

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

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Abstract

The heat capacities of rhodochrosite from Alma, Colorado, having the composition $(\text{Mn}_{0.994}\text{Fe}_{0.005}\text{Mg}_{0.001})\text{CO}_3$ and siderite of composition $(\text{Fe}_{0.956}\text{Mn}_{0.042}\text{Mg}_{0.002})\text{CO}_3$ 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

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

to $\pm 0.3\%$, for the same temperature range, the heat capacity of siderite is

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

also with an average deviation of 0.3%. When we combine our entropy data with extant equilibrium decomposition and aqueous solubility studies, we obtain $\Delta H_{f,298}^\circ = -891.91 \pm 0.52$ kJ/mol and $\Delta G_{f,298}^\circ = -818.13 \pm 0.55$ 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, $H_T^\circ - H_{298}^\circ$, 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 translucent 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 HCl 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 $(\text{Mn}_{0.994}\text{Fe}_{0.005}\text{Mg}_{0.001})\text{CO}_3$.

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 $(\text{Fe}_{0.956}\text{Mn}_{0.042}\text{Mg}_{0.002})\text{CO}_3$. 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 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 | | | | | |
| 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 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 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 | 239.15 | 0.6342 | 38.78 | 0.2230 |
| 331.70 | 0.7493 | 245.19 | 0.6430 | 39.24 | 0.2475 |
| 337.22 | 0.7554 | 251.10 | 0.6518 | 40.21 | 0.1302 |
| | | 256.95 | 0.6602 | 40.91 | 0.1071 |
| Series 2 | | 262.71 | 0.6687 | 41.65 | 0.1035 |
| 52.97 | 0.1373 | 268.42 | 0.6765 | 42.39 | 0.1026 |
| 58.46 | 0.1624 | 274.06 | 0.6810 | Series 13 | |
| 63.30 | 0.1849 | | | 39.30 | 0.2511 |
| 68.22 | 0.2076 | Series 9 | | 39.35 | 0.2549 |
| 73.46 | 0.2316 | 279.50 | 0.6890 | 39.40 | 0.2599 |
| 78.89 | 0.2558 | 285.05 | 0.6954 | 39.45 | 0.2616 |
| 84.48 | 0.2795 | 290.54 | 0.7025 | 39.48 | 0.2620 |
| 89.99 | 0.3018 | 295.99 | 0.7085 | Series 14 | |
| 95.47 | 0.3227 | 301.40 | 0.7150 | 39.53 | 0.2744 |
| Series 3 | | Series 10 | | 39.59 | 0.2799 |
| 101.05 | 0.3428 | 5.95 | 0.000163 | 39.66 | 0.2912 |
| 106.40 | 0.3609 | 6.92 | 0.000254 | Series 15 | |
| 111.63 | 0.3779 | 7.56 | 0.000428 | 46.54 | 0.1105 |
| 116.96 | 0.3943 | 8.34 | 0.000699 | 49.45 | 0.1218 |
| 122.46 | 0.4103 | 9.15 | 0.001418 | Series 16 | |
| 127.97 | 0.4256 | 10.42 | 0.002356 | 39.58 | 0.2783 |
| 133.49 | 0.4400 | 11.71 | 0.003445 | 39.62 | 0.2843 |
| Series 4 | | 12.98 | 0.004883 | 39.66 | 0.2876 |
| 139.02 | 0.4538 | 14.39 | 0.007053 | 39.69 | 0.2961 |
| 144.42 | 0.4666 | 15.93 | 0.01017 | 39.71 | 0.3056 |
| 149.86 | 0.4791 | 17.59 | 0.01449 | 39.85 | 0.2074 |
| 155.36 | 0.4910 | 19.35 | 0.02032 | Series 17 | |
| Series 5 | | 21.29 | 0.02828 | 342.00 | 0.7608 |
| 160.56 | 0.5019 | 23.54 | 0.03950 | 348.20 | 0.7672 |
| 166.09 | 0.5131 | 25.63 | 0.05208 | 354.59 | 0.7739 |
| 171.85 | 0.5244 | 27.87 | 0.06796 | 367.05 | 0.7869 |
| 177.50 | 0.5351 | 30.75 | 0.09262 | 373.26 | 0.7925 |
| 183.05 | 0.5452 | 33.47 | 0.1218 | Series 11 | |
| 188.50 | 0.5550 | 36.29 | 0.1620 | 4.98 | 0.000079 |
| Series 6 | | 43.80 | 0.1072 | 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 $\pm 0.06\%$ above 25 K, whereas those obtained by means of

