

87. The Calcium Oxide-Carbon Dioxide System in the Pressure Range 1-300 Atmospheres.

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The calcium oxide-carbon dioxide equilibrium has been studied at pressures of carbon dioxide up to 304 atm. by using a pressure vessel with an internal heating arrangement. For the reaction $\text{CaCO}_3(\text{s}) = \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$, in the pressure range 1-39.5 atm., the results agree well with those of previous authors and can be expressed by the relation, $\Delta G^\circ = 38,000 - 32.4T$. The eutectic point has been estimated to lie at $1242^\circ \pm 3^\circ$ and 39.5 ± 0.5 atm. Above the eutectic point, the pressure-temperature relations have been plotted for the binary melts in equilibrium with solid calcium carbonate and solid calcium oxide, severally. By means of a special quenching device, the compositions of these melts have been determined and a phase diagram has been derived for the eutectic portion of the system. The eutectic composition has been found to be CaCO_3 88.3 mole %, CaO 11.7 mole %.

THE equilibrium $\text{CaCO}_3 \rightleftharpoons \text{CaO} + \text{CO}_2$ has been well studied at pressures up to 1 atm. and many thermodynamic expressions have been derived for the pressure-temperature relation.^{1,2} At higher pressures, however, the only systematic thermodynamic study has been that of Smyth and Adams³ who used thermal analysis to follow the dissociation up to a pressure of 1000 atm. These workers found that at above 1240° and 39.5 atm. dissociation was accompanied by fusion of the resultant oxide with unchanged carbonate to give a single liquid phase.

Since the system involves both gas-solid and gas-liquid equilibria at high temperatures its study is particularly useful for establishing techniques of general application to molten-salt systems of this type. As a result of the present work on the equilibrium, special apparatus has been developed, for example, a device for quenching samples, and furnaces which are stable in high-pressure carbon dioxide. Knowledge of the equilibrium has been extended by determining the oxide and carbonate contents of the binary melts which are formed and from these results a phase diagram has been constructed for the eutectic portion of the system.

EXPERIMENTAL

Apparatus.—The essential unit of the apparatus was a resistance furnace enclosed in a pressure vessel which could be fitted for thermal analysis, quenching of samples, or thermogravimetric measurements. The rest of the equipment was employed for measuring and controlling temperature and gas pressure.

A sectional view of the high-pressure furnace is shown in Fig. 1. The body was constructed from seamless mild-steel tubing having an internal diameter of 10 cm. and walls of 2 cm. thickness. With these dimensions the yield pressure was estimated to be 700 atm.,⁴ so that a good margin of safety was provided. The device used for introducing thermocouple wires into the pressure-vessel is shown in Fig. 2. Seven wires were introduced this way, but for simplicity only two are shown. This device, the gas inlet, and the power terminals were all screwed into the flange at the top of the pressure-vessel.

The purpose of the long cylinder fitted to the lid was two-fold: It could be fitted with a winding mechanism (as shown) for quenching samples, or it could be used as a housing for a thermogravimetric balance.

Quenching was carried out by operating the winder F so that the whole crucible assembly (E₁-J-K) was withdrawn rapidly out of the furnace tube and into the cool gas in the cylinder.

¹ Hill and Winter, *J. Phys. Chem.*, 1956, **60**, 1361.

² Steiner, "Introduction to Chemical Thermodynamics," McGraw-Hill Book Co., New York, 1948, pp. 330-338.

³ Smyth and Adams, *J. Amer. Chem. Soc.*, 1923, **45**, 1167.

⁴ Newitt, "The Design of High Pressure Plant and the Properties of Fluids at High Pressures," Oxford Univ. Press, 1940, p. 51.

The function of the piston G was to prevent convection currents from entering the cylinder and causing serious heat loss from the furnace.

For thermogravimetric measurements a conventional balance incorporating a Pyrex-glass spring was employed. The spring was suspended in the upper part of the cylinder and was observed with a cathetometer through a Perspex window of 1 cm. thickness (not shown). The lower portion of the cylinder was modified to protect the spring from convection currents from the furnace. A fuller description of the thermogravimetric apparatus will be published subsequently.

