# 739. *The Rate of Dehydration of Chrome Alum.*

By M. M. T. Anous, R. S. Bradley, and (the late) J. Colvin.

The rate of dehydration *in vacuo* of large single crystals of chrome alum of mass *ca.* 1 g. has been studied at thermostat temperatures of 15—35°, a McBain balance being used and special attention being paid to the self-cooling of the crystals. The activation energy is *ca.* 23 kcals. per mole, and the kinetics of dehydration are in rough agreement with the Polanyi–Wigner expression. Pressures of air up to 1 mm. of mercury scarcely affect the rate of dehydration if this is corrected to a uniform temperature to allow for self-cooling; water vapour depresses the reaction at all pressures studied up to 1·7 mm. of mercury. The dehydration has also been studied at $-1{\cdot}7°$ to $-12°$, at which self-cooling is negligible, a silica microbalance being used by means of which velocities of propagation of the interface as low as 0·2 Å sec.$^{-1}$ could be measured. At the low temperatures the activation energy is *ca.* 30 kcals. per mole, and the temperature-independent factor is too large in comparison with the Polanyi–Wigner theoretical value by a factor of $10^{10}$. The heat of decomposition per mole of water lost for the reaction

$$K_2SO_4,Cr_2(SO_4)_3,24H_2O\ (s.) \longrightarrow K_2SO_4,Cr_2(SO_4)_3,12H_2O\ (s.) + 12H_2O\ (g.)$$

has been determined at 25° to be $\Delta H_{298} = 12{\cdot}79$ kcals.

The rate of dehydration of chrome alum *in vacuo* and in the presence of water vapour has been studied by Cooper and Garner (*Proc. Roy. Soc.*, 1940, **174**, *A*, 487) and shows some anomalous features. The activation energy for dehydration *in vacuo* was found to be of the order 31 kcals. per mole; this is much greater than the heat of dissociation (10 kcals. per mole), which is the normal activation energy for the dehydration of hydrates. The temperature-independent factor $B$ in the expression, linear rate of propagation of the interface, $u = Be^{-E/RT}$, where $E$ is the activation energy, is correspondingly very high in comparison with the value deduced by simple theory. The reaction was studied on isolated crystals *in vacuo*, and a large self-cooling occurred, so it seemed worth while to reinvestigate the reaction (*a*) at 15—35°, with particular attention to the measurement of the self-cooling, and (*b*) at temperatures below 0° at which self-cooling is negligible. The second method involved new techniques which are described below.

## Experimental.

*Dehydration* 15—35° in vacuo.—A saturated solution of "AnalaR" chrome alum, prepared at a temperature not exceeding 30°, was filtered and freed from dissolved air by suction, and allowed to crystallize in a dust-free air thermostat at 20°, calcium chloride being used as absorbent. Crystals were turned over periodically, and after growth were dipped in distilled water, dried on filter-paper, and stored over powdered chrome alum in a desiccator. Owing to the influence of the vessel, the crystals had two broad parallel faces with six side faces, all faces being 111; in Fig. 1 the relation of the crystal form to the bipyramid is shown. No difference in behaviour was observed when crystallization was carried out in the presence of dilute sulphuric acid.

The dimensions of the crystals were determined by using a Vickers projection microscope and a micrometer; the weight of the crystal as calculated from the density and volume agreed with the observed weight to within a few units %. The density was found from flotation measurements with benzene to be 1·819 at 15°.

The crystal was nucleated on all faces by rubbing it with a mixture of fine carborundum and dehydrated chrome alum, and was suspended by means of a helical silica spring $A$, Fig. 2 (sensitivity 1 g. ≡ 10 mm.), so that deflection–time curves could be obtained for the loss of water *in vacuo*. From the percentage loss of weight, $w$, the rate of propagation of the interface, $u$, could be found from the geometry of the crystal, the velocity being assumed to be independent of direction. At the end of the reaction, a half of the initial water content is lost, the remainder being presumably co-ordinated to chromium. The zero time and the value of $u$ can best be found by plotting a theoretical curve of $w$ against $ut$, where $t$ is the time, and comparing this with the experimental curve of $w$ against $t_{obs.}$. For the same value of $w$ we have $ut$ and $t_{obs.}$, and hence we can plot $ut$ against $t_{obs.}$ for various values of $w$. Since $ut = u(t_{obs.} - t_0)$, where $t_0$ is a constant, the graph of $ut$ against $t_{obs.}$ should be rectilinear, and from this graph we can determine $u$ from the slope and $t_0$ from the intercept; $u$ is found to be independent of the percentage decomposition, which shows that there is no impedance of the reaction due to the slow diffusion of water vapour through the pseudomorph.

