69. *Kinetics of Salt-hydrate Dissociations:* $MnC_2O_4,2H_2O = MnC_2O_4 + 2H_2O$.

By Bryan Topley and Mervyn L. Smith.

In continuation of previous kinetic studies of salt hydrates (*Proc. Roy. Soc.*, 1931, *A*, **134**, 224; 1932, **136**, 413; *Phil. Mag.*, 1932, **14**, 1030), we have examined in detail over a range of temperature and water-vapour concentration the velocity of dissociation of manganous oxalate dihydrate.

The main interest of the results lies in the unusual dependence of the rate of dissociation upon the concentration of water vapour in the atmosphere surrounding the solid. This dependence, in reactions of the type $\text{Solid}_{\text{I}} \rightleftharpoons \text{Solid}_{\text{II}} + \text{Gas}$, seems normally to be that the reaction velocity constant is a maximum when the concentration of gaseous product is zero and decreases continuously to zero at the equilibrium concentration. The reaction now described is an exception to this generalisation, since there is a strong acceleration of the rate by water vapour within a certain well-defined range of pressures. (The effect does not resemble the catalysis by traces of water vapour associated with the behaviour of intensively dried systems.)

EXPERIMENTAL.

The apparatus and method of experiment are similar to, and the terminology employed in this paper is the same as, those previously used (*loc. cit.*; and J., 1929, 2633). The reaction was followed by weight decrease of a sample of the hydrate contained on a light glass pan hung from a quartz-spring microbalance by means of a quartz thread descending from the microbalance chamber into a long tube kept in a thermostat. When it was desired to remove the water molecules as efficiently as possible after they had left the solid, phosphoric oxide was placed in the tube near the solid, and permanent gas was removed by a mercury-vapour pump and a charcoal–liquid-air trap. For experiments in which the solid decomposed in an atmosphere of known water-vapour concentration, the two methods previously described in detail were used: *i.e.*, for partial pressures of water vapour up to 0·2 mm., the " flow " method with hydrogen as a carrier gas was available, and for higher pressures the " static " method, an ice or water bulb at controlled temperatures being used to maintain known water-vapour pressures. It had been found in the earlier work that the two methods agree in the overlapping range when both are available, and confirmation of this has now been obtained.

Manganous oxalate dihydrate was prepared by addition of finely divided potassium permanganate to hot oxalic acid solution. After thorough washing with boiling water, the product consists of small, white, apparently octahedral crystals, fairly even in size. From the application of Stokes's law to the rate of fall of these through their saturated solution, the radius of the equivalent spherical particle was found to be 0·0044 cm., so that a typical reaction sample of 50 mg. contains about 5×10^4 individual crystals. The low solubility prevents the growth of single crystals large enough for rate measurements. Most of the experiments were done with reaction samples taken from the same preparation, but a second preparation gave rates in excellent agreement with the first. The weight loss after complete dehydration in a stream of nitrogen at 120° corresponded accurately to the composition of the dihydrate; therefore, decomposition of the oxalate was not to be feared in the dehydration experiments, in which the crystals were not heated above 90°.

The reaction curves (wt. loss–time) obtained in a vacuum or in a constant partial pressure of water vapour are of the strongly accelerating type. Spontaneous formation of reaction centres practically does not occur at room temperatures: the crystals are stable for days in vacuum over phosphoric oxide. At 50°, dehydration becomes perceptible only after many hours, whereas at 75° a large number of reaction centres are formed in ½ hour. It is clear, qualitatively, that the process of spontaneous nucleation of the surface has a much higher temperature coefficient than the subsequent propagation of the reaction interface. This is in agreement with the view developed in the earlier papers concerning the activation energy of interface reactions of this type.

Reactions in which the nucleation probability is small relative to the rate of propagation of the interface do not lend themselves to accurate determination of the latter, unless the crystals can be artificially nucleated at many points. Since the manganous oxalate dihydrate crystals are too small for this to be practicable by mechanical means, the following procedure was adopted with each new reaction sample: decomposition was started at 90° in vacuum, and after it had proceeded to the extent of 10—15%, a thermostat at the required reaction temperature ($<90°$) was substituted for the bath at 90°, and at the same time the water-vapour concentration was adjusted to the required value (in " static " experiments) or the hydrogen–water-vapour flow started (in " flow " experiments).

