Kinetic Parameters from Thermogravimetric Data

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Z. Naturforsch. 34 a, 661–663 (1979);
received April 9, 1979

The "differential" method of Achar, Brindley and Sharp (ABS) and the "integral" one of Coats and Redfern (CR) are applied to the dehydration of $BaBr_2 \cdot H_2O$ and $HCOOLi \cdot H_2O$ and to the thermal decomposition of $Pb(SCN)_2$, and the kinetic parameters so obtained are compared with those deduced isothermally.

The results of the ABS method, at the lowest heating rate ($q = 1.2\ K\ min^{-1}$), agree well with the isothermal ones, whereas the CR method leads to satisfactory results only for the $Pb(SCN)_2$ thermal decomposition ($q = 1.2\ K\ min^{-1}$). A possible explanation is given.

In a previous work [1] on the nonisothermal dehydration of $BaBr_2 \cdot 2\,H_2O$ we have found that the α (fractional decomposition) vs. t (time) curves, at low and constant heating rates, satisfy the kinetic equations deduced isothermally [2].

In this note, two of the methods currently used to exploit nonisothermal TG curves, i. e. the Achar, Brindley and Sharp (ABS) [3] "differential" method and the Coats and Redfern (CR) [4] "integral" method are tested.

This is performed by considering three thermal decompositions with very different features (previously or presently studied isothermally in our Institute), i. e. $BaBr_2 \cdot H_2O$ dehydration [2], $HCOOLi \cdot H_2O$ dehydration [5] and $Pb(SCN)_2$ thermal decomposition.

The α vs. t curves (with heating rates, q, between 1.2 and 11 $K\ min^{-1}$) were recorded by using the same apparatus, the same shape, size and amount of sample and the same experimental procedures as employed in the corresponding isothermal studies.

Both the ABS and the CR methods are based on the equation

$$\frac{d\alpha}{dT} = \frac{Z}{q} \exp\left(-\frac{E}{RT}\right)(1-\alpha)^n, \qquad (1)$$

where Z is the frequency factor, E the activation energy, and n the order of the reaction.

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0340-4811 / 79 / 0500-0661 $ 01.00/0

The ABS method utilizes directly the logarithmic form of (1):

$$\log \frac{d\alpha}{dT}\frac{1}{(1-\alpha)^n} = \log \frac{Z}{q} - \frac{E}{4.576\,T}. \qquad (2)$$

In the integration of (1),

$$\int_0^{\alpha} \frac{d\alpha'}{(1-\alpha')^n} = \frac{Z}{q}\int_{T_0}^{T} \exp\left(-\frac{E}{RT'}\right) dT', \qquad (3)$$

the approximation (cf. [6])

$$\int_{T_0}^{T} \exp\left(-\frac{E}{RT'}\right) dT' = \frac{E}{R}\left[x^2(1-2x)\exp\left(-\frac{1}{x}\right) - x_0^2(1-2x_0)\exp\left(-\frac{1}{x_0}\right)\right] \qquad (4)$$

with $x = RT/E$ and $x_0 = RT_0/E$ is valid. In the CR method the second term on the r.h.s. of (4) is neglected, which, as shall be shown, is not always adequate.

a) Dehydration of $BaBr_2 \cdot H_2O$

The α vs. t curves were recorded at five different heating rates ($q = 1.2$, 3, 6, 8, and 11 $K\ min^{-1}$) [1].

The ABS method was employed for the n values 0, 1/2, 2/3, and 1 and gave the best fit for $n = 1/2$, which is shown in Fig. 1 for the different heating rates. In Table I the activation energy and frequency factor values, as deduced by applying the linear regression method to the straight lines of Fig. 1, are reported.

The CR method has been applied for the same n values. It has been observed that the experimental values satisfy the $n = 1$ order whereas for $n = 1/2$ they result in curves (as an example, the results obtained for the heating rates $q = 1.2$ and 6 $K\ min^{-1}$ are reported in Figure 2).

Table I. Results obtained for the $BaBr_2 \cdot H_2O$ dehydration ($0.15 \leq \alpha \leq 0.90$).