Crystal temperatures were measured by means of a thin-junctioned copper–constantan thermocouple which was led out of the vessel $B$ (Fig. 2). The broad faces of two crystals were cemented together by means of "Durofix," in which the thermocouple was embedded with a considerable length of wire between the crystals. After the cement had dried, the pair of crystals was nucleated, suspended in the vessel *B*, and subjected to the same conditions as the crystal in *A*. The pair of crystals in *B* together equalled in weight as nearly as possible the single crystal in *A*. The thermoelectric e.m.f. was measured continuously by means of a Kent recorder, and after an initial variation in general assumed a fairly steady value during the course of the experiment. In Fig. 3 is shown the variation in temperature recorded for a crystal pair of 1·2 g., being dehydrated *in vacuo* in a thermostat at 25°.

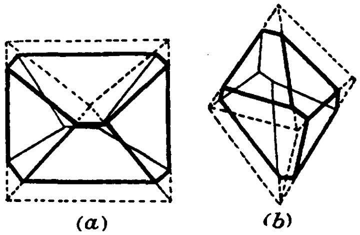


FIG. 1.
*Crystal of chrome alum and its relation to the bipyramid.*

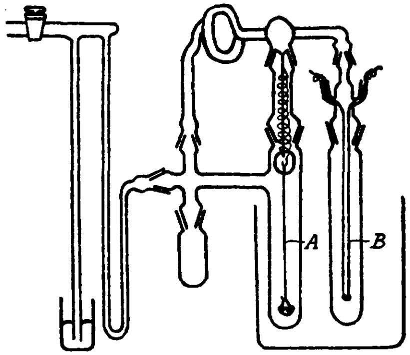


FIG. 2.
*Apparatus for " high "-temperature experiments.*

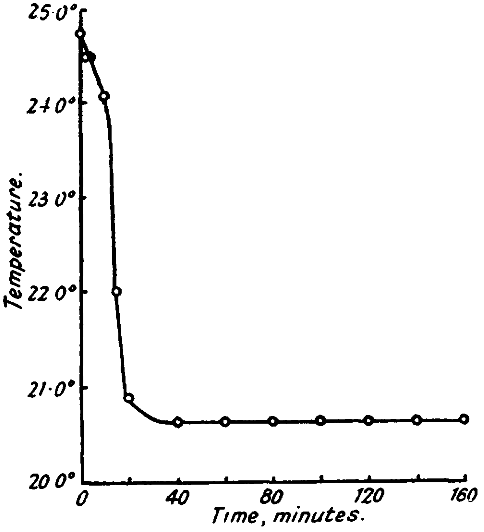


FIG. 3.
*Cooling of a crystal pair of* 1·2 *g. weight. Temperature of bath* 25°.

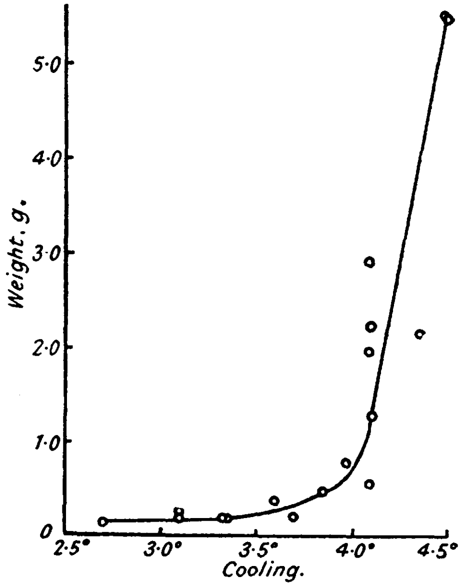


FIG. 4.
*Change of cooling with weight. Temperature of bath* 25°.

Values of the self-cooling for vacuum-dehydration were found at first to be considerably less than those recorded by Cooper and Garner (*loc. cit.*), and this result was confirmed when the thermocouple was inserted in a hole drilled in the crystal in an effort to record the interface temperature: owing to the brittle nature of the crystals and the short length of thermocouple wires embedded in the drilled hole, this method was not generally adopted. This discrepancy with published data was traced to the influence of the size of the crystal on self-cooling, and it was found that the self-cooling increased with increase in size of the crystal, but that for crystals above 1 g. in weight the self-cooling increases only slightly with increasing size of crystal, as shown in Fig. 4; moreover, the temperature was steadier for the large crystals (with only a slight increase in temperature as the reaction proceeded). It may be noted that a steady thermocouple temperature at the centre implies a state of uniform temperature in the crystal and a balance between the heat gained by radiation and conduction down the silica and that lost by reaction; conduction *within* the crystal does not enter into consideration in this steady state. In our experiments the steady state was very nearly achieved (Fig. 3), but it is possible that the temperature was roughly constant because of a balancing of conductivity effects and change in heat absorbed by the reaction as the interfacial surface decreases with time. It was therefore decided to confine the work to large crystals weighing more than 1 g. The self-cooling increased considerably with increase in the thermostat temperature, owing to the increased velocity of reaction, and was slightly dependent on the percentage decomposition, as is seen from Fig. 5, which gives the self-cooling for crystal pairs weighing 1—1·5 g., undergoing dehydration *in vacuo* in a bath at 35° for 20—60% and 40—60% decomposition. The mean self-cooling for 20—60% decomposition is as follows for large crystals (the pair, 1—1·2 g. in weight).

