THERMODYNAMIC DISCUSSION

The relatively large amount of thermo-chemical data available for the system $CaCO_3$–$MgCO_3$ makes possible several detailed calculations of the phase relations encountered at high temperature and pressure. The most useful data are the standard enthalpies of formation and entropies of calcite, magnesite, and dolomite (Robie, ms) and the molar volumes of magnesian calcites, which may be calculated from the unit-cell constants determined by Goldsmith and Graf (1958) and Goldsmith, Graf, and Heard (1961). These data, in conjunction with the measured solubility of $MgCO_3$ in calcite as a function of temperature, allow theoretical calculation of the pressure-temperature locations of the three-phase curves of figure 2 and the effect of pressure on the calcite-dolomite solvus curve.

CaCO₃ system.—The measured slopes of the univariant curves meeting at the triple-point calcite I–calcite II–aragonite (A) determine the volume change per mole of the I $\rightarrow$ II transition. The relation for the volume change is, assuming a first-order transion:

$$\Delta V_{I \rightarrow II} = \frac{-\Delta V_{A \rightarrow I} \left(\dfrac{dp}{dt}_{A \rightleftharpoons I} - \dfrac{dp}{dt}_{A \rightleftharpoons II} \right)}{\dfrac{dp}{dt}_{I \rightleftharpoons II} - \dfrac{dp}{dt}_{A \rightleftharpoons II}}$$

If the transition takes place over a finite temperature and pressure interval, such as would be the case for certain kinds of higher-order transitions, the $\Delta V_{I \rightarrow II}$ would still be calculated by the above expression using the slopes measured on opposite ends of a ΔT interval sufficient to enclose the transition. The values of the slopes presented in the preceding section and the $\Delta V_{A \rightarrow I}$ of 2.78cm³/mole, neglecting any differential compression to 10 kb and differential thermal expansion to 480°C, yield a $\Delta V_{I \rightarrow II}$ of −1.01 cm³/mole. This value is nearly ten times as large as that measured by Bridgman (1939) by the method of piston-displacement at 25°C and might also seem surprisingly large in view of the inability to detect clearly the I $\rightleftharpoons$ II transition by various means in the present study. The I-II transition has a marked effect on the course of the calcite-aragonite boundary, however, and the abrupt change of direction argues persuasively for a first order transition of significant volume change or for a higher order transition of significant net volume change which is complete over a rather small temperature and pressure interval. It is not probable that a few hundred degrees temperature increase could increase $\Delta V_{I \rightleftharpoons II}$ by a factor of nearly 10. The strong indication of the present work is that the ΔV measured by Bridgman was erroneously small because of sluggishness of the transition at the low temperatures at which he worked. Bridgman reported an anomalously high apparent compressibility of calcite II, which would be due to a sluggish transition if the present surmise is correct.

If $\Delta S_{I \rightarrow II}$ is calculated from the Clausius Clapeyron equation the result is $\Delta S = 0.349$ cal/°C mole. This value provides some support for the Jamieson–Boettcher–Wyllie hypothesis of correlating Bridgman's calcite I-II transition with the thermal arrest at 975°C in the 1-atm heating and cooling curves of Boeke (1912). Jamieson estimated a ΔS of 0.273 to 0.409 cal/°C mole for the thermal transition based on the duration of Boeke's signal and the heat capacity of calcite. This relatively large heat effect is not consistent with the small volume change and small dp/dt slope given by Bridgman but is in close agreement with the $\Delta S_{I \rightarrow II}$ of 0.349 cal/°C mole predicted from the measured slopes at the triple-point. The simplest hypothesis, that of the identity of Bridgman's and Boeke's transitions, therefore seems preferable in spite of failure to detect the location of the transition in the pressure-temperature plane by means other than a break in slope of the calcite-aragonite curve.

The $\Delta S_{I \rightarrow II}$ value of 0.349 is smaller than the value of ~ 1.4 cal/°C mole which is the configurational entropy increase due to disordering the planar $CO_3^=$ groups of the calcite structure (Boettcher and Wyllie, 1968). There may also be an entropy decrease attendant on the decrease in volume which could amount to as much as 1 cal°C mole per cc (Fyfe, Turner, and Verhoogen, 1958, p. 30), so that the hypothesis of an order-disorder transition cannot be ruled out on this basis. The percentage entropy and volume changes of the calcite I $\rightleftharpoons$ II transition are quite similar to those at the high-low quartz transition. There is only a slight change in the X-ray powder pattern, assuming that Jamieson's high pressure X-ray data are applicable, as in the α to β quartz case, which is also a non-quenchable transition. A slight bond-angle change in calcite analogous to that in quartz might be a reasonable structural explanation.

If the correlation of Bridgman's calcite I-II transition with the thermal effect of Boeke is made, as the present data seems to favor, neither the DTA arrests encountered by Bell and England (1964) nor the shear-wave velocity anomaly found by Dandekar (ms) at 3 to 4 kb and 25°C in single calcite crystals are elucidated. Alternative $CaCO_3$ pressure-temperature diagrams may be brought forth that explain one or both of these effects by reversible phase changes and that are not wholly ruled out by the present data.

Figure 9A shows the diagram that would result if the observations of Bell and England are due to a first-order phase change which makes a virtual (metastable) triple point with the calcite I-II line inside the field of aragonite. A metastable prolongation of this postulated phase change might be made to explain the observed ultrasonic effects near 3 to 4 kb. The postulated new transition would require a rather small volume change; otherwise it would have been observed in earlier volumetric studies. Bridgman's I-II transition would have to have a substantial volume change under this hypothesis as well, because the "I-X" transition must have a large ΔV in order to deflect the calcite-aragonite curve as it