X.—*The Dehydration of Copper Sulphate Pentahydrate.*

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Measurements of the rates of evaporation of water vapour from salt hydrates have usually been made by placing crystals of the hydrate in an atmosphere of air over a suitable dehydrating agent (compare Rae, J., 1916, **109**, 1229; Crowther and Coutts, *Proc. Roy. Soc.*, 1924, **106**, 215). Under such conditions, an induction period is frequently observed, due to the slow rate at which centres of dehydration are formed on the surface (Langmuir, *J. Amer. Chem. Soc.*, 1916, **38**, 2263). In such cases, the maximum rate of evaporation is not attained until the crystals have undergone considerable decomposition. Removal of the air increases the rate of evaporation, but the induction period is not thereby removed (compare Bružs, *Z. physikal. Chem.*, 1929, *B*, **3**, 434).

The haphazard formation of centres of dehydration on the surfaces of crystals leads to the formation of curved surfaces of evaporation, the areas of which, after a given time, are dependent on the number of centres formed, their position, and their time of origin. The area of the interface from which the water is liberated is thus dependent on chance, and is so uneven that it can neither be measured accurately nor evaluated.

These difficulties can be avoided by employing large single crystals of known area which have been activated by rubbing with the product of the dehydration. For example, a crystal of the pentahydrate of copper sulphate, after being rubbed with the monohydrate and placed in a vacuum, forms innumerable centres all over its surface, and the interface which is ultimately formed between the pentahydrate and the monohydrate consists of a series of planes running parallel to the original surfaces of the crystal. This makes it easy to determine the area of the interface from the dimensions of the crystal and the weight of water which has been lost at any time from the beginning of the dehydration. Thus, values for the rate of evaporation from unit area of interface can be calculated.

For an absolute measurement of rate of evaporation, it is clear that the water molecules must evaporate into a space from which return to the surface is impossible. Such an arrangement cannot readily be obtained in practice, but the rate of return can be made very small by using high vacua and suitably shaped containing vessels. An experimental arrangement is described below, which, as a result of many trials, has been found to be satisfactory for this purpose.

From the temperature coefficient of the rate of evaporation, the critical increment of the process of evaporation can be obtained. The significance of this energy is uncertain, unless the unit process to which it refers is known. There will be at least three possible rates to take into account—(1) the rate of loss of water at the interface $CuSO_4,5H_2O$–$CuSO_4,xH_2O$, where x may be 3, 1, or 0, (2) the rate of diffusion of water vapour across the layer of dehydrated substance, which increases in thickness with time, and (3) the rate of evaporation of water from the external surface of the crystal. If (1) is the rate which determines the velocity of evaporation, then v/A, where v is the velocity and A the area of the interface at any time, will be constant throughout the whole process; if (2) is important, then v/A should decrease as the crystal is dehydrated; and if (3) corresponds to the process measured, then the velocity of evaporation will be independent of the time. Experiment shows that v/A does not change very markedly with the thickness of the dehydrated layer, so that in the case of the pentahydrate of copper sulphate, the slowest process is the change occurring at the interface between the unchanged and the dehydrated substance.

EXPERIMENTAL.

Crystals of the pentahydrate of copper sulphate weighing 0·2—0·5 g. were employed. These were grown slowly from small crystals at room temperature, and during growth, were turned over frequently. In the selection of these crystals, attention was paid to their freedom from defects, and those with numerous facets were rejected. Their thickness was measured by a micrometer screw gauge, and the other dimensions were measured by means of a Zeiss glass scale calibrated in 0·5 mm. The surfaces of these crystals were activated by 15 minutes' rubbing with copper sulphate monohydrate enmeshed in a piece of silk.

The crystals of copper sulphate were suspended singly in the apparatus described below by means of four thin pieces of platinum wire attached to a quartz-fibre spring made after the manner of McBain (*J. Amer. Chem. Soc.*, 1926, **48**, 690).* The quartz springs, made by winding on a steel rod, were calibrated by measuring the elongation under known weights, a Wilson travelling microscope being used for this purpose.

