

## Enthalpy of formation of siderite and its application in phase equilibrium calculation

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### ABSTRACT

The enthalpy of formation of siderite at 298 K has been determined from transposed temperature drop calorimetric measurements of enthalpies of decomposition of siderite at both 978 and 1075 K in an O<sub>2</sub> atmosphere. Synthetic siderite was used for the calorimetric experiments. Enthalpy of formation values from the experimental enthalpies at 978 and 1075 K are consistent, and the final result is  $\Delta H_{f,298}^{\circ} = -750.6 \pm 1.1$  kJ/mol. The heat contents of hematite,  $H_{978} - H_{298}$  and  $H_{1075} - H_{298}$ , determined in the present work, are 1–2 kJ/mol lower than those reported in the literature, but the measured heat content of corundum using the same experimental method is in good agreement with the tabulated values. The consistency of the enthalpy of formation of siderite at 298 K derived from experiments performed at different temperatures indicates that CO (a potential intermediate product of the decomposition of siderite) is completely oxidized. This study provides a new methodology for calorimetric measurements of Fe(II)-bearing carbonates.

The enthalpy of formation of siderite has been used to calculate the univariant curve for the equilibrium: siderite + hematite = magnetite + CO<sub>2</sub>. This curve lies about 100 °C lower than that calculated using thermodynamic data from literature and about 70 °C lower than the recent reversal at 10 kbar (between 863 and 873 K) of Koziol and Newton (1993). Some possible reasons for these discrepancies are discussed, and the thermodynamic data for phases in this system are reevaluated.

### INTRODUCTION

Siderite (FeCO<sub>3</sub>) is the simplest Fe<sup>2+</sup>-bearing carbonate. Although there are several determinations of its enthalpy of formation (Table 1), discrepancies still remain. Values of the enthalpy of formation of siderite at 298 K from the most widely used data bases in the geoscience community range from –737.0 (Robie et al., 1978) to –761.2 kJ/mol (Holland and Powell, 1990). The methods used to determine the enthalpy of formation mainly fall into two categories: (1) from solubility products ( $K_{sp}$ ) of siderite in aqueous solution and (2) from phase equilibrium studies involving siderite. No direct calorimetric determinations have been reported. The value in Robie et al. 1978) is from the solubility products of siderite. Other thermodynamic properties of Fe<sup>2+</sup>, CO<sub>3</sub><sup>2-</sup>, and FeCO<sub>3</sub> [e.g.,  $\Delta G_f$  (Fe<sup>2+</sup>),  $\Delta G_f$  (CO<sub>3</sub><sup>2-</sup>), and  $\Delta S_f$  (FeCO<sub>3</sub>)] have to be used to derive the enthalpy of formation of siderite from solubility products. Different sources of these thermodynamic data (see Table 1) cause the derived enthalpies of formation of siderite to range from –737.0 (Robie et al., 1978) to –749.7 kJ/mol (Helgeson et al., 1978).

The accuracy of the enthalpy of formation derived from phase equilibria depends on the accuracy of many factors such as temperature and pressure brackets, the enthalpies of formation of other phases, assumed entropy values,

and the equation of state of gas phases. The phase equilibria related with siderite in the data base of Holland and Powell (1990) are the decomposition reaction of siderite from Weidner (1972) and the partitioning equilibrium of Fe<sup>2+</sup>/Mg<sup>2+</sup> in ankerite and siderite from Rosenberg (1967) and Anovitz and Essene (1987). The phase equilibrium experiments of Goldsmith et al. (1962) and French (1971) are not included because of apparent inconsistency among the experiments (e.g., the calculated enthalpy of formation of siderite at 298 K was –775.7 kJ/mol; French, 1971).

Recently, Robie et al. (1984) redetermined the heat capacity and entropy of siderite from 5 to 550 K and used solubility-product data and phase equilibria to confine the enthalpy of formation of siderite between –753.2 and –758.6 kJ/mol. Stubbina and Toguri (1989) derived the enthalpy of formation of siderite from the decomposition of siderite in vacuum. Their new data gave –749 kJ/mol. In the present work, the enthalpies of decomposition of siderite in an O<sub>2</sub> atmosphere were measured calorimetrically at 978 and 1075 K, from which the enthalpy of formation of siderite at 298 K was derived. These experiments also will help in the understanding of the mechanism of decomposition of siderite and oxidation of carbon monoxide. The successful measurement of the enthalpy of formation of siderite provides a new meth-

