

dicate a higher value of ΔS°_{298} and correspondingly more positive values of ΔG°_{298} and ΔH°_{298} than are obtained directly from the thermodynamic data themselves.

Because of the large effect of experimental uncertainties on the calculation of the thermodynamic quantities from the experimental results, it is doubtful whether the differences obtained are meaningful or whether these calculations can be used to evaluate the experimental data themselves. The operation of calculating ΔH° (eq 15) involves the quotient of two small difference terms, and even reasonable estimates of experimental uncertainty ($T_{\text{eq}} \pm 10^\circ\text{C}$; $\log K_4 \pm 1.0$) produce uncertainties as large as several hundred percent in the derived value of ΔH° .

The corresponding values of ΔG° are less affected; the stated experimental uncertainties produce an uncertainty in ΔG° of about 5 to 8 percent or about ± 5 kcal/mole, comparable to the uncertainty in the value of ΔG° derived from thermodynamic data (table 1). However, the subtractions and other operations necessary to derive values for ΔG°_{298} (eq 17) multiply this uncertainty to the point where the calculated value of ΔG°_{298} has a minimum uncertainty of about 100 percent.

Because of the large uncertainties, the differences between the various calculated and experimental values in table 6 are probably not significant. The difficulty of using the experimental data to evaluate the experiments themselves is further indicated by the fact that the strongly divergent experimental results of French (ms) and Weidner (ms) give comparable values for the thermodynamic parameters at 298°K.

These results emphasize the extreme difficulty of integrating available thermodynamic data with experimental results in this particular system. The uncertainties in available thermodynamic data make it difficult to calculate equilibrium decomposition temperatures with any pre-

TABLE 6
Calculated thermodynamic data for siderite formation and decomposition to magnetite at 298°K

1. Reaction: $3 \text{FeCO}_3 + 1/2 \text{O}_2 = \text{Fe}_3\text{O}_4 + 3 \text{CO}_2$			
	ΔG°_{298} (kcal)	ΔH°_{298} (kcal)	ΔS°_{298} (cal/mole-deg)
Calculated (French, ms and this study) (table 1)	-42.87	-13.90	+ 96.4
Experimental (French, ms and this study)	-25.49	- 7.60	+111.1
Weidner (ms)	-29.10	- 1.39	+ 93.0
Holland (1965)*	-22.12	+ 7.43	+ 99.3
Yui (1966)*	-29.7	- 0.14	+ 99.3
2. Reaction: $\text{Fe} + \text{C} + 3/2 \text{O}_2 = \text{FeCO}_3$			
	$\Delta G^\circ_{f,298}$ (kcal/mole)	$\Delta H^\circ_{f,298}$ (kcal/mole)	$S^\circ_{298}(\text{siderite})$ (cal/mole-deg)
Calculated (Robie, 1966)	-161.06	-178.20	23.9
Experimental (French, ms and this study)	-166.6	-185.4	17.7

* Recalculated from author's original values for the analogous reaction: $3 \text{FeCO}_3 = \text{Fe}_3\text{O}_4 + 2 \text{CO}_2 + \text{CO}$.

cision (see above, and French, 1970, p. 9-10). Conversely, uncertainties in the experimental stability determinations are sufficient to prevent precise calculation of the thermodynamic properties of siderite from the experimental results, and values so calculated may not be any more accurate than the original data.

New values of thermodynamic parameters of siderite were, however, calculated from the experimental data on the assumptions that the differences between calculated and experimentally derived values of ΔG°_{298} , ΔH°_{298} , and ΔS°_{298} for reaction (4) were real and were due entirely to the thermodynamic data for siderite. With these assumptions, a change of about +7 kcal/mole in $\Delta H^\circ_{f,298}$ and of about +5 kcal/mole in $\Delta G^\circ_{f,298}$ at 600° to 700°K would bring the experimental and calculated values into agreement (table 6). This would correspond to a change of about +4 percent in the present values (Kelley and Anderson, 1935; Robie, 1962).

Thermodynamic data for siderite at elevated temperatures (600°-700°K) are not definite enough to exclude a difference of this magnitude. Current heat-capacity data (Kelley, 1960) are based on studies between 50° and 300°K of a natural siderite containing only 90 percent FeCO_3 (Anderson, 1934); values of C_p were corrected by Anderson for the additional components CaCO_3 , MgCO_3 , and MnCO_3 in the sample. Extrapolation of these data to higher temperatures could produce the indicated difference.

High-temperature heat-capacity data on pure siderite will probably be needed to resolve the question entirely. It should be noted that estimated values of C_p for rhodochrosite (MnCO_3) based on Anderson's data (Kelley and Anderson, 1935) are 5 to 10 percent lower in the range 500° to 700°K than are values determined by direct measurement (Moore, 1943) and that similar differences are observed in values of $\Delta G^\circ_{f,T}$ for rhodochrosite determined from experimental stability data (Huebner, 1969). It is very likely that a similar difference could exist in the thermodynamic data for siderite.

GEOLOGICAL APPLICATIONS

Data on the stability of siderite may be applied to estimate conditions present during the metamorphism of iron formations (French, 1968) and the emplacement of siderite-bearing hydrothermal veins. The experimental results determined here are in a simpler system than present in nature, and application of the experimental data to natural processes is limited by the additional components present in the natural environment.

1. Water is undoubtedly present in significant amounts in any gas phase coexisting with natural siderite. Introduction of water into the gas makes possible the formation of H_2 and CH_4 (French, 1966) and produces a situation in which $P_{\text{CO}_2} + P_{\text{CO}} < P_F$. These effects must be considered in estimating the decomposition temperatures for natural siderite.