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SELF-COOLING EFFECT ON THE KINETICS OF NONISOTHERMAL DEHYDRATION OF LITHIUM SULFATE MONOHYDRATE

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The effects of self cooling on the apparent kinetics of the nonisothermal dehydration of crushed crystals of lithium sulfate monohydrate were investigated using TG accompanied by DTA and power-compensation type DSC. Linearity of the sample heating rate on the TG-DSC system is much better than that on the TG-DTA. Kinetic obedience and Arrhenius parameters obtained from the TG-DTA deviate considerably from those obtained from the TG-DSC; the latter are the more accurate due to the better linearity of the sample heating rate.

Although accurate determination of sample temperature is essential in evaluating reliable kinetic parameters for solid-state reactions, the measurement of temperature has always been and remains a serious problem [1, 2]. This source of error seems to have been overlooked in many and diverse kinetic measurements which have used thermoanalytical equipment, particularly where kinetic parameters for nonisothermal solid-state reactions have been determined. During a reaction proceeding at increasing temperatures, there must inevitably be some temperature lag between the sample and its surroundings [3, 4]. This can be relieved, to some extent, by the use of a smaller sample size and reduced heating rates with enhanced conduction of heat to the sample [1, 3-5].

When the reaction under investigation is endothermic, as in the dehydration of salt hydrates, however, the sample temperature may be much lower than surroundings.

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This effect is known as self-cooling effect [6, 7] and is known to introduce error into the measured kinetic parameters for such endothermic solid-state reactions [8, 9]. One possible way of diminishing the influence of the self-cooling effect is to dilute the sample with an inert substance with high heat conductivity [10]. Another method is to use a power-compensation type DSC, in which the energy supplied maintains the sample temperature equal with that of the reference material.

It is therefore of value to compare the kinetics of dehydration of a given salt hydrate by TG measured simultaneously with DTA and power-compensation type DSC, to determine quantitatively the effect of self cooling on the kinetics of solid-state reactions. Such a kinetic comparison is also of interest in view of the comment of Flynn that the simultaneous analyzer of the TG and DSC apparatus maintains a temperature sensor in good contact with the specimen [1]. In other words, any kinetic difference observed in such measurements is expected to be caused predominantly by the self-cooling effect.

Thermal dehydration of crushed crystals of lithium sulfate monohydrate was identified as a system suitable for the present study, because the kinetics of the dehydration has been investigated comprehensively under various experimental conditions [11]. Kinetic parameters were determined from TG data recorded simultaneously with the DSC and DTA. It was expected that the present approach could further be extended to permit recognition of the effects of self-cooling on the kinetics of solid-state reactions in general.

Experimental

Reagent grade lithium sulfate monohydrate (Katayama Chem. Ind.) was dissolved in water and prolate single crystals were obtained by slow evaporation at ambient temperature. These single crystals were crushed in a pestle and mortar and sieved to separate the 100 to 170 mesh fraction. The sample was characterized by TG and IR, and stored before rate studies for about three weeks to avoid the effects of ageing on the kinetics. 15.0 mg samples were loaded into a platinum crucible of 5.0 mm diameter and 2.5 mm height. Ignited Al_2O_3 was used as a reference material. Simultaneous TG-DSC measurements at various heating rates were carried out on a Rigaku Thermoflex TG-DSC (8085E1) system in a nitrogen flow of 30 ml/min. The simultaneous TG-DTA measurements were made using the same system including the same sample holder unit by switching off the DSC circuit under conditions identical with those of the simultaneous TG-DSC experiments. Sample temperature during the course of reaction was deduced from the temperature difference between the sample and reference material recorded on the DTA trace. All measurements were stored in a microcomputer and the kinetic data calculated by an integral method.

