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Some problems concerning the temperature integral in non-isothermal kinetics.
Part 3. An approximation of the temperature integral through integration over small temperature intervals

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Abstract

This paper gives a new approximation for the integral $\int_{T_1}^{T_2} e^{-E/Ry}\, dy$. If $T_2 - T_1 \leqslant 15$ K, the approximation leads to satisfactory results.

INTRODUCTION

In our previous papers [1–4] we have presented some methods for the evaluation of the non-isothermal kinetic parameters using integration over small temperature intervals. Moreover, in ref. 5 we have shown that integration over small temperature intervals solves the experimental problem of maintaining the programmed heating rate. Until now the following approximation of the temperature integral was used [1]

$$\int_{T_1}^{T_2} e^{-E/R}\, dy \approx (T_2 - T_1)\, e^{-E/RT_{12}} \tag{1}$$

$$T_{12} = \frac{T_1 + T_2}{2} \tag{2}$$

In order to enhance the accuracy of the results, however, better approximations are still necessary. In the following, a procedure to obtain such an approximation is described.

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Dedicated to Professor Joseph H. Flynn in honour of his 70th birthday.

PROCEDURE TO OBTAIN A NEW APPROXIMATION OF THE TEMPERATURE INTEGRAL

In order to simplify the notation, we shall introduce the quantity ε

$$T_2 = T + \varepsilon \tag{3}$$

$$T_1 = T - \varepsilon \tag{4}$$

From eqns. (2), (3) and (4) we get

$$T_{12} = T \tag{5}$$

and

$$\varepsilon = \frac{T_2 - T_1}{2} \tag{6}$$

In terms of this notation, the temperature integral (eqn. (1)) takes the form

$$\int_{T-\varepsilon}^{T+\varepsilon} \mathrm{e}^{-E/Ry}\,\mathrm{d}y \simeq 2\varepsilon\ \mathrm{e}^{-E/RT} \tag{7}$$

This suggests the following new approximation

$$\int_{T-\varepsilon}^{T+\varepsilon} \mathrm{e}^{-E/Ry}\,\mathrm{d}y \approx (2\varepsilon + a)\ \mathrm{e}^{-E/RT} \tag{8}$$

where the correction term a depends on E, T and ε. For a given E and T, taking the derivative of relationship (8) with respect to temperature one obtains

$$\mathrm{e}^{-E/R(T+\varepsilon)} + \mathrm{e}^{-E/R(T-\varepsilon)} = (2 + \mathrm{d}a/\mathrm{d}\varepsilon)\ \mathrm{e}^{-E/RT} \tag{9}$$

Taking into account that

$$-\frac{E}{R(T+\varepsilon)} = -\frac{E}{RT(1+\varepsilon/T)} \tag{10}$$

and

$$-\frac{E}{R(T-\varepsilon)} = -\frac{E}{RT(1-\varepsilon/T)} \tag{11}$$

because $\varepsilon/T \ll 1$, a development of the form [6]

$$\frac{1}{1+x} = 1 - x + x^2 + \cdots + (-1)^n x^n + \ldots \tag{13}$$

$$(-1 < x < 1) \tag{14}$$

can be used in relationship (10) and (11). Actually, because $\varepsilon/T \ll 1$ the development (13) can be reduced to

$$\frac{1}{1+x} = 1 - x \tag{15}$$

In such conditions relationships (10) and (11) become respectively

$$-\frac{E}{R(T+\varepsilon)} \approx -\frac{E}{RT}\left(1-\frac{\varepsilon}{T}\right) \tag{16}$$

and

$$-\frac{E}{R(T-\varepsilon)} \approx -\frac{E}{RT}\left(1+\frac{\varepsilon}{T}\right) \tag{17}$$

Relationship (9), taking into account relationships (16) and (17), takes the form

$$\mathrm{e}^{-E/RT}\,\mathrm{e}^{E\varepsilon/RT^2} + \mathrm{e}^{-E/RT}\,\mathrm{e}^{-E\varepsilon/RT^2} = (2+\mathrm{d}a/\mathrm{d}\varepsilon)\,\mathrm{e}^{-E/RT} \tag{18}$$

or, after simplification

$$\mathrm{e}^{E\varepsilon/RT^2} + \mathrm{e}^{-E\varepsilon/RT^2} = 2 + \mathrm{d}a/\mathrm{d}\varepsilon \tag{19}$$

