

CALCULATED PHASE RELATIONS IN THE SYSTEM $\text{CaCO}_3\text{--SrCO}_3$

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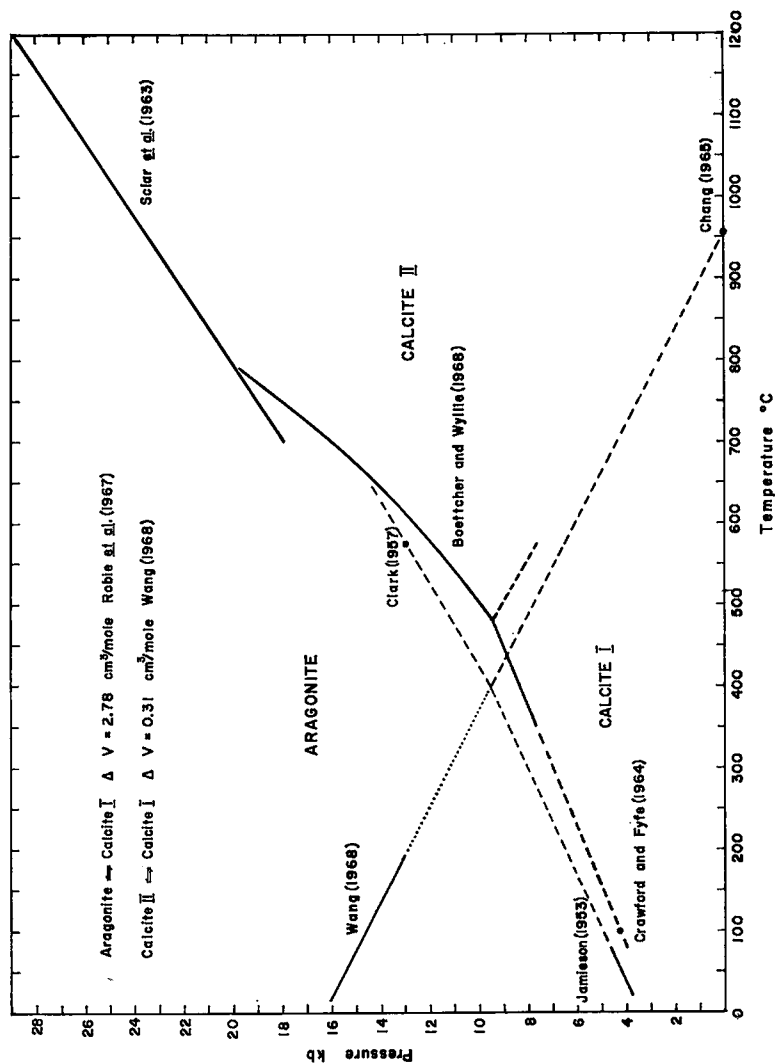
ABSTRACT

The two compounds CaCO_3 and SrCO_3 both exhibit an orthorhombic $\rightleftharpoons$ rhombohedral transition, and, in the system $\text{CaCO}_3\text{--SrCO}_3$, orthorhombic and rhombohedral solid solutions may coexist over a considerable range of pressure and temperature. From existing experimental data, it is possible to derive ΔV and ΔS of the transitions in pure CaCO_3 and SrCO_3 , if it is assumed that these values remain constant and that the solid solutions are ideal. On the basis of the same assumptions, the derived values of ΔV and ΔS may be used to calculate the composition of coexisting solid solutions at any combination of pressure and temperature. In this way, experimentally determined phase relations may be extrapolated to conditions at which no experimental data are available.

INTRODUCTION

The two compounds CaCO_3 and SrCO_3 may exist in orthorhombic and rhombohedral modifications. Over a considerable range of pressure and temperature, orthorhombic and rhombohedral solid solutions coexist and, at certain conditions, complete solid solution series are formed. Phase relations in the system $\text{CaCO}_3\text{--SrCO}_3$ may be shown by means of contours on a P-T diagram or by means of T-X diagrams (at constant P) and P-X diagrams (at constant T). Various experimental data on phase relations in this system are available. In this paper, an attempt is made to express the experimental results by thermodynamic relationships and, on that basis, calculate a complete phase diagram of the system.