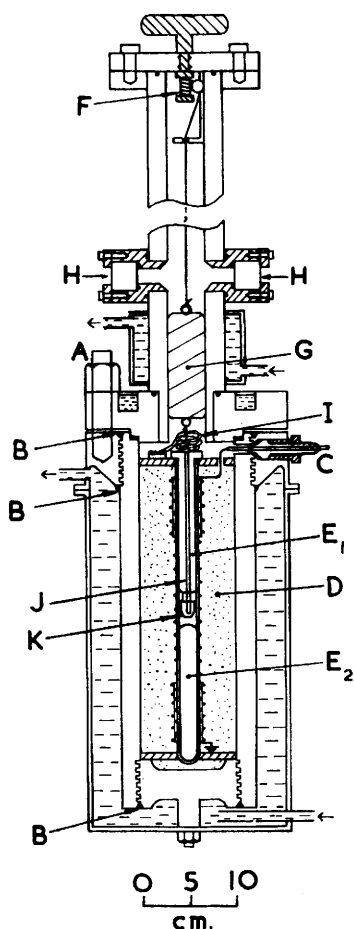


FIG. 1. High-pressure furnace and quenching apparatus.

A, High-tensile bolts (8). B, Welds. C, "Spark-plug" type power terminals (3). D, Alumina powder (100 mesh B.S.S.). E₁ and E₂, Solid alumina baffles. F, Winding mechanism. G, Loosely-fitting piston. H, Perspex windows. I, Coiled thermocouple wires. J, Platinum thermocouple sheath. K, Platinum crucible containing sample.

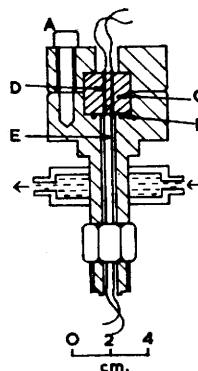


FIG. 2. Device for introducing thermocouple wires.

A, High-tensile bolts (6). B, "O" Ring. C, Laminated Bakelite block. D, Araldite resin. E, Insulated thermocouple wires.

Carbon dioxide for the high-pressure furnace was obtained from a reservoir filled to the requisite pressure by a two-stage compressor (Hofer type 50 HK60). Pressure controllers and needle valves were incorporated in the gas line to allow automatic or manual control of pressure. Drying tubes containing silica gel were also placed in the gas line to remove any traces of moisture. Bourdon test-gauges with scales of 25 cm. diameter were employed for pressure measurement; three gauges were required to cover the pressure range. All the high-pressure apparatus with the exception of the compressor was housed in a cabinet heated to 40° to prevent liquefaction of carbon dioxide in the system. The cooling water for the high-pressure furnace was likewise kept at 40°.

For temperature measurement a potentiometric recorder was used. This was of the two-channel type with a full-scale reading of 1 mv and was equipped with a thermocouple biasing unit⁵ and a potentiometer for calibration purposes.

Performance of the Apparatus.—The pressure gauges were calibrated to an accuracy of

⁵ Jones, Ph.D. Thesis, Imperial College of Science and Technology, London, 1961.

within $\pm 0.25\%$, and pressures could be maintained constant within this accuracy by manual control with needle valves. This method of control was, therefore, used in preference to automatic pressure control.

Temperatures could be measured to $\pm 0.3^\circ$. Thermocouples of Pt-Pt + 13% Rh were used throughout this work and were periodically checked at the gold point.

With increasing pressure, three main problems are encountered in the operation of high-pressure furnaces. These are: fluctuation of the temperature owing to gas turbulence, a tendency for the constant-temperature zone to be displaced upwards by convection, and a narrowing of the zone owing to increased heat losses. The two furnaces used predominantly in this work were designed to overcome these difficulties and will be briefly described.

For the pressure range of 1—40 atm., the furnace used was a conventional one with a single graded winding of platinum alloy, 25 cm. long with an internal diameter of 2.5 cm. Gas turbulence was eliminated by filling the free space in the furnace tube with baffles of solid alumina. With this furnace a constant-temperature zone 3.5 cm. long was obtainable.