**TABLE 1.** A summary of the enthalpy of formation of siderite from the elements at 298 K

Source	Method	$\Delta H_f$ (kJ/mol)
This work	Calorimetry at 978 K in O <sub>2</sub> (FeCO <sub>3</sub> + O <sub>2</sub> → Fe <sub>2</sub> O <sub>3</sub> + CO <sub>2</sub> )	-750.5 ± 0.8
	Calorimetry at 1075 K in O <sub>2</sub> (FeCO <sub>3</sub> + O <sub>2</sub> → Fe <sub>2</sub> O <sub>3</sub> + CO <sub>2</sub> )	-750.7 ± 1.0
Holland and Powell (1990, updated)	Phase equilibria	-760.6 ± 0.5
	Phase equilibria	-761.2 ± 0.9
Holland and Powell (1990)	FeCO <sub>3</sub> → Fe <sub>2</sub> O <sub>4</sub> + C + CO <sub>2</sub> (Weidner, 1972) Fe-dol + mag = dol + sid (Rosenberg, 1967)	
Stubbina and Toguri (1989)	Phase equilibrium (FeCO <sub>3</sub> → Fe <sub>2</sub> O <sub>4</sub> + CO <sub>2</sub> + CO in vacuum)	-749
Robie et al. (1984)	(1) K <sub>sp</sub>	-753.2
	(2) Phase equilibrium	-758.6
Reiterer et al. (1981)	K <sub>sp</sub>	-741.9
Robie et al. (1978)	K <sub>sp</sub>	-737.0 ± 2.3
Helgeson et al. (1978)	K <sub>sp</sub> (Langmuir, 1969)	-749.7
Wagman et al. (1969)	tabulated, no details	-740.6
Kelley and Anderson (1935)	K <sub>sp</sub> (Smith, 1918)	-747.6

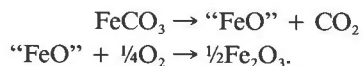
odology for calorimetric measurements for other Fe(II)-bearing carbonates.

#### CALORIMETRIC APPROACH AND THE DECOMPOSITION OF SIDERITE

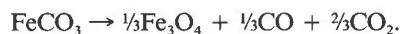
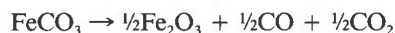
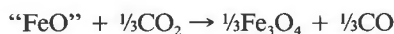
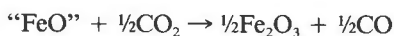
In the present study, we sought calorimetric conditions under which siderite would be converted rapidly to a well-defined phase of known thermodynamic properties upon being dropped from room temperature into a calorimeter at high temperature. This approach was taken after several approaches using oxide melt solution calorimetry were tried. They proved unsuccessful, with uncertain and irreproducible final states, which we believe are related to the mechanism of oxidation and side reactions described below.

The mechanisms of the thermal decomposition of siderite are complicated and depend on the experimental conditions and the purity of the sample (see Chang and Ahmad, 1982, for a review). The final product, generally, is hematite (Fe<sub>2</sub>O<sub>3</sub>) in an oxidizing atmosphere (O<sub>2</sub> or air), magnetite (Fe<sub>3</sub>O<sub>4</sub>) in a CO<sub>2</sub> atmosphere and in vacuum, and magnetite and wüstite ("FeO") in an inert atmosphere.

A two-step mechanism is commonly accepted (Chang and Ahmad, 1982). The decomposition of siderite to "FeO" is followed by oxidation to Fe<sub>2</sub>O<sub>3</sub> in air:



The "FeO" is generally nonstoichiometric. The first step is endothermic and the second exothermic. These enthalpy changes have been observed in DTA studies (Kissinger et al., 1956; Powell, 1965). Wüstite is an intermediate phase and can only be detected by high-temperature X-ray powder diffraction for a short period of time (Kissinger et al., 1956). But the following side reactions are also possible (they may be the main reactions in the nonoxidizing atmosphere):



All these side reactions evolve CO, which indeed has been detected in vacuum and in a He atmosphere by mass spectrometry and gas chromatography (Powell, 1965; Kubas and Szalkowicz, 1971).

The mechanism and kinetics of oxidation of CO are also not well defined, and the oxidation reaction is sensitive to impurities and surface conditions of reactors (see Dixon-Lewis and Williams, 1977, for a review). The reaction time needed for 99% oxidation of CO in a reactor may be estimated from the global equation of Howard et al. (1973), which is based on the rate of oxidation of CO measured in a flow reactor. This estimation may not apply rigorously to different conditions, but some general features of this reaction can be outlined. When temperature or  $f_{\text{O}_2}$  increases, the rate of oxidation increases. At 1073 K in O<sub>2</sub>, 99% of CO can be oxidized to CO<sub>2</sub> within 1 s. On the basis of the above considerations, we chose to perform transposed temperature drop calorimetry in O<sub>2</sub> at two temperatures, 973 and 1073 K. If data obtained at both temperatures led to consistent values of the enthalpy of formation of siderite, this would be further evidence of the completeness of oxidation of FeCO<sub>3</sub> to Fe<sub>2</sub>O<sub>3</sub> (and of CO to CO<sub>2</sub>) in the calorimeter.