After approximately 20% decomposition, the rate falls slowly and then more rapidly, as a consequence of the decreasing area of reaction interface and the increasing " impedance effect " of the solid product (*loc. cit.*). To obtain a common basis for comparison of rates measured at other percentage decompositions than 20%, a set of experimental curves showing the reaction rate at different percentage decompositions was prepared, and used to reduce rates measured at percentage decompositions other than 20% back to this standard amount of decomposition. Since the " impedance effect " must vary somewhat both with temperature and with the concentration of water molecules maintained outside the decomposing crystals, a new curve is in principle required for any change in either of these parameters. In practice it was found sufficient to prepare a few such curves and to use the one most nearly corresponding to the conditions of the experiment in question. The following typical figures indicate the magnitude of the corrections involved:

Decomposition, %	18·4	*20·0*	27·0	36·2	42·0	47·0	57·0
Reduction factor	0·99	*1·00*	1·06	1·15	1·20	1·25	1·37

The sensitivity of the quartz-spring microbalance permitted rate measurements accurate to ± 2% within a range equal to 3% of the weight loss corresponding to complete reaction. These rates, multiplied by the appropriate factor (see above) and then divided by the initial weight of the hydrate in decigrams, gave values which we take as reaction velocity constants. The constants are arbitrary in two respects: they refer to a definite but unknown area of reaction interface, *viz.*, that produced in a 100-mg. sample of the dihydrate which has been decomposed to the extent of 20% in the standardised way explained above; and the " impedance effect " is not eliminated, but only standardised by the procedure adopted. It is probable that the velocity constants are not very seriously affected by the " impedance effect," since the decrease in rate after 20% decomposition in any one experiment is such as may feasibly be attributed mainly to the decreasing area of reaction interface; but in any case the conclusions concerning the general nature of the dependence of rate upon water-vapour concentration are not vitiated by the uncertainty as to the magnitude of this effect.

There is no evidence in the literature suggesting that a hydrate lower than the dihydrate exists. A number of runs under different conditions of water-vapour concentration and temperature were carried through until more than 90% of the combined water had been lost: no deceleration of the reaction in the neighbourhood of a hypothetical monohydrate was detectable.

The Temperature Coefficient.—Table I contains the results of experiments done by the " static " method with phosphoric oxide present in the reaction vessel. The reproducibility of velocity constants at any temperature is about ± 15%. There does not appear to be any

TABLE I.

Temp.	k, exp.	k, interp.	H_2 (mm. Hg).	Temp.	k, exp.	k, interp.	H_2 (mm. Hg).
25·0°	0·00028	0·00028	Mean of several expts. with and without H_2.	59·0°	0·023	0·022	0·19
35·0	0·0013	0·0011		64·8	0·034	0·040	0·40
45·2	0·0032	0·0039	0·26	69·7	0·070	0·070	nil
58·9	0·024	0·021	nil	69·7	0·060	0·070	0·29

effect arising from the presence of hydrogen, other than the conductivity effect, which decreases the self-cooling of the dissociating hydrate. The temperatures (col. 1) have been corrected: a thermal stationary state is established in which the suspended solid is slightly below the thermostat temperatures. (The calculation of this correction, at most 1°, was done as previously described; *Proc. Roy. Soc.*, **1931**, *A*, **134**, 235.) It being assumed that the "impedance effect" can be neglected, the velocity constants in cols. 2 and 3 are the reaction rates (in the units defined above) under the condition that the adsorbed water molecules in the reaction zone are at the lowest concentration consistent with the interfacial nature of the reaction; this concentration cannot in principle be zero (see *Phil. Mag.*, **1932**, **14**, 1080). The constants in col. 3 are obtained from the expression $\log_{10}k = 14{\cdot}83 - 5479/T$, which fits the experimental points. Col. 4 records the presence or absence of hydrogen. Experiments were also made at higher temperatures, and were actually in agreement with these, but have been rejected because analysis of the solid remaining showed that, at any rate in a vacuum, phosphoric oxide sublimed on to the hydrate in detectable quantities. The activation energy is 24·3 kg.-cals. per mol. H_2O.

The Effect of Water Vapour on the Reaction Rate.—The behaviour of a sample of the hydrate suspended in a closed and initially evacuated space shows qualitatively that water vapour can retard or accelerate the net rate of decomposition according to its concentration; as the water vapour produced by the hydrate accumulates in the reaction vessel, the rate of dissociation falls and later reaches a minimum value of the order of one-thirtieth of its previous value. Only a small part of the decrease in rate of loss of weight is attributable to increasing adsorption on the amorphous solid, because the volume and pressure of the water vapour in the reaction vessel corresponded as nearly as could be estimated with the loss in weight of the hydrate. The dissociation proceeds slowly for some time, then gradually accelerates to reach a value several times larger than the minimum rate.

The quantitative dependence of rate upon water-vapour concentration has been closely examined in the range of water-vapour pressure within which the velocity constant passes through a minimum and then a maximum with increasing p_{H_2O}. The smaller partial pressures were obtained by the "flow" method, and the larger by the "static" method; in the overlapping region where rate constants were obtained by both methods, the consistence is nearly as good as that of duplicate experiments by either method. Two series of measurements were made, at 75·9° and 68·0° (Table II).

