

Thermodynamic properties for bunsenite, NiO, magnetite, Fe₃O₄, and hematite, Fe₂O₃, 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:

$$C_p^0 = 4110.720 - 5.302412T + 3.52061 \times 10^{-3}T^2 - 53039.297T^{-0.5} + 2.43067 \times 10^7T^{-2} \quad (\text{valid range } 245\text{--}519 \text{ K})$$

and

$$C_p^0 = -8.776 + 4.2232 \times 10^{-2}T - 7.5267 \times 10^{-6}T^2 + 787.25T^{-0.5} + 3.6067 \times 10^6T^{-2} \quad (\text{valid range } 519\text{--}1800 \text{ K}).$$

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 $\text{Ni} + 0.5\text{O}_2 = \text{NiO}$ is given by the equation $\Delta_r G_T^0 = -238.39 + 0.1146T - 3.72 \times 10^{-3}T \ln T$ (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:

$$C_p^0 = 2659.108 - 2.52153T + 1.36769 \times 10^{-3}T^2 - 3.645541 \times 10^4T^{-0.5} + 2.07344 \times 10^7T^{-2} \quad (\text{valid range } 290\text{--}800 \text{ K}),$$
$$C_p^0 = -3.483016217 \times 10^6 + 944.389435T + 8.866012817 \times 10^7T^{-0.5} - 2.603798463 \times 10^{11}T^{-2} \quad (\text{valid range } 800\text{--}845.5 \text{ K}),$$

and

$$C_p^0 = 11761.609 - 3.8316705T + 6.391782 \times 10^{-4}T^2 - 2.9975290 \times 10^5T^{-0.5} + 1.115308 \times 10^9T^{-2} \quad (\text{valid range } 900\text{--}1800 \text{ K}).$$

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 $2 \text{ magnetite} + 3 \text{ quartz} = 3 \text{ fayalite} + \text{O}_2$ may be calculated from the equation $\Delta_r G_T^0 = 474.155 - 0.16120T$ (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 $6 \text{ hematite} = 4 \text{ magnetite} + \text{O}_2$ may be calculated from the following equations: $\Delta_r G_T^0 = 496.215 - 0.27114T$ (average deviation of the fit is 0.1%, range 298.15–700 K), $\Delta_r G_T^0 = 514.690 - 0.29753T$ (average deviation of the fit is 0.2%, range 700–1100 K), $\Delta_r G_T^0 = 501.348 - 0.2854T$ (average deviation of the fit is 0.4%, range 1100–1600 K).

INTRODUCTION

Bunsenite, NiO, and magnetite, Fe₃O₄, 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, wüstite-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 geologically 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 Grønvold, 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 Grønvold (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 listed in the JANAF tables (Chase et al., 1985), but the value is based upon an analysis completed in 1965 that was not revised in 1985 and is based largely upon the work of Millar (1929). The heat capacities reported by Millar (1929) are significantly lower than those of Westrum and Grønvold (1969), Bartel and Westrum (1976), and Bartel et al. (1976) and account for the lower entropy at 298.15 K calculated from his data. In addition, heat capacities measured by Grønvold and Sveen (1974) at temperatures between 900 and 1040 K are about 6% larger than the values that may be derived from the heat-content data reported by Coughlin et al. (1951). To help

resolve these problems, the heat capacities of magnetite have been measured between 340 and 1000 K.

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). Hydrothermal 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 (BaF₂ internal standard, CuK α 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. Lindley (1976) has shown the variation of the a cell dimension of magnetite with the mole percentage of γ -Fe₂O₃ (maghemite). Using the relationship provided by Lindley (1976), the cleaned magnetite sample would appear to be composed of 87 mol% Fe₃O₄ and 13 mol% of γ -Fe₂O₃.

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-

TABLE 1. Experimental molar heat capacities for bunsenite, NiO (molar mass = 74.6994 g)

