Thermochimica Acta, 54 (1982) 181–186
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands

THE EFFECT OF A PRE-EXPONENTIAL FUNCTION $A = A_nT^n$ ON RISING TEMPERATURE KINETIC PARAMETER CALCULATIONS

D. DOLLIMORE, G.A. GAMLEN and T.J. TAYLOR

Department of Chemistry and Applied Chemistry, University of Salford, Salford, M5 4WT (Gt. Britain)

(Received 26 October 1981)

ABSTRACT

In this study the effect of a pre-exponential function $A = A_nT^n$ on rising temperature kinetic parameter calculations has been shown. The integral methods have been derived using this function and an improvement has been proposed. This eliminates the error induced by introducing more complex temperature integrals and removes the need to recalculate the integral for new values of n.

INTRODUCTION

The application of integral methods in non-isothermal kinetics of solid state reactions usually assumes the temperature independence of the pre-exponential factor A in the Arrhenius equation [1,2] i.e.

$$k = A \exp(-E/RT) \tag{1}$$

where k is the specific reaction rate, R is the gas constant, T is the temperature and E is the activation energy. However, the transition state theory predicts the relationship [3,4]

$$k = \frac{RT}{Nh} K^{\neq} \tag{2}$$

where N is the Avogadro number, h is the Planck's quantum theory constant and $K^{\neq}$ is the equilibrium constant. In the case where $T = \infty$ then from eqn. (1) it can be seen that $k_\infty = A$. Thus from eqn. (2) it is clear that A is temperature dependent.

The transition state theory was developed around a concept of a bimolecular reaction in free space. In reality it is only possible to express A as a function of temperature, thus

$$A = A_nT^n \tag{3}$$

There are two general cases, where $n = \frac{1}{2}$ and $n = 1$, the first describing a surface reaction between a gaseous and a solid reactant and the second a single reactant solid state decomposition. However, other possibilities do exist to describe such reactions as solid–solid, diffusion controlled and pressure dependent interactions.

Thus from eqns. (1) and (3) it can be seen that

$$k = A_n T^n \exp(-E/RT) \tag{4}$$

where A_n is now temperature independent. However, the integral methods of kinetic parameter evaluation implicitly assume that $n = 0$. The aim of this paper is to analyse the effect of real value of n on these methods.

DERIVATION OF INTEGRAL METHODS

In order to understand fully the effect of eqn. (3) on the integral methods it is necessary to repeat the integral derivation using eqn. (4).

Substituting $\mathrm{d}\alpha/\mathrm{d}T = k \cdot \mathrm{f}(\alpha) \cdot \beta^{-1}$ for k into eqn. (4), where α is the fraction decomposed during a reaction with a heating rate β gives

$$\frac{\beta}{\mathrm{f}(\alpha)} \frac{\mathrm{d}\alpha}{\mathrm{d}T} = A_n T^n \exp(-E/RT) \tag{5}$$

Rearranging shows that

$$\int_0^\alpha \frac{1}{\mathrm{f}(\alpha)} \mathrm{d}\alpha = \frac{A_n}{\beta} \int_{T_0}^{T} T^n \exp(-E/RT)\, \mathrm{d}T \tag{6}$$

With the substitution of $x = E/RT$, eqn. (6) can be written as

$$\int_0^\alpha \frac{1}{\mathrm{f}(\alpha)}\, \mathrm{d}\alpha = \frac{A_n E^{n+1}}{\beta R^{n+1}} \int_x^{x_0} x^{-(n+2)} \cdot \exp(-x)\, \mathrm{d}x \tag{7}$$

which after integration becomes

$$\mathrm{g}(\alpha) = \frac{A_n E^{n+1}}{\beta R^{n+1}} p_n(x) \tag{8}$$

In the more usual logarithmic form this becomes

$$\ln \mathrm{g}(x) - \ln p_n(x) = \ln\left(\frac{A_n E^{n+1}}{\beta R^{n+1}}\right) \tag{9}$$

and is the basis of all integral methods. Two general approaches using eqn. (9) are possible, these arising from two methods of expressing the temperature integral $\int_x^{x_0} x^{-(n+2)} \exp(-x)\, \mathrm{d}x$ or $p_n(x)$. The first is based on series expansions of this indefinite integral and the second uses simple approximation.