TABLE II.

p_{H_2O}, mm. Hg.	k.	Method.	p_{H_2O}, mm. Hg.	k.	Method.	p_{H_2O}, mm. Hg.	k.	Method.	p_{H_2O}, mm. Hg.	k.	Method.
(a) *Temperature* 75·9°.											
0	0·135	S	0·0240	0·030	F	0·16	0·0165	S	2·19	0·100	S
0·0042	0·122	F	0·0257	0·024	F	0·163	0·0178	F	2·19	0·111	S
0·0096	0·097	F	0·0402	0·015	F	0·21	0·033	S	2·23	0·111	S
0·0129	0·071	F	0·0510	0·012	F	0·212	0·051	F	2·54	0·102	S
0·0136	0·062	F	0·07	0·011	S	0·33	0·062	S	2·98	0·093	S
0·0141	0·060	F	0·0824	0·0093	F	0·415	0·093	S	3·81	0·084	S
0·0146	0·072	F	0·0858	0·0089	F	0·47	0·100	S	4·58	0·067	S
0·0161	0·045	F	0·09	0·0099	S	0·955	0·132	S	4·58	0·046	S
0·0201	0·040	F	0·111	0·0090	F	1·11	0·121	S	6·54	0·035	S
0·0207	0·037	F	0·125	0·0083	S	2·19	0·121	S	9·21	0·029	S
0·0209	0·039	F	0·141	0·0092	F	2·19	0·111	S	12·79	0·017	S
0·0224	0·032	F				2·19	0·114	S			
(b) *Temperature* 68·0°.											
0	0·059	S	0·0088	0·024	F	0·0182	0·0037	S	0·161	0·0029	S
0·0044	0·041	F	0·0099	0·022	F	0·0217	0·0031	S	0·192	0·0041	S
0·0047	0·038	F	0·0108	0·013	F	0·0243	0·0025	S	0·220	0·0056	S
0·0057	0·037	F	0·0135	0·005	S	0·0305	0·0020	S	0·240	0·0063	S
0·0060	0·034	F	0·0150	0·004	S	0·0385	0·0018	S	0·277	0·0079	S
0·0077	0·020	F	0·0169	0·0077	F	0·0474	0·0016	S	0·324	0·0102	S
0·0080	0·024	F				0·127	0·0033	S			

Col. 1 gives the water-vapour pressure (in "static" experiments) or partial pressure (with hydrogen as carrier gas, in "flow" experiments) in mm. Hg. The corresponding rate constants, in the units already defined, are given in col. 2. The letters F or S indicate the "flow" or the "static" method. The temperature corrections for the crystals were negligible because of the relatively large conductivity of the hydrogen or water vapour present in these particular experiments when the rate was large; in the neighbourhood of the minimum, the cooling was in any case small. Inspection of the data shows that the behaviour is quite complicated, in marked contrast to the other systems whose behaviour in respect of the gaseous product has been studied. The two rates at zero water-vapour pressure are calculated from the formula already given for the rate in vacuum. In spite of one or two irregularities, the main outlines of the phenomenon are quite clear: at 75·9°, the rate falls sharply with small pressures of water vapour to a minimum and then rises less sharply to a maximum about equal to the rate in a vacuum. The minimum, at $p_{H_2O} = 0{\cdot}11$ mm. is very sharp; the maximum at $p_{H_2O} = 0{\cdot}9$ mm. is much less sharp, but definite. The results at 68·0° are similar, but were not followed as far as the maximum. At 75·9° the rate at the minimum is 0·07 of that in a vacuum, and the water-vapour pressure is approximately 0·0014 of the equilibrium vapour pressure. The corresponding figures at 68·0° are 0·03 and 0·00082 respectively.*

DISCUSSION.

The measured reaction velocity is the net rate of escape of water molecules into the gas phase. When the dissociating hydrate is in contact with an arbitrarily fixed concentration of water vapour, we may assume that this is in equilibrium with the adsorbed water molecules on the surface of the finely divided and porous solid product,† and that this equilibrium extends also to the reaction interface. Apart from the small proportion of the original content of combined water carried by the anhydrous product in the form of adsorbed water, the measured rate is simply the algebraic sum of the different unit processes taking place in the reaction zone. It is probable that the main forces causing the adsorption are electrostatic forces between water dipoles and the ions of the anhydrous solid, and secondary forces among the dipoles themselves, oriented by the underlying ions. When the number of water molecules in the reaction zone is sufficient, an appreciable proportion of these (mobile) molecules will occupy adjacent positions (the proportion of pairs of adjacent molecules may be much larger than a purely random distribution would allow, since there may exist a substantial lateral attraction between suitably oriented molecules). The forward and the reverse chemical reaction, in which water molecules in the reaction zone pass over a potential hill from the chemically combined state to the adsorbed state, and inversely, are controlled by the heights of this hill above the two valleys. The height from the valley representing the state of chemical combination in the hydrate lattice is determined, not only by the nature of the binding in the lattice, but also by the adsorption potential on the anhydrous salt, since the molecule surmounts the hill whilst acted upon by a force directed towards the solid reaction product as well as by the restoring force towards the hydrate lattice. If the first of these is relatively important, as it must be in a reaction so definitely of the interfacial type, then the actual energy of activation for a particular water molecule will be a function of the configuration of the adsorbed molecules in the neighbouring part of the reaction zone. The existence of a minimum rate at a certain pressure of water vapour, followed by an increase to a value near the initial (vacuum) rate, indicates that, at any rate in the region of the minimum, the positive catalytic effect increases considerably more than linearly with increasing concentration of water molecules. It seems plausible to associate this with the variation (as the concentration is increased) in the number of spaces

