work of refining the crude material which was carried on by one of us in summer.

Summary

This paper recounts a determination of the atomic weight of gallium by means of the analysis of gallium chloride. The gallium which formed the starting point was very carefully purified, converted into chloride by the action of pure chlorine, and fractionated in this form. The fractionation was effected by distillation and sublimation in chlorine, in nitrogen, and in a vacuum. The salt was analyzed by essentially the same method as that employed in the case of aluminum bromide, and yielded the result Ga = 69.716, if silver is 107.88 and chlorine is 35.458.

Cambridge 38, Massachusetts

[Contribution from the Geophysical Laboratory, Carnegie Institution of Washington]

THE SYSTEM, CALCIUM OXIDE–CARBON DIOXIDE

By F. Hastings Smyth and Leason H. Adams

Received February 10, 1923

Previous Investigations and Purpose of the Present Work

The reaction between calcium oxide and carbon dioxide has long been the subject of investigation. Comparatively few workers, however, have sought the behavior of calcium carbonate when it is subjected to conditions of relatively high temperature and pressure. The reason for this is doubtless found in the fact that difficulties of experimentation at pressures in the neighborhood of a thousand megabars and at temperatures above 1000° are great. Nevertheless, a knowledge of the pressure-temperature relations of this simple system is necessary before further exact knowledge can readily be obtained of systems which contain mixtures of calcium carbonate with other carbonates or with silica. From systems, either with or without the presence of water, would crystallize minerals such as the dolomites and silicate carbonate compounds of which spurrite and cancrinite are examples. We hope that the present work may serve as a basis for the further investigation of the natural conditions which have given rise to the formation of many complex minerals containing calcium carbonate as one constituent.

In the following pages are described an apparatus which has proved reasonably satisfactory for such experimentation, and the results which have been obtained in the 2-component system, calcium oxide–carbon dioxide, the reaction being represented by the equation, $CaCO_3 = CaO + CO_2$.

Of the equilibria data already obtained at lower pressures and temperatures, which may be controlled in apparatus of thin-walled tubes, only the results of Johnston will be cited,[1] since these contain within themselves, or supersede, the results of earlier investigations. We shall show later that these data are consistent with the results of the present work.

At high pressures the most interesting, and probably the first, efforts to determine the conditions under which calcium carbonate may be fused were made by Sir James Hall in the opening years of the nineteenth century, and these early experiments have recently been described by Flett[2] in all necessary detail. Hall heated various charges of ground natural calcite and chalk, and of precipitated calcium carbonate in containers made of sawed-off gun barrels. These containers were closed by welding at one end and by a fusible plug at the other. They were heated in an oil muffle furnace, the end with the plug being allowed to protrude from the furnace in such a way that it could be cooled to prevent fusion of the plug. In the absence of pressure gages, a blow-off valve held down by known weights was provided, by means of which the final pressure before the opening of the valve could be recorded.

With this apparatus Hall found, after 6 or 7 years of careful work, that 52 atmospheres was the lowest pressure at which calcium carbonate might be fused, or at any rate sintered together, and that "a 'complete marble' was formed at a pressure of 86 atmospheres, and carbonate of lime 'absolutely fused' under a pressure of 173 atmospheres."

It may not be out of place to pay tribute again to the skill with which these experiments were conducted with apparatus which we would now call "crude." The results obtained are remarkably close to those which may be had with the use of the elaborate equipment of the modern laboratory.

Other earlier attempts to heat calcium carbonate under high pressures were made with similar apparatus. Le Chatelier[3] and Joannis[4] used a closed bomb made of heavy iron pipe which was heated in a gas furnace. Pressures were developed in these bombs by the partial dissociation of the initial charge of calcium carbonate.

The difficulties inherent in these procedures are that the iron container is so much weakened at high temperatures and that it is impossible to develop really high pressures, good temperature distribution throughout the charge is not obtainable and the temperatures within the charge cannot be accurately measured. Furthermore, the melting point of pure calcium carbonate cannot be obtained, for the charge is partially decomposed during the operation. Le Chatelier has concluded that the melting point of calcium carbonate lies at about 1020°, under a pressure of about 10 megabars.

Great improvement over these methods has been effected by H. E. Boeke,[5] who has constructed a thick-walled bomb enclosing a small platinum-wound furnace. In the walls of this container, which was capable of holding pressures up to 150 megabars, were placed insulating plugs carrying the furnace and thermel[6] leads. An opening for adding and withdrawing carbon dioxide was also provided. The principle of this apparatus is evidently correct. The bomb walls remain cool while the temperatures are generated in a small space surrounding the material to be heated, and can be measured accurately. At the same time the pressure in the system can be controlled without dependence on the carbonate charge as a source of carbon dioxide.

For purposes of reference some of the results of Boeke's work are tabulated in Table I. These results do not cover a sufficient range of pressure and temperature to determine

---

[1] Johnston, This Journal, **32**, 938 (1910).

[2] Flett, *Sci. Monthly*, 13, 308 (1921).

[3] Le Chatelier, *Compt. rend.*, 115, 817, 1009 (1892).

[4] Joannis, *ibid.*, **115**, 934 (1892).

[5] Boeke, *Neues Jahrb. Mineral. Geol.*, **1**, 91 (1912).

[6] Abbreviation for "thermo-element," proposed by W. P. White.

the direction of a curve, and it will develop presently that they are somewhat discordant among themselves, though evidently more nearly correct than any previously obtained. By a method of interpretation of his results which is obscure, Boeke places the melting point of pure undissociated calcium carbonate at 1289°, under a minimum pressure of carbon dioxide of 110 megabars. He finds a eutectic between calcium carbonate and calcium oxide fusing at 1218°. In addition, by using a heating-curve method, Boeke has found a reversible transformation of one form of calcium carbonate into another with accompanying absorption of heat at about 970°.

