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Thermodynamic properties for bunsenite, NiO, magnetite, Fe$_3$O$_4$, and hematite, Fe$_2$O$_3$, with comments on selected oxygen buffer reactions

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ABSTRACT

Smoothed values of the heat capacities and derived thermodynamic functions are given for bunsenite, magnetite, and hematite for the temperature interval 298.15 to 1800 K. The heat capacity [in J/(mol·K)] of bunsenite may be calculated from the equations:

\[
C_p^g = 4110.720 - 5.302412T + 3.52061 \times 10^{-3}T^2 - 53039.297T^{-0.5} + 2.43067 \times 10^1T^{-2} \quad \text{(valid range 245–519 K)}
\]

and

\[
C_p^g = -8.776 + 4.2232 \times 10^{-2}T - 7.5267 \times 10^{-6}T^2 + 787.25T^{-0.5} + 3.6067 \times 10^6T^{-2} \quad \text{(valid range 519–1800 K)}.
\]

The calorimetric values at 298.15 K of 37.99 J/(mol·K) and -239.3 kJ/mol for the entropy and enthalpy of formation, respectively, for bunsenite are shown to be consistent with recent electrochemical data and the equations for heat capacity derived in this study. The Gibbs free energy for the reaction Ni + 0.5O$_2$ = NiO is given by the equation \( \Delta_G^f = -238.39 + 0.1146T - 3.72 \times 10^{-1} \ln T \) (kJ, average deviation of the fit is 0.2%) and is valid from 298.15 K to 1700 K.

The heat capacity [in J/(mol·K)] of hematite may be calculated from the equations:

\[
C_p^g = 2659.108 - 2.521537 + 1.36769 \times 10^{-3}T^2 - 3.645541 \times 10^4T^{-0.5} + 2.07344 \times 10^1T^{-2} \quad \text{(valid range 290–800 K)},
\]

\[
C_p^g = -3.483016217 \times 10^6 + 944.3894357 + 8.8660128 \times 10^1T^2 - 2.603798463 \times 10^6T^{-0.5} \quad \text{(valid range 800–845.5 K)},
\]

and

\[
C_p^g = 11761.609 - 3.8316705T + 6.391782 \times 10^4T^2 - 2.9975290 \times 10^5T^{-0.5} + 1.115308 \times 10^1T^{-2} \quad \text{(valid range 900–1800 K)}.
\]

Good agreement is found between results reported here and the recent results of O’Neill (1987a) from emf studies and also with the earlier phase equilibria results of Hewitt (1978). The Gibbs free energy (in kJ) of the reaction 2 magnetite + 3 quartz = 3 fayalite + O$_2$ may be calculated from the equation \( \Delta_G^f = 474.155 - 0.161207T \) (average deviation of the fit is 0.1%) in kJ and between 800 and 1400 K.

The magnetite-hematite (MH) buffer reaction was also examined. A recent proposal by O’Neill (1988) to adjust the enthalpy of formation of hematite to a more stable value is supported in this study. A value of -826.23 ± 1.25 kJ/mol is recommended. A consistent set of studies upon which earlier estimates of the enthalpy of formation of hematite were based are believed to reflect metastable equilibrium with maghemite or very fine-grained hematite. These findings suggest that care should be exercised in the use of the MH buffer reaction. The Gibbs free energy (in kJ) of the reaction 6 hematite = 4 magnetite + O$_2$ may be calculated from the following equations: \( \Delta_G^f = 496.215 - 0.27114T \) (average deviation of the fit is 0.1%, range 298.15–700 K), \( \Delta_G^f = 514.690 - 0.297537 \) (average deviation of the fit is 0.2%, range 700–1100 K), \( \Delta_G^f = 501.348 - 0.2854T \) (average deviation of the fit is 0.4%, range 1100–1600 K).

INTRODUCTION

Bunsenite, NiO, and magnetite, Fe$_3$O$_4$, are phases that in combination with other phases may fix $f_{O_2}$. As such, these phases have become important components of phase equilibrium studies, studies of igneous and metamorphic rocks, and studies of some hydrothermal systems. The assemblages involving these phases that are important for
buffering O in experimental or natural systems are nickel-bunsenite, iron-magnetite, wüstitie-magnetite, quartz-fayalite-magnetite (QFM) and magnetite-hematite (MH).

