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The thermal dehydration of solid ammonium copper(II) sulphate hexahydrate

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Abstract

The thermal decomposition of ammonium copper(II) sulphate hexahydrate has been studied at temperatures between 339 and 393 K over a range of water vapour pressures. The compound loses four molecules of water of crystallisation in this temperature range, showing Avrami–Erofeyev kinetics at low temperature, changing to contracting-disc kinetics above 350 K. The Arrhenius parameters for the Avrami–Erofeyev region are $E = 170\,\mathrm{kJ\,mol^{-1}}$ and $A = 2.1 \times 10^{21}\,\mathrm{s^{-1}}$, while the contracting-disc kinetics show $E = 82\,\mathrm{kJ\,mol^{-1}}$ and $A = 2.2 \times 10^{8}\,\mathrm{s^{-1}}$. There is no observable effect from variation in water vapour pressure. Microscopy has been used to clarify the kinetics.

Keywords: Alum; Arrhenius; Avrami–Erofeyev parameters; Contracting disc parameters

1. Introduction

The alums are a closely related group of compounds which have formed the basis of a great deal of experimental and theoretical work on the thermal decomposition of inorganic hydrates [1, 2], based in part on the easy growth of good single crystals. The mineral schönite, $K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$ has given its name to another group of materials which can also be crystallised easily. These coumponds, also known as Tutton's salts [3] of which ferrous ammonium sulphate, $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$, is perhaps the best-known chemical example, have been far less studied, despite the fact that a very wide range of isomorphous substitution can occur in the structure. The sulphate group can be replaced by BeF_4^- or SeO_4^{2-}, while most univalent cations can replace NH_4^+. The range of divalent cations includes Mg, Ni, Co, Fe, Cu, Zn and Cd. The unit cells of all of these compounds are very similar, being monoclinic, with

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$a_0 \sim 0.91$ nm, $b_0 \sim 1.25$ nm, $c_0 \sim 0.62$ nm and $\beta = 106°$. The water molecules are arranged octahedrally around the divalent cation [4].

One of this series whose thermal decomposition has been studied is the potassium copper salt [5]. This shows a two-stage decomposition, producing the dihydrate at about 323 K and the anhydrous material at about 400 K. The decomposition is affected by the external water vapour pressure, with high partial pressures producing a crystalline dihydrate intermediate, whereas low partial pressures make the onset of reaction earlier and the intermediate stage very indistinct. No kinetic parameters were determined in this study.

2. Experimental

2.1. Starting material

The starting material was SLR grade material which was twice recrystallised from water, dried on filter paper, and stored in a desiccator before use. This recrystallised material consisted mainly of small cuboid crystals about 1 mm in diameter. The XRD pattern was in very good agreement with that published [6].

2.2. Thermal decomposition

The dehydration studies were carried out using a Stanton TG750 thermobalance with a potentiometric recorder attached. Sample masses were 10 mg ± 10% throughout. Preliminary TG runs gave a total mass loss of 27.1% which agreed very closely with the theoretical loss (27.03%).

The main study was carried out under isothermal conditions, at temperatures between 339 and 393 K, with a current of nitrogen passing over the sample at a rate of 10 cm^{-3} min^{-1}. The humidity of the gas stream was kept constant during any one run by passing the gas through desiccant silica gel or water thermostatted at various temperatures [7]. The mass losses obtained indicated that four molecules of water were lost.

2.3. Microscopy

Single crystals were decomposed on a simple hot stage attached to an optical microscope (Zeiss Orthophot) and examined by both reflected and incident light, before being transferred to the SEM (ISI SS40) after mounting and coating with gold.

3. Results

3.1. Mass losses

Mass losses shown by thermogravimetry totalled 27.1% between 318 and 412 K, with an inflexion at about 367 K corresponding to a mass loss of 18.0%. At higher temperatures (> 449 K) a steady loss in mass was observed, which was shown to be at least partially due to loss of ammonia. The isothermal runs showed a mass loss corresponding to 18.0%, i.e. the first stage in the TG decomposition.

3.2. Kinetics

The isothermal mass-loss curves were analysed by the method of reduced-time plots, based on the time for 50% reaction [8]. The experimental reduced-time plots were compared with models based on nucleation and growth, phase boundary, or diffusion control of the reaction.