Apparatus.—Several forms of apparatus were tried, in all of which the water was removed in a high vacuum by pumping the vapour through U-tubes immersed in liquid air. In the earlier forms, the water was pumped off below the crystal by one exit (Apparatus A),

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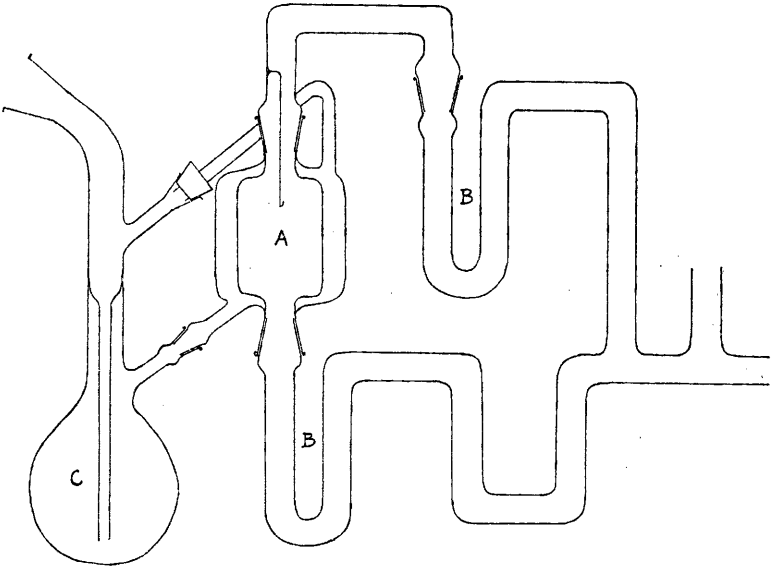
* This balance has been used by Hume and Colvin in a study of the decomposition of potassium hydrogen oxalate hemihydrate (*Proc. Roy. Soc.*, 1929, *A*, **125**, 642).

but in the later types, in order to prevent the return of water molecules to the crystal from above, it was removed by two exits, one above and the other below the crystal (apparatus C; see Fig. 1). The bulb containing the crystal was placed in a constant-temperature oven in the earlier experiments, and surrounded by the vapour from a constant-boiling liquid in the later experiments.

In Fig. 1, A is a Pyrex vessel, 5 cm. in diameter and 15 cm. long, in which the crystal is suspended. It was surrounded by the vapour from C or else by water at a constant temperature. The water vapour was withdrawn through wide tubing 2 cm. in diameter, and *via* the two **U**-tubes B immersed in liquid air.

FIG. 1.



A Hyvac pump and a mercury condensation pump were used in evacuation, and the pressures read on a McLeod gauge. The rates of evaporation were affected when there was a small leak of air into the apparatus, but no effect was observed if the pressure was kept lower than 10^{-4} cm.

The dehydrated crystals were found to consist of $CuSO_4,H_2O$ unless the experiment was unduly prolonged. The rate of loss of water from the monohydrate is very slow: even at 80°, a crystal originally weighing 0·339 g. (see Expt. I) lost only 0·00093 g. per hour after it had been converted into monohydrate.

Partly dehydrated crystals show a core of unchanged hydrate, and the surfaces of this core run parallel to the surfaces of the original crystal. The thicknesses of the dehydrated substance, $CuSO_4,H_2O$, were practically the same on all faces.* This simplified the calculation of the change in the area of the interface with time.

Area of Interface.—The boundaries of the areas of the faces of the crystal and of the area of its chief cross-section were first drawn on squared paper. On the same diagrams were drawn the boundaries of the faces and cross-section of the core of pentahydrate which remained at various stages in the dehydration : the stages chosen were those corresponding to definite thicknesses of the shell of monohydrate. From these diagrams, the areas of the interface and the volumes of the core for four stages in the process of dehydration were evaluated. This treatment gave the volume of unchanged pentahydrate and the area of interface for each of four values of the thickness of the shell of changed salt. The loss of water and the related values, the changes in length of the quartz spring corresponding to the areas of interface so calculated, are readily obtained from the volumes. The values of the area of interface were then plotted against decrease in length of the quartz spring.