| | | | | |
|---|---|---|---|---|
| Bath temp. .............................. | 17·5° | 25° | 30° | 35° |
| Self-cooling .............................. | 2·15° | 4·03° | 6·30° | 8·78° |

We believe this technique to be an improvement on that previously published, for it is to be inferred from Cooper and Garner's work that the crystal pair used to measure the self-cooling did not together equal in weight the single crystal used for kinetic measurements, but were somewhat larger (confirmed by Professor W. E. Garner in private correspondence).

FIG. 5.

*Change of cooling with weight. Temperature of bath* 35°.

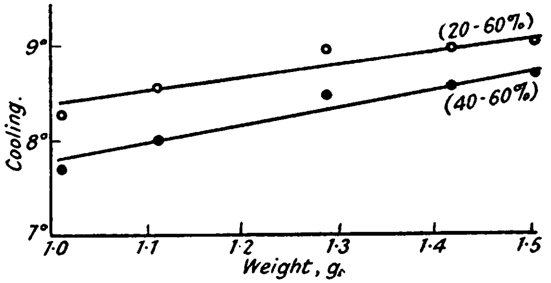
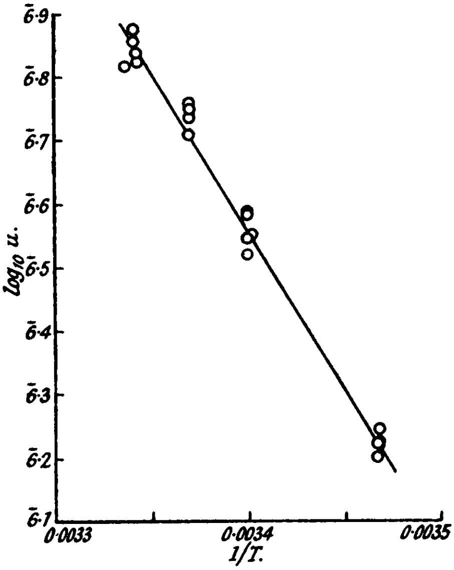


FIG. 6.

$\log_{10} u$ *plotted against* 1/T *for* 20—60% *decomposition.*



The values of $\log_{10} u$ are plotted against $1/T$, where $T$ is the absolute temperature of the crystal, in Fig. 6. Five crystals were studied for each temperature. Activation energies of 22,800 and 22,350 cals. per mole are obtained for 20—60% and 40—60% decomposition, respectively. These values are considerably less than those obtained by Cooper and Garner, but are still much greater than the heat of the reaction. The mean temperature-independent factor $B = 3\cdot6 \times 10^8$, as calculated from $u = Be^{-E/RT}$ by using the experimental value of $E$. The values of $u$ (in cm. sec.$^{-1}$) are shown below.

*Mean linear velocity of propagation of interface.*

| Temp. of crystal | $10^6u$ | Temp. of crystal | $10^6u$ | Temp. of crystal | $10^6u$ | Temp. of crystal | $10^6u$ | Temp. of crystal | $10^6u$ |
|---|---|---|---|---|---|---|---|---|---|
| | | | | 20—60% Decomposition. | | | | | |
| 15·40° | 1·57 | 15·33° | 1·74 | 21·00° | 3·83 | 23·70° | 5·07 | 26·25° | 7·49 |
| 15·40 | 1·65 | 20·98 | 3·49 | 20·97 | 3·29 | 23·70 | 5·63 | 26·50 | 6·51 |
| 15·34 | 1·64 | 21·00 | 3·79 | 23·70 | 5·59 | 23·70 | 5·39 | 26·00 | 6·62 |
| 15·28 | 1·66 | 20·90 | 3·54 | 23·70 | 5·67 | 26·25 | 7·12 | 26·08 | 6·85 |
| | | | | 40—60% Decomposition. | | | | | |
| 15·31 | 1·58 | 15·16 | 1·74 | 21·10 | 3·84 | 24·03 | 5·05 | 26·75 | 7·45 |
| 15·30 | 1·65 | 21·06 | 3·48 | 21·05 | 3·27 | 24·03 | 5·63 | 27·10 | 6·53 |
| 15·19 | 1·65 | 21·04 | 3·78 | 24·03 | 5·61 | 24·03 | 5·35 | 26·35 | 6·67 |
| 15·06 | 1·65 | 20·99 | 3·50 | 24·03 | 5·64 | 26·75 | 7·18 | 26·50 | 6·98 |

