

CCCLIV.—*The Thermal Dissociation of Strontium Carbonate.*

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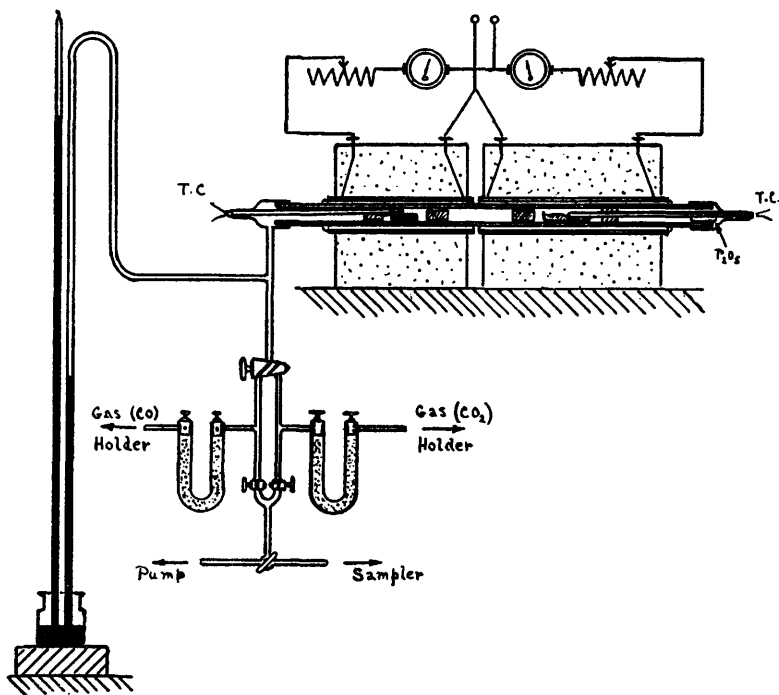
DURING their work on the effect of temperature and pressure on the progress and equilibrium of certain reactions, the authors were faced with the problem of devising a suitable means by which the composition of a gas phase consisting of carbon monoxide and dioxide could be readily determined at any instant. It occurred to one of them (E. O. J.) that a suitable method of attack would be to fix the partial pressure of the carbon dioxide by maintaining the gas phase in contact with a carbonate heated to a known temperature. The pressure of this gas would be the dissociation tension of the carbonate for that particular temperature, and by subtraction from the total pressure of the system the partial pressure of the monoxide could be found.

The alkaline-earth carbonates naturally suggested themselves as being suitable materials for the purpose, and a study of the literature led to the selection of strontium carbonate. The only work on the dissociation tension of this carbonate at different temperatures to which reference could be found was that of Pott (Diss., Freiburg, 1905; see also Mellor, "Treatise on Inorganic and Theoretical Chemistry," III, 655). Two other workers, Brill (*Z. anorg. Chem.*, 1905, 45, 275) and Hedvall (*ibid.*, 1916, 98, 47), record determinations of the temperature at which the tension attains 1 atm. Unfortunately, their work is not in good agreement with that of Pott, and it was further noted that Pott's curve is of quite a different shape from those given for calcium and barium carbonates, and actually cuts the first of these two curves. It

was thought advisable, therefore, to make a series of determinations of the dissociation tension of strontium carbonate at different temperatures in the same apparatus and under the same experimental conditions as those in which it was proposed to use this material for carbon dioxide-pressure control.

During the course of the investigations, two distinct types of apparatus were employed. These are diagrammatically represented in Figs. 1 and 2. The first was designed for use where it was neces-

FIG. 1.