To give relationship (19) a more convenient form we shall use the development

$$\mathrm{e}^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \cdots + \frac{x^4}{n!} + \cdots \tag{20}$$

$$(-\infty < x < \infty) \tag{21}$$

Because

$$E\varepsilon/RT^2 \ll 1 \tag{22}$$

we shall keep only the first four terms from eqn. (20); and by introducing the truncated development of eqn. (20) into eqn. (19), one obtains

$$1 + \frac{E\varepsilon}{RT^2} + \frac{1}{2}\left(\frac{E\varepsilon}{RT^2}\right)^2 + \frac{1}{6}\left(\frac{E\varepsilon}{RT^2}\right)^3 + 1 - \frac{E\varepsilon}{RT^2} + \frac{1}{2}\left(\frac{E\varepsilon}{RT^2}\right)^2 - \frac{1}{6}\left(\frac{E\varepsilon}{RT^2}\right)^3 = 2 + \frac{\mathrm{d}a}{\mathrm{d}\varepsilon} \tag{23}$$

or, after performing the detailed calculations

$$\left(\frac{E\varepsilon}{RT^2}\right)^2 = \frac{\mathrm{d}a}{\mathrm{d}\varepsilon} \tag{24}$$

The integration of the differential equation eqn. (24) leads to

$$a = \frac{1}{3}\frac{E^2\varepsilon^3}{R^2T^4} + C \tag{25}$$

For $\varepsilon \to 0$, $a \to 0$; therefore $C = 0$, thus

$$a = \frac{1}{3}\frac{E^2\varepsilon^3}{R^2T^4} \tag{26}$$

Equation (8), taking into account relationship (26), becomes

$$\int_{T-\varepsilon}^{T+\varepsilon} e^{-E/R} \, dy \approx \left(2\varepsilon + \frac{1}{3} \frac{E^2 \varepsilon^3}{R^2 T^4} \right) e^{-E/RT} \tag{27}$$

or, in terms of the old notation, the approximation has the form

$$\int_{T_1}^{T_2} e^{-E/Ry} \, dy \approx (T_2 - T_1) \left[1 + \frac{1}{24} \left(\frac{E(T_2 - T_1)}{RT_{12}^2} \right)^2 \right] e^{-E/RT_{12}} \tag{28}$$

CHECKING THE OBTAINED APPROXIMATION

To check approximation (28) the value of the integral calculated by it has been compared with that obtained by the more precise but more complicated approximation [7]

$$\int_{T_1}^{T_2} e^{-E/Ry} \, dy = \frac{RT_2^2}{E} e^{-E/RT_2} Q(x_2) - \frac{RT_1^2}{E} e^{-E/RT_1} Q(x_1) \tag{29}$$

where

$$x = E/RT \tag{30}$$

and

$$Q(x) = \frac{x^2 + 5.347x + 1.376}{x^2 + 7.347x + 10.069} \tag{31}$$

For $x > 0$, this leads to relative errors lower than $2 \times 10^{-4}\%$.

TABLE 1

The relative errors of approximation (29) obtained with respect to approximations (28) and (1) for $E = 80$ kJ mol^{-1}

T_1 (K)		T_2 (K)			
		T_1+5	T_1+10	T_1+15	T_1+20
400	(28)	0.030	0.116	0.243	0.396
	(1)	−0.336	−1.300	−2.816	−7.079
500	(28)	0.016	0.062	0.134	0.230
	(1)	−0.136	−0.529	−1.159	−2.005
600	(28)	0.010	0.036	0.080	0.139
	(1)	−0.064	0.252	−0.554	−0.965

TABLE 2

The relative errors of approximation (29) obtained with respect to approximations (28) and (1) for $E = 160$ kJ mol^{-1}

T_1 (K)		T_2 (K)			
		T_1+5	T_2+10	T_1+15	T_1+209
400	(28)	0.056	0.157	0.334	0.504
	(1)	−1.393	−5.276	−11.050	−18.055
500	(28)	0.030	0.110	0.207	0.281
	(1)	−0.572	−2.210	−4.778	−8.103
600	(28)	0.018	0.069	0.141	0.233
	(1)	−0.274	−1.070	−2.345	−4.044

If v_1 is the value of the temperature integral calculated from eqn. (29) and v_2 is the value of the same integral calculated from eqn. (28) or (1), then the relative percent error e is given by

$$e = \frac{v_1 - v_2}{v_1} \times 100\ (\%) \tag{32}$$

Two values of the activation energy E, 80 and 160 kJ mol^{-1} were used, and $R = 8.3143$ J K^{-1} mol^{-1}. The calculated values of e are given in Tables 1 and 2.

DISCUSSION AND CONCLUSION

For a given T_1, the precision is higher the lower the E and $(T_2 - T_1)$ values. For a given E, the precision increases with T_1 ($T_2 - T_1 =$ constant) and decreases with $T_2 - T_1$ ($T_1 =$ constant).

Approximation (28) leads to relative errors lower than 1%; thus this is a good approximation, taking into account its simple form. Values of $T_2 - T_1$ lower than 15 K are recommended.

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