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Note

On the applicability of the p(x)-function to the determination of reaction kinetics under non-isothermal conditions

JAROSLAV ŠESTÁK
Institute of Solid State Physics of the Czech Academy of Sciences in Prague (Czechoslovakia)

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Recent literature[2–4,8–17] indicates a wide use of the function p(x). This has been introduced for non-isothermal kinetic studies by Akahira[1] and popularised by Doyle[2] and Satava[3]. The function p(x) is obtained by integration of the temperature dependent specific rate constant within a temperature interval from 0 to T and is defined as [2–4,20]

$$\int_x^\infty \frac{e^{-x}}{x^2} = p(x) = \frac{e^{-x}}{x} - \int_x^\infty \frac{e^{-x}}{x}\,dx \tag{1}$$

In order to find a suitable analytical formulation of p(x) it is necessary to deploy the function of the exponential-integral $E_1(x) = -\int_x^\infty \frac{e^{-x}}{x}\,dx$. This function, originally used for studying thermal detoriation of insulating materials and thermionic emission[1], can be derived as follows[4]: As the convergent series according to Taylor's formula[19]

$$E_1(x) = 0.577216\ldots + \ln x^4 - x + \frac{x^2}{2\cdot 2!} - \ldots + \frac{(-1)^n x^n}{n\cdot n!} \tag{2}$$

and/or as the semi-divergent series through integration by parts[19]

$$E_1(x) = \frac{e^{-x}}{x}\left(1 - \frac{1}{x} + \frac{2!}{x^2} - \ldots + \frac{(-1)^n n!}{x^n}\right) \tag{3}$$

The factorial-function here increases more steeply for high values of n than the exponent-function. Though less suitable, the last series of Eqn. (3) is frequently used in kinetic evaluations[2–4] as it is most convenient for further mathematical combination with Eqn. (1) yielding p(x) in the form of the following series:

$$p(x) = \frac{e^{-x}}{x^2}\left(1 - \frac{2!}{x} + \frac{3!}{x^2} - \ldots + \frac{(-1)^n (n+1)!}{x^n}\right) \tag{4}$$

The different types of integration under non-isothermal conditions have been discussed by Šesták[4]. Thus using the reverse substitution ($1/x$) in the integration in

Eqn. (1) and solving $E_1(x)$ according to Schölmilch[18]

$$E_1(x) = \frac{e^{-x}}{x}\left(1 - \frac{1}{x+1} + \frac{1}{(x+1)(x+2)} - \ldots + \frac{(-1)^n a_n}{(x+1)\ldots(x+n)}\right) \tag{5}$$

gives p(x) as

$$p(x) = \frac{e^{-x}}{x(x+1)}\left(1 - \frac{1}{x+2} + \frac{1}{(x+2)(x+3)} - \ldots + \frac{(-1)^{n+1} a_n}{(x+2)\ldots(x+n)}\right) \tag{6}$$

(where a_n is the constant[18]) used first by Van Krevelen *et al.*[17] and recently by Ozawa[12]. The tabulation of $E_1(x)$ is presented in the tables of Akahira[1] (e^{-x}/x, $E_1(x)$, $x = 20$ (0.01) 50), Harris[5] ($x = 1(1)4(0.4)8(1)50$), Miller and Hurst[6] ($x = 0.2(0.5)5(0.1)10(0.2)20(0.5)50(1)80$) and p($x$) in the work of Doyle [2,4] ($-\log p(x)$, $x = 10(1)50$), Oberländer[7] ($kT/E \exp(-E/kT)$, $k/E \int_0^T \exp(-E/kT)\,dT$ etc., $E = 0.2(0.2)2$, $T = 25(25)1000, 150(10)390$), Zsako[8] ($-\log p(E/RT)$, $T = 273(10)600$, $E = 10(2)66$) and Šatava and Škvára[9] ($-\log p(E/RT)$, $p(E/RT)$, $T = 273(1)1773$, $E = 5(1)100$, programme in ALGOL available on request). The behaviour of p(x) when using different types of approximations was investigated by Doyle[10], and a limited range formula was introduced[11] and later used by Ozawa[12] and particularly developed by MacCallum and Tanner[13]

$$\begin{aligned} \log p(x) &= -2{,}315 - 0.4567x \qquad \text{(Ref. 11)} \\ &= -0.4828\,\Delta E^{0.4351} - (0.449 + 0.217\,\Delta E)/T10^{-3} \ \text{(Ref. 13)} \end{aligned} \tag{7}$$

where ΔE is the activation energy (in kcal) and T the temperature (°K).