TABLE I

SOME OF BOEKE'S VALUES FOR EQUILIBRIUM PRESSURES FOR CALCIUM CARBONATE ABOVE THE EUTECTIC POINT

t °C.	Pressure megabars	Pressure mm.	*t* °C.	Pressure megabars	Pressure mm.
1275	146	109400	1280	117	87400
1282	124	92700	1271	104	78280
1274	142	106400	1250	74	55480
1272	139	104120	1250	81	60800
1276	101	76000			

Theoretical Outline

From a theoretical standpoint the 2-component system, calcium oxide–carbon dioxide, may be treated as entirely similar to the system, cuprous oxide–oxygen. Since a theoretical discussion of the latter system has been presented with considerable detail in other places,[7] nothing beyond a general statement of the behavior and results to be expected in the system under discussion will be given here.

According to the conditions of pressure and temperature prevailing in the system, we may have the following reactions. (1) Solid calcium carbonate dissociates to give solid calcium oxide and carbon dioxide gas. (2) At and above the temperature at which calcium carbonate and calcium oxide fuse to form a eutectic mixture, dissociation of solid calcium carbonate to form calcium oxide is immediately followed by the fusion of the calcium oxide formed with some of the remaining calcium carbonate to give a liquid instead of a second solid phase. (3) If the solid calcium carbonate disappears entirely, further dissociation at a given temperature must be from the liquid phase and is accompanied by precipitation of calcium oxide, since the removal of calcium carbonate from the solution would otherwise increase the concentration of calcium oxide, which is impossible if the temperature remains unchanged.

These three possibilities of action within the system may be summarized as follows.

$$CaCO_3\ \text{(solid)} \rightleftharpoons CaO\ \text{(solid)} + CO_2\ \text{(gas)} \qquad (1)$$

$$CaCO_3\ \text{(solid)} + xCaCO_3\ \text{(solid)} \rightleftharpoons CaO\ \text{(liquid solution in } xCaCO_3) + CO_2\ \text{(gas)} \qquad (2)$$

$$CaCO_3\ \text{(liquid solution in } xCaO) \rightleftharpoons CaO\text{(solid)} + xCaO\ \text{(solid)} + CO_2\ \text{(gas)} \qquad (3)$$

---

[7] (a) Smyth and Roberts, THIS JOURNAL, **42,** 2582 (1920). (b) Roberts and Smyth, *ibid.*, **43,** 1061 (1921).

The foregoing cases exclude the formation of solid solutions, indications of which have not been found.

The pressure-temperature relations for all three reactions may be followed by means of the Clapeyron equation, $dp/dT = \Delta H/T\Delta V$, in which ΔH represents the heat absorbed in each reaction when 1 mole of carbon dioxide gas is produced. In Reaction 2 this includes the heat which would be absorbed if no fusion took place, plus an additional heat absorption due to the fusion of the x mols of calcium carbonate with the 1 mol of calcium oxide produced. The number of mols of calcium carbonate which fuse with one mol of calcium oxide varies with the pressure and temperature, but for given equilibrium conditions remains constant.

In the case of Reaction 3, on the other hand, the heat which would be absorbed by the reaction if the calcium oxide and calcium carbonate remained both as solid phases, is diminished by the heat evolved when there crystallize from the solution 1 mol of calcium oxide produced and x mols of calcium oxide corresponding to the calcium carbonate lost in the reaction.

In general, ΔH_1 is a positive quantity, ΔH_2 is always greater than ΔH_1 and ΔH_3 is always algebraically less than ΔH_1.

For Reaction 1 this equation may be integrated with a close approximation to the truth by assuming that the total volume change, ΔV, is equal to the volume of carbon dioxide formed which, in turn, may be evaluated in terms of pressure and temperature by the assumption of the ideal gas laws. ΔH may be taken as constant, and with these assumptions the integrated equation is that of a straight line with $\log p$ and $1/T$ as the variables.

Below the eutectic point our experimental data for Reaction 1 nearly justify these assumptions. It is convenient to choose these variables to present the data throughout the temperature range of the experiments, and the equation of the actual graph of the data deviates but slightly from that of a straight line. This actual equation can be determined from the data, and from this and an accurate equation of state for carbon dioxide, ΔH for Reaction 1 may be calculated at any temperature.

In spite of the fact that ΔH is far from constant after fusion takes place to form a solution of composition varying with the temperature, it is still convenient to retain $\log p$ and $1/T$ as variables to present the data in the form of a plot, and this has accordingly been done in Fig. 3.

Equilibrium pressure values for Reaction 1 have been summarized and accurately checked by Johnston,[1] up to a temperature of 894° and a pressure of 716 mm. of mercury. The points determined from these data by plotting the reciprocals of the absolute temperature against the logarithms of the corresponding pressure also lie along a curve which deviates but little from a straight line.

However, as the pressure within the system is raised, the corresponding temperature reaches a point such that the calcium oxide formed by dissociation no longer remains solid, but fuses with part of the remaining calcium carbonate. This is the eutectic point, and here and at higher temperatures Reaction 2 takes place. As long as solid calcium carbonate remains, there are three phases and the system is monovariant. The pressure-temperature curve, however, assumes a steeper slope above the eutectic point, because of increased heat absorption in the fusion, and the logarithmic plot no longer approximates a straight line. As the pressure and temperature continue to rise, larger quantities of calcium carbonate are carried into solution by each mol of calcium oxide formed, until the composition of the liquid approaches that of pure calcium carbonate. Only at this limiting pressure and temperature may we speak of the melting point of pure calcium carbonate. We shall see presently that this point has been approached by us in temperature though perhaps not in pressure, and that it lies considerably above the "melting point" as given by Boeke.

It is in this respect that Boeke's points are discordant among themselves. Above the eutectic an increase in pressure must always be followed by a rise in the temperature at which carbon dioxide gas, solid calcium carbonate and liquid containing calcium carbonate and calcium oxide are in equilibrium. A glance at Table I will show that this is not uniformly the case with the points here recorded. For example, at 76000 mm. pressure, a melting point temperature of 1276° is obtained, while at the higher pressure 109400 mm., the slightly lower temperature of 1275° is found.

As in the general case, when a dissociation product, here calcium oxide, remains the solid phase, and calcium carbonate is present only in the liquid, further dissociation is accompanied by a precipitation of more calcium oxide, and Reaction 3 takes place. The heat effect here is less than that of Reaction 1 and the slope of the pressure-temperature curve is less than that of the curve below the eutectic point. Along a section of this curve, possibly along the major portion, the equilibrium pressure falls with rising temperature. The general form of this curve has also been discussed elsewhere [7a] and, since no actual points on it have yet been found, a further theoretical treatment will not be given here. Its terminal point lies at the high temperature and correspondingly low pressure of the melting point of pure calcium oxide.

