ON THE METHOD OF BAE FOR THE DETERMINATION OF KINETIC PARAMETERS FROM DTA CURVES

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The mathematical error in the method proposed by Bae for the determination of kinetic parameters from DTA curves has been corrected. The proposed equation does not contain thermal constants of the apparatus, and can be applied to DTA curves by an iterative method. The results obtained by the application of this equation to experimental DTA curves for the decomposition of sodium bicarbonate compared well with those from isothermal measurements, even when the DTA sample holder assembly was of the isolated cup-type instead of the block-type assembly recommended by Bae.

Bae [1] extended the theory of Akita and Kase [2] for application to DTA with spherical cells in a block-type assembly, and derived an expression for the differential temperature measured between the centres of the specimens as

$$\Delta T = \frac{a^2}{6\,K_2} \frac{Q W_0}{C_2 W_2} \frac{\mathrm{d}(W/W_0)}{\mathrm{d}t} \tag{1}$$

The reaction rate, $\dfrac{\mathrm{d}(W/W_0)}{\mathrm{d}t}$, for reactions following random nucleation with one nucleus on each particle (Mampel law), was expressed as

$$\frac{\mathrm{d}(W/W_0)}{\mathrm{d}t} = A \exp\left(\frac{A}{\alpha}\right) \exp(\alpha t) \exp\left[-\frac{A}{\alpha} \exp(\alpha t)\right] \tag{2}$$

where

$$A = Z \exp\left(-\frac{E}{RT_0}\right) \tag{3}$$

and

$$\alpha = \frac{E\beta}{RT_0^2} . \tag{4}$$

The symbols except β, the heating rate, have the same significance as in the original paper [1]. Using the condition $\dfrac{\mathrm{d}^2(W/W_0)}{\mathrm{d}t^2} = 0$ at the time of maximum reaction rate, t_{m}, Bae derived expressions for the calculation of kinetic parameters from DTA curves.

At t_m, we have from (2)

$$\alpha t_m = \ln \left(\frac{\alpha}{A} \right) \tag{5}$$

and hence

$$\Delta T_m = \frac{a^2}{6K_2} \frac{QW_0}{C_2 W_2} \frac{1}{e} \alpha \exp \left(\frac{A}{\alpha} \right) \tag{6}$$

The expression for $\Delta T_{\frac{1}{2}m}$ can be derived as follows:

At $t_{\frac{1}{2}m} = 1/2 \, t_m$, (2) can be written as:

$$\left[\frac{d(W/W_0)}{dt} \right]_{t_{\frac{1}{2}m}} = A \exp \left(\frac{A}{\alpha} \right) \exp \left(\frac{\alpha}{2} t_m \right) \exp \left[-\frac{A}{\alpha} \exp \left(\frac{\alpha}{2} t_m \right) \right] \tag{7}$$

Substituting (5) in (7), it can be shown that

$$\left[\frac{d(W/W_0)}{dt_i} \right]_{t_{\frac{1}{2}m}} = \sqrt{A\alpha} \exp \left[\frac{A}{\alpha} - \sqrt{\frac{A}{\alpha}} \right] \tag{8}$$

Substituting (8) in (1), we get

$$\Delta T_{\frac{1}{2}m} = \left[\frac{a^2}{6K_2} \frac{QW_0}{C_2 W_2} \right] \sqrt{A\alpha} \exp \left[\frac{A}{\alpha} - \sqrt{\frac{A}{\alpha}} \right] \tag{9}$$

The expression for $\Delta T_{\frac{1}{2}m}$ derived by Bae (Eq. 29 of ref. 1) is given by

$$\Delta T_{\frac{1}{2}m} = \frac{a^2}{6K_2} \frac{QW_0}{C_2 W_2} (A\alpha)^{\frac{1}{2}} \exp \left(\frac{A}{\alpha} \right)^{\frac{1}{2}} \tag{10}$$

and appears in error.

