

Kinetics of the Isothermal Dehydration of Copper(II) Chloride Dihydrate in High Vacuum

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The isothermal dehydration of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was investigated by weighing on a quartz helix microbalance crystal fractions of dimensions ranging from 0.2 to 2.0 mm at pressures of about 10^{-4} mm Hg, and at temperatures between 20 and 50°C. Although the crystals were strongly elongated, they behaved as cubes in the reaction. A computer programme REAC has been written in Fortran IV for calculating the rate constant. This was found proportional to the equilibrium water vapour pressure and to the surface area of unreacted material. The apparent activation energy was 14 kcal mole⁻¹.

For most of the gas-solid systems of water vapour and metal halides the equilibrium vapour pressures have been well established during the last 30 years. Those that have been investigated, mostly by means of the isoteniscope,⁸ include the chlorides of Mg,¹⁻³ Ca,^{2,4} Mn(II),² Fe(II),^{5,6} Fe(III),⁷ Co(II),^{1,2} Ni(II),^{1,2} and Cu(II).^{1,2} At room temperature, however, the equilibrium vapour pressures are reported to be attained only after several days or weeks. Thus vapour pressure data have shown their insufficiency for the explanation of the reaction products from the rapid halogenations of metals in humid atmospheres.⁹ For this purpose the kinetics of the hydrate transformations must also be known.

While a vast number of papers discuss the thermogravimetry of inorganic salts,¹⁰ comparatively few papers are concerned with the kinetics of the isothermal hydration or dehydration processes. The most thoroughly investigated system seems to be that of magnesium oxide/-hydroxide. Anderson and Horlock^{11,12} have investigated the dehydration of platelets of brucite under varying water vapour pressures, while Bratton and Brindley¹³ studied the hydration of powders of magnesium oxide with different specific surface areas. The chlorides seem only to have been studied by Murgulescu and Segal.¹⁴ They investigated the dehydration of zinc sulfate heptahydrate, cobalt(II) chloride hexahydrate and manganese(II) chloride tetrahydrate, but unfortunately they do not state specific surface areas for the samples. The present

investigation is concerned with the dehydration of copper(II) chloride in high vacuum, where the interference of desorption and gas diffusion are reduced to a minimum.

EXPERIMENTAL

Copper(II) chloride dihydrate of grade MERCK *p.a.*, which consisted of orthorhombic crystals with dimensions ranging from 0.2 to 2 mm, was separated into four fractions by means of sieves of Perlodur with mesh widths of, respectively, 0.2, 0.35, 0.5, and 1.0 mm.

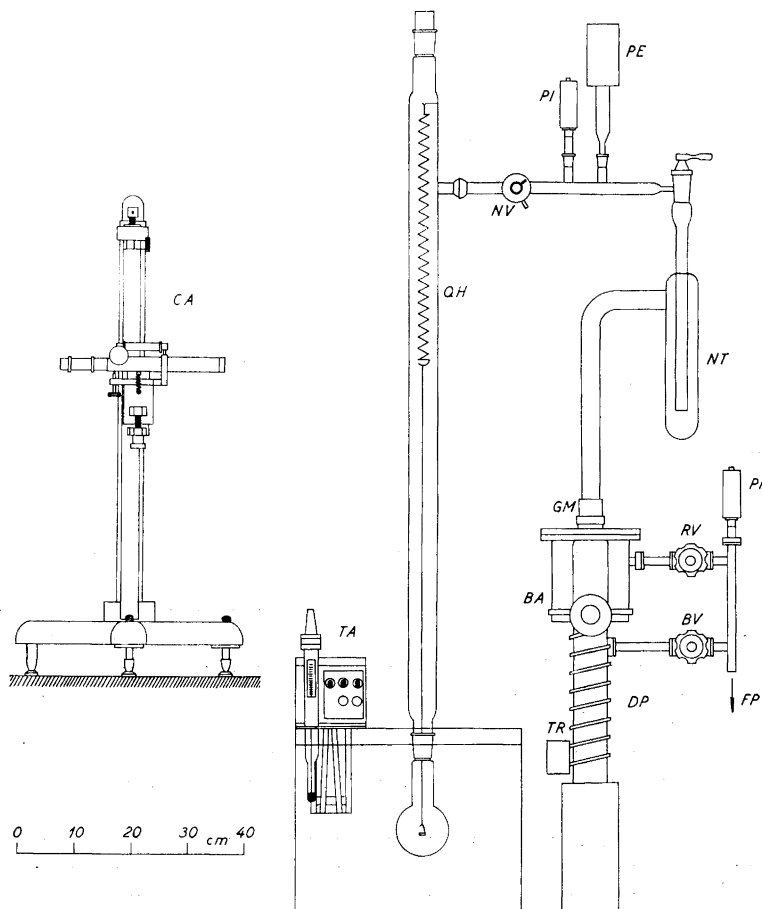


Fig. 1. The vacuum microbalance weighing system. BA: Baffle valve; BV: Backing valve; CA: Cathetometer (Griffin & George, range 0–50 cm, accuracy ± 0.001 cm); DP: Oil diffusion pump (Edwards, Speedivac F 203); FP: To mechanical fore-pump; GM: Glass metal seal; NV: Needle valve for gas inlet; NT: Liquid nitrogen trap; PE: Penning gauge (Speedivac model 5 GH, pressure range 10^{-2} – 10^{-5} mm Hg); PI: Pirani gauge (Speedivac model B4, pressure range 1 – 10^{-3} mm Hg); QH: Quartz helix balance (James A. Jobling & Co., sensitivity 2 m/g and max. load 200 mg); RV: Roughing valve; TA: Thermostating aggregate (Heto, model 623 X, temperatures $\pm 0.01^\circ\text{C}$ in the range 0 – 60°C); TR: Thermal relay switching off the oil-heating during insufficient water cooling.