T K	Heat capacity J/(mol·K)	T K	Heat capacity J/(mol·K)	T K	Heat capacity J/(mol·K)
Series 1		Series 3		Series 5	
338.5	48.44	527.9	60.19	518.0	69.36
348.5	49.04	537.9	58.25	527.9	60.68
358.5	49.88	547.9	57.32	537.9	58.69
368.4	50.54	557.9	56.56	547.9	57.54
378.4	51.33	567.8	56.34	557.9	56.91
388.4	52.20	567.8	56.34	567.8	56.35
398.3	53.02	577.8	56.19	577.8	56.03
408.3	53.92	Series 4		587.8	55.60
418.3	54.52	488.1	62.40	597.8	55.24
428.2	55.53	490.1	62.71	607.7	55.19
438.2	56.19	492.1	63.33	617.7	54.94
448.2	57.26	494.0	63.39	627.6	54.78
458.2	58.33	496.0	63.82	637.6	54.68
468.1	59.63	498.0	64.25	647.6	54.74
478.1	60.93	500.0	64.72	657.6	54.82
488.1	62.38	502.0	64.88	667.5	54.39
498.0	64.25	504.0	65.21	677.5	54.50
Series 2		506.0	65.65	687.5	54.56
338.5	48.32	508.0	66.08	696.4	54.50
348.5	49.17	510.0	66.71	Series 6	
358.5	49.89	512.0	67.51	667.5	55.06
368.4	50.68	514.0	68.28	677.5	54.79
378.4	51.48	516.0	68.91	687.5	54.81
388.4	52.20	518.0	69.29	697.4	54.74
398.3	52.99	520.0	67.16	707.4	54.67
408.3	53.95	522.0	63.49	717.4	54.81
418.3	54.71	524.0	62.21	727.3	54.96
428.2	55.61	526.0	61.43	737.3	55.05
438.2	56.42	527.9	60.93	747.3	54.73
448.2	57.41	529.9	60.23	757.3	55.04
458.2	58.51	531.9	59.72	767.2	55.23
468.1	59.82	533.9	59.17	777.2	55.59
478.1	60.95	535.9	59.03	787.2	55.70
488.1	62.38	537.9	58.77	797.1	55.66
498.0	64.16	539.9	58.73	807.1	55.62
Series 3		541.9	58.47	817.1	55.64
468.1	59.42	543.9	58.39	827.1	55.91
478.1	60.80	545.9	58.19	837.0	55.34
488.1	61.72	546.9	58.10	846.0	55.26

thetic crystal. The final dimensions of the single crystal are $4.0 \times 4.0 \times 0.7$ mm. The sample weighed about 54 mg. The chemical formula is $\text{Fe}_{(3-x)}\text{O}_4$, $x = 0.000$, confirmed by resistivity measurements made by John Koenitzer. A sharp discontinuity (Verwey transition) was observed at 121.5 K, which is consistent with the results obtained from other magnetite samples having $x = 0.000$. This sample will be designated M2. A third sample was provided by Özden Özdemir of the Department of Physics at the University of Toronto. The sample (designated M3) is in the form of a powder composed of single-crystal cubes of approximately single-domain size that was characterized and described by Özdemir and Dunlop (1989).

High-temperature heat capacities were measured by differential scanning calorimetry (DSC) following the procedures outlined by Hemingway et al. (1981). The samples were enclosed in unsealed gold pans. Measurements were made under N_2 gas. Sample weights were checked following each scan to test for sample oxidation. A small increase was observed in sample M3 following several scans to 1000 K. Sample M3 was not used thereafter.

TABLE 2. Molar thermodynamic properties for synthetic bunsenite (molar mass = 74.6994 g)

T K	Heat capacity C_p	Entropy S°	Enthalpy function $(H^\circ - H^\circ_{298})/T$	Gibbs energy function $-(G^\circ - H^\circ_{298})/T$	Formation from elements	
					Enthalpy	Gibbs free energy
					kJ/mol	kJ/mol
298.15	44.49	37.99	0.000	37.99	-239.3	-211.1
300	44.70	38.27	0.275	37.99	-239.3	-211.1
400	53.00	52.38	12.524	39.86	-238.6	-201.6
500	64.90	65.25	21.589	43.66	-237.3	-192.5
519	69.15	67.74	23.250	44.49	-236.8	-190.9
600	56.01	76.07	27.857	48.21	-236.2	-183.7
700	54.21	84.54	31.732	52.81	-235.6	-174.9
800	53.66	91.74	34.498	57.24	-235.0	-166.3
900	53.83	98.06	36.631	61.43	-234.5	-157.8
1000	54.43	103.8	38.378	65.38	-234.0	-149.2
1100	55.29	109.0	39.875	69.11	-233.7	-140.8
1200	56.29	113.8	41.201	72.64	-233.4	-132.3
1300	57.37	118.4	42.403	75.99	-233.0	-124.0
1400	58.48	122.7	43.512	79.17	-232.6	-115.6
1500	59.57	126.8	44.546	82.21	-232.1	-107.2
1600	60.62	130.6	45.518	85.11	-231.6	-98.9
1700	61.61	134.3	46.435	87.90	-231.0	-90.7
1800	62.52	137.9	47.304	90.58	-248.1	-81.4

Based upon the 1975 values for the atomic weights (Commission on Atomic Weights, 1976), the molar masses for stoichiometric bunsenite and magnetite are 74.6994 g and 231.539 g, respectively.