#### EXPERIMENTAL

##### Sample preparation and characterizations

Siderite samples were synthesized by the decomposition of hydrous Fe(II) oxalate (99.99+%, Aldrich) in a CO<sub>2</sub> atmosphere in a cold-seal vessel apparatus (French and Rosenberg, 1965; Rosenberg, 1967). Ag-Pd was used as the capsule material. The synthesis reaction is



This reaction was carried out at 633 K for about 48 h,

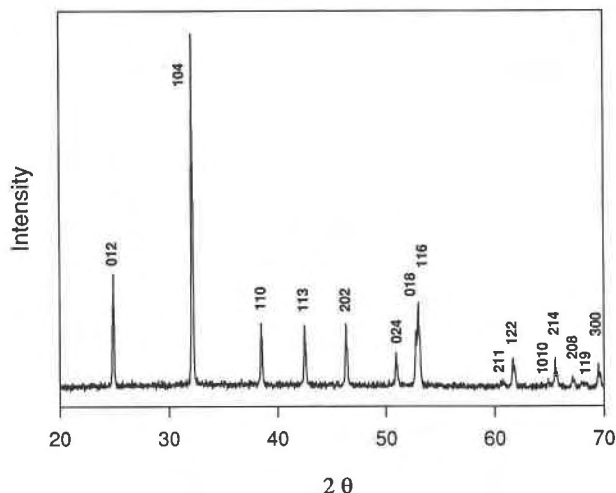


Fig. 1. X-ray powder diffraction pattern of synthetic siderite ( $\text{CuK}\alpha$  radiation). The numbers are the hexagonal indices ( $hkl$ ).

and dry ice was used to provide  $\text{CO}_2$ . The exact pressure is unknown but is estimated as 1–2 kbar.

The synthetic sample has a tan color and was examined by X-ray powder diffraction and optical microscopy. The X-ray diffraction pattern was collected with a Scintag PAD-V diffractometer with  $\text{CuK}\alpha$  radiation (operated at 40 kV and 30 mA) and a solid-state detector. The DMS software and a DEC MicroVax 3100 computer were used to control the diffractometer. Fe-bearing phases fluoresce under Cu radiation. The energy window of the detector was adjusted to reduce the fluorescence without losing much intensity. The step-scan mode was used to collect the data for refinements of lattice parameters, with a step of  $0.02^\circ$  and a preset time of 4.0 s to reduce the fluorescence further. A pattern collected in this way is shown in Figure 1 (a dried siderite sample was used for determination of lattice parameters; see below). Peak positions were calibrated using Si as an external standard, and the least-squares procedures in the controlling DMS software were used for the refinements. Twelve strongest peaks were used to refine the unit-cell parameters (see Table 2). The figure of merit ( $F_{12}$ ) is 43, and the average  $2\theta$  difference is  $0.006^\circ$  (Smith and Snyder, 1979). The lattice parameters for this synthetic sample are slightly smaller than those from natural samples, probably because of the impurities in the natural samples used in the previous studies.  $\text{Mn}^{2+}$  is the common impurity in siderite (2.4 mol% Mn in the sample used by Effenberger et al., 1981, and 1–2% Mn in the sample reported in PDF no. 29-696). Since  $\text{Mn}^{2+}$  is slightly larger than  $\text{Fe}^{2+}$ , it is reasonable that the unit-cell parameters from the previous studies are larger. For routine phase identification, the continuous scan mode was used with a scan rate of  $1^\circ/\text{min}$ . The  $2\theta$  range scanned was usually  $10\text{--}70^\circ$ . Generally, the peak broadness may give information about the crystallinity of the sample. The peak profile was usually analyzed. The full width at half maximum (FWHM) of the (104) peak (hexagonal index) of the above pattern (Fig. 1) is 0.12.

TABLE 2. Lattice parameters of siderite

Sample	$a$ (Å)	$c$ (Å)	Sources
Synthetic	4.6880(3)	15.372(2)	this work
Natural	4.6916(4)	15.3796(16)	Effenberger et al. (1981)
Natural	4.6935(2)	15.386(8)	PDF (no. 29-696)

Note: space group  $R\bar{3}c$ .

The particle size of the synthetic siderite ranges from  $<1$  to about  $10\ \mu\text{m}$ , as inferred from both optical microscopy and a secondary electron image from a Cameca SX-50 microprobe.

Several batches of synthetic siderite were put together and dried at 403 K in vacuum (13 Pa or  $1.3 \times 10^{-4}$  bars). Thermogravimetric analysis (TGA) in an atmosphere of  $\text{H}_2$  showed that the  $\text{H}_2\text{O}$  content was about 0.7 wt% when the sample was dried for 1 h. TGA in an  $\text{O}_2$  atmosphere showed that the  $\text{H}_2\text{O}$  content was 0.05–0.06 wt% when the sample was dried for 5 h. The latter sample was used for lattice-parameter study and calorimetry.

### Calorimetry

The heat effect associated with the decomposition of siderite was measured using two Calvet-type calorimeters (Navrotsky, 1977) operating at 978 and 1075 K, respectively. A flow of  $\text{O}_2$  or dry air was used to control the atmosphere in the calorimeter (flow rate about  $1\ \text{cm}^3/\text{s}$ ). A sample pellet (or sample powder in a Pt capsule) was dropped from room temperature into an empty Pt crucible equilibrated in the calorimeter. The oxidation reaction occurred immediately, and the heat effect was monitored. Typically, the reaction finished within 20–30 min, and the voltage returned to (or close to) the initial values. The area under the voltage-time curve was proportional to the heat effect involved in the reaction. The heat effect was calculated using an appropriate calibration factor (Navrotsky, 1977; Chai and Navrotsky, 1993).

