine structure to a more dense spinel form.[3] Both the equilibria, FQI and FQM, are extensively used as oxygen buffers. The compound Fe_2SiO_4 is reported to exhibit negligible homogeneity range.[4] There have been a large number of studies on FQI and FQM equilibria using different techniques, but the agreement between the results of various investigators has not been entirely satisfactory. The present investigation aims at generating more reliable thermodynamic data on FQI and FQM equilibria at high temperature.

The Gibbs energy change for FQI equilibrium has been determined by Lebedev and Levitskii[5] (1123 to 1423 K) and Schwerdtfeger and Muan[6] (1273, 1373, and 1423 K) by CO/CO_2 gas equilibrium technique. Nafziger and Muan[7] (1423 and 1449 K) and Williams[8] (1198 to 1451 K) employed the CO_2/H_2 gas equilibration tech-
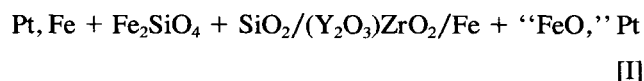
nique, whereas Berliner and Shapovalova[9] (1033 to 1403 K) used a H_2/H_2O gas mixture. Taylor and Schmalzried[10] (1173 to 1373 K), Schwab and Sohnlein[11] (1233 to 1428 K), Schwab and Kustner[12] (1099 to 1414 K), and, recently, O'Neill[13] (1000 to 1400 K) employed an emf technique using stabilized zirconia as the solid electrolyte, whereas Rog and Kozinski[14] (870 to 1200 K) used Fe^{+2} exchanged β-alumina as solid electrolyte in their emf measurements to determine the free energy of formation of Fe_2SiO_4 from stoichiometric FeO and SiO_2. The crystallographic form of silica produced in the reduction studies of Williams[8] was cristobalite, whereas that reported by Berliner and Shapovalova[9] was quartz. In the emf measurements by Schwab and Sohnlein[11] and Schwab and Kustner,[12] the silica had cristobalite form. Recently, O'Neill[13] studied the FQI equilibrium by emf technique with quartz as the crystallographic form of silica. The rest of the investigators[5-7,10,14] did not explicitly report the crystallographic form of silica used in their measurements. The enthalpy of formation of Fe_2SiO_4 from the elements has been determined by King[15] as -1447.7 (±4.6) kJ mol^{-1} at 298 K by hydrofluoric acid solution calorimetry. Hemingway and Robie[16] corrected King's[15] results using more recent data for several of the steps used in his reaction scheme. The corrected value for $\Delta H^\circ_{298} = -1479.4$ (±2.4) kJ mol^{-1} from the elements. The low temperature heat capacity (5.1 to 383 K) for the synthetic crystal of Fe_2SiO_4 was measured by Robie et al.[17] by an intermittent heating method under quasi-adiabatic

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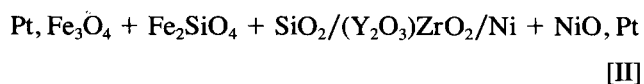Manuscript submitted October 7, 1988.

conditions using a cryostat. The high temperature heat capacity (298 to 1450 K) has been obtained by a least-squares fit of Orr's[18] heat content ($H_T^\circ - H_{298}^\circ$) data combined with the heat capacity measurements of Robie et al.[17] between 300 and 380 K.

The Gibbs energy change for the FQM equilibrium has been determined experimentally by Schwerdtfeger and Muan[6] (1373 K) using CO/CO_2 gas equilibrium technique and by Williams[19] (1395 K) using CO_2/H_2 mixture. Hewitt[20] (923 to 1123 K), Wones and Gilbert[21] (873 to 1073 K), and Chou[22] (873 to 1073 K) measured the Gibbs energy change for FQM equilibrium by a H_2-membrane or sensor technique. The oxygen chemical potential for FQM equilibrium has been measured by the solid-state galvanic cell technique employing calcia-stabilized zirconia as the solid electrolyte by Schwab and Sohnlein[11] (1303 to 1403 K), Schwab and Kustner[12] (1000 to 1400 K), and, very recently, by O'Neill[13] (1050 to 1300 K). The crystallographic form of silica used by Schwab and Sohnlein[11] and Schwab and Kustner[12] was cristobalite, whereas other investigators[13,20–22] used quartz as the starting material. The crystal form of silica was not explicitly specified by Schwerdtfeger and Muan[6] or Williams.[19]

The present investigation aims at redetermination of the Gibbs energy change for FQI and FQM equilibria employing solid-state galvanic cells:

$$Pt, Fe + Fe_2SiO_4 + SiO_2/(Y_2O_3)ZrO_2/Fe + \text{``FeO,''} Pt$$

[I]

and

$$Pt, Fe_3O_4 + Fe_2SiO_4 + SiO_2/(Y_2O_3)ZrO_2/Ni + NiO, Pt$$

[II]

respectively. Yttria-stabilized zirconia is preferred to calcia-stabilized zirconia because it is stable over the temperature range of measurements. The calcia-stabilized zirconia is metastable and the cubic phase is known to undergo a phase transformation at the lower temperature range of the present measurement, giving rise to instabilities.