The eutectic point is the quadruple point of the system, and here calcium carbonate, calcium oxide, liquid and calcium oxide gas can co-exist in equilibrium.

In connection with the equilibrium curve for Reaction 1 it remains to be noted that if there be a transformation point as given by Boeke[8] of one form of calcium carbonate (β form) into another (α form) with absorption

---

[8] Wilhelm Eitel (from advance proof sheets of "Neues Jahrb. Mineral. Geol." furnished by the author), using Boeke's apparatus, has recently obtained thermal evidence similar to that of Boeke that a transformation $\beta CaCO_3 \rightleftharpoons \alpha CaCO_3$ takes place at 970° ± 5°.

of heat, there will be a change in slope of the curve at this point, and the slope of the logarithmic plot between 970° and the eutectic point will be less than that of the line defined by lower temperatures and pressures.

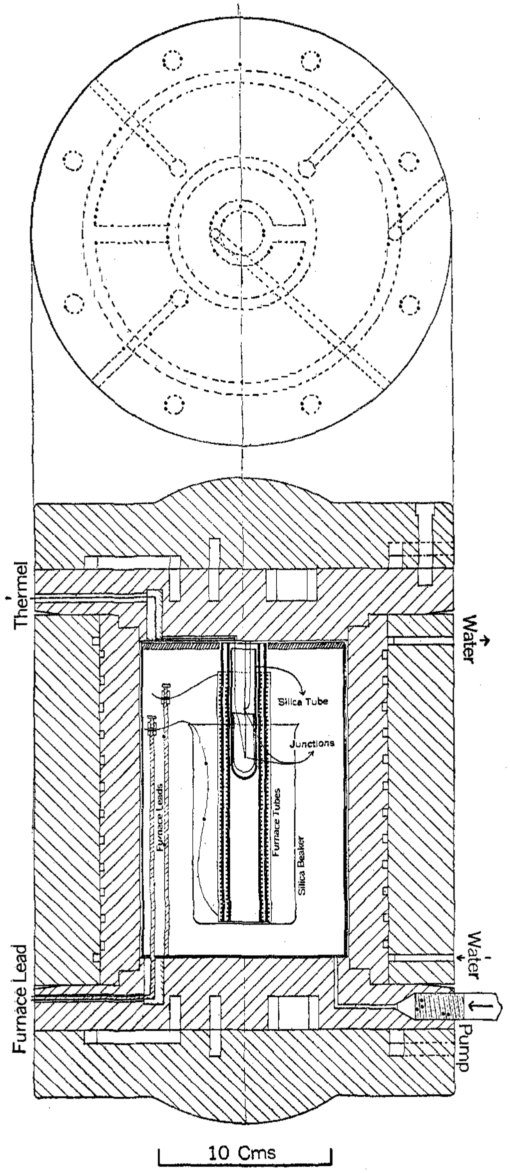

Fig. 1.—Diagram of apparatus for high pressure work, showing section through steel bomb with furnace in place and plan of top and bottom pieces of bomb.

Apparatus

The apparatus used consists essentially of a heavy walled steel container shown diagrammatically in Fig. 1, inside of which is placed a small platinum-wound resistance furnace.

The body of the container or "bomb" is cylindrical, open at both ends, with an internal diameter of 10.5 cm. and an external diameter of 23.5 cm., which gives a wall thickness of 6.5 cm. The top and bottom pieces are separate circular plates, seating against copper gaskets when the bomb is closed.

The cylindrical shell is made in two parts, an outer shell shrunk on an inner cylinder. Around the outer wall of the inner cylinder is cut a spiral groove through which cooling water may be circulated. The top and bottom pieces are also in two parts with a groove between them for the same purpose. Through the bottom plate pass 2 holes for carrying furnace leads, one of which is shown in the figure. These leads are made of silver rod 3 mm. in diameter, which will easily carry a current of 35 amperes without overheating. Similar, though smaller, holes through the top carry 3 thermel leads 0.4 mm. in diameter.

A very satisfactory packing for all these leads is made by ramming into place around each wire, at a pressure of about 2000 kg., a layer of lithographer's stone, a soft rubber washer, and on top of these a layer of talc. The rubber and talc prevent leakage of gas, and the lithographer's stone, while sufficiently soft to crush into place, holds firmly enough to prevent leakage and blow-outs at high pressures. The container and pipe lines, previous to use with gas, were filled with oil and tested up to pressures of 2000 megabars.

The thermel used is of platinum and platinum with 10% rhodium alloy, calibrated at the quartz and gold points.

The resistance furnace is of platinum wire 0.6 mm. in diameter, wound on alundum tubes. The inner tube is about 13 mm. in diameter and the outer tube is chosen to fit closely over its winding. Both tubes are wound over a length of 12.5 cm. and to within 2 cm. of the top of the bomb. The windings are connected in parallel, a useful arrangement at high pressures when large amounts of energy are necessary to attain the higher temperatures.

The principal heat losses at high pressures, with carbon dioxide at least, occur through convection. Therefore, everything possible is done to cut down this effect. The furnace tubes do not reach to the bottom of the bomb and are closed at the lower end and protected from circulating gas by a silica glass beaker embedded in the insulating material which fills the bomb cavity. Within the furnace the small platinum crucible containing the charge is suspended on the thermel leads and is enclosed in a silica glass test-tube which reaches to the top of the furnace. Thus the crucible, though electrically sufficiently well insulated, is practically in solid contact with the inner furnace tube and the heating coils. For the sake of simplicity the thermel junctions only are shown in the diagram. Details of the connection and of the construction of the crucible used are shown in Fig. 2, A and B. The lower junction is within the charge, and the upper junction immediately above the crucible, which gives the temperature outside of and above the charge. The thermel leads pass through alundum disks (not shown in the diagram) which fill the remaining space in the silica test-tube from a point immediately above the crucible to the top of the furnace. An alundum plate screwed to the inner surface of the bomb top protects the steel from the action of the hot gases which leak up through the furnace and around the baffle plates.

