THE THERMAL DISSOCIATION OF CADMIUM CARBONATE.

By P. Y. Narayana and H. E. Watson.

Owing to its comparatively low dissociation temperature, cadmium carbonate is a convenient substance to use for studying the relation between dissociation pressure and temperature, and several papers have been published on the subject.

Centnerszwer and Andrussov (*Z. physikal. Chem.*, 1924, **111**, 79) measured the dissociation pressures by both static and dynamic methods and found that the results could be expressed by the formula

$$\log p = -12\cdot44 + 0\cdot02439\ T.$$

Measurable dissociation occurred at 265° and atmospheric pressure was reached at 357°. Mazzetti (*Atti R. Accad. Lincei*, 1924, [5], **33**, II, 46) found the latter temperature to be 332 and 355° using two different methods. Andrussov (*Z. physikal. Chem.*, 1925, **115**, 273) as the result of a large number of measurements in which equilibrium was approached from both directions found that the formula

$$\log p = -Q_0/4\cdot571\ T + 1\cdot75 \log T - eT/4\cdot571 + 3\cdot2$$

where $Q_0 = 21{,}500$ cals., and $e = 0\cdot003435$, gave an accurate representation of the results. Measurements of the velocity of decomposition and recombination were also made and it was shown that the carbonate became more active, *i.e.*, reached the equilibrium position more rapidly when it had been decomposed and regenerated several times. According to this formula the dissociation temperature is 344°. Jander (*Z. anorg. Chem.*, 1928, **168**, 113) confirmed these results by observing the temperatures at which the substance heated in a closed vessel containing carbon dioxide at different pressures remained constant in weight. The range studied was 340—510° and the value found for the dissociation temperature was 345°.

The results detailed above are more discordant than might be expected and it was, therefore, decided to make additional experiments with the object of ascertaining, if possible, the reason for the discrepancy. A series of measurements by the static method in the region 260—360° yielded results which agreed well with a simple logarithmic equation although differing somewhat from those of former observers, the dissociation temperature being 352°. The investigation was then extended to lower temperatures at which the vapour pressure was of the order of 1 mm. and it was observed that reproducible results could not be obtained in successive experiments with the same material, a marked diminution in pressure being noted. The original experiments were then repeated with improved temperature control and the same phenomenon was observed. It thus became clear that the system was not simple, but that the dissociation pressure was a function of the amount of oxide in the solid phase.

EXPERIMENTAL.

The cadmium carbonate used was prepared by mixing hot aqueous solutions of equimolecular proportions of pure cadmium sulphate and potassium carbonate, filtering and washing the precipitate with hot water, until no trace of sulphate could be detected in the filtrate. The precipitate was then dried at 100° but as it still retained 0·8 per cent. of moisture it was heated at about 300° for four hours in a stream of pure dry carbon dioxide. Estimation of carbon dioxide in the dried preparation gave 25·70 per cent. as a mean of three concordant determinations, theory requiring 25·53 per cent.

The apparatus used is shown in Fig. I. For temperatures up to 200° the substance was sealed into the small soft glass bulb A immersed in an electrically heated oil thermostat the temperature of which remained constant to ± 0 2° over long periods of time. Pressures were measured on a rotating manometer of the type described by Reden (*Physikal Z.*, 1909, **10**, 316) which would read up to 2 mm. with an accuracy of 0·01 mm. For higher temperatures, the double walled pyrex tube B similar to the one described by Brüning (*Chem. Fabrik.*, 1932, 17) was used. The annular space was filled with mercury which formed a thermoregulator and controlled the heating current of the

