Accuracy of Approximations in Kinetic Data Circulation

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Synopsis

Kinetic data can be determined from the relation of two kinetic equations in their integrated form. For the calculation of the exponential integral, approximations are generally used, which allow a simple calculation of the activation energy. With respect of the most frequently used approximations, an evaluation of error produced by their application has been calculated. The best results can be achieved by using the equation

$$\int_0^T \exp\{-E/RT\}dT = (RT^2/E) \exp\{-E/RT\}$$

which permits determination of E to within 1% accuracy.

Introduction

In the study of thermal decompositions we assume that their progress can be described by the equation

$$d\alpha/dt = (Z/\phi) \exp\{-E/RT\}f_{(\alpha)} \tag{1}$$

where the fraction decomposed α is the ratio of weight, volume, or number of moles of the initial mass decomposed to the original quantity, Z is a constant involving frequency factor, and $f_{(\alpha)}$ is only the function α. For polymer pyrolyses the function of $f_{(\alpha)}$ usually has the form $(1 - \alpha)^n$, where n is reaction order. If the heating rate ϕ is constant, eq. (1) rearranged in integral form can be written

$$(\phi/Z) \int_0^\alpha d\alpha/f_{(\alpha)} = \int_0^T \exp\{-E/RT\}dT \tag{2}$$

The activation energy can be determined from the relationship of two sets of eq. (2), where the upper limits of integration on the right-hand side are T_1 and T_2. On the left-hand side of both equations there are different limits of integration,[1-3] α_1 and α_2 or temperature increments[4,5] ϕ_1 and ϕ_2. If the reaction is not of the first order, the left-hand sides can differ by a different Z.[5] If we designate this quantity, which is different in both equations as ζ, we get (see following page)

$$\frac{\zeta_1}{\zeta_2} = \frac{\int_0^{T_1} \exp\{-E/RT\}dT}{\int_0^{T_2} \exp\{-E/RT\}dT} \tag{3}$$

The integral of the exponential function has been calculated by using various methods.

(1) By substitution, integration by parts, and neglecting the third and higher terms of the semidivergent series[6,7] we get

$$\int_0^T \exp\{-E/RT\}dT = (RT^2/E)\exp\{-E/RT\} \tag{4}$$

(2) By neglecting the changes of the quadratic term against the exponential, eq. (4) will be further simplified,[8,9] yielding

$$\int_0^T \exp\{-E/RT\}dT = (RT_s^2/E)\exp\{-E/RT\} \tag{5}$$

where T_s is the mean value of the temperature interval within which the reaction takes place. This approximation has been used by other authors.[5,10]

(3) Horowitz and Metzger[2,11] suggested another relationship:

$$\exp\{-E/RT\} = \exp\{-(E/RT_s)[1 - (\theta/T_s)]\} \tag{6}$$

$$\int_0^{T_1} \exp\{-E/RT\}dT = (RT_s^2/E)\exp\{-(E/RT_s)[1 - (\theta/T_s)]\} \tag{7}$$

where

$$\theta = T_1 - T_s$$

(4) For this calculation, Reich[12] has used the equation

$$\frac{\int_{T_1}^{T_1'} \exp\{-E/RT\}dT}{\int_{T_2}^{T_2'} \exp\{-E/RT\}dT} = \frac{\exp\{-E/RT_1\}}{\exp\{-E/RT_2\}} \tag{8}$$

$T_1' = T_1 = T_2' - T_2 = \Delta T$ is so narrow a temperature interval that the integral can be replaced with a sufficient degree of accuracy by the first term of Taylor's expansion. The application of the above approximations is evident. By substituting, e.g., eq. (4) into eq. (3) we get[1,4]

$$\frac{\zeta_1}{\zeta_2} = \frac{T_1^2}{T_2^2} \exp\left\{-\frac{E(T_2 - T_1)}{RT_2T_1}\right\} \tag{9}$$

where ζ is either the integral[1] $\int_0^\alpha d\alpha/f(\alpha)$ or the heating rate[4] ϕ, or, in a favorable case, Z. The more often used graphical method consists in plotting $\ln \zeta - 2 \ln T$ against $1/T$ and determining the slope of the plotted straight line.

