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Reliability of kinetic measurements for the thermal dehydration of lithium sulphate monohydrate.
Part 1. Isothermal measurements of pressure of evolved water vapour

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Abstract

The thermal dehydration of single crystal and powdered samples of lithium sulphate monohydrate, $Li_2SO_4 \cdot H_2O$, has been selected for detailed examination of the reliability of kinetic parameters obtained from isothermal measurements of the pressure of water vapour evolved in an initially evacuated, constant-volume apparatus.

The reproducibility was examined and various methods of isothermal kinetic analysis, including integral and differential methods and the use of reduced-time scales, were compared.

Arrhenius parameters derived from these experiments are compared with previously published values.

INTRODUCTION

As the quantity of published information concerning the kinetics of thermal decompositions of solids [1] expands, it becomes increasingly important to provide objective assessments of the quality, reliability and significance of the data available. The most frequently reported kinetic observations for such crystolysis [2] reactions are the identification of the rate equation most applicable, and the magnitudes of the calculated Arrhenius parameters (the reaction frequency factor A and the activation energy E). Comparison of the magnitudes of published E and A values reveals [3] that there are often considerable variations between results reported by different workers for the decomposition of nominally identical

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Dedicated to Professor Joseph H. Flynn in honour of his 70th birthday.

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reactants, even when similar experimental methods are used. Many examples of such inconsistency are to be found in the literature and a specific example is the thermal dissociation of calcium carbonate [4]. Garn [5] has stressed the importance of confirming that the experimental conditions employed are capable of providing valid kinetic observations, before such results are interpreted.

Reasons for variations in reported kinetic data include effects arising from the use of different experimental techniques and/or different definitions of the fractional extent of reaction α. Disagreements on the magnitudes of A and E often arise in comparisons between measurements made by isothermal techniques and those from rising temperature techniques. Further variations may result from the use of alternative methods of data analysis [3].

The reactivity of a solid is often significantly influenced by its particle size, the nature, concentration and distribution of its crystal imperfections and impurities, and the damage to crystal surfaces. The observed behaviour may, therefore, be sensitive to the method of reactant preparation, length and conditions of storage, and any pretreatment before decomposition (crushing, abrasion, ageing, irradiation etc.). The kinetics of formation and growth of decomposition nuclei [1] may be sensitive to particle sizes and the distribution of sites at which reaction can be initiated. The criteria used to identify the rate equation [1] that represents the experimental results most precisely [6] can also account for some of the differences to be found in reported results.

This article reports a detailed investigation of the kinetics of dehydration of lithium sulphate monohydrate

$$Li_2SO_4 \cdot H_2O(s) \rightarrow Li_2SO_4(s) + H_2O(g) \qquad (1)$$

This reaction was selected as an apparently simple rate process which proceeds to completion in a single step. Published results [7] show that, following an initial short acceleratory period, the reaction is predominantly deceleratory. This dehydration has been identified as a nucleation-and-growth reaction [7], and the contribution from the reverse reaction is negligible over a wide range of temperatures and at low pressures of water vapour. After the present experimental work had been completed, reaction (1) was selected as the model rate process to be used in an international collaboration investigating the reproducibility of kinetic measurements for solid state reactions by different workers [8].

This article is concerned with the reproducibility of kinetic measurements, the identification of the most applicable rate equation, $f(\alpha) = kt$, and the magnitudes of E and A. The α–time data were obtained from the pressure of water evolved in an initially evacuated constant-volume apparatus under isothermal conditions. Replicate isothermal measurements for both single crystal and powder samples were obtained across the widest practicable temperature range. Data were tested for conformity to all appropriate solid state rate expressions [1] across suitable intervals of α. Kinetic observations are compared with previous studies of reaction (1) [9–17]. A future article will report on α–time data for the same salt obtained under isothermal conditions from thermogravimetry (TG) and differential scanning calorimetry (DSC), and will compare isothermal and non-isothermal observations.

EXPERIMENTAL

$Li_2SO_4 \cdot H_2O$ reactant

The reactant was prepared by procedures identical to those used previously [7] to permit meaningful comparisons of data for the rate of dehydration.

The reactants which are compared are (i) single crystals obtained by the slow evaporation of a saturated solution of reagent grade lithium sulphate and careful removal and storage of the most perfect crystals, (ii) powder, $< 150\ \mu m$, obtained by crushing single crystals and sieving.

Some crystals, referred to here as "aged" samples, were dehydrated in the water vapour pressure apparatus after storage in a closed tube for two years.

Apparatus

The kinetics of dehydration were measured from the changes with time of the pressure of evolved water vapour in an initially evacuated constant-volume glass apparatus. Pressures were measured (0–10 Torr) using a Baratron diaphragm gauge. Readings of pressure, time and temperature were recorded at appropriate intervals and stored in microcomputer memory for later analysis. The apparatus and experimental technique were identical to those used previously [7,18]. For each temperature, replicate experiments were completed without altering the prevailing conditions.

RESULTS AND DISCUSSION

Reaction stoichiometry

The pressure of water evolved in the known volume of the apparatus from the reactions of the single crystals corresponded, on average, to marginally (0.5%) more than the yield expected (14.07%) from complete dehydration of $Li_2SO_4 \cdot H_2O$. There was no trend in the variation of yield with temperature across the interval studied (361–402 K).

Dehydration of the powder samples was investigated in a lower temperature range (323–363 K) and yields corresponding to the constituent water of the monohydrate were observed only for reactions at 340 K and above. At 333 and 323 K the amounts of water corresponded to 90% and 50%, respectively, of expectation. Dehydration, therefore, proceeded to completion at all but the lowest of the temperatures investigated in this study.

KINETICS OF DEHYDRATION

Three aspects of kinetic behaviour were considered:

(i) the reproducibility of pressure–time measurements on similar reactant samples at each of a number of selected reaction temperatures;

(ii) the precise measurement of the final pressure p_f and the calculation of α–time data, $\alpha = (p - p_0)/(p_f - p_0)$;

(iii) the identification of the rate equation, $f(\alpha) = k(t - t_0)$, which most accurately describes the α–time data [1,6].