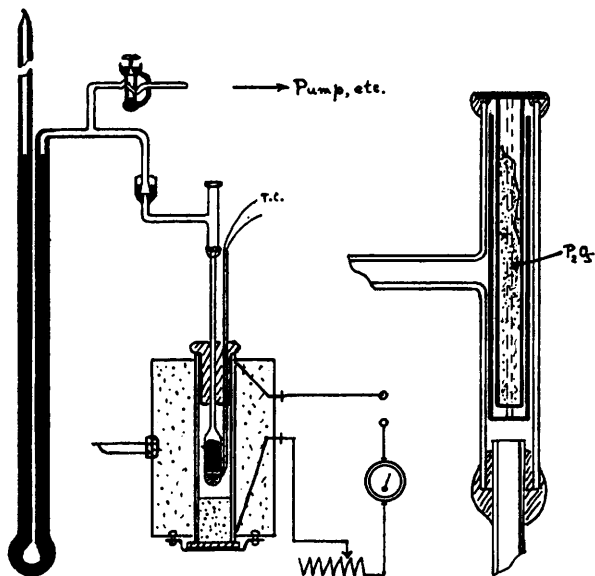
Apparatus No. 1. (Diagrammatic.)

sary to keep the carbonate separate from the other reactants with the gas phase, and where independent temperature control, both of the reactants and of the dissociating carbonate, was desirable. The second, which is simpler, was utilised when the above-mentioned limitations did not apply.

Apparatus 1 consists essentially of a long porcelain tube (800 mm. \times 18 mm. internal diameter) heated by two independently controlled electric resistance furnaces. The ends of the tube were closed by glass caps hermetically sealed to the heating tube by white wax. Each of these caps had a small-bore extension to

take the thermocouple sheath, and one of them was also provided with a side tube which gave connexion to the manometer, evacuating pump, gas holders, etc. The Vitreosil thermocouple sheaths were sealed into the extension tubes of the caps by means of white wax, and it was also found advisable to close the open ends of these sheaths with wax, since, after being maintained at high temperatures for a considerable time, they developed slight porosity at the heated end, due to devitrification. Heat-insulating plugs, made of kieselguhr bonded with a small proportion of sodium silicate, were placed in the furnace tube to lessen heat radiation

FIG. 2.



Apparatus No. 2. (Diagrammatic.)

and to provide zones of uniform temperature. A boat containing phosphorus pentoxide, placed at one end of the tube, served to absorb all the water vapour.

Apparatus 2 is essentially a small, transparent silica bulb of about 10 c.c. capacity fused to a silica tube (30 mm. \times 5 mm.), the other end of which is sealed by white wax into a glass T-piece. This serves to accommodate a small container for phosphorus pentoxide and to give connexion to the manometer, etc. A small resistance furnace, which may be raised or lowered, serves to heat the bulb to the required temperature, which is measured by a thermocouple in contact with the bulb wall.

This second form of apparatus is more suitable for measuring

dissociation tension, since equilibrium conditions are attained much more rapidly as a result of its small volume and its relatively larger carbonate content. Nevertheless, since it was necessary to use the first form of apparatus for some of the investigations, it was considered desirable to study the thermal dissociation of the carbonate in both forms of apparatus as a matter of precaution and for the sake of calibration. The results obtained were found to agree within the limits of experimental error, and this concordance is considered good presumptive evidence of the correctness of the values obtained.

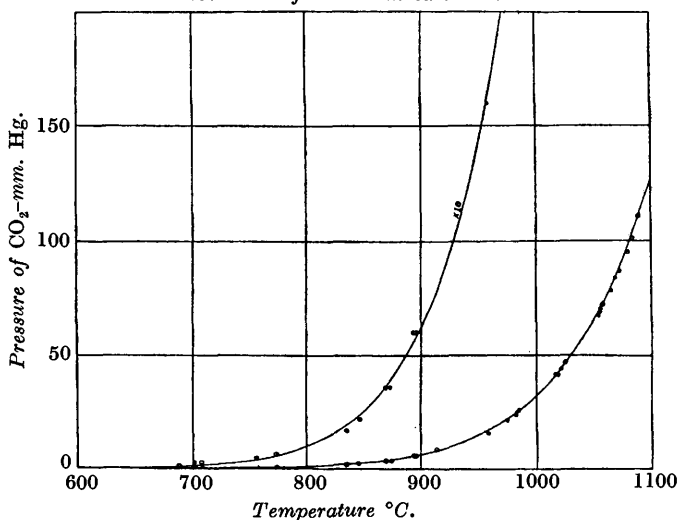
The experimental details were essentially the same for each type of apparatus. A sufficient quantity of pure strontium carbonate (about 1 g. in the case of the bulb, and 4—5 g. in a porcelain boat in the case of the tube) having been introduced, the apparatus was hermetically sealed and then evacuated by means of a "Cenco Hyvac" pump. The temperature was now raised gradually to about 600°, during which time the evolved gases (largely water vapour) were removed at frequent intervals by pumping. When no more gas appeared to be given off, the temperature was raised to 1000° and maintained at this value for about 12 hours. During this time the pressure increased gradually, due probably to further expulsion of occluded gas and to a slow reaction between the carbonate and the silica walls of the bulb where contact occurs, whereby carbon dioxide was liberated. The apparatus was then evacuated rapidly, the tap to the pump closed, and the pressure allowed to attain a steady value. This was lower than the initial one obtained and the process was repeated as often as was necessary to obtain two consecutive equal values for the gas pressure. This procedure ensured (a) removal of all occluded gas, and (b) the presence of more strontium oxide than that equivalent to the carbon dioxide liberated by the slow reaction already mentioned. That this is so is shown by the fact that, on allowing the furnace to cool to 600°, the resulting vacuum was of a higher order than could be obtained by the pump alone, *i.e.*, less than 0.05 mm.