The U.S. Geological Survey (Haas, 1988), with support from the Chemical Thermodynamic Tables Task Group of CODATA, has undertaken an evaluation of the thermodynamically important O buffer systems, including those listed above. During this analysis, questions regarding the thermodynamic properties of bunsenite and magnetite arose. The heat capacities of these phases have been measured to help resolve these questions and to improve the thermodynamic data for these phases.

Heat-content measurements reported for NiO have been interpreted as defining either one (Tomlinson et al., 1955) or two (King and Christensen, 1958) heat-capacity anomalies between 500 and 600 K where both antiferromagnetic ordering (Roth, 1960) and a change from a high-temperature cubic structure to a lower-temperature rhombohedral structure (Rooksby, 1948) have been observed. Lewis and Saunders (1973) have presented graphical results for the thermal conductivity, specific heat, and electrical resistivity of NiO that confirm the single thermal anomaly interpretation. However, the graphical data are not adequate for calculating the thermodynamic properties of NiO in the region of the Néel point, $T_N$. In addition, the results of simultaneous multiple linear regression of experimental data involving bunsenite (Haas, 1988) suggest that the calorimetrically determined entropy at 298.15 K is too large. In order to improve our knowledge of the thermodynamic properties of the Ni-NiO buffer system, the heat capacities of NiO have been measured between 350 and 850 K.

Analysis of an extensive data set involving reactions with magnetite (Haas, 1988) suggested that the heat capacities reported for magnetite between 298.15 K and $T_N$ at about 848 K and between 900 and 1040 K (Grønvold and Sveen, 1974), and the entropy reported for magnetite at 298.15 K (Westrum and Gronvold, 1969; Bartel and Westrum, 1976; and Bartel et al., 1976) were too large. Using the procedures of Haas and Fisher (1976), Haas (1988) estimated an entropy for magnetite of 145.4 J/(mol·K) at 298.15 K. This value may be compared with 146.1 J/(mol·K) calculated by Grønvold and Sveen (1974) from the data of Westrum and Gronvold (1969) and with similar values obtained by Bartel and Westrum (1976) and Bartel et al. (1976). A value of 145.3 J/(mol·K) is given for pure magnetite. Although the uncertainties in the values for the observed cell edge for this sample and for pure magnetite yield an overlap in the possible range of values for each cell edge, the data suggest that the sample is a solid solution of magnetite and maghemite. Lind-sley (1976) has shown the variation of the a cell dimension of magnetite with the mole percentage of $\gamma$-Fe$_2$O$_3$ (maghemite). Using the relationship provided by Lind-sley (1976), the cleaned magnetite sample would appear to be composed of 87 mol% Fe$_3$O$_4$ and 13 mol% of $\gamma$-Fe$_2$O$_3$.

Özdemir and Dunlop (1989) have shown that maghemite alters to hematite at temperatures greater than 725 K in air. This reaction could occur in the differential scanning calorimeter when the magnetite sample is thermally equilibrated at high temperatures.

Two additional magnetite samples were obtained later in this study. A single crystal of magnetite was supplied by John W. Koenitzer and J. M. Honig of the Department of Chemistry at Purdue University. The sample was grown by the skull-melting technique (SM experiment no. 365). A subsolidus anneal was performed at 1000 °C and log $f_{O_2}$ = −9.48 for 119.5 h (anneal no. 227) to ensure the proper stoichiometry. The outer 1 mm was removed when the sample was prepared because cooling the sample from 1000 °C results in minor surface oxidation of the syn-

## Samples and apparatus

The bunsenite sample was prepared by heating Fischer Scientific Company reagent material (lot 784016) for 24 h at 1000 °C. The sample was a portion of the material used by Huebner and Sato (1970) in their study of the Ni-NiO buffer. The sample was 27.914 mg and in the form of a dull green powder that under low magnification showed well-crystallized emerald green grains.

The magnetite sample used for the majority of the heat-capacity measurements was a portion of the sample used by Bartel et al. (1976) that had remained sealed in a glass tube under a reducing atmosphere since the sample was prepared (J. L. Haas, personal communication). Hy-dothermal synthesis and chemical analysis of the sample were described by Bartel et al. (1976). Examination of the portion of the sample made available for this study revealed small, localized volumes of unreacted hematite that were removed by hand picking the sample. Heat-capacity measurements were made with a 38.244-mg sample. Anomalous heat capacities at temperatures greater than 900 K (discussed later) suggested that the sample composition deviated from that assumed by Bartel et al. (1976).