In the pressure range 40—300 atm., to eliminate gas turbulence it was necessary, in addition to using baffles, to reduce the bore of the furnace tube to 1.25 cm. This was done by using a furnace tube with an internal diameter of 2 cm. and sliding another alumina tube inside it. Thermojunctions for checking the temperature distribution were sealed through the wall of the inner furnace tube, the connecting wires being brought out through the space between the two tubes. This furnace incorporated a main element 26 cm. long, over each end of which was wound a subsidiary booster element 6.5 cm. in length. All the elements were wound linearly with platinum-10% rhodium wire of 1.22 mm. diameter; the winding density was 3.5 turns per cm. The use of rather heavy windings was necessitated by the high power inputs required. For example, at the highest pressures a total consumption of about 900 w was required to attain a temperature of 1300°. This is more than twice the power consumed by a laboratory furnace of equivalent size running at this temperature. By independent control of the power input to the three windings, a stable zone was obtainable at all pressures, in which the temperature was constant to within $\pm 2^\circ$ over a distance of at least 5 cm. This furnace is the one shown in Fig. 1.

Satisfactory heating rates for thermal analysis could be obtained manually by operation of Variac transformers connected to the furnace windings. In the pressure range 40—300 atm., the temperature distribution was checked periodically during runs by means of the thermocouples fixed on the inside wall of the furnace tube, above and below the sample. Adjustments could then be made to the power inputs of the booster windings to keep the temperature distribution constant in the region of the sample.

When required, the temperature of the sample could be maintained constant to $\pm 1^\circ$ for an hour or more, by using manual control. With automatic controllers of the proportional type, temperature fluctuations of $\pm 5^\circ$ were frequently observed at the higher pressures.

The thermogravimetric apparatus was designed to measure weight changes of about 0.05 g., which corresponded to a spring extension of about 3 mm. At pressures of about 60 atm., a slight oscillation of the spring was always present owing to gas turbulence. This limited the accuracy of measurement to about $\pm 1\%$. The turbulence was probably present in the furnace tube itself, because the alumina baffles could not be accommodated. More satisfactory operation was obtainable at lower pressures.

Materials.—"AnalaR" calcium carbonate supplied by Hopkin and Williams, and optical grade Iceland spar ground to pass 100 mesh (B.S.S.) were employed. Both of these materials were dried for two days at 120° before use. Carbon dioxide gas of 99.9% purity was obtained from a cylinder.

The Solid Equilibrium Region.—For the study of the thermal dissociation $\text{CaCO}_3(\text{s}) = \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ at different pressures, a differential thermocouple and twin platinum crucibles of 0.8 cm. diameter were employed. The latter were mounted alongside each other in the furnace (internal diam. 2.5 cm.). One crucible contained calcium carbonate (0.8 g.), and the other alumina powder as the reference substance. Both materials were packed to a depth of 1.2 cm. With the D.T.A. unit, both channels of the recorder were utilised so that the differential e.m.f. and the sample temperature were printed alternately.

Operational procedure was as follows: The temperature of the furnace was raised to 450° and the apparatus was purged two or three times with carbon dioxide to remove air. (Pre-evacuation was found to be tedious and did not influence the results, so that it was abandoned.)

Pressurising was then carried out to the desired value and the heating continued at constant pressure. At about 60° below the estimated dissociation temperature the heating rate was adjusted to 1.5° per min. The dissociation point was indicated by a marked inflection in the differential plot, which coincided with a steep arrest in the temperature plot of the sample. Determinations by this method were carried out at pressures up to 30.08 atm.