HIGH-TEMPERATURE HEAT CAPACITIES AND THERMODYNAMIC FUNCTIONS FOR BUNSENITE

The experimental heat capacities for bunsenite are in Table 1. The results were combined with the low-temperature heat capacities of King (1957) and high-temperature heat contents of King and Christensen (1958) and Tomlinson et al. (1955). The data were fit to two equations of the form recommended by Haas and Fisher (1976). The data of Tomlinson et al. (1955) agree with the heat capacities reported here. The results of King and Christensen (1958) were not consistent but represent the only data available for temperatures above 1108 K. Therefore, differences between adjacent heat-content values were used to estimate the heat capacity. **Smoothed values of the heat capacities and derived thermodynamic functions for NiO are in Table 2.**

A 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%:**

$$C_p[\text{J}/(\text{mol} \cdot \text{K})] = 4110.720 - 5.302412T + 3.52061 \times 10^{-3}T^2 - 53039.297T^{-0.5} + 2.43067 \times 10^7T^{-2} \quad (1)$$

(valid range, 245 to 519 K). The heat-capacity and heat-content values for temperatures greater than 519 K were

combined and fit with Equation 2 with an average deviation of 0.9%:

$$C_p^0[\text{J}/(\text{mol} \cdot \text{K})] = -8.776 + 4.2232 \times 10^{-2}T \\ - 7.5267 \times 10^{-6}T^2 + 787.25T^{-0.5} \\ + 3.6067 \times 10^6T^{-2} \quad (2)$$

(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 λ -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 $\langle 111 \rangle$ 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 Comert 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 ± 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

temperature interval 760 to 1400 K and recently reported by Comert and Pratt (1984), Holmes et al. (1986) and O'Neill (1987b). The reaction studied was $\text{Ni} + 0.5\text{O}_2 = \text{NiO}$. Comert and Pratt (1984) derived the following relationship for the Gibbs free energy of formation of bunsenite for the temperature interval 760 to 1275 K: $\Delta_f G_m^\circ (\text{J/mol}) = -232\,450 + 83.435T$. Holmes et al. (1986) reported $\Delta_f G_m^\circ (\text{J/mol}) = -239\,885 + 122.350T - 4.584T \ln T$ for the temperature interval 900 to 1600 K, and O'Neill (1987b) reported $\Delta_f G_m^\circ (\text{J/mol}) = -240\,050 + 122.0T - 4.584T \ln T$ for the temperature interval 800 to 1420 K. The Gibbs free energies calculated from the equation of Comert and Pratt (1984) are 0.4% less negative at the lowest temperatures and identical at the upper temperatures studied, when compared to the Gibbs free energies in Table 2. Those of O'Neill (1987b) are 0.4% more negative at the lower temperatures and about equal at the higher temperatures and those of Holmes et al. (1986) are identical at the lowest temperatures and are 0.4% less negative at the highest temperatures.

Gibbs free energies from the three studies discussed above agree within experimental error in the temperature interval 800 to 1400 K. It is obvious, however, that the slope of each Gibbs free energy curve is somewhat different. Because entropy is a slope term [i.e., $(\partial \Delta_f G / \partial T)_p = -\Delta_f S$], the entropy estimated at 298.15 K from an extrapolation based upon Gibbs free energies obtained from electrochemical data such as that discussed above can be considerably different from the calorimetrically determined entropy for the phase. This can cause a significant adjustment to the entropy calculated at 298.15 K in multiple linear regression analyses of experimental data. This point must be carefully reviewed in such analyses to be sure that the final solution to the least-squares regression of a data set does not contain biased results. The calorimetrically determined entropy at 298.15 K for bunsenite (King, 1957) is shown in this study to be consistent with the recent electrochemical data of Comert and Pratt (1984), O'Neill (1987b), and Holmes et al. (1986) and with the calorimetric enthalpy of formation at 298.15 K (Boyle et al., 1954). Between 298.15 and 1700 K, the free energy for the reaction $\text{Ni} + 0.5\text{O}_2 = \text{NiO}$ is $\Delta_f G_m^\circ = -238.39 + 0.1146T - 3.72 \times 10^{-3}T \ln T$ (kJ, average deviation of the fit is 0.2%). The f_{O_2} can be calculated from the relationship $-\Delta_f G_m^\circ = -RT \ln f_{\text{O}_2}$.