Initially, several containment techniques were tried for the samples. Both open and crimped Pt-foil capsules containing powder and pressed pellets of 3.0 mm diameter were used. The initial concern that the latter might oxidize more slowly was unfounded. Since Pt capsules introduce an additional heat effect from the heat content of Pt, and since the reproducibility of heat effects appeared to depend slightly on capsule geometry, we used pellets for the final experiments. Some initial experiments were conducted in flowing air at 978 K. They appeared consistent with later experiments conducted in  $\text{O}_2$  and are reported in Table 3. The data used to derive  $\Delta H_{f,298}^\circ$  of siderite were produced by pellets dropped in  $\text{O}_2$  at 978 and 1075 K.

## RESULTS AND DISCUSSION

### The completeness of oxidation of siderite and characterization of hematite

There are several lines of evidence indicating that siderite oxidation is complete and that hematite is well crystallized during a calorimetric experiment. First, the en-

**TABLE 3.** Enthalpy of decomposition of siderite

Sample mass (mg)	$\Delta H$ (kJ/mol)
<b>978 K in flowing O<sub>2</sub></b>	
20.19	19.012
23.64	19.113
22.78	18.698
14.80	18.954
25.56	19.880
19.08	19.196
15.44	19.469
20.23	19.367
23.58	20.013
22.55	18.975
22.22	19.688
29.19	19.098
21.44	19.736
28.04	19.126
	av. = 19.31 ± 0.21 (14)*
<b>978 K in flowing air</b>	
13.80	18.540**
19.50	18.970
17.76	18.014
	av. = 18.51 ± 0.55 (3)*
<b>1075 K in flowing O<sub>2</sub></b>	
21.22	31.761
23.80	31.054
21.67	30.343
14.28	28.727
24.58	30.778
27.25	31.363
19.89	30.490
22.55	30.725
	av. = 30.66 ± 0.64 (8)*

\* The error is 2 sd of the mean, and number in parentheses is the number of experiments.

\*\* Using Pt capsule. Other experiments are on pellets (see text).

enthalpy of decomposition measured in an O<sub>2</sub> atmosphere at 978 K is compared with that from a dry-air atmosphere at the same temperature (Table 3). The experimental results are consistent. Second, the weight change of the decomposition product after the calorimetric experiment at 978 K in dry air was monitored (Table 4). A sample with 1-h reaction time was cooled to room temperature immediately after the calorimetric experiment and weighed. Another sample was left in the calorimeter for 4 h after the 1-h reaction time for calorimetry and then cooled to room temperature and weighed. These experimental results show that siderite completely oxidized to hematite within 1 h. The weight changes also confirm that H<sub>2</sub>O and Fe<sup>3+</sup> contents of the synthetic sample are negligible. Third, the decomposition product was characterized by X-ray diffraction after calorimetry. The results are summarized in Table 5. The X-ray pattern of hematite produced from the decomposition of siderite at 978 K in an O<sub>2</sub> atmosphere (labeled hematite-I) is identical with that of a commercial hematite (99.999%, Johnson Matthey) that was heated at 1273 K for 18 h (labeled as hematite-II). The lattice parameters are consistent for both samples and also with those from the PDF card (no. 33-664,  $a = 5.0356 \text{ \AA}$ ,  $c = 13.7489 \text{ \AA}$ ). The FWHM of the strongest peak (104) are 0.139 and 0.120 for hematite-I and hematite-II, respectively. Both samples were also ex-

**TABLE 4.** Decomposition of siderite at 978 K in dry air

Reaction time (h)	FeCO <sub>3</sub> (mg)	Fe <sub>2</sub> O <sub>3</sub> (mg)		Oxidation %*
		Calculated	Experimental	
1	13.80	9.51	9.50	98.95 ± 2.10
5	19.03	13.12	13.12	100.0 ± 1.52

\* The error is estimated from the propagation of weighing error.

amined under the optical microscope. They consist of very fine powder, with a particle size of  $\ll 1 \mu\text{m}$ . Fourth, the energy state of hematite from different sources was characterized by calorimetry. The enthalpy of drop solution,  $\Delta H_{\text{ds}}$ , which corresponds to the enthalpy absorbed when the sample is dropped from room temperature into the hot calorimeter and then dissolves in the solvent, was measured using a calorimeter operated at 1043 K, with molten lead borate as a solvent (see Table 5). A third hematite (hematite-III), from commercial powder heated at 973 K for 18 h, was also measured. The enthalpy values for hematites from commercial powder are the same within experimental error but are slightly different from that of the hematite produced from siderite, although they marginally overlap. It may be worth noting that the color samples with different heat treatments are also different (see Table 5). The heat contents (from 298 to 978 K) of hematite-I and hematite-II were also measured, and they are in good agreement (Table 6). Therefore, the small difference in drop-solution enthalpy appears to be due to the difference in the enthalpy of solution rather than in heat capacities. The particle-size difference between hematite-I and hematite-II may affect the enthalpy of solution and contribute to the enthalpy difference. The strongest peak (104) of hematite-I is slightly broader than that of hematite-II (Table 5). Thus, hematite-I may have higher surface energy because of its fine grain size. Hematite undergoes a  $\lambda$  phase transition at about 955 K (Gronvold and Samuelson, 1975). This magnetic phase transition is probably not involved in the enthalpy difference, since it is a rapid transition and the measured heat contents do not differ between different samples. This observed enthalpy difference between hematite samples is not used below as a correction term in the calculation of the enthalpy of formation of siderite for the following reasons: (1) The observed difference in average value of the enthalpy of drop solution is just slightly beyond the experimental uncertainty, and many of the values of individual experiments actually overlap. (2) The particle size and the energy state of the hematite sample used to determine the enthalpy of formation of hematite are not known (Darken and Gurry, 1946), nor was the particle size of the hematite used in the phase equilibrium studies (Kozioł and Newton, 1993) reported. (3) There is no detectable lattice-parameter difference for the hematite samples. (4) The correction to the enthalpy of formation of siderite would be small (half of the above enthalpy difference, namely, about 1 kJ/mol; see below). (5) The

