American Mineralogist, Volume 69, pages 349–357, 1984

Heat capacities and entropies of rhodochrosite ($MnCO_3$) and siderite ($FeCO_3$) between 5 and 600 K

RICHARD A. ROBIE, H. T. HASELTON, JR. AND BRUCE S. HEMINGWAY

U.S. Geological Survey, Reston, Virginia 22092

Abstract

The heat capacities of rhodochrosite from Alma, Colorado, having the composition $(Mn_{0.994}Fe_{0.005}Mg_{0.001})CO_3$ and siderite of composition $(Fe_{0.956}Mn_{0.042}Mg_{0.002})CO_3$ were measured between 5 and 550 K by combined cryogenic-adiabatic and differential scanning calorimetry. Rhodochrosite has a λ-type transition in C_p° at 34.27±0.05 K, and siderite has a similar heat-capacity anomaly at 39.71±0.03 K, arising from the antiferromagnetic ordering of the magnetic moments of the Mn^{2+} and Fe^{2+} ions, respectively. At 298.15 K, the heat capacity and entropy of rhodochrosite are 80.62±0.10 and 98.03±0.10 J/(mol · K), respectively. For siderite, the equivalent values are 82.44±0.10 and 95.47±0.15 J/(mol · K). Between 298.15 and 600 K, the heat capacity of rhodochrosite measured by differential scanning calorimetry may be represented by the equation

$$C_p^\circ = 149.70 + 0.01876T - 1314.2T^{-.5} + 1.417 \times 10^5T^{-2}$$

to ±0.3%, for the same temperature range, the heat capacity of siderite is

$$C_p^\circ = 257.38 - 0.04620T - 3081.9T^{-.5} + 1.523 \times 10^6T^{-2}$$

also with an average deviation of 0.3%. When we combine our entropy data with extant equilibrium decomposition and aqueous solubility studies, we obtain $\Delta H^\circ_{f,298} = -891.91\pm0.52$ kJ/mol and $\Delta G^\circ_{f,298} = -818.13\pm0.55$ kJ/mol for rhodochrosite.

Introduction

Rhodochrosite and siderite are important sources of manganese and iron respectively. They also occur as common primary gangue minerals in many hydrothermal vein deposits and in some high-temperature metasomatic ore deposits. Equilibria involving these phases are found in many geochemical problems; accordingly, accurate values for their entropies and Gibbs free energies of formation are highly desirable.

Previous attempts by Kelley and Anderson (1935), Robie (1965), and Wagman and others (1969) to reconcile the results of various equilibrium and calorimetric studies on these carbonates have been hindered by the lack of accurate values for the entropies and heat capacities of these phases. Earlier measurements of the low-temperature heat capacities of rhodochrosite and siderite were made by Anderson (1934) between 54 and 297 K, by Kalinkina (1963) between 1.6 and 70 K, and by Kostryakov and Kalinkina (1964) from 70 to 300 K. Moore (1943) has measured the heat content, $H^\circ_T - H^\circ_{298}$, of rhodochrosite at 9 temperatures between 419 and 660 K.

In order to obtain accurate values for their entropies as a function of temperature for use in thermodynamic equilibrium calculations, we have measured the heat capacities of rhodochrosite and siderite by adiabatic calorimetry from 5 to 380 K, and by differential scanning calorimetry in the temperature range 350 to 550 K.

The low-temperature heat capacities of rhodochrosite and siderite are also of interest from a purely physical point of view. Although they are isostructural, the magnetic spin structures of rhodochrosite and siderite below their paramagnetic to antiferromagnetic transition temperatures (Néel temperature, T_N) at 34.3 and 39.7 K, respectively, differ; consequently, $MnCO_3$ becomes weakly ferromagnetic at temperatures below 20 K, whereas $FeCO_3$ remains totally antiferromagnetic below T_N.

We have used our new heat capacity and entropy values for rhodochrosite to reanalyze the high-temperature equilibrium data obtained by Goldsmith and Graf (1957) and Huebner (1969) and the aqueous-solubility results of Garrels et al. (1960) to obtain more accurate values for the enthalpy and Gibbs energy of formation.

Materials

Rhodochrosite ($MnCO_3$)

The rhodochrosite was a coarse-grained polycrystalline mass of transparent to transluscent crystals from Alma, Colorado (USNM no. R-2478). It also contained seams of fine-grained sericite and minor amounts of purple fluorite and chalcopyrite as distinct crystals. Kosnar (1979) has described the mineralogy of the Home Sweet Home Mine at Alma, Colorado, which is probably the source of these rhodochrosite crystals.

The material was crushed into cleavage fragments having a maximum dimension of 5 mm and handpicked free of impurity phases under a binocular microscope. Material less than 35 mesh (0.42 mm) was discarded. The sample was washed in hot 4N HC1 for 2 minutes, rinsed several times in distilled water, and dried at 110°C. An analysis of material from the same hand specimen was provided by J. S. Huebner and is given in column 2 of Table 1. The calculated composition is $(Mn_{0.994}Fe_{0.005}Mg_{0.001})CO_3$.

Siderite *($FeCO_3$)*

The siderite sample was obtained from Research Organic/Inorganic Chemical Company and was labeled "ferrous carbonate-ultra pure." This material was sieved, and the material passing through a 200 mesh screen (i.e., less than 0.075 mm) was discarded. The remaining material was passed thru a Franz magnetic separator 5 times and finally handpicked under a binocular microscope. The resultant sample was approximately 99 percent single-phase siderite and had the composition $(Fe_{0.956}Mn_{0.042}Mg_{0.002})CO_3$. A chemical analysis of this material is given in column 4 of Table 1.

Experimental measurements

Heat capacity measurements were made by means of the intermittent heating method under quasi-adiabatic conditions, using the cryostat described by Robie and Hemingway (1972) and the calorimeter and data acquisition system described by Robie et al. (1976, 1978). For the measurements on rhodochrosite, the low-temperature calorimeter was converted to fully automatic operation (Hemingway *et al.*, 1984). The samples were sealed in the calorimeter under pure helium gas at a pressure of 5 kPa (approximately 4 × 10^{-5} mole) of He.

Our experimental heat capacity measurements on rhodochrosite and siderite obtained by adiabatic calorimetry are listed in their chronological order of measurement in Tables 2 and 3, respectively, and are shown graphically in Figures 1 and 2. The formula weights used were based on the 1975 values for the atomic weights and are 114.947 and 115.856 g/mol for $MnCO_3$ and $FeCO_3$, respectively. The sample weights, corrected for buoyancy, used in our low-temperature measurements were 42.012 and 48.955 g for $MnCO_3$ and $FeCO_3$, respectively.

