137. *The Barium Oxide–Carbon Dioxide System in the Pressure Range* 0·01—450 *Atmospheres.*

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The barium oxide–carbon dioxide system has been studied at pressures of carbon dioxide up to 450 atm. by means of techniques similar to those used previously with molten carbonate systems. Pressure–temperature relations have been determined for the melts in equilibrium with the solid phases above the eutectic point. By means of thermogravimetric measurements, the temperature–composition relations of these melts have been determined. The eutectic composition has been found to be $BaCO_3$ 64 and BaO 36 mole %; these values agree fairly well with those of previous authors.

The equilibrium $BaCO_3 \rightleftharpoons BaO + CO_2$ is similar to the analogous equilibria involving calcium carbonate and strontium carbonate, except that the equilibrium pressures are much lower. With the last two systems, the pressures at which eutectic melting occurs, lie above 1 atmosphere.[1,2] With barium carbonate, the eutectic pressure is about 0·0066 atm.

Despite the fact that they are formed at such low pressures, the barium oxide–carbonate melts have been little studied. This can be attributed to two experimental difficulties, namely, that fusion to an equilibrium melt takes place slowly, and that crucible materials for use in carbon dioxide at high temperatures are all corroded to some extent by the melts. At temperatures up to 1000°, an alloy containing 80% of gold and 20% of palladium has been used successfully with molten carbonates of the alkali metals.[3] However, this alloy melts near 1350°, so that its applicability is restricted. Although platinum is attacked, it appears to be the most satisfactory crucible material for the highest temperatures. The most serious effects of the attack are encountered in the thermogravimetric determinations of the composition of the melts, where prolonged contact between the melts and the crucible is inevitable. When this attack takes place, the measurements show a weight loss in excess of the predicted value, as though an excess of carbon dioxide is being evolved; this is particularly the case at temperatures above 1550°.

The mechanism of the attack on platinum is not clear, many variables are involved, and its study is outside the scope of this work. It is believed, however, that the platinum dissolves in the form of an oxide, because when the melt is quenched a black precipitate is formed; the latter is soluble in hydrochloric acid and is probably platinum dioxide. All the platinum removed from the crucible is recoverable from the melt.

Although this chemical attack naturally limits the accuracy of the measurements, by suitably modifying the techniques used previously with carbonate melts[2] we have derived satisfactory pressure–temperature and temperature–composition relations for the system.

Experimental

Apparatus.—For studies involving gas at barometric pressure, conventional resistance furnaces were employed. These were fitted with impervious alumina tubes through which a stream of the dried gas was passed. For the highest temperatures a winding of 6 : 4 platinum–rhodium alloy was used. For pressures of carbon dioxide of less than 1 atm., accurate mixtures of carbon dioxide and argon were employed. For thermogravimetric measurements the furnaces were fitted with a Pyrex spring balance, the characteristics of which have been described.[2]

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

[2] Baker, *J.*, 1963, 339.

[3] Reisman, Holtzberg, and Banks, *J. Amer. Chem. Soc.*, 1958, **80**, 37; Janz and Lorenz, *J. Electrochem. Soc.*, 1961, **108**, 1052.

Measurements under pressure entailed mainly the use of the high-pressure furnaces and thermogravimetric apparatus used previously.[2] For detection of the fusion points at pressures above 200 atm., a capillary-rise device was used, which was arranged to operate in a horizontal furnace. The latter was 24 cm. long with a bore of 1 cm. and had a single graded winding of 6 : 4 platinum–rhodium alloy. The space in the furnace tube was filled with solid alumina cylinders to reduce gas turbulence. This furnace was accommodated by a water-cooled pressure vessel constructed from a section of auto-frettaged gun-barrel having internal and external diameters of 5·5 and 11 cm., respectively. Particularly stable operation was achieved with this furnace. Electrical leads were introduced into this apparatus by devices similar to, but more substantial than, those used previously.

Barium hydroxide is not easily dehydrated when molten and is particularly corrosive to platinum. To reduce the possibility of any hydroxide formation by pick-up of water vapour by the melt when under pressure, a " breather " containing calcium chloride was fitted into the mouth of the furnace tube. For thermogravimetric measurements this was not possible, but trays of the desiccant were fitted into the space below the water-cooled lid of the pressure vessel.