The Melt Region.—At temperatures above about 1240° and pressures above 39.5 atm., dissociation of calcium carbonate is accompanied by fusion of the resultant oxide with unchanged carbonate to form a melt saturated with respect to calcium carbonate. For the work in this region, the furnace with an internal diameter of 1.25 cm. was used but, because of the restricted space available, a D.T.A. unit could not be accommodated satisfactorily. Fusion

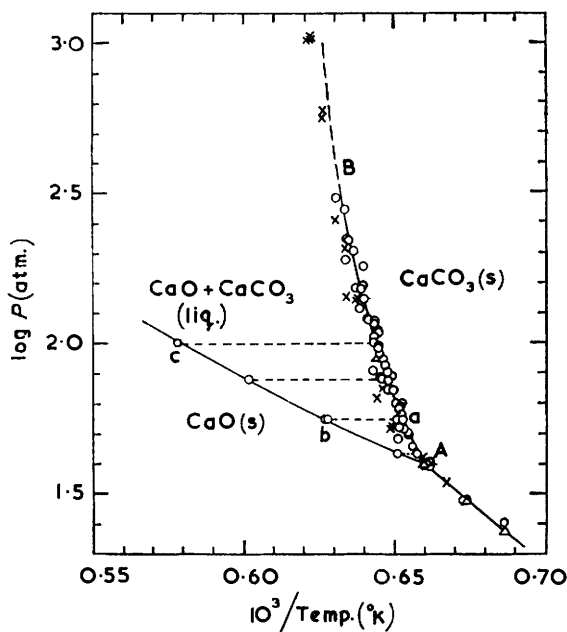


FIG. 3. Pressure-temperature diagram for the melt region.

- "AnalaR" calcium carbonate } (present work).
 △ Iceland spar }
 × Iceland spar (Smyth and Adams).

points were therefore determined from the arrests in the temperature plots obtained from a single shielded thermocouple placed centrally in the samples, a heating rate of about 2° per min. being employed.

Fusion temperatures at pressures up to 304 atm. are plotted in Fig. 3 (portion AB), the temperatures being mostly lower than those of Smyth and Adams. At 1000 atm., where the melt will be practically pure calcium carbonate, these authors give a melting point of 1339°. Even after allowance for extrapolation errors, the present work suggests a lower melting point at this pressure, namely, about 1325°.

The extreme left-hand limb of the plot in Fig. 3 represents equilibrium between solid oxide and melt. It was derived from experiments in which melts obtained by dissociation of calcium carbonate were subjected to further heating at constant pressure, until the increasing oxide contents reached the saturation values and solid lime was precipitated. The saturation temperatures were easily detected by marked arrests in the temperature plots of the melts. The actual heating paths of the melts at various pressures are shown by the isobars (broken lines) across the all-liquid region. For these particular determinations a heating rate of 1° per min. was used. The sharpness of the thermal arrests corresponding to the formation and

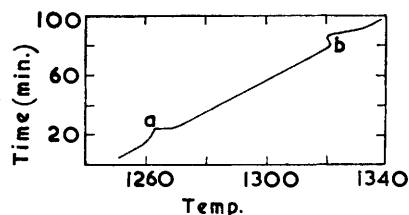


FIG. 4. Temperature plot for the melt at 56 atm.

- a (1263°), Formation of the melt saturated with respect to calcium carbonate. a-b, Heating of the melt accompanied by continuous loss of carbon dioxide. b (1322°), Decomp. of the melt, yielding solid lime.

decomposition of a melt is illustrated by the temperature plot for the isobar at 56 atm. shown in Fig. 4; this corresponds to the path a-b in Fig. 3.

Determination of the Melt Compositions.—For these determinations, "AnalaR" calcium carbonate only was used because of its higher purity. Compositions of the melts in equilibrium with solid calcium carbonate were determined as follows: Calcium carbonate (about 1 g.) was heated under constant pressure until dissociation and fusion took place. The melt was then maintained at the fusion temperature for 45 min. to achieve complete homogeneity of composition. Manual control of temperature to a constancy of $\pm 1^\circ$ was employed during this equilibration period. The melt was then quenched by means of the apparatus described above. Quenching by the cool gas in the cylinder was so effective that the temperature of the melt was reduced to 40° in less than 10 sec. After the pressure had been reduced, the solidified melt was removed, weighed, and dissolved in standard hydrochloric acid. The composition was then determined by titration with standard alkali. Compositions at pressures up to 200 atm. were determined by this method.