It has been suggested[8] that p(x) is a linear function of x in a narrow temperature interval making possible the introduction of a new simple method for the estimation of a probable reaction path from a single non-isotherm[13,14]. A simple plot of ln g(α) *vs.* $1/T$ gives a straight line for the most suitable reaction mechanism[14], being represented by function g(α)[21] for an experimentally determined degree of conversion α (fraction reacted). This procedure is possible owing to the constant difference between the functions ln g(α) and ln p(x), approximated as two parallel straight lines[13,14,16]. However, the validity of this linear behaviour of ln p(x) has not been properly analysed and is as yet limited in the mathematical sense.

From the logarithmic form of Eqn. (4) it can be seen that ln p(x) is predominantly dependent upon x while the effect of the series is suppressed by the logarithm. This, is similar to neglecting ln T with respect to E/RT in the logarithmic expression of the specific rate constant. In order to establish the range of the validity of the linear approximation the well-known Taylor expansion can be put to use:

$$\ln p(x) = \ln p(x)\Big|_{x_1} + \frac{d \ln p(x)}{dx}\Big|_{x_1}(x - x_1) + \frac{d^2 \ln p(x)}{2dx^2}\Big|_{x_1}(x - x_1)^2 + \ldots \tag{8}$$

where x_1 is the chosen point of the approximation. Neglecting terms of the exponent above two in Eqn. (8), after substitution

$$\ln \mathrm{p}(x) = \ln \mathrm{p}(x_1)+\rho(x_1)(x-x_1)+\tfrac{1}{2}\xi(x_1)(x-x_1)^2 \tag{9}$$

where (see Appendix)

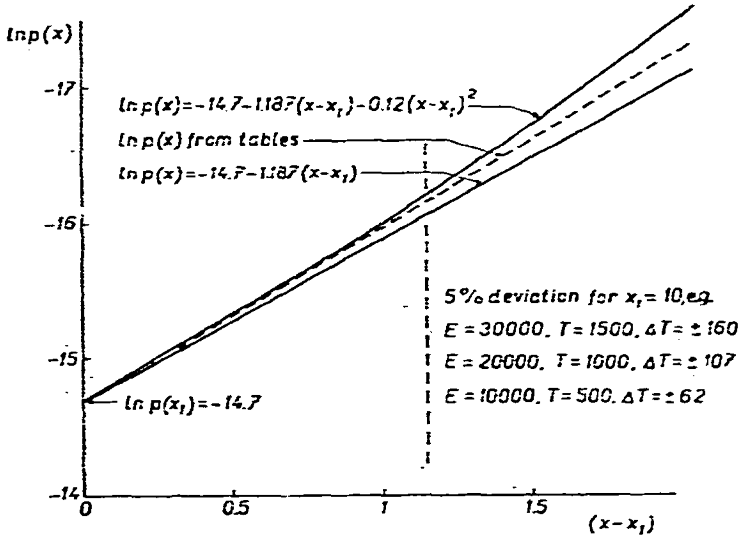
$$\rho(x_1) = -(e^{x_1}x_1^2\mathrm{p}(x_1))^{-1} \tag{10}$$

$$\xi(x_1) = -(\rho(x_1))^2-(x_1+2)\rho(x_1)/x \tag{11}$$

In practice the graphical comparison of the linear with the parabolic substitution (in Eqn. (9)) gives evidence for the validity range of the linear approximation. The following table provides data of $\mathrm{p}(x)$, e^x, $E_1(x)$ and $-\log \mathrm{p}(x)$.

x	10	20	30	40	50
$-\ln \mathrm{p}(x)$	14.7	26.1	36.8	47.4	57.5
$-\rho(x)$	1.187	1.102	1.064	1.049	1.032
$-\frac{1}{2}\xi(x)$	0.123	0.065	0.033	0.025	0.013

The most unfavorable case, $x_1 = 10$, is illustrated diagramatically in Fig. 1 with regard to $(x-x_1)$ in Eqn. (9). It is easily seen that the parabolic term has a negligible influence for $(x-x_1)$ below about one, which means that for a normal temperature interval within about 100°C the straight line is really an excellent approximation.