Method	q/K min^{-1}	T_0/K	n	E/kcal mole^{-1}	Z/min^{-1}
ABS	1.2	377.5	1/2	25.3	$4.88 \cdot 10^{12}$
ABS	3	380	1/2	22.2	$1.05 \cdot 10^{11}$
ABS	6	385	1/2	21.5	$4.69 \cdot 10^{10}$
ABS	8	390	1/2	20.3	$1.10 \cdot 10^{10}$
ABS	11	395	1/2	20.2	$1.04 \cdot 10^{10}$
Isothermal			1/2	25.3	$2.24 \cdot 10^{12}$

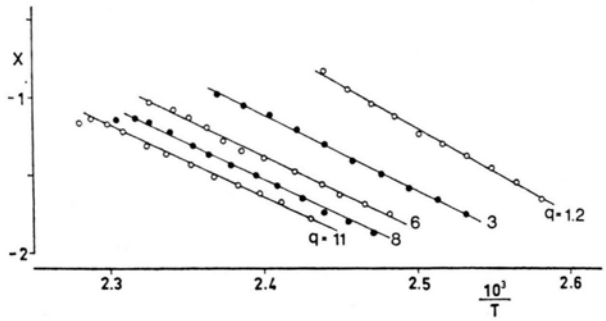

Fig. 1. Dehydration of $BaBr_2 \cdot H_2O$: data calculated by the ABS method for $n = 1/2$.

$$X = \log\left(\frac{d\alpha}{dT}\frac{1}{(1-\alpha)^{1/2}}\right).$$

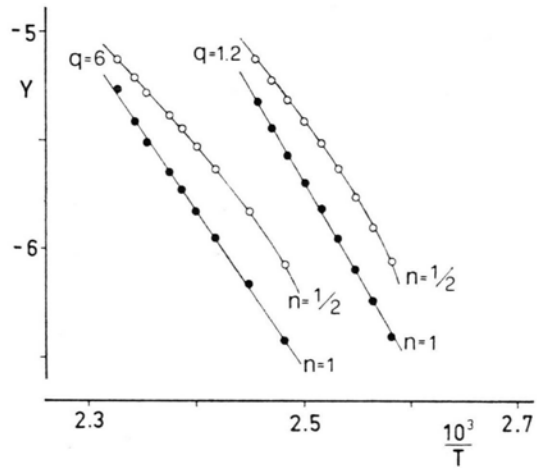

Fig. 2. Dehydration of $BaBr_2 \cdot H_2O$: data calculated by the CR method for $n = 1/2$ and $n = 1$.

$$Y = \log\frac{1-(1-\alpha)^{1/2}}{T^2/2} \text{ and } \log\left[-\frac{\log(1-\alpha)}{T^2}\right], \text{ respectively.}$$

b) Dehydration of $HCOOLi \cdot H_2O$

The isothermal study [5], performed in vacuo with single crystals in the temperature range 44 – 80 °C, showed that the experimental data fit the equation $\alpha = k\,t$ in the range $0.05 \leqq \alpha \leqq 0.50$. For $\alpha > 0.50$ we found a decay period whose interpretation was difficult.

The α vs. t curves have been recorded at the heating rates $q = 1.2$ and 6 K min^{-1}.

In Table II the results obtained by applying the ABS method for the order $n = 0$, which gives the best fit, are reported. Also in this case, the application of the CR method, for $n = 0$, gives curvilinear trends.

Table II. Results obtained for the $HCOOLi \cdot H_2O$ dehydration ($0.05 \leqq \alpha \leqq 0.50$).

Method	q/K min^{-1}	T_0/K	n	E/kcal mole^{-1}	Z/min^{-1}
ABS	1.2	325	0	14.2	$9.79 \cdot 10^7$
ABS	6	325	0	9.7	$1.14 \cdot 10^5$
Iso-thermal			0	14.0	$1.10 \cdot 10^8$

c) Thermal decomposition of $Pb(SCN)_2$

Investigations on the thermal decomposition of $Pb(SCN)_2$ are in progress in this Institute. We can anticipate here some of the results obtained isothermally in air in the temperature range 237 – 280 °C. The samples were prepared by recrystallization of the commercial salt (Merck Suprapur). The grain size averaged 44 – 63 μm. In the range $0.05 \leqq \alpha \leqq 0.80$ * the experimental data fit the equation $\alpha = k\,t$.

The α vs. t curves were recorded at the heating rates $q = 1.2$ and 6 K min^{-1}. Table III presents the results obtained applying both methods for the order $n = 0$, which gives the best fit.

From the results with the ABS method it appears that, at least for the lowest heating rate ($q = 1.2$ K min^{-1}), the activation energy and frequency factor values of the three reactions studied are in good agreement with those deduced from the isothermal study.

As concerns the CR method, only for the $Pb(SCN)_2$ thermal decomposition (Table III) the results agree with the isothermal ones, at least for $q = 1.2$ K min^{-1}.

To evaluate the validity of the mentioned neglection in the CR method we calculated for the three

Table III. Results obtained for the $Pb(SCN)_2$ thermal decomposition ($0.05 \leqq \alpha \leqq 0.80$).