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* The whole water-vapour pressure range covered by these experiments is a comparatively small fraction of the complete range up to the saturated vapour pressure of the hydrate–anhydrous salt system. The latter amounts to approximately 78 mm. and 49 mm. at the higher and the lower temperature respectively. The vapour pressure (in mm. Hg) is approximately given by $\log_{10}p = 10{\cdot}438 - 2982/T$. The system approaches equilibrium extremely slowly in a tensimeter, and this formula is derived from a single prolonged experiment at 45·20° combined with calorimetric measurements previously reported (J., 1932, 1977). The calculation of the cooling corrections was based on these measurements also.

† The assumption implied is that the desorption and adsorption processes are rapid in comparison with the dissociation of the hydrate lattice; this is very probable, since the activation energy for dissociation is in the neighbourhood of 24 kg.-cals., whereas the adsorption potential cannot exceed 8 or 9 kg.-cals., for if it were larger than this, the adsorption would tend to saturation at pressures of water vapour at which, as the reaction kinetics show, saturation is not being approached. We are, of course, assuming here that the adsorption potential is also the activation energy for the desorption process, and that the temperature-independent factor is of the same order of magnitude for the dissociation and for the desorption processes.

unoccupied by adsorbed molecules, ***which are situated between occupied spaces in the reaction zone.*** One possibility is that an unoccupied space, available for a molecule dissociating over the potential hill, is associated with a lower hill if it falls between two (or more) adsorbed water molecules oriented with their outer poles having the opposite sign to that presented by the escaping water molecules. With a suitable configuration the activation energy might be lowered by several kg.-cals.; at the same time, the mutual potential of oppositely oriented molecules adsorbed within range of each other's attraction will increase the activation energy required to pass from the adsorbed to the combined state; and diminish correspondingly the probability of the recombination. It does not seem extreme to suppose a change in the height of the hill of as much as 4 kg.-cals., which would correspond to an increased probability of dissociation over the hill, or a decreased probability of the reverse reaction, of over 300-fold. As the reaction zone becomes still more densely occupied, the number of spaces of any sort available to receive molecules from the hydrate lattice will decrease until finally the rates of dissociation and of recombination become equal. No quantitative development of this view is possible in the absence of knowledge of the intermolecular and interionic distances involved; but if it is correct to attribute the (net) positive catalysis by water vapour to a modification of the activation energy as suggested, then it is to be anticipated that the whole effect will depend very much upon a suitable spacing of the positive and negative ions of the solid reaction product.

Menzies and Potter (*J. Amer. Chem. Soc.*, 1912, **34**, 1452) describe qualitatively the behaviour of the hydrate $3As_2O,5H_2O$ on dehydration, which is apparently similar to that of the $MnC_2O_4,2H_2O$. They found that at 170° the dehydration was more rapid and more thorough in the presence of 300 mm. than of 20 mm. of water vapour, and still more so than in the presence of 10 mm.

SUMMARY.

The dissociation reaction $MnC_2O_4,2H_2O = MnC_2O_4 + 2H_2O$ has been studied kinetically. Spontaneous nucleation of the surface of the crystals is comparatively infrequent at temperatures suitable for measurements of the rate of propagation of the interface, and rate measurements have been confined to samples of the hydrate nucleated at a higher temperature.

The activation energy for the dissociation in vacuum is 24·3 kg.-cals.

The rate of dissociation is a complicated function of the concentration of water vapour surrounding the solid; with increasing concentration, the rate constant at first decreases strongly, passes through a minimum, and increases strongly to a maximum of the same order of magnitude as the rate in vacuum, and then falls more slowly. The interpretation of this is discussed in general terms.

THE SIR WILLIAM RAMSAY LABORATORIES OF INORGANIC AND PHYSICAL CHEMISTRY,
UNIVERSITY COLLEGE, LONDON, W.C. 1. [*Received, January 11th*, 1935.]