CCCLIV.—*Chemical Kinetics of the System* $Ag_2CO_3 \rightleftharpoons Ag_2O + CO_2$.

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The object of this work was to study the reaction rate in a reversible chemical change involving solid reactants. The dissociation of silver carbonate was selected on the following grounds: it was expected that the decomposition and recombination would be free from the complication of consecutive and side reactions (actually it was found that the oxide decomposed into metallic silver to a very slight extent during the time of an experiment at the highest temperature used, but this had no effect upon the primary reaction); the material can be crystallised under conditions such that it should be very free from adsorbed impurities other than water; and the reaction takes place at a measurable speed within a temperature range where equilibrium in the system corresponds to conveniently measurable pressures of carbon dioxide. The reaction has been studied from the following points of view: (1) the importance of the interface between the two solid phases; (2) the kinetic nature of the equilibrium; (3) the influence of water vapour; (4) the influence of temperature; (5) variations in the behaviour of different preparations of silver carbonate.

Previous observations on the dissociation of silver carbonate include those of Colson (*Compt. rend.*, 1901, **132**, 467; 1905, **140**, 865), Centnerszwer and Bruzs (*Z. physikal. Chem.*, 1926, **123**, 111; *J. Physical Chem.*, 1925, **29**, 733), Centnerszwer and Krustinson (*Z. physikal. Chem.*, 1926, **124**, 225). Where a comparison is possible, our observations are in agreement with the previous work, but the conditions of the kinetic measurements in the earlier experiments are not precisely specified.

EXPERIMENTAL.

The reaction was followed by the change in weight of a sample of the solid lying in a very light concave glass container attached to a quartz spring balance of the type used by McBain. The details of its construction were similar to those described by Topley and Whytlaw-Gray (*Phil. Mag.*, 1927, **4**, 873), with the addition of an optically plane glass window and a reaction vessel sealed to the glass microbalance case. The sensitivity of the quartz spring and cathetometer was one part in 10,000 parts of the load of 100 mg. carried by the spring, so that the method is both direct and sensitive. The reaction vessel was a hard-glass tube attached vertically below the microbalance case by means of a wide mercury-sealed ground joint. The total volume of reaction vessel, microbalance case, manometer, and connecting tubes was large enough to make the concentration of the carbon dioxide formed in a reaction negligible in those experiments in which it was not immediately pumped off. The temperature was controlled by hand regulation of a vertical tubular electric furnace, and measured by means of copper–constantan thermocouple junctions. The furnace, lined with a thick copper tube to equalise the temperature, was counterpoised by four weights and pulleys built into an iron frame, so that it could be raised and lowered smoothly round the reaction vessel. The latter communicated by all-glass connexions with a mercury-vapour and a " Hyvac " pump, and with a manometer, McLeod gauge, and reservoir of carbon dioxide. The carbon dioxide was stored over phosphoric oxide, and could be admitted at any pressure up to 800 mm. Water vapour was admitted when required, either in traces from a small gas container, or up to 15 mm. from a bulb containing liquid water. Between the microbalance case with its attached reaction vessel and the remainder of the apparatus a glass spiral was inserted, which could be cooled in liquid air acting as a mercury-vapour trap when prolonged evacuation was necessary. The method of starting an experiment was to admit carbon dioxide to a pressure exceeding the dissociation pressure corresponding to the selected temperature, and then to raise the furnace; when the temperature had become steady the carbon dioxide was pumped out and the reaction started—the uncertainty in the time of starting was less than one minute.

Preparation of Silver Carbonate.—Crystalline silver carbonate was prepared from a solution of the bicarbonate. Amorphous silver carbonate (from equivalent volumes of *N*/10-solutions of silver nitrate and potassium or sodium carbonate) was well washed and suspended in 10 l. of water into which carbon dioxide was passed for some days. Carbon dioxide was removed from the filtered solution in a large vacuum desiccator; silver carbonate was then deposited on standing as small crystals showing little tendency to twinning, and these were dried in a vacuum at room temperature. The same amorphous silver carbonate was used repeatedly in this way for the preparation of fresh crops of crystals, in the expectation that the successive products would become rather more free from ionic impurities adsorbed in the amorphous material.

Various other preparations were made by a method which should favour the retention of adsorbed ions: *N*/60-solutions of silver nitrate and of potassium bicarbonate were saturated with carbon dioxide, cooled in ice, and mixed very slowly while carbon dioxide was passed through the solution; the crystalline product which separated over-night was similar to that obtained by the other method.

Centnerszwer and his co-workers (*locc. cit.*) give complete analyses of samples prepared in ways similar to these, and also by crystallisation from ammonia solution; the results show that the product is too pure for adsorbed impurity to be detected by a discrepancy in the analysis. As a confirmation, one of the samples used in the present work was ignited (Found: Ag, 78·19. Calc.: Ag, 78·24%).

The average radius of the crystals, assumed spherical, was determined by Stokes's law and found to be of the order 0·003 cm. for all the preparations used.