The performance and accuracy of the equipment for measuring and controlling temperature and pressure have been described.[1,2] Six Bourdon test gauges were required to cover the pressure range of 1—450 atm.

Materials.—Barium carbonate of " Specpure " grade was supplied by Johnson Matthey Ltd. This was dried for 2 days at 120° before use. Barium oxide was prepared by calcining " AnalaR " barium carbonate in a graphite boat in argon. Carbon dioxide gas of 99·9% purity and technical argon were used.

Determination of the Fusion Temperatures.—The basis of operation was similar to that employed previously: the pressure of carbon dioxide was kept constant, whilst the barium carbonate was heated until dissociation to an oxide–carbonate melt took place.

For visual detection of the fusion point,[2] an irregular pellet of the carbonate of about 4 mm. diameter was supported on a thin wire of 87 : 13 platinum–rhodium alloy. Fusion was shown by collapse of the outside of the pellet furthest from the wire inwards as rivulets of liquid formed. A heating rate of ~0·5° per min. was used. A ceramic support of sintered thoria and yttria was tested, and was found to be fairly satisfactory at temperatures up to 1400°. In both cases, renewal of the supporting material was necessary for each determination. Platinum wire occasionally gave low fusion points at temperatures and pressures below 1320° and 0·4 atm., but at higher temperatures and pressures it was the most satisfactory material.

The device used for detecting fusion by capillary-rise in the range 1—200 atm. was almost identical with that used previously,[2] except that no channel was formed in the platinum capillary tube; the latter was of seamless construction. This modification was necessary because, owing to a slight dissolution of the platinum, a minute amount of ternary melt was always formed at a temperature slightly lower than the fusion temperature of the binary melt. If a seam was present, the ternary melt could climb up it and cause a spasmodic contact with the electrode at an incorrectly low temperature. With this modification, however, the fusion temperatures were readily determinable; the resistance reading fell from *ca.* 100,000 Ω to *ca.* 3000 Ω when contact was made. For pressures above 200 atm. the horizontal furnace was used, and the material was contained in a platinum boat. The electrode portion of the capillary tube was mounted horizontally over the boat, whilst the other end of the tube was bent down into the material. An average heating rate of 1° per min. was used with both the vertical and the horizontal device.

For thermogravimetric studies of fusion, the crucible employed was the same size as that used previously;[2] the weight of barium carbonate used was about 0·6 g. New crucibles were found to be attacked less than old ones, probably because the true surface area of the newly rolled platinum was lower; a new crucible was consequently employed for nearly every run. Operational procedure was as follows: The temperature was raised until a slight weight loss, equivalent to ~1 mole %, was observed. The temperature was then raised by steps of 10—20° and was kept constant until a constant weight was obtained. Complete fusion to the melt saturated with respect to the solid phase was shown by a larger weight change, a time of about 15 min. being required for constant weight to be obtained. Subsequent temperature increases then gave smaller weight changes which became constant within about 6 min. This showed that the material was molten and equilibrium was being established more rapidly by loss of carbon dioxide from the melt. At the lowest pressures, the temperature interval between the onset of detectable decomposition (*i.e.*, a change of ~1 mole %) and complete fusion was about 120°; at higher pressures (5—20 atm.) it was about 80°.

Fusion temperatures in the range 0·01—450 atm. are plotted in Fig. 1 (portion BC).

Determination of the Melt Compositions.—The thermogravimetric method gives both the fusion temperatures and the composition of the melts which are formed. Some of the thermogravimetric plots are shown in Fig. 2; the different symbols used show the reproducibility of the runs. In the plot at 1 atm. for example, the initial portion a—b is considered to represent the variation in composition with temperature of a solid solution of the oxide in the carbonate. The inflexion (point c) corresponding to the formation of the melt was not sharply defined at any pressure employed in the range 0·035—20 atm. Attack on the crucible at the fusion points was insignificant, most of the attack took place during the subsequent excursion into the all-liquid region (*e.g.*, along c—d). This was particularly the case above 1550° when the oxide content was high, and a considerable time was required to reach this temperature region. Under these conditions as much as 0·005 g. of platinum was dissolved, and excessive weight losses were observed from which the compositions were estimated to be 10—20% in error.