It was also necessary to determine whether an incorrect estimation of the magnitude of p_f (point (ii) above) had a significant effect on the identification of the rate equation (iii). These interdependent features of the kinetic analysis cannot be treated separately because variations in the values of rate coefficients (k) obtained from different kinetic expressions (iii) provide a measure of the reproducibility (point (i) above).

The procedure used in each experiment was to estimate the magnitude of p_f by extrapolation of the later pressure–time values, convert the pressure values to α values and then test the α–time values for conformity to five different deceleratory kinetic expressions, $f(\alpha) = k(t - t_0)$ [1]. These were the contracting geometry models (R3 and R2), the first-order model (F1) and two diffusion models (D3, diffusion in three-dimensions and D4, the Ginstling–Brounshtein model). Of the many possible ways of testing conformity of isothermal data to a rate equation [1], probably the most frequently used is the critical comparison of plots (linear regression) of $f(\alpha)$ against t to identify the expression which gives an acceptable linear fit over the largest α range (Table 1, Method 1).

TABLE 1

Summary of isothermal methods of kinetic analysis used

Method no.	Explanation
1	Plot of $f(\alpha)$ against t
2	Plot of $k = f(\alpha)/(t - t_0)$ against t
3	Plot of $(\mathrm{d}\alpha/\mathrm{d}t)$ against $f'(\alpha)$
4	Plot of $(\mathrm{d}\alpha/\mathrm{d}t)$ against α (only linear if $n = 1$)
5	Plot of $\ln(\mathrm{d}\alpha/\mathrm{d}t)$ against $\ln(1 - \alpha)$
6	Reduced-time plots

Rate coefficients, k (s^{-1}) can then be calculated from the slopes of these linear regions. In the present work, the "best fit" was identified from the calculated correlation coefficients r and examination of the plots of the residuals ($f(\alpha)$(expt.)–$f(\alpha)$(theory)) for the absence of definite trends [6]. The effects of variations (errors) in the values of p_f used in the calculations were also examined.

Kinetic behaviour

Crystals

Isothermal pressure–time curves for dehydrations of single crystals, 362–402 K, show an initial, very brief acceleratory region which does not vary appreciably in shape, extent or duration (about 5 min) with changing values of the isothermal reaction temperature. All pressure–time plots were predominantly deceleratory and, because the approach of reaction to completion was usually slow, values of p_f were often estimated by extrapolation.

Powder

Isothermal pressure–time curves for the powder samples, 323–363 K, are similar in shape to those of single crystals, but the temperature at which dehydration proceeded at the same rate as in a crystal was significantly lower. At 363 K the approximate half-life for dehydration of a crystal is 220 ± 10 min compared with 12 ± 1 min for the powder.

Comparison of fit of data to various kinetic models

Crystals

Quantitative measures of the excellence of fit of data to the five deceleratory rate equations, for dehydration of crystals at 373 K, are given in Table 2. The contracting-volume model (R3) provides the most accurate fit across the most extensive α range (Fig. 1).

Powder

A similar analysis of the measured α–time data for dehydration of powder samples at 342 K is included in Table 2. The first-order equation (F1) gave the most satisfactory fit, being marginally better than the contracting-volume expression (Fig. 2). The diffusion model (D4) was applicable over a more restricted α range, but there was no additional evidence suggesting a diffusion-controlled rate process.

Also included in Table 2 are the rate coefficients calculated using Method 2 in Table 1.

TABLE 2

Comparison of kinetic models for isothermal dehydration of $Li_2SO_4 \cdot H_2O$

Model	r^2	Method 1 k (10^{-4} s^{-1})	Method 2 k (10^{-4} s^{-1})
Crystals: $T = 373$ K; $p_f = 4656$ mTorr; mass, 30.0 mg			
		($0.01 < \alpha < 0.99$)	($0.56 < \alpha < 0.97$)
R3	0.9986	1.1880 ± 0.0024	1.1859 ± 0.0093
R2	0.9862	0.9528 ± 0.0066	1.051 ± 0.052
F1	0.9752	1.965 ± 0.021	1.555 ± 0.160
D3	0.9278	0.4208 ± 0.0078	
D4	0.9821	0.2358 ± 0.0020	0.172 ± 0.029
Powder: $T = 342$ K; $p_f = 1750$ mTorr; mass, 14.2 mg			
		($0.01 < \alpha < 0.93$)	($0.50 < \alpha < 0.91$)
R3	0.9936	2.596 ± 0.023	2.551 ± 0.048
R2	0.9823	2.190 ± 0.032	2.31 ± 0.11
F1	0.9956	3.750 ± 0.028	3.16 ± 0.17
		($0.12 < \alpha < 0.93$)	
D3	0.9675	0.824 ± 0.018	
D4	0.9940	0.5070 ± 0.0045	0.333 ± 0.058

Reproducibility of kinetic behaviour

Data from several series of replicate experiments were analysed using the more applicable kinetic expressions identified in Table 2 (R3 and F1).

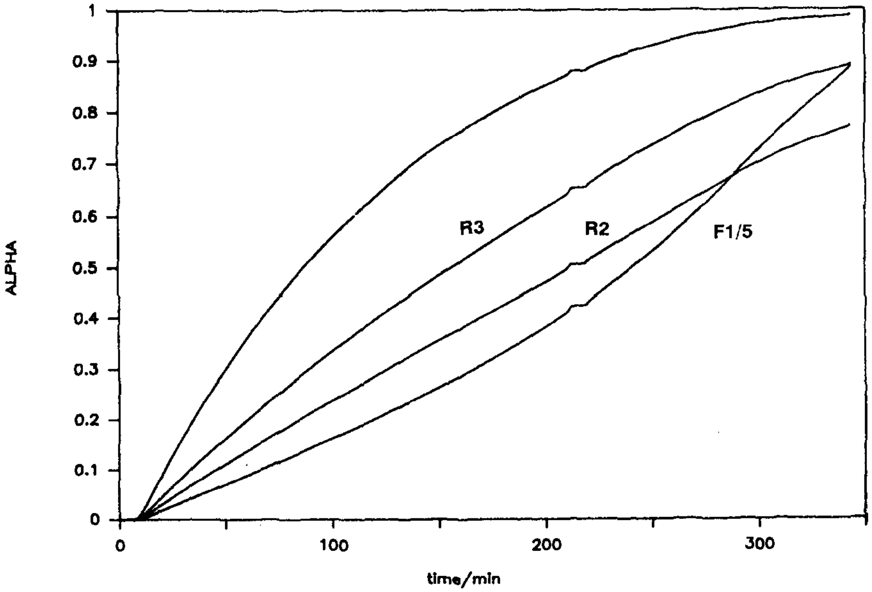

Fig. 1. α–time and $f(\alpha)$–time plots (R3, R2 and F1 models) for the isothermal dehydration of lithium sulphate monohydrate crystals at 373 K.