The orthorhombic $\rightleftharpoons$ rhombohedral transition in pure CaCO_3 has been investigated by several workers (Fig. 1). For some time, the phase boundary obtained by joining the determinations of Jamieson (1953) and Clark (1957) was widely accepted. But recently Boettcher & Wyllie (1968) presented a different boundary which displayed, as a novel feature, an appreciable inflection at a suggested triple point between calcite I, calcite II, and aragonite. They made use of their own experimental work and the determination obtained by Crawford & Fyfe (1964). At about the same time, Goldsmith & Newton (1969) published a phase diagram very similar to that of Boettcher & Wyllie (1968). Calcite II is a polymorph of CaCO_3 characterized by a *c* cell dimension half that of calcite I. Its structure represents a minor modification of the normal calcite structure (Jamieson 1957). The transition calcite I $\rightleftharpoons$ calcite II has been observed at one atmosphere (Chang 1965) and metastably in the aragonite field (Bridgman 1939; Davies 1964; Jamieson 1957; Wang 1968). The existence of the triple point was suggested by Jamieson (1957) who argued that

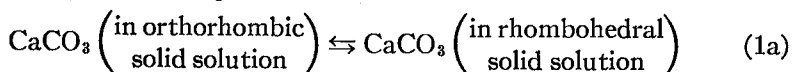
FIG. 1. Phase relations in the system CaCO_3 .

only a very slight inflection of the calcite-aragonite boundary would be demanded by the calcite I—calcite II transition because the two calcite polymorphs have very similar properties. Since the volume change of the calcite I—aragonite transition is known (Robie *et al.* 1967), Goldsmith & Newton (1969) calculated the volume change of the calcite I—calcite II transition from their phase diagram. They obtained a value of $1.01 \text{ cm}^3/\text{mole}$. For a minor change in structure, this seems rather high and is, in fact, contradicted by direct measurement of the volume change by Bridgman (1939) and Wang (1968). Accepting the value of $0.31 \text{ cm}^3/\text{mole}$ obtained by Wang (1968), the points of Jamieson (1953) and Clark (1957) on the calcite—aragonite boundary, and the location of the calcite I—calcite II boundary as determined by Chang (1965) and Wang (1968), the inflection of the calcite-aragonite curve is only very slight, as shown in Fig. 1. A small volume change of the calcite I—calcite II transition is also indicated by continuous lattice parameters of rhombohedral $(\text{Ca,Sr})\text{CO}_3$ solid solutions (Chang 1965) and by the absence of differential solubility of Sr and Mg in calcite I and calcite II (Chang 1965; Goldsmith & Newton 1969). Furthermore, the slope of Boettcher & Wyllie's (1968) curve is not consistent with the phase boundary of Sclar *et al.* (1963) at higher temperatures. For these reasons, the Clark-Jamieson boundary of the calcite—aragonite transition is accepted in this paper.

In the system $\text{CaCO}_3\text{--SrCO}_3$, phase relations at one atmosphere, including the orthorhombic $\rightleftharpoons$ rhombohedral transition in pure SrCO_3 at 912°C , have been determined by Chang (1965). His experimental data based on identification of phases by means of high-temperature x-ray diffraction are shown in Fig. 2. Due to the difficulty of quenching rhombohedral $(\text{Ca,Sr})\text{CO}_3$ solid solutions, results obtained by examining quenched products were not used. Therefore, the equilibrium curves shown in Fig. 2 differ somewhat at lower temperatures from the phase diagram presented by Chang (1965). Froese & Winkler (1966) have investigated the phase relations at 560°C and 655°C and pressures up to 13 kb. Due to quenching difficulties, it was impossible to determine the composition of rhombohedral solid solutions coexisting with orthorhombic solid solutions. Recently, Chang (1969) reported further work in this system.