In connexion with some of the experimental work, accurate data were required for the dissociation pressure of the crystalline material. The available measurements are those of Colson (*loc. cit.*), over the range 132—218°, and of Centnerszwer and Krustinson, by a more accurate dynamical method, over the range 190—220°. The latter authors give a formula of the Nernst approximation type, which, however, is not quite in agreement with their own results at the highest temperatures or with the data of Colson at lower temperatures; we have therefore interpolated from their data and extrapolated to lower temperatures by the Ramsay–Young formula, using mercury as a reference substance, and have obtained the following values, which agree with those given by Colson below 190° :

Temp.	130°	140°	150°	160°	170°	180°	190°	200°	210°	216·3°
Press. (mm.)	20·7	33·7	53·0	81·5	123	192	284	416	603	760

The Decomposition of Crystalline Silver Carbonate in the Absence of Carbon Dioxide.—To avoid confusion we have throughout used the words " decomposition " and " recombination " to refer to the chemical change actually measured; for the separate and simultaneous reactions $Ag_2CO_3 \rightleftharpoons Ag_2O + CO_2$ we have used the terms " forward " and " reverse " reactions.

Experiments have been made with different preparations of silver carbonate, at different temperatures, and with different concentrations of water vapour present in the reaction vessel. In general there is a slight induction period, followed by a smooth curve, the slope of which decreases gradually at first and then more rapidly towards the end of the reaction. The curves can be divided roughly into two groups—" normal," in which the form agrees with a theoretical equation discussed in the next paragraph, and " abnormal," in all of which the rate falls off much more rapidly than corresponds to the equation. This complication arises from the fact that the progress of the reaction is influenced by the presence of water vapour; it is not here a question of intensive drying—the effect is characteristic rather of an adsorption equilibrium in which pressures of water vapour up to several mm. of mercury are required to produce an approach to saturation. The action of water vapour is discussed later, but it may be stated here that whether or not the actual chemical reaction is catalysed by water vapour, the progressive retardation of decomposition which appears in the curves referred to as " abnormal " can be diminished or prevented by having present in the reaction vessel a sufficient concentration of water vapour. The minimum concentration necessary varies with different preparations of silver carbonate and increases with the temperature of decomposition. The " normal " form of decomposition curve is a limiting form to which the decomposition can be made to approximate by suitable adjustment of the conditions—apart from the initial short period of acceleration, which only becomes important at the lowest temperatures employed.

It is a very probable assumption that decomposition takes place from the outside of a particle inwards, and further, that, provided the carbon dioxide is able to escape rapidly from the region of chemical change, the reaction spreads inwards at a constant linear rate. The different types of decomposition curve to be expected in these circumstances have been discussed by Topley and Hume (*Proc. Roy. Soc.*, 1928, *A*, **120**, 211). For the case in which reaction begins at many points simultaneously on the surface of each particle, we have

$$v/r = \{1 - \sqrt[3]{1 - \alpha}\}/t \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where α is the fraction decomposed at time t, v the linear rate of propagation of the reaction, and r the radius of the particles. This applies strictly only to spherical particles of uniform size, but is approximately true as an average result when factors such as the irregular shape and the difference of rate parallel to different crystal axes are averaged over the large number of particles (10^5—10^6) contained in the reacting material.

Tables I and II contain the results of typical experiments. The first two columns give the time t in minutes and the corresponding value of α, and the third contains values of the " linear reaction velocity coefficient " v/r (min.$^{-1}$ × 1000), calculated by equation (1). The pressure of water vapour admitted at the beginning of each experiment (p_{H_2O}) is in mm. of mercury. For convenience in discussion, the experiments are labelled " normal " or " abnormal," according to the type of curve which represents them (see p. 2636). Some experiments, really of an intermediate type, are classed as " normal " because, although v/r decreases somewhat during the course of the reaction,* the fall is much less pronounced than in the " abnormal " experiments. It is not implied that the two types of reaction curve correspond to any essential difference in reaction mechanism.

It is shown later that the velocity of decomposition is very sensitive to the presence of carbon dioxide; when, therefore, the decomposition is of the " normal " type, it follows that the carbon

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* Lack of uniformity of crystal size would cause v/r to decrease during the reaction, although not in the rapid way characteristic of the " abnormal " curves; but if, owing to micro-fissures in the crystals, the effective particle size is much smaller than the crystal size, then it becomes a question of the uniformity of the former, and probably the chemical reaction is itself the only source of information about this.

TABLE I.

Expt. 1.

Prep. A. $p_{H_2O} = 0$ mm.
Temp. 147·0°. Normal.

t.	*a.*	*v/r.*
5	0·002	0·1
10	0·036	1·2
20	0·110	1·9
50	0·274	2·0
80	0·424	2·1
120	0·580	2·1
160	0·716	2·1
200	0·817	2·2
250	0·894	2·1
300	0·940	2·0

Expt. 2.

Prep. A. $p_{H_2O} = 0$ mm.
Temp. 158·0°. Normal.

t.	*a.*	*v/r.*
5	0·056	3·8
10	0·115	4·0
20	0·243	4·4
30	0·365	4·7
50	0·572	4·9
80	0·778	5·0
100	0·860	4·8
120	0·910	4·6

Expt. 3.

Prep. A. $p_{H_2O} = 0$ mm.
Temp. 168·8°. Normal.

t.	*a.*	*v/r.*
5	0·130	9·0
10	0·247	9·0
20	0·468	9·5
30	0·642	9·7
40	0·750	9·3
60	0·847	7·7
80	0·908	6·7

Expt. 4.

Prep. A. $p_{H_2O} = 0$ mm.
Temp. 179·3°. Normal.

5	0·197	14·1
10	0·410	16·1
15	0·575	16·6
20	0·690	16·2
30	0·812	14·2
50	0·895	10·6

Expt. 5.