The term in the first square bracket of (9) can be eliminated on dividing by (6), whence

$$\frac{\Delta T_{\frac{1}{2}m}}{\Delta T_m} = e \left(\frac{A}{\alpha} \right)^{\frac{1}{2}} \exp \left[-\sqrt{\frac{A}{\alpha}} \right] \tag{11}$$

Substitution of (5) in (11) leads to

$$\frac{\Delta T_{\frac{1}{2}m}}{\Delta T_m} = e \exp \left[-\left(\frac{1}{2} \alpha t_m + e^{-\frac{1}{2}\alpha t_m} \right) \right] \tag{12}$$

or

$$1 - \ln \left[\frac{\Delta T_{\frac{1}{2}m}}{\Delta T_m} \right] = \frac{1}{2} \alpha t_m + \exp \left[-\frac{1}{2} \alpha t_m \right] \tag{13}$$

Knowing t_m, ΔT_m and $\Delta T_{\frac{1}{2}m}$, (13) can be iterated to obtain the value of α and hence E. The value of α can then be substituted in (5) to obtain A, from which Z can be calculated using (3). (13) has been tested with DTA curves obtained for the decomposition of sodium bicarbonate.

Experimental

DTA curves were recorded with an assembly consisting of a D. C. Microvolt-meter (Rikadenki Kogyo Co. Ltd., Model A-10), an X—Y Recorder (Houston Omnigraphic Corporation — Model HR-101) and an on-off program controller (Hartmann and Braun-Indin 192 controller, coupled with timed program unit RMZ and thermal two-position feed-back unit RMT1). The sample holders were platinum cups (6 g each) supported on silica spaghetties [3]. A differential thermo-couple circuitry [3] was used to measure ΔT as well as the temperature of the reference material. The thermocouple junctions were placed in the depressions at the base of the platinum cups and were located at the centre of the sample without being in contact with it. The platinum cups were provided with sleeves fitting snugly over the silica spaghetties, so that positioning of the cups was re-producible. Since good baselines were obtained at a sensitivity of 2 μV ($\simeq 0.05$ K) per division on the ΔT axis using chromel-alumel thermocouples (30 gauge), experiments were carried out with 10 mg samples at a heating rate of $4.5-5$ K/min. The sample (B.D.H. AnalaR, -200 mesh) was diluted with 190 mg cal-cined alumina (B.D.H. AnalaR), the reference material, and hence Bae's assump-tion of equal thermal diffusivities was nearly true for the present experimental conditions. The peak heights of the DTA curves were reproducible to within 2 μV, and the peak areas to within 5 per cent.

With a view to confirming the results obtained by DTA, a separate series of iso-thermal weight loss measurements were also performed, using the Little Gem' TG kit supplied by Cahn Instrument Co. The small diameter of the furnace and

Table 1

Kinetic parameters for the decomposition of sodium bicarbonate from isothermal weight loss measurements

T, K	$k \times 10^4$, sec^{-1}*	E, kcal/mole	Z, sec^{-1}
387	8.6		
397	18.0		
		23.9	2.6×10^{10}
403	30.3		
410	47.9		

* Mechanism of decomposition corresponded to the Mampel unimolecular decay law.

Kinetic parameters for the decomposition

Curve No.	Sample weight, mg	Heating rate, K/min	T_0, K	t_m, sec	T_m, K	$t_{1/2 m}$, sec
1.	10.2	4.8	388.0	448	423.8	224
2.	10.1	4.9	382.5	510	422.5	255
3.	10.2	4.5	386.0	510	422.0	255
4.	10.2	4.4	387.5	519	424.5	259
5.	10.2	4.3	390.0	459	423.5	230

* One chart division corresponds to 2 μv. Values of ΔT were measured with respect to the

hangdown tube allowed precise measurements at a sensitivity of 10 μg, and hence sample weights of $1-2$ mg were used in these studies. Since the thermal inertia of the system was relatively small, temperatures could be easily controlled at the desired value. The temperature-measuring thermocouple was located within 2 mm of the sample pan positioned in the uniform temperature zone of the furnace. The sample could be heated to the desired temperature within three minutes.

Results and discussion

The isotherms obtained at 387, 397, 403 and 410 K were analyzed using the Mampel equation for random nucleation with one nucleus on each particle. The plot of $-\log(1 - \sigma)$ vs. time, where σ is the fraction decomposed, indicated an excellent fit $(0-99\%)$ of the data. The small sample weight might have ensured the agreement between theory and experiment by reducing self-cooling of the sample due to the endothermic reaction, and also by favouring diffusion of the product gases away from the sample environment. The rate constants obtained as the slopes of the plots of $-\lg(1 - \sigma)$ vs. time, are listed in Table 1. The Arrhenius plot yielded values of 23.9 kcal/mole for the activation energy, and 2.6×10^{10} sec^{-1} for the pre-exponential factor.