II. EXPERIMENTAL PROCEDURE

A. Materials

Puratronic grade Fe, Fe_3O_4, Fe_2O_3, Ni, and NiO powders were obtained from Johnson and Matthey Chemicals Ltd. Silica of 99.99 pct purity was obtained from Ventron. The iron orthosilicate was prepared by intimately mixing the appropriate molar mixture of Fe, Fe_2O_3, and SiO_2, pressing it into pellets, and sintering it at 1373 K for 7 days in a platinum crucible which was sealed inside an evacuated quartz capsule. The pellets were ground, pelletized, and sintered again under the same conditions. The product was ground and subjected to X-ray examination. The X-ray analysis indicated single-phase Fe_2SiO_4, in agreement with the FeO-SiO$_2$ phase diagram.[23] By subjecting the iron orthosilicate powder thus obtained to a magnetic field, it was verified that there was no unreacted iron present in the sample.

The three-phase electrode for cell-I was prepared by

intimately mixing an equimolar mixture of Fe, Fe_2SiO_4, and SiO_2, pelletizing it under pressure, and sintering it at 1400 K in a platinum crucible sealed inside an evacuated silica capsule. The three-phase electrode for cell-II was prepared by a similar procedure at 1373 K. The flat surfaces of the working electrodes were polished before being used in the cell for emf measurements. The metal + metal oxide reference electrodes were taken inside an yttria-stabilized zirconia solid electrolyte tube and sintered in situ at 1400 K under prepurified argon gas with platinum leads buried in the mixture.

B. Apparatus and Procedure

A schematic diagram of the apparatus using an $(Y_2O_3)ZrO_2$ tube as the solid electrolyte is shown in Figure 1. The two-phase reference electrode was taken in the solid electrolyte tube. The three-phase electrode pellet was spring loaded against the outside of the solid electrolyte tube by a supporting system of alumina slabs and rods. The platinum gauze was placed between the three-phase electrode and the solid electrolyte for good electrical contact. The platinum lead was spot welded to the gauze. Both electrodes were flushed separately with streams of argon gas which were dried and deoxidized prior to their use.

The emf of the cells was measured with a high impedance ($>10^{12}$ Ω) digital voltmeter. The reversibility of each cell was checked by passing small currents (~50 μA) through the cell in either direction for 200 seconds. In each case, the emf was found to return to its original value before the titration. The emf was found to be independent of the flow rate of argon through the cell in the range of 1 to 4 ml s^{-1}. The emf was reproducible during the heating and cooling cycles.

The temperature of the cell was measured by a Pt/Pt-13 pct Rh thermocouple placed adjacent to the three-phase electrode. The absence of a thermal gradient was checked by constructing a symmetric cell with Ni + NiO as electrodes. The emf of this cell was found to be ±0.20 mV over the temperature range 900 to 1400 K. At the end of the experiment, the pellets were subjected to X-ray diffraction analysis. The phase composition of the electrode pellets was found to be unaltered during the experiment for both cells. The silica particles retained their quartz structure and did not transform to cristobalite during the experiment.

The steady-state emf was obtained in 2 to 8 ks, depending on the temperature. The slow response at lower temperatures was probably due to the sluggish kinetics of the reaction involving the three condensed phases.

III. RESULTS

The reversible emf of cell-I is plotted as a function of temperature in Figure 2 and that of cell-II is shown in Figure 3. The numbers on the plot indicate the sequence of measurement. The least-squares regression analysis of emf of cell-I gives