The dimensions of the three crystal edge lengths perpendicular to each other, a , b , and c have been determined from microphotographs of 10–50 mg crystal samples. Only the two dimensions in the photographical plane, a and c , could be measured directly, while b was evaluated from the shadows. As the crystals were of prismatic shape, the total volume V and surface area A could be calculated from following expressions

$$V = \sum abc \quad (1)$$

$$A = 2(\sum ab + \sum bc + \sum ca) \quad (2)$$

The weighing system, shown in Fig. 1, consisted of a quartz helix microbalance the deflections of which were determined by a cathetometer. As the helix used had a sensitivity of 2 m/g and the deflections could be measured with an accuracy of 0.001 cm, mass changes of 0.005 mg could be observed. Depending on crystal size samples of 15–40 mg $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ were used. The sample was placed in a crucible of aluminium, plated with copper after the method of Buchner,¹⁵ and suspended under the helix in a glass fibre (0.15 mm diam.).

RESULTS AND DISCUSSION

When a solid decomposes into a gas and another solid, the volume generally proves to be smaller than that of the starting material. The porosity thus produced may facilitate the gas transport from the solid zone of reaction to the outer surface of the crystals so much that this ceases to be the rate-determining step. In the following we shall restrict ourselves to consider the kinetics due to the reaction at the surface boundary.

Firstly, let us consider the kinetics of crystals with shapes of cubes with edge-length a_0 . If x denotes the thickness of product layer, the degree of reaction α is defined by

$$a_0^3 \alpha = a_0^3 - (a_0 - 2x)^3 \quad (3)$$

when the same decomposition rate prevails along the three surface normals. Further, when the rate is dependent on the surface area of unreacted material, it must be valid that

$$a_0^3 \frac{d\alpha}{dt} = kA = 6k(a_0 - 2x)^2 \quad (4)$$

By differentiating eqn. (3) and comparing the result with eqn. (4), it is seen that $x = kt$. By insertion of this in eqn. (3) we get

$$\alpha = 1 - \left(1 - \frac{2kt}{a_0}\right)^3 \quad \text{or} \quad \frac{2kt}{a_0} = 1 - (1 - \alpha)^{1/3} \quad (5)$$

It can be easily shown that the same relations will hold for spheres of equal size, when a_0 is the diameter.

For crystal needles, however, represented by a model of quadratic prism of infinite length, the expected kinetics should be given by

$$\alpha = 1 - \left(1 - \frac{2kt}{a_0}\right)^2 \quad \text{or} \quad \frac{2kt}{a_0} = 1 - (1 - \alpha)^{1/2} \quad (6)$$

The kinetic crystal edge-length a_0 for cubes and the specific surface area S have been calculated from the definitions $a_0 = 6V/A$ and $S = A/w$. The results obtained in this manner are shown in Table 1, which also includes in the last

Table 1. Dimensions of the crystals used for dehydrations.

Sieve/mesh (mm)	S (m ² /g)	a_0 (mm)	\bar{a}	\bar{b}	\bar{c}
0.20—0.35	0.0107	0.220 ± 0.002	0.18	0.10	0.68
0.35—0.5	0.0077	0.30 ₈ ± 0.01 ₃	0.25	0.15	0.97
0.5—1.0	0.0052	0.45 ₈ ± 0.01 ₃	0.34	0.19	1.19
1.0—2.0	0.0031	0.76 ₈ ± 0.09	0.71	0.52	2.38

3 columns the mean values of the crystal edge-lengths. It should be noted that the relative standard deviations for the a_0 's of the 2nd and 3rd crystal fractions are four times greater than those for the first and 4th crystal fractions due to a more diffuse crystal size distribution.

To test the kinetics given above, all data were transformed to the same curve, Fig. 2, by dividing the time values by the best rate constants, which have been found by plotting the data according to the right hand eqn. (5). For comparison the theoretical curves for prisms and cubes are also shown in the figure together with their slope at zero time. Although the crystals geometrically resembled prisms more than cubes, it must be concluded that the crystals in the kinetic sense acted as cubes.

