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On the Linearity of the Energy of Activation in the *Eyring* Theory of Kinetics

I. A. Stepanov

Juglas 1a/20, Riga-24, Latvia

Summary. A result obtained earlier implies that – if the *Eyring* theory is correct – the energy of the transition state is less than $U + E_a$ where U is the sum of the internal energies of the chemical reactants and E_a is the energy of activation. The energy of the transition state for the forward reaction is not equal to that of the inverse reaction; it varies linearly with the temperature.

Keywords. Kinetics; *Arrhenius* equation; Energy of activation; Transition state.

Zur Linearität der Aktivierungsenergie in der *Eyring*schen Theorie

Zusammenfassung. Aus einem früher erhaltenen Ergebnis folgt, daß – Richtigkeit der *Eyring*-Theorie vorausgesetzt – die Energie des Übergangszustands geringer ist als $U + E_a$ (U: Summe der inneren Energien der Reaktanden; E_a: Aktivierungsenergie). Die Energie des Übergangszustands ist für Hin- und Rückreaktion unterschiedlich und hängt linear von der Temperatur ab.

Introduction

In the *Arrhenius* equation (Eq. (1)), k is the reaction rate constant and E is the effective energy of activation. E is not equal to the true energy of activation, and its exact meaning is somewhat unclear.

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

In Refs. [1, 2] it has been shown that the *Arrhenius* equation has the form

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

where Z is the number of molecular collisions, $E_0 + BT$ is the true energy of activation, and B is the coefficient of proportionality. E_0 is the energy of activation when $T = 0$. Obviously, $E = E_0$. The present paper deals with the application of this result to the *Eyring* theory.

Methods

According to Ref. [3]

$$k = \frac{k_0 T}{h} \cdot \frac{Q^{\#}}{Q_1 Q_2 \ldots} \cdot \exp(-E_0/\mathrm{R}T) \tag{3}$$

where k is the reaction rate constant, k_0 is the *Boltzmann* constant, h is the *Planck* constant, Q_i is the statistical sum of the initial particles, and $Q^{\#}$ is the statistical sum of the transition state; E_0 is the energy of activation when $T = 0$ K. From Eq. (1) it follows that

$$\partial/\partial T \ \ln k = E/\mathrm{R}T^2 \tag{4}$$

From Eq. (3) it is easy to obtain Eq. (5) [4].

$$\mathrm{R}T^2 \partial/\partial T \ \ln k = \mathrm{R}T + \mathrm{R}T^2 \partial/\partial T \ \ln Q^{\#} - \mathrm{R}T^2 \Sigma \partial/\partial T \ \ln Q_i + E_0 \tag{5}$$

From statistical mechanics we know that

$$\mathrm{R}T^2 \partial/\partial T \ \ln Q_i = U_i - U_0 \tag{6}$$

where U_i is the internal energy of the corresponding degree of freedom and U_0 is its energy when $T = 0$. Taking into account Eq. (4), Eq. (5) turns to

$$E = \mathrm{R}T + E^{\#} - E_0^{\#} - (\Sigma U_i - U_0) + E_0 \tag{7}$$

where U_i are the energies of the chemical reactants.

Results and Discussion

Equation (7) has not yet been applied for thermodynamical calculations because of its rather diffuse nature. In the *Eyring* theory, it is supposed that $E \neq E_0$ [3, 4]. From Eq. (2), $E = E_0$; therefore, Eq. (7) can be written as

$$E^{\#} - E_0^{\#} = \Sigma U_i - U_0 - \mathrm{R}T \quad \text{and} \quad E^{\#} - E_0^{\#} = \Sigma U'_i - U'_0 - \mathrm{R}T. \tag{8,9}$$

From Eq. (8), Eq. (10) can be obtained.