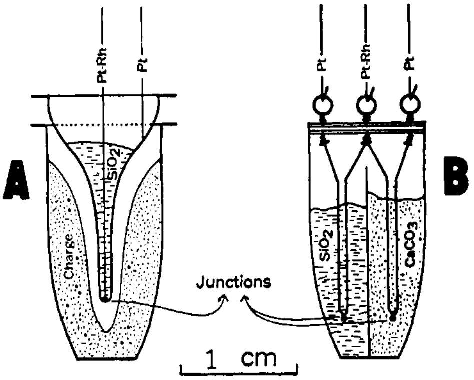

Fig. 2.—Platinum crucibles used for heating and fusing $CaCO_3$. A. Covered crucible, the cover itself being part of thermel. B. Divided crucible with differential thermel used to detect small heat effects.

The entire cavity of the bomb together with the lower part of the furnace is filled with powdered alundum ground to 60 mesh.

The furnace, at pressures up to 200 megabars, provides a heated section of about 15 mm. in length, within which the temperature difference is not more than 2° at 1400°. However, at 1000 megabars the temperature gradient is much larger and the hottest portion of the furnace moves continually upwards with increasing pressure, until sometimes at 1000 megabars the best location for the crucible is at the very top of the furnace tube, above the winding altogether. The heat losses are also large. The furnace, which at atmospheric pressure requires 10 amperes at 22 volts to attain a temperature of 1400°, requires 30 amperes at 75 volts for the same temperature at 1200 megabars. The charges used were not more than 5 to 7 mm. deep, and were, therefore, assured of a reasonably uniform temperature distribution within the platinum crucible.

It is necessary to circulate hot water through the bomb walls at high pressures, so that all of the gas may be above its critical temperature. If the walls are kept cool, extraordinary sudden temperature fluctuations as great as 50° to 100° may be noted within the furnace. The reason for this is not clear, though it is not impossible that liquid carbon dioxide may assume a spheroidal state and this cool liquid may penetrate at times the hot furnace. If the walls of the bomb are heated, however, the temperature of a crucible and charge may be controlled readily within a few tenths of a degree over periods of an hour or more by using storage battery current and regulating from time to time with a hand rheostat. Satisfactory smooth heating curves are also obtained with this apparatus.

Gas pressures up to 60 megabars may be obtained readily from a cylinder of commercial carbon dioxide. We can obtain higher pressures up to 1000 megabars by using a hand pump with a small steel piston, the pump being cooled by ice in order to keep the carbon dioxide passing through it in the liquid state. The compressibility of liquid carbon dioxide at pressures above 100 megabars does not appear to be great, so that large quantities of liquid do not have to be pumped into the bomb to give the pressures which we have required.

While in use, the bomb with the top and bottom pieces in place is set upright in a 500-ton oil press, and sufficient pressure is applied to hold the end pieces against their seats and to prevent leakage around the copper gaskets. At 1000 megabars this requires about 200 tons.

The types of crucibles used are shown in Fig. 2 at A and B. The crucible A has a cover which extends down inside the crucible, which is entirely made of pure thermel platinum and is joined to the platinum thermel lead. Inside the lower tip of the cover, well within the interior of the charge when it is in place, is fused the rhodium-alloy wire. Thus the tip of the cover itself becomes the thermel junction, an arrangement which gives the temperature of the inside of the charge and at the same time keeps the crucible covered. The depression in the cover is filled with ground quartz or alundum to prevent exposure of the junction to convection currents. The cover is held in place by small pieces of platinum foil bent as clamps around the edges of the flanges of the crucible and its cover. These flanges, shown in the figure, fit tightly together when the cover is in place.

In order to register very slight heat effects, a divided crucible (Fig. 2, B) is also used, with two junctions, one compartment of which holds the charge and the other ground quartz. By means of a suitable potentiometer the difference in the temperature of these junctions and the actual temperature of the charge can be read practically simultaneously. The double thermel junction tips are made separately and carried on a bit of porcelain capillary as shown, which also serves as a support for the crucible. Connections with the thermel leads are made by pinching the wires together through loops as shown in the figure.

The gas pressures are read on gages of the Bourdon type, which have been carefully calibrated during use against an absolute gage with weights. The various scales of these gages reading in pounds and atmospheres are converted into megabars and millimeters of mercury for the sake of uniformity and convenience in plotting. Pressures between 50 and 1000 pounds per square inch are read to an accuracy of 1 pound, and above this point an accuracy of 1 megabar is obtained.

Materials

The calcium carbonate used is natural Iceland spar. This material is in the form of large, colorless crystals showing the correct index of refraction for calcite and found by analysis in this Laboratory to be free from iron and manganese and to contain less than 0.05% of magnesium oxide.

The carbon dioxide gas is from commercial cylinders and shows practically complete absorption in potassium hydroxide solution. The gas is dried before use by passing through a steel tube containing fused calcium chloride. Now and then a cylinder of carbon dioxide contains oil which is troublesome if it enters a heated furnace. An oily cylinder is, however, easily detected and discarded.

Experimental Detail and Results

In general, in determining points on the pressure-temperature curve, a charge of ground calcium carbonate is heated in the bomb at a constant pressure until dissociation begins. By recording the heating curve, the point of dissociation, or fusion, as the case may be, is evident by the slowing or stopping of the temperature rise. At higher temperatures this method gives accurate results without difficulty, and above 1100° the charge is usually held in the covered crucible of Fig. 2, A, with a single junction registering the temperature. It is particularly necessary to have the crucible covered through a range of about 30° above the eutectic point, for within this range fusion is accompanied by so much dissociation that the charge usually blows out of the crucible. Even a covered crucible does not prevent the loss of fusions made at or near the eutectic point.