3.3. Reaction mechanisms

At temperatures between 350 and 393 K, the best fit between experimental and model reduced-time plots was in terms of the two-dimensional phase boundary equation (contracting disc)

$$(1-(1-\alpha)^{1/2}=kt$$

where α is the proportion decomposed.

Fig. 1 shows a reduced-time plot for the data gathered in this temperature range. At lower temperatures, the best fit was with the Avrami–Erofeyev equation

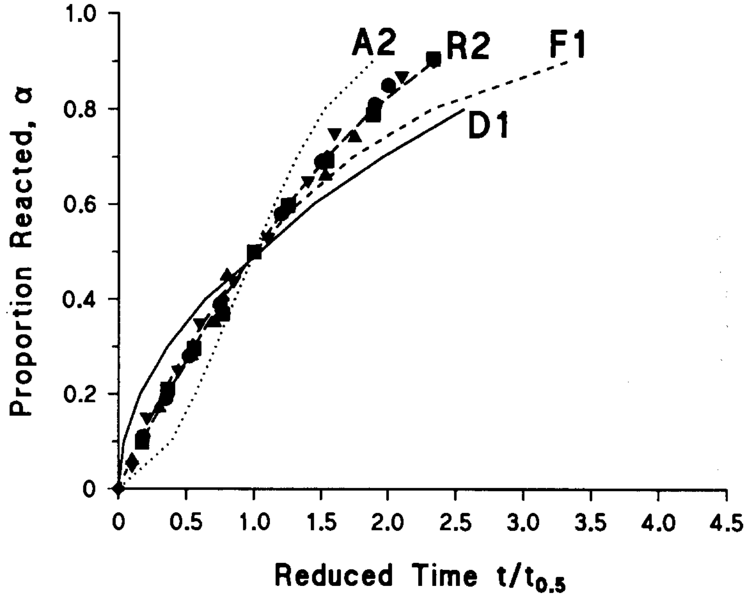

Fig. 1. Reduced-time plot for the high-temperature dehydration of ammonium copper(II) sulphate hexahydrate: ■, 353 K and $1\times10^{-3}\,\mathrm{N\,m^{-2}}$; ▼, 363 K and $44.8\,\mathrm{N\,m^{-2}}$; ▲, 373 K and $172\,\mathrm{N\,m^{-2}}$; ◆, 383 K and $542\,\mathrm{N\,m^{-2}}$; ●, 393 K and $172\,\mathrm{N\,m^{-2}}$.
A2, Avrami–Erofeyev equation, $n=2$; R2, contracting-disc equation; F1, first-order equation; D1, parabolic law.

with $n = 2$

$$-\ln(1-\alpha) = kt^2$$

A reduced-time plot is shown in Fig. 2 for this temperature range. No effects were noted with variation of water vapour pressure. The derived rate constants have been converted into an Arrhenius plot shown in Fig. 3.

3.4. *Microscopy*

Single crystals were decomposed on a hot stage at two temperatures, corresponding to the nucleation and growth and contracting disc regions (340 and 370 K respectively). Usually, the stage temperature was set to the chosen value and was constant before the chosen crystal was placed in position. A few experiments were undertaken in which the stage (with a crystal in position) was warmed from room temperature to the lower of the two chosen temperatures. Little difference was noted between the two treatments, except for occasional disintegration of crystals during rapid heating.

Low-temperature decomposition

The starting material exhibited reasonably flat faces, which within a few minutes at 340 K, showed multiple small nuclei which were not uniformly distributed across the

