Notes

COMMENTS ON THE DEHYDRATION OF $Li_2SO_4 \cdot H_2O$ AS A MODEL SUBSTANCE IN KINETIC STUDIES

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$Li_2SO_4 \cdot H_2O$ is an important model substance that is frequently used in research to solve problems of TG measurements and their kinetic evaluation. The article by Huang and Gallagher [1] is one of the best examples of the many levels of the problems and the problem-solving efforts *via* well-organized measurements and their accurate kinetic evaluations on powdered, pressed pellet, plate and cubic crystal samples. Sample masses ranged from 36 to 38 mg. The purge gases were dry or wet N_2 for TG measurements, and dry N_2 for DSC ones. The apparent kinetic constants were calculated on the basis of the Ozawa method at different heating rates: 10, 2 or 0.5 and 10, 5 or $2°C$ min^{-1} for TG and DSC measurements, respectively.

The data in Tables 1–5 illustrate the kinetic compensation effect (CE), though they contain the effect of the different heating rates, i.e. the changes in the internal rates of the partial processes, too. For the data relating to dry and wet powder, pellet, plate and cubic samples, the regression coefficients of the straight lines are greater than 0.999, while for the DSC measurements they are greater than 0.996. This means that, by using the constants of CE ($logA=aE-b$) for all four dry samples and all the data in Tables 1–4 as one series ($a=0.3303$; 0.33426 and $b=-3.3185$; -3.31623), the E and $logA$ values (e.g. $a=0.14$ (powdered) and $a=0.85$ (cubic crystal)) can be recalculated and compared with the results published in Tables 1 and 4 as follows:

$0.14E=219.74,$ $logA=70.2$ $0.85E=71.44,$ $logA=19.8$ given,

$0.14E=218.70,$ $logA=70.6$ $0.85E=68.74,$ $logA=20.7$ recalculated,

$0.14E=219.93,$ $logA=70.1$ $0.85E=69.16,$ $logA=20.6$ recalculated.

Table 1 Constants calculated *via* Eq. (1) from data in Tables 1–5 [1]

Purge gas	TG measurements					
	Dry N_2			Wet N_2		
Parameters	E	T	Int	E	T	Int
Powder	7.73	362.7	−2.5616	12.44	340.1	−4.4001
Pellet	5.05	366.4	−1.6571	9.81	353.4	−3.3726
Plate crystal	14.49	344.2	−5.0636	12.06	361.4	−4.0139
Cubic crystal	17.29	327.6	−6.3504	11.72	366.0	−3.8521

Purge gas	DSC measurements		
	Dry N_2		
Powder	18.76	288.8	−7.8099
Pellet	6.93	346.3	−2.4055
Plate crystall	17.15	317.6	−6.6677
Cubic crystal	30.28	241.2	−15.1005

E=kJ mol^{-1}, T=temperature/ K, Int=intersection of log$A$

Consequently, the statement "that the kinetic mechanism changes during the course of the dehydration" (p. 39 [1]) is not verifiable with the measure of the formal kinetic constants. In spite of this, the mechanism is essentially very similar in each case.

To solve the problem, it has to be taken into consideration that an analogy exists between the component, the heat and the momentum streams. This is the basis of the dimensionless kinetic analysis and its application in the following equation [2]:

$$\ln A \cong \overline{(1/RT_i)E_i} - \overline{n\ln(1-\alpha)_i} + \overline{\ln(d\alpha/dt)_i} \tag{1}$$

A=1 and n=1 are the original conditions for the elimination of the physicochemical preconceptions relating with the partial processes like diffusion, heat conduction, etc. These are present and affect on the "pure" chemical reaction but inseparable manner. An analogy obviously exists between CE and the Eq. (1), but in a very formal manner.

$$a \cong \overline{(1/RT_i)E_i}, \quad \text{and} \quad b \cong \overline{-n\ln(1-\alpha)_i} + \overline{\ln(d\alpha/dt)_i,}$$

so the Eq. (1) is not an indefinite phenomenon only, like CE today, but characterizes both the thermal process and the relations of the measured data directly. This allows a quantitative determination of the similarity and differences of the different measurements. Besides establishing some set of criteria for the ideal ki-

netic study, it is justifiable to look for and to determine the effects of factors of thermal processes quantitatively. It is possible to obtain a perfect match between the two sets of TG and DSC curves, too.

Another aspect is that it has to agree with most of the qualitative findings about the measured data in the article. These statements are proved by the data in Table 1.

References

1 J. Huang and P. K. Gallagher, Thermochim. Acta, 192 (1991) 35.
2 Z. Adonyi, J. Thermal Anal., 47 (1996) 577.