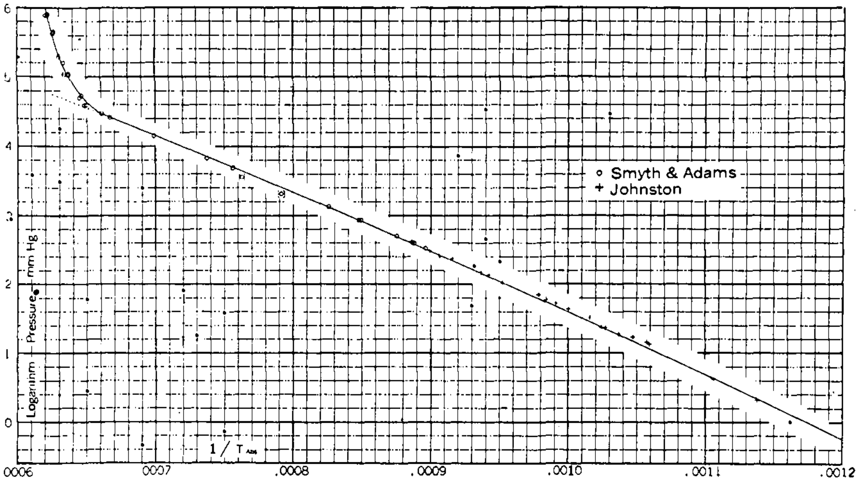

Fig. 3.—$\mathrm{Log}_{10}\, p - 1/T_{\mathrm{abs}}$. Plot of experimental data throughout range covered by Johnston and by Smyth and Adams. The equation of the curve below the eutectic is: $\mathrm{Log}_{10}\, p = -11355/T - 5.388 \log T + 29.119$.

At lower temperatures and pressures, between 900° and 1100° there is a great tendency for calcium carbonate to superheat, and it is only at temperatures much above the true dissociation temperature for a given pressure that the heating curve begins to show a definite heat absorption. Therefore, points determined by this method are always too high in temperature. The points in brackets in Table II and shown in Fig. 3 are typical of many such results.

But by using a divided crucible with a differential element, the point of incipient dissociation is readily recognized before the effect in the heating curve is noticeable. Fig. 4 shows such a heating curve with the accompanying difference in temperature of the two junctions plotted with it. The temperature of dissociation judged from the heating curve would be read at 10,225 microvolts, whereas the differential shows that already at 10,140 microvolts the charge is dissociating. The differential also brings out the interesting fact that slight dissociation does start promptly at the equilibrium temperature. The calcium oxide formed, however, must coat the surface of the calcium carbonate grains, causing further loss of carbon dioxide to cease, so that heat absorption actually falls off again, although the temperature continually rises. It is only at still higher temperatures that the carbon dioxide pressure in the calcium carbonate crystals is able to crack this coating or to burst the crystals open, when dissociation begins in earnest and the heat effect is unmistakable.

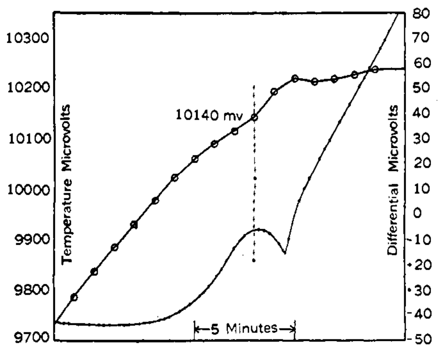

Fig. 4.—Typical plot of behavior of the differential thermel with $CaCO_3$ used in divided crucible. Left-hand curve shows recorded temperature of $CaCO_3$ in microvolts. Right-hand curve shows difference in temperature between the two junctions.

The Eutectic Point

As already noted, for about 30° above the eutectic point it is very difficult to get results, owing to the fact that the charge always blows out of the crucible, but when the pressure reaches 150 megabars and the temperature about 1300° quiet fusion is usually assured. The eutectic point itself has been most difficult to locate for this reason. In such cases two kinds of superheating are possible. First, the calcium carbonate itself may (though rarely) be heated above the dissociation point without forming appreciable quantities of calcium oxide and, second, the calcium oxide and calcium carbonate may remain unfused for some time even above the eutectic temperature. However, after repeated trial by approaching the eutectic pressure from both directions, we believe that the true pressure of the quadruple point is now known within about 600 mm., which corresponds to a temperature range of little over 2°. The method of locating this pressure consists in taking heating curves on successive charges of calcium carbonate, starting at a pressure of 28,000 mm., where no fusion takes place, and increasing the pressure by about 50 mm. at each experiment until dissociation is immediately followed by fusion. The same process is followed by reducing the pressure gradually from about 32,000 mm., until the charge at the end of the experiment shows that dissociation,

TABLE II

EQUILIBRIUM PRESSURES AND TEMPERATURES FOR THE REACTIONS

$CaCO_3$ (solid) $\rightleftharpoons$ CaO (solid) + CO_2 (gas) and

$CaCO_3$ (solid) $\rightleftharpoons$ CaO (liquid solution in $CaCO_3$) + CO_2 (gas)

Temp. °C.		Temp. °Abs.	$\frac{1}{T} \times 10^3$	Pressure Mm. Hg		Pressure Megabars	Log10 p (mm.)
$CaCO_3$ (solid) $\rightleftharpoons$ CaO (solid) + CO_2 (gas)							
842.3[a]		1115.3	0.8966	343.0		...	2.5353
852.9[a]		1125.9	0.8882	398.6		...	2.6005
854.5[a]		1127.5	0.8869	404.1		...	2.6065
868.9[a]		1141.9	0.8757	510.9		...	2.7083
904.3[a]		1177.3	0.8494	879.0		...	2.9440
906.5[a]		1179.5	0.8478	875.0		...	2.9424
937.0[a]		1210.0	0.8258	1350		...	3.1303
937.0[a]		1210.0	0.8258	1340		...	3.1271
[990.6[b]		1263.6	0.7914	2053		2.73	3.3124]
[1038.2[b]		1311.2	0.7627	3604		4.80	3.5568]
1049.3[c]		1322.3	0.7563	4894		6.52	3.6897
1082.5[c]		1355.5	0.7377	6758		9.90	3.8298
1157.7[c]		1430.7	0.6990	14202		18.94	4.1523
1226.3		1499.3	0.6670	26093		34.8	4.4166
1226.2		1499.2	0.6670	26093		34.8	4.4166
1240.9	eutectic temp.	1513.9	0.6605	29718	eutectic pressure	39.6	4.4730
1238.9[c]		1511.9	0.6614	30579		40.7	4.4854
$CaCO_3$ (solid) $\rightleftharpoons$ CaO (liquid solution in $CaCO_3$) + CO_2 (gas)							
1244.5		1517.5	0.6589	31528		42.0	4.4987
1244.9		1517.5	0.6588	31528		42.0	4.4987
1267.2		1540.2	0.6492	39690		52.9	4.5988
1270.1		1543.1	0.6480	39535		52.7	4.5971
1275.6		1548.6	0.6457	53505		71.4	4.7284
1278.1		1551.1	0.6441	49875		66.5	4.6980
1296.0		1569.0	0.6373	107262		142.9	5.0305
1296.9		1569.9	0.6369	106228		141.6	5.0263
1304.8		1577.8	0.6338	108296		144.3	5.0264
1306.4		1579.4	0.6332	157411		209.8	5.1971
1314.0		1587.0	0.6301	193800		258.4	5.2874
1324.2		1597.2	0.6260	449160		598.8	5.6524
1325.0		1598.0	0.6257	426360		568.4	5.6298
1334.7		1607.7	0.6220	798760		1065	5.9024
1336.1		1609.1	0.6214	779000		1039	5.8915
1338.9		1611.9	0.6203	779000		1039	5.8915