Table 1. Chemical analysis of rhodochrosite and siderite samples used for heat-capacity measurements

	1	2	3	4
Fe_2O_3	—	—	—	59.8
FeO	—	0.30	62.01	—
MgO	—	0.04	—	0.11
CaO	—	0.00	—	0.05
Na_2O	—	—	—	0.08
MnO	61.71	61.11	—	2.6
CO_2	38.29	38.50	37.99	37.5
	100.00	99.95	100.00	100.14

1. $MnCO_3$
2. Rhodochrosite calorimetry sample Alma, Colorado, USNM (U.S. Natl. Museum) No. R-2478, U.S. Geol Survey analysis 68-Wo-9, analyst J.R. Fahey.
3. $FeCO_3$
4. Siderite calorimetry sample Research Organic/ Inorganic Chemical Co., Fe-85, U.S. Geol. Survey analysis W-209826: analysts Z. Hamlin, and J. Marinenko.

Table 2. Experimental molar heat capacities of rhodochrosite crystals from Alma, Colorado

Temp. K	Heat capacity J/(mol·K)	Temp. K	Heat capacity J/(mol·K)	Temp. K	Heat capacity J/(mol·K)
Series 1		Series 4		Series 5	
5.38	0.6072	34.28	29.24	210.02	66.53
6.04	0.9112	34.53	18.68	215.48	67.55
6.56	1.165	34.70	17.14	220.93	68.38
7.30	1.558	34.90	15.91	226.38	69.35
8.16	2.116	35.10	15.32	231.84	70.43
9.00	2.651	35.31	14.74	237.30	71.28
9.91	3.241	35.52	13.95	242.75	72.08
10.82	3.776	35.74	13.16	248.18	73.24
11.71	4.317	36.17	12.89	253.61	73.86
12.90	4.963	36.39	12.39	259.05	74.83
14.35	5.776	36.61	12.94	264.47	76.27
15.80	6.567	36.82	12.36	269.86	77.08
17.30	7.367	37.04	12.06	275.27	77.46
18.79	8.185	37.26	11.94	280.66	78.33
20.27	9.043	37.47	11.80	286.01	78.76
22.15	10.18	38.31	11.41	291.34	79.67
24.53	11.83	40.10	11.05	296.66	80.38
27.12	14.01	42.20	11.12	301.95	81.29
30.01	17.24	44.31	11.48	307.23	81.78
33.22	22.19	46.47	11.97	312.47	82.46
38.32	12.01	48.66	12.62	317.70	83.13
44.31	11.47	50.86	13.45	322.91	83.88
48.56	12.61	53.06	14.09	328.10	84.50
		55.29	14.77		
Series 2		59.30	16.34	Series 6	
		65.00	19.48		
4.51	0.2017	70.78	22.78	332.85	85.10
4.81	0.3780	76.86	25.83	337.93	85.79
4.99	0.5441	83.02	28.74	342.87	86.30
5.63	0.7206	89.13	31.59	347.84	87.04
6.51	1.164	95.23	34.34	352.96	87.57
7.29	1.594	101.30	36.94	358.06	88.02
8.21	2.127	107.33	39.41	363.15	88.63
9.16	2.724	113.31	41.71	368.22	89.33
		119.24	43.82	373.28	89.90
Series 3		125.15	45.74	378.32	90.69
		131.02	47.72		
31.98	20.40	136.88	49.58	Series 7	
32.42	21.37	142.71	51.26		
32.87	22.08	148.53	52.91	310.50	82.50
33.41	23.62	154.32	54.37	319.52	83.52
33.94	25.99	160.09	55.73	323.77	84.04
34.55	20.05	165.84	57.16	328.69	84.78
35.27	14.56	171.57	58.62	333.62	85.28
35.89	13.33	177.30	59.76	343.78	86.55
36.35	12.72	183.01	60.96	348.92	87.13
Series 4		Series 5		Series 8	
33.55	23.96	188.62	62.30	303.09	81.38
33.65	24.46	194.11	63.36	305.62	81.93
33.94	25.83	199.31	64.44	307.88	81.91
34.06	27.18	204.54	65.41	310.15	82.38
34.17	27.93				

Table 3. Experimental specific heats of siderite

Temp. K	Specific heat J/(g·K)	Temp. K	Specific heat J/(g·K)	Temp. K	Specific heat J/(g·K)
Series 1		Series 7		Series 12	
300.06	0.7125	222.09	0.6089	35.29	0.1458
305.01	0.7185	227.95	0.6177	36.47	0.1647
310.12	0.7243	234.09	0.6269	37.42	0.1832
315.42	0.7306			37.99	0.1968
320.78	0.7367	Series 8		38.32	0.2064
326.22	0.7429			38.78	0.2230
331.70	0.7493	239.15	0.6342	39.24	0.2475
337.22	0.7554	245.19	0.6430	40.21	0.1302
		251.10	0.6518	40.91	0.1071
Series 2		256.95	0.6602	41.65	0.1035
		262.71	0.6687	42.39	0.1026
52.97	0.1373	268.42	0.6765		
58.46	0.1624	274.06	0.6810	Series 13	
63.30	0.1849				
68.22	0.2076	Series 9		39.30	0.2511
73.46	0.2316			39.35	0.2549
78.89	0.2558	279.50	0.6890	39.40	0.2599
84.48	0.2795	285.05	0.6954	39.45	0.2616
89.99	0.3018	290.54	0.7025	39.48	0.2620
95.47	0.3227	295.99	0.7085		
		301.40	0.7150	Series 14	
Series 3					
		Series 10		39.53	0.2744
101.05	0.3428			39.59	0.2799
106.40	0.3609	5.95	0.000163	39.66	0.2912
111.63	0.3779	6.92	0.000254		
116.96	0.3943	7.56	0.000428	Series 15	
122.46	0.4103	8.34	0.000699		
127.97	0.4256	9.15	0.001418	46.54	0.1105
133.49	0.4400	10.42	0.002356	49.45	0.1218
		11.71	0.003445		
Series 4		12.98	0.004883	Series 16	
		14.39	0.007053		
139.02	0.4538	15.93	0.01017	39.58	0.2783
144.42	0.4666	17.59	0.01449	39.62	0.2843
149.86	0.4791	19.35	0.02032	39.66	0.2876
155.36	0.4910	21.29	0.02828	39.69	0.2961
		23.54	0.03950	39.71	0.3056
Series 5		25.63	0.05208	39.85	0.2074
		27.87	0.06796		
160.56	0.5019	30.75	0.09262	Series 17	
166.09	0.5131	33.47	0.1218		
171.85	0.5244	36.29	0.1620	342.00	0.7608
177.50	0.5351	43.80	0.1072	348.20	0.7672
183.05	0.5452			354.59	0.7739
188.50	0.5550	Series 11		367.05	0.7869
				373.26	0.7925
Series 6		4.98	0.000079		
		5.45	0.000167		
194.09	0.5645	6.04	0.000224		
199.73	0.5740	7.00	0.000277		
205.24	0.5828	7.70	0.000504		
210.82	0.5916	8.62	0.001119		
216.49	0.6021	9.78	0.001909		
		10.92	0.002721		
		12.12	0.003874		
		13.47	0.005568		