Calculation of Errors

We express the activation energy as a function of $\zeta_1/\zeta_2 = \zeta_{12p}$:

$$E = \varphi_{(\zeta_{12p})}$$

$$\zeta_{12p} = f_{(E)}$$

(10)

where f is a inverse function to φ. In this case f is a transcendental function and in the interval at hand can be replaced by a simpler function of f_{ap}

$$\zeta_{12ap} = f_{ap(E)}$$

$$E = \varphi_{ap(\zeta_{12ap})}$$

(11)

We define E_{ap} as a function of ζ_{12p}:

$$E_{ap} = \varphi_{ap(\zeta_{12p})}$$

$$\zeta_{12p} = f_{ap(E_{ap})}$$

(12)

If the difference between true and approximate value of activation energy ΔE is small we can write

$$E - E_{ap} = \Delta E$$

$$= \varphi_{ap(\zeta_{12ap})} - \varphi_{ap(\zeta_{12p})}$$

$$= \varphi'_{ap(\zeta_{12})}(\zeta_{12ap} - \zeta_{12p})$$

(13)

where

$$\zeta_{12} \in \langle \zeta_{12ap}, \zeta_{12p} \rangle$$

(14)

For the first approximation the following expressions may be obtained

$$f_{ap(E)} = (T_1{}^2/T_2{}^2) \exp \left\{ -E(T_2 - T_1)/RT_1T_2 \right\}$$

(15)

$$\varphi_{ap(\zeta_{12})} = -[RT_1T_2/(T_2 - T_1)] \ln (T_2{}^2/T_1{}^2)\zeta_{12}$$

(16)

$$f_{(E)} = f_{ap(E)} \frac{1 - \dfrac{2!}{x_1} + \dfrac{3!}{x_1{}^2} - \dfrac{4!}{x_1{}^3} \cdots \dfrac{(-1)^n(n-1)!}{x_1{}^{n-2}}}{1 - \dfrac{2!}{x_2} + \dfrac{3!}{x_2{}^2} - \dfrac{4!}{x_2{}^3} \cdots \dfrac{(-1)^n(n-1)!}{x_2{}^{n-2}}}$$

(17)

$$= f_{ap(E)} \frac{1 - (2/x_1)\vartheta_1}{1 - (2/x_2)\vartheta_2}$$

where

$$\vartheta_1 = 1 - \frac{3!}{2x_1} + \frac{4!}{2x_1{}^2} \cdots \frac{(-1)^{n-1}(n-1)!}{2x_1{}^{n-3}}$$

(18)

$$\vartheta_2 = 1 - \frac{3!}{2x_2} + \frac{4!}{2x_2{}^2} \cdots \frac{(-1)^{n-1}(n-1)!}{2x_2{}^{n-3}}$$

(19)

and

$$x_1 = E/RT_1 \qquad\qquad n \leq x$$
$$x_2 = E/RT_2 \qquad\qquad n > x - 1 \tag{20}$$

$$d\varphi_{ap}/d\zeta_{12} = -[RT_1T_2/(T_2 - T_1)](1/\zeta_{12}) \tag{21}$$

If $T_1 > T_2$ it follows that

$$E \leqslant \frac{RT_1T_2}{T_1 - T_2} \frac{2R(\vartheta_1 T_1 - \vartheta_2 T_2)}{E[1 - (2RT_1/E)\vartheta_1]} \tag{22}$$

By using the second approximation it follows in the same way that

$$E \leqslant \left| -\frac{RT_1T_2}{T_2 - T_1} \frac{T_2{}^2 - T_1{}^2 - (2RT_2{}^3/E)\vartheta_2 + (2RT_1{}^3/E)\vartheta_1}{T_2{}^2[1 - (2RT_2/E)\vartheta_2]} \right| \tag{23}$$

The third approximation leads to a rather cumbersome expression. In illustration, if only the first five terms are considered, we get

$$\frac{\Delta E}{E} \leqslant \left| -\frac{1}{x(h_1 - h_2)} \right.$$

$$\times \left. \frac{a(h_1 - h_2) + b(h_1{}^2 - h_2{}^2) + c(h_1{}^3 - h_2{}^3) + d(h_1{}^4 - h_2{}^4)}{1 - \dfrac{2}{x} + \dfrac{6}{x^2} - \dfrac{24}{x^3} + \dfrac{120}{x^4} - \dfrac{720}{x^5} \cdots + ah_2 + bh_2{}^2 + ch_2{}^3 + dh_2{}^4} \right|$$

$$\tag{24}$$

where

$$a = 2 - \frac{6}{x} + \frac{24}{x^2} - \frac{120}{x^3} + \frac{720}{x^4} - \frac{5040}{x^5} + \frac{40320}{x^6} \cdots$$

$$b = -x + 3 - \frac{12}{x} + \frac{60}{x^2} - \frac{360}{x^3} + \frac{2520}{x^4} - \frac{20160}{x^5} \cdots$$

$$c = -x + 4 - \frac{20}{x} + \frac{120}{x^2} - \frac{840}{x^3} + \frac{6720}{x^4} \cdots$$