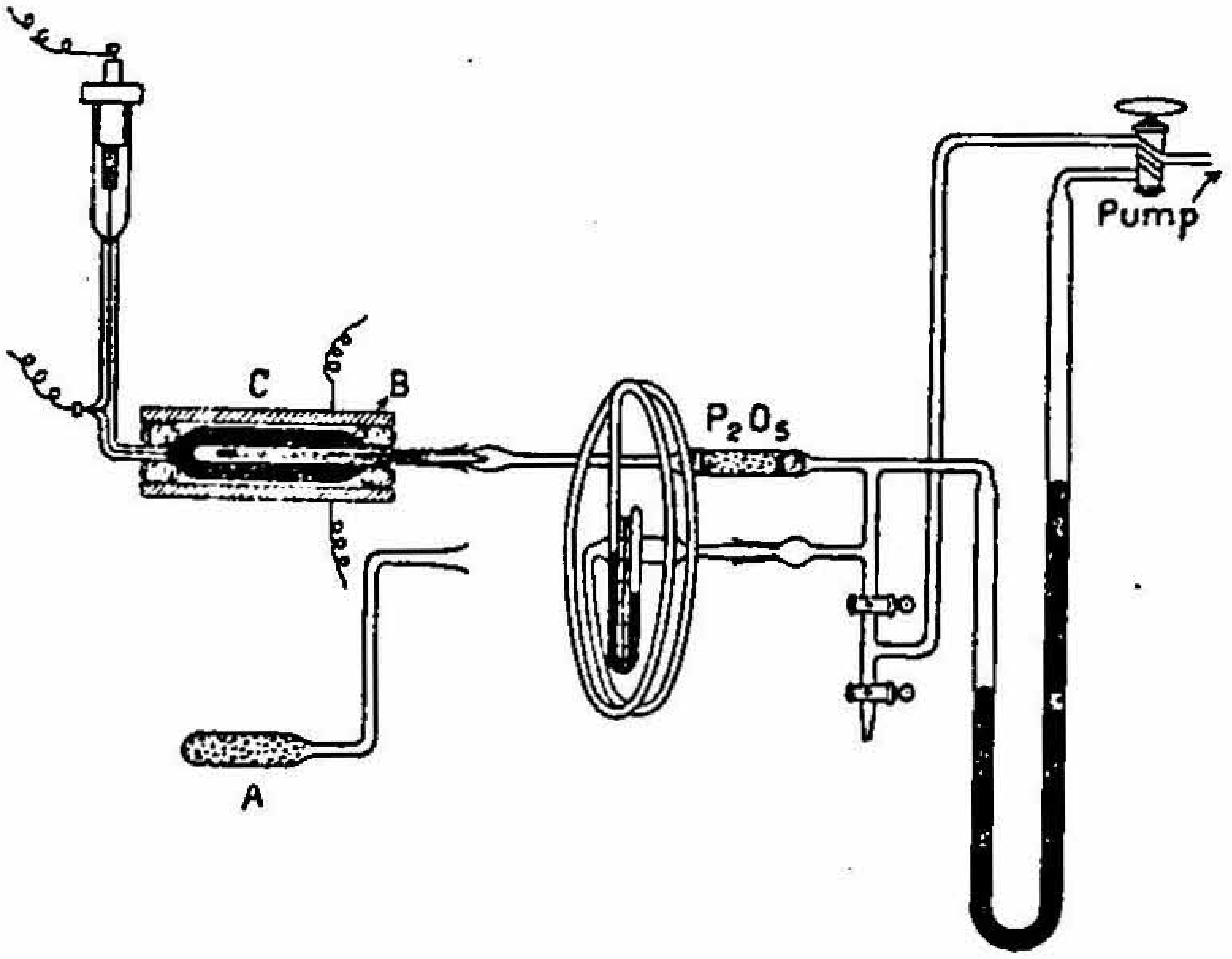

Fig. I.

oven C by means of a relay. The main disadvantage of this arrangement was the distinct lag which occurred between the switching on or off of the current and the corresponding heating or cooling of the tube. This was minimised as far as possible by allowing a steady current to pass, just insufficient to maintain the tube at the required temperature and arranging for the relay to short circuit a resistance when the temperature became too low. The range of temperature was about ± 0·5° at 300° and ± 0·7° at 335°, the temperatures being determined by means of a calibrated mercury thermometer enclosed inside the apparatus.