$$E_I = 101.4 - 0.0404\,T\,(\pm 0.3)\quad mV \qquad [1]$$

For cell-II,

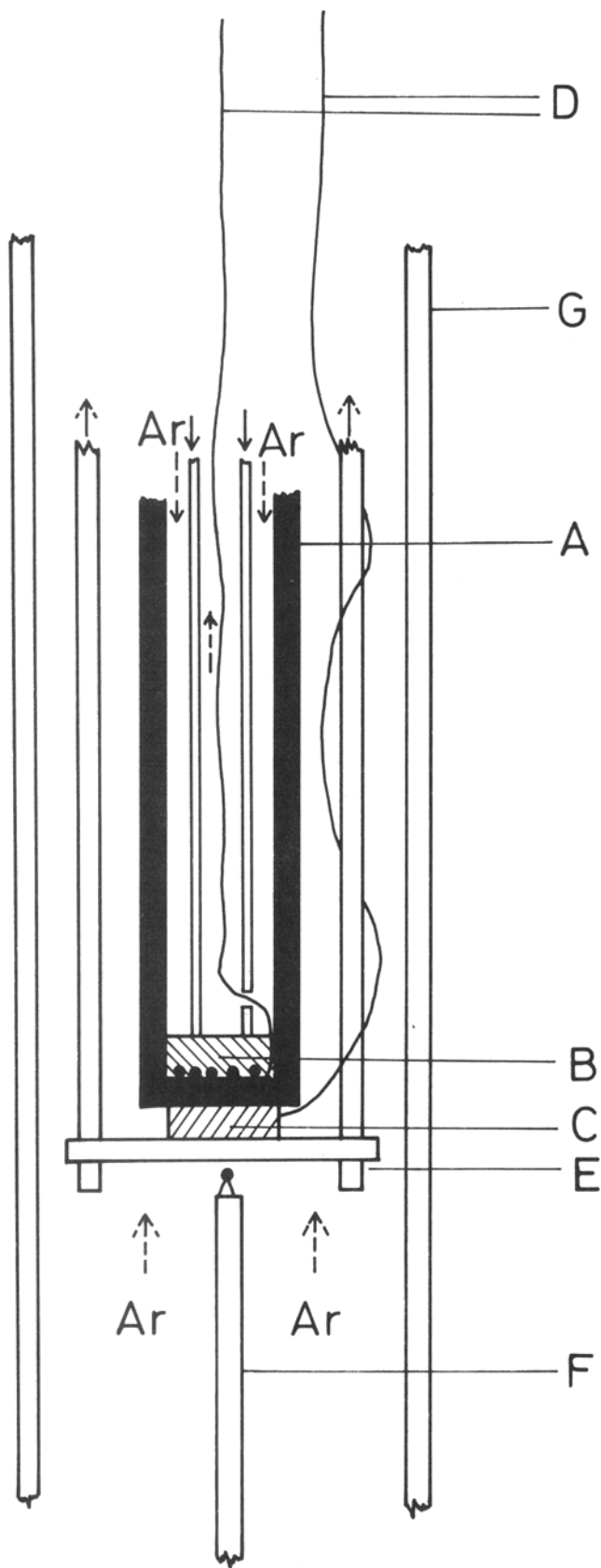$$E_{II} = 8.9 + 0.0252\,T\,(\pm 0.2)\quad mV \qquad [2]$$

Fig. 1—A schematic diagram of the solid-state galvanic cell. (A) $(Y_2O_3)ZrO_2$ electrolyte tube; (B) reference electrode (Fe/"FeO" or Ni/NiO); (C) working electrode; (D) Pt leads; (E) alumina supports for spring loading; (F) Pt/Pt-13 pct Rh thermocouple; and (G) alumina tube housing the cell, inside which an inert atmosphere is maintained.
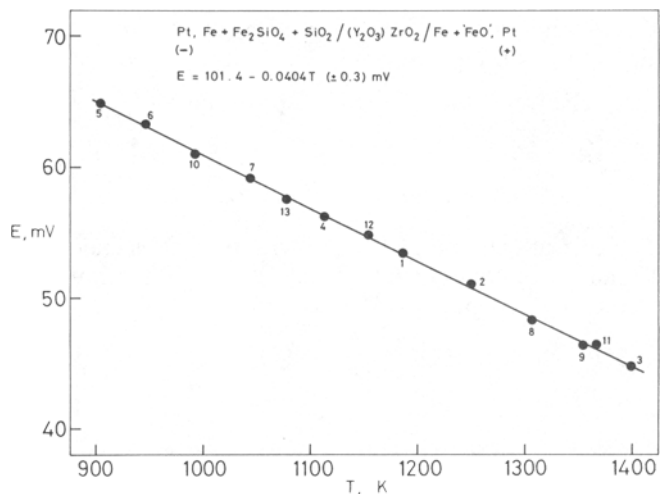

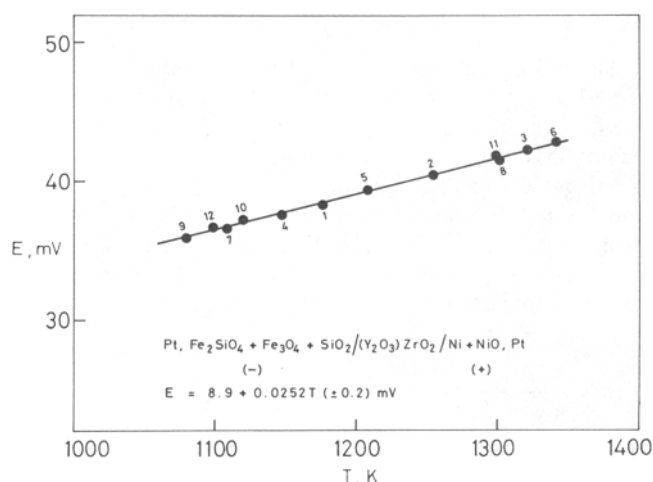Fig. 2—Temperature-dependence of the emf of cell-I.

