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A NEW APPROXIMATION OF THE p(x) FUNCTION

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ABSTRACT

A new approximation of the p(x) function has been developed giving an easy determination of the activation energy of solid-state reactions from a plot of ln g(α) vs. the reciprocal temperature, with an error lower than 6% when $E/RT = 2$.

INTRODUCTION

The basic equation for the kinetic analysis of chemical reactions under a linear heating program can be expressed in the following well-known form

$$\mathrm{g}(\alpha) = \frac{A}{\beta}\int_{T_0}^{T} \exp(-E/RT)\,\mathrm{d}T = \frac{AE}{\beta R}\,\mathrm{p}(x) \tag{1}$$

where β is the heating rate; E is the activation energy; A is the Arrhenius pre-exponential factor; T is the absolute temperature; R is the gas constant; and p(x) represents the following function

$$\mathrm{p}(x) = \int_{x}^{\infty} \frac{\mathrm{e}^{-x}}{x^2}\,\mathrm{d}x \tag{2}$$

where $x = E/RT$.

The p(x) function cannot be expressed in a closed form, but must be evaluated by numerical integration. This is why a number of authors [1,2] attempted to achieve empirical approximations of the p(x) function that make log p(x) a linear function of the reciprocal of the temperature, so that the activation energy can be simply obtained from the slope of the plot of ln g(α) vs. $1/T$, according to eqn. (1). The most popular of these approximations are those of Doyle [3], Coats and Redfern [4], Gyulai and Greenhow [5], and MacCallum and Tanner [6]. The literature [1,7–11] has shown that these approximations are adequate, provided that $E/RT > 15$. However, the accuracy of these methods becomes poorer as E/RT decreases, the error in the activation energy being of the order of 200–300% when $E/RT = 2$.

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Therefore, the use of conventional methods of kinetic analysis for non-isothermal data of the desorption reactions of gases from solid surfaces is very restricted, if these reactions usually take place at low temperatures, generally indicating small values of E/RT.

The aim of the present paper is to develop an approximation of the $p(x)$ function which calculates the activation energy of solid-state reactions with a high accuracy from a plot of $\ln g(\alpha)$ vs. $1/T$ in an E/RT range far greater than that possible for similar methods available in the literature.

THEORETICAL

In order to investigate the linear relationship between $\log p(x)$ and $1/T$, the fourth-degree rational approximation of the $p(x)$ function derived by Senum and Yang [10] is used

$$p(x)=\frac{\exp(-x)}{x}\,\frac{x^3+18x^2+88x+96}{x^4+20x^3+120x^2+240x+120} \tag{3}$$

which involves an error lower than $10^{-5}\%$.

A procedure similar to that previously outlined by MacCallum and Tanner [6] is followed. According to these authors, $\log p(x)$ and $1/T$ are related through the following relationship

$$-\log p(x)=X+a/T \tag{4}$$

where a is the slope of the line, and X is the intercept on the $-\log p(x)$ axis. Values of a and X were determined [6] for a series of values of E ranging from 14 to 64 kcal mol^{-1}.

However, Gorbachev [12] and Sestak [13] pointed out that the linear relationship between $\log p(x)$ and $1/T$ has not been properly analysed and is limited in the mathematical sense. In fact, Fig. 1 indicates that a plot of $-\log p(x)$, calculated from eqn. (3), vs. $1/T$, for a given value of E, in the range investigated by MacCallum and Tanner, shows an important deviation from linearity, which could lead to a large error in the calculation of the activation energy.

On the other hand, since Coats and Redfern [4] pointed out that the function $\log p(x)-2\log T$ shows a better linear correlation with $1/T$ than $-\log p(x)$, it is considered that an expression of the form

$$\log p(x)-m\log T=X+a/T \tag{5}$$

where m is a constant, would be a more comprehensive approximation of $\log p(x)$ than eqn. (4).

Equation (5) has been systematically investigated for a series of activation energy values ranging from 1 to 100 kcal mol^{-1} in order to find the value of m which best fits a plot of the left-hand side of eqn. (5) vs. $1/T$. The same

TABLE 1

Values of the constants of eqns. (6) and (7) evaluated by the least-squares method

Y	b	c	d
−14.16	−218.8	−1.876	−5.03

value ($m = 1.81$) was obtained by the method of least-squares for the same E values. Figure 1 shows that the linear correlation between ($\log p(x) - 1.8 \log T$) and $1/T$, proposed here, is far better than that between $\log p(x)$ and $1/T$.

