



Fig. 9. Possible alternative CaCO_3 stability diagrams. Figure 9A shows possible relations if a hypothetical phase "X" makes a metastable triple point with aragonite and calcite II in the field of aragonite. Metastable portions are indicated by dotted and broken lines. Figure 9B shows possible relations if a hypothetical phase "X" has a stable invariant relation with respect to calcite I and calcite II.

does, and the $\Delta_{\text{I-II}}$ must be the sum of $\Delta V_{\text{I-X}}$ and $\Delta V_{\text{X-II}}$. This hypothesis would also eliminate the need for curvature in the calcite I-II curve. A deflection of the calcite-aragonite curve by the II-X transition as it crosses it might be too small to be easily observed.

Figure 9B is a diagram that would result if there is a "II-X" transition that makes a stable invariant point with the I-II transition. The observations of Bell and England could be explained by this hypothesis, but the observation of Dandekar could not. Again the I-II transition would have to have a large ΔV and need not have much curvature.

It is conceivable that both calcite II and a "calcite X" might have a calcite I-like X-ray diffraction powder pattern with the (113) line missing, whether or not an anion-rotation phenomenon is responsible for the line deletion. Thus a diagram involving three calcite phases is not eliminated as a possibility by the present data. The scientists' prejudice for the simplest workable hypothesis may lend favor to the relatively straightforward calcite I-II interpretation as shown in figure 1.

Binary system.—Many of the features of the pressure-temperature diagram of the system $\text{CaCO}_3\text{--MgCO}_3$ can be investigated by using the theory of regular solutions. Following Robie (1957), CaCO_3 (cc)- MgCO_3 (mc) solutions in the calcite structure are treated as regular solutions, so that:

$$\begin{aligned}\mu_{cc} &= \mu_{cc}^{\circ} + RT \ln (1-X_{mc}) + \Omega X_{mc}^2 \\ \mu_{mc} &= \mu_{mc}^{\circ} + RT \ln X_{mc} + \Omega (1-X_{mc})^2\end{aligned}$$

where μ denotes the partial molal Gibbs energy of the components, R is the gas constant per mole, T is the absolute temperature, X is the mole fraction of a component, Ω is the "inter-change energy" per mole (Guggenheim, 1952), and a superscript zero refers to the pure component.

The equilibrium relation of the solvus is given by:

$$\mu_{cc}^c + \mu_{mc}^c - \mu^d = 0$$

Here the superscript C represents calcite, and D represents dolomite. Inserting the regular solution equations gives:

$$0 = \Delta\mu^{\circ} + RT \ln X_{mc} (1-X_{mc}) + \Omega [X_{mc}^2 + (1-X_{mc})^2]$$

The standard Gibbs energy change for the pure substances, $\Delta\mu^{\circ}$, is evaluated by:

$$\Delta\mu^{\circ} = \Delta H^{\circ}_{298} - T\Delta S^{\circ}_{298}$$

where ΔH°_{298} is the standard enthalpy change, and ΔS°_{298} is the corresponding entropy increment. The latter equation assumes that ΔS° is constant over the temperature interval 298°K-T, an assumption that is necessary because of the lack of high-temperature heat content data for magnesite and dolomite. This assumption is likely to be valid with a high degree of accuracy in the temperature range of interest, as evidenced by the fact that the heat capacity of dolomite in the range 70 to 300°K is equal to the sum of the heat capacities of calcite and magnesite to within 0.2 percent (Robie, ms, p. 73). Hence,

$$\Omega = \frac{-\Delta H^{\circ}_{298} + T\Delta S^{\circ}_{298} - RT \ln X_{mc}(1-X_{mc})}{2X_{mc}^2 - 2X_{mc} + 1}$$

The values of $\Delta H^{\circ}_{298} = 3150$ cal/mole and $\Delta S^{\circ}_{298} = 0.81$ cal/°C-mole used by Robie are adopted. Table 4 shows the values of Ω that are calculated at several temperatures when the best solvus data of the present work, reduced to a 1-atm basis by applying the measured pressure correction, are used. The Ω values fall within a fairly narrow spread, which is some justification for the use of the regular solution theory.

The effect of total pressure on the MgCO_3 solubility can be calculated as follows. The total variation at constant temperature of the Gibbs energy change of the solvus reaction, $\Delta\mu = \mu_{cc}^c + \mu_{mc}^c - \mu^d$,