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

where the uncertainty limits correspond to twice the standard deviation. The response of cell-II was more sluggish than that of cell-I. It was difficult to measure the emf below 1080 K. Schwab and Kustner[12] observed a significant change in slope of their plot of log (P_{O_2}) vs the reciprocal of absolute temperature at 1187 K. The lack of reproducibility at lower temperature may be related to a small solubility (~4 mol pct) of Fe_2SiO_4 (ol) in Fe_3O_4. On decreasing the temperature, Fe_2SiO_4 tries to precipitate from the supersaturated solid solution. The resulting gradients in the chemical potentials of cations and oxygen in the electrode pellets are probably responsible for the irreproducible emf. From the emf of cell-I, the Gibbs energy change for the reaction

$$0.106Fe\ (s) + 2Fe_{0.947}O\ (r.s.)$$

$$+ SiO_2\ (qz) \rightarrow Fe_2SiO_4\ (ol) \qquad [3]$$
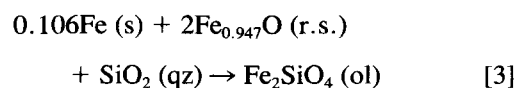
is obtained as

$$\Delta G_3^\circ = -39,140 + 15.59\ T\ (\pm 150) \quad J\ mol^{-1}$$

$$(900 \leq T \leq 1400\ K) \qquad [4]$$

Combining this with the free energy of formation of $Fe_{0.947}O$ given by Steele,[24]

$$2Fe \text{ (s)} + O_2 \text{ (g)} + SiO_2 \text{ (qz)} \rightarrow Fe_2SiO_4 \text{ (ol)} \quad [5]$$
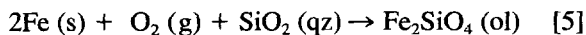
$$\Delta G_5^\circ = -568,290 + 146.39\, T\, (\pm 1050) \quad J\, mol^{-1}$$

$$(900 \leq T \leq 1400 \text{ K}) \quad [6]$$

The emf of cell-II is combined with the Gibbs energy of formation of NiO given by Steele[24] to give the standard free energy change for the reaction

$$3Fe_2SiO_4 \text{ (ol)} + O_2 \text{ (g)} \rightarrow 2Fe_3O_4 \text{ (sp)} + 3SiO_2 \text{ (qz)}$$
$$[7]$$
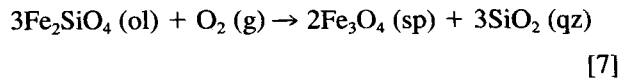
$$\Delta G_7^\circ = -471,750 + 160.06\, T\, (\pm 1100) \quad J\, mol^{-1}$$

$$(1080 \leq T \leq 1340 \text{ K}) \quad [8]$$

IV. DISCUSSION

A. The Fayalite-Quartz-Iron (FQI) Equilibrium

The Gibbs energy change for FQI equilibrium obtained in the present study is compared in Figure 4 with the earlier measurements reported in the literature. The values given by Eq. [6] are in excellent agreement with the CO/CO_2 gas equilibrium measurements of Lebedev and Levitskii[5] and Schwerdtfeger and Muan.[6] The recent measurements of O'Neill[13] are also in good agreement with the present results. The emf measurements of Taylor and Schmalzried[10] and Schwab and Kustner[12]
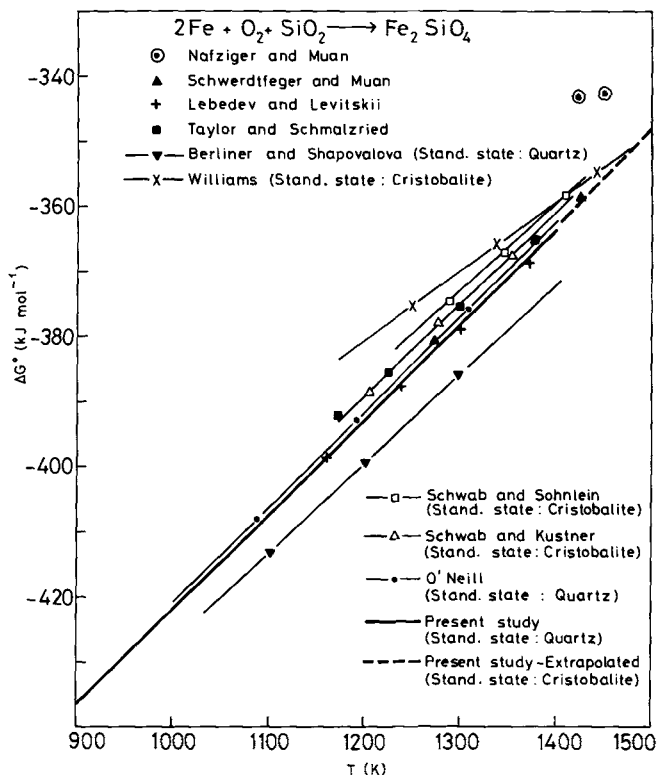

Fig. 4—Comparison of the Gibbs energy of formation of Fe_2SiO_4 (ol) from Fe, O_2, and SiO_2 obtained in this study with the data reported in the literature.

are in fair agreement with the results obtained in this study. The results of CO_2/H_2 gas equilibrium measurements of Schwab and Sohnlein[11] are more positive than the present results, whereas the H_2/H_2O gas equilibrium measurements of Berliner and Shapovalova[9] are more negative. The results of CO_2/H_2 gas equilibrium studies of Nafziger and Muan[7] are more positive by nearly 15 kJ mol^{-1}.