THEORY

The components CaCO_3 and SrCO_3 may be freely transferred between orthorhombic and rhombohedral solid solutions. For component CaCO_3 , the following reaction equation is valid:



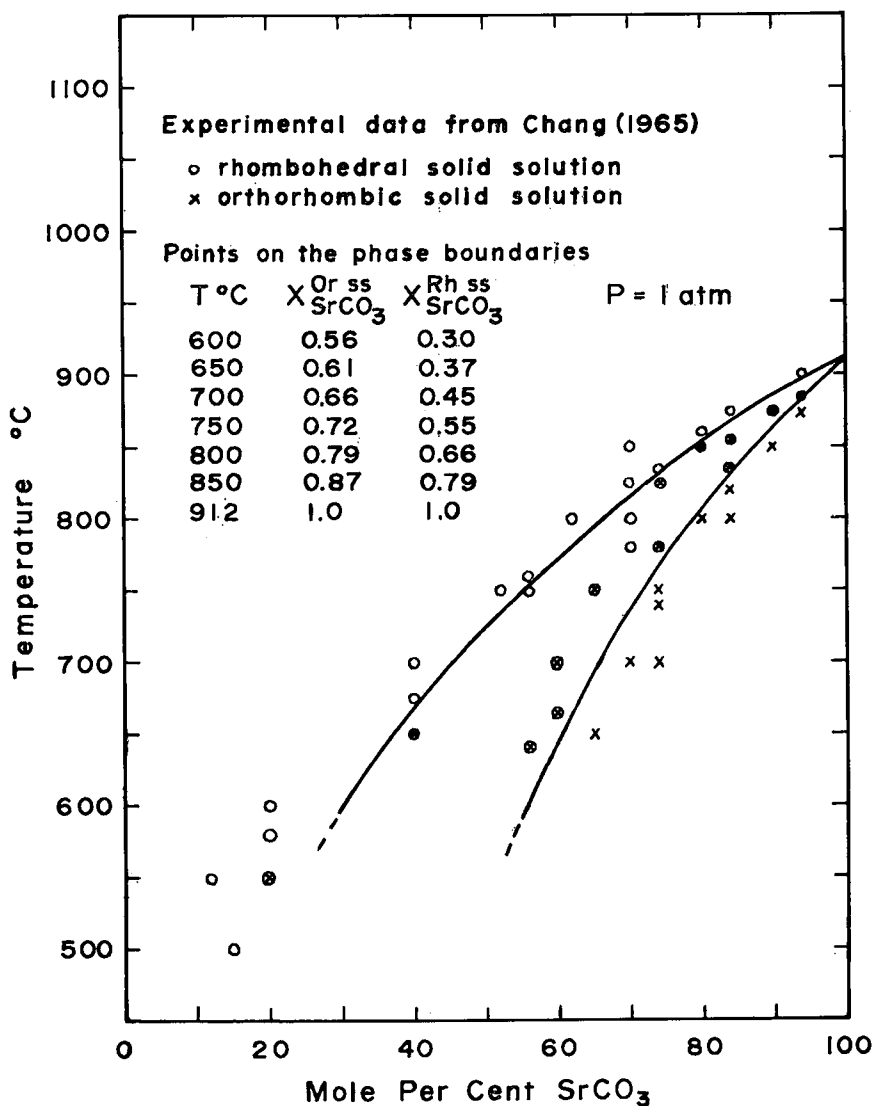


FIG. 2. Phase relations in the system $\text{CaCO}_3\text{-SrCO}_3$ at 1 atm based on experimental data from Chang (1965).

At equilibrium, the free energy change of this reaction must be zero, *i.e.* the partial molar free energy of CaCO_3 in the two phases must be equal:

$$\bar{G}_{\text{CaCO}_3}^{\text{Or ss}} = \bar{G}_{\text{CaCO}_3}^{\text{Rh ss}} \quad (1b)$$

If pure rhombohedral CaCO_3 , at any specified pressure and temperature, is defined as the standard state of rhombohedral CaCO_3 and, similarly, pure orthorhombic CaCO_3 as the standard state of orthorhombic CaCO_3 , the following equation may be written:

$$G_A^\circ + RT \ln a_{\text{CaCO}_3}^{\text{Or ss}} = G_C^\circ + RT \ln a_{\text{CaCO}_3}^{\text{Rh ss}} \quad (1c)$$

where

G_A° = molar free energy of pure orthorhombic CaCO_3 (aragonite) at any specified pressure and temperature

