

Fig. 10. Partial molal volumes of CaCO_3 and MgCO_3 in calcite as functions of composition, as obtained from quenched solid solutions at 1 atm and room temperature.

transition. The present data fail to establish clearly a discontinuity in the solubility versus pressure curves but place an upper limit of 0.3 to 0.5 mole percent on an increase of MgCO_3 solubility going into the calcite II structure. This number is itself quite useful in determining the location of the calcite I-calcite II-dolomite line in the pressure-temperature projection, as will be seen shortly.

Theoretical curves for the calcite I-dolomite-aragonite and calcite II-dolomite-aragonite pressure-temperature projections can be constructed from the regular solution theory starting with the diagram for pure CaCO_3 . By setting the chemical potential of CaCO_3 in magnesian calcite equal to the chemical potential of aragonite, one finds the increase in pressure necessary to produce the calcite-aragonite transition when MgCO_3 is saturated in the calcite structure so that dolomite is present:

$$P-P^I = \frac{1}{\Delta V_{A \rightarrow I}} \left[-RT \ln (1-X_{mc}^I) - \Omega X_{mc}^{I^2} \right]$$

$$P-P^{II} = \frac{1}{\Delta V_{A \rightarrow II}} \left[-RT \ln (1-X_{mc}^{II}) - \Omega X_{mc}^{II^2} \right]$$

where P^I is the equilibrium transition pressure from pure calcite I to

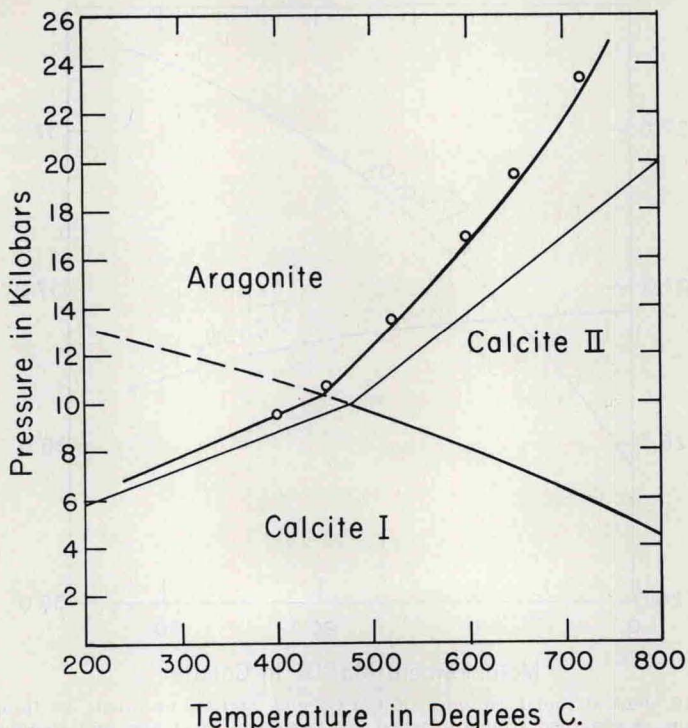


Fig. 11. Computed points on the calcite-aronite-dolomite curve, compared with the experimentally determined curve. Phase boundaries for pure CaCO_3 are shown. The metastable portion of the calcite I-calcite II curve is dashed.

aragonite at a given temperature and P^{II} is the corresponding pressure for pure calcite II. The fundamental finding that there is a negligible solubility difference of MgCO_3 in calcite I and calcite II is now applied. A corollary of this is that the Ω values for calcite I and calcite II are very nearly the same. The X_{mc} values are given an appropriate incremental increase in Mg-content due to the pressure increase from the 1-atm values to the pressure of the pure CaCO_3 calcite-aronite curve. Figure 11 shows the calculated points compared with the least-square fit to the data: The agreement is surprisingly good. The calculated points lie a few hundred bars above the experimental curve, but the discrepancy is within the combined error limits. A change of ΔV of the calcite-aronite transition with temperature and pressure or a change of Ω with temperature and pressure might also be responsible for the slight discrepancy.

An independent estimate of $\Delta V_{\text{I} \rightarrow \text{II}}$ in pure CaCO_3 can be made from the two preceding equations by comparing the dispositions of the univariant curves around the triple points in the pure CaCO_3 and the MgCO_3 saturated system. The experimental determinations of the univariant curves are shown enlarged in the region of the univariant points in the pressure-temperature diagram in figure 12. The pressures P , P^{I} ,