[a] Determined in glass apparatus with mercury manometer.

[b] Results which show superheating by heating-curve method with single thermel.

[c] Differential thermel used.

but no fusion, has taken place. The average values which come from these results are: eutectic pressure, 30,000 mm. ± 300 mm.; eutectic temperature, 1240° ± 1°.

It has been found possible to extend the Johnston series of data which stops at 894° and 716 mm. of mercury up to 937° and 1350 mm., in the low-pressure quartz-tube apparatus which had been used previously in the work on copper oxide[7a] in this Laboratory. The lowest determination made in the pressure bomb is at a temperature 100° higher than this. But since the latter determinations are consistent with the extrapolation of the curve determined by the lower points, it was not thought necessary to construct a special gage to use with the high pressure apparatus which would read with accuracy pressures between 1400 and 5000 mm. of mercury. Even with such a gage, the heating curve method would not be satisfactory much below 1050°. Pressures and temperatures between 940° and 1050° can best be read from the curve which the other points determine.

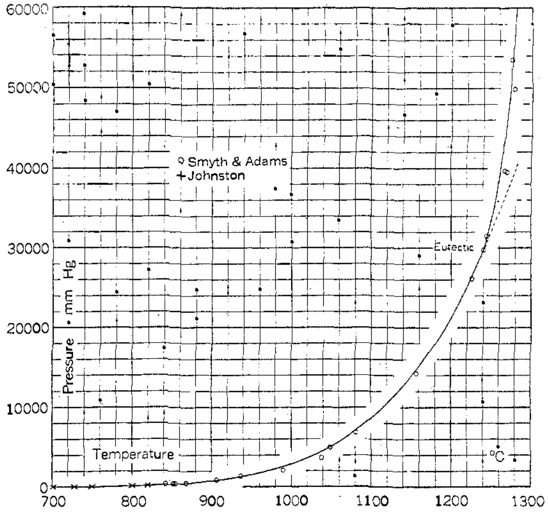

Fig. 5.—Direct pressure temperature curve taken from the logarithmic plot of Fig. 3 together with experimental points of Johnston and of Smyth and Adams, up to 53,500 mm. and 1276°.

The final experimental results together with logarithms of pressures and reciprocals of absolute temperatures are given in Table II, and are plotted in Figs. 3 and 5.

The direct pressure-temperature plot of Fig. 5 does not extend above 60,000 mm. and 1280°, but the logarithmic plot is extended to the maximum pressure and temperature recorded. This final temperature of 1339° at a pressure of 779,000 mm. (1040 megabars) must be very close to the true melting point of calcium carbonate, since the loss in weight of the charge after fusion corresponded to the formation of only 0.38% of calcium oxide. Examination of the fused material under the microscope[9] indicates the presence of not more than this quantity of lime.

To get rid of the last traces of calcium oxide in the melt would doubtless require a very much greater pressure, but we do not believe that the fusion temperature would be greatly raised. 1340° is thought to be a close approximation to the melting point of pure calcium carbonate.

The microscope also shows that the eutectic mixture fusing at 1240° contains about 50% of calcium oxide. This mixture has not been analyzed directly since, after fusion, sufficiently large quantities have not yet been recovered. The fused mixture has, however, a typical "honeycomb" eutectic structure, without predominantly large crystals of either calcium carbonate or calcium oxide, which is also an evidence that the charges examined, and from which the eutectic temperature has been obtained, have been fused at the proper eutectic pressure (30,000 mm.) and that the liquid and solid phases in equilibrium were of the same composition. In charges fused at higher pressures, large crystals of calcium carbonate, which is the primary phase, are readily seen under the microscope.

In order to determine the form and the constants of the logarithmic equation which best represents the curve passing through the experimental points recorded for Reaction 1, we may start, as suggested in the discussion above, with the Clapeyron equation

$$\mathrm{d}p/\mathrm{d}T = \frac{\Delta H}{T\Delta V} \tag{1}$$

Assuming the ideal gas laws and that $\Delta V =$ the volume of the gas alone, we have $\Delta H = \Delta H_0 + \Delta C_p T$, if ΔC_p, the difference in the heat capacity of $CaCO_3$ and $CaO + CO_2$ is assumed to remain constant throughout the temperature range studied, up to the eutectic point.

With these assumptions we obtain on integrating,

$$ln\ p = -\frac{\Delta H_0}{RT} + \frac{\Delta C_p}{R} ln\ T + \text{const.} \tag{2}$$

which may be written in the general form, after converting to ordinary logarithms,

$$\log p = A\ \frac{1}{T} + B \log T + C \tag{3}$$

The constants A, B, and C can be determined directly from the data available by dividing the determined points, including those of Johnston, into three groups, averaging the variables ($\log p$ and $1/T$) in each group to give three average points at different parts of the curve, and solving for the constants by direct substitution in the equation. This method utilizes the experimental results only and involves no assumption concerning the actual value of ΔH or of ΔC_p.