G_C° = molar free energy of pure rhombohedral CaCO_3 (calcite) at any specified pressure and temperature

$a_{\text{CaCO}_3}^{\text{Rh ss}}$ = activity of CaCO_3 in rhombohedral solid solution

$a_{\text{CaCO}_3}^{\text{Or ss}}$ = activity of CaCO_3 in orthorhombic solid solution

This equation may be rearranged:

$$G_C^\circ - G_A^\circ = \Delta G_{A \rightleftharpoons C}^\circ = -RT \ln \frac{a_{\text{CaCO}_3}^{\text{Rh ss}}}{a_{\text{CaCO}_3}^{\text{Or ss}}} \quad (1d)$$

Where $\Delta G_{A \rightleftharpoons C}^\circ$ is the standard free energy change of reaction (1a), *i.e.* the free energy change of the orthorhombic $\rightleftharpoons$ rhombohedral transition in pure CaCO_3 at any specified pressure and temperature. Deviations from ideal behaviour of a solution are commonly expressed by an activity coefficient defined as $\gamma = a/X$, where X is the mole fraction. Therefore, equation (1d) may be written:

$$\Delta G_{A \rightleftharpoons C}^\circ = -RT \ln \frac{X_{\text{CaCO}_3}^{\text{Rh ss}}}{X_{\text{CaCO}_3}^{\text{Or ss}}} \cdot \frac{\gamma_{\text{CaCO}_3}^{\text{Rh ss}}}{\gamma_{\text{CaCO}_3}^{\text{Or ss}}} \quad (1e)$$

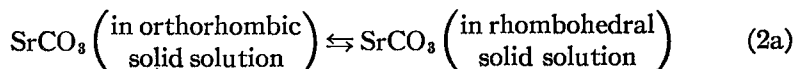
If it be assumed that the solution is ideal (*i.e.* $\gamma = 1$) or, at least, that the ratio of the activity coefficients in equation (1e) is one, the equation reduces to:

$$\Delta G_{A \rightleftharpoons C}^\circ = -RT \ln \frac{X_{\text{CaCO}_3}^{\text{Rh ss}}}{X_{\text{CaCO}_3}^{\text{Or ss}}} \quad (1f)$$

For a solid solution consisting only of CaCO_3 and SrCO_3 , the relationship holds that $X_{\text{CaCO}_3} + X_{\text{SrCO}_3} = 1$, and equation (1f) may be written in the form:

$$\Delta G_{A \rightleftharpoons C}^\circ = -RT \ln \frac{1 - X_{\text{SrCO}_3}^{\text{Rh ss}}}{1 - X_{\text{SrCO}_3}^{\text{Or ss}}} \quad (1g)$$

Equilibrium relationships analogous to those developed for CaCO_3 also exist for component SrCO_3 . The following reaction equation is valid:



For this equilibrium, the relationship may be deduced:

$$\Delta G_{S \rightleftharpoons R}^\circ = -RT \ln \frac{X_{\text{SrCO}_3}^{\text{Rh ss}}}{X_{\text{SrCO}_3}^{\text{Or ss}}} \quad (2b)$$

Where $\Delta G_{S \rightleftharpoons R}^\circ$ is the standard free energy change of reaction (2a), *i.e.* the free energy change of the orthorhombic $\rightleftharpoons$ rhombohedral transition in pure SrCO_3 at any specified pressure and temperature.

If the free energy change of the transitions in pure CaCO_3 and pure SrCO_3 are known at a given pressure and temperature, equations (1g) and (2b) may be solved simultaneously for the two unknowns $X_{\text{SrCO}_3}^{\text{Rh ss}}$ and $X_{\text{SrCO}_3}^{\text{Or ss}}$. If the pure components, at any specified pressure and temperature, are chosen as the standard state, the standard free energy change along the transition boundary must be zero. The free energy change at other conditions of pressure and temperature may be calculated from the relations:

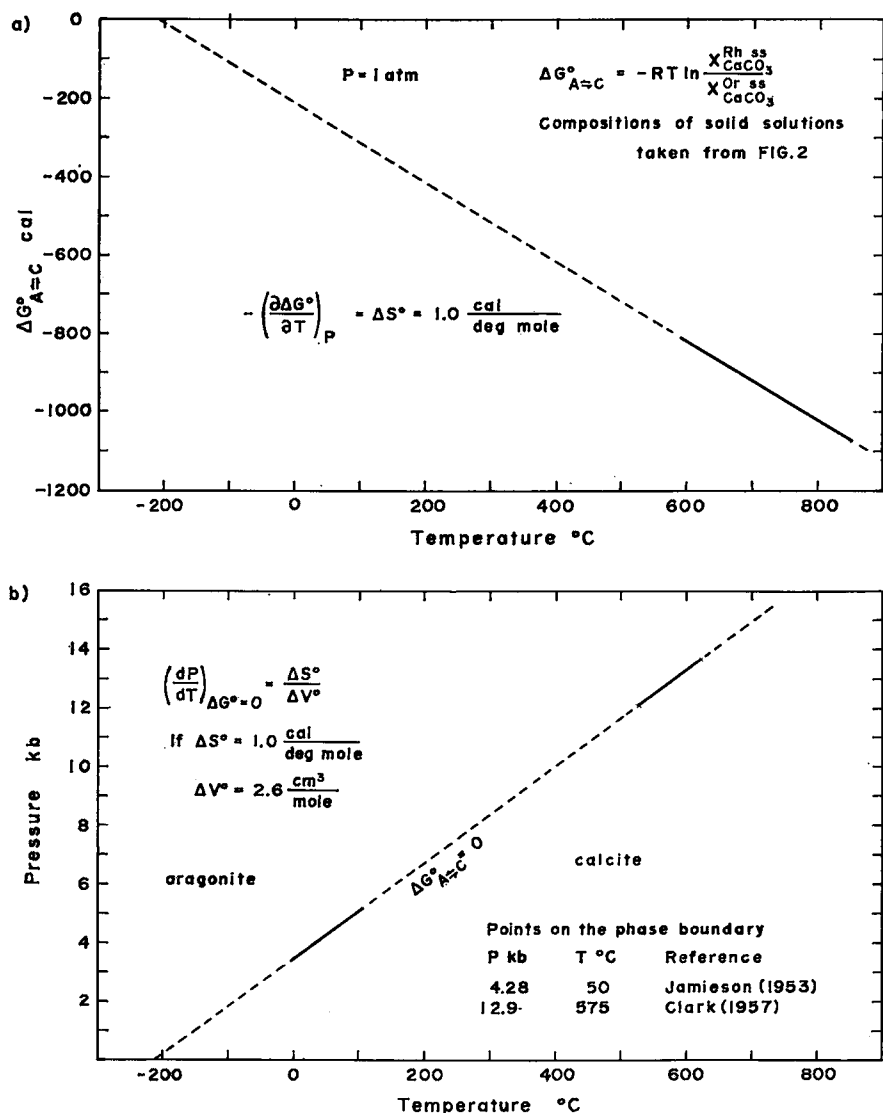
$$\left(\frac{\partial \Delta G^\circ}{\partial P} \right)_T = \Delta V^\circ$$