Before making measurements at higher pressures, the volume of the apparatus and manometer was determined at different pressures by filling it with air which was then pumped off and measured. In this way an estimate could be formed of the amount of gas which had been evolved by the cadmium carbonate at any stage.

RESULTS.

The results obtained at the lower temperatures are shown in Table I.

TABLE I.

	Temperature	Time in days		Equilibrium pressure mm.
(1)	175 ± 0·2°	60	(i)	0·425
		60	(ii)	0·284
(2)	192·5 ± 0·2°	34	(i)	1·75
		44	(ii)	1·35
		38	(iii)	0·71
		40	(iv)	0·135

Before commencing the measurements the bulb containing the carbonate was evacuated and heated. At a temperature below 100° the pressure rose to 20 mm. probably owing to adsorbed gas since a bicarbonate of cadmium has not been recorded. The gas was pumped off, any water vapour being removed by the phosphorus pentoxide, and the pressure fell to a very low value. The temperature was then raised to 175° when a further small evolution of gas took place owing to decomposition of the carbonate itself. Pumping was continued at intervals for two hours. From the quantity of carbon dioxide obtained it was estimated that not more than 1 per cent. of the carbonate was decomposed at this stage. The pump was shut off and the pressure allowed to rise. Attainment of equilibrium was very slow but after 60 days an approximately constant pressure was reached. The gas was then removed and the experiment repeated, when it was found that the rate of decomposition and the final pressure were much less than before. The temperature was next raised to 192·5° and results i–iv obtained in succession, the gas being pumped off when the pressure had become approximately constant. The progress of these experiments is shown in greater detail in Fig. II. The quantity of carbonate