The cleaned magnetite sample was examined by X-ray diffraction analysis (BaF$_2$ internal standard, CuKα radiation), and the a cell dimension, 8.392 Å, was calculated from the 440 lattice reflection. No diffraction peaks other than those consistent with magnetite were observed; however, the calculated cell edge is smaller than the value given for pure magnetite. Although the uncertainties in the values for the observed cell edge for this sample and for pure magnetite yield an overlap in the possible range of values for each cell edge, the data suggest that the sample is a solid solution of magnetite and maghemite. Lind-sley (1976) has shown the variation of the a cell dimension of magnetite with the mole percentage of $\gamma$-Fe$_2$O$_3$ (maghemite). Using the relationship provided by Lind-sley (1976), the cleaned magnetite sample would appear to be composed of 87 mol% Fe$_3$O$_4$ and 13 mol% of $\gamma$-Fe$_2$O$_3$.

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were made under N₂ gas. Sample weights were checked following each scan to test for sample oxidation. A small thermal anomaly associated with the antiferromagnetic-paramagnetic transformation was observed in the heat capacity of NiO at 519 K. The heat-capacity and heat-content data for temperatures below 519 K were combined and fit with Equation 1 with an average deviation of 0.45%:

\[
C_p[J/(mol-K)] = 4110.720 - 5.3024127T + 3.52061 \times 10^{-7}T^2 - 53039.297T^{-0.5} + 2.43067 \times 10^{-7}T^{-2}
\]  

(valid range, 245 to 519 K). The heat-capacity and heat-content values for temperatures greater than 519 K were obtained from other magnetite samples having \(x = 0.000\). The chemical formula is Fe₃₋ₓOₓ x = 0.000, consistent with the results of Christensen (1958) which were not consistent but represent the only data available for temperatures above 1108 K.

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\[
C_p [J/(mol\cdot K)] = -8.776 + 4.2232 \times 10^{-2} T - 7.5267 \times 10^{-6} T^2 + 787.257 T^{-0.5} + 3.6067 \times 10^6 T^{-2}
\]  

(valid range, 519 to 1800 K). The agreement between Equation 1 and the measured heat capacities is good to near 519 K. Equation 2 represents a reasonable least-squares fit to the experimental data. The form of the equation will not allow an exact match to the form of the measured heat-capacity data. Between 550 and 650 K the smoothed curve overestimates the heat capacities by about 1%. Between 519 and 540 K Equation 2 underestimates the measured values. If precise heat-capacity values are required in the region of the anomaly, the equations derived by Haas (1988) should be used.

King and Christensen (1958) observed two breaks in the slope of the heat-content data for NiO in the region of the antiferromagnetic-paramagnetic transformation. The atypical behavior of the second slope change in the heat-content data led King and Christensen (1958) to infer a second transition. The results presented here clearly show that the interpretation of King and Christensen (1958), although reasonable, is incorrect. Unlike the typical \(\lambda\)-type anomaly associated with antiferromagnetic ordering (e.g., Robie et al., 1982, 1984) or that associated with a structural change (e.g., Hemingway et al., 1986) that rapidly decrease in heat capacity from a peak value, the heat capacity of NiO decreases slowly over nearly 100 K (Table 1).

The Néel temperature, \(T_N\), observed in this study was 519 K as compared with the values of 523 K from King and Christensen (1958), 525 and 520 K from specific heat and electrical resistivity data reported by Lewis and Saunders (1973), 523 K from Tomlinson et al. (1955), and 520 K from Perakis and Parravano (1960). Perakis and Parravano (1960) examined the effect of excess O on the Néel temperature of NiO and found a shift from about 520 to 543 K for the addition of 0.003 atoms of O per mole of NiO. Although variations in the O content may result in changes in the observed Néel temperature, it is more likely that the observed differences are the consequence of small offsets in the practical temperature scales used in each laboratory, coupled with the difficulty in determining the exact transition temperature from some experimental techniques (e.g., heat-content measurements).

