Thermochimica Acta, 42 (1980) 357—361
Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

Note

THE TEMPERATURE INTEGRAL FOR PRE-EXPONENTIAL FACTORS GIVEN BY $A = A_r T^r$

E. SEGAL

Chair of Physical Chemistry and Electrochemical Technology, National Institute of Chemistry, Bd. Republicii 13, Bucharest (Romania)

(Received 29 May 1980)

One of the most important problems connected with the application of the integral methods in nonisothermal kinetics consists of an accurate evaluation of the temperature integral [1,2]. A lot of work has been done to approximate the temperature integral for the case of pre-exponential factors independent of temperature, i.e. when the rate constant is given by the classical Arrhenius relationship [3]

$$k = A\, e^{-E/RT} \tag{1}$$

Approximations of the temperature integral were also performed for the following two cases [4]

$$A = A_{1/2}\, T^{1/2} \tag{2}$$

$$A = A_1 T \tag{3}$$

The transition state theory [5], as well as other modern theories of reaction rate, predict the following general relationship [5] for the temperature dependence of the rate constant

$$k = A_r T^r\, e^{-E/RT} \tag{4}$$

where r are real positive or negative numbers, integers or half integers. Consequently, in this work, we aim to obtain general approximations of the temperature integral, mainly based on the general equation (4). In spite of the quite unimportant influence of the factor T^r with respect to the factor $e^{-E/RT}$ on the rate constant, the integral kinetic equations, based on the general relationship (4), are supposed to describe more correctly the evolution of the chemical reaction in time or with temperature under nonisothermal conditions.

$r = m/2$; $m = 2q + 1$; q IS A POSITIVE INTEGER

The temperature integral

$$I = \int_{T_0}^{T} T^{m/2}\, e^{-E/RT}\, dT \tag{5}$$

with the substitution

$$y = \frac{E}{RT} \tag{6}$$

can be written in the form

$$I = \left(\frac{E}{R}\right)^{(m/2)+1} \int_{y}^{y_0} \frac{e^{-y}}{y^{(m/2)+2}}\, dy \tag{7}$$

Taking into account the following notation

$$M_{(m/2)+2}(y) = \int_{y}^{\infty} \frac{e^{-y}}{y^{(m/2)+2}}\, dy \tag{8}$$

relationship (7) becomes

$$I = \left(\frac{E}{R}\right)^{(m/2)+1} [M_{(m/2)+2}(y) - M_{(m/2)+2}(y_0)] \tag{9}$$

An integration by parts in eqn. (8) leads to

$$\int_{y}^{\infty} \frac{e^{-y}}{y^{(m/2)+2}}\, dy = \frac{2}{m+2}\left(\frac{e^{-y}}{y^{(m/2)+1}} - \int_{y}^{\infty} \frac{e^{-y}}{y^{(m/2)+1}}\, dy\right) \tag{10}$$

or

$$M_{(m/2)+2}(y) = \frac{2}{m+2}\left[\frac{e^{-y}}{y^{(m/2)+1}} + M_{(m/2)+1}(y)\right] \tag{11}$$

which is a recurrence formula between the functions $M_{(m/2)+2}(y)$ and $M_{(m/2)+1}(y)$.

Repeating the integrations by parts, the function $M_{(m/2)+2}(y)$ can finally be expressed by means of the function $M_{5/2}(y)$, which has been tabulated for different values of y [4]. The integral kinetic equation for the considered case is then

$$F(\alpha) = \frac{A_{m/2}}{a}\left(\frac{E}{R}\right)^{(m/2)+1} \int_{y}^{y_0} \frac{e^{-y}}{y^{(m/2)+2}}\, dy \tag{12}$$

or

$$F(\alpha) = \frac{A_{m/2}}{a}\left(\frac{E}{R}\right)^{m+1} p_{(m/2)+2}(y) \tag{13}$$

where $F(\alpha)$ is the conversion integral [6] ($F(\alpha) = (A_r/a)I$), a is the heating rate and