TABLE 5. Characteristics of hematites

	Hematite-I (from siderite) (978 K)	Hematite-II (1273 K)	Hematite-III (973 K)
XRD pattern*	same as no. 33-664	same	same
Color	dark red	brownish black	dark red
Size ( $\mu\text{m}$ )	<1	<1	<1
FWHM of (104)	0.139	0.120	
a ( $\text{\AA}$ )	5.0357(3)	5.0362(2)	
c ( $\text{\AA}$ )	13.7523(12)	13.7509(8)	
Figure of merit ( $F_{10}$ )	53	88	
	( $\Delta 2\theta = 0.008$ )	( $\Delta 2\theta = 0.005$ )	
$\Delta H_{\text{ds}}$ (kJ/mol)	173.53 $\pm$ 1.27(7)	177.14 $\pm$ 1.53(8)	176.01 $\pm$ 1.57(10)

\* Data were collected using the step-scan mode and a 4-s preset time.

magnitude of this correction would not remove the discrepancies in calculated equilibrium (see below); indeed, it would make the misfit slightly worse.

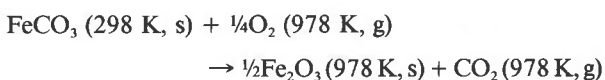
### Heat content of hematite

The heat content of hematite is needed for calculations to recover the enthalpy of decomposition at room temperature. To check older literature values (see Robie et al., 1978; Berman, 1988), to characterize different samples of hematite, and to estimate uncertainties better, the heat content of hematite was also measured in this study. Heat content measurements on pellets were performed in static air at both 978 and 1075 K. The average sample weight was 20–30 mg. The hematite samples from different sources have the same heat content (see Table 6), but the measured heat contents of hematite from room temperature to 978 and 1075 K are 1–2 kJ/mol smaller than those from the literature (Robie et al., 1978; Berman, 1988). The experimental values at 978 K marginally overlap those from the literature if the error from the literature is assumed to be 1%, but the values do not overlap at 1075 K. To check the method used in this work, the heat content of corundum was also measured at 1075 K under the same conditions. The experimental value of the heat content of corundum is in good agreement with those in the literature (Table 6). The heat contents of hematite in the literature (Robie et al., 1978; Berman, 1988) are mainly based on the calorimetric measurements from 298 to 1050 K of Gronvold and Samuelson (1975) and those from 298 to 1757 K of Coughlin et al. (1951). Well-characterized and pure samples were used in both studies. Although the magnetic disordering of hematite at about 955 K may play a role, the source of the discrepancy is unknown. However, it should be pointed out that the uncertainty for the enthalpy of reaction and the enthalpy of formation of siderite at room temperature, introduced by using different data for the heat content of hematite, is only 0.5–1 kJ/mol because of the coefficients of the reactions (see next section). The heat contents from the present work are used for the latter calculations, and this choice does not introduce major uncertainties.

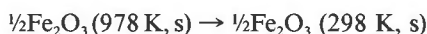
### Enthalpy of reaction and enthalpy of formation of siderite at 298 K

The individual calorimetric measurements from the decomposition of siderite at 978 and 1075 K are listed in Table 3. Corrected for the heat contents of  $\text{Fe}_2\text{O}_3$ ,  $\text{CO}_2$ , and  $\text{O}_2$  ( $\text{CO}_2$  and  $\text{O}_2$  data from Robie et al., 1978), the enthalpy of the decomposition reaction at room temperatures is  $-55.37 \pm 0.47$  (from 978 K) and  $-55.10 \pm 0.72$  kJ/mol (from 1075 K). The thermodynamic cycles used to derive these values are (in kJ/mol) as follows:

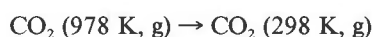
From 978 K,



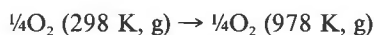
$$\Delta H_1 = 19.31 \pm 0.21$$



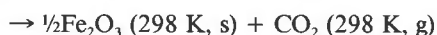
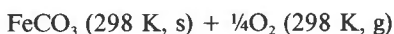
$$\Delta H_2 = \frac{1}{2} \cdot (-95.92) = -47.96 \pm 0.42$$



$$\Delta H_3 = -32.20$$

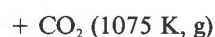
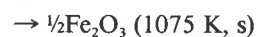
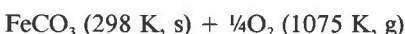


$$\Delta H_4 = \frac{1}{4} \cdot 21.91 = 5.48$$

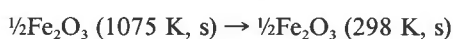


$$\Delta H_{\text{R}} = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 = -55.37 \pm 0.47.$$