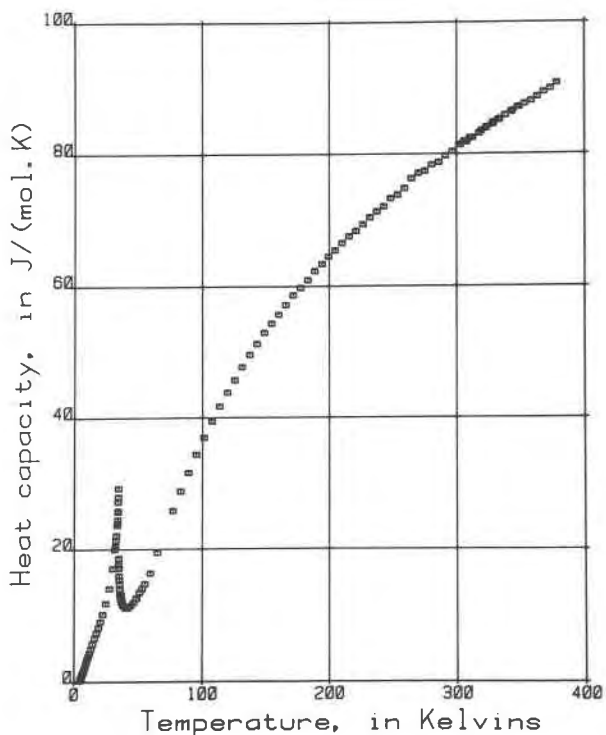


Fig. 1. Experimental heat capacities of 114.947 g of rhodochrosite from Alma, Colorado, having the composition $(\text{Mn}_{0.994}\text{Fe}_{0.005}\text{Mg}_{0.001})\text{CO}_3$.

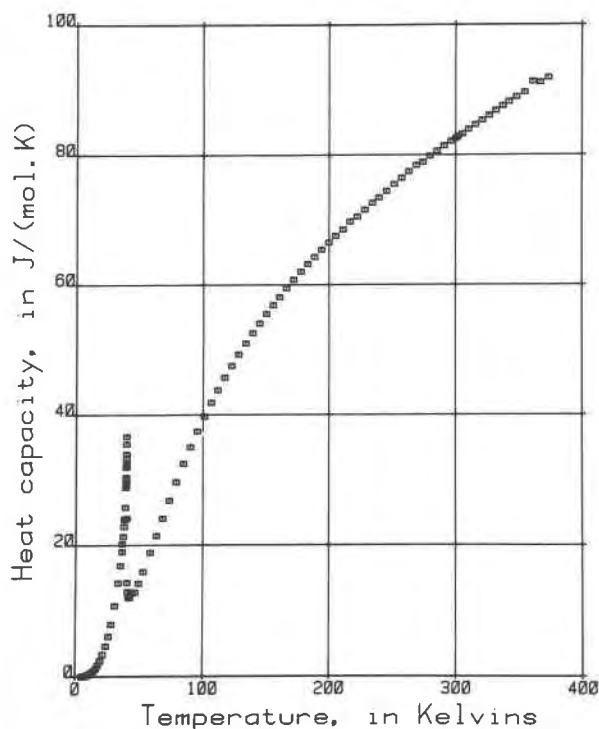


Fig. 2. Experimental heat capacities of 115.586 g of siderite of the composition $(\text{Fe}_{0.956}\text{Mn}_{0.04}\text{Mg}_{0.002})\text{CO}_3$.