Experimental Results.

The decrease in the length of spring depends on the weight of the crystal and the sensitivity of the spring ; on an average, it was about 0·6 cm. Such a change could be measured to about 1 part in 600 parts. The dehydration was in general followed until the pentahydrate was completely converted into the monohydrate ; beyond this point, loss of water was very slow, and the crystal became dark. The decrease in length of spring, calculated from the original weight of the crystal, assuming that dehydration proceeds to monohydrate, was in two cases 0·602 and 0·374 cm. The observed values were 0·604 and 0·370 cm., respectively. Typical curves of length of spring plotted against time are given in Fig. 2. The curve for 56° (Curve II) is curious in that, when 2 mols. of water had been lost, there was a marked decrease in the rate of evaporation (see later).

The following results (Expts. I and II) were obtained with an early form of the apparatus in which water was removed by one exit only. The tables give the dimensions of the crystals, the time in hours,† the decrease in length of the spring (x), the change in length of spring *per hour* (dx/dt), the area of the interface, A, and the velocity of dehydration, k, expressed as g. of water lost *per*

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* These were measured by breaking a partly dehydrated crystal and examining the depth of penetration under the microscope. These depths were the same within 10%.

† The first of the times given for each experiment includes that required to heat the crystal to the temperature of the experiment, and hence has little significance.

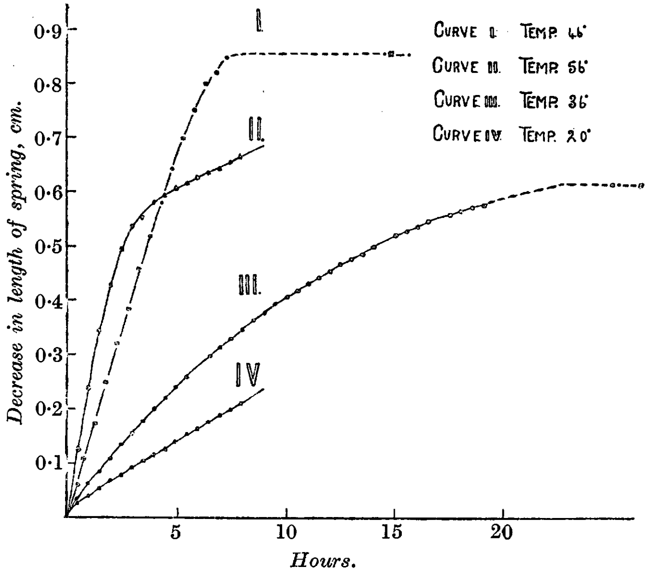
minute from unit area of interface. The total elongation given is the change in length of spring at the end of the dehydration to $CuSO_4,H_2O$.

Expt. I. Temp. = 36·5°; weight = 0·339 g.; area of crystal = 2·40 cm.^{2}; thickness = 0·205 cm.; sensitivity of spring = 6·15 cm./g.; total elongation = 0·60 cm.

t	0·75	1·8	2·8	4·0	5·2	6·6	9·7	13·8
x, cm.	0·05	0·10	0·15	0·20	0·25	0·30	0·40	0·50
dx/dt	0·050	0·048	0·046	0·042	0·038	0·036	0·030	0·023
A, cm.^{2}	2·32	2·29	2·20	2·11	2·00	1·85	1·52	1·13
$k \times 10^5$	5·8	5·7	5·7	5·4	5·2	5·3	5·3	5·5

FIG. 2.

Dehydration curves for $CuSO_4,5H_2O$.



The loss of water was measured up to a composition of $CuSO_4,H_2O$, at which the rate of evaporation decreased abruptly to about 0·0002 g. per hour. The extrapolated value for k at zero time is $5·8 \times 10^{-5}$, and its value is practically constant throughout.