HIGH-TEMPERATURE HEAT CAPACITIES AND THERMODYNAMIC FUNCTIONS FOR MAGNETITE

Heat capacities for magnetite were measured between 340 and 1000 K. A λ -type 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 (Grønvold and Samuelsen, 1975), suggesting that the sample contained hematite. The excess enthalpy for the interval 910 to 1000 K was cal-

culated. This value, converted to the composition $\alpha\text{-Fe}_2\text{O}_3$, was compared with the excess enthalpy of pure $\alpha\text{-Fe}_2\text{O}_3$, calculated in a similar manner. The result of this calculation suggested that the magnetite sample contained 13 mol% of $\gamma\text{-Fe}_2\text{O}_3$, 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 Grønvold (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 $\gamma\text{-Fe}_2\text{O}_3$ 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 Grønvold (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 $\gamma\text{-Fe}_2\text{O}_3$, 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 Grønvold (1969) and Bartel and Westrum (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%:**

$$C_p^\circ [\text{J}/(\text{mol} \cdot \text{K})] = 2659.108 - 2.52153T + 1.36769 \times 10^{-3}T^2 - 3.645541 \times 10^4 T^{-0.5} + 2.07344 \times 10^7 T^{-2}. \quad (3)$$

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

$$C_p^\circ [\text{J}/(\text{mol} \cdot \text{K})] = -3.483016217 \times 10^6 + 944.389435T + 8.866012817 \times 10^7 T^{-0.5} - 2.603798463 \times 10^{11} T^{-2}. \quad (4)$$

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%:

$$C_p^\circ [\text{J}/(\text{mol} \cdot \text{K})] = 11761.609 - 3.8316705T + 6.391782 \times 10^{-4}T^2 - 2.9975290 \times 10^5 T^{-0.5} + 1.115308 \times 10^9 T^{-2}. \quad (5)$$

Smoothed values of the thermodynamic properties for magnetite derived from Equations 3–5 and the hand integration are in Table 4.

TABLE 3. Experimental molar heat capacities for synthetic **magnetite (molar mass = 231.539 g)**

T K	Heat capacity J/(mol·K)	T K	Heat capacity J/(mol·K)	T K	Heat capacity J/(mol·K)
Series 1		Series 5		Series 7	
540.2	197.9	731.5	235.7	844.2	326.9
550.2	200.7	741.5	239.0	845.2	329.0
560.4	201.8	750.6	243.0	846.1	325.4
570.4	203.7	Series 6		847.1	312.5
580.5	205.8	761.7	246.4	848.1	299.6
590.6	207.2	771.7	250.4	849.1	287.6
600.6	209.3	781.8	256.0	850.0	280.6
610.7	210.3	791.9	259.8	851.0	276.1
619.7	213.5	801.9	266.8	852.0	270.9
Series 2		Series 7		853.0	268.9
620.8	212.3	804.9	271.9	853.9	264.7
630.8	214.5	806.0	274.5	854.9	263.4
640.9	215.5	807.0	274.6	855.9	258.8
651.0	217.6	808.0	275.7	856.9	261.4
661.0	219.7	809.0	275.6	857.8	255.7
671.1	222.0	810.0	279.3	858.8	253.4
681.1	224.0	811.0	280.8	859.8	253.2
691.2	226.8	812.0	281.5	860.8	248.8
Series 3		813.0	281.0	861.7	247.5
338.9	161.9	814.0	283.2	862.7	246.5
349.0	164.5	815.0	281.8	863.7	245.1
359.1	166.9	816.0	283.6	864.7	242.4
369.1	169.0	817.0	285.5	865.6	241.7
379.2	171.4	818.0	286.8	866.6	239.8
389.3	173.8	819.0	288.3	867.6	236.8
399.3	175.8	820.0	290.3	868.5	234.7
409.4	177.8	821.1	291.4	869.5	233.8
419.5	179.4	822.1	290.6	870.5	233.6
429.5	181.1	823.1	291.4	871.0	228.0
439.6	182.5	824.1	294.5	Series 8	
448.6	184.6	825.1	295.4	876.3	228.0
Series 4		826.1	296.3	881.2	224.0
439.6	182.9	827.1	297.8	886.1	220.8
449.6	185.0	828.1	299.2	891.0	220.0
459.7	186.5	829.1	299.4	895.8	216.1
469.8	188.1	830.1	300.1	900.7	216.0
479.8	189.9	831.1	301.9	905.6	213.6
489.9	191.4	832.1	304.5	910.4	213.0
500.0	192.9	833.1	306.5	915.3	213.7
510.0	194.6	834.1	308.8	Series 9	
520.1	196.3	835.1	308.2	919.9	212.2
530.2	197.6	836.1	309.8	929.9	217.3*
540.2	198.7	837.2	310.5	939.7	214.2
549.3	199.9	838.2	313.7	949.4	217.8*
Series 5		839.2	313.9	959.1	213.8
701.3	226.8	840.2	317.3	968.9	213.9
711.3	229.8	841.2	318.8	978.6	206.9
721.4	232.6	842.2	321.4	988.4	209.5
		843.2	323.3	997.0	206.7