The pseudomorph product was pink, but the outer layer was greenish to bluish-grey, a phenomenon observed with mixed chromium and aluminium potassium alums by Acock, Garner, Milsted, and Willavoys (*Proc. Roy. Soc.*, **1947**, **189**, *A*, 508). The water content of each layer was determined by means of a micro-technique by heating at 300—350° to constant weight, and appeared to be the same. This identity was confirmed by *X*-ray examination of the powders, kindly undertaken by Mr. P. Markey, of this Department. In addition, $Cr_2(SO_4)_3,12H_2O$ was prepared by dehydration of violet $Cr_2(SO_4)_3,18H_2O$ *in vacuo*, and when it was mixed with potassium sulphate in molecular proportions it gave an *X*-ray powder photograph which differed considerably from that given by the two layers, suggesting that the result of the dehydration was not a mixture of separate crystals of $K_2SO_4$ and $Cr_2(SO_4)_3,12H_2O$, but a solid solution not yet prepared in the form of large crystals. An attempt to prepare the double salt was made by crystallizing a solution of chrome alum in a concentrated solution of sulphuric acid; green crystals were obtained, and were washed with benzene and alcohol and dried. The *X*-ray powder photograph differed slightly from that of the pseudomorph.

FIG. 7.

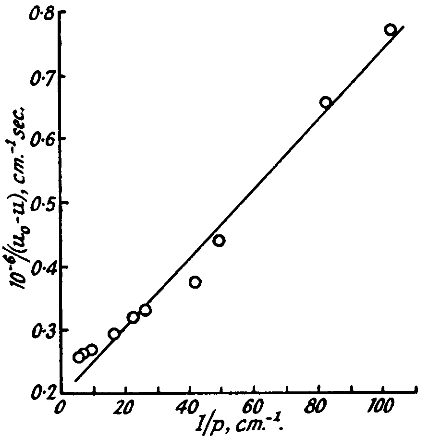
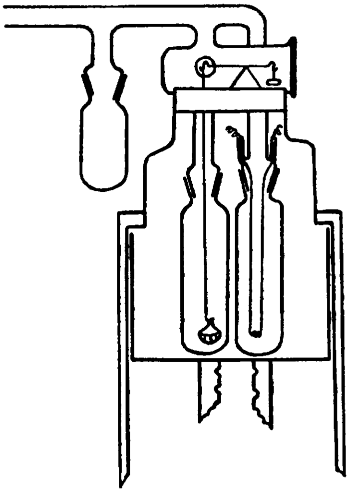


FIG. 8.

*Apparatus for low-temperature experiments.*



*Effect of Air and of Water Vapour on the Rate of Dehydration.*—The experiments described above were repeated at a bath temperature of 25° in the presence of air up to a pressure of $10^{-1}$ cm. of mercury, with very little influence on the rate after allowance for the self-cooling, except for a shallow maximum, as shown by the following data corrected to a crystal temperature of 25°:

| Pressure, cm. of Hg | $1·34 \times 10^{-6}$ | $1·63 \times 10^{-3}$ | $5·63 \times 10^{-3}$ | $1·46 \times 10^{-2}$ | $8·84 \times 10^{-2}$ | $1·06 \times 10^{-1}$ |
|---|---|---|---|---|---|---|
| $10^6u$ (cm. sec.$^{-1}$) ... | 6·36 | 6·42 | 7·68 | 7·62 | 6·79 | 6·19 |

These results suggest that the rate of loss of water is not controlled by a diffusion process through channels in the pseudomorph, since air at 1 mm. pressure would make such a process considerably slower.

The rate of dehydration was also studied at a bath temperature of 25° in the presence of water vapour at low pressures provided by a sample of water cooled by acetone and solid carbon dioxide, the temperature of which was recorded by means of a sulphur dioxide vapour-pressure thermometer. Results are given in Table I; crystals of mass 1·2 g. were used, and there is a small scatter inevitable when dealing with different crystals (see below). It will be seen that when the results are corrected to 25° there is no trace of the maximum for rate as a function of pressure reported by Cooper and Garner from their experiments on the rate of growth of *nuclei*. The normal decrease in rate due to a back pressure of water vapour is observed as with the dehydration of $CuSO_4,5H_2O$. It is possible that the water vapour acts as a depressant by forming an adsorbed layer just above the reaction zone and thereby favouring the reverse reaction, since the reaction is reversible in the region of the interfacial reaction zone. On applying Langmuir's adsorption isotherm it would be expected that $u = u_0 - k_2p/(k_3 + p)$,

TABLE I.

