52. *The Strontium Oxide–Carbon Dioxide System in the Pressure Range 0·3—400 Atmospheres.*

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The strontium oxide–carbon dioxide system has been studied at pressures of carbon dioxide up to 400 atm. by using pressure vessels with internal heating arrangements. For the reaction $SrCO_3(s) = SrO(s) + CO_2(g)$ in the temperature range 1149—1259°, the results can be expressed by the relation $\Delta G^\circ = 46{,}500 - 30{\cdot}36T$. The eutectic point is estimated to lie at 1270° and 1·12 atm. Above the eutectic point, the pressure–temperature relations have been plotted for the binary melts in equilibrium with the solid phases. By means of thermogravimetric and quenching techniques, the temperature–composition relations have been derived for the eutectic portion of the system. The eutectic composition has been found to be $SrCO_3$ 79·3 and SrO 20·7 moles %.

The equilibrium $SrCO_3 \rightleftarrows SrO + CO_2$ has been studied mainly at 1 atm. pressure or less, where only gas and solid phases are present, and several pressure–temperature relations have been derived for this pressure region.[1] For completeness, a brief study of the solid–gas equilibrium from 1149° to 1259° has been included in the present work.

The present work shows that above 1270° and 1·12 atm. dissociation of strontium carbonate is accompanied by fusion of the resultant oxide with unchanged carbonate to form melts. However, fusion to an equilibrium melt is slower than with calcium carbonate[5] and less obvious. Decomposition begins at a certain temperature and then ceases. A temperature increase of 1—2° causes little further decomposition, and it is only after the temperature has been raised several degrees that collapse of the material to a melt is complete. This effect is found mainly at the lowest pressures, where the oxide content of the melts is higher; above 10 atm. it is much less significant. The reason for this incipient decomposition is not clear. It may be fusion below the equilibrium temperature or decomposition of the solid preceding fusion, whereby a very small amount of oxide (*ca.* 1 mole %) is retained in solid solution. The latter proposition is, however, somewhat speculative in view of the structures of the carbonate and the oxide lattice.

These complications hinder detection of the fusion points by thermal methods. Consequently other methods have been devised. These involve measurement of the change in conductance of the material during melting, thermogravimetric determination during melting, visual observation of the fusion process, and a detection of the melt by its rise in a capillary tube. The last method depends on the high surface tension and low viscosity of these melts. In these ways we have derived pressure–temperature and temperature–composition relations for the eutectic region of the system.

Experimental

Apparatus.—The apparatus was essentially that used for the study of calcium carbonate[2] and was operated on the same general basis: the pressure of carbon dioxide was maintained constant whilst the strontium carbonate was heated until decomposition occurred. For pressure measurement, Bourdon test-gauges with scales 25 cm. in diameter were used. They were calibrated within ±0·25%, and the pressure could be maintained constant within these limits by means of needle valves. The performance and accuracy of the electrical controls and measuring instruments have been described.[2]

Fig. 1 is a sectional view of the high-pressure furnace fitted with improved power terminals,

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[1] Jones and Becker, *J.*, 1927, 2669; Tamaru and Siomi, *Z. phys. Chem.*, 1932, **159**, 227; Lander, *J. Amer. Chem. Soc.*, 1951, **73**, 5794; Brusset, " Nouveau Traité de Chimie Minérale," Masson et Cie, Paris, 1958, Vol. IV, p. 730.

[2] Baker, *J.*, 1962, 464.

and shows the thermogravimetric balance. The extension of the Pyrex glass spring was observed relative to a reference point (B) with a cathetometer through a Perspex window of 1 cm. thickness. The reference point was attached to the suspending hook for the spring. Both windows were 1 cm. wide and were clamped against gaskets, fitted to slots 5 mm. wide, in the spring housing. Baffles were fitted below the spring to protect it as far as possible from convection currents from the furnace. To facilitate setting-up, the spring assembly and baffles were fixed in a thin-walled tube which slid into the main housing. The free-space between the lid and the top of the furnace was packed with asbestos wool. The portion of the platinum suspending wire in the hottest zone was 0·3 mm. in diameter. The platinum crucible was 8 mm. in diameter and 18 mm. long, and the top was crimped to prevent loss of material. The position of the crucible in the furnace tube (internal diam. 2 cm.) was adjusted by means of levelling screws under the pressure vessel.