The corresponding values of a and X have also been determined by the least-squares method from plots of $\log p(x) - 1.8 \log T$ vs. $1/T$ for different values of E. Thus, it has been verified that, according to ref. 6, the constant a and the activation energy show an excellent linear correlation. Thus

$$a = Y + bE \tag{6}$$

where Y and b are the a axis intercept and slope, respectively. The values of Y and b evaluated by the method of least-squares are given in Table 1.

MacCallum and Tanner [6] found that the values of $\log X$ determined from eqn. (4) were linear in relation to $\log E$. This relationship is not evident for those X values determined from eqn. (5). However, an excellent linearity between X and $\log E$ has been found, as shown by Fig. 2. Therefore, we can write

$$X = c \log E + d \tag{7}$$

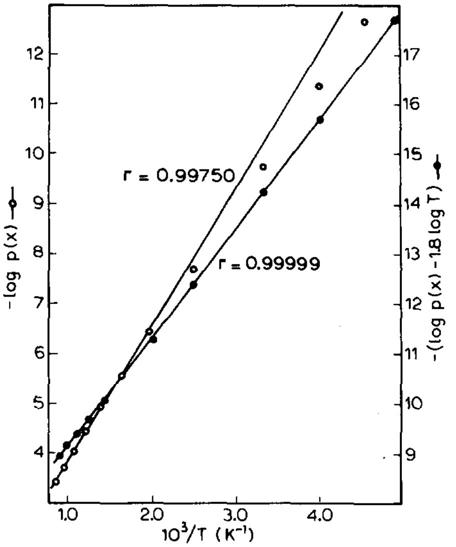

Fig. 1. Plots of $\log p(x) - 1.8 \log T$ and $-\log p(x)$ vs. $1/T$ for $E = 10$ kcal mol^{-1}.

the values of the constants c and d, determined as before, are given in Table 1.

From eqns. (5), (6) and (7), after substituting the constants collected in Table 1, we get

$$\log \mathrm{p}(x) - 1.8 \log T = -5.03 - 1.876 \log E - \frac{14.16 + 218.8E}{T} \tag{8}$$

where E is expressed in kcal mol^{-1}.

From eqns. (1) and (8) we obtain

$$\log \mathrm{g}(\alpha) - 1.8 \log T = \log \frac{9.3 \times 10^{-6} A E^{-0.876}}{\beta R} - \frac{14.16 + 218.8E}{T} \tag{9}$$

TABLE 2

The percentage error in the activation energy using the new approximation of the p(x) function

T(K)	$E/RT = 2$	5	10	20	50	100
300	5.62	0.63	−0.14	−0.05	0.03	0.02
400	6.10	0.72	−0.02	−0.04	0.02	0.03
600	5.69	0.64	−0.06	−0.08	0.02	0.02
800	5.63	0.53	−0.16	−0.11	0.01	0.01
1000	5.28	0.36	−0.22	−0.14	−0.02	0.01
1200	5.07	0.25	−0.28	−0.19	−0.03	−0.01
1400	4.94	0.13	−0.36	−0.22	−0.05	−0.01

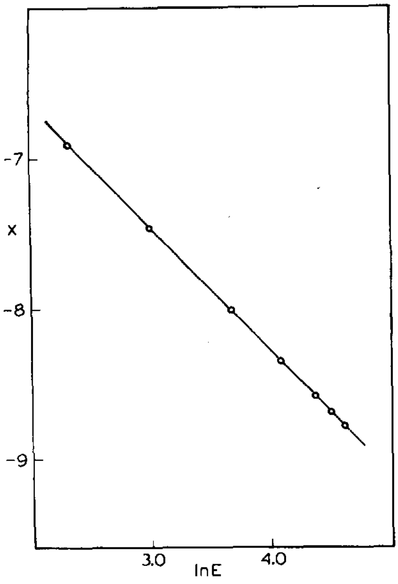

Fig. 2. Plot of X vs. ln E according to eqn. (7).

which can be used for calculating the kinetic parameters of solid-state reactions.