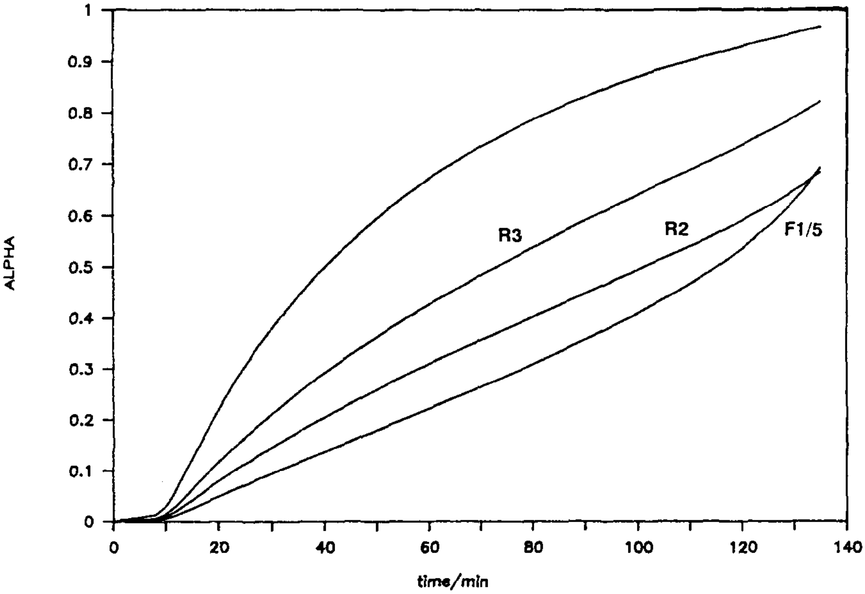

Fig. 2. α-time and $f(\alpha)$-time plots (R3, R2 and F1 models) for the isothermal dehydration of lithium sulphate monohydrate powder at 342 K.

The scatter in the estimated rate coefficients was used to measure the reproducibility of the kinetics of isothermal dehydration. The results for crystals at 373 K and for powder (< 100 mesh) at 353 and 343 K, are given in Table 3.

The scatter in the values of k, as measured by the standard deviations, was greater in each case for the model which had been identified in Table 2 as giving the better fit. For powder samples the reproducibility deteriorated markedly at the lower temperatures.

Influence of p_f *measurement on kinetic analysis*

The magnitude of p_f used for the calculation of α values can significantly influence the kinetic expression identified as most satisfactorily representing the data.

Crystals

For the experiment reported in Table 2, the use of $p_f = 4656$ mTorr resulted in the most satisfactory fit being given by the contracting-volume expression (R3). If the p_f value was increased by 10% ($p_f = 5120$ mTorr), the calculated α-time values were more accurately represented by the first-order expression (F1). This trend emphasizes the importance of establishing the true reaction yield within $\pm 2\%$ if a distinction is to be made between a contracting-geometry model and first-order behaviour.

TABLE 3

Reproducibility of isothermal dehydration of $Li_2SO_4 \cdot H_2O$ in the constant-volume system

T (K)	Mass (mg)	p_f/mass	Rate coefficient (10^{-4} s^{-1})	
			R3	F1
Crystals at 373 K			$(0.01 < \alpha < 0.99)$	
373.2	30.0	155.2	1.188	1.97
373.5	43.6	165.5	0.990	1.77
373.6	34.9	160.6	1.281	2.00
374.8	36.4	156.9	1.119	1.77
Mean 373.8 ± 0.7		159.6 ± 4.6	1.15 ± 0.13	1.88 ± 0.12
± error		(2.9%)	(10.9%)	(6.6%)
Powder at 353 K			$(0.01 < \alpha < 0.93)$	
353.1	21.6	139.4	3.801	6.399
353.2	18.5	149.7	3.978	7.493
353.3	21.7	151.6	3.732	6.351
353.7	16.7	152.7	4.083	7.198
Mean 353.3 ± 0.3		148.4 ± 6.1	3.90 ± 0.15	6.87 ± 0.57
± error		(4.1%)	(4.1%)	(8.3%)
Powder at 343 K			$(0.01 < \alpha < 0.93)$	
341.8	14.2	123.2	2.596	3.750
342.1	13.9	145.3	1.211	1.987
343.0	20.2	138.6	1.305	2.266
343.3	17.6	148.3	0.967	1.515
Mean 342.6 ± 0.7		138.9 ± 11.2	1.52 ± 0.73	2.38 ± 0.96
± error		(8.1%)	(48.1%)	(40.3%)

Powder

The first-order expression was identified (see Table 2) as the preferred kinetic representation. It is clearly unrealistic to consider data calculated using p_f values lower than those measured.

Measurement of the total yield of product corresponding to completion of the rate process being investigated is always uncertain. A final slow evolution of product could in principle be either first-order behaviour or an alternative rate process resulting from an impurity or atypical structure. To distinguish between the applicability of the contracting-volume or contracting-area model and first-order behaviour, thus requires accurate data measurements during the final stages of reaction.