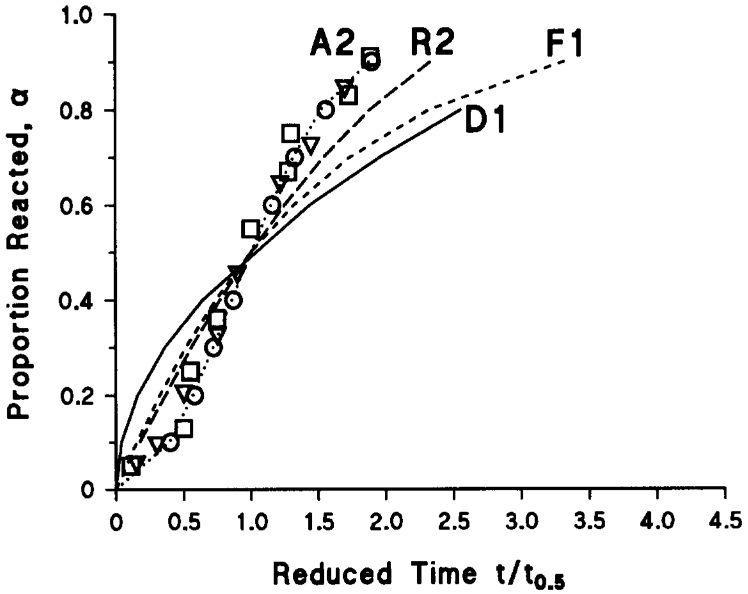

Fig. 2. Reduced-time plot for the low-temperature dehydration of ammonium copper(II) sulphate hexahydrate: □, 339 K and 1×10^{-3} N m^{-2}; ○, 345 K and 44.8 N m^{-2}; ▽, 342 K and 172 N m^{-2}; ◇, 342 K and 44.8 N m^{-2}. Other symbols as in Fig. 1.

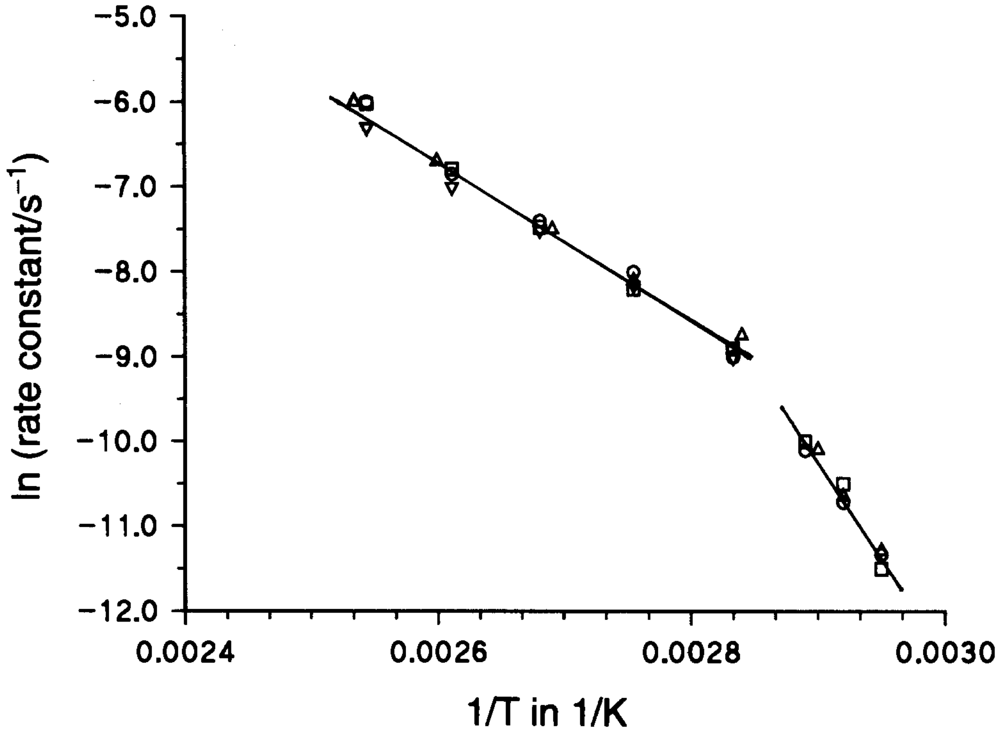

Fig. 3. Arrhenius plot for the dehydration of ammonium copper(II) sulphate hexahydrate: △, 1×10^{-3} N m^{-2}; ▽, 44.8 N m^{-2}; □, 172 N m^{-2}; ○, 542 N m^{-2}.

crystal face (Fig. 4). Cracks appeared between the initial nuclei, which grew with time (Fig. 5).