Specific heat data for $MnCO_3$ and $FeCO_3$ obtained by differential scanning calorimetry in the temperature interval 350 to 550 K are listed in Table 4. The operation and calibration of the scanning calorimeter have been discussed previously by Krupka et al. (1979). For our measurements, the samples were encapsulated in gold sample pans. We used a heating rate of 10 K/min and a range setting of 2.5 J/min; sample weights were 28.87 and 34.57 mg for rhodochrosite and siderite, respectively. The adiabatic calorimetry measurements have a precision of ±0.06% above 25 K, whereas those obtained by means of

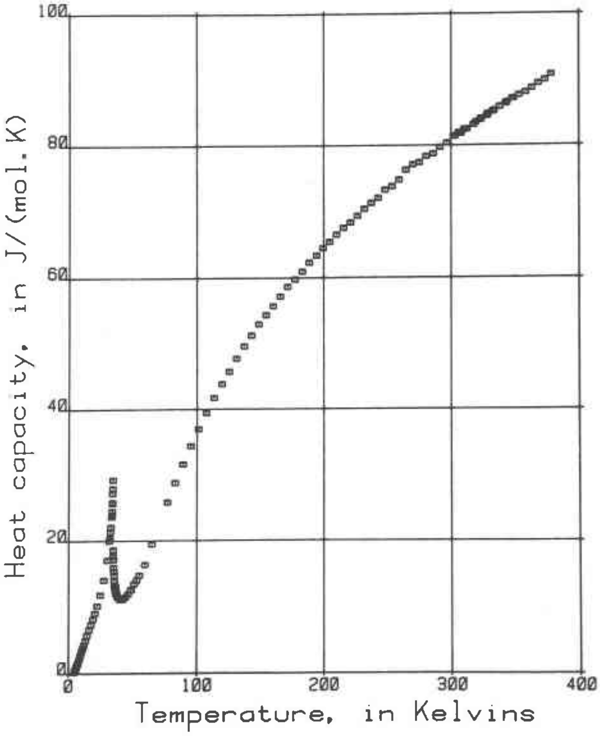

Fig. 1. Experimental heat capacities of 114.947 g of rhodochrosite from Alma, Colorado, having the composition $(Mn_{0.994}Fe_{0.005}Mg_{0.001})CO_3$.

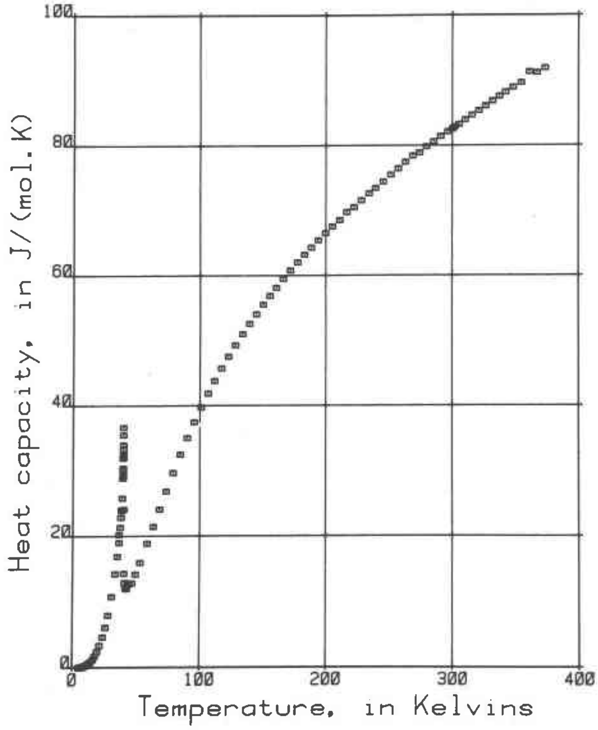

Fig. 2. Experimental heat capacities of 115.586 g of siderite of the composition $(Fe_{0.956}Mn_{0.04}Mg_{0.002})CO_3$.

Table 4. Experimental specific heats of siderite and rhodochrosite measured by differential scanning calorimetry

Temp. K	C_p° J/(g·K)	Temp. K	C_p° J/(g·K)
Series 1		Series 2	
Siderite			
339.8	.7445	339.8	.7565
349.8	.7573	349.8	.7671
359.9	.7695	359.9	.7761
369.9	.7797	369.9	.7854
379.9	.7906	379.9	.7931
389.9	.8000	389.9	.8037
399.9	.8096	399.9	.8123
409.9	.8187	409.9	.8210
419.9	.8271	419.9	.8292
429.9	.8346	429.9	.8389
439.9	.8428	439.9	.8448
449.9	.8494	449.9	.8536
Rhodochrosite			
350	.7466	420	.8168
360	.7570	430	.8257
370	.7685	440	.8343
380	.7773	450	.8430
390	.7872	460	.8509
400	.7979	470	.8602
410	.8068	480	.8657
420	.8347	490	.8717
430	.8243	500	.8804
440	.8324	510	.8860
450	.8411	520	.8921
460	.8498	530	.8969
470	.8586	540	.9012
		550	.9063

the differential scanning calorimeter have a precision of ±1.0%. Our experimental results for siderite are reported as specific heats because of the small deviations of our samples from exact stoichiometry.

Rhodochrosite as a sharp λ-type anomaly in C_p° with a maximum at 34.27±0.05 K (T_N) and also a "broad shoulder" in the heat capacity in the range 7 to 16 K (see Figure 3). At T_N, C_p° is 29.5 J/(mol · K) and decreases precipitously to 14 J/(mol · K) at 36 K. The λ anomaly arises from the antiferromagnetic ordering of the magnetic moments of the Mn^{2+} ions below T_N. The broad maximum is presumably related to the slight canting of the magnetic moments on the four magnetic sublattices away from exact antiparallelism (Alikhanov (1959) and Brown and Forsyth (1967)), which causes $MnCO_3$ to become weakly ferromagnetic at temperatures below about 20 K.