$$\left(\frac{\partial \Delta G^\circ}{\partial T} \right)_P = -\Delta S^\circ$$

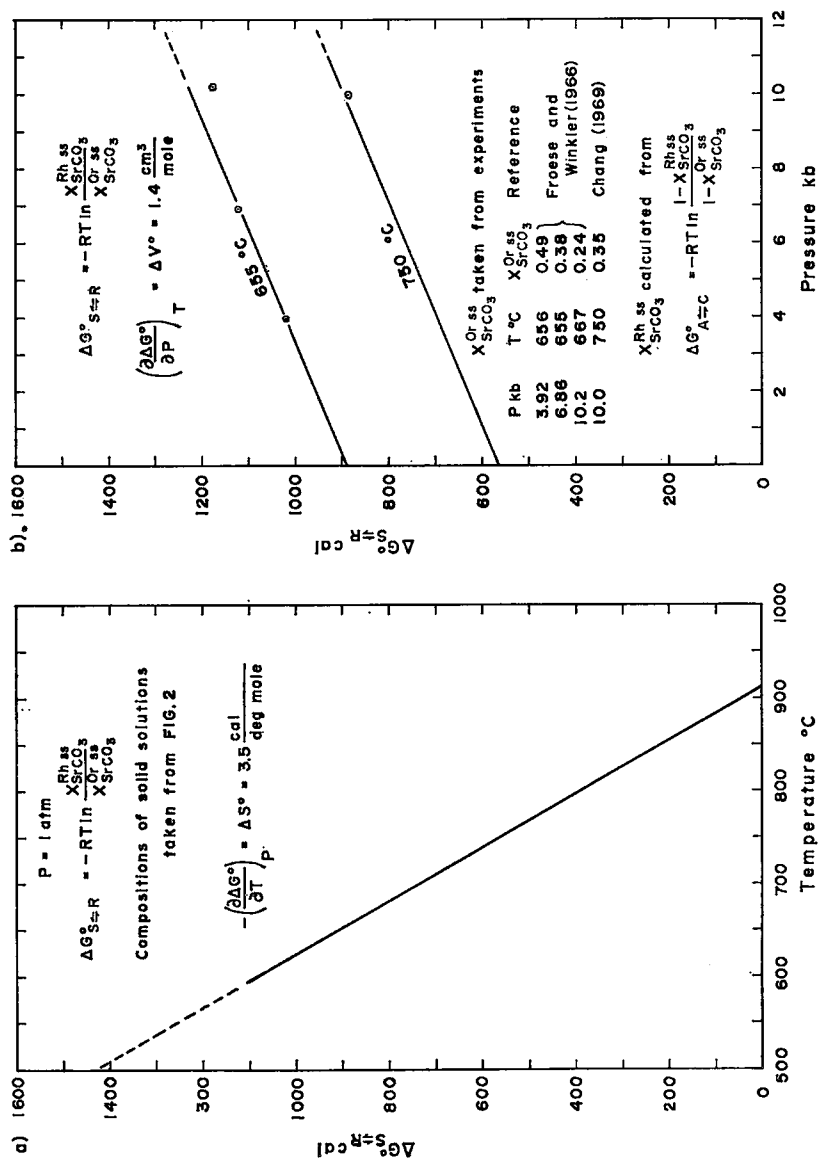
DERIVATION OF THERMODYNAMIC PROPERTIES

As has been shown, a rather simple relationship exists, in the case of ideal solutions, between the free energy change of the aragonite $\rightleftharpoons$ calcite and strontianite $\rightleftharpoons$ rhombohedral SrCO_3 transitions, on the one hand, and the compositions of coexisting solutions, on the other. Also, the variation of the free energy change with pressure and temperature is easily calculated, if ΔV and ΔS remain constant in the pressure and temperature range under consideration. As has been discussed by Thompson (1955), this is usually a good approximation for reactions involving solids only. It probably is a reasonable assumption in the case of the two transitions of interest. Unfortunately the degree of departure from ideality of the two solution series is not known. Nevertheless, it is of interest to see if the simple relationships valid for ideal solutions is consistent with the available experimental data.

From the compositions of coexisting solutions (Fig. 2), $\Delta G_{A \rightleftharpoons C}^\circ$ may

FIG. 3. Derivation of ΔS and ΔV of the aragonite $\rightleftharpoons$ calcite transition.

be calculated according to equation (1g) and plotted against temperature (Fig. 3a). These values show a linear variation. The slope of this line, equal to $-\Delta S$, is consistent with the slope of the Clark-Jamieson boundary (Fig. 3b), which in turn gives the ratio $\Delta S/\Delta V$. Thus ΔV may be obtained.

FIG. 4. Derivation of ΔS and ΔV of the strontianite $\rightleftharpoons$ rhombohedral SrCO_3 transition.