Prep. B. $p_{H_2O} = 8$ mm.
Temp. 172·3°. Normal.

10	0·087	3·0
20	0·165	2·9
40	0·278	2·6
60	0·364	2·3
100	0·514	2·1
150	0·637	1·9
200	0·765	1·9
250	0·885	2·1
300	0·938	2·0

Expt. 6.

Prep. B. $p_{H_2O} = 10$ mm.
Temp. 193·3°. Normal.

5	0·102	7·1
10	0·217	7·8
20	0·403	7·9
30	0·534	7·8
50	0·749	7·4
70	0·883	7·3
100	0·971	6·9

Expt. 7.

Prep. B. $p_{H_2O} = 10$ mm.
Temp. 204·0°. Normal.

5	0·170	12·1
10	0·353	13·1
15	0·497	13·7
20	0·630	14·1
25	0·737	14·4
30	0·817	14·4
40	0·920	14·2
50	0·963	13·3

Expt. 8.

Prep. C. $p_{H_2O} = 1$ mm.
Temp. 172·8°.
Abnormal.

5	0·021	1·4
10	0·038	1·3
20	0·067	1·2
30	0·087	1·0
40	0·104	1·0
50	0·121	0·8
60	0·137	0·7
70	0·150	0·8

Expt. 9.

Prep. C. $p_{H_2O} = 1$ mm.
Temp. 183·2°.
Abnormal.

5	0·030	2·0
10	0·056	1·9
20	0·098	1·7
30	0·130	1·5
40	0·158	1·4
50	0·184	1·3

Expt. 10.

Prep. C. $p_{H_2O} = 5$ mm.
Temp. 193·6°. Normal.

5	0·055	3·8
10	0·115	4·0
15	0·163	3·9
20	0·196	3·5
30	0·263	2·9
40	0·323	3·1
50	0·366	2·8

Expt. 11.

Prep. C. $p_{H_2O} = 10$ mm.
Temp. 204·0°. Normal.

5	0·097	7·6
10	0·189	6·7
15	0·261	6·4
20	0·320	6·1
25	0·366	5·6
30	0·408	5·4
40	0·467	4·7

Expt. 12.

Prep. C. $p_{H_2O} = 10$ mm.
Temp. 214·3°. Normal.

5	0·152	10·8
10	0·297	11·1
15	0·396	10·3
20	0·462	9·3
25	0·523	8·8
30	0·568	8·1

dioxide must at all stages of the reaction be able to escape into the gas phase and be removed from the region of reaction as soon as it is produced. On the other hand, when a reaction is progressively retarded and virtually comes to an end before all the silver carbonate

TABLE II.

Experiments at 224·5° with Preparation C, and with different concentrations of water vapour present.

Expt. 13.			Expt. 14.			Expt. 15.		
p_{H_2O} = 0 mm.			p_{H_2O} = 2 mm.			p_{H_2O} = 3 mm.		
t.	*a.*	*v/r.*	*t.*	*a.*	*v/r.*	*t.*	*a.*	*v/r.*
2	0·074	12·7	2	0·098	16·9	2	0·078	13·5
5	0·149	10·5	5	0·154	10·8	5	0·156	11·0
10	0·247	9·0	10	0·230	8·3	10	0·271	10·1
17	0·330	7·4	17	0·306	6·8	17	0·368	8·3
25	0·406	6·2	25	0·381	5·9	25	0·449	7·2
35	0·491	5·8	35	0·454	5·2	35	0·517	6·2
50	0·562	4·8	50	0·570	4·9	50	0·591	5·2
100	0·687	3·2	70	0·684	4·6	100	0·774	3·9
			100	0·830	4·6			

Expt. 16.			Expt. 17.			Expt. 18.		
p_{H_2O} = 4·5 mm.			p_{H_2O} = 6 mm.			p_{H_2O} = 9 mm.		
2	0·079	13·6	2	0·079	13·6	2	0·090	15·5
5	0·216	15·6	5	0·188	13·4	5	0·263	17·3
10	0·366	14·1	10	0·348	13·3	8	0·373	18·0
17	0·505	12·3	17	0·483	11·6	12	0·492	16·8
25	0·602	10·6	25	0·574	9·9	16	0·561	15·0
35	0·700	9·5	32	0·629	8·8	20	0·625	14·0
50	0·818	8·7	40	0·684	8·0	25	0·697	13·1
						30	0·742	12·1

Expt. 19 (p_{H_2O} = 13 mm.).			Expt. 20 (p_{H_2O} = 15 mm.).		
t.	*a.*	*v/r.*	*t.*	*a.*	*v/r.*
2	0·080	14·0	2	0·086	14·8
5	0·208	15·0	4	0·216	19·5
8	0·320	15·0	6	0·307	19·2
10	0·370	14·3	8	0·382	18·5
15	0·484	13·2	11	0·465	17·1
20	0·560	12·0	15	0·557	15·9
25	0·612	10·8	20	0·636	14·3
30	0·660	10·0	28	0·730	12·6
			35	0·780	11·3

has decomposed, there are two possibilities. (1) The carbon dioxide is not able to escape through the surrounding oxide fast enough to prevent the accumulation of a certain local concentration of gas in the reaction zone, until the increasing rate of diffusion outwards balances the decreasing rate of formation; this diffusion rate must then be considered to be a function of the amount of adsorbed water in the outer layer of silver oxide, and hence of the water-vapour concentration. (2) The retardation arises from a failure of water vapour to penetrate through the increasing thickness of oxide into the reaction region, it being now assumed that the presence of water actually at the seat of the reaction is essential. These two possibilities, which are, of course, not mutually exclusive, are referred to later; in the meantime, the mechanism of reaction and the nature of the equilibrium will be discussed in terms of the uncatalysed reaction, since the conclusions reached are easily restated to include an intermediate step in the reaction, involving, for example, silver hydroxide.