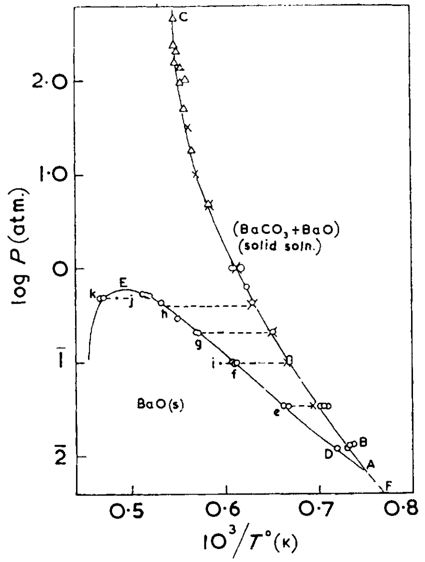

Fig. 1. Pressure–temperature diagram for the melt regions. Determinations were by (○) visual assessment, (×) thermogravimetry, (Δ) capillary rise.

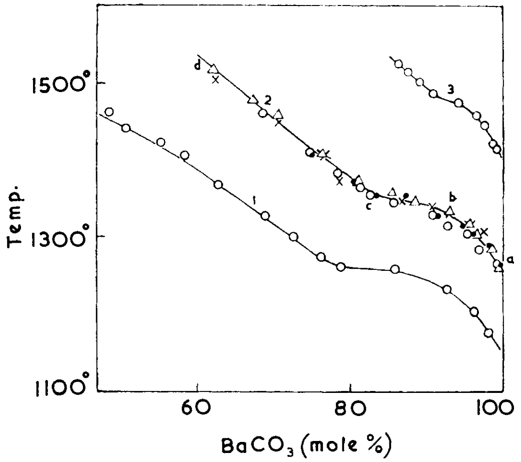

Fig. 2. Typical thermogravimetric plots.

(1) 0·208, (2) 1, (3) 10 atm. (a) point of detectable decomp. (a—b) Solid–solution region. (b—c) Formation of the melt of final composition (c) saturated with respect to the solid phase. (c—d) Heating of the melt accompanied by successive losses of carbon dioxide.

Because of the above difficulties, measurements were confined to temperatures below 1550°, and the total time of a run was limited to about 3½ hr. The maximum time allowed for measurements in the all-liquid region was 1½ hr. With these restrictions, only about 0·0008 g. of platinum was dissolved in a run, and the shape and reproducibility of the plots indicated that errors were not large.

For an unknown reason, the crucible was badly attacked during the runs at 0·035 atm., although temperatures were low. No thermogravimetric determination was attempted at carbon dioxide pressures of less than 0·035 atm.

Determination of the Oxide–Melt Relation.—The line DE in Fig. 1 represents equilibrium between the melts and solid oxide, and would normally be derived by heating the melts at constant pressure until saturation with oxide occurred and the latter was precipitated.[1,2] Owing to the slowness of precipitation and the attack of the platinum, this method was unsatisfactory and a modified visual one was used: A fragment of barium oxide was supported on a platinum ring and heated in argon to a temperature about 40° above the oxide–melt equilibrium temperature. The requisite mixture of argon and carbon dioxide was then admitted, and the furnace was cooled at the rate of 2° per min. When the equilibrium temperature for melt formation was reached, combination with the carbon dioxide took place and the surface of the oxide collapsed inwards as small amounts of liquid were formed. A typical cooling path is the one at 0·098 atm. (i—f) in Fig. 1.

The point k at 1860° on the other side of the curve was obtained by heating the oxide fragment in argon to about 1730°, then admitting the gas mixture and heating the whole further (path j—k) until liquid was formed. The supporting ring was of 3 : 2 platinum–rhodium alloy, and the thermocouple combination was of 4 : 1 and 3 : 2 platinum–rhodium. The pressure plotted, *i.e.*, 0·497 atm., has been corrected for the thermal dissociation of carbon dioxide.