Expt. II. Temp. = 36·5°; weight = 0·216 g.; area of crystal = 1·96 cm.^{2}; thickness = 0·144 cm.; sensitivity = 6·15 cm./g.; total elongation = 0·35 cm.

t	1·0	2·2	3·5	5·1	6·9	9·2
x, cm.	0·05	0·10	0·15	0·20	0·25	0·30
dx/dt	0·044	0·040	0·036	0·030	0·023	0·0175
A, cm.^{2}	1·85	1·72	1·60	1·40	1·25	1·00
$k \times 10^5$	6·4	6·3	6·1	5·4	5·0	4·8

In Expt. II, the crystal was smaller than that in Expt. I, and it had a greater ratio of area to volume. The values of k decreased with time from 6·4 to 4·8 × 10^{-5} g./min. Similar decreases occurred in Expts. III and IV, and a drift is also observable in Expt. VII.

Apparatus B.—The results given in Expt. III were obtained with an apparatus similar to that shown in Fig. 1, except that the constant temperature was obtained by placing the apparatus in an air thermostat. The water was removed both above and below the crystal, without, however, changing the magnitude of k appreciably.

Expt. III. Temp. = 36·5°; weight = 0·282 g.; area of crystal = 2·33 cm.^{2}; thickness = 0·150 cm.; sensitivity = 6·91 cm./g.; total elongation = 0·57 cm.

t	1·6	3·1	5·2	7·6	9·2	10·8
x, cm.	0·1	0·2	0·3	0·4	0·45	0·50
dx/dt	0·063	0·054	0·046	0·036	0·030	0·024
A, cm.^{2}	2·22	2·00	1·74	1·48	1·30	1·10
$k \times 10^5$	6·8	6·5	6·4	5·9	5·6	5·3

Apparatus C.—A further change was then made in which the dehydration chamber was jacketed and the crystal maintained at constant temperature by the vapour of boiling ether.

Expt. IV. Temp. = 35·1°; weight = 0·479 g.; area of crystal = 3·10 cm.^{2}; thickness = 0·190 cm.; sensitivity = 6·91 cm./g.; total elongation = 0·95 cm.

t	1·25	2·5	4·1	5·8	7·7	9·9	12·4	15·4
x, cm.	0·10	0·20	0·30	0·40	0·50	0·60	0·70	0·80
dx/dt	0·076	0·070	0·062	0·055	0·049	0·042	0·037	0·033
A, cm.^{2}	3·00	2·85	2·7	2·52	2·32	2·15	1·95	1·75
$k \times 10^5$	6·1	5·9	5·5	5·3	5·1	4·7	4·6	4·6

Expt. V. Temp. = 35·1°; weight = 0·205 g.; area of crystal = 1·86 cm.^{2}; thickness = 0·1135 cm.; sensitivity = 10·52 cm./g.; total elongation = 0·60 cm.

t	1·4	3·1	5·0	7·2
x, cm.	0·1	0·2	0·3	0·4
dx/dt	0·060	0·057	0·050	0·0425
A, cm.^{2}	1·75	1·60	1·47	1·35
$k \times 10^5$	5·5	5·7	5·4	5·3

Expt. IV shows a very appreciable fall in the values of k. In the calculation of the critical increment, it will therefore be necessary to use the value for the velocity coefficient obtained by extrapolation back to zero time. In Expt. V, with a much smaller crystal, the rates per unit area are practically constant.

Experiments in the Neighbourhood of Room Temperature.—At this temperature, the rate of evaporation is so slow that the dehydration was not followed up to the monohydrate stage, so that there is not so large a drift in the values of k.

Expt. VI. Temp. = 26·5°; weight = 0·266 g.; area of crystal = 2·10 cm.^{2}; thickness = 0·134 cm.; sensitivity = 6·91 cm./g.

t	1·1	2·8	4·6	6·6	8·6	10·8
x, cm.	0·05	0·10	0·15	0·20	0·25	0·30
dx/dt	0·030	0·027	0·027	0·025	0·0245	0·0205
A, cm.^{2}	2·05	2·00	1·90	1·84	1·73	1·62
$k \times 10^5$	3·5	3·3	3·5	3·3	3·4	3·1

Expt. VII. Temp. = 21·5°; weight = 0·348 g.; area of crystal = 2·31 cm.^{2}; thickness = 0·156 cm.; sensitivity = 10·52 cm./g.