Evidence that the Reaction is of the " Interface " Type.—The fact that in the " normal " curves the quantity v/r is constant shows that the reaction takes place in the surface layers of the silver carbonate still remaining, and that the carbon dioxide does not accumulate in that place. An important question is whether the reaction involves an actual interface between the silver carbonate and the silver oxide, or whether it is sufficient that there should be a free silver carbonate surface from which carbon dioxide escapes by a process analogous to evaporation. Langmuir (*J. Amer. Chem. Soc.*, 1916, **38**, 2222) has pointed out that the fact that the equilibrium pressure is independent of the relative amounts of the two solid phases could be accounted for by assuming that the reaction (in both directions) takes place only at an interface between the two solids, so that the area available for reaction is always the same for both. Langmuir's suggestion does not take into account the adsorption phenomena associated with the chemical reaction, but the point remains that the non-formation of solid solutions of oxide and carbonate makes it very probable that the seat of the reaction is the interface between the two solids. But there is more direct evidence based upon the acceleration in the reaction rate which can be observed in the system $Ag_2CO_3 \rightleftharpoons Ag_2O + CO_2$ in certain circumstances. The argument is that, if it can be shown that under some conditions an interface reaction does actually occur in this system, then it is reasonable to suppose that the reaction is mainly conditioned by the interface, even when direct proof of this is lacking. The spontaneous formation of " nuclei " of the second solid phase is of course equivalent to the reaction proceeding to some extent without the intervention of the interface; but such reaction centres might form only on exceptional spots on the surface (*e.g.*, where the effective curvature is very great) and yet be present in numbers sufficient to obscure the acceleration expected in an interface reaction, very shortly after the beginning of the reaction. The accelerating period observed at the beginning of a decomposition is usually very slight, but in some circumstances it becomes much more pronounced. At low temperatures the decomposition curve of the crystalline carbonate begins to show the characteristic sigmoid shape. Expt. 1 at 147° shows a marked acceleration up to above 10% of the complete reaction. With the " synthetic " silver carbonate produced in the recombination of the oxide with carbon dioxide, pronounced sigmoid curves are obtained in the decomposition at low temperatures or in the presence of small concentrations of carbon dioxide. Again, in the recombination reaction very definite accelerations are obtained in reactions carried out with pressures of carbon dioxide not greatly in excess of the equilibrium pressure. Further evidence that the recombination reaction is essentially of the interface type is obtained in experiments in which carbon dioxide is introduced into the reaction vessel after the decomposition has begun, and is referred to later.

Accelerating reaction in a system of the type $\text{Solid}_{(1)} = \text{Solid}_{(2)} +$ Gas is most reasonably interpreted as being due to the spreading outwards of the reaction from centres at which it is initiated; the tendency to react in this way must arise from the forces operating in the two solids concerned, and is therefore proper to the system, at least over the range of temperature in question.

The Influence of Water Vapour in promoting the Reactivity.—It is well known that the reactivity of carbonates and oxides in general is greatly influenced by water vapour ; in the case of silver carbonate, the catalytic effect of water vapour has frequently been reported. Colson (*loc. cit.*) noticed that although the system silver carbonate–silver oxide would establish a reproducible dissociation pressure when equilibrium was approached from the silver carbonate side, a satisfactory equilibrium could not be realised by the combination of silver oxide and carbon dioxide unless moisture was present, and also that equilibrium from either side was approached more slowly if the system had been dried by phosphoric oxide. We have found that both decomposition and recombination are affected by water, but not in the same way. Much smaller partial pressures produce the full effect in the latter case, which is kinetically different from the decomposition. In this paper only the decomposition measurements with crystalline silver carbonate are discussed. The results of a large number of observations may be summarised as follows : the retardation in the absence of added water vapour is much more marked in the later stages of a reaction than at the beginning; a reaction without added water vapour may start at about the same rate as when water is present, but then become slower and appear to come almost to an end before all the carbonate is decomposed. The effect varies with different preparations, and is usually more pronounced at the higher temperatures (200—230°) than at the lower (150—200°).

The experiments in Table II, performed at a relatively high temperature and with Preparation C, so that the definitely "abnormal" type of curve is obtained in the absence of water vapour, may be summarised as follows, the rates (as percentage decomposition per min.) being given at specified proportions of complete decomposition :

p_{H_2O}	0	2·0	3·0	4·5	6·0	9·0	13·0	15·0
Rate at 0%	3·7	4·9	3·9	4·0	4·0	4·5	4·0	4·3
,, 10%	2·6	2·8	2·6	4·7	3·9	5·1	4·5	5·3
,, 50%	0·6	0·7	0·6	1·6	1·3	2·3	1·7	2·3
Ratio, 50%/10%	0·23	0·24	0·24	0·34	0·33	0·45	0·38	0·43

The influence of water vapour becomes more marked as the amount of silver oxide increases; the results, in spite of their irregularity, also indicate that the effect of water tends towards a limit in a manner suggesting that it depends upon adsorption tending to saturation. The actual amount of water vapour adsorbed by the reaction sample is too small to be measured in the case of the carbonate, and is about 0·1% of the weight of silver oxide at $p_{H_2O} =$ 10 mm.