Again, using the compositions of coexisting solutions (Fig. 2), $\Delta G_{s \rightleftharpoons R}^\circ$ may be calculated according to equation (2b) and plotted against temperature (Fig. 4a). This also results in a straight line the slope of which is equal to $-\Delta S$. In order to derive ΔV of the strontianite-rhombohedral SrCO_3 transition, it is necessary to plot $\Delta G_{s \rightleftharpoons R}^\circ$ against pressure at constant temperature. To solve equation (2b) the composition of both solid solution must be known. The composition of orthorhombic solutions at various pressures and two temperatures is given by Froese & Winkler (1966). Using these values and knowing $\Delta G_{A \rightleftharpoons C}^\circ$ at any given pressure and temperature, the composition of the coexisting rhombohedral solution may be calculated from equation (1g). It is now possible to solve equation (2b) for $\Delta G_{s \rightleftharpoons R}^\circ$ and plot this value against P. This has been done for the experimental results at 655° C and ΔV is obtained from the slope of the line. The results at 560° C are less reliable and were not used. Also shown is a determination at 750° C reported by Chang (1969) which gives a ΔV about the same as the results at 655° C.

CALCULATION OF THE PHASE DIAGRAM

Knowing ΔS and ΔV of both transitions, it is possible to calculate $\Delta G_{A \rightleftharpoons C}^\circ$ and $\Delta G_{s \rightleftharpoons R}^\circ$ at any combination of pressure and temperature and then solve equations (1g) and (2b) simultaneously for $X_{\text{SrCO}_3}^{\text{Rh ss}}$ and $X_{\text{SrCO}_3}^{\text{Or ss}}$. Thus the complete phase diagram of the system $\text{CaCO}_3\text{-SrCO}_3$ may be calculated (Fig. 5). Essentially this represents an extrapolation of experimental results in the T-X section at 1 atm and the P-X section at 655° C to other pressure-temperature conditions on the basis of assuming ideal solution and constancy of ΔS and ΔV . These assumptions impose a certain curvature on the solvus curves which is in good agreement with the experimental results. Also, the calculated P-X section at 560° C agrees well with the interpreted curve based on somewhat scattered experimental results not used in deriving thermodynamic properties. It is concluded that the available experimental results in the system $\text{CaCO}_3\text{-SrCO}_3$ are consistent and not in conflict with the assumptions inherent in the calculation procedure.

COMPARISON OF THERMODYNAMIC PROPERTIES

Although the accuracy of the derived thermodynamic properties is not known, their values agree well with those based on direct measurements (Table 1). An exception to this is ΔS of the calcite-aragonite transition at higher temperatures. Using the heat capacity measurements of Kobayashi (1951a and 1951b), ΔS may be calculated at higher temper-