High-temperature decomposition

Decomposition at 370 K gave no sign of decomposition nuclei, but crystals rapidly became opaque, with the production of very large cracks, many of which were at approximately right angles to the crystal axes (Fig. 6).

4. Discussion

4.1. Mass losses

All of the runs gave mass losses very close to the theoretical value for the loss of four water molecules. The resulting dihydrate was not stable over a wide range of temperature because of the relatively easy loss of ammonia, unlike the potassium copper salt [5].

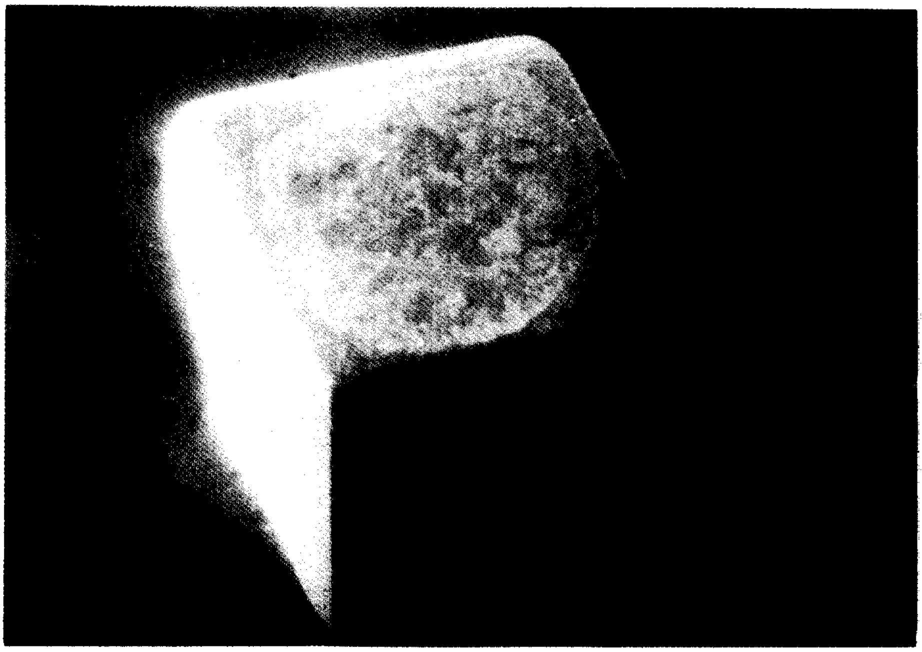

Fig. 4. 340 K, 180 s. Magnification × 20.

Fig. 5. 340 K, 240 s. Magnification × 1000.

Fig. 6. 370 K, 300 s. Magnification × 30.

4.2. Reaction mechanisms

A normal kinetic interpretation of the reduced-time plots shown in Fig. 1 would indicate that the Avrami–Erofeyev equation describes the low-temperature dehydration, and the contracting-disc equation describes the high-temperature behaviour. These together suggest that two-dimensional geometry is important in the reaction, and that the rate of nucleus formation increases greatly with temperature, giving rise to the rapid formation of the decomposed surface layer at higher temperatures. The course of the early reaction is therefore likely to be that two-dimensional nuclei are formed and that these grow to cover the surface of the decomposing crystal. The reactant/product interface should then move inwards through the crystal till the reaction is finished. Such a simple process should give rise to contracting volume kinetics: the observed kinetics are contracting disc.

The Arrhenius parameters derived from Fig. 4 give activation energies of 82 and 170 kJ mol^{-1} for the high- and low-temperature stages, respectively, and values of 2.2×10^8 and 2.1×10^{21} s^{-1} respectively, for the high- and low-temperature frequency factors. These values would suggest that both the nucleation and the growth stages in the dehydration reaction have approximately the same activation energies, i.e. 88 and 82 kJ mol^{-1} respectively. The frequency factors indicate that the transition state for the low-temperature step has more degrees of freedom than the higher temperature one. This latter point would suggest that the transition state does not involve any surface states, and may even involve free translation over the surface [9].