The conclusion that, qualitatively, the concentration of water vapour required to produce the maximum decomposition rate increases as the amount of silver oxide increases, is borne out by other experiments in which the water was introduced at various stages of the "dry" decomposition. This effect receives a very simple explanation if it is supposed that the removal of carbon dioxide from the reaction interface by surface diffusion on the silver oxide particles is facilitated by the adsorption of water vapour upon the oxide, possibly in a form equivalent to a surface layer of silver hydroxide (see Riley, *Phil. Mag.*, 1927, **3**, 459). The necessary condition for a "normal" reaction uninhibited by the overlying oxide is that carbon dioxide should diffuse away rapidly in comparison with its rate of formation; the fact that, in general, a larger concentration of water vapour is required at the higher temperatures is in keeping with this, since the adsorption of water vapour will presumably be less, and the rate of the interface reaction increases more rapidly with temperature than the rate of the diffusion process. It seems to us that these considerations provide a possible explanation of the negative temperature coefficient found by Centnerszwer and Bruzs (*loc. cit.*) for the decomposition of amorphous silver carbonate between 240° and 260°. At these temperatures the amount of water vapour required might be considerable, and water vapour was not added. As the temperature is increased, the *relative* state of dryness of the material is increased, so that the reaction is actually made slower; above 260° the exponential increase of reaction rate with temperature again outweighs the effect of dryness; hence the apparent anomaly of a temperature coefficient being first positive, then negative, then again positive.

It does not seem possible by experiments upon crystalline silver carbonate to decide whether there is a true catalysis of the reaction itself, such as would be represented by the scheme $Ag_2CO_3 + H_2O \longrightarrow [2AgOH + CO_2] \longrightarrow Ag_2O + H_2O + CO_2$ (or some less definite mechanism depending upon the field of force round an adsorbed water molecule), or whether the function of the water is merely subsidiary, its action being to facilitate movement of carbon dioxide away from the interface. (An attempt will be made to measure the rate of surface diffusion of carbon dioxide upon silver oxide in the presence of different concentrations of water vapour.) Silver carbonate prepared from aqueous solution, however, is certain to contain some included water, so that as the decomposition is propagated through the crystals there will probably always be some water present in the interface. The case is different with the " synthetic " silver carbonate which can be prepared in a very dry state by carbonating the oxide, and results with this suggest that water is not required for the interface reaction or for the formation of " nuclei " which initiate it.

Differences in the Behaviour of Different Preparations.—With any one preparation the results are reproducible within certain limits: in Table II the initial velocities vary from 13 to 17, and in Table III (R_0) from about 2 to 4. It was noticed that the length of time during which the sample is heated in dry carbon dioxide above the dissociation pressure has some (rather irregular) influence upon the subsequent rate; a possible reason is the " annealing out " of strains produced in the crystal lattice during growth. Another point is that during the heating in the atmosphere of carbon dioxide there is a slight decomposition which stops completely after a time. This is almost certainly due to the higher dissociation pressure at the edges and corners of the crystals; at relatively low temperatures, where the pressure of carbon dioxide is from 5 to 20 times the dissociation pressure, this slight decomposition does not take place, but when the external pressure exceeds the dissociation pressure by only 10—20% it invariably occurs.

When a comparison is made of the behaviour of different preparations made in as nearly as possible the same way, very considerable differences appear. Thus, under the same conditions of temperature and water-vapour concentration, Preparation A decomposed 4 times more rapidly than B and 8 times faster than C. These are average results, unaffected by the random irregularities referred to above. The influence of water vapour was more marked with C than with the other preparations.

It is known that the rate of chemical change in solids may be profoundly modified by the adsorption of ions during growth (Macdonald and Hinshelwood, J., 1925, **127**, 2764). The possibility that, with silver carbonate, ions from the solution are included in the lattice and affect the rate, was tested by using excess of one or other of the reagents in the precipitation, but in no case could a correlation between behaviour and mode of preparation be traced. (This applies to the definitely crystalline material; amorphous silver carbonate and the product obtained by recarbonating the oxide show a somewhat different kinetic behaviour.)

Mechanism of the Forward and Reverse Reactions, and the Equilibrium.—Experiments in which the effect upon the reaction rate of a partial pressure of carbon dioxide different from the equilibrium pressure was studied suggested the following view of the reaction mechanism. Carbon dioxide is assumed to have free access to the interface by rapid diffusion on the surface of the silver oxide. The limitations of this assumption have already been discussed in connexion with the action of water, but the important point is that under " normal " conditions the carbon dioxide must be able to penetrate the silver oxide layers freely, as is proved by the form of the " normal " curves. We assume that an adsorption equilibrium is set up, by which a fraction of the area of the carbonate–oxide interface is covered by a unimolecular layer of carbon dioxide. Adsorption of *more* than one layer does not come into question, because if there is space available for more than one layer between the oxide and the carbonate the distance separating carbonate and oxide ions would exceed the range of the forces round the ions, and this would not constitute an interface effective for chemical reaction. The adsorption reaches equilibrium in a time short compared with the duration of the reaction which is being measured; consequently, as the reaction proceeds and the interface moves through the silver carbonate, the adsorption equilibrium is unchanged, the concentration of carbon dioxide in the gas phase being kept sensibly constant. The assumption of a ready transfer of carbon dioxide to and from the interface does not seem to present a difficulty, in view of the work of Volmer (*Z. physikal. Chem.*, 1925, **115**, 253) and of Adhikari and Felman (*ibid.*, 1928, **131**, 347) on the surface diffusion of molecules adsorbed on solid surfaces.