Method	q/K min^{-1}	T_0/K	n	E/kcal mole^{-1}	Z/min^{-1}
ABS	1.2	480	0	45.4	$1.62 \cdot 10^{16}$
ABS	6	480	0	41.2	$2.77 \cdot 10^{14}$
CR	1.2	480	0	46.7	$6.38 \cdot 10^{16}$
CR	6	480	0	39.1	$4.26 \cdot 10^{13}$
Iso-thermal			0	44.9	$1.02 \cdot 10^{16}$

* The α values were calculated assuming PbS as the only solid product (as verified by X-ray diffraction).

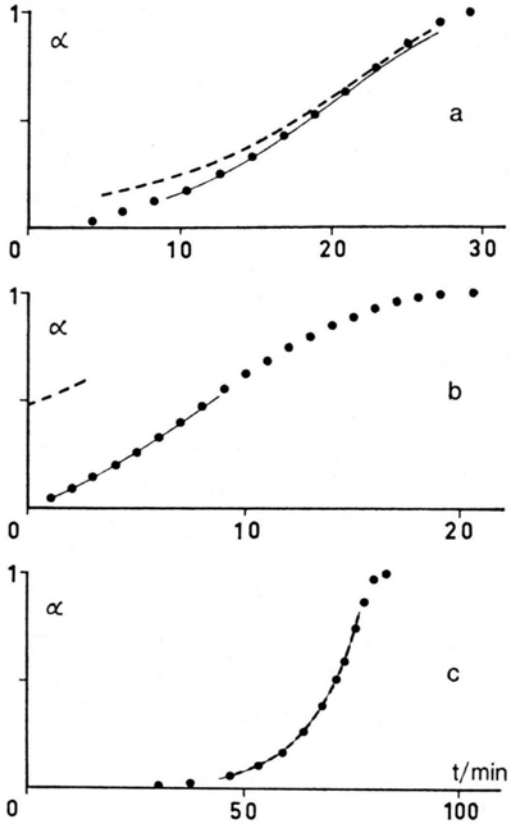

Fig. 3. Comparison between the experimental (full circles) and calculated α vs $\cdot t$ curves. Full lines: exponential integral calculated between the boundaries T_0 and T. Dashed lines: exponential integral calculated between the boundaries 0 and T; a) Dehydration of $BaBr_2 \cdot H_2O$, b) Dehydration of $HCOOLi \cdot H_2O$, c) Thermal decomposition of $Pb(SCN)_2$.

processes the α vs. t curves ($q = 1.2\,K\,min^{-1}$) by using the correct and the approximate form of (4). This was accomplished by employing the kinetic parameters isothermally deduced.

The results obtained are reported, along with the experimental data, in Figure 3 a, b, c. It can be seen that only for the $Pb(SCN)_2$ thermal decomposition (Fig. 3 c) the two calculated curves agree with the experimental data.

As regards the $BaBr_2 \cdot H_2O$ (Fig. 3 a) and $HCOOLi \cdot H_2O$ (Fig. 3 b) dehydrations, we observe that only the curves calculated assuming T_0 as the lower boundary for the exponential integral agree with the experimental data; a different trend, on the contrary, is apparent when 0 and T are taken as the boundaries. The disagreement is larger for the $HCOOLi \cdot H_2O$ dehydration which has the lower activation energy.

It seems therefore that the neglection as regards the exponential integral adopted by CR (and by other Workers [7] who also proposed "integral" methods) is not generally adequate; this probably can be the reason of the discrepancies existing among literature results obtained by means of "integral" methods [8].

In particular, the CR method appears to be inadequate when applied to the non-isothermal study of reactions, such as dehydrations, which have activation energy values not higher than 20 – 25 kcal $mole^{-1}$ and develope in temperature ranges between room temperature and about 200 °C.

[1] G. Flor, A. Marini, and V. Berbenni, Z. Naturforsch. (in press).
[2] G. Flor, Atti Soc. Peloritana **16,** 11 (1970).
[3] B. N. Achar, G. W. Brindley, and J. H. Sharp, Proc. Int. Clay Conf. Jerusalem **1,** 67 (1966).
[4] A. W. Coats and J. P. Redfern, Nature London **201,** 68 (1964).
[5] G. Flor, V. Berbenni, and P. Ferloni, "Journées de Calorimétrie et d'ADT", Torino, 28–30 juin 1978.
[6] E. D. Rainville, Special Functions, McMillan, London 1960, p. 44.
[7] J. Zsako, J. Phys. Chem. **72,** 2406 (1968). – V. Satava and F. Skvara, J. Am. Ceram. Soc. **52,** 591 (1969). – T. Ozawa, Bull. Chem. Soc. Japan **38,** 1881 (1965).
[8] J. Zsako and H. E. Arz, J. Thermal Anal. **6,** 651 (1974). – J. Simon, J. Thermal Anal. **5,** 271 (1973).