From 1075 K



$$\Delta H_1 = 30.66 \pm 0.64$$



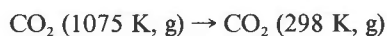
$$\Delta H_2 = \frac{1}{2} \cdot (-109.19) = -54.60 \pm 0.32$$

TABLE 6. The heat contents of hematite and corundum

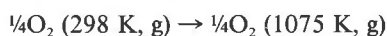
Sample*	This work** (kJ/mol)	Robie et al. (1978) (kJ/mol)	Berman (1988) (kJ/mol)
$H_{978}-H_{298}$ hematite-I	95.83 ± 0.62 (7)	97.31	97.35
hematite-II	95.92 ± 0.85 (9)	97.31	97.35
$H_{1075}-H_{298}$ hematite-II	109.19 ± 0.64 (10)	111.41	111.29
corundum	87.18 ± 0.11 (14)	87.29	87.49

\* Hematite-I is the decomposition product of siderite at 978 K in an O atmosphere, and hematite-II is from a commercial powder heated at 1273 K for 18 h.

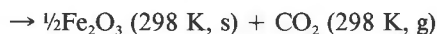
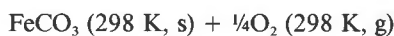
\*\* The error is 2 sd of the mean, and numbers in parentheses are the number of experiments.



$$\Delta H_3 = -37.49$$



$$\Delta H_4 = \frac{1}{4} \cdot (25.30) = 6.33$$



$$\Delta H_R = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 = -55.10 \pm 0.72.$$

The average value of the enthalpy of decomposition of siderite at room temperature is  $-55.24 \pm 0.86$  kJ/mol. The consistency of the enthalpy of decomposition derived from different temperatures indicates that CO is completely oxidized during the reaction, the first reactions in the above cycles indeed represent what happens under calorimetric conditions.

The enthalpy of decomposition of siderite at room temperature may be related to the summation of enthalpies of formations at 298 K:

$$\Delta H_R = \frac{1}{2}\Delta H_f^\circ (\text{Fe}_2\text{O}_3) + \Delta H_f^\circ (\text{CO}_2) - \frac{1}{4}\Delta H_f^\circ (\text{O}_2) - \Delta H_f^\circ (\text{FeCO}_3).$$

Therefore, the enthalpy of formation of siderite at 298 K can be derived from the enthalpy of reaction and the enthalpies of formation of other phases (Robie et al., 1978):

$$\begin{aligned} \Delta H_f^\circ (\text{FeCO}_3) &= \frac{1}{2}\Delta H_f^\circ (\text{Fe}_2\text{O}_3) + \Delta H_f^\circ (\text{CO}_2) \\ &\quad - \frac{1}{4}\Delta H_f^\circ (\text{O}_2) - \Delta H_R \\ &= \frac{1}{2}(-824.64 \pm 1.26) + (-393.51 \pm 0.13) \\ &\quad - 0.0 - (-55.24 \pm 0.86) \\ &= -750.6 \pm 1.1 \text{ (kJ/mol)}. \end{aligned}$$

This value is in good agreement with those from Helgeson et al. (1978) and from Stubbina and Toguri (1989) and slightly less negative than those from Robie et al. (1984) (see Table 1).

### Calculation of the univariant curve for the reaction siderite + hematite = magnetite + CO<sub>2</sub>

One of the important applications of thermodynamic data is to calculate phase diagrams. A pressure and temperature reversal of the reaction siderite + hematite = magnetite + CO<sub>2</sub> has been determined recently by Koziol and Newton (1993). Figure 2 shows this reversal (squares) and the univariant curve of this equilibrium, calculated using the data in the updated data set of Holland and Powell (1990) (thin solid curve). This updated data set is from the computer program Thermocalc (v2.2b1), provided by R. Powell (1994 personal communication) and produced in 1993, hereafter referred to as Holland and Powell (1990, updated) in this paper to distinguish this data set from the original one. A new set of coefficients for the heat-capacity equation of siderite ( $a = 0.1722$ ,  $b = 0.0477$ ,  $c = 95.389$ ,  $d = -1.5731$  for  $C_p = a + bT + c/T^2 + d/T^{0.5}$ ), provided by T. Holland, was used for the calculation. These new coefficients result in a well-behaved heat capacity above 800 K, whereas the coefficients of the heat capacity of siderite from Robie et al. (1978) and Holland and Powell (1990, updated), which were fitted to experimental data from 5 to 550 K (Robie et al., 1984), cause the heat capacity to decrease above about 1000 K. Thus, the new coefficients were used in the present calculation. The temperature of the univariant curve at about 10 kbar, calculated from the data set of Holland and Powell (1990, updated), is slightly higher than the reversal from Koziol and Newton (1993) because of this heat-capacity correction.