| Press. of $H_2O$ vapour, cm. Hg | Self-cooling | $10^6u$ (uncorr.), cm. sec.$^{-1}$ | $10^6u$ (corr.), cm. sec.$^{-1}$ | Press. of $H_2O$ vapour, cm. Hg | Self-cooling | $10^6u$ (uncorr.), cm. sec.$^{-1}$ | $10^6u$ (corr.), cm. sec.$^{-1}$ |
|---|---|---|---|---|---|---|---|
| 0·0 | 4·03° | 3·59 | 6·03 | 0·0761 | 1·50° | 2·21 | 1·66 |
| 0·00966 | 2·67 | 3·31 | 4·73 | 0·1219 | 0·31 | 1·64 | 1·70 |
| 0·02375 | 2·02 | 2·61 | 3·36 | 0·1691 | 0·87 | 1·89 | 2·12 |
| 0·0439 | 1·42 | 2·42 | 2·88 | | | | |

where $u_0$ is the velocity when the pressure $p = 0$, or $u_0 - u = k_2p/(k_3 + p)$. Hence $1/(u_0 - u)$ should be a linear function of $1/p$, as is found (see Fig. 7) to be very nearly true from the data of Table I (cf. Acock, Garner, Milsted, and Willavoys, *loc. cit.*).

The values of the self-cooling observed with water vapour were compared with theoretical predictions, the kinetic theory being used in a manner similar to that used by Birks and Bradley (*Proc. Roy. Soc.*, 1949, **198**, *A*, 226) but with an additional term to allow for radiation owing to the high values of the self-cooling. Cooper and Garner discussed only the latter term. The loss of heat per second due to reaction is $-(\mathrm{d}m/\mathrm{d}t)\Delta H/M$, where $-(\mathrm{d}m/\mathrm{d}t)$ is the rate of loss of mass, $\Delta H$ the reaction heat per mole of water lost, and $M$ the molecular weight of water. The gain of heat in ergs per second is $5{\cdot}735 \times 10^{-5}A(T_1^4 - T_0^4)$ from radiation, where $T_1$ is the temperature of the thermostat and $T_0$ that of the crystal and $A$ is the crystal area, and $2k(T_1 - T_0)aAp/\sqrt{2\pi mkT_1}$ from molecular bombardment, where $p$ is the gas pressure, $a$ the thermal accommodation coefficient, and $m$ the mass of a water molecule. Hence, at thermal equilibrium, if $\Delta H$ is expressed in ergs per mole

$$\frac{p}{(2\pi mkT_1)^{\frac{1}{2}}} \cdot 2k(T_1 - T_0)aA + 5{\cdot}735 \times 10^{-5}A(T_1^4 - T_0^4) = -\frac{\mathrm{d}m}{\mathrm{d}t} \cdot \frac{\Delta H}{M}$$

or, approximately,

$$\frac{p}{(2\pi mkT_1)^{\frac{1}{2}}} \cdot 2k \,.\, \Delta T \,.\, aA + 5{\cdot}735 \times 10^{-5}A\Delta T \,.\, 4T_1^3 = -\frac{\mathrm{d}m}{\mathrm{d}t} \cdot \frac{\Delta H}{M}$$

since $\Delta T = T_1 - T_0 \ll T_1$ or $T_0$. The approximation $T_1^4 - T_0^4 = 4T_1^3 \,.\, \Delta T$ is in error to only 3% in the extreme case. Hence the self-cooling

$$\Delta T = -\frac{\mathrm{d}m}{\mathrm{d}t} \cdot \frac{\Delta H}{M} \cdot \frac{1}{\theta_1 + \theta_2} \text{ (app.)},$$

where

$$\theta_1 = \frac{p}{(2\pi mkT_1)^{\frac{1}{2}}} \cdot 2kaA, \text{ and } \theta_2 = 5{\cdot}735 \times 10^{-5} \,.\, 4T_1^3A$$

Calculations of the theoretical value of $\Delta T$ by using the experimental mean values of $\mathrm{d}m/\mathrm{d}t$ for 20—60% decomposition for crystals of area approximately 5 cm.² for $a = 0{\cdot}3$, $0{\cdot}5$, and $1{\cdot}0$, are made and are compared with the experimental results in the following table. It will be seen that, apart from experimental scatter, the experimental results are in reasonable accord with $a = 1{\cdot}0$. It should be noted that black-body radiation and no conduction by the silica fibre are assumed, and that a condition of thermal equilibrium is assumed.

| | | Theoretical $\Delta T$ : | | |
|---|---|---|---|---|
| Press. of water vapour, cm. Hg | Experimental self-cooling, $\Delta T$ | $a = 1{\cdot}0$ | $a = 0{\cdot}5$ | $a = 0{\cdot}3$ |
| 0·0 | 4·03° | 4·00 | 4·00 | 4·00 |
| 0·00966 | 2·67 | 3·02 | 3·11 | 3·15 |
| 0·02575 | 2·02 | 2·31 | 2·50 | 2·59 |
| 0·0439 | 1·42 | 2·61 | 2·95 | 3·12 |
| 0·0761 | 1·50° | 1·66 | 2·00 | 2·19 |
| 0·1219 | 0·31 | 1·06 | 1·42 | 1·64 |
| 0·1691 | 0·87 | 0·93 | 1·28 | 1·50 |