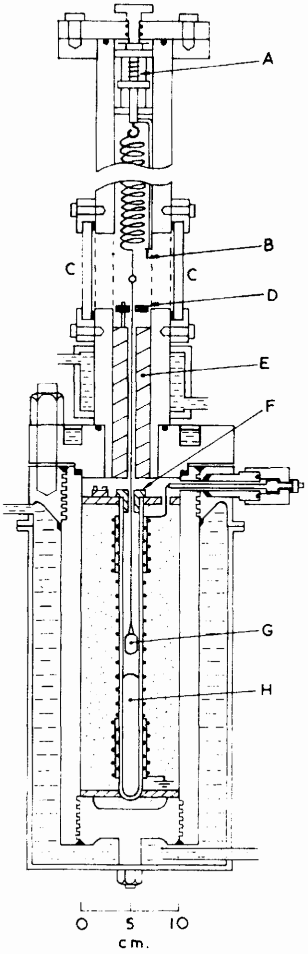

FIG. 1. High-pressure furnace and thermogravimetric balance.

A, Winder. B, Reference point. C, Perspex window. D, Bakelite baffle. E, Aluminium baffle. F, Refractory plug with hole of 3 mm. diameter. G, Platinum crucible containing sample. H, Solid alumina baffle. (For other details see ref. 2.)

Extension of the spring by 1 cm. corresponded to a weight change of 0·175 g. When loaded, the spring was ~35 cm. in length. The total load was 1·7 g., of which the sample accounted for 0·7 g. This somewhat heavy load helped to damp oscillation of the spring due to convection currents, particularly at the highest pressures (*ca.* 40 atm.) used in this work. Since both the cooling water and the cabinet enclosing the apparatus were kept at 40°, the spring housing remained within about ±2° of this temperature during a run. As measurements were made at constant pressure, the gas in the spring housing was also at a virtually constant density and buoyancy correction was unnecessary. The change in buoyancy of the load caused by the volume change on fusion of the carbonate was considered to be insignificant. The average accuracy of the weight changes measured was estimated to be ±1%. (For greater accuracy the spring would need to be hung in a longer housing further from the furnace.)

By means of thermocouples (not shown) placed alongside, above, and below the sample, both the sample temperature and the temperature distribution in the hottest zone were continuously checked. At the lowest pressures, the sample temperature could be determined within ±0·5°; at 40 atm. the limits were about ±2°. The thermal characteristics of the platinum-alloy furnace have been described.[2]

For determinations of the fusion points by differential thermal analysis and by the capillary-rise method, at pressures up to 200 atm., a water-cooled lid was fitted to the pressure vessel, and solid alumina baffles were incorporated in the furnace tube above and below the sample to eliminate gas turbulence. For measurements above 200 atm. the furnace was enclosed in a pressure vessel constructed from a section of a gun-barrel, having internal and external diameters of 12 and 23 cm., respectively. To remove gas turbulence in this pressure region, alumina baffles were used as above, and also the diameter of the furnace tube was reduced to 12 mm. by sliding an alumina tube inside it. Leads for electrical measurements were introduced into both the pressure vessels by devices similar to those used for thermocouple wires.[2]

Materials.—Dried strontium carbonate of " Specpure " grade supplied by Johnson Matthey, and carbon dioxide gas of 99·9% purity, were used.

The Solid Equilibrium Region.—The equilibrium $SrCO_3(s) = SrO(s) + CO_2(g)$ was studied thermogravimetrically. The apparatus, however, was open to air, and a slow stream of the dried gas was passed up from the bottom of the furnace tube; the total pressure was thus the barometric pressure. For pressures of carbon dioxide of less than 1 atm., accurate mixtures of carbon dioxide and argon were used.

Procedure was as follows: The carbonate was heated at the rate of 2° per min. until a weight loss showed that dissociation had begun. Heating was continued for a further 20—30° until about 25% of the material had decomposed. The oxide–carbonate mixture was then cooled, until a weight gain showed that combination had started. The true equilibrium temperature lay somewhere between the decomposition and the combination temperature, the separation of which ranged from 5° to 15°. By continually heating and cooling the mixture above and below the estimated equilibrium point whilst observing the weight changes, the exact equilibrium temperature was ultimately obtained. For this operation, 1—2 hr. were required before superheating and supercooling effects disappeared. When true equilibrium was attained, repeated temperature variations of ±1° immediately gave corresponding weight decreases or increases, so that the true equilibrium temperature could be ascertained accurately.