Results and discussion

Figure 1 shows typical curves of the fractional reaction, α, against time, t, together with the heating curves, obtained from TG accompanied by DSC and DTA at a programmed constant heating rate of 3.8 deg/min. We see that sample temperature on the TG-DSC system rises relatively more rapidly. It is noted that the heating curve for the TG-DTA is far from linear, particularly during initial and final stages of reaction [4]. The slight depression in the slope of this curve around $\alpha = 0.5$ is clearly due to the rapid endothermic reaction. The accelerated heating rate during the later stage is attributed to recovery from the transient temperature diminution and restoration of equilibration with the surroundings. We also note that there are considerable differences in the shapes (slopes) of the α - t curves between the two experiments. Figure 2 shows conventional α - temperature T curves of TG accompanied by DSC and DTA at various heating rates.The shapes and the slopes of TG curves are quite different at each comparable heating rate, particularly during the early stage of the reaction. Longer induction periods are observed for the TG curves accompanied by DTA. This may be ascribed to the longer time required for the sample to attain reaction temperature, together with the influence of endothermic water removal from the sample [11]. The difference in the shape of TG curves indicates the possibility that the appropriate kinetic model function, $F(\alpha)$, and Arrhenius parameters are considerably different between the TG measurements accompanied by DSC and by DTA.

It is of interest here to calculate from these data the Arrhenius parameters for this reaction using the Ozawa method. This method has already been shown to be fairly reliable for the present system [12] and TG traces at various heating rates are available. According to Ozawa, the following equations hold [13-15].

$$\ln\left(\frac{\beta}{T^2}\right) \doteqdot -\frac{E}{RT} + \ln\left(\frac{R}{\theta E}\right) \tag{1}$$

with

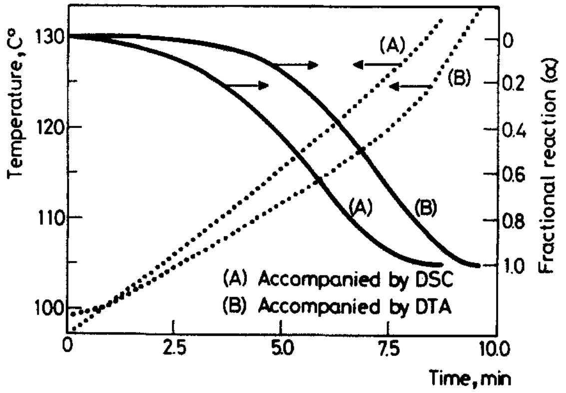

Fig. 1 Typical TG and temperature curves accompanied by DSC and DTA at a programmed heating rate of 3.8 deg/min

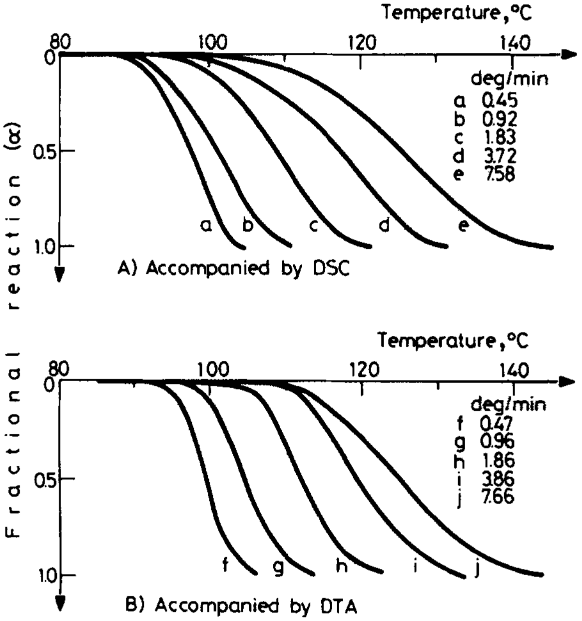

Fig. 2 Heating rate dependence of α vs. T curves of TG accompanied by DSC and DTA

$$\theta \doteqdot \left(\frac{RT^2}{\beta E}\right) \exp\left(-\frac{E}{RT}\right) \tag{2}$$

where β is the heating rate, θ is the reduced time or generalized time and other symbols have usual meaning. The following equation is used to obtain the Arrhenius preexponential factor, A [14, 16].

$$F(\alpha) = A\,\theta \tag{3}$$

Figure 3 shows a comparison of the apparent activation energies, E, obtained using Eq.(1) at various values of α. Although both E values decrease as reaction advances, the values of E obtained from the TG-DTA experiments are about 10 kJ/mol larger throughout the reaction than those from the TG-DSC runs. The θ values were calculated from Eq.(2), using the mean value of E over the α range of 0.1-0.9. According to Eq.(3), the appropriate $F(\alpha)$ and the values of A were determined by plotting various $F(\alpha)$ against θ. Table 1 lists the values of A obtained for all the possible $F(\alpha)$, together with correlation coefficient, γ, of the linear regression analysis of the plot. It is noted that the values of A obtained from the TG-DTA runs are also larger than those from the TG-DSC runs, as for the E values. Because of the so-called kinetic compensation behavior [16], a comparison of apparent values of E is rather meaningless, because it contributes little to the understanding of the kinetics of solid-state reactions.