Differential methods for testing kinetic expressions

Differential methods (using $d\alpha/dt$) may provide a more sensitive test of applicability of a kinetic expression than integral methods. Such analyses are possible only when the precision of measurements is sufficient to

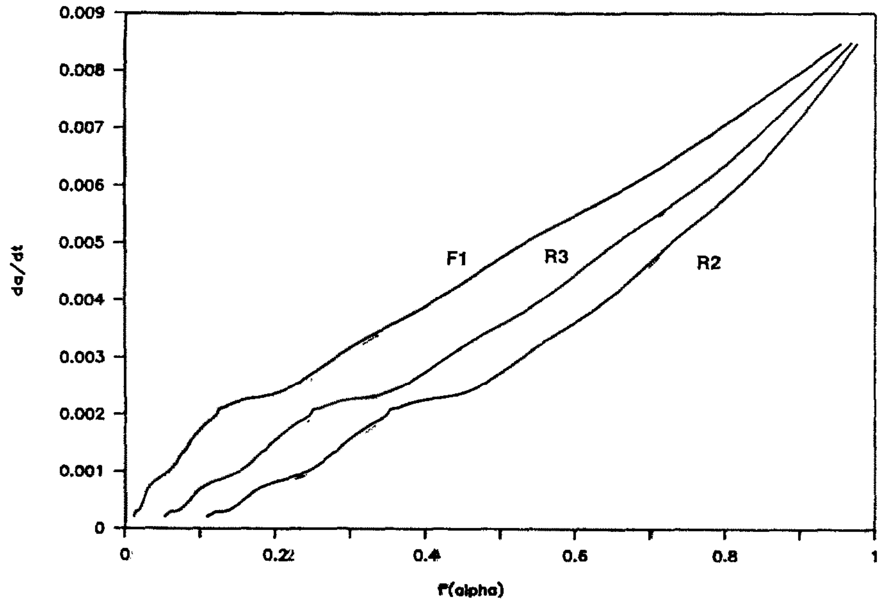

Fig. 3. Rate vs. $f'(\alpha)$ plots (R3, R2 and F1 models) for the isothermal dehydration of lithium sulphate monohydrate crystals at 373 K.

prevent trends being obscured by noise. The use of automatic recording methods has allowed larger numbers of measurements to be made, sometimes with increased precision. This, together with the possibility of digital smoothing, has improved the reliability of analyses using rate data. Previous recommendations of this approach [1] have included comparison of plots of experimental values of $(\mathrm{d}\alpha/\mathrm{d}t)$ against α with model plots [19] (Table 1, Method 4) and the use of $(\mathrm{d}\alpha/\mathrm{d}t)$ against reduced-time values [20].

A further method (Method 3, Table 1), which does not appear to have been considered previously in a general form, was used to analyse the data. If the rate expression has been correctly identified, a plot of $(\mathrm{d}\alpha/\mathrm{d}t)$ against $f'(\alpha)$ should be linear and pass through the origin ($\mathrm{d}\alpha/\mathrm{d}t = 0$, $f'(\alpha) = 0$). The slope of the line gives the rate coefficient k. Magnitudes of α are, however, controlled by the value chosen for p_f and so there are interdependences between the features discussed here. An advantage of this method is that contributions from *initial* errors in the magnitudes of induction periods (t_0) or initial reactions (α_0) will be small.

Plots of $(\mathrm{d}\alpha/\mathrm{d}t)$ (smoothed once using a 12-point cubic spline algorithm) against $f'(\alpha)$, i.e. $(1-\alpha)^{2/3}$ (R3 model), $(1-\alpha)^{1/2}$ (R2 model), and $(1-\alpha)$ (F1 model) (Method 3), are shown in Fig. 3 (crystals) and Fig. 4 (powder). The discrimination between alternative possible rate equations is found to be better for the powder than for the crystals.

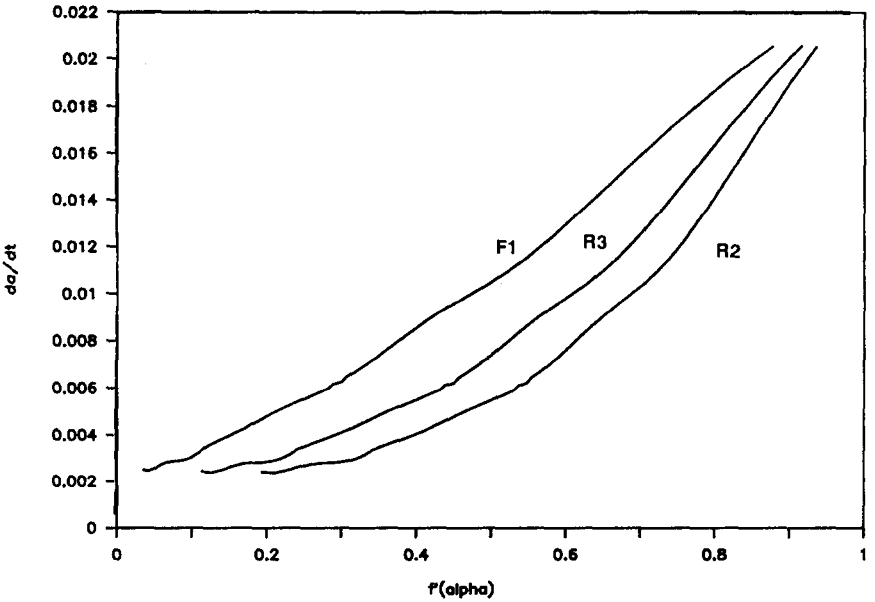

Fig. 4. Rate vs. $f'(\alpha)$ plots (R3, R2 and F1 models) for the isothermal dehydration of lithium sulphate monohydrate powder at 342 K.

Plots of $(\mathrm{d}\alpha/\mathrm{d}t)$ against α (Method 4, Table 1) will be linear only in the special case of first-order behaviour and then the slope of the line is $-k$ and the intercept is k.

On the assumption that $f'(\alpha) = (1-\alpha)^n$, a value of n may be obtained [21] from the slope of a plot of $\ln(\mathrm{d}\alpha/\mathrm{d}t)$ against $\ln(1-\alpha)$ (Method 5, Table 1). This method has the advantage that there is no constraint on the value of n. Results of application of these differential tests are summarized in Table 4.