$$p_{(m/2)+2}(y) = \int_{y}^{y_0} \frac{e^{-y}}{y^{(m/2)+2}}\, dy \tag{14}$$

$r = -m/2$; $m = 2q + 1$; q IS A POSITIVE INTEGER

The temperature integral

$$I = \int_{T_0}^{T} \frac{e^{-E/RT}}{T^{m/2}}\, dT \simeq \int_{0}^{T} \frac{e^{-E/RT}}{T^{m/2}}\, dT \tag{15}$$

with the change of variable (6), can be written as follows

$$I = \left(\frac{R}{E}\right)^{(m/2)-1} \int_{y}^{\infty} y^{(m/2)-2}\, e^{-y}\, dy \tag{16}$$

or, introducing the notations

$$\int_{y}^{\infty} y^{(m/2)-2}\, e^{-y}\, dy = M_{2-(m/2)}(y) = p_{2-(m/2)}(y) \tag{17}$$

it is found that

$$I = \left(\frac{R}{E}\right)^{(m/2)-1} M_{2-(m/2)}(y) = \left(\frac{R}{E}\right)^{(m/2)-1} p_{2-(m/2)}(y) \tag{18}$$

From eqn. (17), through integration by parts, we get

$$\int_{y}^{\infty} y^{(m/2)-2}\, e^{-y}\, dy = \frac{2}{2-m}\left(\frac{e^{-y}}{y^{1-(m/2)}} - \int_{y}^{\infty} y^{(m/2)-1}\, e^{-y}\, dy\right) \tag{19}$$

$$M_{2-(m/2)}(y) = \frac{2}{2-m}\left[\frac{e^{-y}}{y^{1-(m/2)}} - M_{1-(m/2)}(y)\right] \tag{20}$$

For $m = 1$

$$M_{3/2}(y) = 2\left[\frac{e^{-y}}{y^{1/2}} - M_{1/2}(y)\right] \tag{21}$$

Thus, it is possible to express the function $M_{3/2}(y)$ using the tabulated function $M_{1/2}(y)$ which could be tabulated.

Taking into account eqn. (18), the integral kinetic equation for the considered case is

$$F(\alpha) = \frac{A_{-(m/2)}}{a}\left(\frac{R}{E}\right)^{(m/2)-1} p_{2-(m/2)}(y) \tag{22}$$

$r = m$; m IS A POSITIVE INTEGER

For the considered case, the temperature integral

$$I = \int_{T_0}^{T} T^{m}\, e^{-E/RT}\, dT \tag{23}$$

in terms of the variable $x = -E/RT$, can be written as

$$I = (-1)^m \left(\frac{E}{R}\right)^{m+1} \int_{-\infty}^{x} \frac{e^x}{x^{m+2}}\, dx \tag{24}$$

or, with the notation

$$p_{m+2}(x) = \int_{-\infty}^{x} \frac{e^x}{x^{m+2}}\, dx \tag{25}$$

$$I = (-1)^m \left(\frac{E}{R}\right)^{m+1} p_{m+2}(x) \tag{26}$$

From eqn. (25), integrating by parts, one gets

$$p_{m+2}(x) = -\frac{1}{m+1}\left(\frac{e^x}{x^{m+1}} - \int_{-\infty}^{x} \frac{e^x}{x^{m+1}}\, dx\right) \tag{27}$$

by means of which relationship (26) may be written as

$$I = (-1)^{m+1} \left(\frac{E}{R}\right)^{m+1} \frac{1}{m+1}\left(\frac{e^x}{x^{m+1}} - \int_{-\infty}^{x} \frac{e^x}{x^{m+1}}\, dx\right) \tag{28}$$

Taking this result into account, the integral kinetic equation takes the form

$$F(\alpha) = (-1)^{m+1} \frac{A_m}{a}\left(\frac{E}{R}\right)^{m+1} \frac{1}{m+1}\left(\frac{e^x}{x^{m+1}} - \int_{-\infty}^{x} \frac{e^x}{x^{m+1}}\, dx\right) \tag{29}$$