METHODS UTILISING SERIES EXPANSIONS

These methods [5,6] use the fact that since $\ln p_n(x)$ is simply the logarithmic form of the increase in area of an exponential function of $1/T$ then a plot of $\ln p_n(x)$ vs. $1/T$ is linear. Thus since

$$\frac{\mathrm{d} \ln p_n(x)}{\mathrm{d}x} = \frac{1}{p_n(x)} \cdot \frac{\mathrm{d}p_n(x)}{\mathrm{d}x} \tag{10}$$

then

$$\frac{\mathrm{d}\ln p_n(x)}{\mathrm{d}x}=\frac{E}{Rx^{n+2}\,\mathrm{e}^x p_n(x)} \tag{11}$$

incorporating the original definitions of $p_n(x)$ and x. Therefore the activation energy can be found by either an iterative process from the gradient of a plot of $\ln p_n(x)$ vs. $1/T$ [7] or from tabulated $\ln p_n(x)$ values for particular ranges of x [8].

Since, from eqn. (9), the difference between $\ln g(\alpha)$ and $\ln p_n(x)$ is constant then, assuming the reaction to be isokinetic, a plot of $\ln g(\alpha)$ and $\ln p_n(x)$ vs. $1/T$ should give two parallel lines, the distance between them being $\ln(A_n E^{n+1}/\beta R^{n+1})$ so allowing A_n to be calculated.

There are many series expansions of $p_n(x)$ where $n=0$, these having been reviewed by Wendlandt et al. [8]. Recent papers [9–11] have compared these expressions and shown that a Schloemilch series is the most accurate for $x>15$. However, these expansions are based on the partial integration of $p_n(x)$, a process not applicable for non integer values of n. Thus Varhegyi [12] using work by Bateman [13] has shown, for complete integration, the Schloemilch series to be

$$p_n(x)=\frac{\exp(-x)}{x^{n+2}}\left(1+\frac{a_1}{x+1}+\frac{a_2}{(x+1)(x+2)}+\frac{a_3}{(x+1)(x+2)(x+3)}+\dots\right) \tag{12}$$

where the values of a_n corresponding to n are shown in Table 1 (taken, in part, from ref. 12). In addition Varhegyi has shown how to use Pade approximations and Legendre fractions for any value of n. Also Segal [14] has derived approximations to the temperature integral assuming any positive values of n.

In order to satisfy the requirements of eqn. (9), it is clear that $\ln g(\alpha)$ and $\ln p_n(x)$ vs. $1/T$ must be parallel for any isokinetic reaction. However, although not immediately obvious the two lines will be parallel for any value of n whether correct or not. This is because the RHS of eqn. (9) is always constant. Figure 1 shows a graph of $\ln g(\alpha)$ and $\ln p_n(x)$ vs. $1/T$ for $n=0$, 0.5, 1.0, 1.5 and 2.0 for the decomposition of 1.0% nickel nitrate on fumed silica (wt./wt.%) calculated for $g(\alpha)=1-(2\alpha/3)-(1-\alpha)^{2/3}$ using eqn. (12) with constants from Table 1 [15]. All

TABLE 1

Coefficients to eqn. (12) (taken, in part, from ref. 12)

n	a_1	a_2	a_3	a_4
0	−2.0	4.0	−10.0	30.0
0.5	−2.5	6.25	−18.125	61.563
1.0	−3.0	9.0	−30.0	114.0
1.5	−3.5	12.25	−46.375	190.985
2.0	−4.0	16.0	−68.0	314.0