The enthalpy of formation of siderite from our present work, together with other data from Holland and Powell (1990, updated) and the revised heat-capacity coefficients for siderite, was also used to calculate the univariant curve of the equilibrium (thick solid curve in Fig. 2). The temperature of this univariant curve at 10 kbar is about 100 °C lower than that from Holland and Powell (1990, updated) and about 70 °C lower than the reversal of Koziol and Newton (1993). Although the apparently slightly different energy state of hematite from the decomposition of siderite relative to other hematites may affect the value of the enthalpy of formation of siderite, as discussed above, the magnitude of this correction is small. If this difference is corrected, the value of the enthalpy of formation of siderite from the elements at 298 K is  $-748.8 \pm 1.8$  instead of  $-750.6 \pm 1.1$  kJ/mol. This corrected value is consistent with the uncorrected value within experimental error, but it makes the discrepancy with Holland and Powell (1990, updated) worse, since their value is  $-760.6 \pm 0.5$  kJ/mol (see Table 1). The heat contents of hematite from this study are also slightly different from those in the literature. The enthalpy of formation of siderite from the elements at 298 K would be  $-749.7 \pm 0.9$  kJ/mol if the heat content of hematite from the literature were used. Again, this correction would make the above discrepancy with phase equilibrium worse. It should be emphasized that the enthalpy of formation of siderite at 298 K derived in this study depends on the enthalpy of



formation values of hematite and  $\text{CO}_2$ . To compare with the univariant curve produced from Holland and Powell (1990, updated), the enthalpy of formation value of hematite ( $-825.72 \pm 0.66$  kJ/mol) in Holland and Powell (1990, updated) should be used. This gives the enthalpy of formation of siderite at 298 K as  $-751.1$  kJ/mol. This value is consistent with that using the enthalpy of formation of hematite from Robie et al. (1978). Therefore, the discrepancy in the univariant curves produced using calorimetric and the phase equilibrium data cannot be explained by the uncertainties in our experiments or in the state of the hematite produced.

Other thermodynamic data have to be used to calculate the univariant curve. Many efforts have been made to evaluate those data. The uncertainties discussed below may account, fully or in part, for the discrepancy in the univariant curves calculated using data from calorimetry and from phase equilibrium for the siderite + hematite = magnetite +  $\text{CO}_2$  reaction.

Siderite, as other rhombohedral carbonates, crystallizes in the calcite structure ( $R\bar{3}c$ ) (see Reeder, 1983).  $\text{CO}_3$  groups in the calcite structure have the same orientation in the plane perpendicular to the  $c$  direction. Rotation of  $\text{CO}_3$  groups may occur at high temperature. This rotational disordering in calcite has been studied by Redfern et al. (1989). Significant increase of heat capacity, entropy, and heat content result from the disordering of  $\text{CO}_3$  groups. The disordering of  $\text{CO}_3$  groups in siderite has not been studied, presumably because of experimental difficulty (siderite is not stable at high temperature and ambient pressure). Therefore, it is not known whether such a disordering transition exists in siderite; if it does, the increased enthalpy and entropy resulting from it could decrease the discrepancy between calculated and observed  $P$ - $T$  reversals.

The entropy of siderite at 298 K in Holland and Powell (1990, and 1990, updated) is from Robie et al. (1984), in which the heat capacity of a siderite sample ( $\text{Fe}_{0.956}\text{Mn}_{0.042}\text{Mg}_{0.002}\text{CO}_3$ ) was measured by combined adiabatic and differential scanning calorimetry between 5 and 550 K. This entropy value [ $95.50$  J/(mol·K)] is significantly different from that [ $105.0$  J/(mol·K)] in Robie et al. (1978). The latter is from earlier heat-capacity measurements using an impure siderite sample ( $\text{Fe}_{0.883}\text{Mn}_{0.052}\text{Mg}_{0.045}\text{Ca}_{0.019}\text{CO}_3$ ) plus the estimated excess entropy from the low-temperature (about 40 K)  $\lambda$  phase transition (Robie, 1965; Robie et al., 1978). It is interesting to note that when the old value of the entropy of siderite at 298 K [ $105.0$  J/(mol·K)] from Robie et al. (1978) is used, together with the enthalpy of formation of siderite from this study, the calculated univariant curve is in good agreement with the reversal from Koziol and Newton (1993) (the dashed curve in Fig. 2). If this entropy value [ $105.0$  J/(mol·K)] is used to calculate the enthalpy of formation of siderite from solubility measurements near room temperature (e.g., Robie et al., 1984), the enthalpy of formation of siderite at 298 K is  $-750.3$  kJ/mol. The same entropy value was used by Helgeson et al. (1978) to de-