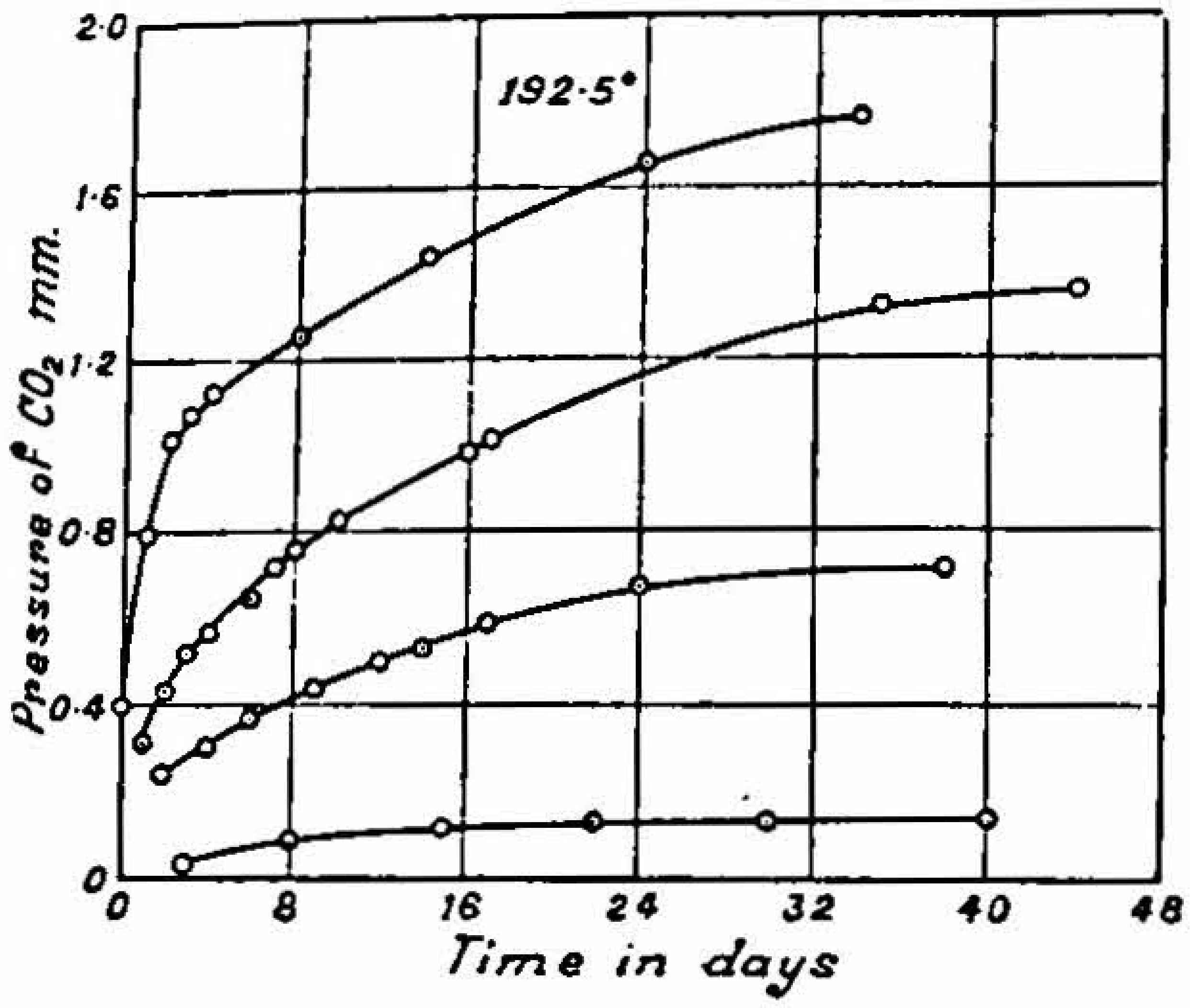

Fig. II.

decomposed at the end was not determined with certainty but was of the order of two per cent.

Before making measurements at the higher temperatures the carbonate was heated at 200° at a low pressure to remove adsorbed gas and moisture, and carbon dioxide admitted into the apparatus until the pressure reached 104 mm. so that the amount of carbonate decomposed on heating would be small. Equilibrium was attained after heating for 3–4 days, the rate of rise in pressure being shown in Figs. III and IV.