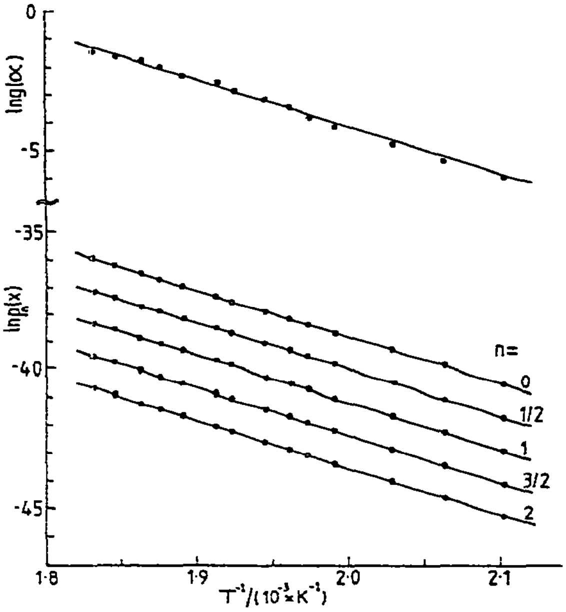

Fig. 1. A plot of ln g(α) and ln $p_n(x)$ vs. $1/T$ for varying values of n.

six lines shown on the graph have equal slopes. The Arrhenius parameters calculated from Fig. 1 are shown in Table 2, the activation energies showing a decreasing trend with increasing values of n. This can be understood by referring to eqn. (11), the RHS requiring the values of $p_n(x)$ and x^{n+2} to be known.

However, E is recognised as being temperature independent, although Gorbachev [16] has postulated an algorithm for the case where $E(T) = E_0 + RBT$. However, the initial proof of this is in error. Thus Table 2 shows that the activation energy can be miscalculated by up to 6% depending on the choice of n. In addition some of the expansions for $p_n(x)$ [12] are invalid [17] for non integer values of n. A proposal for

TABLE 2

Arrhenius parameters calculated from Fig. 1

n	Calc. using eqn. (12)		Calc. using eqn. (14)	
	E (kJ mole^{-1})	A_n (s^{-1})	E (kJ mole^{-1})	A_n (s^{-1})
0	13.2	5.80 E10	13.2	5.80 E10
0.5	13.0	1.57 E09	13.2	1.45 E09
1.0	12.8	4.25 E07	13.2	3.64 E07
1.5	12.6	1.10 E06	13.2	9.12 E05
2.0	12.4	3.13 E04	13.2	2.29 E04

a modified method of calculating the Arrhenius parameters is based on the following argument.

If we consider a distance between the two plots of d_n as

$$d_n = \ln\left(\frac{A_n E^{n+1}}{\beta R^{n+1}}\right) \tag{13}$$

then for any expansion of $p_n(x)$ for $n = 0$, A_n can be calculated from d_0 by

$$\ln A_n = d_0 + \ln\left(\frac{E^{n+1}}{\beta R^{n+1}}\right) \tag{14}$$

for any value of n. Thus using the normal integral methods outlined earlier for $n = 0$, A_n can be calculated for any value of n using eqn. (14) with eqn. (9). Recalculated results using this method and the data used previously are shown in Table 2. As can be seen, the activation energies are the same for any value of n and thus A_n is calculated to a slightly different value.

METHODS UTILISING SIMPLE APPROXIMATIONS

These approaches to integral methods of kinetic parameter evaluation utilise simple approximations to the temperature integral. They either use equations of the type $y = mx + c$ or more complex series expansions truncated after one or two terms. The following equation is an example of the first type of approximation

$$\ln p_n(x) = -c - mx \tag{15}$$

where, according to Doyle [18], $m = 0.4567$ and $c = 2.315$ when $n = 0$ and $x > 20$. Ozawa [19] using the Doyle approximation combined eqns. (15) and (9) to show that a plot of ln β vs. $1/T$ will give a linear plot. However, looking at the equation for any value of n

$$\ln \beta = -\frac{mE}{RT} - c + \ln\left(\frac{A_n E^{n+1}}{g(\alpha) R^{n+1}}\right) \tag{16}$$

shows that an incorrect choice of n will affect the slope $(-mE/R)$ since the constants in eqn. (15) vary with n. This possible error in the calculation of E will, however, be insignificant compared with the error introduced by utilising this type of approximation.