Compositions of the melts lying on the isobars at 56 and 100 atm. in the all-liquid region were determined similarly. Since the oxide contents of these melts were somewhat higher than those described above, steps were taken to reduce the possibility of carbonation of some of the oxide during quenching. This was done by using a platinum crucible equipped with a narrow tail portion at the bottom, in which the melt collected when fusion took place. The length of the tail portion was 1.5 cm., but its diameter was only 6 mm. so that only a small area of melt was exposed to the gas phase during quenching. In view of the narrowness of the sample, the equilibration period was increased to 60 min. Some compositions on the 56 atm. isobar were determined thermogravimetrically from the weight changes caused by evolution of carbon dioxide from the melts. With this method, however, the temperature of the melts could only be estimated to within $\pm 5^\circ$ by means of thermocouples placed around the crucible. This inaccuracy was caused by lateral thermal gradients probably resulting from the absence of baffles in the furnace tube. When a reasonably constant temperature was obtained, the composition of the melt became constant within 10 min. This showed that the equilibration periods employed in the quenching method were more than adequate.

RESULTS AND DISCUSSION

For the reaction, $\text{CaCO}_3(\text{s}) = \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$, the pressures and dissociation temperatures for Iceland spar and "AnalaR" calcium carbonate are given in Table 1; temperatures are given to the nearest degree. The temperatures recorded for 1 atm. pressure are the mean values obtained from a number of determinations. Temperatures marked with an asterisk refer to the reverse reaction and were obtained by slowly cooling

TABLE 1.

Equilibrium pressures and temperatures for the reaction $\text{CaCO}_3(\text{s}) = \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$.													
$P(\text{atm.}) \dots$	1.00	1.00 †	2.30 †	3.00	4.29 †	7.94 †	10.12	11.95 †	14.94	14.94	17.00 †	17.00	17.0
Temp. (c)	902°	898°	959°	997°	1012°	1071°	1093°	1107°	1139°	1137°	1142°	1153°	1148°
$P(\text{atm.}) \dots$	17.00	17.00	19.90	20.00	20.00	21.80 †	23.78 †	25.30	30.00	30.00	30.00	30.08 †	
Temp. (c)	1152°	1144° *	1164°	1164°	1163° *	1168°	1185°	1185°	1214°	1212° *	1211°		

* Reverse reaction (see text). † Iceland spar; others, "AnalaR" calcium carbonate.

the calcium oxide resulting from complete dissociation of the carbonate, until combination took place. A plot of $\log P_{(\text{atm.})}$ against $10^3/\text{Temp.}(\text{°K})$ for all these values shows a linear relation, and the agreement with the results of Smyth and Adams is excellent. Some of the values for pressures just below the eutectic point have been included in Fig. 3.

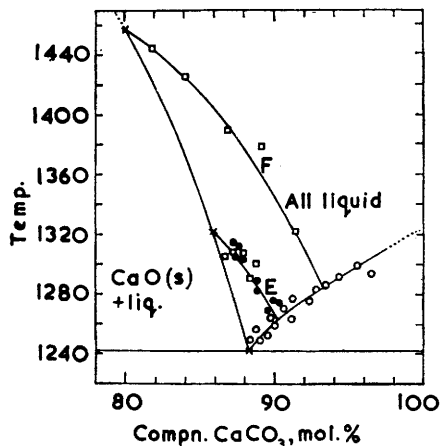
From the method of least squares, the best straight line drawn through the plotted values can be expressed by $\log P_{(\text{atm.})} = 7.079 - 38,000/4.574T$. In deriving this relation, the pressures have been considered to be accurate and the dissociation temperatures subject to error. For the temperature range of 1173–1515°K, the value of $\Delta H = 38,000$ cal. is considered to be accurate within ± 500 cal., and the entropy of reaction, $\Delta S = 32.4$ e.u., accurate within ± 0.2 e.u. The accuracy limits have been calculated from the standard deviations of the dissociation temperatures. In this pressure and temperature