RESULTS AND DISCUSSION

From the intersection of the curves in Fig. 1, the eutectic point A is considered to lie at 1060° at a pressure of 0·00661 atm. Hackspill and Wolff[4] give the eutectic temperature as ~1100° at approximately this pressure; Lander[5] gives the temperature as 1030°.

Immediately below the eutectic point, the solid equilibrium will be characterised by a straight line. This should intersect the eutectic point and roughly bisect the angle between the two curves. For the solid equilibrium in this region, Lander[6] gives an expression, but the line produced rises too steeply and coincides with the curve AB. However, this author also measured calorimetrically the heat contents of the oxide and the carbonate in this temperature region. The results, which are probably fairly accurate, when combined with the value[7] $\Delta H_{298} = 63,850$ cal. mole^{-1}, give a heat of dissociation for this region of ~53,000 cal. mole^{-1}. This is a realistic value and the line AF has been interpolated on this basis. With the latter value and the eutectic parameters, ΔS is found to be ~30 e.u.; this is a reasonable value for the entropy change because it is almost equal to that for the dissociation of strontium carbonate in the high-temperature region.[2] The small solubility of the oxide in the solid carbonate should not greatly affect these values.

The vertical trend of the curve AC in Fig. 1 at the highest pressures shows that the melting point of barium carbonate has been attained. The best value for the melting point is considered to be 1555°.

The temperature of 1740° which is often quoted for the melting point of barium carbonate, is an estimated value obtained by Boeke,[8] who measured the fusion temperature of mixed carbonates of barium and calcium, and extrapolated the results by about 300° to the composition of 100 mole % barium carbonate. Although the melting point from the present work may have been lowered owing to a slight attack of the platinum capillary, the extent of this is believed to be small because the overall platinum contents of the melts at the ends of the runs were only ~0·1 mole %. Since the capillary device itself had been modified slightly for this work, the vertical type was tested with " Specpure " strontium carbonate, to study the effects of the alterations. At pressures of 154 and 220 atm. the redetermined melting points were 1502° and 1500°, respectively; the previous values at these pressures were 1495° and 1494°. Fusion temperatures at lower pressures, however, agreed with previously determined values. It is likely that the melting point of strontium carbonate lies between 1494° and 1502°, and a maximum error of ±5° might be expected to result from variations in the design of the device. These considerations suggest that the melting point of barium carbonate is not greatly in error.

At a pressure of 1 atm. the fusion temperature of 1360° agrees fairly well with the values, 1350° and 1380° obtained by Finkelstein[9] and Boeke,[10] respectively.

[4] Hackspill and Wolff, *Compt. rend.*, 1937, **204**, 1820.

[5] Lander, *J. Amer. Chem. Soc.*, 1951, **73**, 5893.

[6] Lander, *J. Amer. Chem. Soc.*, 1951, **73**, 5794.

[7] U.S. Nat. Bur. Stand., Circular No. 500, Washington D.C., 1952, pp. 99, 413, 424.

[8] Boeke, *Mitt. Naturf. Ges. Halle*, 1913, **3**, 13.

[9] Finkelstein, *Ber.*, 1906, **39**, 1585.

[10] Boeke, quoted in Mellor, " A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans and Co., London, 1923, Vol. III, p. 836.

The peak of the curve at the point E in Fig. 1 lies at ~0·6 atm. and 1770°. With increasing temperature and diminishing pressure, the line will drop steeply and intersect the melting point of the oxide (1925°) at a very low pressure. The oxide–melt curves of the calcium carbonate and the strontium carbonate system should behave similarly. In these cases, however, the equilibrium pressures are high and the melting points of the oxides are well above 2000°. The peaks of the curves probably lie near 2000° and would be difficult to realise experimentally.

The compositions of the melts at the fusion points are plotted in Fig. 3 (portion GI); pressures have been omitted to allow a two-dimensional representation. These compositions were obtained from the inflections in the thermogravimetric plots which correspond to point c in Fig. 2.