t	1·5	2·0	2·5	3·5	4·0	6·5	8·0
x, cm.	0·068	0·084	0·103	0·140	0·153	0·230	0·270
dx/dt	0·040	0·037	0·035	0·034	0·031	0·030	0·028
A, cm.^{2}	2·22	2·20	2·16	2·10	2·07	1·98	1·94
$k \times 10^5$	2·9	2·7	2·6	2·6	2·4	2·4	2·3

Expt. VIII. Temp. = 20·5°; weight = 0·202 g.; area of crystal = 1·75 cm.^{2}; thickness = 0·106 cm.; sensitivity = 10·52 cm./g.

t	2·20	3·25	5·25	7·30
x, cm.	0·075	0·10	0·15	0·20
dx/dt	0·0265	0·0245	0·0245	0·024
A, cm.^{2}	1·67	1·65	1·60	1·55
$k \times 10^5$	2·5	2·35	2·4	2·45

Results at the Temperature of Boiling Carbon Disulphide, 46°.—Expts. IX, X, and XI were carried out at 46°. On account of the rapidity of the change, no measurements could be made of the rate in the very early stages of the dehydration. At this temperature, the values of k do not decrease with time in the manner found with some of the experiments at 36°. There was, however, evidence of an induction period. Only the early part of Expt. XI was satisfactory.

Expt. IX. Temp. = 46·25°; weight = 0·263 g.; area of crystal = 2·49 cm.^{2}; thickness = 0·111 cm.; sensitivity = 10·52 cm./g.; total elongation = 0·85 cm.

t	1·08	1·78	2·8	3·6	4·8	5·7
x, cm.	0·15	0·25	0·40	0·50	0·65	0·75
dx/dt	0·140	0·149	0·138	0·123	0·119	0·102
A, cm.^{2}	2·30	2·17	1·97	1·80	1·64	1·42
$k \times 10^5$	9·7	11·0	11·1	10·8	11·5	11·3

Expt. X. Temp. = 46·0°; weight = 0·325 g.; area of crystal = 2·41 cm.^{2}; thickness = 0·152 cm.; sensitivity = 10·52 cm./g.; total elongation = 0·99 cm.

t	2·4	3·25	4·1	5·1	6·1	7·2	8·4	9·0
x, cm.	0·25	0·35	0·45	0·55	0·65	0·75	0·85	0·90
dx/dt	0·117	0·114	0·109	0·102	0·093	0·087	0·085	0·071
A, cm.^{2}	2·12	2·00	1·86	1·70	1·60	1·45	1·30	1·12
$k \times 10^5$	8·9	9·1	9·4	9·6	9·2	9·5	10·3	10·0

Expt. XI. Temp. = 45·7°; weight = 0·282 g.; area of crystal = 2·31 cm.^{2}; thickness = 0·143 cm.; sensitivity = 10·52 cm./g.

t	1·0	2·5	3·5
x, cm.	0·118	0·307	0·417
dx/dt	0·125	0·121	0·101
A, cm.^{2}	2·14	1·91	1·79
$k \times 10^5$	9·3	9·9	9·0

Results at the Temperature of Boiling Acetone, 56°.—At this temperature also, the dehydration proceeds at a constant rate per unit area of interface, but there is a curious difference between the dehydration at this temperature and that at lower temperatures (see Fig. 2). A break occurs on the dehydration curve at the composition $CuSO_4,3H_2O$, and if the crystal is broken at this stage, there is no core of pentahydrate. The interface thus moves into the crystal at a relatively faster rate than is the case for experiments at lower temperatures, since only 2 mols. of water are lost instead of 4. The dehydration of $CuSO_4,3H_2O$ proceeds slowly, and after partial dehydration to $CuSO_4,H_2O$, the crystal shows a more amorphous structure than when it has been dehydrated to $CuSO_4,H_2O$ directly. In the latter case, the pseudomorph breaks along the old cleavage planes of the crystal, but crystals dehydrated at 56° do not show this feature when broken.