Coats and Redfern [20,21] used an approximation of

$$p_0(x) = \exp(-x)[(1/x - 2/x^2)] \tag{17}$$

and obtained from eqn. (9)

$$\ln\left(\frac{g(\alpha)}{T^2}\right) = \ln\left(\frac{A_o R}{\beta E}\right)\left(1 - \frac{2RT}{E}\right) - \frac{E}{2.3RT} \tag{18}$$

This method of treatment is, however, dependent on the type of approximation used. Using eqn. (18) a plot of $\ln[g(\alpha)/T^2]$ vs. $1/T$ will yield a straight line over a narrow temperature interval. The approximation is obtained through partial integration of the temperature integral and is not valid for non integer values of n. In addition it is not one of the more accurate approximations, being truncated after the second term.

CONCLUSION

Thus in conclusion it must be noted that in any calculation of E care must be taken to ensure that the uncertainty of n in the pre-exponential function does not affect the accuracy to which E is calculated. Also series expansions of the temperature integral must be checked for validity with non-integer values of n. A method of calculating A_n and E for any value of n has been proposed for use with the "dual plot" method of calculating Arrhenius parameters. This removes the need to formulate complex $p_n(x)$ functions since only one expansion is needed.

Methods of kinetic parameter evaluation utilising simple approximations are very dependent on the type of approximation used. The nature of the approximations introduces an error into the calculations. In addition they are specifically for one value of n.

REFERENCES

1 J.H. Flynn and L.A. Wall, J. Res. Natl. Bur. Stand. Sect. A, 70 (1966) 487.
2 J. Sestak, Silikaty, 11 (1967) 153.
3 K. Laidler, Chemical Kinetics, McGraw Hill, London, 1961.
4 R.D. Shannon, Trans. Faraday Soc., 60 (1964) 1902.
5 C.D. Doyle, J. Appl. Polym. Sci., 5 (1961) 285.
6 V. Satava and F. Skvara, J. Am. Ceram. Soc., 52 (1966) 591.
7 J. Szako, J. Therm. Anal., 2 (1970) 145.
8 W.W. Wendlandt, V. Satava and J. Sestak, Thermochim. Acta, 7 (1973) 450.
9 C.D. Doyle, Nature (London), 207 (1965) 290.
10 G. Gyulai and E.J. Greenhow, Thermochim. Acta, 6 (1973) 239.
11 J. Norwisz and N. Hajduk, J. Therm. Anal., 13 (1978) 223; 16 (1979) 193.
12 G. Varhegyi, Thermochim. Acta, 25 (1978) 201.
13 H. Bateman, in A. Erdelyi (Ed.), Higher Transcendental Functions, Vol. 2, McGraw Hill, New York, 1953.
14 E. Segal, Thermochim. Acta, 42 (1980) 357.
15 T.J. Taylor, to be published.
16 V.M. Gorbachev, J. Therm. Anal., 10 (1976) 447.
17 A. Erdelyi, Asymptotic Expansions, Dover Publ. Inc., New York, 1956.
18 C.D. Doyle, J. Appl. Polymer Sci., 6 (1962) 639.
19 T. Ozawa, Bull. Chem. Soc. Jpn., 38 (1965) 1881.
20 A.W. Coats and J.P. Redfern, Nature (London), 20 (1964) 88.
21 A.W. Coats and J.P. Redfern, Polym. Lett., 3 (1965) 917.