Monatshefte für Chemie 128, 1219–1221 (1997)

Monatshefte für Chemie
Chemical Monthly

Printed in Austria

A New Factor in the *Arrhenius* Equation

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Summary. It could be shown that there is a factor in the *Arrhenius* equation taking into account the history of a chemical reaction, *i.e.* its development from 0 K to the actual temperature.

Keywords. Kinetics; *Arrhenius* equation; History of chemical reaction.

Ein neuer Faktor in der *Arrhenius*-Gleichung

Zusammenfassung. Es konnte gezeigt werden, daß die *Arrhenius*-Gleichung einen Faktor enthält, der die Vergangenheit einer chemischen Reaktion berücksichtigt, d.h. ihre Entwicklung von 0 K bis zur aktuellen Temperatur.

Introduction

In the *Arrhenius* equation (Eq. (1))

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

where k is the reaction rate constant, E_0 is a constant. According to Refs. [1, 2],

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

where Z is the number of molecular collisions per unit time, $E_0 + BT$ is the actual energy of activation, and B is a constant. In the present article it is demonstrated that there is an additional factor in the *Arrhenius* equation:

$$k = ZL\ \exp\left(-(E_0 + BT)/\mathrm{R}T\right) \tag{3}$$

L takes into account 'the history' of chemical reaction, *i.e.* its development from 0 K up to the actual temperature.

Methods

According to Refs. [3–5], $K = k_0 = \mathrm{const}$ 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 $T_2 < T \leq T_3, \ldots, k = A_\mathrm{n} \exp\cdot (-E_0/\mathrm{R}T)$ for $T_n < T$ where $f(T)$ is a function of the temperature, whereas A_i and E_i are constants. *Arrhenius* obtained his equation in the form $\partial/\partial T\ \ln k = E_0/\mathrm{R}T^2$ [8].

According to Eq. (2), $k_0 = \mathrm{const}$ for $0 < T \leq T_0, k_1 = f(T)$ for $T_0 < T \leq T_1, k_2 = Z\ \exp(-(E_1 + B_1T)/\mathrm{R}T)$ for $T_1 < T \leq T_2, k_3 = Z\ \exp\,(-(E_2 + B_2T)/\mathrm{R}T)$ for $T_2 < T \leq T_3, \ldots, k_{n+1} = Z\ \exp\,(-(E_0 + BT)/\mathrm{R}T)$ for $T_n < T$.

It may be assumed that

$$f(T_1) \neq Z\exp\left(-(E_1 + B_1T_1)/\mathrm{R}T_1\right) \tag{4}$$

and

$$Z\exp\left(-(E_1 + B_1T_2)/\mathrm{R}T_2 \neq Z\exp\left(-(E_2 + B_2T_2)/\mathrm{R}T_2\right)$$

If

$$Z\exp\left(-(E_{i+1} + B_{i+1}\,T_{i+1})/\mathrm{R}T_{i+1}\right)\, Z\exp\left(-(E_i + B_iT_{i+1})\ \mathrm{R}T_{i+1}\right) = \Delta_{\mathrm{i}} \neq 1 \tag{5}$$

and

$$\int_0^T \partial/\partial T \ln k\,\mathrm{d}T = \ln k - \ln k_0,$$

then

$$\begin{aligned}\ln k &= \ln k_0 + \int_0^{T_0} \partial/\partial T \ln k_0 \mathrm{d}T + \int_{T_0}^{T_1} \partial/\partial T \ln k_1 \mathrm{d}T + \cdots + \int_{T_n}^{T} \partial/\partial T \ln k_{n+1} \mathrm{d}T\\ &= \ln k_{n+1}/(\Delta_1\Delta_2 \ldots \Delta_n).\end{aligned} \tag{6}$$

Results and Discussion

From the above equations, one obtains

$$k = Z/(\Delta_1\Delta_2 \ldots \Delta_n)\exp\left(-(E_0 + BT)/\mathrm{R}T\right) = ZL\exp\left(-(E_0 + BT)/\mathrm{R}T\right). \tag{7}$$

The factor $L = 1/(\Delta_1\Delta_2 \ldots \Delta_n)$ is the result of integration from 0 K up to the current temperature and is related to 'the history' of the chemical reaction as defined in the introduction.

For the forward and reverse reaction, Eq. (8) holds with $i = 1$ and 2.

$$k_i = ZL_i\exp\left(-(E_{0i} + B_iT)/\mathrm{R}T\right) \tag{8}$$

Usually, $Z_1 \approx Z_2$ [1]. For the equilibrium constant of chemical reaction,

$$\ln K = \ln k_1/k_2 = -Q/\mathrm{R}T + \ln L_1/L_2 = (-Q + \mathrm{R}T\ln L_1/L_2)/\mathrm{R}T \tag{9}$$

where Q is the heat of reaction.

$$\partial/\partial T(-Q + \mathrm{R}T\ln L_1/L_2) = B_2 - B_1 + \mathrm{R}\ln L_1/L_2 = \mathrm{const} \tag{10}$$

On the other hand, $\ln K = -\Delta G^0/\mathrm{R}T$. In numerous cases where ΔG^0 has been measured electrochemically, for example in Refs. [9–15], it has been shown with high accuracy that

$$\Delta G^0 = a + bT \tag{11}$$

where a and b are constants. For example, according to Ref. [9]

$$\Delta_f G^0(\mathrm{CaCr_2O_4}) = -1356.6 + 0.31641T \pm 0.63\mathrm{kJ/mole}\ (788 < T < 1070\,\mathrm{K}) \tag{12}$$

$$\Delta_f G^0(\mathrm{SrCrO_4}) = -1359.1 + 0.32998T \pm 0.30\mathrm{kJ/mole}\ (851 < T < 1116\,\mathrm{K}) \tag{13}$$

$$\Delta_f G^0(\mathrm{BaCrO_4}) = -1323.7 + 0.31159T \pm 0.34\mathrm{kJ/mole}\ (850 < T < 1168\,\mathrm{K}) \tag{14}$$

The error is less than 0.06% (Eq. (12)) or 0.03% (Eqs. (13), (14)), respectively. For (Eqs. (12–14)), $\partial \Delta G^0/\partial T = b = \mathrm{const}$ which is in accordance with the present result (Eq. (10)).

The following conclusion may be drawn: If the number of molecular collisions Z and the energy of activation are known, it is not sufficient to write the equation for the reaction rate constant in the form of Eq. (2), but it is necessary to take into account the term L.

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Received March 14, 1997. Accepted April 7, 1997