During the heating from room temperature, the powdered carbonate always contracted away from the crucible wall and formed as a close-packed pellet. In one determination, in order to reduce this effect, platinum wool was mixed with the sample, but no significant variation of the equilibrium temperature or its ease of attainment was observed.

The Melt Region.—At temperatures above about 1270° and pressures above 1 atm., dissociation of strontium carbonate is accompanied by fusion of the resultant oxide with unchanged carbonate to form a melt saturated with respect to the carbonate.

For detection of the fusion points by differential thermal analysis the crucible arrangement and the quantities employed were those used for the study of the solid transitions.[3] With a heating rate of 2° per min., the fusion was shown by a loop in the differential plot. The initial inflection of the loop, however, was poorly defined and no marked arrest was shown in the temperature plot of the sample. Variations in heating rate of 1—4° per min. gave no improvement. Examination of the material after cooling showed that complete fusion appeared to correspond with the second inflection of the differential loop, *i.e.*, where it turned back towards the base line. By using this point as an indication of fusion it was possible to obtain an initial assessment of the pressure–temperature relation up to 50 atm.

For detection of the fusion points by conductance change, a Pye conductance bridge was used, at a frequency of 5 kc./sec. Conductance was measured between a platinum-ring electrode immersed in the carbonate, and the platinum crucible containing it. The crucible was earthed; so was a platinum-sheathed thermocouple immersed in the material. Readings were made at a heating rate of 0·5° per min.; the instrument was connected only at the instant of measurement, to avoid electrolysis of the material. The first marked change in conductance was observed

[3] Baker, *J.*, **1962**, **2525**.

at ~15° below the fusion point, the value subsequently increasing sharply from *ca.* 10^{-2} to *ca.* 0·2 mho at the fusion point. The conductance then remained nearly constant with temperature owing to the high conductance of the melt. The results obtained with this method were better than those given by differential thermal analysis.

For thermogravimetric studies of fusion, the carbonate was heated slowly until a slight weight loss showed that incipient decomposition had started. The temperature was then raised by steps of 2° and was kept constant ($\pm 1°$) manually in each case until a constant weight was obtained. Complete fusion to the melt saturated with respect to the carbonate was indicated by a large weight change for a temperature rise of 2—3°, a time of 20—50 min. being required for a constant weight to be obtained. Subsequent temperature increases then gave only small weight changes, in which constant weight was obtainable within 5 min. This result showed that the material was molten and that equilibrium was being established rapidly by loss of carbon dioxide from the melt. At the lowest pressures, the temperature interval between the onset of decomposition and complete fusion was often as much as 10°; at higher pressures (10—40 atm.) it was about 3°. The results at 4 atm. pressure are illustrated by the portion abc of the plot in Fig. 2.

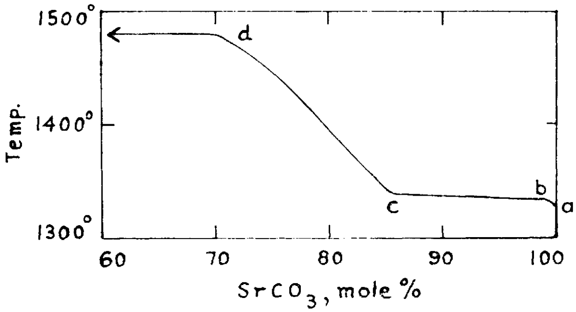

FIG. 2. Thermogravimetric plot at 4 atm.

a—b, Incipient decomp. b—c, Formation of the melt of final composition c saturated with respect to strontium carbonate. c—d, Heating of the melt accompanied by successive losses of carbon dioxide. d, Decomp. of the melt, yielding solid oxide.