Roth (1960) and Slack (1960) have studied the crystallographic and magnetic structure of NiO in the region of the Néel temperature (see also Roth and Slack, 1960). Antiferromagnetic ordering of the magnetic moments in cubic NiO is accomplished by a slight rhombohedral distortion that is the result of contraction along one of the (111) axes of the original cubic cell. However, Shimomura et al. (1954) have shown that as the amount of excess O increases, less rhombohedral deformation occurs and the NiO becomes somewhat ferromagnetic. The spins lie in the (111) plane, and the direction of magnetization is reversed in neighboring planes. Ordering is accomplished through superexchange coupling between Ni ions on opposite sides of O ions. The contraction perpendicular to the antiferromagnetic sheets results in crystallographic twinning and the formation of antiferromagnetic domains. Domain walls are also created by rotation of the direction of the magnetic moments with respect to adjacent crystal regions. Thus, the thermal anomaly in the heat capacity of NiO is associated with the degree of crystallographic change and with the ordering of spins on the magnetic sublattices.

Heat-capacity values obtained for temperatures above the Néel temperature (e.g., 650 to 850 K) exhibit a larger scatter than is usual for the experimental technique and appear to contain some excess heat capacity related to thermal disequilibrium. Roth (1960) observed changes in the location of the twin walls in crystals heated well into the paramagnetic region (e.g., to 770 K) and then cooled below the Néel temperature. Roth (1960) also observed that the time required to move a twin wall was shorter than that required to redistribute the spin states. These results suggest that heat capacities measured above \(T_N\) reflect differences in crystal structure and magnetic ordering that arise from differences in the short-term thermal history of the sample, for example, the length of time the sample was equilibrated prior to the DSC scan of the temperature range, the maximum temperature to which the sample was heated before the scan, the length of time the sample was held at the highest temperature before cooling to the initial scan temperature, and the rate at which the sample was cooled to the initial scan temperature. Therefore, the heat capacities measured at temperatures above 650 K were given less weight in establishing Equation 2.

The Gibbs free energy of formation of bunsenite may be estimated from calorimetric data and from electrochemical measurements. Results from recent electrochemical measurements compare favorably with the calorimetric data. Results from earlier electrochemical studies are less consistent with the calorimetric results and with recent electrochemical results. The older electrochemical measurements have been reviewed by Colmert and Pratt (1984) and Holmes et al. (1986) and will not be reviewed here.

The calorimetric Gibbs free energy of formation of bunsenite as a function of temperature may be estimated from the enthalpy of formation at 298.15 K, \(-239.7 \pm 0.4\) kJ/mol (Boyle et al., 1954), the entropy at 298.15 K, 37.99 J/mol (King, 1957), and the heat-capacity equations given above. Comparison with electrochemical data (see below) suggests that \(-239.3\) kJ/mol is the most appropriate value for the enthalpy of formation of bunsenite at 298.15 K. This value, together with the entropy reported by King (1957) and Equations 1 and 2, were used to calculate the enthalpy and Gibbs free energy of formation of bunsenite listed in Table 2.

Electrochemical measurements have been made in the
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Heat capacities for magnetite were measured between 340 and 1000 K. A lower-case thermal anomaly was observed with a maximum heat-capacity value measured near 845.5 K. A small, rounded peak centered at about 950 K was also observed. Although the cleaned sample of magnetite appeared to be free of hematite, the small anomaly at 950 K is consistent with an antiferromagnetic to paramagnetic transition in hematite (Gronvold and Samuelsen, 1975), suggesting that the sample contained hematite. The excess enthalpy for the interval 910 to 1000 K was calculated. This value, converted to the composition $\alpha$-Fe$\text{O}_3$, was compared with the excess enthalpy of pure $\alpha$-Fe$\text{O}_3$, calculated in a similar manner. The result of this calculation suggested that the magnetite sample contained 13 mol\% of $\gamma$-Fe$\text{O}_3$, in agreement with the estimate based upon the a cell dimension discussed earlier. In support of this calculation, the enthalpies of the Verwey transition measured by Bartel et al. (1976) and Westrum and Gronvold (1969) were compared. This was done because the sample used in this study was a portion of the sample prepared for Bartel et al. (1976). Thus, if $\gamma$-Fe$\text{O}_3$, is uniformly distributed in the sample, the enthalpy of the Verwey transition (577.4 J/mol) observed by Bartel et al. (1976) should be smaller than that observed (661.1 J/mol) by Westrum and Gronvold (1969) for a magnetite with essentially ideal composition. Using this comparison, one would estimate that the sample measured by Bartel et al. (1976) was only 88 mol\% magnetite. If one assumes the diluent to be $\gamma$-Fe$\text{O}_3$, the calculation confirms the earlier estimates.

