



Fig. 11. Comparison of calculated and experimentally determined values of  $\Delta H^\circ$  for the reaction: 3 siderite +  $1/2 \text{O}_2 = \text{magnetite} + 3 \text{CO}_2$  (eq 4), derived from plotting the equilibrium constant against  $1/T$ . Values of  $\log K_4(T)$  ( $\equiv \log K_B$ ) derived from thermodynamic data are shown by solid lines for  $P_T = 1$  bar and 2000 bars. Dashed lines indicate values of the quantity:  $3 \log f_{\text{CO}_2} - 1/2 \log f_{\text{O}_2}$  as a function of temperature, using  $f_{\text{O}_2}$  values along the hematite-magnetite (HM) (long dashes) and graphite (Gr) (short dashes) buffers. Intersections of the dashed lines with the solid lines correspond to calculated equilibrium temperatures for a particular pressure.

Values of  $\log K_4$  ( $\equiv \log K_B$ ) calculated from experimental results (table 4) are plotted as solid circles (the open circle indicates an extrapolated value for the SHMG point at 2000 bars). Boxes around the points indicate the estimated uncertainty ( $\log K_4 \pm 1.0$ ;  $1/T \times 10^3 \pm 0.03$ ). Values of  $\Delta H^\circ$  obtained from the experimental equilibrium constants by connecting points at the same total pressures differ significantly from the calculated values and are opposite in sign. However, the fact that the error boxes overlap the entire range of variation in  $\log K_4$  suggests that the derived values of  $\Delta H^\circ$  may not be meaningful.

for siderite. Eugster and Wones (1962) applied the same method to calculate thermodynamic data for the iron-biotite, annite.

Experimentally determined values of  $\log K_4$  (table 4; fig. 11) are quite closely grouped and are considerably smaller than values calculated from  $\Delta G^\circ$  for 1 bar and 2000 bars. The lines that connect each pair of experimental points at the same total pressure have high negative slopes

which become more negative at lower pressures, in contrast to the positive slopes of the calculated lines (fig. 11).

Values of  $\Delta H^\circ$  calculated from the experimental results are positive and range from +7 to +12 kcal/mole between 500 and 2000 bars, in sharp contrast to the values of -13 to -16 kcal/mole derived from thermodynamic data (fig. 11). These differences are too great to be caused by the effect of changing total pressure on  $\Delta H^\circ$  (see Orville and Greenwood, 1965), because the differences exist between calculated and experimental data for the same total pressure, and because the effect of total pressure on this reaction can be calculated to be only about -2 kcal/mole between 1 bar and 2000 bars.

Similar differences exist between calculated and experimental values of  $\Delta G^\circ$  (table 4); the experimental results are about 10 kcal/mole more positive. Assuming that  $\Delta S^\circ$  is constant with temperature, the experimental results yield a value of  $\Delta S^\circ = +111$  cal/mole-deg, in contrast to a calculated value of about +96 cal/mole-deg (table 1).

Using the relationship:

$$\Delta G^\circ_{298^\circ\text{K}} = \Delta G^\circ_T + \Delta S^\circ (T - 298) \quad (17)$$

the experimental data yield a value of  $\Delta G^\circ_{298^\circ\text{K}} = -25.5$  kcal/mole and  $\Delta H^\circ = +7.6$  kcal/mole, in contrast to the calculated values of -42.9 kcal/mole and -13.9 kcal/mole, respectively (table 5).

Approximate values of  $\Delta G^\circ$  and  $\Delta H^\circ$  can be calculated from Weidner's (ms) data by assuming that  $f_{\text{CO}_2} = P_F$  (French and Eugster, 1965) and neglecting the change in  $f_{\text{O}_2}$  of the buffers with changing  $P_F$  (Eugster and Wones, 1962). The errors introduced by these two effects are opposite in sign and will probably not produce uncertainties greater than those in the experimental data themselves. With these assumptions, Weidner's (ms) data yield values of  $\Delta G^\circ_{298} = -29.1$  kcal/mole,  $\Delta H^\circ = -1.4$  kcal/mole,  $\Delta S^\circ = +93$  cal/mole-deg (table 6).

Thermodynamic data for the decomposition of siderite to magnetite (eq 4) derived from these two experimental studies are given in table 6, together with values calculated by other workers (Holland, 1965; Yui, 1966) for the same reaction. The latter two values are not completely independent, having been based on the earlier results of French and Rosenberg (1965). The results calculated from experimental data appear to in-

TABLE 5  
Calculated and experimentally determined values of  $\Delta H^\circ$  for the reaction: 3 siderite +  $\frac{1}{2}$  O<sub>2</sub> = magnetite + 3 CO<sub>2</sub>

$P_F$ (bars)	$\Delta H^\circ$ (kcal)	
	calc	expt.
1	-13.9 ± 7.0	—
500	—	+12.5
1000	—	+7.6
2000	-16.1 ± 7.0	+1.8(*)

(\*) Based on estimated temperature of 370°C for the SHMG curve at 2000 bars.