The heat capacity of $MnCO_3$ was previously measured by Anderson (1934) between 55.3 and 296.8 K on material of composition $(Mn_{0.979}Ca_{0.020}Fe_{0.001})CO_3$ and by Kalinkina (1963) between 1.6 and 70 K. Our values are 2% larger than Anderson's (1934) at 55 K and 1% less than his at 300 K. Anderson's (1934) *measured* entropy increment ($S_{298.1}^\circ - S_{56.2}^\circ$) and our equivalent value agree to 0.5%. Kalinkina gave only a graph of his data and a temperature of 29.4 K for the Néel temperature. Kostryakov and Kalinkina (1964) reported S_{298}° = 112.9 J/(mol · K) obtained by combining their C_p° data for the range 70 to 298 K with the earlier results of Kalinkina. This result is 15% larger than our value, 98.03±0.10 J/(mol · K).

Siderite has a sharp λ-type anomaly in the heat capacity at 39.71±0.03 K corresponding to the paramagnetic to antiferromagnetic transition (see Fig. 3). The heat capacity of siderite was measured at 13 temperatures by Anderson (1934) on material with a composition of $(Fe_{0.883}Mn_{0.052}Mg_{0.046}Ca_{0.019})CO_3$ Anderson's measurements covered only the temperature range 54 to 297 K; thus, his calculated entropy value at 298.15 K did not include the magnetic contribution. Anderson's C_p° values average 1.5% greater than ours between 55 and 280 K, above which they cross over and become smaller than ours by 0.4%. The measurements by Kalinkina (1963), on a sample described as "97%-pure natural siderite," gave a Néel temperature of 30.6 K. Kostryakov and Kalinkina (1964) reported a value for S_{298}° of 96.1 J/(mol · K) based on Kalinkina's measurements between 1.6 and 70 K and their own from 70 to 298 K. Neither of these reports presented numerical values for the C_p° results. Kostryakov and Kalinkina's entropy at 298 K for siderite is in good agreement with our value, 95.29±0.20 J/(mol · K).

Inasmuch as we wished to utilize the high-temperature equilibrium studies on the stability of rhodochrosite and siderite to derive values for the Gibbs free energies of

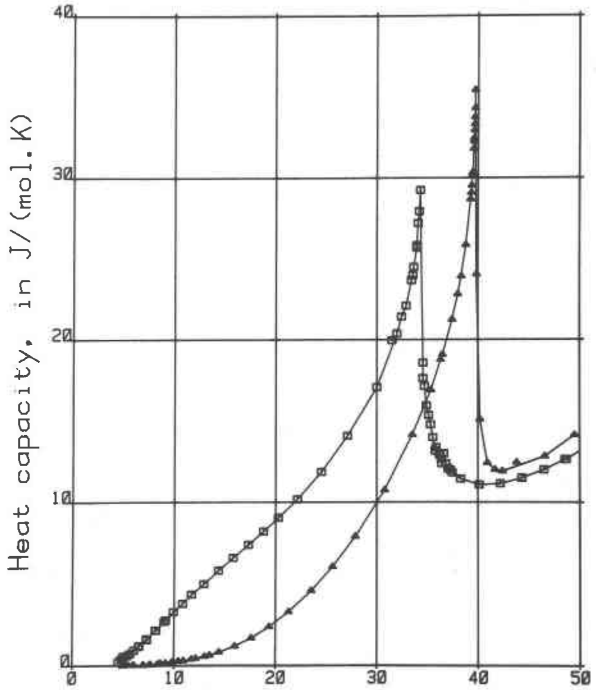

Fig. 3. Molar heat capacities of $MnCO_3$ (squares) and $FeCO_3$ (triangles) in the region of the λ transition.

formation of these carbonates, we also measured the heat capacities of rhodochrosite and siderite between 350 and 550 K by differential scanning calorimetry. Rhodochrosite can be represented between 350 and 600 K by the equation

$$C_p^\circ = 149.70 + 0.01876T - 1314.2T^{-.5} + 1.417 \times 10^5 T^{-2}$$

with an average deviation of 0.3%, and siderite over the same temperature range by

$$C_p^\circ = 257.38 - 0.04620T - 3081.9T^{-.5} + 1.523 \times 10^6 T^{-2}$$

also with an average deviation of 0.3%. Our C_p° data suggest the beginning of decomposition of siderite between 500 and 550 K.

Table 5. Molar thermodynamic properties of $MnCO_3$. [Formula weight = 114.947 g mol^{-1}]

Temp.	Heat capacity	Entropy	Enthalpy function	Gibbs energy function
T	C_P°	$S_T^\circ - S_0^\circ$	$(H_T^\circ - H_0^\circ)/T$	$-(G_T^\circ - H_0^\circ)/T$
Kelvin		J/(mol·K)		
5	0.499	0.163	0.116	0.047
10	3.273	1.270	0.936	0.334
15	6.134	3.156	2.206	0.950
20	8.909	5.300	3.533	1.766
25	12.22	7.622	4.921	2.702
30	17.08	10.24	6.505	3.735
35	18.52	13.47	8.581	4.887
40	11.08	15.10	9.033	6.069
45	11.60	16.44	9.291	7.146
50	13.02	17.72	9.585	8.139
60	17.33	20.46	10.50	9.961
70	22.34	23.50	11.83	11.67
80	27.33	26.82	13.46	13.36
90	32.03	30.31	15.26	15.05
100	36.38	33.91	17.16	16.75
110	40.40	37.57	19.09	18.48
120	44.07	41.25	21.02	20.22
130	47.42	44.91	22.93	21.98
140	50.48	48.54	24.79	23.75
150	53.24	52.12	26.60	25.52
160	55.77	55.63	28.34	27.29
170	58.16	59.09	30.02	29.06
180	60.40	62.47	31.65	30.82
190	62.54	65.80	33.22	32.58
200	64.56	69.06	34.74	34.32
210	66.47	72.25	36.20	36.05
220	68.28	75.39	37.62	37.77
230	70.03	78.46	38.99	39.47
240	71.74	81.48	40.32	41.16
250	73.45	84.44	41.61	42.83
260	75.18	87.36	42.87	44.49
270	76.80	90.23	44.10	46.13
280	78.20	93.04	45.29	47.75
290	79.52	95.81	46.45	49.36
300	80.87	98.53	47.57	50.96
310	82.18	101.2	48.67	52.53
320	83.47	103.8	49.74	54.10
330	84.75	106.4	50.78	55.64
340	85.99	109.0	51.79	57.17
350	87.18	111.5	52.79	58.69
360	88.34	114.0	53.76	60.19
370	89.55	116.4	54.71	61.68
273.15	77.26	91.12	44.48	46.64
298.15	80.62	98.03	47.37	50.66