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

| Temp. K | C_p^o J/(g·K) | Temp. K | C_p^o 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 $\pm 1.0\%$. 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^o 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^o 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 ($S_{298.1}^o - S_{56.2}^o$) and our equivalent value agree to 0.5%. Kalinkina gave a graph of his data and a temperature

of 29.4 K for the Néel temperature. Kostryakov and Kalinkina (1964) reported $S_{298}^o = 112.9$ J/(mol · K) obtained by combining their C_p^o 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^o 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}^o 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^o 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

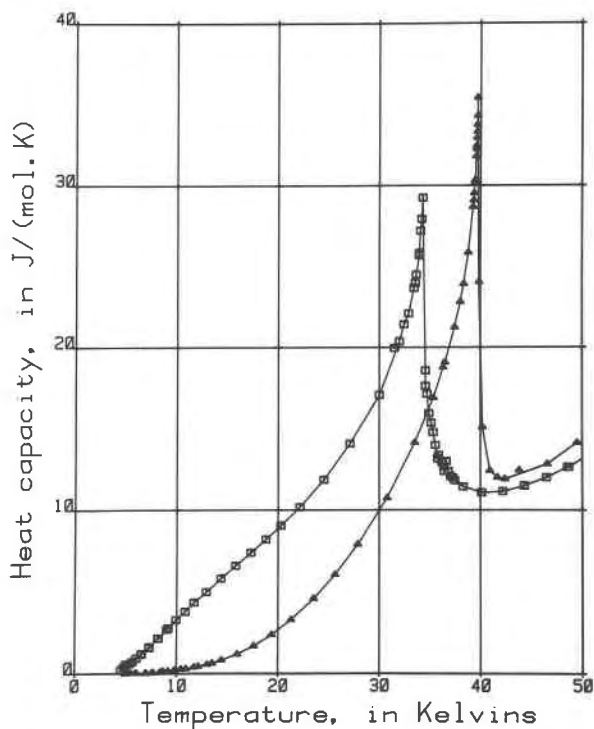


Fig. 3. Molar heat capacities of $MnCO_3$ (squares) and $FeCO_3$ (triangles) in the region of the λ transition.

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.

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



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)

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

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

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

Table 5. Molar thermodynamic properties of $MnCO_3$. [Formula weight = 114.947 g mol⁻¹]

| Temp. T Kelvin | Heat capacity C_p° | Entropy $S_T^\circ - S_0^\circ$ | Enthalpy function $(H_T^\circ - H_0^\circ)/T$ | Gibbs energy function $-(G_T^\circ - H_0^\circ)/T$ |
|----------------------|------------------------------|------------------------------------|--|---|
| 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 |

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 9825¹ 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 FeCO₃. [Formula weight = 115.856 g mol⁻¹]

| Temp. | Heat capacity | Entropy | Enthalpy function | Gibbs energy function |
|--------|-----------------------------|--|---|--|
| T | C _p ^o | S _T ^o -S ₀ ^o | (H _T ^o -H ₀ ^o)/T | -(G _T ^o -H ₀ ^o)/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 | 43.12 | 38.43 |
| 260 | 77.04 | 84.55 | 44.4 | 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 $\Delta[(G_T^o - H_{298}^o)/T]$ 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 $\Delta H_{r,298}^o$, 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 $\Delta H_{f,298}^o$ of MnO and CO₂ and the entropies of Mn, C, and O₂ from Robie et al. (1979), we obtain $\Delta H_{f,298}^o = -891.91 \pm 0.52$ kJ/mol and $\Delta G_{f,298}^o = -818.13 \pm 0.55$ kJ/mol for MnCO₃.

An independent check on the value of $\Delta G_{f,298}^o$ for MnCO₃ is possible by utilizing aqueous solubility data. The solubility of MnCO₃ in H₂O under various CO₂ 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 manganese 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 Mn²⁺) and a crystalline MnCO₃ prepared in a salt bridge.

The Gibbs free energy of formation of MnCO₃ 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 MnCO₃, yield $\Delta G_{f,298}^o$ 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 $\Delta G_{f,298}^o = -814.6$ kJ/mol. Obviously, accurate solubility data for pure synthetic crystals of MnCO₃ 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 $\Delta G_{298}^o = 60.50 \pm 0.30$ kJ for the reaction



Using $\Delta G_{f,298}^o = -527.90 \pm 0.12$ kJ/mol for CO₃²⁻ from Wagman et al. (1969) and -9.63 ± 0.50 kJ/mol for Fe²⁺

