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ON THE EXPEDIENCE FOR PRACTICE TO SEARCH FOR A MORE ACCURATE ANALYTICAL SOLUTION OF THE INTEGRAL IN THE ARRHENIUS EQUATION IN NON-ISOTHERMAL KINETICS

V. M. Gorbachev

Institute of Inorganic Chemistry, Sibirian Department of the Academy of Sciences of the U.S.S.R.
Novosibirsk

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The existing methods of approach to solve the integral in the Arrhenius equation (Coats—Redfern, Gorbachev, Zsakó, Balarin etc.), when the standard linearization method of the integral kinetic equation

$$\ln \frac{g(\alpha)}{T^2}\ vs.\ \frac{1}{T}$$

is applied in order to determine the value of the activation energy E, yield factually identical results. Hence attempts to find more accurate approaches have no practical sense.

A large number of papers [1—11 and others are found in the literature proposing various approaches for the integral in the Arrhenius equation

$$g(\alpha) = \frac{A}{q}\int\limits_0^T \exp\left(\frac{-E}{RT}\right) dT \tag{1}$$

where α is conversion, and q the linear heating rate. Among the papers listed in the references the following, most successful approaches may be cited:

Coats—Redfern [1]:

$$\int\limits_0^T \exp\left(\frac{-E}{RT}\right) dT \simeq \left(1-\frac{2\,RT}{E}\right)\frac{RT^2}{E}e^{\frac{-E}{RT}}. \tag{2}$$

Gorbachev [2]:

$$\int\limits_0^T \exp\left(\frac{-E}{RT}\right) dT \simeq \frac{RT^2}{E+2\,RT}\exp\left(\frac{-E}{RT}\right). \tag{3}$$

Zsakó [3]:

$$\int\limits_0^T \exp\left(\frac{-E}{RT}\right) dT \simeq \frac{E}{R}p(x), \text{ where } x=\frac{E}{RT}.$$

$$p(x) = \frac{e^{-x}}{(x-d)(x+2)} \quad \text{and} \quad d=\frac{16}{x^2-4x+8}. \tag{4}$$

Balarin [4]:

$$\int_0^T \exp\left(\frac{-E}{RT}\right) \mathrm{d}T \simeq \frac{RT^2}{E\sqrt{1+\frac{4\,RT}{E}}}\, e^{\frac{-E}{RT}}. \tag{5}$$

A comparison of Eqs (2), (3), (4) and (5) will allow to separate the common factors:

$$\int_0^T \exp\left(\frac{-E}{RT}\right) \mathrm{d}T = \frac{RT^2}{E}\, e^{\frac{-E}{RT}}\, \Delta p(x)\,, \tag{6}$$

and hence, for the above equations, $\Delta p(x)$ is

$$\Delta p_1(x) = 1 - \frac{2\,RT}{E} = \frac{x-2}{x}\,,$$

$$\Delta p_2(x) = \frac{E}{E+2\,RT} = \frac{x}{x+2}\,,$$

$$\Delta p_3(x) = \frac{x^2}{(x-d)(x+2)} \quad \text{and}$$

$$\Delta p_4(x) = \frac{1}{\sqrt{1+\frac{4\,RT}{E}}} = \frac{1}{\sqrt{1+\frac{4}{x}}}\,.$$

The numerical values of $\Delta p_1(x)$, $\Delta p_2(x)$, $\Delta p_3(x)$ and $\Delta p_4(x)$ are listed in Table 1, demonstrating that these values *vs.* the non-dimensional criterium of Arrhenius $x = \frac{E}{RT}$ are practically identical.

Table 1

Relationship $\Delta p(x)$ *vs.* x

x	$\Delta p_1(x)$	$\Delta p_2(x)$	$\Delta p_3(x)$	$\Delta p_4(x)$
4	0.5	0.67	1.33	0.71
8	0.75	0.80	0.85	0.82
12	0.83	0.86	0.87	0.87
16	0.87	0.89	0.89	0.89
20	0.90	0.91	0.91	0.91
24	0.92	0.92	0.92	0.92
28	0.93	0.93	0.93	0.93
32	0.94	0.94	0.94	0.94
36	0.94	0.95	0.95	0.95
40	0.95	0.95	0.95	0.95

In the general case the integration of the Arrhenius equation is necessary to perform the linearization process of the kinetic Eq. (6) in order to establish the value of the activation energy E according to

$$\ln \frac{g(\alpha)}{T^2} = - \frac{E}{RT} + \ln \frac{AR}{qE} \Delta p(x).$$

If the value $\Delta p(x)$ is factually independent of the value x *in the temperature interval in which the transformation of the substance in question proceeds,* one may state that the above approaches will yield identical values for the activation energy E.

It is obvious that an analogous statement will be also valid for the more complex case $K(T)$, that is,

$$g(\alpha) = \frac{A}{q} \int_0^T T^b \exp\left(\frac{-E}{RT}\right) dT. \tag{7}$$

Using the general solution of these integrals proposed earlier by us [11, 12] in the form

$$\int_0^T T^b \exp\left(\frac{-E}{RT}\right) dT \simeq \frac{RT^{b+2}}{E + (b+2)RT} e^{\frac{-E}{RT}},$$

one obtains, by analogy

$$\int_0^T T^b \exp\left(\frac{-E}{RT}\right) dT = \frac{RT^{b+2}}{E} e^{\frac{-E}{RT}} \Delta p(x), \tag{8}$$

where

$$\Delta p(x) = \frac{x}{x+b+2} \quad \text{and} \quad \ln \frac{g(\alpha)}{T^{b+2}} = \frac{-E}{RT} + \ln \frac{AR}{qE} \Delta p(x).$$

In conclusion, it is important to note that the true form of the function

$$K(T) = AT^b \exp\left(\frac{-E}{RT}\right)$$

is not *a priori* known for every factual transformation. The utilization of the simple Arrhenius equation appears a suitable first approach in the given situation. The lack of knowledge of the true model of $K(T)$ results in the general case, according to [13], to some uncertainty in the determination of the activation energy E. In [14], e.g., assuming two models for the function $K(T)$, namely that of active collisions ($b = 1/2$) and that of activated complexes ($b = 1$), respectively, the non-detectable difference between the activation energies, at an experimental accuracy of ±5%, may attain a value as high as 5 kcal/mol. It is self-evident that this situation will not be improved by whatever accuracy of the solution of the integral in the Arrhenius equation. In our opinion, it is preferable to utilize a more general model $K(T) = AT \exp\left(\frac{-E}{RT}\right)$ in the kinetic calculations.

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