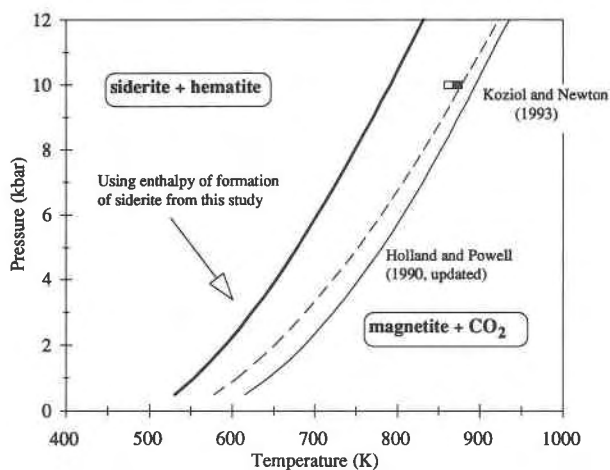


Fig. 2. The univariant equilibrium curves for siderite + hematite = magnetite +  $\text{CO}_2$ . The squares are the reversal from Koziol and Newton (1993); the thin solid curve was calculated from data in Holland and Powell (1990, updated) (see text); the thick solid curve was calculated using the enthalpy of formation of siderite from this study; and the dashed curve was calculated using the enthalpy of formation of siderite from this study and the entropy of siderite from Robie et al. (1978).

rive the enthalpy of formation of siderite,  $-749.7$  kJ/mol (see Table 1). Both are in excellent agreement with the value from this study. Because there is still a significant amount of Mn in the siderite sample used by Robie et al. (1984) that tends to lower the low-temperature  $\lambda$  phase transition (Robie et al., 1984) and therefore makes the entropy smaller, the entropy of siderite at room temperature may be possibly larger than that reported by Robie et al. (1984).

The thermodynamic data for hematite and magnetite also affect the calculated univariant curve for siderite + hematite = magnetite +  $\text{CO}_2$ . Both hematite and magnetite undergo magnetic phase transitions at high temperature (955 and 848 K, respectively). These phase transitions have been well documented (Berman, 1988; Holland and Powell, 1990). As pointed out by Berman (1988), the pressure effect on these phase transitions, and therefore on the enthalpies, entropies, and heat capacities, is not clear, since heat-capacity measurements were performed at ambient pressure. These may also contribute to the discrepancy.

Finally, the above discussions are based on the assumption that the enthalpies of formation of hematite and magnetite are well known. It is worth noting that the uncertainties of the enthalpy of formation of hematite and magnetite would also affect the calculated results. Any change in the enthalpy of formation of hematite affects the univariant curve in two ways: by affecting the value of enthalpy of formation of siderite from this study and by affecting the enthalpy of the reaction siderite + hematite = magnetite +  $\text{CO}_2$ .

The above discussion suggests that the thermodynamic

values and equations determined at low temperature and ambient pressure should be used with caution to reproduce phase equilibria at high temperature and high pressure. The discrepancies seem to indicate that the behavior of one or more of the minerals participating in the equilibrium is different at high temperature and pressure from what has been assumed. Further work to resolve the present discrepancy needs to be done. We believe that the current directly determined enthalpy of formation of siderite may help anchor values for other thermodynamic properties in internally consistent data sets, which, by their very nature, have all their numerical parameters interrelated such that a change in one value causes corresponding changes in many others.

#### Application to other Fe<sup>2+</sup>-bearing carbonates

Several calorimetric measurements have been made successfully for Fe<sup>2+</sup>-bearing phases using oxide melt solvents (Navrotsky et al., 1979; Wood and Kleppa, 1981; Chatillon-Colinet et al., 1983; Brown and Navrotsky, 1994). In those experiments, an inert atmosphere (usually Ar) was used to prevent the oxidation of Fe<sup>2+</sup>. However, Fe<sup>2+</sup>-bearing carbonates behave differently from other Fe<sup>2+</sup>-bearing phases when they dissolve in an oxide melt solvent because of the possible spontaneous oxidation of Fe<sup>2+</sup> by CO<sub>2</sub>. Our experiments showed that the dissolution products of siderite in lead borate solvent in an inert atmosphere appear to contain a mixture of Fe<sup>2+</sup> and Fe<sup>3+</sup>. At the same time, solution-calorimetric experiments of siderite using lead borate as a solvent are always accompanied by base-line shifts (the final voltage does not return to the initial values). These shifts make the final state uncertain and make it difficult to interpret the results. Calorimetry of siderite in an alkali borate solvent in an inert atmosphere also did not result in a single valence state of Fe. A more fruitful approach to calorimetry of Fe-bearing carbonates may consist of two steps: decomposition in an O<sub>2</sub> atmosphere to products fully oxidized to Fe<sup>3+</sup> followed by solution calorimetry of these products. We are now exploring this methodology for carbonates in the calcite-magnesite-siderite system.

#### ACKNOWLEDGMENTS

We thank E. Muromachi for helpful discussions on the calorimetric method, J. DiCarlo for the TGA analysis in an H<sub>2</sub> atmosphere, E. Smelik for the help in hydrothermal synthesis, M. Rodriguez for assistance in X-ray diffraction, and E. Vicenzi for microprobe analysis. We are grateful to N. Ross, R. Newton, and an anonymous reviewer for their critical reviews and valuable suggestions; the manuscript was improved by these suggestions. We would like to thank T. Holland, R. Powell, and K. Bose for the helpful discussions on phase equilibrium calculation. This paper benefited from telecommunications with T. Holland and R. Powell. However, the authors take full responsibility for this paper. This work was supported by the Department of Energy (grant DE-FG02-85ER13437).

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MANUSCRIPT RECEIVED OCTOBER 7, 1993

MANUSCRIPT ACCEPTED APRIL 29, 1994