The most appropriate $F(\alpha)$ was identified from the most satisfactory linearity of the $F(\alpha)$ *vs.* θ plot, by scanning the values of n and m in the R_n and A_m laws. Linear plots of the appropriate functions $F(\alpha)$ against θ are shown in Fig. 4. Kinetic obedience is described by either $R_{2.17}$ or $A_{1.59}$ law and either $R_{3.00}$ or $A_{1.18}$ law for the runs of TG-DSC and TG-DTA, respectively. Table 2 shows changes in kinetic obedience and Arrhenius parameters across different ranges of α. For all the α ranges examined, the different kinetic obediences are observed between the runs of TG-DSC and TG-DTA. The change in the Arrhenius parameters is accompanied by variation in the kinetic obedience. Such variation in the kinetic parameters precludes establishment of the so-called quantitative kinetic compensation effect, which is the case with a constant kinetic obedience [17].

It is evident that the above kinetic difference is caused by the different temperature variations within the sample, because the experimental conditions are practically identical for the TG-DSC and the TG-DTA experiments. In addition, any distortion in linearly increasing temperature also

Table 1 The preexponential factor *A* calculated by the Ozawa Method in terms of all the F(α) examined for the monisothermal dehydration of crushed crystals of $Li_2SO_4 \cdot H_2O$ (–100 + 170 Mesh) within the α range of 0.1-0.9

$F(\alpha)$	accompanied by DSC			accompanied by DTAC		
	A, 1/s	γ^a	$\sigma^b \cdot 10^2$	*A*, 1/s	γ^a	$\sigma^b \cdot 10^2$
D_1	$5.55 \cdot 10^{12}$	0.9959	2.32	$1.28 \cdot 10^{14}$	0.9964	2.20
D_2	$4.40 \cdot 10^{12}$	0.9859	3.47	$1.02 \cdot 10^{14}$	0.9954	1.98
D_3	$1.74 \cdot 10^{12}$	0.9576	2.42	$4.08 \cdot 10^{13}$	0.9786	1.73
D_4	$1.18 \cdot 10^{12}$	0.9782	1.16	$2.75 \cdot 10^{13}$	0.9917	0.72
A_u	$2.64 \cdot 10^{13}$	0.9889	18.4	$5.99 \cdot 10^{14}$	0.9762	26.9
R_1	$5.39 \cdot 10^{12}$	0.9890	3.73	$1.22 \cdot 10^{14}$	0.9729	5.84
R_2	$4.17 \cdot 10^{12}$	0.9999	0.33	$9.52 \cdot 10^{13}$	0.9950	1.93
R_3	$3.26 \cdot 10^{12}$	0.9993	0.56	$7.47 \cdot 10^{13}$	0.9987	0.78
A_1	$1.37 \cdot 10^{12}$	0.9904	8.87	$3.18 \cdot 10^{14}$	0.9986	3.43
A_2	$7.52 \cdot 10^{12}$	0.9982	2.07	$1.71 \cdot 10^{14}$	0.9909	4.69
A_3	$5.29 \cdot 10^{12}$	0.9920	3.13	$1.20 \cdot 10^{14}$	0.9793	5.00
A_4	$4.09 \cdot 10^{12}$	0.9868	3.11	$9.26 \cdot 10^{13}$	0.9716	4.56

[a] Correlation coefficient of the linear regression analysis of the *F*(α) *vs.* θ plot, [b] Standard deviation of eath point from the line

affects the apparent kinetic parameters, because these are calculated by assuming a linear heating of the sample [6, 8]. Figure 5 shows plots of $\Delta T/\Delta t$ against α, which is measure of the temperature fluctuation from linear heating of the sample. We see that the irregularity increases with the rise in heating rate and that the curves for the TG-DSC are much smoother than those for the TG-DTA. This suggests that the kinetic parameters determined from the TG-DSC runs are more reliable than those from the TG-DTA runs. It is also noted that it is preferable to heat the sample at as low a heating rate as possible, when undertaking nonisothermal kinetic investigations [1,4].