At temperatures above 1500 K, the cristobalite form of silica is expected to prevail. The Gibbs energy change for the reaction

$$2Fe \text{ (s)} + O_2 \text{ (g)} + SiO_2 \text{ (crist)} \rightarrow Fe_2SiO_4 \text{ (ol)} \quad [9]$$
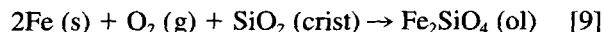
can be calculated from Eq. [6] and the data of Richet et al.[25] for the crystallographic transformation of silica as

$$\Delta G_9^\circ = -570,490 + 148.37\, T\, (\pm 1120) \quad J\, mol^{-1}$$

$$(900 \leq T \leq 1600 \text{ K}) \quad [10]$$

The standard Gibbs energy change for Reaction [9] is shown as the broken line in Figure 4. There has been no measurement of the high temperature enthalpy of formation of Fe_2SiO_4 by calorimetry.

The third-law analysis is an accurate indicator of temperature-dependent errors in emf measurement. The standard enthalpy change for Reaction [3] can be calculated from the measured free energy change at each temperature using the expression

$$\Delta H_{298}^\circ = \Delta G_T^\circ - T\, \Delta \Phi \quad [11]$$

where

$$\Phi = \frac{G_T^\circ - H_{298}^\circ}{T} = -S_{298}^\circ - \int_{298}^{T} \frac{C_p^\circ}{T}\, dT$$
$$+ \frac{1}{T} \int_{298}^{T} C_p^\circ\, dT \quad [12]$$

The value for ΔH_{298}°, corresponding to Reaction [3], is evaluated from the results of the present study and the thermal functions for Fe_2SiO_4 (ol) calculated from S_{298}° and high temperature heat capacity from Robie et al.,[17] for quartz from Richet et al.,[25] and for Fe and $Fe_{0.947}O$ from Pankratz.[26] The analysis gives $\Delta H_{298}^\circ = -35.22$ kJ mol^{-1}, independent of temperature, over the entire temperature range of measurement. The third-law analysis of the measurements of O'Neill[13] shows a small temperature-dependence given by the equation

$$\Delta H_{298}^\circ = -34,730 + 2.65 \times 10^{-1}\, T \quad J\, mol^{-1} \quad [13]$$

Combining the corrected value[16] of King[15] for the calorimetric enthalpy of formation of fayalite with the enthalpy of formation of quartz from Richet et al.[25] and $Fe_{0.947}O$ from Pankratz[26] gives $\Delta H_{298}^\circ = -36.1\, (\pm 0.11)$ kJ mol^{-1} for Reaction [3]. This is 0.88 kJ mol^{-1} more negative than that obtained from the results of this study.

B. The Fayalite-Quartz-Magnetite (FQM) Equilibrium

The Gibbs energy change for the FQM equilibrium obtained from the present measurements is compared as a function of temperature in Figure 5 with the earlier
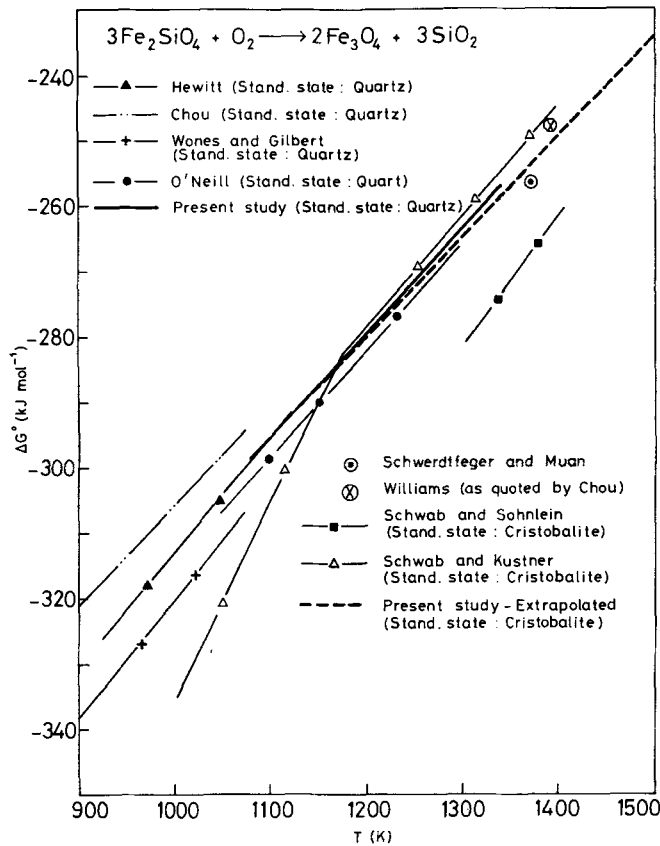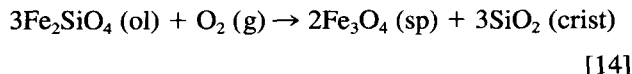
Fig. 5—Comparison of the Gibbs energy change for the fayalite-quartz-magnetite equilibrium as a function of temperature.