Thermodynamic properties

Our experimental heat capacity data (corrected for curvature) were corrected for deviations from the exact compositions of $MnCO_3$ and $FeCO_3$ by assuming that the impurities are present as carbonates and by using the C_p° data of Hemingway et al. (1977) for $MgCO_3$ and of Staveley and Linford (1969) for $CaCO_3$. The corrections to C_p° for deviations from exact stoichiometry had a maximum value of 0.05% for the $MnCO_3$ sample and 0.4% for $FeCO_3$. The corrected values were extrapolated to 0 K by using a plot of C_p°/T versus T^2, and the combined data were smoothed by computer by using the orthogonal polynomial program of Justice (1969). The derived thermodynamic functions C_p°, $S_T^\circ - S_0^\circ$, $H_T^\circ - H_0^\circ$, and $-(G_T^\circ - H_0^\circ)/T$ are listed in Tables 5 and 6 for temperatures between 5 and 380 K. At 298.15 K, the heat capacity and entropy of $MnCO_3$ are 80.62±0.10 and 98.03±0.10 J/(mol · K) respectively. For siderite, the equivalent values are 82.44±0.10 and 95.47±0.15 J/(mol · K).

Robie (1965) obtained 110.54±0.63 kJ for the enthalpy of the reaction

$$MnCO_3 = MnO + CO_2 \qquad (1)$$

on the basis of the equilibrium data obtained by Goldsmith and Graf (1957) and an estimate for the entropy of $MnCO_3$, which included an estimate of the magnetic contribution to S_{298}°. We have repeated this calculation, using our more accurate *measured* entropy and high-temperature heat capacity values for $MnCO_3$. We have also included the data of Huebner (1969) for this equilibrium, data that were obtained by a totally different experimental procedure than that used by Goldsmith and Graf (1957). We used the relation (Robie, 1965)

$$-\Delta H_{298}^\circ/T = \Delta[(G_T^\circ - H_{298}^\circ)/T] + (P - 1)\,\Delta V_{298}^\circ/T + R\ln f_{CO_2} \qquad (2)$$

to calculate a value of ΔH_{298}° for reaction (1) from *each* equilibrium point (or bracket). In (2) the bracketed term is calculated from

$$(H_T^\circ - H_{298}^\circ)/T - S_T^\circ \qquad (3)$$

and is obtained exclusively from heat capacity and/or heat content measurements; the ΔV_{298}° term refers to the solid phases only. The fugacity of CO_2 was calculated from the modified Redlich-Kwong equation given by Kerrick and Jacobs (1981). The calculations were made using the FORTRAN program FLUIDS of Jacobs and Kerrick (1981) after rewriting it in HPL for use on a Hewlett-Packard 9825[1] computer. We note in passing that over the temperature range of 600 to 1300 K and for pressures of 100 to 2000 bars, this equation gives values for the free energy of CO_2 that agree with those tabulated by Shmulovich and Schmonov (1978) and Bottinga and Richet (1981)

---

[1] Any use of trade names in this report is for descriptive purposes only and does not constitute endorsement by the U.S. Geological Survey.

Table 6. Molar thermodynamic properties of $FeCO_3$. [Formula weight = 115.856 g mol^{-1}]

Temp.	Heat capacity	Entropy	Enthalpy function	Gibbs energy function
T	C_P°	$S_T^\circ - S_0^\circ$	$(H_T^\circ - H_0^\circ)/T$	$-(G_T^\circ - H_0^\circ)/T$
Kelvin	J/(mol·K)			
5	0.012	0.004	0.003	0.001
10	0.236	0.050	0.040	0.010
15	0.953	0.255	0.203	0.052
20	2.649	0.732	0.576	0.156
25	5.576	1.612	1.260	0.352
30	9.935	2.988	2.318	0.669
35	16.46	4.967	3.833	1.134
40	22.86	7.980	6.197	1.783
45	12.70	9.418	6.866	2.552
50	14.48	10.81	7.505	3.308
60	19.79	13.92	9.109	4.809
70	25.12	17.37	11.02	6.354
80	30.27	21.06	13.10	7.959
90	35.03	24.91	15.28	9.628
100	39.38	28.83	17.47	11.35
110	43.31	32.77	19.65	13.12
120	46.84	36.69	21.77	14.92
130	50.05	40.57	23.82	16.74
140	52.96	44.38	25.80	18.58
150	55.64	48.13	27.70	20.43
160	58.12	51.80	29.53	22.27
170	60.44	55.40	31.28	24.12
180	62.63	58.91	32.96	25.95
190	64.69	62.36	34.58	27.78
200	66.64	65.72	36.13	29.59
210	68.50	69.02	37.63	31.39
220	70.31	72.25	39.07	33.18
230	72.05	75.41	40.47	34.94
240	73.75	78.52	41.82	36.69
250	75.43	81.56	43.13	38.43
260	77.04	84.55	44.4[illegible]	40.15
270	78.56	87.49	45.64	41.84
280	80.00	90.37	46.84	43.53
290	81.36	93.20	48.01	45.19
300	82.69	95.98	49.14	46.84
310	84.01	98.72	50.25	48.47
320	85.34	101.4	51.32	50.08
330	86.66	104.0	52.37	51.67
340	87.95	106.7	53.40	53.25
350	89.19	109.2	54.41	54.82
360	90.39	111.8	55.39	56.36
370	91.55	114.2	56.35	57.89
380	92.67	116.7	57.29	59.41
273.15	79.02	88.40	46.02	42.38
298.15	82.44	95.47	48.94	46.53

to better than 650 joules/mol. The use of equation (2), known also as the "third-law method," is predicated on the fact that the term $\Delta[(G_T^\circ - H_{298}^\circ)/T]$ is a very slowly varying function of temperature and may therefore be extrapolated above the limits of the measured heat capacities without introduction of significant error. For reaction (1), this term varies by less than 1.0% between 298 and 800 K. Numerical details of the calculation are listed in Table 7. The derived values for $\Delta H_{r,298}^\circ$, based on data over a range of 400 K and four orders of magnitude in P_{CO_2}, show no systematic variation with equilibrium temperature and yield -113.18 ± 0.16 kJ. When combined with the $\Delta H_{f,298}^\circ$ of MnO and CO_2 and the entropies of Mn, C, and O_2 from Robie et al. (1979), we obtain $\Delta H_{f,298}^\circ = -891.91 \pm 0.52$ kJ/mol and $\Delta G_{f,298}^\circ = -818.13 \pm 0.55$ kJ/mol for $MnCO_3$.

