Thermochimica Acta, 54 (1982) 377–379
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands

Note

THE QUESTIONABLE USE OF THE ARRHENIUS EQUATION TO DESCRIBE CELLULOSE AND WOOD PYROLYSIS

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(Received 29 October 1981)

The Arrhenius equation has been used widely to describe the variation with temperature of the reaction rate constant for the pyrolysis of cellulose and wood.

It may be written

$$k = A\ \mathrm{e}^{-E/RT}$$

where k is the reaction rate constant, A is the pre-exponential factor or 'reaction frequency factor', E is the 'energy barrier for reaction', R is the gas constant, and T is the absolute temperature.

It has been suggested [1] that there are three groups of results for the pyrolysis of cellulose alone or as a constituent of wood

$$A_1 = 4 \times 10^{17}\ \mathrm{s}^{-1};\ E_1 = 234.5\ \mathrm{kJ\ (g\ mole)}^{-1} \tag{1}$$

$$A_2 = 6 \times 10^{7}\text{–}7.5 \times 10^{8}\ \mathrm{s}^{-1};\ E_2 = 125.6\ \mathrm{kJ\ (g\ mole)}^{-1} \tag{2}$$

$$A_3 = 1.5 \times 10^{3}\ \mathrm{s}^{-1};\ E_3 = 62.8\ \mathrm{kJ\ (g\ mole)}^{-1} \tag{3}$$

These results follow the relationship

$$\log A = aE + b$$

with $a = 0.084$ and $b = -2.1$.

Other cellulose and wood data for E and A may be fitted to this relationship [2], exhibiting the 'kinetic compensation effect' which has been found to apply for many other reaction systems [3] including homogeneous reactions in solution, reactions on electrodes, decomposition of cobalt complexes and oxidation of metal films. The apparent kinetic parameters depend upon procedural variables but the values of a $(= 1/2.3RT_c)$ and b $(= \log k_c)$ do not.

Results of a study of the pyrolysis of cellulose fabrics [4] may be shown to exhibit the 'kinetic composition effect' also. In this case, some at least of the values of $(E, \log A)$ are an artefact of the method used to calculate first E and then A from E. One method of calculation involved weight loss data only at the temperature of maximum decomposition rate, a temperature which could change with slight changes in heating rate and other procedural variables. The values of $(E, \log A)$ obtained for the fabrics ranged from (78.7, 2.99) to (604.6, 49.73).

TABLE 1

Variation of (E, log A) with T_0

T_0 (K)	E [kJ (g mole)$^{-1}$]	log A
500	24.10	4.10
550	38.83	5.06
580	63.10	6.76
590	84.13	8.28
595	106.78	9.94

Linked values of (E, log A) might be obtained also from an application of the Arrhenius equation mistakenly in conditions where another relationship should be used. Let us assume, for example, that there is heat transfer control of reaction rate constant of the form

$$k = C(T - T_0) \quad \text{(a)}$$

or

$$k = C(T^4 - T_0^4) \quad \text{(b)}$$

Paired values of $k_1 = C(T_1 - T_0)$ and $k_2 = C(T_2 - T_0)$ may be used to derive values of (E, log A) from the Arrhenius equation. When this is done, a series of linked values results from the variation of T_0, which could represent a sample temperature.

For $C = 1$, with $T_1 = 600$ and $T_2 = 700$ K, the results obtained with variation of T_0 are shown in Table 1.

It should be noted that a 10-fold change in C changes log A by one unit and E not at all, the most important effect being that of the temperature difference.

The Arrhenius equation is remarkably insensitive and has been widely used without critical consideration of the inherent significance of E and A. Turning again to the equation of the form $k = C(T - T_0)$, with $T_0 = 673$ K and $C = 0.2$, the

TABLE 2

Variation of k with T

k	log k	T	$10^3(T)^{-1}$
1	0	678	1.475
4	0.602	693	1.443
8	0.903	713	1.403
12	1.079	733	1.364
16	1.204	753	1.328
20	1.301	773	1.294

variation of k with T is shown in Table 2, as are some calculated values of log k and $(T)^{-1}$.

Plotting log k vs. $(T)^{-1}$, the results give a curve but for small, say three-fold, changes of K, a portion of the curve might be mistaken for either one straight line or two straight lines intersecting at a 'reaction transition point' and the appropriate Arrhenius parameters calculated.

Until there is a better understanding of the effect of procedural variables on kinetic parameters, values of (E, log A) for pyrolysis of cellulose and wood should be used with caution. They should be treated as useful numbers describing the behaviour of specific systems under particular conditions, and no more.

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