Expt. XII. Temp. = 56·0°; weight = 0·423 g.; area of crystal = 2·57 cm.^{2}; thickness = 0·180 cm.; sensitivity = 10·52 cm./g.; elongation at break = 0·65 cm.

t	1·0	1·45	1·95	2·55
x, cm.	0·25	0·35	0·45	0·55
dx/dt	0·236	0·231	0·183	0·163
A, cm.^{2}	2·12	1·85	1·64	1·40
$k \times 10^5$	17·7	19·8	17·8	18·4

Expt. XIII. Temp. = 55·85°; weight = 0·325 g.; area of crystal = 2·31 cm.^{2}; thickness = 0·145 cm.; sensitivity = 10·52 cm./g.; elongation at break = 0·48 cm.

t	0·75	1·25	1·75
x, cm.	0·180	0·290	0·390
dx/dt	0·226	0·208	0·174
A, cm.^{2}	2·00	1·75	1·49
$k \times 10^5$	18·0	18·9	18·5

Expt. XIV. Temp. = 56°; weight = 0·249 g.; area of crystal = 2·26 cm.^{2}; thickness = 0·206 cm.; sensitivity = 10·52 cm./g.; elongation at break = 0·56 cm.

t	1·0	2·0	2·5	3·0
x, cm.	0·252	0·392	0·460	0·518
dx/dt	0·180	0·133	0·126	0·103
A, cm.^{2}	1·77	1·36	1·16	0·93
$k \times 10^5$	16·1	15·5	17·3	17·6

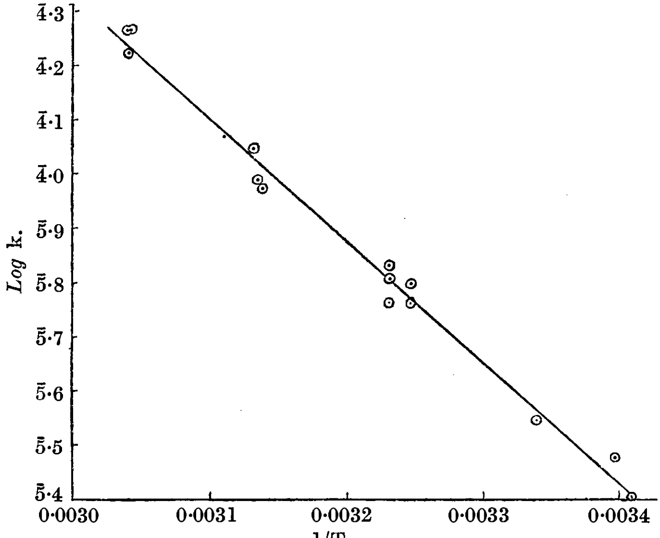
The dehydration of $CuSO_4,3H_2O$ occurs at the following rates: For Expt. XII, 0·0022 g./hour; for XIII, 0·0019 g./hour; and for XIV, 0·0021 g./hour.

Temperature Coefficient of the Dehydration.—The following table gives the rates of evaporation per unit area. Where the rates show a drift, the value for zero time has been taken, but where there is evidence of an induction period, this has been ignored in the evaluation of *k*.

Temp.......	20·5°	21·5°	26·5°	35·1°	36·5°	46·0°	56·0°
$k \times 10^5$ ...	2·55	3·0	3·5	5·8	5·8	9·4	16·8
				6·3	6·4	9·7	18·4
					6·8	11·1	18·4

FIG. 3.

Temperature coefficient of rate of dehydration of $CuSO_4,5H_2O$.



The values of log *k* are plotted against the reciprocal of absolute temperature ($1/T$) in Fig. 3, and the values at 56·0° lie on the same straight line as those for the other temperatures. The value for the critical increment is 10,300 * calories, and the value of μ calculated from this is 2·77, which corresponds to one of the vibration frequencies of the water molecule.

Discussion.