---

[9] Microscopic work performed by H. E. Merwin, to whom we are indebted for much valuable assistance.

The eutectic point itself (1240° and 30,000 mm.), which we think is determined with considerable accuracy, is chosen as a definite point on the curve. The other two groups used are our own data between 842° and 937° and the data of Johnston between 587° and 711°.

The equation of the curve thus found is

$$\log p = -11355/T - 5.388 \log T + 29.119 \qquad (4)$$

This curve is the one plotted up to the eutectic point in Fig. 3 and it fits the data within the limits of experimental error throughout the range covered by both Johnston's and our own results.

It is interesting to note that the curve given by Johnston as determined from his results alone with the aid of separately determined values for ΔH and ΔC_p, would give a eutectic pressure of 24,770 mm., and that the best representative straight line through all the points as determined by the method of least squares gives a eutectic pressure of 32,360 mm. The experimentally determined pressure being 30,000 mm., a straight line appears to fit the data for the whole range better than does the extrapolation of the curve given by Johnston.

Table III contains the equilibrium pressures at even temperatures from 500° to 1360° as read from the logarithmic plot. Below the eutectic, the pressures have been calculated from the equation of the curve.

TABLE III

PRESSURES AT EVEN TEMPERATURES CALCULATED FROM THE CURVE

$\log p = -11355/T - 5.388 \log T + 29.119$

Temp. ° C.	Temp. °Abs.	Pressure Mm.	Pressure Megabars	Temp. ° C.	Temp. °Abs.	Pressure Mm.	Pressure Megabars
500	773	0.073	.....	1150	1423	13750	18.3
550	823	0.41	.....	1200	1473	21797	29.0
600	873	1.84	.....	1240[a]	1513	30149	40.2
650	923	6.90	.....	Pressures above eutectic point read from logarithmic plot			
700	973	22.2	.....	1250	1523	33490	44.6
750	1023	63.2	.....	1260	1533	39090	52.1
800	1073	167	.....	1270	1543	47210	62.9
850	1123	372	.....	1280	1553	59170	78.8
897	1170	760	(1 atm.)1.013	1290	1563	77630	103.4
900	1173	793	1.1				
950	1223	1577	2.1	1300	1573	108400	144.4
1000	1273	2942	3.9	1310	1583	162200	216.1
				1320	1593	288400	384.2
1050	1323	5196	6.9	1330	1603	588900	784.4
1100	1373	8739	11.6	1340	1613	851200	1133.8

[a] Eutectic.

Equation 4 may perhaps best be regarded as an empirical equation chosen to represent the data; but we may note that in general $\Delta H = RT^2 \dfrac{d\, ln\, p}{dT}$, provided only that the gas follows the ideal gas laws and that the volumes of the solids are negligible in comparison with that of the gas. Hence, from Equations 3 and 4 it follows that $\Delta H = —2.3026\ RA - RBT = 51990 - 10.71T$. At several temperatures the values of ΔH as calculated from this relation are as follows: 48,800, 45,850, 42,640, 40,500, 38,360, and 36,210 calories at 25°, 300°, 600°, 800°, 1000° and 1200°, respectively. At 898.6°, the temperature at which $p = 760$ mm., $\Delta H = 39{,}440$ cal. and at the eutectic temperature, 1240°, $\Delta H = 35790$ calories.

The values of ΔH at 25°, 300°, 800° and 1000° calculated from the curve given by Johnston are 42,870, 42,150, 38,740 and 34,010 calories, respectively. The Johnston value at 25° is in agreement with the experimental value of Thomson (42,900 cal.) since the Johnston pressure-temperature curve is based on this value. The curve which we have developed, while it gives to ΔH at 25° a much higher value, is nevertheless in better agreement with the actual low temperature results of Johnston than is his own curve.

Furthermore, from the general relation, $\Delta C_p = \frac{d\Delta H}{dT}$, it follows that $\Delta C_p = —RB = —10.71$, which is constant on account of the form of the equation chosen to represent p as a function of T. This value, however, is not to be thought of as more than a rough determination of the mean value of ΔC_p over the range of temperatures at which measurements have been made. This is because we have differentiated Equation 4 twice in order to obtain ΔC_p, and, as is well known, small errors in the original data become magnified enormously when we pass to the second differentials. Nevertheless, we may note that at 900°—about the middle of the total experimental range of temperature—ΔC_p calculated from the equation which Johnston[10] took to represent the change of ΔC_p with T is —11.8. There is thus an agreement between the mean values of ΔC_p as determined directly from the dissociation pressures and as calculated from Johnston's equation for ΔC_p.

The values calculated for ΔH, on the other hand, depend on the first derivative of p with respect to T and probably represent the true values of ΔH with fair accuracy, but only for temperatures within the experimental range. Extrapolation to temperatures outside this range may, and probably does, lead to serious error. In the absence of directly determined values of the specific heats for each of the substances involved and over the whole desired range of temperature, it is unsafe to extrapolate heats of reaction, dissociation pressures, equilibrium constants or free energies.

The above calculation of ΔH involves the assumption that the carbon dioxide follows the perfect gas law and that the volume of the calcium carbonate and of the calcium oxide may be neglected.

It is interesting to compare these values of ΔH with some of the values of

---

[10] Ref. 1, p. 943.

ΔH for Reaction 1 which may be calculated directly from the Clapeyron equation $dp/dT = \frac{\Delta H}{T\Delta V}$ by determining the value of dp/dT from the experimental curve (Equation 4), and the value of ΔV from the Keyes equation of state[11] for carbon dioxide. This equation has been shown to apply to carbon dioxide with considerable accuracy within the ranges of available experimental data.

By differentiation of Equation 4 after conversion to natural logarithms we obtain,

$$\frac{dp}{dT} = p\left[\frac{2.3026 \times 11355}{T^2} - \frac{5.388}{T}\right] \tag{4a}$$

which expresses the change in equilibrium pressure for Reaction 1, in millimeters of mercury per degree at any given absolute temperature. Values for dp/dT may be found by direct substitution in this equation of corresponding values of p and T taken from the experimental logarithmic curve (Equation 4).

At 1513° abs. and 30,000 mm. (the eutectic point) $dp/dT = 237.02$ mm. = 0.3157 megabars per degree.