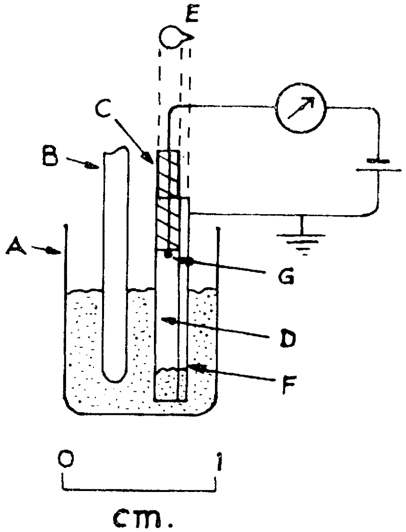

FIG. 3. Arrangement for detection of fusion by capillary rise.

A, Platinum crucible. B, Platinum-sheathed thermocouple. C, Alumina insulator. D, Platinum capillary-tube (cross section, E). F, Channel formed in side of the tube. G, Platinum wire electrode.

Visual observation of the fusion point entailed the use of a pellet of the carbonate in the form of a 6 mm. cube. This was supported on a platinum ring alongside a thermocouple in the hottest zone of the furnace, the lower alumina baffle being removed. The mouth of the furnace tube was closed by a glass disc, and the pellet was observed with a telescope by means of a mirror fixed at 45° behind the Perspex window of the balance housing. The bottom of the furnace tube appeared as a black background against which the pellet was clearly outlined. The fusion point was indicated by the material's finally collapsing into a round bead and flowing along the supporting wire. A heating rate of 0·3° per min. was used. Above 20 atm., gas turbulence destroyed visibility.

The arrangement used for the detection of fusion by capillary rise is shown in Fig. 3. When fusion occurred, the melt rose rapidly up the platinum tube (internal diam. 1·5 mm.) and made contact with the central electrode (G); a narrow channel in the side of the tube assisted this rise. When contact was made, the highly conductive melt completed an electric circuit, and a reading was shown on the meter. The meter was an Avometer switched to the resistance range; the reading dropped from *ca.* 0·1 megohm to *ca.* 40 ohms when contact was made. An average heating rate of 0·2° per min. was used with this method, which was the only one suitable for the highest pressures.

Fusion temperatures at pressures up to 400 atm. are plotted in Fig. 4 (portion ABC).

The line AD in Fig. 4 represents equilibrium between the melt and solid strontium oxide.

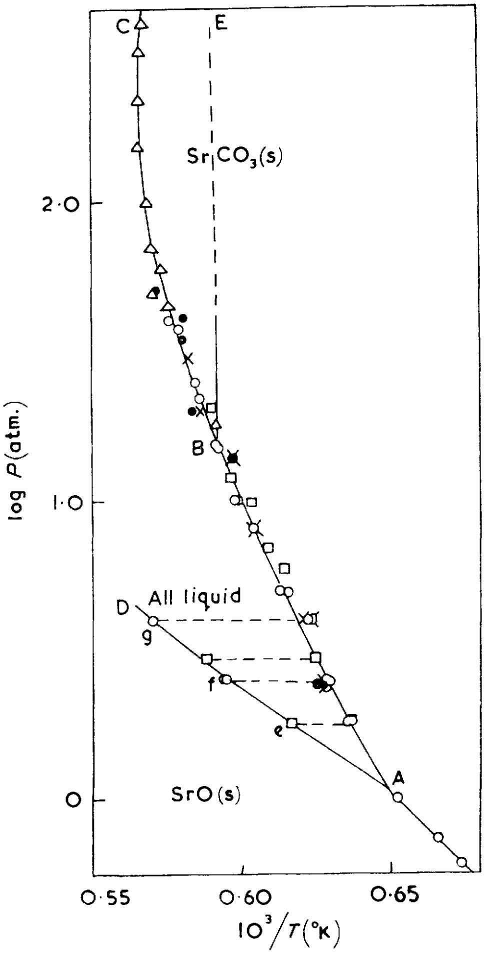

Fig. 4. Pressure–temperature diagram for the melt regions.

Determinations were by (●) differential thermal analysis, (×) conductance change, (○) thermogravimetry, (□) visual assessment, or (△) capillary rise.