An independent check on the value of $\Delta G_{f,298}^\circ$ for $MnCO_3$ is possible by utilizing aqueous solubility data. The solubility of $MnCO_3$ in H_2O under various CO_2 pressures has been measured by Ageno and Valla (1911), Haehnel (1924), Garrels et al. (1960), and Gamsjager et al. (1970). All these measurements were made on precipitated manganous carbonate with the exception of some experiments by Garrels et al. (1960), who also measured the solubility of a natural rhodochrosite (containing approximately 5 mole% of cations other than Mn^{2+}) and a crystalline $MnCO_3$ prepared in a salt bridge.

The Gibbs free energy of formation of $MnCO_3$ calculated from Garrels et al. (1960) data on natural rhodochrosite crystals is −818.8 kJ/mol and agrees well with the value calculated above from the high-temperature equilibrium studies by Goldsmith and Graf (1957) and by Huebner (1969). The solubility values of Ageno and Valla (1911), Haehnel (1924), and Gamsjager et al. (1970), which were all obtained on *precipitated* $MnCO_3$, yield $\Delta G_{f,298}^\circ$ values in the range of −809.0 to −812.1 kJ/mol, whereas the value of Garrels et al. (1960) for "better crystallized synthetic rhodochrosite" grown in a salt bridge leads to $\Delta G_{f,298}^\circ = -814.6$ kJ/mol. Obviously, accurate solubility data for pure synthetic crystals of $MnCO_3$ are highly desirable.

The Gibbs free energy of formation of siderite can be calculated from the aqueous solubility measurements of Smith (1918), Langmuir (1969), and Hepler (written comm., Dec. 1980). These results lead to $\log K_{sp} = -10.60 \pm 0.05$ or $\Delta G_{298}^\circ = 60.50 \pm 0.30$ kJ for the reaction

$$FeCO_3 = Fe^{2+} + CO_3^{2-}. \quad (4)$$

Using $\Delta G_{f,298}^\circ = -527.90 \pm 0.12$ kJ/mol for CO_3^{2-} from Wagman et al. (1969) and -9.63 ± 0.50 kJ/mol for Fe^{2+}

Table 7. "Third-law" calculation of $\Delta H_{r,298}$ for the reaction $MnCO_3 = MnO + CO_2$ from the equilibrium measurements of Goldsmith and Graf (1957) and Huebner (1969)

T	P	$\Delta(G_T^\circ - H_{298}^\circ)/T$	$(P-1)\Delta V_{298}^\circ/T$	f_{CO_2}	$R\ln f_{CO_2}$	$\Delta H_{r,298}^\circ$
K	bars	J/K	J/K	bars	J/K	kJ
Data of Goldsmith and Graf (1957)						
649	1	-174.53	-0.000	1	0	-113.27
783	34	-173.84	-0.075	34	29.32	-113.22
836	103	-173.56	-0.218	104	38.60	-113.01
908	350	-173.18	-0.686	372	49.21	-113.19
959	681	-172.92	-1.266	798	55.56	-113.76
1012	1378	-172.64	-2.429	2035	63.34	-113.07
1050	1996	-172.44	-3.392	3629	68.15	-113.07
Data of Huebner (1969)						
979	973	-172.81	-1.772	1254	59.31	-112.85
1020	1500	-172.60	-2.624	2309	64.39	-113.05
1051	1973	-172.44	-3.350	3559	67.98	-113.31
$\Delta V_{298}^\circ = -1.785$ J/bar				Average ΔH_{298}° =		-113.18 kJ ± 0.16

from Larson et al. (1968) and Sweeton and Baes (1970), we calculate $\Delta G^\circ_{f,298}$ + -680.03 ± 0.60 kJ/mol for siderite, and using our entropy value and those of Robie et al. (1979) for Fe, C, and O_2, we calculate -753.22 ± 0.61 kJ/mol for $\Delta H^\circ_{f,298}$. French (1971) and Weidner (1972) have studied the equilibrium

$$6FeCO_3 = 2Fe_3O_4 + 5CO_2 + C \qquad (5)$$

at temperatures between 450° and 760°C. Inasmuch as the Gibbs free energies of formation of Fe_3O_4 and CO_2 are accurately known, we wish to use these high-temperature equilibrium studies together with our high-temperature C°_p data in an attempt to confirm the $\Delta G^\circ_{f,298}$ value for siderite obtained from the solubility data. Unfortunately, these two high-temperature equilibrium studies differ significantly; they also differ from the stability of $FeCO_3$ obtained from the solubility measurements. Furthermore, they imply a ΔS°_T for the reaction considerably different from that obtained by the much more accurate and direct ΔS°_T obtained from the heat capacity measurements. I-Ming Chou (private comm., June 1983, and ms.) has reinvestigated the reaction $3FeCO_3 + 1/2O_2 = Fe_3O_4 + 3CO_2$ along the magnetite–hematite buffer. The data represent only the decomposition of $FeCO_3$. It should therefore be considered only as an upper stability limit for siderite. Chou's curve is in reasonable agreement with the uppermost (2000 bar) point of French (1971). The method of preparation of the $FeCO_3$ used for the solubility studies made by Smith (1918) probably resulted in an extremely fine-grained product; accordingly, the value of $\Delta G^\circ_{f,298}$ calculated from these data would be too positive. Based upon these considerations we assume that the solubility data represent a lower limit for the stability of siderite and that the decomposition studies of Chou are an upper bound. Therefore we believe $\Delta G^\circ_{f,298}$ for siderite should fall within the limits -680.0 to -685.5 kJ/mol. The corresponding (limiting) values for $\Delta H^\circ_{f,298}$ are -753.1 and 758.6 kJ/mol. We are unable to explain the cause of this discrepancy and until a direct calorimetric determination of ΔH°_f for $FeCO_3$ is available we suggest an average value of -682.8 ± 5.5 kJ/mol for $\Delta G^\circ_{f,298}$.

Magnetic heat capacities and entropies of $MnCO_3$ and $FeCO_3$

At temperatures below the respective maxima in C°_p, the magnetic moments (spins) of the Fe^{2+} ions in $FeCO_3$ are aligned, antiferromagnetically, parallel to the $\bar{3}$ axis [111], whereas in $MnCO_3$ they are aligned, antiferromagnetically, normal to [111] (Alikhanov, 1959). $FeCO_3$ and $MnCO_3$ are isostructural with calcite, space group $R\bar{3}c$ (167), and their magnetic unit cells are the same as the X-ray unit cell. Dzyaloshinsky (1958) has shown that because of the alignment of the spins normal to [111] in $MnCO_3$ a weak ferromagnetism can be produced in the (111) plane because of the slight canting of the magnetic sublattices away from exact antiparallelism (see also Moriya, 1960). In $FeCO_3$, this is not possible because the spins are aligned parallel to [111], and any canting would violate the observed (magnetic) trigonal symmetry.