4.3. Compensation effect

The Arrhenius parameters for the two mechanisms may indicate the operation of a compensation effect [10, 11] in which high activation energies are compensated for, in rate terms, by high frequency factors, according to the relationship

$$\operatorname{Log} A = B + eE$$

where A and E are the frequency factor and the activation energy, and B and e are constants, the compensation parameters. While the present two values cannot be given much weight, the compensation parameters determined from them ($B = -3.8$, $e = 0.15$) lie reasonably close to those derived for a range of carbonate decomposition reactions ($B = -5.02$, $e = 0.067$ [12]) and dehydrations ($B = -3.0$, $e = 0.067$ [13]) and, particularly in the value of B, are very different from those derived from catalytic reactions ($16.6 < B < 19.9$; $0.099 < e < 0.118$) [11].

4.4. Microscopy

The kinetic parameters determined suggest that two-dimensional geometry is important in the decomposition. However, the Avrami–Erofeyev equation is composite [14], and the integer power is the sum of terms which describe the time dependence of nucleation γ and the number of dimensions of growth δ

$$-\ln(1-\alpha) = kt^n$$

where $n = \gamma + \delta$. When $n = 2$ the following possibilities arise: $\gamma = 0$, $\delta = 2$; $\gamma = 1$, $\delta = 1$; $\gamma = 2$, $\delta = 0$. The last of these is only a theoretical possibility because the growth of nuclei must occur in at least one dimension.

The micrographs show that the nuclei are two-dimensional, suggesting that γ should be zero. This means that the number of nuclei does not change with time, i.e. $dN/dt = 0$, where N is the number of nuclei. All of the potential nuclei must therefore be present at the start of the dehydration, and at any particular time all of the nuclei should be of the same size. It can be seen from the micrographs that this is generally true. These nuclei all show cracking from the centre, usually in the form of a cross, and presumably triggered by the volume changes on loss of water. In addition to the obvious nuclei, cracking of the crystal surface occurs in regions which are apparently undecomposed (Fig. 5). These cracks are short and tend to lie parallel to each other and are roughly oriented with the edges of the crystal. They are very approximately 10 µm apart: after high-temperature heating, they are the most obvious feature (Fig. 6). This cracking may be the key to the observed high-temperature contracting-disc kinetics. The observed crystal shape would suggest contracting-volume kinetics, as described previously. The observed cracking will produce instead a series of thin slabs of hydrate which, having their thickness much less than the other two dimensions, will be likely to show contracting-disc kinetics rather than contracting volume. The variable nucleus density shown in Fig. 4 may be related to the observation that many crystals had a cloudy core, with clearer faces and apices. This suggests that the initial crystallisation was rapid, producing relatively defect-rich material, followed by slower secondary growth, with fewer defects.

References

[1] W.E. Garner (Ed.), Chemistry of the Solid State, Butterworth, London, 1955, Chap. 8.
[2] A.K. Galwey, R. Spinicci and G.G.T. Guarini, Proc. R. Soc. London Ser. A, 378 (1981) 477.
[3] See A.E.H. Tutton, J. Chem. Soc., 71 (1897) 842.
[4] R.W.G. Wyckoff, Crystal Structures, Vol. 3, 2nd edn., Interscience Publishers, New York, 1960, p. 824.
[5] M. Tardy and G. Pannetier, Bull. Soc. Chim. Fra., 9 (1968) 3651.
[6] JCPDS Card No. 11-660.
[7] J.F. Young, J. Appl. Chem., 17 (1967) 24.
[8] J.H. Sharp, G.W. Brindley and B.N.N. Achar, J. Am. Ceram. Soc. 49 (1966) 379.
[9] H.F. Cordes, J. Phys. Chem., 72 (1968) 2185.
[10] A.K. Galwey, Adv. Catal., 26 (1977) 247.
[11] A.K. Galwey and M.E. Brown, J. Catal., 60 (1979) 335.
[12] M.C. Ball and M.J. Casson, J. Therm. Anal., 28 (1983) 371.
[13] M.C. Ball and L. Partwood, J. Therm. Anal., 41 (1994) 347.
[14] C.H. Breennan and C.F.H. Tipper (Eds.), Reactions in the Solid State, Comprehensive Chemical Kinetics, Vol. 22, Elsevier, Amsterdam, 1980, p. 41.