The results from the isothermal studies justified the use of Eq. (13), for which the validity of the Mampel law is an important assumption. Data pertaining to five DTA curves for sodium bicarbonate were iterated in accordance with (13). The results presented in Table 2 gave values of E and Z in good agreement with those obtained by the isothermal method, thereby justifying the use of (13).

Solving (6) and (10), Bae derived an expression (Eq. 30 of ref. 1)

$$A = \frac{(\Delta T_{\frac{1}{2}m})^2}{\Delta T_m} \frac{1}{e} \frac{6K_2}{a^2} \frac{C_2 W_2}{Q W_0} \tag{14}$$

of sodium bicarbonate by the modified method

$T_{\frac{1}{2}}m$, K	*ΔTm, div.	$\Delta T_{\frac{1}{2}}m$ div.*	$\alpha \times 10^{4}$	E, kcal/mole	Z, sec^{-1}
405.5	24.7	12.7	63.488	23.8	5.5×10^{10}
401.5	25.2	9.5	71.163	25.1	4.3×10^{10}
403.0	25.0	12.0	59.370	23.6	6.5×10^{9}
405.5	25.3	11.8	59.868	24.3	1.5×10^{10}
407.0	24.4	13.0	59.887	25.2	5.1×10^{10}

baseline constructed using the straight line approximation discussed by Smith [4].

for calculating E and Z from a single DTA curve for reactions following the Mampel law. The error in (10), however, invalidates (14). Since the thermal constants in (14) are usually not known, an alternative expression based on DTA curves obtained at different heating rates was also suggested by Bae. This has also been shown to lead to erroneous results [5] because of the difference in magnitude by which DTA and σ vs. temperature curves are affected by the heating rate. However, it should be emphasized from the successful application of (13) to DTA curves of sodium bicarbonate presented here that the basis of the method suggested by Bae is valid.

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References

1. J. H. BAE, J. Thermal Anal., 4 (1972) 261.
2. K. AKITA and M. KASE, J. Phys. Chem., 72 (1968) 906.
3. K. S. SUBRAMANIAN, Report, B. A. R. C.-429 (1969).
4. G. W. SMITH, Thermochim. Acta, 21 (1977) 431.
5. P. V. RAVINDRAN, T. P. RADHAKRISHNAN and A. K. SUNDARAM, Report, B. A. R. C. — 873 (1976).

RÉSUMÉ — On a corrigé l'erreur mathématique de la méthode proposée par Bae pour la détermination des paramètres cinétiques à partir des courbes d'ATD. L'équation proposée ne contient pas de constantes thermiques relatives à l'appareil et peut être appliquée aux courbes d'ATD par une méthode itérative. Les résultats obtenus en appliquant cette équation aux courbes d'ATD expérimentales pour la décomposition du bicarbonate de sodium sont en bon accord avec ceux obtenus à partir de mesures isothermes, même si le porte-échantillon de l'appareil d'ATD est du type coupelle isolée au lieu du type bloc recommandé par Bae.

ZUSAMMENFASSUNG — Der mathematische Fehler der von Bae zur Bestimmung kinetischer Parameter aus DTA-Kurven vorgeschlagenen Methode wurde korrigiert. Die vorgeschlagene Gleichung enthält keine thermischen Konstanten der Geräte und kann für DTA-Kurven durch eine iterative Methode angewandt werden. Die durch Anwendung dieser Gleichung bei experimentellen DTA-Kurven der Zersetzung von Natriumbicarbonat erhaltenen Ergebnisse sind mit den aus isothermen Messungen erhaltenen gut vergleichbar, selbst wenn die DTA-Probenbehälter-Zusammenstellung dem isolierten Bächertyp und nicht dem von Bae empfohlenen Blocktyp entsprach.

Резюме — Исправлена математическая ошибка в методе, предложенном Би для определения кинетических параметров из кривых ДТА. Предложенное уравнение не содержит термических констант прибора и может быть использовано для кривых ДТА с помощью итерационного метода. Результаты, полученные при использовании этого уравнения к экспериментальным кривым ДТА разложения бикарбоната натрия, хорошо сравнимы с результатами изотермических измерений и даже в том случае, когда держатель образца в ДТА был изолированного чашечного типа, вместо держателя образца блочного типа, как было предложено Би.