*Rate of Dehydration at Low Temperatures.*—Since the self-cooling $\Delta T$ decreases as the thermostat temperature decreases ($\log_{10} \Delta T$ is a linear function of $T$), the self-cooling at temperatures less than 0° should be negligible, and this should provide an ideal method of studying solid reactions. Owing, however, to the low velocities at low temperatures a much more refined apparatus is necessary, and we have used the microbalance and technique described by one of us and others (Bradley, Evans, and Whytlaw-Gray, *Proc. Roy. Soc.*, 1946, *A*, **286**; Birks and Bradley, *ibid.*, 1949, *A*, **198**, 226; Bradley and Shellard, *ibid.*, p. 239; Bradley, *ibid.*, 1951, *A*, **205**, 553; Bradley and Waghorn, *ibid.*, 1951, *A*, **206**, 65). We have succeeded in making accurate measurements on velocities as low as 0·2 Å per second; much lower linear speeds could be measured if necessary.

The silica microbalance had a sensitivity of 107·1 µg. per mm., and the deflection could be read to 0·002 mm. The apparatus is shown in Fig. 8. The lower limb of the balance case dipped into a thermostat containing concentrated calcium chloride solution, provided with a thermoregulator coupled to a small heater, and a cooling unit consisting of a glass tube 5 cm. in diameter which could be filled with solid carbon dioxide. By means of a rack and pinion the thermostat tank could be raised or lowered.

It was first shown by means of the microbalance that no change in the character of dehydration occurs at low temperatures. The loss of weight of a small quantity of powdered chrome alum *in vacuo* at −5·6° corresponded to one-half the water content. Changes of weight were observed by following the deflection, and to avoid buoyancy errors initial and final readings were taken in a few mm. of air. It was also shown that a negligible self-cooling occurred: the crystal temperature was, however, slightly higher than that of the thermostat.

Owing to the fact that the whole course of the microbalance beam deflection corresponded to a very small fraction of the weight of the crystal, the method gives the linear velocity at a given percentage decomposition, and both the experimental technique and method of calculation differed from those employed with the helical spring. The correct experimental procedure was found after the following exploratory research, which was subsequently modified. A crystal of known dimensions and weight was nucleated, suspended in a silica cage from the balance, and counterpoised; by means of the side window, silica was then added to the hook on the fibre which held the crystal, the weight of the silica corresponding to 20% decomposition of the crystal. The apparatus was evacuated at 15° until the microbalance beam began to swing, air was admitted, the cold thermostat was raised into position, and after ½ hour the apparatus was evacuated and readings were taken. More than one run could be made on the same crystal by opening the case and adding quartz to replace the water lost. This procedure gave curved plots of deflection against time with poor reproducibility, a result attributed to the absorption of air by the thick layer of finely divided pseudomorph.

The percentage decomposition studied at first was therefore lowered to 5%, and the apparatus evacuated at 15° with the *thermostat in position* until the beam began to lift off the arrestment. The thermostat was then cooled by adding powdered solid carbon dioxide to the calcium chloride solution, and after 2 hours at the required temperature, during which time the apparatus was evacuated, deflection–time readings were taken. This procedure was necessary to prevent any oscillation of the balance *in vacuo*. Runs could be repeated by opening the balance, adding a small piece of silica to replace the water lost, and repeating the procedure. Percentage decompositions in the region 5—40% were studied. Good straight lines were obtained on plotting deflection against time.

The temperature of the crystal was determined as before: it was also shown that a thermocouple hanging freely inside the evacuated vessel acquired the same temperature as the crystal, and an economy of labour was effected by the use of the hanging thermocouple to measure the crystal temperature, which was slightly higher than that of the bath, possibly owing to radiation.

The linear rate of propagation could be calculated from the area of the interface $A$, which could be determined from the geometry of the crystal and the percentage decomposition. Since $A$ is virtually constant during a run,

$$-\mathrm{d}m/\mathrm{d}t = 0{\cdot}2165 A u \rho$$

where $\rho$ is the density, and the factor 0·2165 gives the loss of weight of 1 g. of chrome alum on complete decomposition.

Four crystals were studied over a range of temperature. The activation energies for all four were in fair agreement, but there was considerably greater scatter of experimental points than at the higher temperatures; it may be noted that at the "high" temperatures the value of $u$ was obtained as a mean over a large range of decomposition, and hence might be expected to show less scatter than at low temperatures. Values of the temperature-independent factor $B$ were calculated as before. The results for the four crystals are given in Table II, $u$ being in cm. sec.$^{-1}$.