TABLE 4

Further kinetic analyses of the dehydration of lithium sulphate monohydrate: plots of $(\mathrm{d}\alpha/\mathrm{d}t)$ against $f'(\alpha)$ (Method 3, Table 1)

Model	k (10^{-4} s^{-1})	Std. error	r^2	Intercept (10^{-4} s^{-1})	Std. error
Crystals at 373 K					
F1	1.344	0.013	0.9797	0.12	0.05
R2	1.496	0.023	0.9524	−0.23	0.08
R3	1.398	0.016	0.9524	−0.06	0.06
Powder at 342 K					
F1	3.66	0.06	0.9819	0.06	0.11
R2	4.07	0.14	0.9033	−0.92	0.26
R3	3.78	0.11	0.9425	−0.44	0.21

TABLE 5

Further kinetic analyses of the dehydration of lithium sulphate monohydrate

T (K)	Method 5		Method 4 ($n = 1$)		$(r_5)^2$	$(r_4)^2$
	n	k_5 (10^{-4} s^{-1})	−Slope (10^{-4} s^{-1})	Intercept (10^{-4} s^{-1})		
Crystals						
361.9	0.78	0.4592	0.4833	0.5105	0.9763	0.9876
362.5	1.40	0.6583	0.8317	0.6565	0.9854	0.9716
373.2	0.73	1.3200	1.3117	1.4425	0.9512	0.9930
373.5	0.84	1.3053	1.5183	1.5333	0.9657	0.9687
374.8	0.73	1.2470	1.4583	1.5192	0.9287	0.9753
383.8	0.72	3.4161	3.2583	3.6578	0.9630	0.9732
384.5	0.53	3.5023	3.0317	3.8877	0.9938	0.9516
385.0	0.57	4.1747	3.7017	4.5625	0.9620	0.9547
393.0	0.55	6.6762	5.8183	7.3037	0.9785	0.9506
393.1	0.48	5.8552	4.9567	6.5910	0.9345	0.8813
393.1	0.53	6.1085	5.4817	6.8782	0.9428	0.9484
394.2	0.55	6.4552	5.5717	7.0732	0.9107	0.9323
402.1	0.62	12.3850	11.3450	13.3955	0.9734	0.9189
402.5	0.59	6.3038	6.0167	7.1837	0.9742	0.9823
Powder						
324.1	1.18	0.6010	0.7417	0.6517	0.9417	0.9314
324.3	1.11	0.5763	0.6483	0.5967	0.9708	0.9708
331.9	1.24	1.5758	1.6483	1.5138	0.9752	0.9817
332.7	1.57	1.0645	1.2833	1.0558	0.9728	0.9155
334.0	1.29	2.1437	2.5383	2.2172	0.9659	0.9368
334.1	1.69	1.7337	2.1167	1.6862	0.9688	0.9139
334.2	1.12	1.8532	2.1750	1.9840	0.9637	0.9618
334.5	1.74	1.0478	1.1550	0.9710	0.9718	0.8392
341.8	0.89	3.4300	3.7833	3.7790	0.9763	0.9847
342.1	1.24	3.1035	3.4083	3.1320	0.9906	0.9649
343.0	1.51	5.2563	5.1433	4.5470	0.9932	0.9649
343.3	1.90	5.8298	5.1983	4.3107	0.9934	0.9457
353.1	0.99	6.5652	6.9433	6.8867	0.9960	0.9980
353.2	0.98	7.4190	8.1017	8.0108	0.9952	0.9964
353.3	1.00	6.6995	7.0633	6.9863	0.9922	0.9978
353.7	1.09	8.7918	9.0200	8.7728	0.9974	0.9948
363.7	0.87	14.7208	14.0933	14.7923	0.9968	0.9864
364.3	0.95	20.2357	19.9633	19.5003	0.9958	0.9976
364.4	0.85	15.3420	16.6117	17.0185	0.9990	0.9960
364.7	0.99	19.9033	19.3383	19.5003	0.9958	0.9976

Plots of $(d\alpha/dt)$ against α (Method 4) for powder samples gave excellent agreement between k values calculated from the slope and from the intercept (Table 5) (intercept = $(0.9969 \pm 0.0093) \times (-\text{slope})$, with $r = 0.9983$). For crystals, the relationship is somewhat skewed (intercept = $(1.25 \pm 0.02) \times (-\text{slope})$, with $r = 0.9950$).

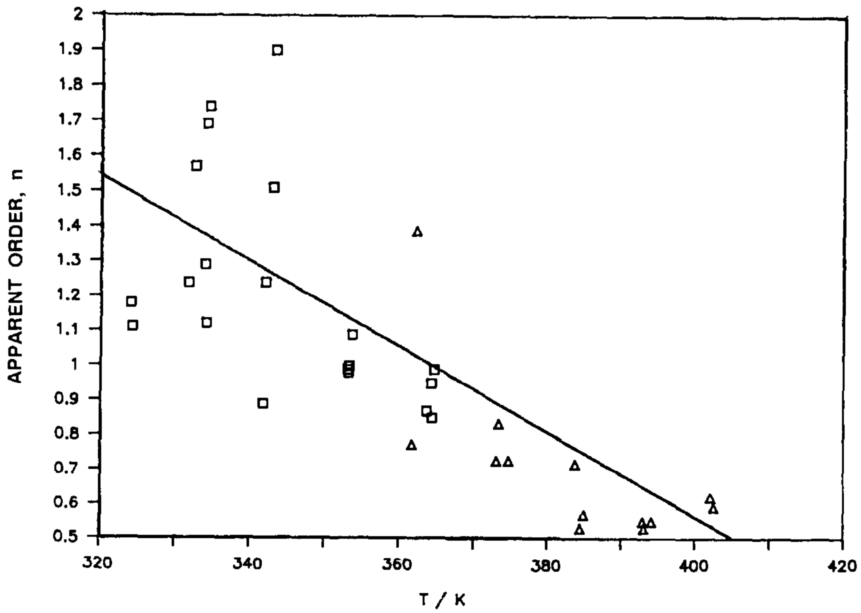

Fig. 5. Apparent "order of reaction" n (Method 5) against temperature for isothermal dehydration of lithium sulphate monohydrate: △, crystals (360–400 K); □, powder (320–360 K).