In the interface, ions belonging to the silver carbonate lattice vibrate towards the surface of the silver oxide lattice; in so doing they lose some of the stability proper to ions of the carbonate lattice. If the kinetic and potential energy conditions are favourable, there will be a tendency for these ions, when they closely approach the oxide lattice side of the interface, to assume a new stable arrangement appropriate to the oxide lattice; a carbon dioxide molecule set free in this rearrangement becomes indistinguishable from any other carbon dioxide molecule taking part in the adsorption equilibrium.

On this view, the vibration of ions from the carbonate lattice on to a part of the oxide lattice *not covered by adsorbed carbon dioxide* may (subject to unknown energy and steric conditions) result in chemical reaction in the sense of the equation $Ag_2CO_3 \longrightarrow Ag_2O(CO_2)_{\text{adsorbed}} \rightleftharpoons Ag_2O + CO_2$. But if the part of the oxide lattice towards which the vibrating ions move happens at that moment to be covered by an adsorbed molecule, then the essential condition for chemical change is not satisfied, and no contribution to the progress of the reaction is made. The reverse reaction $Ag_2O + CO_2 \rightleftharpoons Ag_2O(CO_2)_{\text{adsorbed}} \longrightarrow Ag_2CO_3$ is analogous, the formation of carbonate occurring only where adsorbed carbon dioxide happens to be in immediate juxtaposition to the ions vibrating from the oxide on to the carbonate lattice.

Writing R_1 and R_2 for the separate velocities of the two simultaneous reactions, and σ for the total area of the interface, we have $R_1 = K_1(1 - \gamma)\sigma$ and $R_2 = K_2\gamma\sigma$, where γ is the fraction of the oxide surface in the interface which is covered by adsorbed carbon dioxide at the pressure p of carbon dioxide in the gas phase. The observed rate of decomposition is the difference, *i.e.*,

$$R = R_1 - R_2 = \sigma\{K_1 - \gamma(K_1 + K_2)\} \quad . \quad . \quad (2)$$

The fraction γ is related to the pressure of carbon dioxide in the gas phase. Since only adsorption in a single molecular layer is considered, it seems reasonable to try an adsorption equation of the Langmuir type, $k\gamma = k'(1 - \gamma)p$, where k and k' are constants depending on temperature and characteristic of the adsorption of carbon dioxide in the interface (not on the free surface of silver oxide). This is equivalent to

$$\gamma = p/(p + k/k') \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The rate of decomposition when $p = 0$ is $R_0 = \sigma K_1$, hence $R/R_0 = 1 - \gamma(1 + 1/K)$, where $K = K_1/K_2$. Substitution of the value of γ from (3) then gives

$$R/R_0 = (1 - k'p/Kk)/(1 + k'p/k) \quad . \quad . \quad . \quad (4)$$

At the equilibrium (dissociation) pressure p_e, R becomes 0, therefore $1 - k'p_e/Kk = 0$ or $k/k' = p_e/K$. Substituting this value of k/k' in equation (4), we have

$$R/R_0 = (p_e - p)/(p_e + Kp) \quad . \quad . \quad . \quad . \quad (5)$$

The equilibrium dissociation pressure is thus a function of the adsorption constants in the Langmuir isotherm and of the ratio of the coefficients for the forward and reverse reaction rates per unit area of the interface respectively free from, and covered by, adsorbed carbon dioxide. Two points require mention. (1) The use of an adsorption equation of the Langmuir type is compatible with the assumption of rapid diffusion of the adsorbed molecules in the interface, although in the present case the adsorption equilibrium must be considered to be reached through the " three-phase line " discussed by Schwab and Pietsch (*Z. Elektrochem.*, 1929, **35**, 135) and by Bradley (*Phil. Mag.*, 1929, **8**, 202). (2) The hypothesis that decomposition occurs only in the part of the interface which is free (at any moment) from adsorbed carbon dioxide implies also that if an indifferent gas is adsorbed in the interface, then to the extent to which silver oxide is covered, the forward reaction is inhibited. But since the area so covered is available neither for the forward nor for the reverse reaction, it is easily shown that the equilibrium pressure is unaltered. This is a condition which a theory of the reaction mechanism must fulfil, because a change in the equilibrium pressure compensated for by the free-energy change on adsorption of the indifferent gas would not be a permissible assumption, since the latter is a function of the area of the interface, whereas the mass of silver carbonate decomposed is thermodynamically independent of this area.

Equation (5) has been tested by the data of three series of experiments carried out as follows : the decomposition is started under a negligibly small pressure of carbon dioxide, 8 mm. of water vapour being added to ensure the course of the decomposition being of the " normal " type. After reaction has proceeded to the extent of about 30%, carbon dioxide is introduced into the reaction vessel at a measured partial pressure. This causes an abrupt change in the rate. When the new rate has been measured the reaction vessel is evacuated, 8 mm. of water vapour again admitted, and the rate measured again. This could be repeated, a different pressure of carbon dioxide being admitted. In this way the rate of decomposition in the absence of carbon dioxide was measured immediately before and after the measurement in the presence of a known pressure; by taking the mean of the two rates in the absence of carbon dioxide as R_0, then the ratios R/R_0 are independent of any factors affecting the effective area of the interface in the particular sample experimented upon, *i.e.*, particle size, the fortuitous way in which the crystals touch one another, or the fraction of the interface covered by water vapour, if it acts in this respect as an inert adsorbed substance.