The heat capacities reported here have been corrected for the thermal anomaly observed at about 950 K by assuming the impurity to be hematite. The corrected experimental heat capacities for magnetite are in Table 3. The experimental results were combined with the low-temperature heat capacities of Westrum and Gronvold (1969) and Bartel et al. (1976) and the high-temperature heat contents of Coughlin et al. (1951). For temperatures between 290 and 800 K, Equation 3 fit the combined data set with an average deviation of 0.34%:

$$C_I(J/(mol \cdot K)) = 2659.108 - 2.52153T$$
$$+ 1.36769 \times 10^{-9}T^2$$
$$- 3.64554 \times 10^{-9}T^{-0.5}$$
$$+ 2.07344 \times 10^{-9}T^{-2}. \quad (3)$$

Equation 4 provides a least-squares fit with an average deviation of 0.34% for heat capacities measured between 800 and 845.5 K:

$$C_I(J/(mol \cdot K)) = -3.483016217 \times 10^6$$
$$+ 944.389435T$$
$$+ 8.866012817 \times 10^4T^{-0.5}$$
$$- 2.603798463 \times 10^4T^{-2}. \quad (4)$$

The slopes of Equations 3 and 4 were not constrained to be consistent at 800 K. The heat capacities in the interval 845.5 to 900 K could not be fit with an equation of the form used above and consequently were integrated by hand. For temperatures between 900 and 1800 K, Equation 5 fit the combined data set, with an average deviation of 0.61%:

$$C_I(J/(mol \cdot K)) = 11761.609 - 3.8316705T$$
$$+ 6.39178 \times 10^{-4}T^2$$
$$- 2.9975290 \times 10^{-9}T^{-0.5}$$
$$+ 1.115308 \times 10^{-9}T^{-2}. \quad (5)$$

Smoothed values of the thermodynamic properties for magnetite derived from Equations 3–5 and the hand integration are in Table 4.
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In an effort to establish the best value for the heat capacity of magnetite at 1000 K, the heat capacity of stoichiometric FeO, (samples M2 and M3) was determined. The observed heat capacities were 205.8 and 205.5 J/(mol·K), respectively, for samples M2 and M3. These values are consistent with the recommended value in Table 4. The results are about 3% lower than the value reported by Gronvold and Sveen (1974) and are about 3% larger than the value derived from the heat-content measurements reported by Coughlin et al. (1951).

The heat capacities of magnetite samples M2 and M3 also were measured over the temperature interval of 340 to 500 K to ensure that the values reported here and those of Gronvold and Sveen (1974) were consistent with the heat capacities of stoichiometric FeO,. The results are in good agreement (Table 5).

The heat capacities reported in this study may be compared with those reported by Gronvold and Sveen (1974). Tn, observed in this study, 845.5 K, is slightly lower than the temperatures assigned by Gronvold and Sveen (1974) of 848.04 K. Tn was also measured for sample M2. The resulting value, 845.1 K, is in good agreement with the value reported in Table 3. The observed differences in Tn most likely represent variations in the practical temperature scales employed in each laboratory. The heat capacities measured between 340 and about 650 K are in good agreement; however, between 650 and 800 K and between 845 and 1000 K, the heat capacities measured in this study are somewhat lower than those reported for the same intervals by Gronvold and Sveen (1974). Consequently, integration of C and C/T yield slightly lower values (0.7 and 0.3%, respectively) for H,000 - H,000 in this study.

Most of the observed differences in the heat contents and entropies arise from differences in the heat capacities measured at temperatures above Tn. An examination of the experimental data reported by Gronvold and Sveen (1974) suggests the presence of a small, rounded heat-capacity anomaly above 900 K and the possible presence of FeO as an impurity. Because the specific heats of FeO, and FeO are similar below 850° for magnetite, the largest corrections for the heat capacities of magnetite are for those measured above about 750 K. The corrections increase the heat capacities in the interval 750 to about 860 K and reduce the observed heat capacities in the temperature interval 860 to 1000 K. Such corrections to the heat capacities reported by Gronvold and Sveen (1974) would result in better agreement among heat capacities measured above 860 K.