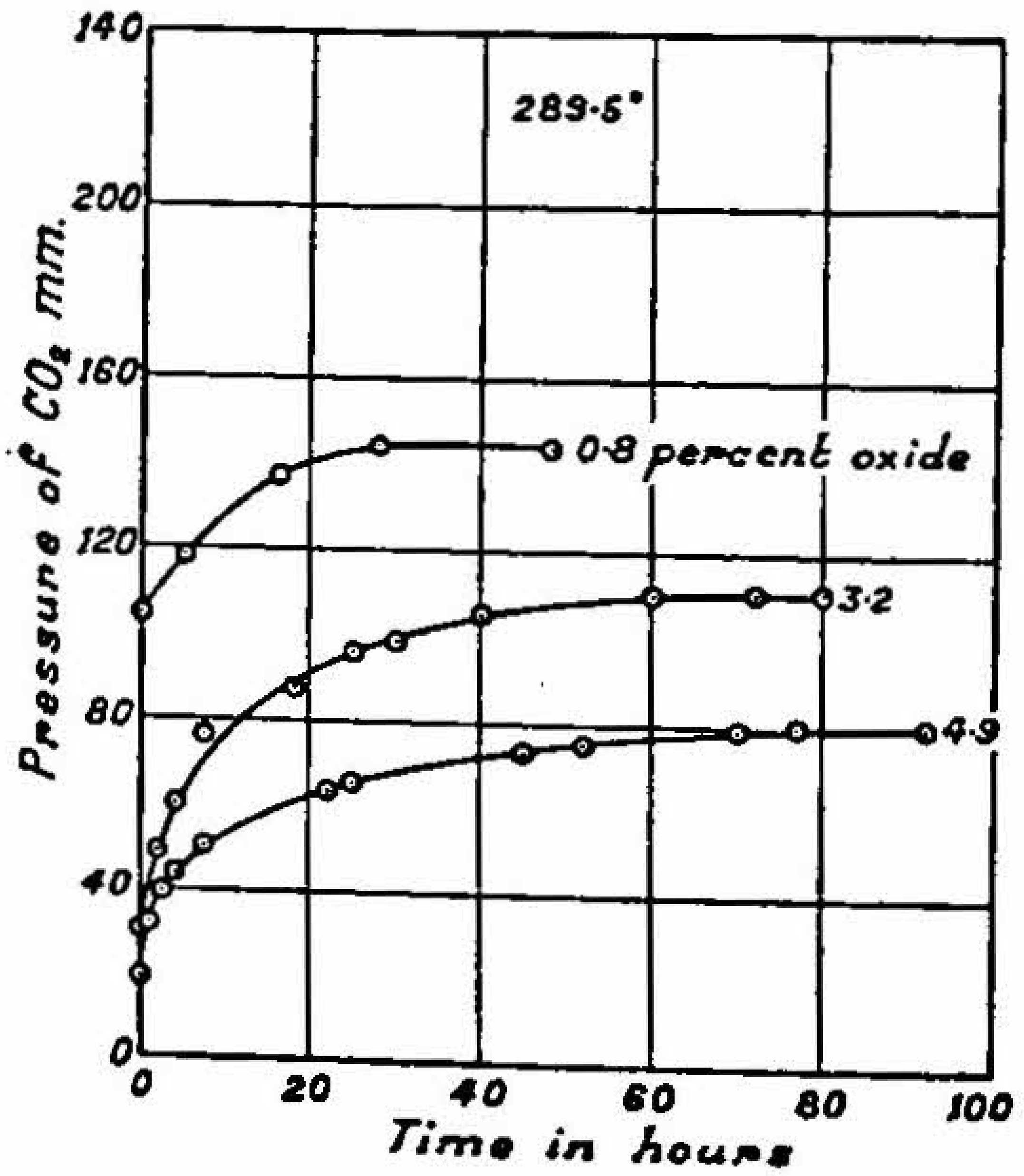

Fig. III.

