Fig. 10. Partial molal volumes of CaCO₃ and MgCO₃ 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:

$$P-P^I = \frac{1}{\Delta V_{A \to I}} \left[-RT \ln (1-X^I_{mc}) - \Omega X^{I\,2}_{mc} \right]$$

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

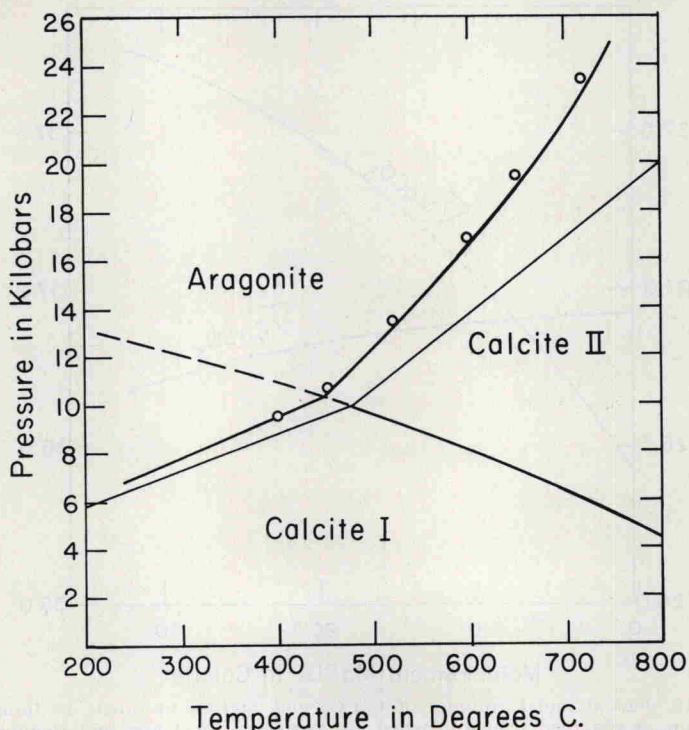where P^I is the equilibrium transition pressure from pure calcite I to

Fig. 11. Computed points on the calcite-aragonite-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-aragonite 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-aragonite 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 $\Delta V_{I \rightarrow II}$ 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,