### Table 3. Experimental molar heat capacities for synthetic magnetite (molar mass = 231.539 g)

<table>
<thead>
<tr>
<th>T K</th>
<th>Heat capacity J/(mol·K)</th>
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<th>T K</th>
<th>Heat capacity J/(mol·K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Series 1</td>
<td>540.2</td>
<td>197.9</td>
<td>731.5</td>
<td>235.7</td>
<td>844.2</td>
</tr>
<tr>
<td>Series 2</td>
<td>620.8</td>
<td>212.3</td>
<td>833.3</td>
<td>213.0</td>
<td>936.5</td>
</tr>
<tr>
<td>Series 3</td>
<td>700.4</td>
<td>218.5</td>
<td>925.6</td>
<td>215.0</td>
<td>1028.5</td>
</tr>
<tr>
<td>Series 4</td>
<td>570.4</td>
<td>203.7</td>
<td>717.6</td>
<td>246.1</td>
<td>846.1</td>
</tr>
<tr>
<td>Series 5</td>
<td>590.6</td>
<td>207.2</td>
<td>717.1</td>
<td>250.4</td>
<td>849.1</td>
</tr>
<tr>
<td>Series 6</td>
<td>600.6</td>
<td>209.3</td>
<td>718.1</td>
<td>256.0</td>
<td>850.0</td>
</tr>
<tr>
<td>Series 7</td>
<td>610.7</td>
<td>210.3</td>
<td>719.5</td>
<td>259.8</td>
<td>851.0</td>
</tr>
<tr>
<td>Series 8</td>
<td>691.7</td>
<td>213.5</td>
<td>801.9</td>
<td>266.8</td>
<td>952.0</td>
</tr>
<tr>
<td>Series 9</td>
<td>786.0</td>
<td>217.3</td>
<td>881.0</td>
<td>278.6</td>
<td>1052.0</td>
</tr>
<tr>
<td>Series 10</td>
<td>871.0</td>
<td>228.0</td>
<td>967.0</td>
<td>285.6</td>
<td>1152.0</td>
</tr>
</tbody>
</table>

**Note:** Results corrected for FeO, (see text). Not used in computer fit to data above 900 K.

**Discussion**

The O buffer reactions involving magnetite are important both for establishing fO2 in phase-equilibrium experiments and in interpreting conditions of temperature and fO2 in rock-forming processes (e.g., Spencer and Lindsay, 1981 and Anovitz et al., 1985). In addition to the revised thermodynamic properties for magnetite reported here, new experimental data that bear upon the QFM buffer reaction have been published since Robie et al. (1982) compared values derived from calorimetric, phase equilibria, and emf studies. Hemingway (1988) has published a revision of the thermodynamic properties for quartz. O'Neill (1987a, 1988) has studied the QFM buffer reaction and has determined the enthalpies and free energies of formation of fayalite and magnetite using an electrochemical method, Rögg and Kozinski (1983) have determined the free energy of formation of fayalite using an electrochemical method, and Myers and Eugster (1983) have studied the QFM buffer reaction using a thermogravimetric gas-mixing furnace. The results reported here, those of Hemingway (1988), and those of O'Neill (1987a,
are consistent with the data set used by Robie et al. (1982) and thus provide only refinement to the recommended QFM buffer reaction. The data of Rög and Kozinski (1983) and Myers and Eugster (1983) are not consistent. The results of Myers and Eugster (1983) have been shown to be internally inconsistent (O'Neill, 1987a) and thus to contain systematic errors. The data of Rög and Kozinski (1983) are incomplete because the results are provided for the reaction 2FeO + SiO₂ = Fe₃SiO₆, but the exact composition of the FeO is not defined. At 1000 K, the difference in Gibbs free energy between stoichiometric FeO and wüstite (Fe₉₋ₓO) is about 6 kJ/mol (Robie et al., 1979), which means that the Gibbs free energy of formation of Fe₃SiO₆ calculated from the data of Rög and Kozinski (1983) can vary by up to 12 kJ and thus is not of sufficient accuracy to be useful.

Using the Gibbs free energies of magnetite (this study), quartz (Hemingway, 1988) and fayalite (Robie et al., 1982), the Gibbs free energy of the QFM buffer reaction (2 magnetite + 3 quartz = 3 fayalite + O₂) at 1 bar may be calculated (in kJ) from the equation ΔG° = 474.155 - 0.161207T between 800 and 1400 K. The equation fits the data to ±0.1%. The equation is in agreement (±0.4%) with Gibbs free energies calculated from the equation given by Hewitt (1978), although the slope calculated from Hewitt's data is greater than that derived in this study. The Gibbs free energies calculated from this equation are in good agreement with Gibbs free energies calculated from the equation for the QFM buffer given by O'Neill (1987a); however, the values systematically differ by about 0.6%. This difference arises from the values for the enthalpies and Gibbs free energies for magnetite and fayalite utilized by O'Neill (1987a).