The region of the λ-transitions in $FeCO_3$ and $MnCO_3$ is seen in more detail in Figure 3, which shows that below T_N, the heat capacity of $MnCO_3$ decreases much less rapidly with temperature than does that of $FeCO_3$, even though they are isostructural, and that $FeCO_3$ and $MnCO_3$ differ by only 0.8% in their formula weights and differ by less than 6% in molar volumes. At 10 K, for example, $MnCO_3$ has a heat capacity almost 14 times that of $FeCO_3$. We suspect that this very large difference in C°_p is related to the canting of the spins in $MnCO_3$. A similar difference is observed between the heat capacities of Mn_2SiO_4 (Robie et al., 1982b) and Fe_2SiO_4 (Robie et al., 1982a), which are known to exhibit spin-canting at very low temperatures, and that of isostructural Co_2SiO_4 (Robie et al., 1982b) which remains exactly antiferromagnetically ordered at least down to 4.2 K. It seems unlikely that the difference in C°_p at $T < T_N$ for $FeCO_3$ and $MnCO_3$ could be accounted for in terms of the difference in the spin-wave contributions to C°_p (see for example, Gopal, 1966).

Our values for the Néel temperature obtained from C°_p measurements (to within 0.05 K of T_N) are 39.71 ± 0.03 and 34.27 ± 0.05 K for $FeCO_3$ and $MnCO_3$, respectively. These values are significantly higher than those obtained by Kalinkina (1963): 30.6 and 29.4 K for $FeCO_3$ and $MnCO_3$, respectively. These values may also be compared with Néel temperatures obtained from magnetic-susceptibility measurements. (Note that the Néel temperature obtained from susceptibility measurements, T'_N should be slightly higher than T_N (Carlin and van Duyneveldt, 1977, p. 123).

The magnetic susceptibility of rhodochrosite has been measured by Maartense (1969, 1971) and by Meijer et al. (1970). Maartense (1971) gives a value for T'_N of 34.5 ± 0.1 K from ac susceptibility measurements on 250-μm-sized synthetic crystals. Meijer et al. (1970) obtained T'_N = 32.55 and 32.69 K by static (dc) susceptibility measurements on rhodochrosite from Sonora, Mexico, containing appreciably less manganese than required by $MnCO_3$.

The Néel temperature of $FeCO_3$ was given as 38.4 ± 0.2 K by Forester and Koon (1969) from Mössbauer measurements on siderite that contained 4.5 atomic percent Mn. Ok (1969) obtained 38.5±.3 K and Jacobs (1963) 38.0 K on the basis of both powder and single-crystal susceptibilities on the Roxbury, Connecticut, siderite $(Fe_{0.83}Mn_{0.05}R_{0.12})CO_3$.

Acknowledgments

This work was supported by the U.S. Department of Energy through the Los Alamos Scientific Laboratory, contract X69-9915-F-3. We thank our U.S. Geological Survey colleagues for their many useful suggestions for improving the manuscript. We thank John S. White, Jr. of the U.S. National Museum of Natural History, Washington, D.C., for providing the samples of rhodochrosite from Alma, Colorado, and J.S. Huebner of the U.S. Geological Survey for the unpublished analysis of this material.

References

Ageno, F. and Valla, E. (1911) Contributo allo studio dell'idrolisi. I. Idrolisi dei carbonati. Atti Accademia dei Lincea, Ser. 5, 20:2, 706–712.

Alikhanov, R. A. (1959) Neutron diffraction investigation of the antiferromagnetism of the carbonates of manganese and iron. Journal of Experimental and Theoretical Physics, 9, 1204–1208. (Translation of Zhurnal eksperimental'noi i teoreticheski fiziki 36, 1690–1696, 1959.)

Anderson, C. T. (1934) The heat capacities of magnesium, zinc, lead, manganese and iron carbonates at low temperatures. Journal of the American Chemical Society, 56, 849–851.

Bottinga, Y. and Richet, P. (1981) High pressure and temperature equation of state and calculation of the thermodynamic properties of gaseous carbon dioxide. American Journal of Science, 281, 615–660.

Brown, P. J. and Forsyth, J. B. (1967) The spatial distribution of ferromagnetic moment in $MnCO_3$. Proceedings of the Physical Society, 92, 125–135.

Carlin, R. L. and van Duyneveldt, A. J. (1977) Magnetic Properties of Transition Metal Compounds. Springer-Verlag, New York.

Dzyaloshinsky, I. (1958) A thermodynamic theory of "weak" ferromagnetism of antiferromagnetics. Journal of the Physics and Chemistry of Solids, 4, 241–255.

Forester, D. W. and Koon, N. C. (1969) Mössbauer investigation of metamagnetic $FeCO_3$. Journal of Applied Physics, 40, 1316–1317.

French, B. M. (1971) Stability relations of siderite ($FeCO_3$) in the system Fe–C–O. American Journal of Science, 271, 37–78.

Gamsjager, H., Kraft, W., and Schindler, P. (1970) Zur Thermodynamik der Metallcarbonate. 4. Mitteilung. Potentiometrische Untersuchungen am System Mn^{2+}–CO_2–H_2O. Helvetica Chimica Acta, 53, 290–299.

Garrels, R. M., Thompson, M. E., and Siever, R. (1960) Stability of some carbonates at 25°C and one atmosphere total pressure. American Journal of Science, 258, 402–418.

Goldsmith, J. R. and Graf, D. L. (1957) The system CaO–MnO–CO_2: Geochimica et Cosmochimica Acta, 11, 310–333.

Gopal, E. S. R. (1966) Specific Heats at Low Temperatures. Plenum Press, New York.

Haehnel, O. (1924) Uber die Löslichkeit der Carbonate des Strontiums des Bariums und der Schwermetalle in Wasser unter hohen Kohlendioxyddrucken sowie über die Eigenschaften solcher Lösungen. Journal für Praktical Chemie, Ser 2, 108, 187–193.

Hemingway, B. S., Kittrick, J. A., Grew, E. S., Nelen, J. A., and London, D. (1984) The thermodynamic properties of two natural chlorites to 500 K, the heat capacities of osumilite from 298.15 to 1000 K and the thermodynamic properties of petalite to 1800 K. American Mineralogist, 69, in press.

Hemingway, B. S., Robie, R. A., Fisher, J. R., and Wilson, W. H. (1977) Heat capacities of gibbsite, $Al(OH)_3$, between 13 and 480K and magnesite, $MgCO_3$, between 13 and 380K and their entropies at 298.15K, and the heat capacities of Calorimetry Conference benzoic acid between 12 and 316K. U.S. Geological Survey Journal of Research, 5, 797–806.