TABLE II.

| Crystal $a$: $E = 30{,}400$ cals./mole; $B = 6 \times 10^{16}$ | | Crystal $b$: $E = 29{,}930$ cals./mole; $B = 5 \times 10^{16}$ | | Crystal $e$: $E = 29{,}700$ cals./mole; $B = 3 \times 10^{16}$ | | Crystal $d$: $E = 33{,}100$ cals/mole; $B = 1{\cdot}5 \times 10^{19}$ | |
|---|---|---|---|---|---|---|---|
| Crystal temp. | $10^9u$ | Crystal temp. | $10^9u$ | Crystal temp. | $10^9u$ | Crystal temp. | $10^9u$ |
| − 3·48° | 13·3 | − 1·71° | 32·3 | − 2·50° | 26·2 | −1·70° | 24·9 |
| − 3·60 | 11·4 | − 3·30 | 26·4 | − 3·75 | 16·3 | −3·95 | 21·4 |
| − 5·05 | 7·76 | − 5·50 | 13·6 | − 4·75 | 29·3 | −4·28 | 23·9 |
| − 6·75 | 6·04 | − 5·80 | 15·2 | − 5·35 | 16·0 | −4·28 | 12·8 |
| − 8·65 | 2·94 | − 6·30 | 10·3 | − 5·50 | 15·7 | −5·20 | 14·2 |
| −11·94 | 1·93 | − 7·38 | 10·0 | − 7·85 | 7·52 | −7·05 | 7·44 |
| | | −10·50 | 5·18 | − 8·18 | 4·39 | −7·65 | 5·19 |
| | | −11·45 | 4·87 | − 8·65 | 6·30 | −9·90 | 3·73 |
| | | −12·05 | 2·54 | −12·10 | 2·91 | | |

*Heat of Dissociation.*—In normal hydrate dissociations the activation energy for dehydration is equal to the heat of dissociation. For alums, however, it is doubtful if there is a true dissociation pressure, since irreversible phenomena occur on rehydration (Bielanski and Tompkins, *Trans. Faraday Soc.*, 1950, **46**, 1072), and hence the heat of dissociation when measured by the vapour pressure may be anomalous. Following a suggestion by Professor W. E. Garner, we have determined the heat of decomposition by measuring the heats of solution of chrome alum and of the dehydration product, using a thermostated Dewar flask as calorimeter, the calorimeter constant being determined by electrical heating; 0·0028 mole of $K_2SO_4,Cr_2(SO_4)_3,24H_2O$ was dissolved in 14—20 moles of water. The alum was finely powdered and rehydrated over saturated solution in a desiccator and was added to the stirred water in small quantities during 2 minutes. The heat of solution per mole of $K_2SO_4,Cr_2(SO_4)_3,24H_2O$ did not vary with the different dilutions used and was found to be:

$$\Delta H_{298} = 14{\cdot}53,\ 15{\cdot}03,\ 14{\cdot}27,\ 15{\cdot}55,\ 14{\cdot}39;\ \text{mean} = 14{\cdot}75 \text{ kcals.}$$

The heat of solution of the powdered dehydrated product was determined under the same conditions and for the same concentrations of solutions as chrome alum and was found to be:

$$\Delta H_{298} = -12{\cdot}07,\ -11{\cdot}34,\ -12{\cdot}13;\ \text{mean} = -11{\cdot}85 \text{ kcals. per mole of } K_2SO_4,Cr_2(SO_4)_3,12H_2O.$$

It follows that the heat of the reaction:

$$K_2SO_4,Cr_2(SO_4)_3,24H_2O\ (s.) \longrightarrow K_2SO_4,Cr_2(SO_4)_3,12H_2O + 12H_2O\ (l.)$$

is given by $\Delta H_{298} = 26{\cdot}60$ kcals., or 2·22 kcals. per mole of water lost. Hence the heat of decomposition per mole of water lost for the reaction:

$$K_2SO_4,Cr_2(SO_4)_3,24H_2O\ (s.) \longrightarrow K_2SO_4,Cr_2(SO_4)_3,12H_2O + 12H_2O\ (g.)$$

is given by $\Delta H_{298} = 2{\cdot}22 + 10{\cdot}57 = 12{\cdot}79$ kcals., which is somewhat higher than the figure determined by Cooper and Garner from vapour-pressure measurements at 20—35°, *viz.*, 10·03 kcals. Our value, however, agrees to within 4% with that calculated from the heats of formation quoted by Bichowsky and Rossini (" The Thermochemistry of the Chemical Substances," Reinhold Publ. Corp., 1936), *viz.*, $Q_f$ $KCr(SO_4)_2,12H_2O$ = 1384·9 kcals.; $Q_f$ $KCr(SO_4)_2,6H_2O$ = 958·0 kcals.; $Q_f$ $H_2O$ (g.) = 57·8 kcals. This gives for the heat of reaction :

$$K_2SO_4,Cr_2(SO_4)_3,24H_2O\ (s.) \longrightarrow K_2SO_4,Cr_2(SO_4)_3,12H_2O + 12H_2O\ (g.)$$

$\Delta H$ per mole of water lost = 13·3 kcals. It seems probable, moreover, that the heat of reaction should be greater than the latent heat of vaporization of liquid water.

