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The Compensation Effect as a Result of Integration of the *Arrhenius* Equation

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Summary. It has been shown that joined segments of straight lines are observed upon plotting the logarithm of the rate constant against the reciprocal temperature, exhibiting sharp breaks at so-called 'critical' temperatures indicating sudden changes in activation energy [3, 5–8]. If the integration of the differential form of the *Arrhenius* equation from 0 to T K is taken into account, the compensation effect can easily be explained.

Keywords. Kinetics; Energy of activation; Compensation effect.

Der Kompensationseffekt als Ergebnis der Integration der *Arrhenius*-Gleichung

Zusammenfassung. Wenn man den Logarithmus der Geschwindigkeitskonstante gegen die reziproke Temperatur aufträgt, erhält man aufeinanderfolgende Teilstücke von Geraden mit scharfen Knicks bei sogenannten kritischen Temperaturen, welche jeweils eine Änderung der Aktivierungsenergie anzeigen [3, 5–8]. Integration der *Arrhenius*-Gleichung zwischen 0 und T K führt zu einer zwanglosen Erklärung des Kompensationseffekts.

Introduction

Chemical reactions obey the *Arrhenius* equation

$$k = A\ \exp(-E_0/\mathrm{R}T) \qquad (1)$$

where k is the reaction rate constant and A and E_0 are constants. According to Ref. [1, 2],

$$k = Z\ \exp(-(E_0 + BT)/\mathrm{R}T) \qquad (2)$$

where Z is the number of thermal molecular collisions, $(E_0 + BT)$ is the veritable energy of activation, and B is the coefficient of proportionality.

For reactions of the same type (*i.e.*, the same reaction in different solutions or with different catalyst etc.), the following correlation holds [3]:

$$\log A = a + bE_0 \qquad (3)$$

In Eq. (3) which is called the compensation effect, a and b are constants. The compensation effect is also observed in physical and biological processes which obey the *Arrhenius* equation, *e.g.* diffusion, crystal growth, desorption, electric conductivity, viscosity, etc. [3]. The reason of the compensation effect is unknown. In the present article, an attempt is made towards an explanation.

Methods

All articles dealing with an explanation of the compensation effect use Eq. (1) [3]. Nevertheless, *Arrhenius* obtained his equation in the form of Eq. (4) [4].

$$\mathrm{d}/\mathrm{d}T \ln k = E_0/\mathrm{R}T^2 \tag{4}$$

In Refs. [3, 5–8] it has been claimed that joined segments of straight lines are observed on plotting the logarithm of the rate constant against the reciprocal temperature, exhibiting sharp breaks at certain temperatures. This effect has been observed rather frequently [3, 6] and indicates that sudden changes of the activation energy E_0 occur. According to Refs. [3, 5–8], $k = \mathrm{const}$ for $0 < T \leq T_0, k = f(T)$ for $T_0 < T \leq T_1, k = A_1 \exp(-E_1/\mathrm{R}T)$ for $T_1 < T \leq T_2, k = A_2 \exp(-E_2/\mathrm{R}T)$ for $T_2 < T \leq T_3, \ldots, k = A_\mathrm{n} \exp(-E_n/\mathrm{R}T)$ for $T_n < T$. Therefore, $\partial/\partial T \ln k = 0$ for $< T \leq T_0, \partial/\partial T \ln k = f'(T)$ for $T_0 < T \leq T_1, \partial/\partial T \ln k = E_1/\mathrm{R}T^2$ for $T_1 < T \leq T_2, \partial/\partial T \ln k = E_2/\mathrm{R}T^2$ for $T_2 < T \leq T_3, \ldots., \partial/\partial T \ln k = E_n/RT^2, T_n < T$. From this, one obtains

$$\begin{aligned} k &= \exp\left(\int_0^T \partial/\partial T \ln k \,\mathrm{d}T\right) = k_0 + C' \exp(-E_{n-1}/\mathrm{R}T_n) \exp(E_n/\mathrm{R}T_n) \exp(-E_n/\mathrm{R}T) \\ &= C \exp(E_n/\mathrm{R}T_n) \exp(-E_n/\mathrm{R}T) \end{aligned} \tag{5}$$

where C and C' are constants. When $T \to 0$, the reaction rate is very small; hence, k_0 can be neglected.

Results and Discussion

From Eq. (5), $A = \mathrm{C} \exp(E_n/\mathrm{R}T_n)$ and $\log A = a + bE_n$. If there is a number of reactions of the same type, they obey Eq. (6) where i is the number of reaction.

$$k^i = A^i \exp(-E^i/\mathrm{R}T) \tag{6}$$

For all of them, Eq. (5) can be applied: $\log A^i = a^i + b^i E^i$. Actually, $C^i \neq C^j$, however, it is very likely that $\log C^i \approx \log C^j \approx a^i \approx a^j$ because the reaction under consideration is the same under different conditions.

The dependence of the reaction rate on the temperature consists of a few segments, each of them obeying the *Arrhenius* equation. Every segment extends over a few dozen degrees. Hence, the values of T_n^i do not differ very much from each other (T_n^i is the temperature at which the energy of activation abruptly changes), and $b^i \approx b^j$ with sufficient accuracy. Therefore, $\log A^i \approx a + bE_n$.

The above result offers a simple explanation of the compensation effect, demonstrating its origin as a result of the *Arrhenius* equation.

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