The volumes at the eutectic point are

$$\begin{array}{ccccc} CaCO_3 & \longrightarrow & CaO & + & CO_2 \\ 36.89 \text{ cc.} & & 18.15 \text{ cc.} & & 3208.33 \text{ cc.} \end{array}$$

and $\Delta V = +3190$ cc.

Substituting in the Clapeyron equation, $0.3157 = \frac{\Delta H}{1513 \times 1390}$ whence $\Delta H = 1{,}523{,}605$cc. megabars = 36,440 cal.

Similarly, $\Delta H(897°) = 39{,}420$ cal.

The use of the Dieterici equation of state would indicate a volume of the carbon dioxide nearer to the ideal volume than would the Keyes equation. Indeed, the former equation yields a volume which departs from the ideal by an amount which nearly compensates for the difference in volume between calcium carbonate and calcium oxide.

From Equation 4 also we obtain the equation for the free energy change ($-\Delta F$) for the reaction $CaCO_3 \longrightarrow CaO + CO_2$ (1 atm.), in terms of the absolute temperature at which the change takes place.

This equation is: $-\Delta F = 120.136\ T - 24.670\ T \log T - 51991$; or, if the final gas pressure be 1 megabar: $-\Delta F = 120.149\ T - 24.670\ T \log T - 51991$.

From these equations: at 1240°, $-\Delta F = 11{,}085$ cal.

The Non-existence of Two Forms of Calcite

In none of the many experiments carried out in the course of this investigation were we able to detect the slightest evidence in the thermal behavior of the calcium carbonate that a transition from one form to another

---

[11] Compare Keyes and Kenney, *J. Am. Soc. Refrig. Eng.*, **3**, No. 4, 1–25 (1917).

takes place at or about 970° as found by Boeke,[5] and recently by Eitel,[12] using Boeke's apparatus.

There is threefold evidence that no transition takes place.

First, large crystals of natural calcite may be heated and cooled repeatedly through the supposed transition point under sufficient pressure to prevent dissociation, without subsequently betraying under the microscope signs that they have been changed in any manner. If a molecular rearrangement takes place at 970°, evidences of twinning should be present in calcite which has been heated above that point, which do not exist in the natural calcite before heating. The analogy for this result would be the behavior of quartz which has been heated above 575°, the changes in which may be used as a "geologic thermometer," as pointed out by Wright and Larsen.[13] These latter changes are certainly, from a crystallographic standpoint, very slight, yet the evidences of change which remain in a quartz crystal which has been heated are unmistakable. No such analogous evidence is discernible in the case of calcite. Large crystals of natural calcite are not shattered after being repeatedly passed through the supposed transition temperature, nor do the crystal surfaces when etched with dilute acid after such heating show any change as is the case with quartz.

Second, on thermodynamic grounds, there is no evidence of transformation. The pressure-temperature equilibrium curve shows no break until the eutectic point is reached. On the logarithmic curve which is almost a straight line, a sudden change in slope could be readily detected if the heat absorption at the supposed transition is even a part of that suggested by the heating curves of Boeke and Eitel.

Third, we have direct experimental evidence that no transition exists. In one side of the divided crucible (Fig. 2, B) was packed pure powdered quartz, and in the other powdered calcite. The temperature of the crucible was read simultaneously with the difference in temperature between the calcite and quartz. All other conditions were identical with those of other high pressure experiments. With this arrangement the transition from α to β quartz at 575° is readily discerned even with rapid heating at a pressure of 60 megabars. This absorbs only about 3.5 calories per gram of quartz; yet with 0.5 g. of quartz in the crucible, a rapid increase of the difference in temperature between the two junctions of the double thermel could be noted of 17 to 20 microvolts, during the transition process. A heat absorption of $^1/_{10}$ of this quantity would be readily recognized by this means. Nevertheless, the crucible could be heated through the range 900° to 1100° without any corresponding sign whatever of heat absorption by the calcite.

[12] Compare Ref. 8.

[13] Wright and Larsen, *Am. J. Sci.*, **27**, 421 (1909).

To us the evidence seems conclusive that two forms of calcite do not exist, but that the heat effect at 970° in the apparatus used by Boeke and by Eitel must be due to some other material present near the thermel junction or to some condition peculiar to the furnace used.

Summary

1. An apparatus has been built with which the pressure-temperature relations in the system, calcium oxide, carbon dioxide can be studied up to 1390° and 1000 megabars pressure.
2. Equilibrium pressures have been determined which, with the previously determined data of Johnston, define the system experimentally from 587° to 1389°, and from 1.0 mm. to 779,000 mm. pressure.
3. An equation for the pressure-temperature curve which fits all data within limits of experimental error up to the eutectic point for the system, calcium carbonate–carbon dioxide is given.
4. The melting point of calcium carbonate containing only 0.38% of calcium oxide is given as 1389° at 779,000 mm. pressure. This is probably very near to the melting point of pure calcium carbonate.
5. The eutectic, experimentally determined, between calcium carbonate and calcium oxide lies at 1240° ± 1°, and 30,000 mm. ± 300 mm. The composition as judged from microscopic examination is about 50% of calcium carbonate: 50% of calcium oxide.
6. ΔH and $-\Delta F$ for the reaction, $CaCO_3 \rightleftarrows CaO + CO_2$, have been calculated at various temperatures, and equations giving these two quantities in terms of the temperature are discussed.
7. It has been shown by thermodynamic and experimental evidence that only one crystalline form of calcium carbonate exists within the temperature range investigated.

Washington, D. C.

[Contribution from the Coastal Laboratory of the Carnegie Institution of Washington]

THE REDUCTION OF CARBON DIOXIDE BY ULTRAVIOLET LIGHT

By H. A. Spoehr

Received February 12, 1923

In the many applications of chemistry to biology there is probably no other purely hypothetical suggestion which has served as such a lure for further speculation as the Baeyer[1] formaldehyde theory of photosynthesis. Attention is here confined to a discussion of some experiments on the reduction of carbonic acid to formaldehyde in glass by means of ultraviolet light. Although the conclusions drawn from these experiments can only

---

[1] Baeyer, *Ber.*, 3, 63–78 (1870).