Note: Results corrected for Fe₂O₃ (see text).

* Not used in computer fit to data above 900 K.

In an effort to establish the best value for the heat capacity of magnetite at 1000 K, the heat capacity of stoichiometric Fe₃O₄ (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 recommended by Grønvold 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 Grønvold and Sveen (1974) were consistent with the heat capacities of stoichiometric Fe₃O₄. The results are in good agreement (Table 5).

The heat capacities reported in this study may be compared with those reported by Grønvold and Sveen (1974). T_N observed in this study, 845.5 K, is slightly lower than the temperatures assigned by Grønvold and Sveen (1974) of 848.04 K. T_N 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 T_N 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 845.5 and 1000 K, the heat capacities measured in this study are somewhat lower than those reported for the same intervals by Grønvold and Sveen (1974). Consequently, integration of C_p and C_p/T yield slightly lower values (0.7 and 0.3%, respectively) for $H_{1000} - H_{298}$ and S_{1000} 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 T_N . An examination of the experimental data reported by Grønvold and Sveen (1974) suggests the presence of a small, rounded heat-capacity anomaly above 900 K and the possible presence of Fe₂O₃ as an impurity. Because the specific heats of Fe₃O₄ and Fe₂O₃ are similar below T_N 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 Grønvold and Sveen (1974) would result in better agreement among heat capacities measured above 860 K.

DISCUSSION

The O buffer reactions involving magnetite are important both for establishing f_{O_2} in phase-equilibrium experiments and in interpreting conditions of temperature and f_{O_2} in rock-forming processes (e.g., Spencer and Lindsley, 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. Róg and Kozłowski (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,

TABLE 4. Molar thermodynamic properties for synthetic magnetite (molar mass = 231.539 g)

T K	Heat capacity C_p	Entropy S_f°	Enthalpy function $(H_f^\circ - H_{298}^\circ)/T$ J/(mol·K)	Gibbs energy function $-(G_f^\circ - H_{298}^\circ)/T$	Formation from elements	
					Enthalpy kJ/mol	Gibbs free energy kJ/mol
298.15	150.87	146.14	0.000	146.14	-1115.726	-1012.566
300	151.4	147.1	0.932	146.1		
400	176.1	194.2	41.800	152.4	-1113.024	-977.690
500	192.9	235.4	70.440	165.0	-1109.125	-944.253
600	207.9	271.9	92.062	179.8	-1104.598	-911.684
700	228.6	305.4	109.983	195.4	-1099.275	-880.015
800	260.7	337.8	126.679	211.1	-1092.504	-849.086
845.5	330.5	354.0	135.656	218.4	-1087.840	-835.264
900	213.9	369.1	142.054	227.1	-1085.098	-819.167
1000	206.0	391.2	148.809	242.4	-1085.610	-789.566
1100	201.5	410.6	153.779	256.8	-1089.593	-759.711
1200	199.3	428.0	157.647	270.4	-1091.361	-729.794
1300	198.8	444.0	160.821	283.1	-1088.937	-699.804
1400	199.4	458.7	163.548	295.2	-1086.823	-670.134
1500	201.0	472.5	165.988	306.5	-1084.778	-640.256
1600	203.2	485.6	168.243	317.3	-1082.846	-610.750
1700	206.0	498.0	170.380	327.6	-1084.473	-581.263
1800	209.2	509.8	172.445	337.4	-1083.585	-551.606