Method 5 (plots of $\ln(d\alpha/dt)$ against $\ln(1-\alpha)$) gave the values of n and k recorded in Table 5. The value of n determined by this method varies with temperature. For crystals, n tends towards 1.0 (i.e. the F1 model), with decreased reproducibility at the lower temperatures (360 K) (Fig. 5), but decreases to between 0.5 (R2 model) and 0.6 ($n = 0.667$ is R3 model) at higher temperatures (400 K). The values of n obtained for powder samples were generally less reproducible at a given temperature (Fig. 5) and the values were generally higher (> 1) than those for crystals. The combined sets of data are shown in Fig. 5.

Rate coefficients calculated by Methods 1–5 in Table 1 for the R3 and F1 rate equations for crystals at 373 K and powder at 342 K (data from Table 2) are compared in Table 6.

Reduced-time plots (Method 6, Table 1)

Isothermal α–time curves (discounting the problem of the determination of p_f and consequent errors in α) were converted to a reduced-time scale [1], t_{red}, based on the times (corrected for any heat-up period, t_0) so that $t_{red} = (t - t_0)/(t_{0.50} - t_0)$, where $t_{0.50}$ is the time at which $\alpha = 0.50$.

The experimental values of α were then compared with the α values predicted by the rate equations.

TABLE 6

Comparison of rate coefficients calculated by different methods

Method	k (10^{-4} s^{-1}) for model	
	R3 ($n = 0.667$)	F1 ($n = 1.00$)
Crystals at 373 K		
1 $f(\alpha)$ vs. t	1.188 ± 0.0024	1.965 ± 0.021
2 k vs. t	1.186 ± 0.0093	1.555 ± 0.160
3 Rate vs. $f'(\alpha)$	1.398 ± 0.016	1.344 ± 0.013
4 Rate vs. α	–	1.3117–1.4425
5 ln(rate) vs. $\ln(1-\alpha)$	($n = 0.73$)	$k = 1.320 \times 10^{-4}$ s^{-1}
Powder at 342 K		
1	2.596 ± 0.023	3.750 ± 0.028
2	2.551 ± 0.047	3.157 ± 0.174
3	3.78 ± 0.11	3.66 ± 0.06
4	–	3.783–3.779
5	($n = 0.89$)	$k = 3.430 \times 10^{-4}$ s^{-1}

Crystals

Reduced-time plots for crystals at 373 K were examined together with plots of the residuals (α(model)–α(expt.) on the same time scale. The value of t_0 was determined by minimizing the sum of the squares of the residuals (see Table 6) for the different models. For crystals at 373 K, the R3 model with $t_0 = 5.5$ min (Fig. 6) gave the best fit.

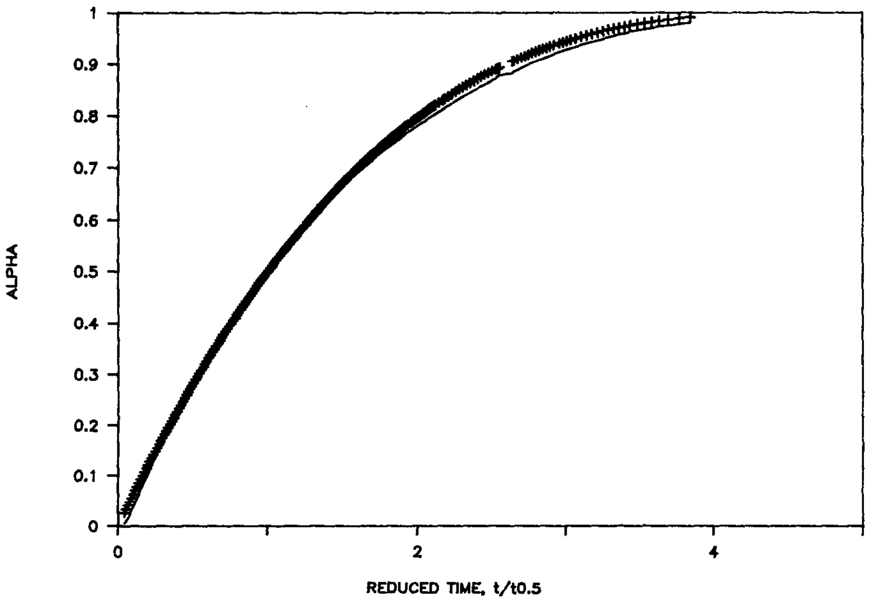

Fig. 6. α vs. reduced-time plot for the isothermal dehydration of lithium sulphate monohydrate crystals at 373 K: ———, experimental; +, R3 model with $t_0 = 5.5$ min.

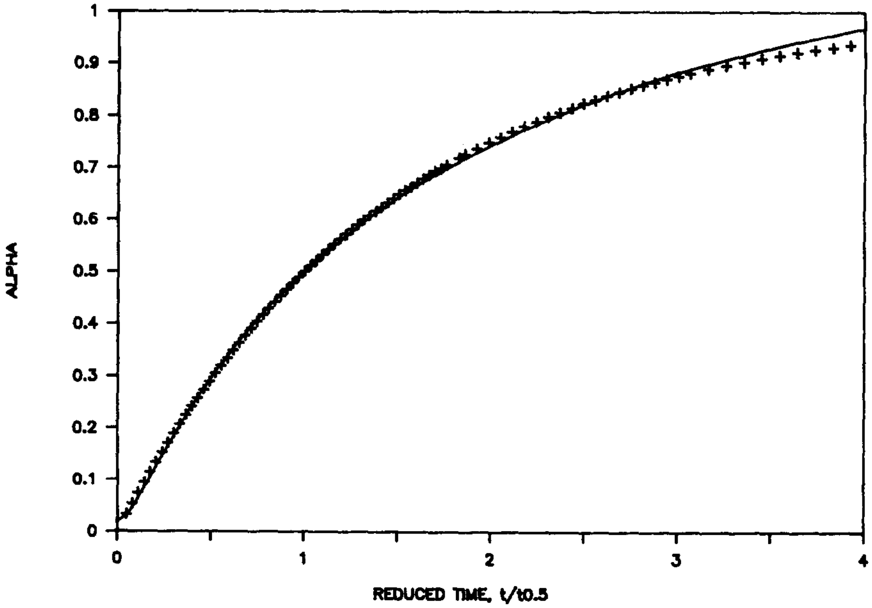

Fig. 7. α vs. reduced-time plots for the isothermal dehydration of lithium sulphate monohydrate powder at 342 K: ———, experimental; +, F1 model with $t_0 = 9.5$ min.