Good agreement exists between thermodynamic data derived from calorimetric, phase equilibrium, and emf experimental methods for the QFM buffer, although slight differences remain in the absolute values of the formation properties calculated from the various experimental data sets. These differences are themselves within the experimental uncertainty of the data.

O'Neill (1988) has proposed a significant change in the enthalpy (−826.0 kJ/mol) and Gibbs free energy (−744.0 kJ/mol) of formation of hematite at 298.15 K and 1 bar based upon electrochemical studies. O'Neill's (1988) electrochemical data are in agreement with the results reported by Blumenthal and Whitmore (1961) and Roth (1929), and with some of the results reported by Chou (1978) and Moriyama et al. (1969). The proposed change would result in a decrease in log fO₂ of 0.5 for the magnetite-hematite equilibrium at 1000 K.

The enthalpies of formation of hematite (about −824.6 kJ/mol) recommended in the JANAF tables (Chase et al., 1985), the NIST (formerly NBS) 270 series (Wagman et al., 1982) and in USGS Bulletin 1452 (Robie et al., 1979) are derived from studies of the MH buffer reaction and from a set of experimental results that are fairly consistent (ten references in Chase et al., 1985 and O'Neill, 1988). It should be noted that the value for the enthalpy of formation of hematite listed in Chase et al. (1985) is

<table>
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<tr>
<th>Temperature K</th>
<th>M2 C$</th>
<th>M3 C$</th>
</tr>
</thead>
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<td>338.9</td>
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<td>161.7</td>
</tr>
<tr>
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<td>163.9</td>
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<td>166.3</td>
</tr>
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<td>499.0</td>
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HEMINGWAY: THERMODYNAMIC PROPERTIES FOR NiO, Fe₂O₃, AND Fe₃O₄

Table 6. Molar thermodynamic properties for hematite (molar mass = 159.692 g)

<table>
<thead>
<tr>
<th>T K</th>
<th>Heat capacity C_p</th>
<th>Entropy S</th>
<th>Enthalpy function (H° - H°_f)/T</th>
<th>Gibbs energy function (G° - G°_f)/T</th>
<th>Formation from elements</th>
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<tbody>
<tr>
<td></td>
<td>J/(mol·K)</td>
<td>J/(mol·K)</td>
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<tr>
<td></td>
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<tr>
<td>298.15</td>
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<td>0.000</td>
<td>87.40</td>
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<tr>
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<td>120.91</td>
<td>120.50</td>
<td>28.800</td>
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<thead>
<tr>
<th></th>
<th>Enthalpy</th>
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<tr>
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<td>kJ/mol</td>
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<tr>
<td>298.15</td>
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<td>1800</td>
<td>-790.719</td>
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</table>

1 kJ more negative than that given by the other sources listed. This difference results from the adoption of a more negative value for the enthalpy of formation of magnetite than that listed by the other sources. Recalculation of the JANAF data set using a consistent value for the enthalpy of formation of magnetite (Table 4) shows the JANAF evaluation to actually predict a lower stability (less negative) for hematite than the other sources. The JANAF tabulations were compiled in the mid-1960s and were not reevaluated for the 1985 publication. More recent experimental data (see references in O'Neill, 1988) utilized by the other sources indicated a slightly lower f0₂.

O'Neill (1988) has reviewed the potential sources of error in his experiments and has concluded that if his experiments are correct, then the discrepancy between the two data sets discussed above likely rests with the failure of earlier workers to equilibrate magnetite and hematite. O'Neill (1988) considers it more likely that the oxidized phase was maghemite (γ-Fe₂O₃), a phase less stable than hematite, or very fine-grained hematite (O'Neill, personal communication; see also Özdemir and Dunlop, 1989) and, therefore, likely to equilibrate at a higher f0₂. O'Neill (1988) supports this hypothesis by noting that enthalpies of formation calculated by the third law method from his experimental data measured at temperatures above 1150 K become less negative (less stable) than the constant average value typical of values calculated from the measurements made in the 1000 to 1150 K temperature interval. O'Neill (1988) suggests that the explanation for this trend lies in the fact that a stable solid solution of Fe₂O₃ in magnetite exists at temperatures above 1150 K (e.g., Linsley, 1976).

