Journal of Thermal Analysis, Vol. 10 (1976) 447—449

ALGORISM FOR THE SOLUTION OF THE EXPONENTIAL INTEGRAL IN NON-ISOTHERMAL KINETICS AT LINEAR HEATING

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(Received March 11, 1976)

The solution of the exponential integral at linear heating for the general case that the activation energy linearly depends on temperature according to $E(T) = E_0 + RBT$ is

$$\frac{A}{q}\int_0^T T^B \exp\left(-\frac{E_0}{RT}\right) \mathrm{d}T = \frac{A}{q}\left(\frac{RT^{B+2}}{E_0 + (B+2)RT}\right) \exp\left(-\frac{E_0}{RT}\right).$$

In an earlier paper [1] we presented the solution of the exponential integral for the particular case when the activation energy is independent of temperature:

$$F(\alpha) = \frac{A}{q}\int_0^T \exp\left(-\frac{E}{RT}\right) \mathrm{d}T = \frac{A}{q}\left(\frac{RT^2}{E + 2RT}\right) \exp - \left(\frac{E}{RT}\right). \tag{1}$$

It is interesting to note that this solution of the temperature integral had already implicitly been reported in the literature [2] in the form of the function $P(x)$:

$$F(\alpha) = \frac{AE}{qR} P(x) \tag{2}$$

where, as the best approach of the function, the following expression had been proposed:

$$P(x) = (x + 2)^{-1} x^{-1} e^{-x} \tag{3}$$

where $x = E/RT$. In fact, if Eq. (3) is substituted into Eq. (2) and some simple transformations are performed, we arrive to the known solution Eq. (1):

$$F(\alpha) = \frac{AE \exp(-E/RT)}{qR(E/RT + 2)E/RT} = \frac{A}{q}\left(\frac{RT^2}{E + 2RT}\right) \exp\left(-\frac{E}{RT}\right). \tag{4}$$

It is surprising why Doyle [2] did not carry out these simple operations to obtain the final analytical relationship. He also pointed out the high accuracy of the approach $P(x) = (x + 2)^{-1} x^{-1} e^{-x}$, as demonstrated by the table in [2].

In the followings, we propose an algorism of the solution of the exponential integral for the more general case when activation energy depends, as a first approach, linearly on temperature:

$$E(T) = E_0 + RBT \,. \tag{5}$$

Substitution of this equation into the differential form of the Arrhenius equation yields

$$\frac{\mathrm{d}\ln K}{\mathrm{d}T} = \frac{E(T)}{RT^2} = \frac{E_0 + RBT}{RT^2} \tag{6}$$

or, after integration

$$K = AT^B \exp\left(-\frac{E_0}{RT}\right). \tag{7}$$

It is known that in the theory of active collisions $B = 1/2$, in the theory of activated complexes $B = 1$. Under real conditions the value of the temperature exponent presumably can assume other values too.

Let us consider the solution of the temperature integral for the case of $B = 1$ (theory of activated states):

$$F(\alpha) = \frac{A}{q} \int_0^T T \exp\left(-\frac{E_0}{RT}\right) \mathrm{d}T \,. \tag{8}$$

Let us assume that the following expression is the solution of Eq. (8):

$$F(\alpha) = \frac{A}{q} Z \frac{RT^3}{E_0} \exp\left(-\frac{E_0}{RT}\right) \tag{9}$$

with the condition that the value Z is dependent only to a very slight extent on temperature, which in turn leads to the condition $\mathrm{d}Z/\mathrm{d}T \approx 0$. Let us now differentiate Eq. (9):

$$\left(\frac{\mathrm{d}Z}{dT}\right) \frac{RT^3}{E_0} + Z \frac{3RT^2}{E_0} + ZT = T \,,$$

and, taking into account the above conditions:

$$Z \frac{3RT^2}{E_0} + ZT = T \,,$$

so that finally

$$Z = \frac{E_0}{E_0 + 3RT} \,,$$

and the solution of the integral equation (8) will assume the form

$$F(\alpha) = \frac{A}{q} \left(\frac{RT^3}{E_0 + 3RT}\right) \exp\left(-\frac{E_0}{RT}\right). \tag{10}$$

To test the correctness of Eq. (10), let us redifferentiate Eq. (10):

$$\frac{\mathrm{d}F(\alpha)}{\mathrm{d}T} = \frac{A}{q}\left\{1 - \frac{3R^2T^2}{(E_0 + 3RT)^2}\right\} T \exp\left(-\frac{E_0}{RT}\right). \tag{11}$$

The expression

$$\frac{3R^2T^2}{(E_0 + 3RT)^2} \ll 1 .$$

For any arbitrary value of B this same algorism of integration leads to the general expression

$$F(\alpha) = \frac{A}{q}\int\limits_0^T T^B \exp\left(-\frac{E_0}{RT}\right)\mathrm{d}T = \frac{A}{q}\left\{\frac{RT^{B+2}}{E_0 + (B+2)RT}\right\}\exp\left(-\frac{E_0}{RT}\right). \tag{12}$$

If subsequently the activation energy of the transformation is determined by plotting the linear relationship

$$\ln\frac{F(\alpha)}{T^{B+2}} = -\frac{E_0}{RT} + \ln\left[\frac{AR}{q[E_0 + (B+2)RT]}\right],$$

then the value E_0 can be calculated from the slope, since the effect of the temperature dependence of the term

$$\ln\left\{\frac{AR}{q[E_0 + (B+2)RT]}\right\}$$

on linearity can be neglected. Hence, independently of what model is assumed for $K(T)$, experimental data will yield the value of the activation energy E_0, and not that of $E(T)$.

References

1. V. M. Gorbachev, J. Thermal Anal., 8 (1975) 349.
2. C. D. Doyle, Nature, 207 (1965) 290.