range, the departure of the gas from ideal behaviour is not considered significant enough to warrant correction of the pressures. Smyth and Adams combine their results with some earlier ones of Johnston⁶ for pressures below 1 atm. and derive an expression containing a ΔC_p term to cover a greater temperature range. The value of ΔH obtained from the above expression lies between the enthalpy values $\Delta H_{1170^\circ\text{K}} = 39,440$ cal. and $\Delta H_{1513^\circ\text{K}} = 35,790$ cal., given by their expression for 1 atm. pressure and their eutectic point, respectively. The latter values, however, are indicative of a rather large variation in enthalpy for a temperature range of only 343° . This can be ascribed to the difficulty in interpreting ΔC_p satisfactorily in this temperature range, from limited thermal data. Actually, the results of these authors for this region are better expressed by a straight-line plot.

FIG. 5. Temperature-composition diagram for the eutectic region. Curves E and F are isobars at 56 and 100 atm., respectively.

× Extrapolated compositions. Isobaric compositions: □ detd. by quenching; ● detd. thermogravimetrically.

Compositions in equilibrium with solid phases are at varying pressure.



From the intersection of the three limbs of the plot in Fig. 3, the eutectic point is considered to lie at $1242^\circ \pm 3^\circ$ and 39.5 ± 0.5 atm. These values show a good agreement with those obtained by Smyth and Adams solely for Iceland spar, namely, $1240^\circ \pm 1^\circ$ and 39.5 ± 0.5 atm.

Compositions of the melts in equilibrium with solid calcium carbonate at different temperatures are shown in Fig. 5, (○) pressures having been omitted to enable a two-dimensional diagram to be used.

Compositions of the melts lying on the 56 and 100 atm. isobars are also plotted in Fig. 5 (curves E and F, respectively) and these have been extrapolated to the temperatures of saturation with calcium oxide at these pressures. These temperatures are 1322° and 1457° , respectively, and are represented by the points *b* and *c* in Fig. 3. The line intersecting these extrapolated values and the eutectic point, in Fig. 5, thus gives the compositions of melts in equilibrium with solid lime. The best fit of all these curves gives the eutectic composition as CaCO_3 88.3 mole %, CaO 11.7 mole %. These values show a fair agreement with those estimated microscopically by Wyllie and Tuttle⁷ during their isobaric synthesis of carbonatite magma. They estimate the composition to lie near CaCO_3 90 mole %, CaO 10 mole %. The compositions plotted in Fig. 5 are considered to be accurate within ± 1 mole %.

The exact representation of the system requires a three-dimensional model in which equilibrium compositions are represented by points on a surface. For completeness, therefore, compositions of the melts in equilibrium with the solid phases are given in Table 2 with the corresponding temperatures and pressures. The values tabulated are smoothed ones obtained from the curves in Figs. 3 and 5, pressures being given to the nearest 0.5 atm.

⁶ Johnston, *J. Amer. Chem. Soc.*, 1910, **32**, 938.

⁷ Wyllie and Tuttle, *J. Petrology*, 1960, **1**, 1.

The success of the quenching method naturally depends on the fact that any carbonation of the lime in the solidified melt must take place only to a small extent during the 10-minute period required to reduce the pressure and open the apparatus. The fair agreement between the results obtained by quenching and those obtained thermogravimetrically suggests that this is so. It is considered therefore that the quenching method gives reasonably reliable results, and compositions of the binary melts in the strontium oxide-carbon dioxide system are at present being studied by this method.

TABLE 2.

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

<i>Melts in equilibrium with CaCO₃(s).</i>			<i>Melts in equilibrium with CaO(s).</i>			Eutectic point		
Temp. (c)	<i>P</i> (atm.)	CaCO ₃ , mole %	Temp. (c)	<i>P</i> (atm.)	CaCO ₃ , mole %	Temp. (c)	<i>P</i> (atm.)	CaCO ₃ , mole %
1300°	200	95.8	1450°	98.5	80.3	1242°	39.5	88.3
1290	135	94.2	1400	79	82.7			
1280	96	92.6	1350	63	84.8			
1270	72	91.1	1300	50	86.5			
1260	55	89.9	1250	40.5	88.1			
1250	45.5	88.9						

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