Compositions of the melts lying on the isobars in the all-liquid region are also plotted in Fig. 3. The compositions on the isobars at 0·035, 0·098, 0·208, and 0·4 atm. have been extrapolated to the temperatures of saturation with the oxide at these pressures. These isobars correspond to the broken lines across the all-liquid region in Fig. 1, and the temperatures of saturation (1235°, 1362°, 1478°, and 1590°) are represented by the points e—h, respectively. In Fig. 3, the line GH intersecting these extrapolated values and the eutectic point thus gives the compositions of the melts in equilibrium with solid barium oxide. The eutectic composition, which is $BaCO_3$ 64 and BaO 36 moles %, agrees well with the value $2BaCO_3,BaO$ suggested by other authors [4,5] from the heat changes involved during fusion at the eutectic point.

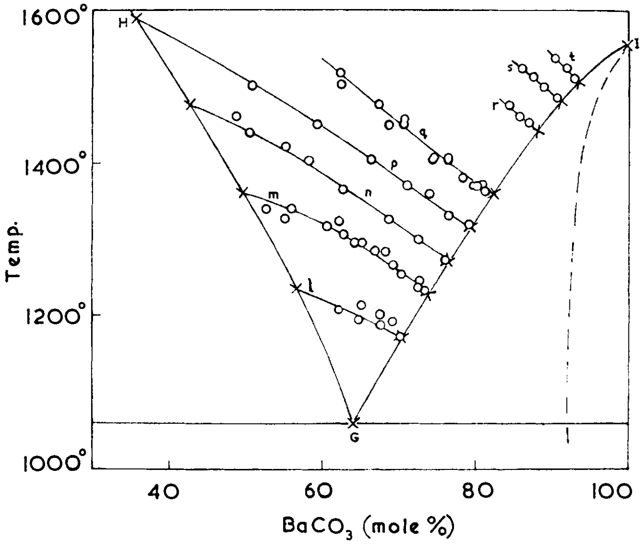

FIG. 3. Temperature–composition diagram for the eutectic region.

(×) Interpolated compositions. (○) Compositions on the isobars: (l) 0·035, (m) 0·098, (n) 0·208, (p) 0·4, (q) 1, (r) 5, (s) 10, (t) 20 atm. Compositions lying on GH and GI in equilibrium with the solid phases are at various pressures.

At temperatures above 896°, barium carbonate exists in a cubic (rock-salt) form, so that acceptance of some oxide in solid solution is likely. The portions of the thermogravimetric plots corresponding to a—b in Fig. 2 are considered to represent the region where solid solutions are formed, because heating or cooling in this region involved a loss or gain in weight, and the quenched material was found to be unmelted. The character of the material under the conditions represented by b—c is uncertain; when quenched, the material formed a hard shiny block which showed signs of incipient fusion. In all cases, however, it was necessary to raise the temperature to the point corresponding to c to obtain complete fusion. In Fig. 1, an approach to the line AC from the right corresponds to an increase in solid solubility of the oxide; the maximum oxide contents of the solid phase are represented approximately by the broken line in Fig. 3. At the eutectic temperature, Lander [5] gives the maximum solid solubility as 4% ± 1% of oxide; the present work suggests a value of *ca.* 8 mole %, but this may be high.

To co-ordinate the pressure–temperature and temperature–composition relations, the parameters of the melts in equilibrium with the solid phases are given in the annexed Table, being smoothed values interpolated from Figs. 1 and 3. Owing to the experimental difficulties, they are probably less accurate than those for calcium carbonate and strontium carbonate. In common with these two systems, however, the melts of the barium carbonate system show negative departure from ideal behaviour. Details of these aspects will be published shortly.

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

Melts in equil. with $BaCO_3$ (solid soln.)			Melts in equil. with BaO (s)			Eutectic point		
Temp.	*P* (atm.)	$BaCO_3$ (mole %)	Temp.	*P* (atm.)	$BaCO_3$ (mole %)	Temp.	*P* (atm.)	$BaCO_3$ (mole %)
1500°	15·8	93·0	1600°	0·417	35·0	1060°	0·00661	64·0
1400	1·94	85·1	1400	0·123	47·3			
1300	0·347	78·6	1200	0·0243	58·4			
1200	0·070	72·2						

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