

Christ, 1965; Holland, 1959, 1965; Mel'nik, 1964; Yui, 1966). The stability field of siderite is considered to be bounded by six possible reactions (table 1, eqs 3-8).

Reactions (7) and (8) can be stable only at  $f_{\text{O}_2}$  values below that of the graphite buffer; they lie entirely within the condensed region and do not involve  $\text{CO}_2$  or  $\text{CO}$  (French and Eugster, 1965). Calculated stability fields of siderite, bounded by reactions (3), (4), and (6), have been presented by Garrels (1960) for 298°K and by Holland (1959) for 300° to 600°K. Neither author considered possible reactions involving siderite and graphite.

In the present study,  $\Delta G^\circ_{f,T}$  data for siderite were calculated from thermodynamic data (Kelley and Anderson, 1935). Values of  $\Delta G^\circ_T$  for each reaction were calculated using values for the oxides tabulated by Coughlin (1954). The calculated values of  $\Delta G^\circ_T$  are essentially linear functions of  $T$  from 298° to 1200°K (table 1). Uncertainties in the values were calculated from the stated uncertainties of Coughlin (1954) for the oxide data, and a 1 percent uncertainty was assumed for the siderite data; the total uncertainty in  $\Delta G^\circ_T$  is thus only a minimum value. Data on the other physical properties of the phases involved are summarized elsewhere (Eugster and Wones, 1962; French, ms, 1970).

Values of  $\Delta S^\circ$  and  $\Delta H^\circ$  for each reaction (table 1) were calculated from the free energy data, using the relations:

$$\left( \frac{\partial \Delta G^\circ}{\partial T} \right)_P = -\Delta S^\circ \quad (9)$$

$$\left( \frac{\partial \frac{\Delta G^\circ}{T}}{\partial \frac{1}{T}} \right)_P = \Delta H^\circ \quad (10)$$

(Lewis and others, 1961, p. 165).  $\Delta S^\circ$  and  $\Delta H^\circ$  for all reactions are virtually independent of  $T$  over the temperature range 298° to 1200°K.

The equilibrium constants  $K(T)$  for each reaction were calculated from the relation:

$$\begin{aligned} \Delta G^\circ_T &= -2.303 RT \log K(T) \\ \log K(T) &= \frac{-\Delta G^\circ}{2.303 RT} \end{aligned} \quad (11)$$

and are given in table 1.

Values of equilibrium  $f_{\text{O}_2}$  as a function of  $T$  can then be calculated from the equilibrium constant for any specified total pressure. In those reactions in which  $\text{CO}_2$  also participates, it is reasonable to assume that  $P_F = P_{\text{CO}_2}$  for temperatures below 600°C and  $f_{\text{O}_2}$  values above those of the graphite buffer (French and Eugster, 1965). Values of  $f_{\text{CO}_2}$  were cal-

TABLE 1  
Calculated thermodynamic data for siderite decomposition reactions

Reaction	$\Delta G^\circ_{298}$ (cal)	$\Delta G^\circ_T$ (cal)	$\log K_1(T)$
3. Siderite + O <sub>2</sub> = hematite + CO <sub>2</sub> 2 FeCO <sub>3</sub> + $\frac{1}{2}$ O <sub>2</sub> = Fe <sub>2</sub> O <sub>3</sub> + 2 CO <sub>2</sub> $\log K_3(T) = 2 \log f_{\text{CO}_2} - \frac{1}{2} \log f_{\text{O}_2}$	- 43,850 $\pm$ 4,500	- 26,500 - 54.29 T	+ 6012/T + 11.87
4. Siderite + O <sub>2</sub> = magnetite + CO <sub>2</sub> 3 FeCO <sub>3</sub> + $\frac{1}{2}$ O <sub>2</sub> = Fe <sub>3</sub> O <sub>4</sub> + 3 CO <sub>2</sub> $\log K_4(T) = 3 \log f_{\text{CO}_2} - \frac{1}{2} \log f_{\text{O}_2}$	- 42,870 $\pm$ 6,200	- 13,900 - 96.44 T	+ 3039/T + 21.08
5. Siderite + O <sub>2</sub> = wüstite + CO <sub>2</sub> 0.947 FeCO <sub>3</sub> + 0.026 O <sub>2</sub> = Fe <sub>0.947</sub> O + 0.947 CO <sub>2</sub> $\log K_5(T) = 0.947 \log f_{\text{CO}_2} - 0.026 \log f_{\text{O}_2}$	+ 4,490 $\pm$ 1,800	+ 16,300 - 39.6 T	- 3564/T + 8.66
6. Siderite = iron + CO <sub>2</sub> + O <sub>2</sub> FeCO <sub>3</sub> = Fe + CO <sub>2</sub> + $\frac{1}{2}$ O <sub>2</sub> $\log K_6(T) = \log f_{\text{CO}_2} + \frac{1}{2} \log f_{\text{O}_2}$	+ 66,780 $\pm$ 1,700	+ 84,600 - 59.65 T	- 18,495/T + 13.04
7. Siderite = magnetite + graphite + O <sub>2</sub> 3 FeCO <sub>3</sub> = Fe <sub>3</sub> O <sub>4</sub> + 3 C + 5/2 O <sub>2</sub> $\log K_7(T) = 5/2 \log f_{\text{O}_2}$	+ 239,910 $\pm$ 6,100	+ 268,300 - 91.69 T	- 58,656/T + 20.05
8. Siderite = iron + graphite + O <sub>2</sub> FeCO <sub>3</sub> = Fe + C + 3/2 O <sub>2</sub> $\log K_8(T) = 3/2 \log f_{\text{O}_2}$	+ 161,040 $\pm$ 1,600	+ 178,700 - 58.97 T	- 39,068/T + 12.89