Fig. 6—Comparison of the temperature-dependence of ΔH°_{298} for fayalite-quartz-magnetite equilibrium.

measurements reported in the literature. The present results when extrapolated to 1400 K are in excellent agreement with the results of Williams[19] at 1395 K obtained from CO_2/H_2 gas equilibrium studies. The reduction studies employing H_2-membrane technique by Hewitt[20] agree exactly at 1100 K. The emf measurements of Schwab and Kustner[12] are in fair agreement with the present study above 1187 K but begin to deviate significantly at lower temperatures. The emf measurements of O'Neill[13] are more negative by ~3 kJ mol^{-1} at 1080 K and ~2 kJ mol^{-1} at 1340 K compared to the values obtained in this study. The CO/CO_2 gas equilibrium result of Schwerdtfeger and Muan[6] is 4.5 kJ mol^{-1} more negative than the present results, extrapolated to 1373 K. The Gibbs energies suggested by Schwab and Sohnlein[11] and Wones and Gilbert[21] are more greatly negative, while that of Chou[22] is much more positive, than that obtained in this study. The present results for FQM equilibrium when combined with the data for quartz to cristobalite transformation from Richet et al.[25] give for the reaction

$$3Fe_2SiO_4 \text{ (ol)} + O_2 \text{ (g)} \rightarrow 2Fe_3O_4 \text{ (sp)} + 3SiO_2 \text{ (crist)}$$

[14]

$$\Delta G^{\circ}_{14} = -465,150 + 154.1\,T\,(\pm 1025) \quad J\,mol^{-1} \quad [15]$$

The standard Gibbs energy change for Reaction [14] is shown in Figure 5 as a broken line.

The third-law analysis of the earlier FQM equilibrium studies is given in Figure 6 in comparison with the results of this study and selected calorimetric data. The thermal functions of Fe_3O_4 used in this plot are from Pankratz.[26] The thermal functions for Fe_3O_4 given in the
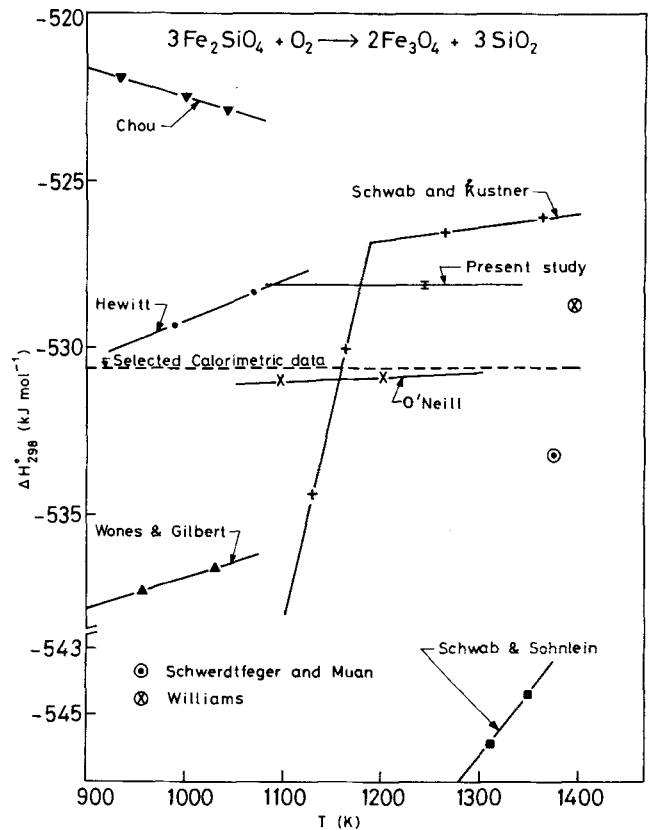
standard tables[28,29,30] are in considerable disagreement with the reported data of Pankratz.[26] The calorimetric value for ΔH°_{298}, obtained by using the corrected value for Fe_2SiO_4 from Hemingway and Robie,[16] quartz from Richet et al.,[25] and Fe_3O_4 from Pankratz,[26] is -530.6 (± 1.0) kJ mol^{-1}. It can be seen from Figure 6 that the present results give $\Delta H^{\circ}_{298} = -528.10$ (± 0.1) kJ mol^{-1} for FQM equilibrium, independent of temperature. The ΔH°_{298} obtained from the measurements of O'Neill[13] shows only a small temperature-dependence given by the equation

$$\Delta H^{\circ}_{298} = -532,740 + 1.6\,T \quad J\,mol^{-1} \quad [16]$$

Data of other investigators[10,11,18-20] show significant temperature variation.