The apparatus was now ready for use. The strontium carbonate was slowly heated, and pressure and temperature readings were taken. In the case of the bulb apparatus, the rate of heating was sufficiently slow to ensure that the pressure corresponding to a given temperature was the equilibrium pressure until about 900° had been reached. Beyond this temperature, the furnace was allowed to reach a steady state before readings were taken. In the case of the tube furnace, the method of allowing the furnace to reach a steady temperature was practised from the beginning, as the gas evolution involved was so much larger.

The temperature was measured by means of carefully calibrated thermocouples and is considered accurate to within $\pm 3^\circ$; pressures less than 10 mm. were read by means of a cathetometer to within ± 0.05 mm.; higher pressures were read directly on a metre scale fixed alongside the manometer. This gave readings to within ± 0.5 mm., which is as close as is justified by the accuracy of the temperature measurements.

Values of the dissociation tension for given temperatures were obtained on both ascending and descending temperature scales and

FIG. 3.
Dissociation of strontium carbonate.



further checked by haphazard alteration of the temperature; the concordance was good. In view of this agreement, there is no need to quote more than one set of results. Those obtained by one of the authors (M. L. B.) are recorded in Table I (in mm. Hg) and shown graphically in Fig. 3.

TABLE I.

Temp.	<i>p</i> , obs.	<i>p</i> , calc.	Temp.	<i>p</i> , obs.	<i>p</i> , calc.
689°	0.1	0.07	975°	21	21.5
708	0.3	0.12	984	25	24.5
756	0.5	0.35	1020	42	42
775	0.6	0.55	1027	47.5	47
835	1.7	1.85	1059	72.5	72
846	2.2	2.3	1070	84	84
869	3.6	3.5	1081	95	97
896	6.0	5.8	1090	111	110
913	8.8	7.8	1103	123	130
958	16.0	16.3			

The dissociation tensions of calcium and barium carbonates determined by various workers have been found to fit closely to curves of the form

$$\log p_1 - \log p_2 = -K(1/T_1 - 1/T_2)$$

where p_1 and p_2 are the pressures (mm. Hg), T_1 and T_2 the absolute temperatures, and K is a constant. It was of interest, therefore, to see whether the dissociation of strontium carbonate could be similarly expressed. If the value of the dissociation tension at 928° be taken as 10 mm. and K as 1.05×10^4 , then the values of the carbon dioxide pressure for other temperatures can be calculated. The resulting graph, as will be seen, agrees very satisfactorily with the observed values over the entire range investigated. Table II gives calculated values of the dissociation pressure for temperature increments of 50° .

TABLE II.