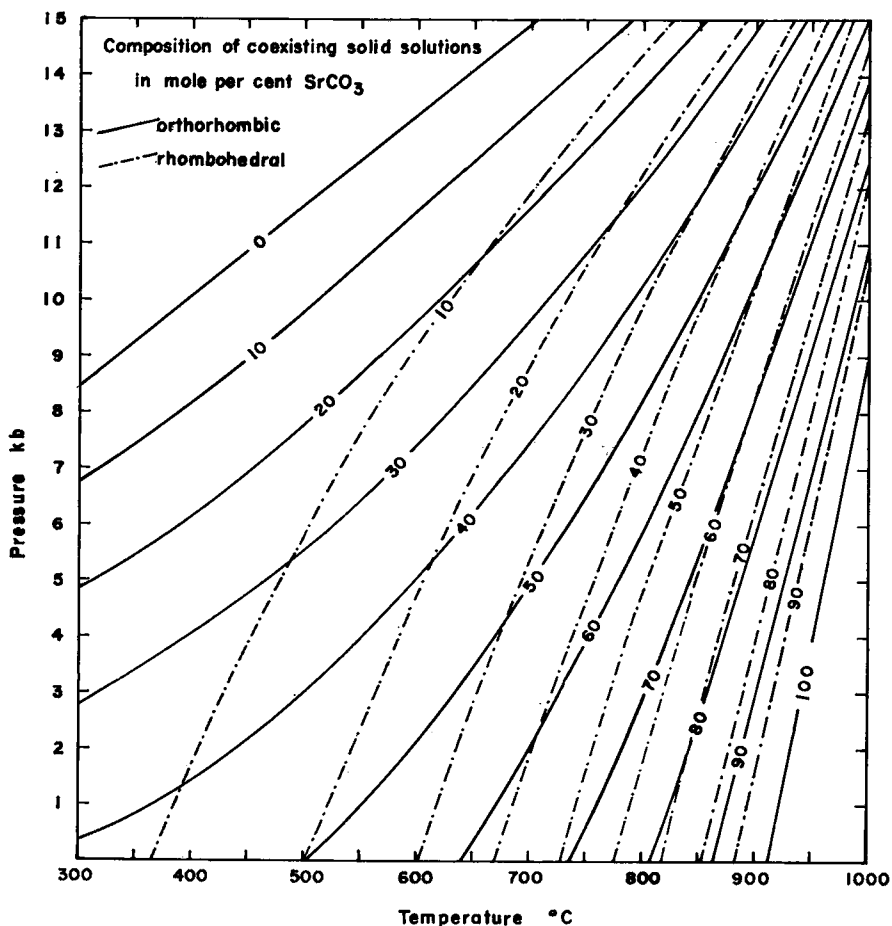


FIG. 5. Phase relations in the system CaCO_3 - SrCO_3 at various pressures and temperatures.

TABLE 1. THERMODYNAMIC PROPERTIES

	Derived from experimental data	Reported values (all at 1 atm)	Reference
Aragonite $\rightleftharpoons$ calcite transition			
ΔS	1.0 cal/deg mole	1.0 cal/deg mole at 25° C	Kelley & King (1961)
ΔV	2.6 cm^3/mole	2.78 cm^3/mole at 26° C	Robie <i>et al.</i> (1967)
ΔH at 1 atm	60 cal/mole	48 cal/mole at 50° C	Roth & Chall (1928)
Strontianite $\rightleftharpoons$ rhombohedral SrCO_3 transition			
ΔS	3.5 cal/deg mole	—	
ΔV	1.4 cm^3/mole	—	
ΔH at 1 atm	4100 cal/mole	4700 cal/mole at 924° C	Lander (1951)

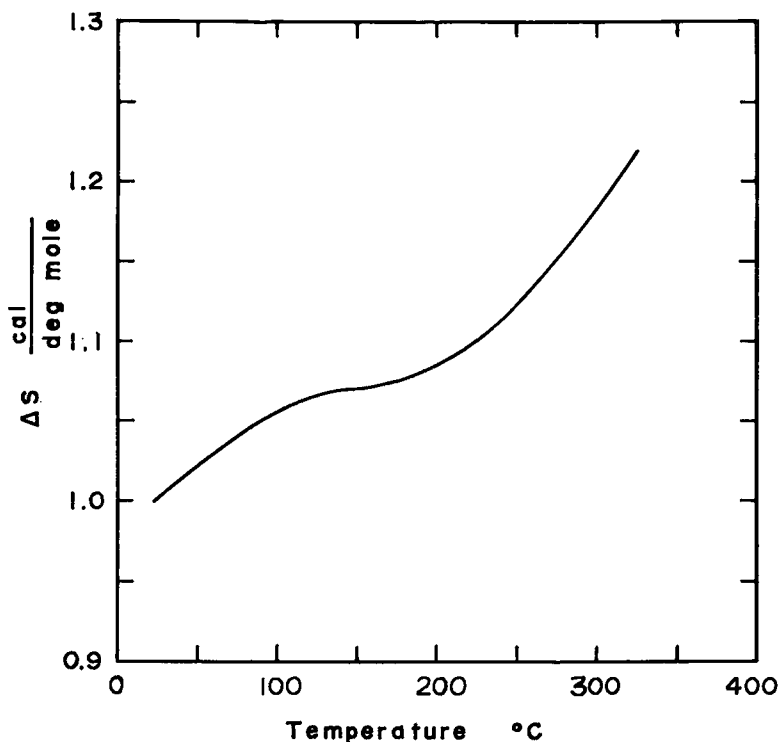


FIG. 6. The variation with temperature of ΔS for the aragonite $\rightleftharpoons$ calcite transition.

atures. The variation of ΔS with temperature, shown in Fig. 6, displays an anomaly. At first, ΔS approaches a constant value as would be expected (Thompson 1955) but then it rises rapidly. This rise probably is due to errors in the heat capacity of aragonite.

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