The error in the activation energy determined from eqn. (9) can be calculated by resolving the equation

$$\log p(x) = \log p_a(x_a) \qquad (10)$$

where $p(x)$ is the accurate value of the function calculated from eqn. (3), and $p_a(x_a)$ is the approximate value given by eqn. (8). Values of $x_a = E_a/RT$ have been determined as a function of both E/RT and T, because the mathematical form of eqn. (8) does not allow $p_a(x_a)$ to be evaluated as a function of x_a only. The percentage error, ϵ, has been calculated from the expression

$$\epsilon = \frac{E_a/RT - E/RT}{E/RT} \times 100 = \frac{E_a - E}{E} \times 100 \qquad (11)$$

The values of ϵ determined as a function of both E/RT and T are given in Table 2.

The results included in Table 2 suggest that the errors in the activation energy calculated from the method outlined here are much lower than those reported in the literature [2,5,7,10] for other methods based on a linear relationship between log g(α) and $1/T$.

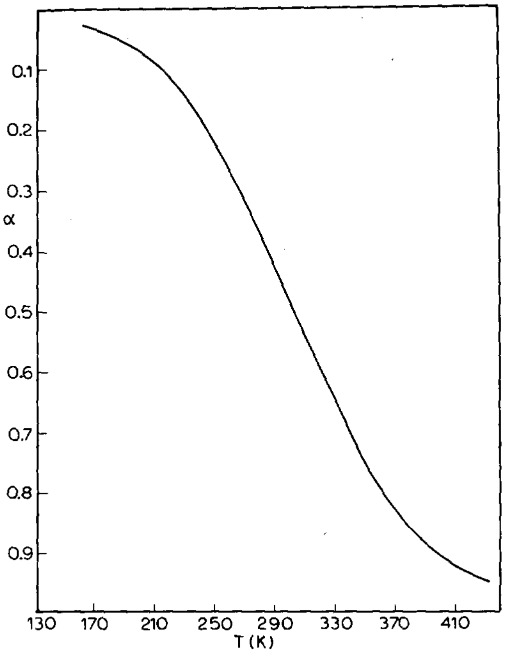

Fig. 3. Theoretical $\alpha - T$ curve calculated by assuming a first-order kinetic law, a heating rate of 16 °C min^{-1} and the following kinetic parameters: $E = 2$ kcal mol^{-1}, $A = 5$ min^{-1}.

TABLE 3

Kinetic parameters and errors calculated from the theoretical data of Fig. 3 by means of different methods; actual values of kinetic parameters $E = 2$ kcal mol^{-1}, $A = 5$ min^{-1}

Method	E (kcal mol^{-1})	ϵ (%)	A (min^{-1})
Coats–Redfern	1.80	10	2.23
MacCallum–Tanner	0.91	54	9.7
Doyle	2.80	40.7	223
Gyulai–Greenhow	2.5	25.0	1.01
New approximation	1.89	5.5	3.42

In order to check the above statement, eqn. (9) has been used to perform the kinetic analysis of the theoretical curve in Fig. 3, which was calculated from eqns. (1) and (3) by assuming a first-order kinetic law (i.e., $g(\alpha) = -\ln(1-\alpha)$) and the following kinetic parameters: $E = 2$ kcal mol^{-1}; $A = 5$ min^{-1}; and heating rate, $\beta = 16\,^{\circ}$C min^{-1}.

The data from Fig. 3, according to eqn. (9), are used in Fig. 4, showing the excellent linear correlation between $\log g(\alpha) - 1.8 \log T$ and $1/T$. The values of both the kinetic parameters and the errors involved are given in Table 3, where they are compared with the corresponding values of the kinetic analysis of the same kinetic data by the methods of various workers.

The above results confirm that with the present method, the kinetic parameters of a chemical reaction can be calculated with a larger accuracy than with other similar methods.

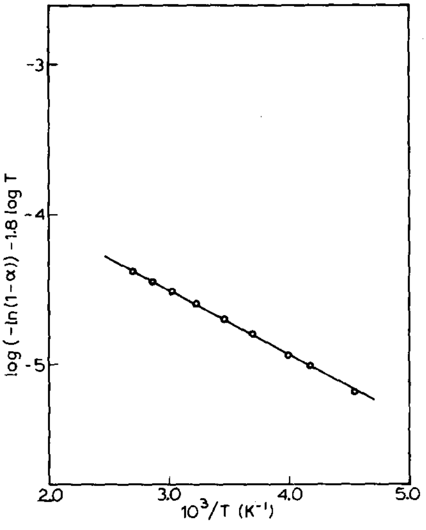

Fig. 4. Kinetic analysis of data taken from Fig. 3 according to eqn. (9).

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