Through repeated integrations by parts, eqn. (25) leads to [7]

$$p_{m+2}(x) = -e^x \sum_{k=1}^{m+1} \frac{1}{(m+1)\, m(m-1)\, ...(m+2-k)\, x^{m+2-k}} + \frac{1}{m+1} E_i(x) \tag{30}$$

so that the temperature integral and the conversion integral will be given, respectively, by

$$I = (-1)^{m+1} \left(\frac{E}{R}\right)^{m+1} \left[e^x \sum_{k=1}^{m+1} \frac{1}{(m+1)\, m(m-1)\, ...\, (m+2-k)\, x^{m+2-k}} + \frac{1}{m+1} E_i(x)\right] \tag{31}$$

$$F(\alpha) = (-1)^{m+1} \frac{A_m}{a}\left(\frac{E}{R}\right)^{m+1} \left[e^x \sum_{k=1}^{m+1} \frac{1}{(m+1)\, m(m-1)\, ...(m+2-k)\, x^{m+2-k}} + \frac{1}{m+1} E_i(x)\right] \tag{32}$$

$r = -m$; m IS A POSITIVE INTEGER

As in the former case, the temperature integral

$$I = \int_0^T T^{-m}\, e^{-E/RT}\, dT \tag{33}$$

can be brought to the form

$$I = (-1)^m \left(\frac{R}{E}\right)^{m-1} \int_{-\infty}^{x} x^{m-2}\, e^x\, dx \tag{34}$$

which by repeated integrations by parts leads to [8]

$$I = (-1)^m \left(\frac{R}{E}\right)^{m-1} e^x [x^{m-2} - (m-2)\, x^{m-3} + (m-2)(m-3)\, x^{m-4} - \ldots$$
$$+ (-1)^{m-3}(m-x)\,!x + (-1)^{m-2}(m-2)\,!] \tag{35}$$

Thus, for the conversion integral $F(\alpha)$, we get

$$F(\alpha) = (-1)^m \frac{A_{-m}}{a} \left(\frac{R}{E}\right)^{m-1} P_{2-m}(x) \tag{36}$$

where

$$P_{2-m}(x) = \int_{-\infty}^{x} x^{m-2}\, e^x\, dx$$
$$= e^x [x^{m-2} - (m-2)\, x^{m-3} + (m-2)(m-3)\, x^{m-4} - \ldots + (-1)^{m-3}$$
$$\times (m-x)\,!x + (-1)^{m-2}(m-2)\,!] \tag{37}$$

REFERENCES

1 J.H. Flynn and L.A. Wall, J. Res. Natl. Bur. Stand. Sect. A, 70 (1966) 487.
2 J. Šesták, V. Satava and W.W. Wendlandt, Thermochim. Acta, 7 (1973) 333.
3 J. Šesták, Thermochim. Acta, 3 (1971) 150.
4 P. Vallet, Thermogravimétrie, Gauthier-Villars, Paris, 1972, pp. 192—194.
P. Vallet, Tables Numériques Permettant l'Intégration des Constantes de Vitesse par Rapport à la Température, Gauthier-Villars, Paris, 1961.
5 K. Laidler, Chemical Kinetics, McGraw-Hill, London, 1965.
I.G. Murgulescu, T. Oncescu and E. Segal, Introduction to Physical Chemistry, Vol. II, Part 2, Editura Academiei, Bucharest. (In Romanian.)
6 D. Fătu, Stud. Cercet. Chim., Acad. R.S.R., 19 (1971) 849.
7 I.M. Rijik and I.S. Gradstein, Tabele de Integrale, Sume, Serii si Produse, Editura Tehnică, Bucharest, 1955, p. 103.
8 M.L. Smolianskii, Tablitsi Neopredelennih Integralov, F.M., Moscow, 1963, p. 90.