Table 7. "Third-law" calculation of $\Delta H_{r,298}^o$ for the reaction MnCO₃ = MnO + CO₂ from the equilibrium measurements of Goldsmith and Graf (1957) and Huebner (1969)

| T | P | $\Delta(G_T^o - H_{298}^o)/T$ | $(P-1)\Delta V_{298}^o/T$ | f_{CO_2} | $R \ln f_{CO_2}$ | $\Delta H_{f,298}^o$ |
|-----------------------------------|------|-------------------------------|---------------------------|------------|------------------|----------------------|
| 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 |
| $\Delta V_{298}^o = -1.785$ J/bar | | Average $\Delta H_{298}^o =$ | | | | -113.18 kJ |
| | | | | | | ± 0.16 |

from Larson et al. (1968) and Sweeton and Baes (1970), we calculate $\Delta G_{f,298}^{\circ} + -680.03 \pm 0.60$ kJ/mol for siderite, and using our entropy value and those of Robie et al. (1979) for Fe, C, and O₂, we calculate -753.22 ± 0.61 kJ/mol for $\Delta H_{f,298}^{\circ}$. French (1971) and Weidner (1972) have studied the equilibrium



at temperatures between 450° and 760°C. Inasmuch as the Gibbs free energies of formation of Fe₃O₄ and CO₂ 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 $\Delta G_{f,298}^{\circ}$ value for siderite obtained from the solubility data. Unfortunately, these two high-temperature equilibrium studies differ significantly; they also differ from the stability of FeCO₃ obtained from the solubility measurements. Furthermore, they imply a $\Delta S_{f,298}^{\circ}$ for the reaction considerably different from that obtained by the much more accurate and direct $\Delta S_{f,298}^{\circ}$ obtained from the heat capacity measurements. I-Ming Chou (private comm., June 1983, and ms.) has reinvestigated the reaction $3\text{FeCO}_3 + 1/2\text{O}_2 = \text{Fe}_3\text{O}_4 + 3\text{CO}_2$ along the magnetite-hematite buffer. The data represent only the decomposition of FeCO₃. 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 FeCO₃ used for the solubility studies made by Smith (1918) probably resulted in an extremely fine-grained product; accordingly, the value of $\Delta G_{f,298}^{\circ}$ 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 $\Delta G_{f,298}^{\circ}$ for siderite should fall within the limits -680.0 to -685.5 kJ/mol. The corresponding (limiting) values for $\Delta H_{f,298}^{\circ}$ 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 $\Delta H_{f,298}^{\circ}$ for FeCO₃ is available we suggest an average value of -682.8 ± 5.5 kJ/mol for $\Delta G_{f,298}^{\circ}$.

Magnetic heat capacities and entropies of MnCO₃ and FeCO₃

At temperatures below the respective maxima in C_p^o, the magnetic moments (spins) of the Fe²⁺ ions in FeCO₃ are aligned, antiferromagnetically, parallel to the $\bar{3}$ axis [111], whereas in MnCO₃ they are aligned, antiferromagnetically, normal to [111] (Alikhanov, 1959). FeCO₃ and MnCO₃ 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 MnCO₃ 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 FeCO₃, 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 FeCO₃ and MnCO₃ is seen in more detail in Figure 3, which shows that below T_N, the heat capacity of MnCO₃ decreases much less rapidly with temperature than does that of FeCO₃, even though they are isostructural, and that FeCO₃ and MnCO₃ differ by only 0.8% in their formula weights and differ by less than 6% in molar volumes. At 10 K, for example, MnCO₃ has a heat capacity almost 14 times that of FeCO₃. We suspect that this very large difference in C_p^o is related to the canting of the spins in MnCO₃. A similar difference is observed between the heat capacities of Mn₂SiO₄ (Robie et al., 1982b) and Fe₂SiO₄ (Robie et al., 1982a), which are known to exhibit spin-canting at very low temperatures, and that of isostructural Co₂SiO₄ (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^o at T < T_N for FeCO₃ and MnCO₃ could be accounted for in terms of the difference in the spin-wave contributions to C_p^o (see for example, Gopal, 1966).

Our values for the Néel temperature obtained from C_p^o measurements (to within 0.05 K of T_N) are 39.71 ± 0.03 and 34.27 ± 0.05 K for FeCO₃ and MnCO₃, respectively. These values are significantly higher than those obtained by Kalinkina (1963): 30.6 and 29.4 K for FeCO₃ and MnCO₃, 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 Duijneveldt, 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 MnCO₃.

The Néel temperature of FeCO₃ 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})CO₃.

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