From the slope of the linear approximation of $\mathrm{p}(x)$ the variable x may be calculated. In the case of a kinetic investigation the value of the activation energy E in $x = E/RT$ (where R is the gas constant 1.987) can easily be derived mathematically. There appear to be several ways of determining this slope. As $\rho(x)$ in the table has an almost constant value of about 1.08, the semiempirical approximations introduced in the form of Eqn. (7) are justified. Thus after the derivation of Eqn. (7) with respect to $1/T$ and rearrangement:

$$E = -\frac{449 + \text{tg}\,\beta/2.303}{217}\,10^3\ [\text{cal/mol}] \tag{12}$$

the activation energy can be calculated from the slope tg β of the straight line approximation of the plot of ln g(α) *vs.* $1/T$. Another method used by Satava[14] employs the first two terms of the series in Eqn. (A19) and expresses E as the root of the derived quadratic equation:

$$E = \frac{1.987}{2}\left(-\text{tg}\,\beta + \sqrt{\text{tg}^2\beta + 8\ \text{tg}\,\beta\ \bar{T}}\right)[\text{cal/mol}] \tag{13}$$

This second, more complicated method, seems to be a more appropriate approximation because it takes into consideration the position of the line in the temperature scale ($\bar{T}_{\text{aver.}}$). Through the check-evaluation made on the theoretically calculated and plotted thermogravimetric curve[15] ($E = 27{,}000$ and $g(\alpha) = -\ln(1-\alpha)$) as scanned from $\alpha = 0.05$ by steps of 0.05 to 0.95 yielding log g(α) *vs.* $T^{-1}\ 10^{-3}$ as follows: −1.23/2.610, −0.977/2.559, −0.789/2.53, −0.651/2.51, −0.541/2.493, −0.448/2.478, −0.366/2.466, −0.292/2.455, −0.223/2.443, −0.159/2.433, −0.098/2.423, −0.038/2.414, 0.021/2.405, 0.081/2.396, 0.142/2.387, 0.207/2.375, 0.278/2.363, 0.362/2.351, 0.477/2.335; Eqn. (12) gives $E = 27{,}700 \pm 1{,}100$ and Eqn. (13) $E = 31{,}000 \pm 600$. Both values compare well with the values of E obtained by conventional methods[15]. Equation (13) yields a little higher value of E (but with a lower error) probably due to neglecting terms with exponents langer than two in the series of Eqn. (A19). It may be corrected by introducing a suitable constant or by iterations through Eqn. (A15) and/or Eqn. (A19).

This method described[13,14] for the handy evaluation of the reaction mechanism[21] as well as for the determination of associated kinetic parameters from a single non-isothermal run is believed to be well founded and, because of its simplicity, may become a basic method in regular kinetic investigations[16].

APPENDIX

On considering Eqns. (1), (3) and (4)

$$\frac{d}{dx}\int_x^{\infty}\frac{e^{-x}}{x^b}\,dx = \frac{d}{dx}\int_0^{\infty}\frac{e^{-x}}{x^b}\,dx - \frac{d}{dx}\int_0^{x}\frac{e^{-x}}{x^b}\,dx = -\frac{e^{-x}}{x^b}\Bigg) \tag{A14}$$

$$\frac{d\ln p(x)}{dx} = -\frac{1}{e^x x^2 p(x)} = -\frac{1}{x(1 - x\,e^x E_1(x))} \tag{A15}$$

$$\frac{d^2 \ln p(x)}{dx^2} = \frac{p(x)(1+2/x)+dp(x)/dx}{e^x x^2 (p(x))^2} \tag{A16}$$

$$\frac{dp(x)}{dx} = \left[-p(x) + \frac{e^{-x}}{x^2}\left(-\frac{2!}{x} + \frac{3!}{x^2} - \ldots + \frac{(-1)^n (n+1)!}{x^n}\right)\right] = -\frac{e^{-x}}{x^2} \tag{A17}$$

$$\frac{d^2 \ln p(x)}{dx^2} = -\left(\frac{1}{e^x x^2 p(x)}\right)^2 + \frac{1+2/x}{e^x x^2 p(x)} \tag{A18}$$

$$\frac{d \ln p(x)}{dx} = -\left(1 - \frac{2!}{x} + \frac{3!}{x^2} - \ldots + \frac{(-1)^n (n+1)!}{x^n}\right)^{-1} = \frac{R}{E} \operatorname{tg} \beta \tag{A19}$$

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