The results of experiments at three temperatures are recorded in Tables III, IV, and V. The actual reaction rates R' (before admission of carbon dioxide), R (in the presence of carbon dioxide), and R'' (after removal of carbon dioxide), expressed as percentage reaction per minute, are included in Table III, and only the ratios

R/R_0 in the other tables. The rates in the columns R' and R'' should all be about the same, instead of varying from about 2 to 4; this far exceeds the experimental error, and the reason has not been satisfactorily traced, but these irregularities do not obscure the nature of the influence of carbon dioxide.

TABLE III.

Temperature 214·3°. Dissociation pressure 700 mm.

p.	R'.	R.	R''.	R_0.	R/R_0.	p/p_e.	K.
7	3·74	2·53	2·57	3·15	0·803	0·010	—
10	3·12	1·80	1·84	2·48	0·726	0·014	—
26	2·80	1·65	1·65	2·22	0·743	0·037	8
48	4·37	1·90	2·79	3·58	0·531	0·069	11
85	3·12	1·20	2·51	2·82	0·426	0·121	9
112	3·48	1·11	3·07	3·27	0·339	0·160	9
210	3·94	0·83	3·94	3·94	0·211	0·300	8
292	3·45	0·46	4·26	3·85	0·117	0·416	10
392	2·36	0·16	2·00	2·18	0·073	0·560	9
392	3·22	0·27	4·14	3·68	0·073	0·560	9
492	3·51	0·11	3·86	3·69	0·030	0·703	13
592	2·70	0·04	3·59	3·15	0·013	0·846	—
						Mean	9·6

TABLE IV.

Temp. 193·6°.
Diss. press. 325 mm.

R/R_0.	p/p_e.	K.
0·490	0·049	19
0·379	0·098	14
0·110	0·308	17
0·047	0·615	12
0·033	0·892	—
0·005	0·984	—
−0·032	1·108	—
−0·038	1·277	—
−0·234	1·461	—
	Mean	15·5

TABLE V.

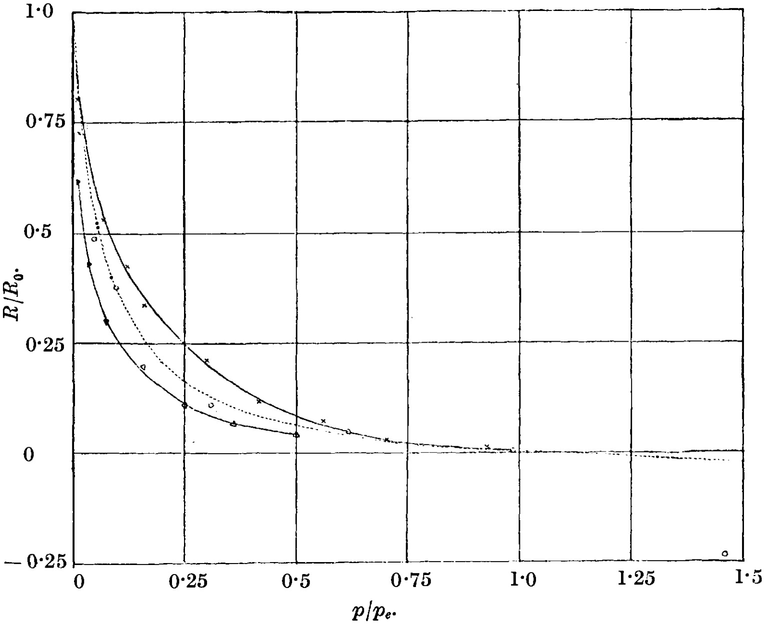
Temp. 172·8°.
Diss. press. 140 mm.

R/R_0.	p/p_e.	K.
0·619	0·014	—
0·432	0·036	27
0·303	0·075	28
0·197	0·157	21
0·120	0·250	21
0·067	0·357	24
0·044	0·500	21
	Mean	23·7

The values of K in the last column, calculated by equation (5), are greatly affected by small experimental errors or irregularities in the rate both when the pressure of carbon dioxide is small and when it approaches the equilibrium value. In the latter case, in particular, the values of K become extremely sensitive to small errors in the temperature. For this reason, significance can only be attached to those values of K corresponding to values of p/p_e between the limits 0·02—0·7.

The three series were unfortunately not done with the same preparation of silver carbonate, the small solubility of silver bicarbonate making it difficult to obtain a sufficient quantity in a single crystallisation; but, as judged by the rate at a standard temperature, the different preparations used were all similar, and sufficient water was always present to eliminate variations due to different amounts of it.

The way in which carbon dioxide affects the rate of decomposition is best seen in the curves in the diagram. This represents the data of Tables III, IV, and V, including the experiments at pressures of carbon dioxide above the dissociation pressure. The curve indicated by the broken line is calculated from equation (5), K being taken as 15·5 from Table IV, and the circles represent the experimental figures; the continuous lines are smooth curves drawn through the experimental points of the other two series. In these, the experimental points lie a little below the line calculated with the average value of K, when p/p_e is small, *i.e.*, the smaller partial pressures of carbon dioxide have relatively too great an influence. But at all three temperatures the equation reproduces the experimental results as closely as could be expected in view of the fact that conditions in the interface are probably not as uniform as has been postulated.