C. Gibbs Energy of Formation of Fe_2SiO_4 (Sp)

The olivine-spinel phase boundary has been determined by quench experiments using a tetrahedral anvil type of high-pressure apparatus by Akimoto et al.[32,33] Recently, Yagi et al.[34] studied the olivine-spinel transformation by in situ X-ray studies using a cubic anvil type high-pressure apparatus coupled with synchrotron radiation in the temperature range 1073 to 1473 K. The results of Akimoto et al.[32] are unreliable because at the end of their experiments above 1123 K, the presence of $FeSiO_3$ was also detected in their samples. In their subsequent study, Akimoto et al.[33] were able to avoid the formation of $FeSiO_3$ by containing the samples in iron and graphite capsules. They[33] raised the temperature of Fe_2SiO_4 samples after compressing them to desired

pressures. The change in pressure in the sample chamber during heating was ignored. Yagi et al.[34] used NaCl as an internal pressure marker in their experiments. The Gibbs energy change for the olivine to spinel transition can be calculated from the high-pressure data. The effects of pressure and temperature on molar volumes can be corrected using the bulk moduli of olivine and spinel phases given by Sumino[35] and Sato[36] and the thermal expansivity data of Yagi et al.[34] The Gibbs energy change for the reaction

$$Fe_2SiO_4 \text{ (ol)} \rightarrow Fe_2SiO_4 \text{ (sp)} \qquad [17]$$

is computed using the relation

$$\Delta G_T^\circ = - \int_{P_1}^{P_2} \Delta V^\circ \, dP \qquad [18]$$

where

$$\Delta V^\circ = V_T^{\circ,P} \text{ (sp)} - V_T^{\circ,P} \text{ (ol)} \qquad [19]$$

and

$$V_T^{\circ,P} = V_{298}^\circ + \int_{298}^{T} \alpha V_{298}^\circ \, dT - \int_{P_1}^{P_2} \kappa \, V_T^\circ \, dP \qquad [20]$$

The symbols α and κ represent the coefficient of thermal expansion and isothermal compressibility, respectively. The free energy change for Reaction [17] computed from the P-T equation suggested by Yagi et al.[34] and the temperature-dependence of the molar volume of spinel and olivine at high pressure from Yagi et al.[34] and Sumino,[35] respectively, is

$$\Delta G_{17}^\circ = 8350 + 10.72 \, T$$

$$+ 4.6 \times 10^{-4} \, T^2 \, (\pm 500) \quad \text{J mol}^{-1} \qquad [21]$$

Navrotsky et al.[37] measured the enthalpy of transition as 2940 ($\pm$830) J mol^{-1} by oxide melt solution calorimetry at 986 K. The calorimetric data does not agree with the "second-law" enthalpy obtained from the high-pressure studies of Yagi et al.[34] Although an inert atmosphere was maintained over the melt in the calorimetric study of Navrotsky et al.,[37] the residual partial pressure of oxygen was not monitored. Because of the possibility of oxidation of Fe^{+2} ions in the melt, a weighted value of 5200 ($\pm$1000) J mol^{-1} is chosen for the enthalpy of transition. This, when combined with ΔG° for the transition at the mean temperature of high-pressure studies of Yagi et al.,[34] gives the relation

$$\Delta G_{17} = 5200 + 13.62 \, T \, (\pm 700) \quad \text{J mol}^{-1} \qquad [22]$$

It is interesting to note that Eq. [22] does not violate any of the data points of Yagi et al.[34] Combining Eqs. [4] and [22] gives the reaction

$$0.106Fe \text{ (s)} + 2Fe_{0.947}O \text{ (r.s.)} + SiO_2 \text{ (qz)}$$

$$\rightarrow Fe_2SiO_4 \text{ (sp)} \qquad [23]$$
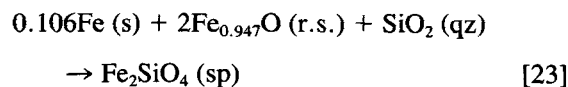
$$\Delta G_{23}^\circ = -33,940 + 29.21 \, T \, (\pm 550) \quad \text{J mol}^{-1}$$

$$(900 \leq T \leq 1400 \text{ K}) \qquad [24]$$

The corresponding expression for the Gibbs energy of formation of the spinel form of Fe_2SiO_4 from iron, oxygen, and quartz is

$$2Fe \text{ (s)} + O_2 \text{ (g)} + SiO_2 \text{ (qz)} \rightarrow Fe_2SiO_4 \text{ (sp)} \qquad [25]$$
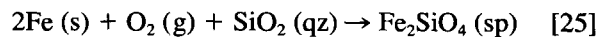
$$\Delta G_{25}^\circ = -563,090 + 160.01 \, T \, (\pm 1200) \quad \text{J mol}^{-1} \qquad [26]$$