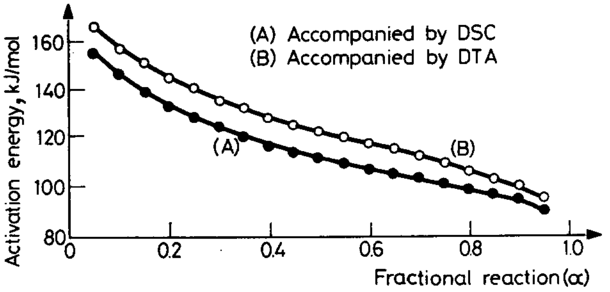

Fig. 3 Values of E at various α calculated by the Ozawa method for TG accompanied by DSC and DTA

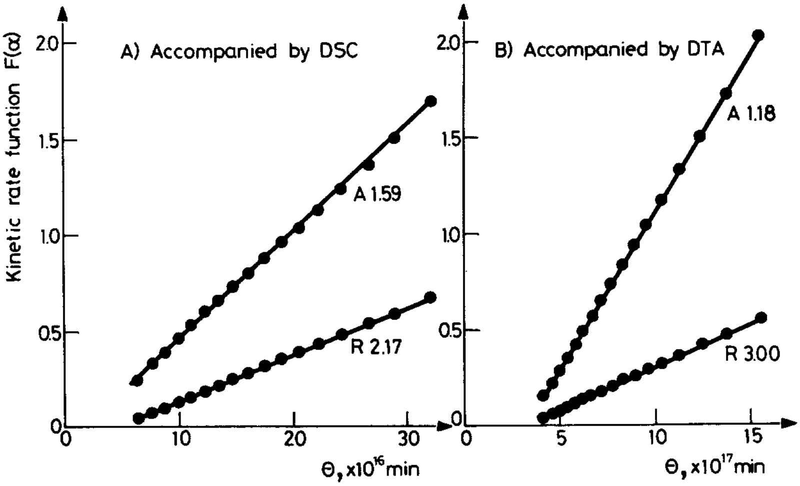

Fig. 4 The linear plots of the appropriate $F(\alpha)$ against θ

Table 2 Appropriate kinetic rate function, $F(\alpha)$, and Arrhenius parameters, E and A, calculated by the Ozawa method for the nonisothermal dehydration of crushed crystals of $Li_2SO_4 \cdot H_2O$ (–100 + 170 Mesh) within the various ranges of α

apparatus	range of	E,	$R_n = 1 - (1-\alpha)^{1/n}$				$A_m = [-\ln(1-\alpha)]^{1/m}$			
	α	kJ/mol	n	A, 1/s	γ^a	$\sigma^b \cdot 10^3$	m	A, 1/s	γ^a	$\sigma^b \cdot 10^3$
TG-DSC	0.1-0.9	114.1±2.5	2.17	$3.98 \cdot 10^{12}$	0.9999	2.01	1.59	$9.16 \cdot 10^{12}$	0.9997	10.4
	0.1-0.5	125.0±3.2	2.22	$1.20 \cdot 10^{14}$	0.9999	0.28	1.16	$3.17 \cdot 10^{14}$	0.9999	1.47
	0.2-0.6	117.7±2.7	2.00	$1.34 \cdot 10^{13}$	0.9999	0.31	1.33	$3.12 \cdot 10^{13}$	0.9999	1.16
	0.3-0.7	112.0±2.4	1.64	$2.55 \cdot 10^{12}$	0.9999	0.58	1.69	$4.46 \cdot 10^{12}$	0.9999	1.66
	0.4-0.8	107.3±2.2	2.27	$4.81 \cdot 10^{11}$	0.9999	1.36	1.72	$1.00 \cdot 10^{12}$	0.9999	1.76
	0.5-0.9	103.1±2.0	2.27	$1.33 \cdot 10^{11}$	0.9999	1.20	2.44	$1.92 \cdot 10^{11}$	0.9998	2.80
TG-DTA	0.1-0.9	124.0±2.1	3.00	$7.47 \cdot 10^{13}$	0.9987	7.80	1.18	$2.74 \cdot 10^{14}$	0.9999	4.23
	0.1-0.5	136.3±3.0	2.63	$4.33 \cdot 10^{15}$	0.9999	1.34	1.16	$1.31 \cdot 10^{16}$	0.9999	3.17
	0.2-0.6	128.8±2.2	3.00	$3.63 \cdot 10^{14}$	0.9997	1.52	1.06	$1.28 \cdot 10^{15}$	0.9999	1.60
	0.3-0.7	122.6±1.7	3.00	$5.17 \cdot 10^{13}$	0.9998	1.42	1.15	$1.81 \cdot 10^{14}$	0.9999	1.97
	0.4-0.8	117.0±1.4	3.00	$8.72 \cdot 10^{12}$	0.9998	1.83	1.27	$2.91 \cdot 10^{13}$	0.9999	0.80
	0.5-0.9	111.6±1.2	3.00	$1.56 \cdot 10^{12}$	0.9995	3.59	1.37	$5.05 \cdot 10^{12}$	0.9999	2.49