It was interpolated by means of the thermogravimetric and the visual technique as follows: The temperature of the melt produced by decomposition of the carbonate was raised in stages, and the weight loss accompanying the loss of carbon dioxide was measured at each constant temperature. Constant weight was obtained at each successive temperature within 5 min. Eventually a small temperature rise gave a large weight change; this change continued even after 30 min. or more; it indicated that 45—90 moles % of oxide were present; it showed that the point of saturation with the oxide had been reached and that oxide was being precipitated. The process at 4 atm. pressure is illustrated by the path cd in Fig. 2. For visual observation the molten bead produced by dissociation of the carbonate was further heated at a rate of about 1° per min. until decomposition took place. The latter was shown by effervescence, followed by deposition of oxide on the platinum ring. The heating paths corresponding to the last determinations are shown in Fig. 4 by the isobars (broken lines) across the all-liquid region.

The thermogravimetric, visual, and capillary rise methods are considered to be the most accurate of those employed, and the curves in Fig. 4 have been interpolated mainly from the results of these methods. At the lowest pressures the average accuracy of the fusion temperatures is about ±5°. Above 60 atm., where fusion takes place sharply, the fusion temperatures are considered to be accurate within ±3°; decomposition temperatures are of comparable accuracy.

RESULTS AND DISCUSSION

In the study of the reaction $SrCO_3(s) = SrO(s) + CO_2(g)$, it was necessary to heat and cool the material continuously above and below the estimated equilibrium point before true equilibrium could be obtained. A likely reason for this is that the operation ultimately produced considerable amounts of oxide and carbonate in the form of crystals containing many surface defects. With such material of high surface reactivity, decomposition or combination could then take place readily, so that superheating and supercooling were reduced; true equilibrium was then readily established.

Pressures and equilibrium temperatures for the solid equilibrium are given in Table 1; temperatures are given to the nearest degree. The plot of log P against $10^3/T$°(K). for these values is linear, as shown for those in Fig. 4. The best straight line drawn through these points can be expressed by $\log P(\text{atm}) = 6{\cdot}638 - 46{,}500/4{\cdot}574T$. In deriving this relation, the pressures have been considered to be accurate and the temperatures subject to error. For the temperature range 1149—1259°, the heat of reaction $\Delta H = 46{,}500$ cal. mole^{-1} is considered to be accurate within ±1000 cal. mole^{-1}, the limits being assessed from the accuracy of measurement of the equilibrium temperatures. This value of ΔH is somewhat lower than the value, 49,090 cal. mole^{-1}, obtained by Tamaru and Siomi[1] for this temperature region.

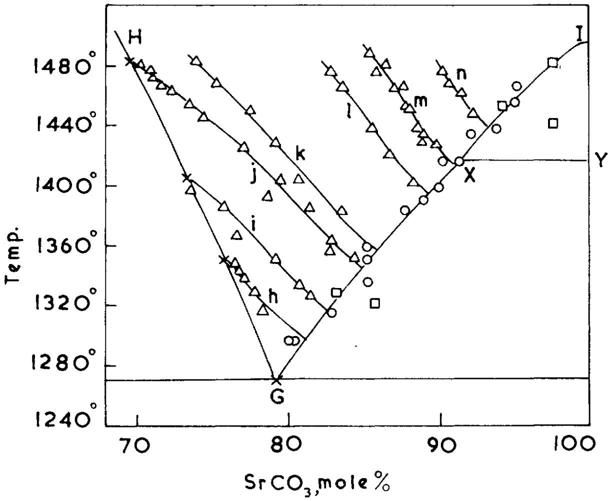

FIG. 5. Temperature–composition diagram for the eutectic region.

(×) Extrapolated compositions. (△) Compositions on the isobars: (h) 1·8, (i) 2·5, (j) 4, (k) 5, (l) 10, (m) 15, and (n) 25 atm., respectively. Compositions lying on GH and GI, in equilibrium with the solid phases, are at varying pressure. XY represents the transition, hexagonal to probably cubic, at 1416°.

TABLE 1.

Equilibrium pressures and temperatures for the solid reaction.

P (atm.)	0·309	0·477	0·614	0·738	1·00
Temp. (c)	1149°	1188°	1211°	1228°	1259°

From the intersection of the three limbs of the plot in Fig. 4, the eutectic point is estimated to lie at 1270° and 1·12 atm. Owing to the difficulty of obtaining accurate melt–solid equilibrium temperatures just above the eutectic point, these values are probably less precise than those for the calcium carbonate system.