D. Gibbs Energy of Formation of Fayalite

Rog and Kozinski[14] determined the Gibbs energy of formation of fayalite from stoichiometric FeO and SiO_2 by using Fe^{+2} substituted β-alumina as solid electrolyte from 870 to 1200 K. Rog and Kozinski[14] used the cell

$$Pt/O_2/FeO//Fe_{0.26}Na_{0.48}Al_9O_{14}//Fe_2SiO_4$$

$$+ SiO_2/O_2/Pt \qquad [27]$$
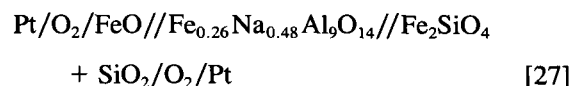
An inert gas flow was maintained over the assembly. The residual oxygen in the inert gas was used to fix the oxygen partial pressure over both electrodes. The stoichiometry of FeO in the left-hand electrode is, therefore, uncertain. The investigators did not establish the ionic conduction characteristics of their partially stabilized β-alumina but assumed that Fe^{+2} ions are the predominantly mobile species. The crystallographic form of SiO_2 used in their study was also unspecified. The present values of the free energy of formation of Fe_2SiO_4 from $Fe_{0.947}O$ and SiO_2 (qz) are compared in Table I with the values of Rog and Kozinski.[14] It can be seen that their values are more positive by approximately 6 kJ mol^{-1} over the entire temperature range of measurement.

The Gibbs energy of formation of the olivine form of Fe_2SiO_4 from the elements

$$2Fe \text{ (s)} + 2O_2 \text{ (g)} + Si \text{ (s)} \rightarrow Fe_2SiO_4 \text{ (ol)} \qquad [28]$$
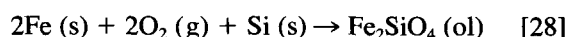
obtained by combining Eq. [6] with the free energy of formation of quartz from Richet et al.[25] is

$$\Delta G_{28}^\circ = -1,472,180 + 320.20 \, T \, (\pm 1100) \quad \text{J mol}^{-1} \qquad [29]$$

Table II shows the values obtained from this equation in comparison with those given in standard tables.[27,28,29] It is clear that the data for fayalite given in the compilation by Barin and Knacke[29] are incorrect. The Gibbs energy of formation of the spinel form of Fe_2SiO_4 from elements represented by the equation

Table I. Standard Gibbs Energy of Formation of Fe$_2$SiO$_4$ from Component Oxides

	ΔG° (kJ mol^{-1})			
Source	900 K	1000 K	1100 K	1200 K
Present study (Eq. [4])	−25.11	−23.55	−21.99	−20.43
Rog and Kozinski[14]	−19.01	−16.01	−14.81	−12.71

Table II. Standard Gibbs Energy of Formation of Fe_2SiO_4 from Elements

Source	$\Delta G°$ (kJ mol^{-1})					
	900 K	1000 K	1100 K	1200 K	1300 K	1400 K
Present study	−1184.14	−1151.98	−1119.89	−1087.88	−1055.93	−1024.04
Pankratz et al.[27]	—	−1153.96	—	−1090.04	—	−1026.38
Robie et al.[28]	−1182.92	−1150.8	−1118.53	−1086.24	−1054.10	−1022.20
Barin and Knacke[29]	−1160.91	−1127.86	−1094.60	−1061.30	−1028.09	− 995.16

$$2\text{Fe (s)} + 2O_2 \text{ (g)} + \text{Si (s)} \rightarrow Fe_2SiO_4 \text{ (sp)} \quad [30]$$
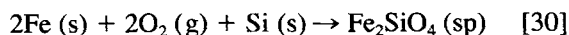
is obtained from Eqs. [22] and [29] as

$$\Delta G_{30}^{\circ} = -1,466,980 + 333.82 \, T \, (\pm1400) \quad \text{J mol}^{-1}$$

$$[31]$$

V. SUMMARY

The Gibbs energy changes for FQI and FQM equilibria have been redetermined using a solid-state galvanic cell technique. Unlike most previous measurements, the third-law analysis of the present results gives temperature-independent values for ΔH_{298}° for both equilibria. The thermal data for Fe_3O_4 given in the recent compilation of Pankratz[26] are most consistent with the present measurements. The standard free energy of formation of Fe_2SiO_4 from elements for both olivine and spinel forms has been deduced from present measurements and other information available in the literature. The Gibbs energy of formation of Fe_2SiO_4 given by Barin and Knacke[29] appears to be incorrect.

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