The values of the constants calculated from the plot of $1 - (1 - \alpha)^{1/3}$ against t can only be first approximations, however. This is because of the uncertainty in the determination of the zero length of the spring balance. Necessarily,

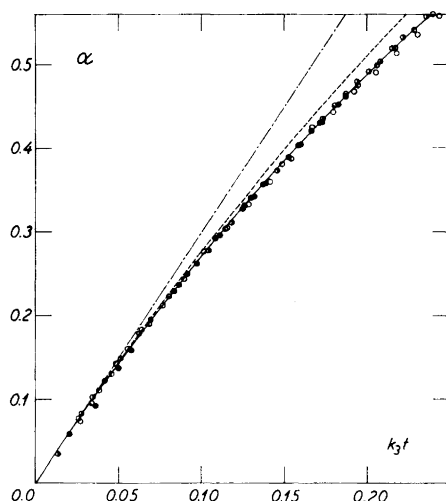


Fig. 2. The reduced dehydration curve. Comparison of reduced data with theoretical curve for cubes eqn. (7) (full drawn) and needles, eqn. (8) (dotted) of identical initial slope (dot and dashed).

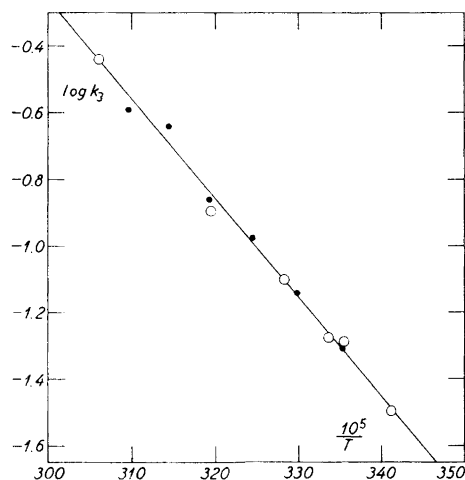


Fig. 3. The temperature dependency of the rate constant k_3 for the 0.5—1.0 mm crystal fraction (filled circles). For comparison $\log P_w$ (mm Hg) — 2.17 is plotted against $1/T$ (open circles), where P_w is the equilibrium water vapour pressure.

this length had to be determined at atmospheric pressure, while the value needed for calculation of the degree of reaction should be that under high vacuum. Compared to the measured length, the required zero length should be greater due to buoyancy, but less due to desorption of gases from the spring balance.

Therefore the final rate constants and zero heights were determined by successive iterations from linear regression analyses of $y=1-(1-\alpha)^{1/3}$ against t . The calculations have been performed on the IBM 7090 computer at the NEUCC with program REAC, written in FORTRAN IV for this purpose. The standard deviation of the measured heights was found to be about 0.0016 cm, *i.e.* comparable to the cathetometer reading accuracy of 0.0010 cm.

The final values of $2k/a_0$ are given in Table 2. It is noted that the values of k for the 0.220 and 0.765 mm crystal fractions are in excellent agreement

Table 2. Rate constants for the dehydration. The data marked * are from measurements with a spring balance of 5 times lower sensitivity.

Crystal fraction a_0 (mm)	Temperature T (°C)	Reaction rate constants	
		$k_3 = \frac{2k}{a_0}$ (h ⁻¹)	k (cm/h)
0.456	20.16 *	0.020 ± 0.001	
	25.16 *	0.060 ± 0.001	
	30.03	0.0747 ± 0.0003	
	34.98	0.0992 ± 0.0002	
	39.99	0.1393 ± 0.0002	
	44.82	0.2280 ± 0.0002	
	49.77	0.2473 ± 0.0003	
0.220	30.05	0.1908 ± 0.0003	$2.1_0 \times 10^{-3}$
0.308	30.05	0.1982 ± 0.0005	$3.0_0 \times 10^{-3}$
0.456	30.03	0.0747 ± 0.0003	$1.7_0 \times 10^{-3}$
0.765	30.05	0.0537 ± 0.0001	$2.0_0 \times 10^{-3}$

with each other while the corresponding values for the 0.308 and the 0.456 mm fractions deviate considerable from each other and from the two first cited rate constants.

This is well explained, when it is considered that the relative standard deviation of the edge-length a_0 for the two latter crystal fractions is 4 times greater than that for the two former. By multiplying the rate constants with factors equal to the square of the reciprocal relative standard deviations the weighted mean for the absolute rate constant is calculated to be

$$k(30^\circ\text{C}) = (2.0_9 \pm 0.0_4) \times 10^{-3} \text{ cm/h}$$

From the plot of $\log k_3$ against $10^5/T$ given in Fig. 3 the Arrhenius activation energy is determined to $E_a = 14 \pm 2$ kcal/mole. For comparison is in Fig. 3 also given the logarithmic equilibrium water vapour pressures after Derby

and Yngve¹ and Diesnis.² By subtraction of a constant from the vapour pressure data, these are seen to be concentrated along the same line as the rate constant. Consequently, the activation energy does not differ significantly from the heat of gaseous hydration, which may be calculated either by linear regression analysis of the vapour pressure data or from the heat of water vapourisation (10.58 kcal/mole¹⁶) and the heat of liquid hydration of copper(II) chloride (3.43 kcal/mole¹⁷) giving 13.85 kcal mole⁻¹ (at 40°C) and 14.01 kcal mole⁻¹ (at 18°C), respectively.

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