1988) 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 Róg and Koziński (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 Róg and Koziński (1983) are incomplete because the results are provided for the reaction $2\text{FeO} + \text{SiO}_2 = \text{Fe}_2\text{SiO}_4$, but the exact composition of the FeO is not defined. At 1000 K, the difference in Gibbs free energy between stoichiometric FeO and wüstite ($\text{Fe}_{0.947}\text{O}$) is about 6 kJ/mol (Robie et al., 1979), which means that the Gibbs free energy of formation of Fe_2SiO_4 calculated from the data of Róg and Koziński (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 ($2\text{magnetite} + 3\text{quartz} = 3\text{fayalite} + \text{O}_2$) at 1 bar may be calculated (in kJ) from the equation $\Delta_r G_f^\circ = 474.155 - 0.16120T$ between 800 and 1400 K. The equation fits the data to $\pm 0.1\%$. The equation is in agreement ($\pm 0.4\%$) 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 $\log f_{\text{O}_2}$ 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 5. Heat capacities of magnetite samples M2 and M3

Temperature K	M2 C_p J/(mol·K)	M3 C_p J/(mol·K)
338.9	161.9	161.7
349.0	164.1	163.9
359.1	166.5	166.3
369.1	168.7	168.4
379.2	171.0	170.7
389.3	173.4	173.2
399.3	175.4	175.4
499.0	192.2	192.5

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

T K	Heat capacity C _p ^o	Entropy S _p ^o	Enthalpy function (H _p ^o - H ₂₉₈ ^o)/T	Gibbs energy function -(G _p ^o - H ₂₉₈ ^o)/T	Formation from elements	
					Enthalpy	Gibbs free energy
			J/(mol·K)		kJ/mol	
298.15	103.85	87.40	0.000	87.40	-826.230	-744.273
Uncertainty		0.21	—	0.21	1.250	1.250
400	120.91	120.50	28.800	91.70	-824.560	-716.489
500	131.39	148.69	48.338	100.35	-822.155	-689.720
600	139.01	173.34	62.833	110.51	-819.478	-663.476
700	146.53	195.33	74.241	121.09	-816.703	-637.746
800	156.06	215.48	83.844	131.64	-813.875	-612.367
900	169.20	234.58	92.556	142.02	-810.949	-587.293
950	177.51	243.81	96.224	147.59	-809.326	-575.339
950	151.69	245.76	98.168	147.59	-807.478	-575.339
1000	148.49	252.71	100.551	152.16	-808.590	-562.544
1100	143.55	266.61	104.666	161.94	-810.813	-537.791
1200	140.74	278.96	107.772	171.19	-811.736	-513.004
1300	140.07	290.18	110.267	179.91	-809.958	-488.255
1400	141.42	300.60	112.429	188.17	-808.365	-463.613
1500	144.64	310.45	114.459	195.99	-806.666	-438.989
1600	149.58	319.93	116.489	203.44	-804.766	-414.561
1700	156.06	329.19	118.618	210.57	-804.839	-390.174
1800	163.95	338.32	120.909	217.41	-802.719	-365.757

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 f_{O_2} .

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 f_{O_2} . 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., Lindsley, 1976).

Oxidation of magnetite to form hematite appears to be a two-step process, regardless of the temperature of oxida-

tion (Davis et al., 1968). Step 1 involves the formation of a solid solution of Fe₂O₃ in magnetite (M_{ss}) 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 f_{O_2} associated with the magnetite-hematite equilibrium. M_{ss} 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 M_{ss} undergoes disproportionation to Fe₃O₄ and Fe₂O₃, which promotes nucleation and growth of hematite (Columbo et al., 1965). At temperatures greater than 1150 to 1200 K, stability of M_{ss} 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 f_{O_2} . 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 M_{ss} 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 ± 1.25 and -744.273 ± 1.25 kJ/mol, 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 ($6 \text{ hematite} = 4 \text{ magnetite} + O_2$) may be calculated from the following equations: $\Delta_r G_T^\circ = 501.348 - 0.2854T$ (range 1100–1600 K, average deviation of fit is 0.4%), $\Delta_r G_T^\circ = 514.690 - 0.29753T$ (range 700–1100 K, average deviation of fit is 0.2%), and $\Delta_r G_T^\circ = 496.215 - 0.27114T$ (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 M_{ss} 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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