Oxidation of magnetite to form hematite appears to be a two-step process, regardless of the temperature of oxidation (Davis et al., 1968). Step 1 involves the formation of a solid solution of Fe₂O₃ in magnetite (M₉) through the process of diffusion of Fe³⁺ ions to the surface of the grain resulting from a gradient in the O₂ potential. Over time, and with a strong gradient in the O₂ potential, this process can produce Fe₂O₃ with the spinel structure (maghemite) on the outer surface of the grain. Step 2 involves inversion of maghemite to hematite. The phase diagram for the system Fe-O (Lindsley, 1976) provides information that is useful in interpreting how the oxidation process described above may affect the measurement of the f0₂ associated with the magnetite-hematite equilibrium. M₉ is shown to be stable at temperatures greater than about 1000 K; however, substantial solubility of Fe₂O₃ in magnetite does not develop until about 1150 K to 1200 K. Metastable M₉ undergoes disproportionation to Fe₂O₃ and Fe₃O₄, which promotes nucleation and growth of hematite (Columbo et al., 1965). At temperatures greater than 1150 to 1200 K, stability of M₉ allows the development of maghemite without providing a mechanism for nucleation of hematite. Therefore, the inversion of maghemite to hematite is the rate-limiting step, and maghemite is likely to be the phase controlling the f0₂. Columbo et al. (1965) has shown that the inversion of maghemite to hematite occurs rapidly if hematite is in intimate contact with the maghemite, which makes the disproportionation reaction critically important. Within the temperature interval of 1000 to 1150 K, one would expect some disproportionation of M₉ to occur and thus provide some nucleation of hematite. At lower temperatures than 1000 K, one would expect the reaction rates (e.g., diffusion of Fe³⁺ and disproportionation) to decrease, resulting in larger times for equilibrium to be attained.

The hypotheses presented by O'Neill (1988) to explain
the disparate data appear to be correct. Third law treatment of the experimental data of O'Neill (1988) and Chou (1978) collected at temperatures less than about 950 K show a dependence upon temperature of the calculated enthalpy of the MH buffer reaction at 298.15 K (see O'Neill, 1988), which indicates a failure of the reactions to reach equilibrium. Of the experimental data for the MH buffer reaction suggesting more oxidizing conditions than that recommended by O'Neill (1988), most were determined at temperatures greater than 1100 K, where the formation and persistence of maghemite is expected. Finally, measurements made between about 1000 and 1150 K are likely to be the only measurements that come close to recording the equilibrium \( f_{o_2} \) for the MH buffer reaction. However, these results may tend to overestimate the equilibrium \( f_{o_2} \) and, in the calculation procedure cited above, yield a slightly less stable value for the enthalpy and Gibbs free energy of formation of hematite.

The results presented by O'Neill (1988) have been combined with the data for magnetite reported here to provide an estimate of the stability of hematite. The enthalpy and Gibbs free energy of formation are \(-826.23 \pm 1.25 \text{ and } -744.273 \pm 1.25 \text{ kJ/mole, respectively.}

The thermodynamic properties of hematite derived from these values and the heat capacity functions of Robie et al. (1979) are given in Table 6.

The Gibbs free energy of the MH buffer reaction (6 hematite = 4 magnetite + O₂) may be calculated from the following equations: \( \Delta G^\circ_f = 501.348 - 0.28547 T \) (range 1100–1600 K, average deviation of fit is 0.4%), \( \Delta G^\circ_f = 514.690 - 0.297537 T \) (range 700–1100 K, average deviation of fit is 0.2%), and \( \Delta G^\circ_f = 496.215 - 0.27114T \) (range 298.15–700 K, average deviation of fit is 0.1%).

The problems discussed above suggest that the MH buffer reaction should be used with caution. Because the \( f_{o_2} \) may be affected by nonequilibrium processes, the buffer must be carefully applied in experimental studies. The nonequilibrium processes may themselves be affected by other processes, such as dissolution and precipitation of Fe³⁺ from the surface of the grain by aqueous solutions that might facilitate conversion of magnetite to hematite, or the presence of chemical impurities that might stabilize \( \text{M}_2 \) to lower temperatures, and hence extend the range over which metastable maghemite may control \( f_{o_2} \). Similarly, care should be exercised in estimating temperatures and \( f_{o_2} \), from natural assemblages.

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