$$d = \frac{x^2}{2} - x + 5 - \frac{30}{x} + \frac{210}{x^2} - \frac{1680}{x^3} \cdots$$

and

$$h_1 = (T_1 - T_s)/T_s$$
$$h_2 = (T_2 - T_s)/T_s$$
$$h_1 > h_2$$
$$x = E/RT_s$$

The error of the last method is given by

$$\frac{\Delta E}{E} \Bigg| \leqslant \frac{T_1 T_2}{T_2 - T_1} \frac{\Delta T[(\vartheta_1/T_1{}^2) - (\vartheta_2/T_2{}^2)]}{2[1 + (E\Delta T/2RT_1{}^2)\vartheta_1]} \Bigg| \tag{25}$$

where

$$\vartheta_1 = 1 + 1/3 \frac{\Delta T}{T_1} (x_1 - 2) + \frac{1}{12} \left(\frac{\Delta T}{T_1}\right)^2 (x_1{}^2 - 6x_1 + 6)$$

$$+ \frac{1}{60} \left(\frac{\Delta T}{T_1}\right)^3 (x_1{}^3 - 12x_1{}^2 - 36x_1 - 24) \ldots$$

$$\vartheta_2 = 1 + 1/3 \frac{\Delta T}{T_2} (x_2 - 2) + \frac{1}{12} \left(\frac{\Delta T}{T_2}\right)^2 (x_2{}^2 - 6x_1 + 6)$$

$$+ \frac{1}{60} \left(\frac{\Delta T}{T_2}\right)^3 (x_2{}^3 - 12x_2{}^2 + 36x_2 - 24) \ldots$$

Discussion

The use of the first approximation leads to a lower E value; in view of the fact that x is generally greater than 20, the error varies within tenths of one per cent. This conclusion is in accordance with the tabulated ratios between true and approximate values of the exponential integral.[13] When applying the second method, the error is in the opposite sign and its value can exceed 10%. This is obviously the reason for the very high activation energy calculated by Ingraham and Marier.[11] The third approximation with small h is approaching the second one, and roughly the same applies to its error. By a suitable choice of T_s, however, a substantially greater accuracy can be achieved, because the first two terms of the numerator can mutually cancel. This happens, if we choose $h_2 = 0$ and $h_1 = 0.10$ for $x = 20$, $h_1 = 0.067$ for $x = 30$, $h_1 = 0.05$ for $x = 40$. The requirement that T_s should be the temperature at which the rate of reaction reaches it maximum value cannot, therefore, in this case be justified. By using the last method we obtain a lower activation energy. By substituting T' for T in the exponential function, the error will have the opposite sign and will be somewhat greater. In both cases, its size will be directly proportional to ΔT and inversely proportional to the difference $T_2 - T_1$.

van Krevelen et al.[3] have suggested a more complex approximation, which has not been widely used

$$\int_0^T \exp\{-E/RT\} dT = [RT_s{}^2 e/(RT_s + E)](T/eT_s)^{(E/RT_s)+1}$$

If the activation energy error is calculated in this manner, it leads to a complex formula, which does not allow a simple evaluation of its size. If we choose T_s in the center of the temperature interval within which the reaction is being studied, E is greater than its actual value, the error being of the order of several per cent.

We can conclude that the first method gives excellent results, provided x is not too small. The same applies for the last approximation, provided $T_2 - T_1$ against ΔT is sufficiently great. In both cases, the error lies far below the experimental error, which produces variations of activation energy in the range of 5–10%.

References

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Résumé

Des données cinétiques peuvent être déterminées au départ de la relation existant entre deux équations cinétiques sous leurs formes intégrées. Pour le calcul de l'intégrale exponentielle, des approximations sont généralement utilisées, qui permettent un calcul simple de l'énergie d'activation. En regard des approximations les plus fréquemment utilisées, une évaluation des erreurs produites par leur application a été calculée. Le meilleur résultat peut être obtenu en utilisant la formule indiquée dans le résumé anglais et permet de déterminer E avec une précision à 1% près.

Zusammenfassung

Kinetische Daten können aus der Beziehung zwischen zwei kinetischen Gleichungen in ihrer integrierten Form bestimmt werden. Zur Berechnung des exponentiellen Integrals werden im allgemeinen Näherungen verwendet, welche eine einfache Berechnung der Aktivierungsenergie erlauben. Für die am häufigsten verwendeten Näherungen wird der durch ihre Anwendung erzeugte Fehler ermittelt. Die besten Ergebnisse werden mit der in der englischen Zusammenfassung angegebenen Formel erhalten, nach welcher E mit einer Genauigkeit von 1% bestimmt wird.