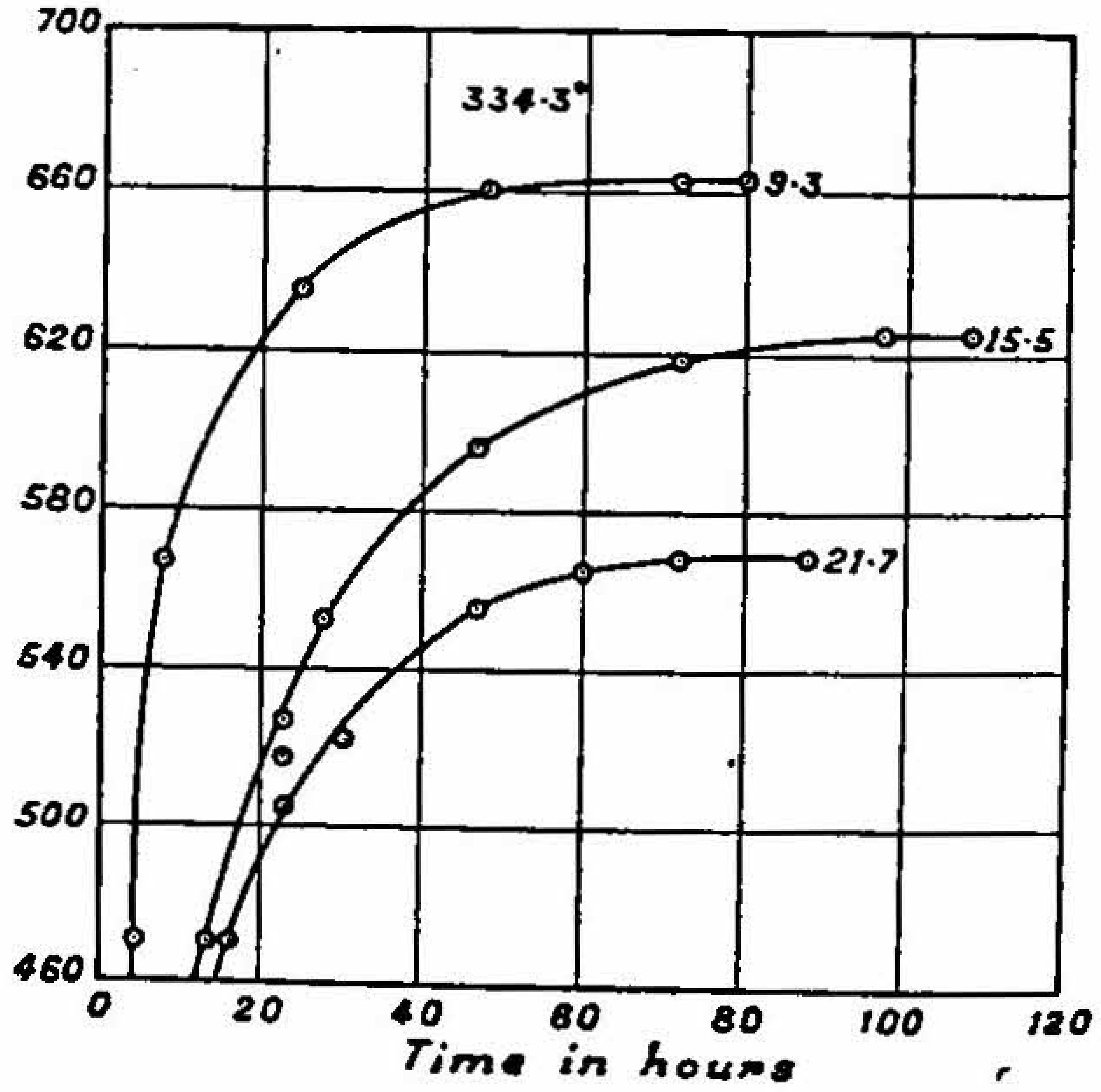

Fig. IV.

The final pressures p and the number of grams g of cadmium oxide in 100 g. of undissociated carbonate at equilibrium are shown in Table II.

TABLE II.

Equilibrium pressures of different mixtures.

T	g	p	$(p_0 - p)/g$
289·5	0·0	(159)	
,,	0·8	144	18·7
,,	3·2	111	15·0
,,	4·9	80	16·1
334·3	0·0	(730)	
,,	9·3	664	7·1
,,	15·5	625	6·8
,,	21·7	577	7·1

If the values of p are plotted against those of g, an approximation to a straight line is obtained in each case so that p_0 the dissociation pressure of the undecomposed carbonate can be obtained by extrapolation. The figures in the last column show the fall in dissociation pressure due to 1 per cent. of oxide and it is remarkable that the change is much greater not only relatively but absolutely, at the lower temperature. Fig. II shows that at still lower temperatures the relative change is very great, about one per cent. of oxide reducing the pressure to 1/14th of its initial value. The exact relation between the relative lowering of pressure produced by a given amount of oxide and the temperature is obscure and cannot be determined without further experimental results. These are somewhat difficult to obtain owing to the long period required for the attainment of equilibrium at the lower temperatures. It is evident, however, that Raoult's law is not obeyed. When the vapour pressure is very low, the results may be complicated by the slow evolution of adsorbed gas from the carbonate and walls of the tube and since the rate of formation of the carbonate is exceedingly small, the observed values may be too high. Too much reliance must not therefore be placed upon the figures of table I.

While the present experiments were in progress Afanasiew and Roginsky in a preliminary communication (*Z. physikal. Chem.*, 1932, **18**, 360), stated that an X-ray examination indicated the existence of solid solutions of the oxide in the carbonate, a phenomenon which is in accordance with the results we have obtained.

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SUMMARY.

The dissociation pressure of cadmium carbonate has been measured at various temperatures by a static method and has been found to depend upon the quantity of oxide present.

No simple relation between the lowering of pressure and the amount of oxide has been found, the actual depression for the same proportion of oxide being more at 290° than at 334°. The effect is very marked at lower temperatures.

Department of General Chemistry,
Indian Institute of Science.

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