Powder

Reduced-time plots and residuals for powder samples at 342 K were examined and the value of t_0 was determined, as above, by minimizing the sum of the squares of the residuals (see Table 7) for the different models. The effect of increasing the value of p_f used in the calculation of α from 1750 mTorr to 1900 mTorr was also examined (Table 6). The F1 model with $t_0 = 8.5$ min gave the best fit for the powder sample (Fig. 7). Increasing the value used for p_f did not significantly improve the fit of model F1, even with adjustment of t_0 (Table 7).

Isokinetic behaviour

The correlation coefficients (r) obtained by fitting the F1 and R3 rate equations to the α–time data were examined for variations with temperature. The only trend observed was that r values for the fit of the F1 equations to the data for crystals decreased with increasing temperature.

Experiments on aged samples

Samples of the original crystals that had been stored in a sealed tube for a further year were dehydrated at 401 ± 1 K in the pressure apparatus under conditions similar to the original experiments. This material is

TABLE 7

Reduced-time plots (Method 6, Table 1)

t_0 (min)	Sum of the squares of the residuals (on same number of points)	
	R3 model	F1 model
Crystals at 373 K; $p_f = 6546$ mTorr; $t_{0.50} = 86.5$ min		
0	0.0723	0.4012
2	0.0489	0.3207
4	0.0371	0.2496
4.5	0.0361	0.2336
5	0.0360	0.2182
5.5	0.0368	0.2037
6	0.0385	0.1899
8		0.1437
10		0.1136
11		0.1056
12		0.1028
13		0.1058
14		0.1151
Powder at 342 K; $p_f = 1750$ mTorr; $t_{0.50} = 40.0$ min		
0	0.1198	0.2350
2	0.0876	0.1567
4	0.0708	0.0888
4.5	0.0696	0.0741
5	0.0697	0.0604
5.5	0.0714	0.0480
6	0.0746	0.0369
8	0.1065	0.0088
8.5	0.1200	0.0068
9	0.1361	0.0072
9.5	0.1550	0.0104
10	0.1770	0.0166
Powder at 342 K; $p_f = 1900$ mTorr; $t_{0.50} = 44.5$ min		
0	0.1454	0.1342
1	0.1390	0.1080
2	0.1358	0.0840
2.5	0.1355	
3	0.1362	0.0627
4	0.1408	0.0446
5	0.1501	0.0304
6	0.1650	0.0207
6.5	0.1747	0.0178
7	0.1861	0.0164
7.5	0.1993	0.0167
8	0.2145	0.0187

referred to as "aged" crystals. The rate coefficients for dehydration of aged crystals at 401 ± 1 K are compared with the earlier values in Table 8. Any effect of ageing is at a level that is below that of the reproducibility.

TABLE 8

Rate coefficients k (10^{-4} s^{-1}) for dehydration of aged crystals at 401 ± 1 K (Method 1, Table 1)

Notes	R3 model	R2 model	F1 model
Original crystals	3.98	4.68	21.46
Original crystals	2.26	2.72	11.23
Aged crystals		2.87	9.33
Aged crystals, exp. H_2O, 24 h		3.20	11.33
Aged crystals		4.27	12.00
Aged crystals, exp. H_2O, 24 h		3.58	11.17
Aged crystals		5.38	15.50
Aged crystals, exp. H_2O, 24 h		4.57	18.50
Aged crystals, 4 min evac.		5.00	20.83

Arrhenius parameters

The several studies of the rate of dehydration of $Li_2SO_4 \cdot H_2O$ to be found in the literature [7,9–17] report kinetic observations that show significant differences. Vasilev and Ershova [9] found sigmoid isothermal α–time curves and the apparent value of E decreased with decreasing pressure in the apparatus, from 66 to 59 kJ mol^{-1}. The α–time data for the reaction were also reported [10,11] as fitting the contracting-volume equation, but E values were not quoted. Okhotnikov and co-workers [13–15,17], working with single crystals, found nucleation to be instantaneous and the activation energy for the subsequent dehydration was 85 ± 2 kJ mol^{-1}.

TABLE 9

Arrhenius parameters for the dehydration of lithium sulphate monohydrate

	Evolved $p(H_2O)$			Previous values [7]		
	R3	R2	F1	R3	R2	F1
E (kJ mol^{-1})	106.3	105.3	109.7	79.9	80.1	
Std. error	7.0	6.7	7.9	3.4	3.4	
ln A (s^{-1})	24.07	23.94	26.75	15.70	15.90	
Std. error	0.29	0.28	0.32	1.20	1.20	
r^2	0.9392	0.9421	0.9285	0.9692	0.9694	
k_{370} (10^{-4} s^{-1})	0.280	0.340	1.364	0.323	0.413	
Powder						
E (kJ mol^{-1})	87.0	85.2	91.7	93.0		92.2
Std. error	5.7	5.9	5.6	1.9		1.8
ln A (s^{-1})	20.71	20.27	23.94	22.80		23.95
Std. error	0.33	0.34	0.32	0.69		0.69
r^2	0.9316	0.9254	0.9413	0.9880		0.9882
k_{370} (10^{-4} s − 1)	5.150	5.950	28.240	5.388		22.826

Tanaka and co-workers [7,12,16] reported significantly higher values of E, about 110 kJ mol^{-1}. The magnitude of E varied with particle size and the α range investigated.