## DISCUSSION.

The activation energy at low temperatures is considerably greater than that at " high " temperatures, and the former value supports that given by Cooper and Garner from their " high " temperature measurements. Two possibilities arise : either our technique gives the true value at high temperatures, so that some change in reaction mechanism occurs on cooling, or, in spite of our improvements in technique the crystal temperature is not known exactly at the " high " temperatures and the low-temperature measurement gives the true activation energy at all temperatures.

It may be thought that a change in mechanism over as small a range of temperature as 15° is unlikely, but Cooper and Garner observed that below 20° unstable nuclei may form, and these have no radial cracks, have a higher activation energy for growth, and occur more frequently below 20° than above. It is noteworthy, in support of the view that the mechanism changes, that the " high " temperature measurements are in better accord with Polanyi and Wigner's expression (*Z. physikal. Chem.*, 1928, Haber Band, 439) than the measurements at low temperatures. This gives for the linear rate of the reaction $u = 2\nu d(E/\mathbf{R}T)e^{-E/\mathbf{R}T}$ where $\nu$ is a vibration frequency of a water molecule in the interface and $d$ is a molecular diameter. Now $\nu$ is of the order $10^{12}$ (Bradley, *Phil. Mag.*, 1931, **12**, 290) and hence the temperature-independent factor should be of the order $2 \times 10^6$, which is in rough agreement with the value found from the " high " temperature measurements, *viz.*, $3{\cdot}6 \times 10^8$, but much lower than the low temperature value, *viz.*, $(3\text{—}5) \times 10^{16}$ (cf. Table II).

Such large values of the temperature-independent factor have received a partial explanation by Garner (*Discuss. Faraday Soc.*, " Crystal Growth," 1949, **5**, 194; cf. also Hartshorne and Roberts, *J.*, 1951, 1097), who assumes that the reaction proceeds relatively rapidly through the crystal mosaic blocks and is then delayed at the gaps between the blocks. If the time taken for the reaction to pass through the block is neglected in comparison with that to bridge the gap, the reaction proceeds a distance $w'$, the width of block and gap, in time $k_4e^{-E/\mathbf{R}T}$, *i.e.*, the time taken to bridge the gap, hence $u = (w'/k_4)e^{-E/\mathbf{R}T}$. The onus of explanation of the large value of $B$ is then placed on the factor $k_4$. Although this theory gives a clear explanation of the scatter of experimental results when different crystals were compared, since the block structure may differ, the precise significance of $k_4$ is not clear. It is possible that the delay at the gap is due to the necessity to nucleate the virgin surface opposite the resultant, but if $w'$ were $10^{-5}$ cm. and $k_4$ were $10^{-12}$ sec.$^{-1}$, $w'/k_4$ would be $10^7$ instead of the observed value at low temperatures ($10^{16}$); lower values of $k_4$ would result if nucleation required the simultaneous loss from the surface of more than one water molecule.

A further possibility is that the reaction is governed by the diffusion of water molecules in the solid, so that holes may accumulate round the nuclei (cf. Acock, Garner, Milsted, and Willavoys, *loc. cit.*). This is unlikely in view of the high activation energy measured, since the activation energy for the diffusion would be expected to be less than the heat of dissociation.

On the whole, we are inclined to believe that on cooling there is some change of reaction mechanism, the nature of which requires further experimental study, but in view of the difficulty of measuring crystal temperatures the possibility of spurious temperature measurements in the region of large self-cooling of the crystals cannot be ruled out.

This work was submitted in partial fulfilment of the requirements for a Ph.D. degree at the University of Leeds by one of us (M. M. T. A.), and our thanks are due to the Egyptian Government for a grant to this author. Our thanks are also due to Professor E. G. Cox for his interest and encouragement, and to Professor W. E. Garner for helpful discussions.

This work was begun in October 1946 by M. M. T. Anous and J. Colvin. It was interrupted by a long illness of M. M. T. Anous and was resumed in July 1949. On the death of Dr. J. Colvin in September 1949 the work was resumed by M. M. T. Anous and R. S. Bradley and was completed in June 1951.

DEPARTMENT OF INORGANIC AND PHYSICAL CHEMISTRY,
THE UNIVERSITY OF LEEDS.

[*Received, July* 13*th*, 1951.]