At 1416° strontium carbonate shows a solid-state transition from hexagonal to another form which is probably cubic;[3] the region of stability of the latter lies to the left of the line BE in Fig. 4. In the pressure range 20—50 atm., where the transition was studied, any change of the transition temperature with pressure was too small to be detected.[3] With greater pressure increases, however, it is possible that the transition temperature will be raised detectably, consequently the upper portion of the line BE has been drawn schematically with a slight veer to the left.

At the highest pressures studied, namely, 154, 220, 320, and 400 atm., the observed fusion temperatures are 1495°, 1494°, 1493°, and 1489°, respectively. These results suggest that the melting point of the strontium carbonate has been reached near 1495° and that fusion temperatures are subsequently lowered as equilibrium is established with respect to molten strontium carbonate in which increasing amounts of carbon dioxide are dissolved. However, the fusion temperatures in this region are considered to be accurate only within ±3°, so that this implication must be treated with reserve. The almost vertical trend of the fusion curve in this region nevertheless confirms the vicinity of the melting point of strontium carbonate. The best value for the melting point is considered to be 1494°. Boeke[4] obtained a melting point of 1497° for the carbonate under 60 atm. pressure. The present work gives a fusion temperature of 1474° at this pressure, but when the experimental difficulties are considered, the result from this early work is not unreasonable.

The compositions of melts in equilibrium with strontium carbonate, which were determined thermogravimetrically, are plotted for temperatures up to 1494° as circles in Fig. 5; pressures have been omitted to allow a two-dimensional representation. Some of the compositions (marked by squares) were determined by quenching and analysing the solidified melts by the methods previously described.[2]

TABLE 2.

Temperatures, pressures, and compositions of melts in equilibrium with the solid phases.

Melts in equilibrium with $SrCO_3$(s)			Melts in equilibrium with SrO(s)			Eutectic point		
Temp. (c)	*P* (atm.)	$SrCO_3$ (moles %)	Temp. (c)	*P* (atm.)	$SrCO_3$ (moles %)	Temp. (c)	*P* (atm.)	$SrCO_3$ (moles %)
1470°	53·7	96·6	1470°	3·77	70·3	1270°	1·12	79·3
1440	25·9	93·5	1400	2·46	73·6			
1416	16·0	91·5	1350	1·80	75·9			
1400	11·5	90·0	1300	1·32	78·1			
1350	4·52	85·5						
1300	1·85	81·6						

Compositions of the melts lying on the isobars in the all-liquid region are also plotted (as triangles) in Fig. 5. The compositions on the isobars at 1·8, 2·5, and 4 atm. pressure have been extrapolated to the corresponding temperatures of saturation with the oxide at these pressures. These temperatures (1350°, 1404°, and 1482°) are represented by the points e, f, and g, in Fig. 4. The line GH intersecting these extrapolated values and the eutectic point in Fig. 5, thus gives the compositions of melts in equilibrium with solid strontium oxide. The best fit of all these curves gives the eutectic composition as $SrCO_3$ 79·3 and SrO 20·7 moles %.

For the melts in equilibrium with the solid carbonate, the experimental errors are such that the compositions plotted are probably high in oxide content. These, however, and the compositions in equilibrium with the solid oxide, are estimated to be accurate within ±1 mole %. For the isobaric compositions in the all-liquid region, the accuracy limits are believed to be nearer ±0·5 mole %. The slight loss of weight of the platinum crucible observed at the end of each thermogravimetric run is also taken into account in the accuracy limits.

To co-ordinate the pressure–temperature and temperature–compositions relations, the

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Boeke, *Mitt. naturf. Ges. Halle*, 1913, **3**, 13.

parameters of the melts in equilibrium with the solid phases are given in Table 2. The values tabulated are smoothed ones interpolated from the curves in Figs. 4 and 5.

The similarity between the phase diagrams of the calcium carbonate and the strontium carbonate system extends also to the thermodynamic properties of the melts. From estimated heats of fusion of the solid phases, the calculated oxide and carbonate activities in the melts show that both systems, on a molar basis, exhibit negative departure from Raoult's law. Details of this aspect of the work will be published later.

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