TABLE 4

Calculated interchange energy for regular solution
calcite-dolomite solvus

T, °K	Xmc (1 atm) mole. fraction	Ω cal/mole
673	0.022	2650
723	0.032	2615
773	0.043	2605
823	0.055	2630
873	0.069	2680
923	0.089	2630
973	0.111	2605
993	0.117	2705
1053	0.152	2690
1173	0.245	2740

must remain zero under arbitrary differential changes in pressure and composition of the calcite phase:

$$d\,(\Delta\mu) = 0 = \left(\frac{\partial\Delta\mu}{\partial p}\right)_{T,X_{mc}} dp + \left(\frac{\partial\Delta\mu}{\partial X_{mc}}\right)_{P,T} dX_{mc}$$

$$\therefore\ \left(\frac{\partial X_{mc}}{\partial P}\right)_{T} = -\ \frac{\left(\dfrac{\partial\Delta\mu}{\partial P}\right)_{T,X_{mc}}}{\left(\dfrac{\partial\Delta\mu}{\partial X_{mc}}\right)_{T,P}}$$

The numerator may be evaluated as:

$$\frac{\partial\Delta\mu}{\partial P}\bigg|_{T,X_{cm}} = V_{cc}{}^{c} + V_{cm}{}^{c} - V^{D}$$

where ∇ indicates partial molal volume, and V is volume per mole. If the denominator is evaluated by differentiating the regular solution expressions, the pressure effect becomes:

$$\left(\frac{\partial X_{mc}}{\partial P}\right)_{T} = \frac{V_{cc}{}^{c} + V_{mc}{}^{c} - V^{D}}{(2X_{mc}\text{-}1)\left[\dfrac{RT}{X_{mc}\,(1\text{-}X_{mc})} - 2\Omega\right]}$$

In order to evaluate the partial molal volumes, a plot of volume per mole of calcite solid solution versus mole fraction of $MgCO_3$ in solid solution was made using the unit cell data of Goldsmith, Graf, and Heard (1961). Table 5 gives the molar volumes of the solid solutions and dolomite. The partial molal volumes are the intercepts on the calcite and magnesite axes of the tangents to the molar volume curve. Very careful plotting on large sheets of millimeter paper and careful straightedge measurements were necessary in order to get acceptable values be-

TABLE 5

Molar volumes of magnesian calcite and dolomite

Composition, mole % $MgCO_3$	a_o, Å	c_o, Å	V, cm^3	Source*
Calcite	4.9900	17.062	36.931	1
(Johnson-Mathey Spec-Pure $CaCO_3$)				
4.94	4.9691	16.952	36.386	1
9.89	4.9440	16.851	35.805	1
10.0	4.9483	16.870	35.908	2 (avg)
19.78	4.9022	16.637	34.755	1
20.0	4.9122	16.699	35.027	2 (avg)
30.0	4.8760	16.514	34.131	2
40.0	4.8419	16.283	33.184	2 (avg)
42.5	4.8328	16.235	32.962	2
45.0	4.8244	16.167	32.710	2 (avg)
47.5	4.8152	16.111	32.472	2
50	4.8050	16.061	32.234	2
Magnesite, synthetic	4.6331	15.015	28.018	1
Dolomite, ordered, Gabbs, Nev.	4.8064	23.102	32.139	2
Dolomite, disordered, Gabbs, Nev.	4.8031	16.037	32.161	2
Dolomite, ordered, Serra das Eguas, Brazil	4.8065	16.004	32.140	2
Dolomite, disordered, Serra das Eguas, Brazil	4.8017	16.037	32.142	2

*Source 1 is Goldsmith and Graf (1958); source 2 is Goldsmith, Graf, and Heard (1961).

cause of the slight departure from Vegard's Law. Two separate plots were made, and the tangent-intercepts averaged.

Figure 10 shows the averaged partial molal values of $MgCO_3$ and $CaCO_3$ in solid solution in the composition range 0 to 30 mole percent $MgCO_3$. It should be remembered that the data are taken from samples at room temperature and at 1 atm pressure. The correction of the values to the elevated temperature and pressure of the desired calculation was necessarily ignored. The present solubility data, reduced to 1-atm values, were used in the pressure-effect calculation. The computed increases of solubility due to pressure are 0.52 mole percent/10 kb at 520°, 0.82 mole percent/10 kb at 650°, and 0.82 mole percent/10 kb at 780°. These values may be compared with the measured values of approximately 0.9 mole percent/10 kb at 500°C, of 1.2 mole percent/10 kb at 650°, and of 1.4 mole percent/10 kb at 780°. The agreement is close enough to indicate that the regular solution theory provides a nearly quantitative estimate of the pressure effect on the solvus. The discrepancies could be due to the several obvious sources of error, such as ignoring the pressure and temperature effects on the molar volume curve, the difficulty of obtaining accurate tangents to it by graphical means, or not taking into account any slight increase of solubility of $MgCO_3$ at the calcite I-II