Any detailed discussion of the results can have but little value until further hydrates have been studied. The main features which

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* This critical increment is very much smaller than that found by Topley and Hume (*Proc. Roy. Soc.*, 1928, *A*, **120**, 211) for the decomposition of $CaCO_3,6H_2O$.

are of interest may, however, be examined. It is rather surprising that the rate of evaporation is so little affected by the thickness of the dehydrated salt. Experiment shows that there is a constant unidirectional streaming of molecules from unit area of the interface $CuSO_4,5H_2O$–$CuSO_4,H_2O$ to the surface of the crystal. The structure of the material through which the molecules escape can only be guessed. Its nearest analogue is probably that of the structure of amorphous carbon. The molecules probably escape through capillary passages, the diameter of which is of the same order as that of the molecular diameter of water. Thus the movement occurs within the range of the attractive forces of the molecules forming the capillaries, and will thus correspond to that which occurs in an adsorbed gas film. There will be a pressure gradient in the adsorbed film which lies between the interface and the surface of the crystal. This is necessarily the case, since the molecules after leaving the interface expand from regions of small to regions of greater volume. The rate of return of water molecules to the interface will depend on the pressure exerted by the water molecules at the interface, just as in the case of a three-dimensional system, and this rate will be negligible only if the pressure in the neighbourhood of the interface is negligible. It is unlikely that this is the case when the interface is covered by a layer of dehydrated substance, so that the constancy of the values of k may mean that the pressure in the neighbourhood of the interface is constant at constant temperature and independent of the thickness of layer of dehydrated salt. Thus the values of k so far obtained may not be the true rates, and hence the temperature coefficient may not give the true critical increment of the dehydration process. Evidence for this view must be sought in measurements of the rate of evaporation in the very early stages of the dehydration of the crystal, when the dehydrated layer is thin, and such measurements can be accurately made only at low temperatures. The curves obtained for 20° (compare curve IV, Fig. 2) are practically linear, but if the linear portion of the curves be extrapolated back to $t = 0$, they do not pass through the origin. The rate of dehydration over the first hour is much larger than the steady rate reached subsequently.

The change in the nature of the dehydration phenomena which occurs between 46° and 56° also provides an indication that the constant rates are not true rates. At 56° the dehydration product is the trihydrate, whereas at 46° it is the monohydrate. This behaviour can be explained in terms of the pressure of the water molecules in the surface gas film of the dehydrated layers. As the temperature rises, this pressure increases until it may become greater than the equilibrium pressure of water over the trihydrate.

Since at 56°, this hydrate is not dehydrated until the whole of the pentahydrate has disappeared, it is evident that the surface pressures in the dehydrated layers must be greater than the dissociation pressure of the trihydrate. If such pressures prevail, then the possibility of return of water molecules to the interface is always present.

The slow rates of dehydration of the monohydrate and the trihydrate are also of interest. The trihydrate on dehydration does not give a visible interface similar to that obtained when the pentahydrate is dehydrated. Evaporation appears to proceed from the whole of the internal surface of the pseudomorph. The movement of the water molecules may therefore be restricted by the production of discontinuities in the internal surface of the dehydrated substance.

Summary.

The rates of dehydration of single crystals of $CuSO_4,5H_2O$ have been measured in a vacuum over a range of temperatures from 20° to 56°. Crystals of known weight and area were activated by rubbing with the powder of the monohydrate. Such crystals after partial dehydration gave a core of pentahydrate, the surfaces of which ran parallel to the original surfaces of the crystal. The rate of loss of water divided by the area of the interface between the pentahydrate and the dehydrated product was practically constant for the higher temperatures, but in some experiments at the lower temperatures, the velocity coefficient decreased as dehydration proceeded.

Below 46° the dehydrated product was the monohydrate, which remains in the form of a pseudomorph which loses water very slowly. At 56°, the first product of the dehydration is the trihydrate, which does not decompose until all of the pentahydrate has disappeared. The trihydrate then slowly gives up its water at a constant rate.

A straight line is obtained by plotting log k against the reciprocal of the absolute temperature, k being the velocity coefficient per unit area of interface. The critical increment of the process is 10,300 calories, and $\mu = 2{\cdot}77$, which corresponds to one of the vibration frequencies of the water molecule.

It is concluded that the rates measured may not be the true rates of evaporation, and that the critical increment may not be the true value for the unit process which occurs at the interface.

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