Observations in the literature, therefore, report differences in isothermal kinetic behaviour, with the α–time data being described by kinetic expressions as diverse as the Avrami–Erofeev equation and the deceleratory models. Reported magnitudes of E vary by a factor of almost 2, from about 60 [9] to about 110 kJ mol^{-1} [16].

Rate coefficients, k (s^{-1}), measured in the present study by Method 1 (linear $f(\alpha)$ against time plots) were used to calculate the activation energy values recorded in Table 9. These values were then compared with previous results obtained by similar experiments and analysis [7]. Values of rate coefficients k lay in similar ranges but the magnitudes of E values showed relatively large variations.

CONCLUSIONS

The dehydration of both single crystals and powdered (< 150 μm) lithium sulphate monohydrate

$$Li_2SO_4 \cdot H_2O(s) \rightarrow Li_2SO_4(s) + H_2O(g)$$

is confirmed as proceeding to completion in a single step at all but the lowest temperatures (below 340 K) investigated, provided that the water vapour pressure in the surrounding atmosphere is kept low.

The rate of isothermal dehydration of powder, in the pressure apparatus, was significantly higher than the rate in crystals at the same temperature (Figs. 1 and 2).

Isothermal α–time curves for both single crystals and powder reactant samples were almost entirely deceleratory. The short apparent acceleratory period does not vary significantly with reaction temperature and is probably due to the time lag in the sample reaching the reaction temperature and/or a temporarily high local water vapour pressure due to desorption of surface water.

Preparation, ageing and grinding all influence the kinetics of dehydration.

Reproducibility

The ratio of the measured p_f to the sample mass at a fixed T had a standard deviation of about 3% for crystals and there was a similar variation for powder, although the average ratio was lower and decreased further as the reaction temperature decreased. The rate coefficients for the various models applied to the curves for crystals varied in replicate runs by up to 10% and this variation was greater for powders, increasing to up to 50% at low temperatures (343 K).

Most applicable rate equation

The contracting-volume model (R3) provides the most accurate fit to α–time data across the most extensive α range for dehydration of crystals in the pressure apparatus at 373 K (Fig. 1). A similar analysis of the results for dehydration of powder samples at 342 K (Table 2) showed that for this reactant form the fit of the first-order equation (F1) was marginally better than the contracting-volume expression (Fig. 2).

The scatter in the values of k, as measured by the standard deviations, was greater in each case for the rate equation which had been identified in Table 2 as giving the better fit. For powder samples the reproducibility deteriorated markedly at the lower temperatures.

Influence of choice of p_f

The magnitude of p_f used for the calculation of α values can significantly influence the kinetic expression identified as most satisfactorily representing the data. If the p_f value for the reaction of crystals was increased by around 10%, the most satisfactory fit changed from being the contracting-volume expression (R3) to the first-order expression (F1). This emphasizes the importance of establishing the reaction yield within ±2% if a distinction is to be made between a contracting-geometry model and first-order behaviour. Fit of the α–time data for crystals by the contracting-volume rate equation is consistent with the observation, in the electron microscope, of a reaction interface. The distribution of particle sizes in the powder samples explains the slightly different shape of the α–time curve during the latter stages, when data are better fitted by the first-order rate equation.

Method of analysis

Rate coefficients calculated by the various methods in Table 1 for the R3 and F1 models for crystals at 373 K and powder at 342 K are compared in Table 6. The integral methods gave rate coefficients with the lowest standard deviations. Method 2 (testing the constancy of k with t) revealed the averaging effect of determining the value of k by Method 1 and emphasized the small but non-random drifts in the values of k calculated for all of the models tested.

Use of differential methods (Methods 3 and 4 in Table 1) does not provide clearer discrimination amongst models and noise in the signal is a problem. Differential plots do reveal overlapping stages more clearly.

Method 5 (plots of $\ln(d\alpha/dt)$ against $\ln(1-\alpha)$) provided evidence that the value of the apparent order of reaction n, varies with temperature. For crystals, n tends towards 1.0, i.e. the F1 model, with decreased reproducibility at the lower temperatures (360 K) (Fig. 5), but decreases to between 0.5 (R2 model) and 0.6 ($n = 0.667$ is R3 model) at higher temperatures (400 K). The values of n obtained for powder samples were generally less reproducible at a given temperature (Fig. 5) and the values were generally higher (> 1) than those for crystals.

Reduced-time plots (method 6 in Table 1) require accurate knowledge of the values of α and hence of p_f. Assessment of the fit of a proposed model has to be based on plots of the residuals (α(model)–α(expt.)) and allowance has to be made for a correction t_0 to the original time scale. This time correction was determined by minimizing the sum of the squares of the residuals (over a constant number of data points) (see Table 6) for the different models. For examples, for crystals at 373 K, the R3 model with $t_0 = 5.5$ min gave a better fit than the F1 model with $t_0 = 12.0$ min. If an independent estimate of t_0 was available, based on some other criteria, the problem would be simplified.

For powder samples at 342 K, the value of t_0 was determined, as before, by minimizing the sum of the squares of the residuals (see Table 7) for the different rate equations. The effect of increasing the value of p_f used in the calculation of α from 1750 mTorr ($t_{0.50} = 44.5$ min) to 1900 mTorr ($t_{0.50} = 40.0$ min) was also examined (Table 7). The F1 model with $t_0 = 8.5$ min gave a better fit than the R3 model with $t_0 = 4.5$ min. Increasing the value used for p_f did not significantly improve the fit of model F1, even with adjustment of t_0 (Table 7).

Rate coefficients, k (10^4 s^{-1}), measured using Method 1 (linear $f(\alpha)$ against time plots) were used to calculate the activation energy values recorded in Table 9. These values were compared with previous results and relatively large variations were observed.

In Part 2 of this series [22], these measurements of α and t based on pressures of evolved water vapour will be compared with similar measurements (and analyses) obtained using isothermal thermogravimetry and isothermal differential scanning calorimetry.

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