Temp.	p , mm.	Temp.	p , mm.	Temp.	p , mm.
650°	0.023	900°	6.19	1150°	231
700	0.090	950	14.36	1200	411
750	0.30	1000	31.22	1258	760
800	0.91	1050	63.98	1300	1167
850	2.47	1100	124.5		

It has already been pointed out that good concordance existed between the results obtained in the different apparatus, and further confirmation, particularly of the lower values as corrected to the calculated curve, is given by later work on the C-CO-CO₂ equilibrium where the carbon dioxide pressure is controlled by means of strontium carbonate. The values of the equilibrium constant thus determined for this system at different temperatures lie closely on Tigerschiöld's curve (*Jernkontoret's Annaler*, 1923, 67; see also Johansson and von Seth, *J. Iron and Steel Inst.*, 1926, **114**, 313) which correlates satisfactorily the work of Boudouard (*Ann. Chim. Phys.*, 1901, **24**, 5), Schenck (*Ber.*, 1905, **38**, 2139), and Rhead and Wheeler (*J.*, 1910, **97**, 2178) on this equilibrium. This agreement justifies the acceptance of the results, and, in particular, the validity of the formula for calculating the dissociation tension in the lower temperature range.

The authors' value for the temperature at which the dissociation pressure is equal to 1 atm. is approximately 100° higher than those reported by Brill (*loc. cit.*) and Hedvall (*loc. cit.*). Although the authors' result has been obtained by extrapolation of the curve, whereas the others have experimental basis, it is regarded as more accurate for the following reasons. (a) Brill noted the temperature at which loss of weight just occurred from calcium carbonate in a

carbon dioxide atmosphere of approximately 760 mm. pressure, and obtained a value 75—100° lower than those recorded by other workers who measured the actual dissociation tension. This discrepancy for calcium carbonate is of the same order as the difference between Brill's result for strontium carbonate and the one put forward in this paper.

(b) Hedvall, who used the thermal arrest in the heating curve for fixing the dissociation temperature, gives 1141° as the temperature at which carbon dioxide evolution commences. It is of interest, however, that he quotes 1255° (only 3° different from the value put forward by the authors) as the temperature at which carbon dioxide evolution becomes rapid, and further states that a small quantity of strontium carbonate was not completely decomposed on being heated for 5 minutes at temperatures between 1141° and 1255°.

The authors' curve lies wholly between the accepted curves for calcium carbonate (Johnston, *Z. physikal. Chem.*, 1908, **62**, 330; *J. Amer. Chem. Soc.*, 1910, **32**, 938) and barium carbonate (Finkelstein, *Ber.*, 1906, **39**, 1585), thus differing from that of Pott. It is suggested that the higher values obtained by Pott in the lower temperature range are due to the absence of sufficient oxide phase to absorb the excess carbon dioxide liberated by some such slow carbonate-silica reaction as was noticed by the authors in their work. At higher temperatures, where the extent of dissociation involves the production of larger quantities of strontium oxide, this source of error tends to disappear, and it is of interest to note that Pott's results for 1256° and 1263° (744 mm. and 785 mm., respectively) would lie satisfactorily on the extrapolated portion of the authors' curve.

In view of the fact that Finkelstein (*loc. cit.*) obtained evidence of the formation of a basic barium carbonate ($\text{BaO}, \text{BaCO}_3$), the authors sought for indications of a similar basic strontium carbonate. When the dissociation tensions at 1000° and 1100° were being measured, a known volume (approximately one-sixth of the available carbon dioxide) was drawn off and the system allowed to return to equilibrium. The resulting pressure was the same as in the initial determination. This process was repeated until six withdrawals had been made. In every case, except the last, the pressure returned to the recorded equilibrium value, whilst on the last occasion the pressure only rose a few mm., showing that the solid phase was now wholly the oxide. This series of experiments shows that over the range 15—85 mols. % of strontium oxide the solid phase does not change in character, and therefore affords no evidence for the existence of a basic carbonate under these conditions.

The work here described was carried out in the Metallurgical Department, Manchester University, and the authors desire to express their thanks to Prof. F. C. Thompson, D.Met., for the facilities provided and also for his interest and helpful criticisms and suggestions during the course of the work. Acknowledgment is also due to the Department of Scientific and Industrial Research and to the British Cast Iron Research Association for their financial grants and for their permission to publish the results.

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[Received, September 7th, 1927.]