[a] Correlation coefficient of the linear regression analysis of the $F(\alpha)$ *vs.* θ plot, [b] Standard deviation of each point from the line

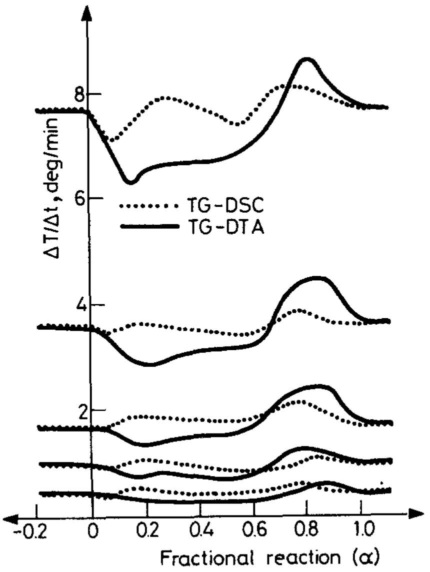

Fig. 5 Plots of $\Delta T/\Delta t$ against α during the course of reaction

Consequently many kinetic results already reported in the literature using dynamic TG (TG-DTA) measurements may thus be rather dubious and unreliable. Another serious problem arises because most of Arrhenius parameters for nonisothermal reactions are calculated by supposing a linear heating of the sample and uniform temperature of the sample. We conclude, therefore, that isothermal methods of determining kinetics of solid-state reactions are to be strongly preferred and should be always used to obtain the most reliable rate parameters [12, 18], although self-cooling or self-heating of the sample cannot be ignored here, either [8].

Conclusion

The kinetic equation obeyed and Arrhenius parameters determined from TG for the nonisothermal dehydration of $Li_2SO_4 \cdot H_2O$ were markedly influenced by the distortion from linearity of increasing temperature during rate measurements. The power-compensation type DSC and the simultaneous TG-DSC have the great advantage over TG or TG-DTA in characterizing the nonisothermal kinetic behavior of solid-state decompositions. Kinetic parameters determined nonisothermally from thermal analysis without use of DSC tend to be rather unreliable, particularly when they are obtained at higher heating rates and with larger sample sizes.

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Zusammenfassung — Mittels TG, ergänzt durch DTA und DSC mit Leistungskompensation wurde der Einfluß des Self-cooling-Effektes auf die scheinbare Kinetik der nichtisothermen Dehydratation von zerkleinerten Kristallen aus Lithiumsulfat-Monohydrat geschätzt. Die mittels TG-DTA erhaltene Kinetik und die Arrheniusschen Parameter weichen erheblich von denen ab, die mittels TG-DSC ermittelt wurden. DSC mit Leistungskompensation und TG-DSC haben gegenüber TG oder TG-DTA den großen Vorteil, das nichtisotherme kinetische Verhalten von Feststoffzersetzungen zu charakterisieren. Mittels Thermoanalyse nichtisotherm ermittelte kinetische Parameter sind ohne Anwendung von DSC eher unreell, besonders wenn sie bei größeren Aufheizgeschwindigkeiten und Probengrößen bestimmt wurden.