× = *Expts. at* 214·3°. ⊙ = *Expts. at* 193·6°. △ = *Expts. at* 172·8°.

Equation (5) predicts for the recombination reaction a limiting velocity when the external pressure of carbon dioxide is very much greater than the dissociation pressure; the interface is then completely covered by adsorbed carbon dioxide so that the forward reaction is entirely suppressed, and $R/R_0 = -1/K$. In the diagram the calculated curve corresponding to $K = 15{\cdot}5$ is continued beyond the equilibrium pressure. It is not, however, possible to realise this part of the curve experimentally. The recombination rates observed are much greater than the calculated, and the divergence increases rapidly as the excess pressure over the equilibrium value is increased. The reason for this is clear. As the pressure of the carbon dioxide is increased the normal reaction in the original interface becomes a (net) recombination, but added to this there is the formation of fresh " nuclei " of carbonate at points on the surface of the silver oxide and the growth of these. A study of the recombination reaction has shown that the tendency for fresh reaction centres of carbonate to form increases rapidly as the excess pressure over the equilibrium value increases; the form of the recombination reaction curve passes through a stage in which it has the sigmoid shape characteristic of an interface reaction spreading from rather few centres, to a stage in which the maximum velocity is at the beginning of the reaction showing that many " nuclei " are obtained almost immediately after the gas is admitted.

The Temperature Coefficient of the Reaction Rate.—The effect of temperature upon the rate at which silver carbonate decomposes in the presence of carbon dioxide is complicated, as can be seen by differentiating equation (5), since R_0, K, and p_e are all very sensitive to temperature. With an appropriate value of p/p_e the temperature coefficient can become very large. The temperature coefficient found by Centnerszwer and Bruzs is considerably higher than the value found by us, and this is explained by the fact that they worked with carbon dioxide at atmospheric pressure in the decomposition apparatus.

The influence of temperature upon the rate of decomposition in the absence of carbon dioxide is simply the influence upon R_0, which is proportional to the linear reaction velocity coefficient v/r. The values found for the three preparations were :

	Prep. A.				Prep. B.		
Temp.	147·0°	158·0°	168·8°	179·3°	172·3°	193·6°	204·0°
$v/r \times 1000$...	2·1	4·9	9·4	15·8	2·8	7·5	14·0

	Prep. C.					
Temp.	172·8°	183·2°	193·6°	204·0°	214·0°	224·5°
$v/r \times 1000$...	1·4	2·0	3·8	6·9	10·7	15·0

The corresponding values of the empirical quantity $A = -1{\cdot}98 d\log_e(v/r)/d(1/T)$ are : Preparation A 23,400, preparation B 22,800, and preparation C 22,500.

Relationship of the Temperature Coefficient to the Absolute Velocity of the Reaction.—Part of the interest of " topochemical " reactions is the question how far the conceptions of the detailed mechanism of chemical change which have emerged from the study of gas reactions can properly be transferred to the solid state, and how far modification is necessary on account of forces operating in solids which are absent in gases. A correlation of absolute reaction rate and its variation with temperature has been attempted with only one reaction of this type, *viz.*, $CaCO_3,6H_2O = CaCO_3 + 6H_2O$ (Topley and Hume, *Proc. Roy. Soc.*, 1928, *A*, **120**, 211). In that case the interesting point was that the linear rate of propagation of the reaction through the solid was 10^{20} times as great as corresponded to the assumption that ions or ionic groups vibrating in the interface are activated when they possess an energy exceeding A, the fraction activated being taken as $\beta = e^{-A/RT}$. Kassel (*J. Amer. Chem. Soc.*, 1929, **51**, 1136) has examined for this reaction the possibility of activation in a large number of degrees of freedom, and finding that the coincidence of large reaction velocity and high temperature coefficient cannot be explained in this way, suggests that the reaction may take place in stages (lower hydrates); by postulating suitable reaction rates with quite moderate temperature coefficients, the large " over-all " temperature effect is accounted for, and also the fact that the intermediate stages are not detectable.

It is therefore of interest to repeat the calculation of β for the simpler case of silver carbonate decomposing in the absence of carbon dioxide. From the data of Expt. 1 (p. 2638), $v/r = 2{\cdot}1 \times 10^{-3}$ (min.$^{-1}$) at $T = 420°$ (Abs.); $r = 0{\cdot}003$ cm.; $A = 23{,}400$. Taking for the vibration frequency (ν) 5×10^{12} sec.$^{-1}$ and for the spacing of the ionic layers in the carbonate (λ) 5×10^{-8} cm., then we have $\beta' = v/\nu\lambda = 4 \times 10^{-13}$, whereas from the temperature coefficient $\beta = 6 \times 10^{-13}$. The value 0·003 cm. for the average particle size is an upper limit; and it is known that crystals frequently contain microfissures, so that the effective particle size may be considerably less, and consequently the calculated value of β' is an upper limit. The main point, however, is that the enormous discrepancy found in the case of calcium carbonate hexahydrate between the observed value of β and that calculated from the temperature coefficient using the simple exponential function is not found in the simpler decomposition of silver carbonate. Both reactions are endothermic.

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