Huebner, J. S. (1969) Stability of rhodochrosite in the system manganese-carbon-oxygen. American Mineralogist, 54, 457–481.

Jacobs, G. K. and Kerrick, D. M. (1981) APL and FORTRAN programs for a new equation of state for H_2O, CO_2 and their mixtures at supercritical conditions. Computers and Geosciences, 7, 131–143.

Jacobs, I. S. (1963) Metamagnetism of siderite ($FeCO_3$)*. Journal of Applied Physics, 34, 1106–1107.

Justice, G. H. (1969) Thermal data fitting with orthogonal functions and combined table generation. The FITAB program. U.S. Atomic Energy Commission COO-1149-143.

Kalinkina, I. N. (1963) Magnetic heat capacity of antiferromagnetic Co, Ni, Mn, and Fe carbonates: Journal of Experimental and Theoretical Physics, 16, 1432–1438. (Translation of Zhurnal eksperimental'roi i teoreticheski fiziki 43, 2028–2037, 1962.)

Kelley, K. K. and Anderson, C. T. (1935) Contributions to the data on theoretical metallurgy. IV. Metal carbonates-correlations and applications of thermodynamic properties: U.S. Bureau of Mines Bulletin 384.

Kerrick, D. M. and Jacobs, G. K. (1981) A modified Redlick-Kwong equation for H_2O, CO_2 and H_2O–CO_2 mixtures at elevated pressures and temperatures. American Journal of Science 281, 735–767.

Kosnar, R. A. (1979) The Home Sweet Home mine. Mineralogical Record, 10, 333–338.

Kostryakov, V. N. and Kalinkina, I. N. (1964) Heat capacity and entropy for manganese, iron, cobalt, and nickel carbonates at low temperatures. Zhurnal Fizicheskoi Khimii, 38, 780–781. (In Russian)

Krupka, K. M., Robie, R. A., and Hemingway, B. S. (1979) High-temperature heat capacities of corundum, periclase, anorthite, $CaAl_2Si_2O_8$ glass, muscovite, pyrophyllite, $KAlSi_3O_8$ glass, grossular, and $NaAlSi_3O_8$ glass. American Mineralogist, 64, 86–101.

Langmuir, D. (1969) The Gibbs free energies of substances in the system Fe–O_2–H_2O–CO_2 at 25°C. U.S. Geological Survey Professional Paper 650-B.

Larson, J. W., Cerutti, P., Garber, H. B., and Hepler, L. G. (1968) Electrode potentials and thermodynamic data for aqueous ions. Copper, zinc, cadmium, iron, cobalt, and nickel. Journal of Physical Chemistry, 72, 2902–2907.

Maartense, I. (1969) Magnetism of synthetic and natural $MnCO_3$. Physical Review, 188, 924–929.

Maartense, I. (1971) A note on the critical behavior of $MnCO_3$ and NiF_2. Solid State Communications, 9, 2071–2076.

Meijer, H. C., Pimmelaar, L. M. W. A., Brouwer, S. R., and Van den Handel, Jr. (1970) Some magnetic properties of $MnCO_3$ at low field strength: Physica, 46, 279–290.

Moore, G. E. (1943) Heat content of manganese dioxide and carbonate at high temperatures. Journal of the American Chemical Society, 65, 1398–1399.

Moriya, T. (1960) Anisotropic superexchange interaction and weak ferromagnetism. Physical Review, 120, 91–98.

Ok, H. N. (1969) Relaxation effects in antiferromagnetic $FeCO_3$. Bulletin of the American Physical Society, 14, 729.

Robie, R. A. (1965) Heat and free energy of formation of herzenbergite, troilite, magnesite, and rhodochrosite calculated from equilibrium data. U.S. Geological Survey Professional Paper 525-D, 65–72.

Robie, R. A., Finch, C. B., and Hemingway, B. S. (1982a) Heat capacity and entropy of fayalite (Fe_2SiO_4) between 5.1 and 383

K: comparison of calorimetric and equilibrium values for the QFM buffer. American Mineralogist, 67, 463–469.

Robie, R. A. and Hemingway, B. S. (1972) Calorimeters for heat of solution and low-temperature heat capacity measurements. U.S. Geological Survey Professional Paper 755.

Robie, R. A., Hemingway, B. S., and Fisher, J. R. (1979b) Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10^5 pascals) pressure and at higher temperatures. U.S. Geological Survey Bulletin 1452.

Robie, R. A., Hemingway, B. S., and Takei, H. (1982b) Heat capacities and entropies of Mg_2SiO_4, Mn_2SiO_4, and Co_2SiO_4 between 5 and 380 K. American Mineralogist, 67, 470–482.

Robie, R. A., Hemingway, B. S., and Wilson, W. H. (1976) The heat capacities of Calorimetry Conference copper and of muscovite $KAl_2(AlSi_3)O_{10}(OH)_2$, pyrophyllite $Al_2Si_4O_{10}(OH)_2$, and illite $K_3(Al_7Mg)(Si_{14}Al_2)O_{40}(OH)_8$ between 15 and 374 K and their standard entropies at 298.15 K. U.S. Geological Survey Journal of Research, 4, 631–644.

Robie, R. A., Hemingway, B. S., and Wilson, W. H. (1978) Low-temperature heat capacities and entropies of feldspar glasses and of anorthite. American Mineralogist, 63, 109–123.

Shmulovich, K. I. and Schmonov, V. M. (1978) [Tables of thermodynamic properties of gases and liquids (carbon dioxide).] Gosdarstvennaya Sluzhba Standartrykh Dannykh. (In Russian).

Smith, H. J. (1918) On equilibrium in the system ferrous carbonate, carbon dioxide, water. Journal of the American Chemical Society, 40, 879–883.

Staveley, L. A. K. and Linford, R. G. (1969) The heat capacity and entropy of calcite and aragonite, and their interpretation. Journal of Chemical Thermodynamics, 1, 1–11.

Sweeton, F. H. and Baes, C. F., Jr. (1970) The solubility of magnetite and hydrolysis of ferrous ion in aqueous solutions at elevated temperatures: Journal of Chemical Thermodynamics, 2, 479–500.

Wagman, D. D., Evans, W. H., Parker, V. B., Halow, I., Bailey, S. M., and Schumm, R. H. (1969) Selected values of chemical thermodynamic properties: U.S. National Bureau of standards Technical Note 270–4.

Weidner, J. R. (1972) Equilibria in the system Fe–C–O. Part I: Siderite–magnetite–carbon–vapor equilibrium from 500 to 10000 bars. American Journal of Science, 272, 735–751.

Manuscript received, February 14, 1983;
accepted for publication, September 19, 1983.