$$E^{\#} = \Sigma U_i + E_0^{\#} - U_0 - \mathrm{R}T \tag{10}$$

Obviously, $E^{\#}$ must not necessarily equal $\Sigma U_i + E_a$ where $E_a = E_0 + BT$ is the true energy of activation. $E^{\#}$ can be greater than or less than $\Sigma U_i + E_a$. This fact can easily be explained: if the substance acquires energy and the energy of the molecules becomes equal to $\Sigma U_i + E_a$, it loses steadiness, and latent energy is released (for example as chemical energy, energy of internal electronic shells, or nuclear energy) which increases the energy of the transition state. If energy of the transition state is absorbed, on the other hand (turning, for example to chemical energy), its energy becomes less than $\Sigma U_i + E_a$. It can be seen from Eq. (10) that the energy of the transition state can be less than the sum of the internal energies of the chemical reactants if $\mathrm{R}T$ is greater than $E_0^{\#} - U_0$ assuming Eq. (3) to be true.

If $E^{\#} = \Sigma U_i + E_a$ and $E_0^{\#} = U_0 + E_0$, Eq. (8) turns to

$$BT = -\mathrm{R}T \tag{11}$$

In reality, B can differ from $-\mathrm{R}$ very much; In Ref. [2], for example, $B = 13.5\mathrm{R}$. The discrepancy between the experiment and Eq. (11) is due to the incorrectness of the assumption that $E^{\#} = \Sigma U_i + E_a$ or to the incorrectness of Eq. (3) [3]. If the *Eyring* theory is assumed to be more or less correct, the discrepancy must mainly be due to the assumption that $E^{\#} = \Sigma U_i + E_a$.

If $E^{\#} = \Sigma U_i + E_a + A + CT$ (A, C: constants) and $E_0^{\#} = U_0 + E_0 + a$ (a is a constant) and these relations are introduced into Eq. (8), Eq. (12) is obtained.

$$BT + CT + A - a = -\mathrm{R}T \tag{12}$$

From Eq. (12), $A = a$; if $B = 13.5\mathrm{R}$ [2], then $C = -14.5\mathrm{R}$. So, most probably $E^{\#} < \Sigma U_{\mathrm{i}} + E_{\mathrm{a}}$. As $192.8 \leq 14.5\mathrm{R}T \leq 361.5$ kJ/mole [2] ($1600 \leq T \leq 3000$ K), the energy of the transition state can be much less than $\Sigma U_{\mathrm{i}} + E_{\mathrm{a}}$. In Ref. [2], $E_0 = 131$ kJ/mole.

We do not have to assume that $E^{\#} = \Sigma U_{\mathrm{i}} + E_{\mathrm{a}} + A + CT$. Using $E^{\#} = \Sigma U_{\mathrm{i}} + E_{\mathrm{a}} + g(T)$ where $g(T)$ is a function of temperature and introducing this formula into Eq. (8) one obtains

$$BT + g(T) - a = -\mathrm{R}T \tag{13}$$

From Eq. (13) follows that $g(T) = a + CT$.

In Ref. [5], expressions (14)–(18) have been derived:

$$E_{\mathrm{a}} = E^{\#} - \Sigma U_{\mathrm{i}} \tag{14}$$

$$E'_{\mathrm{a}} = E^{\#} - \Sigma U'_{\mathrm{i}} \tag{15}$$

$$E'_{\mathrm{a}} - E_{\mathrm{a}} = \Sigma U_{\mathrm{i}} - \Sigma U'_{\mathrm{i}} \tag{16}$$

$$\Sigma U_i = U_0 + f(T) + DT, \tag{17}$$

$$\Sigma U'_{\mathrm{i}} = U'_0 + f(T) + D'T \tag{18}$$

Eq. (18) can be written as

$$\Sigma U'_{\mathrm{i}} = U'_0 + f'(T) + D'T \tag{19}$$

where

$$f'(T) = f(T) \tag{20}$$

As reactants and products are different substances, $f(T)$ must not be equal to $f'(T)$. If $f(T) = f'(T)$, this means that $f(T) = f'(T) = 0$. Therefore, Eqs. (17) and (18) turn to

$$\Sigma U_{\mathrm{i}} = U_0 + DT \tag{21}$$

and

$$\Sigma U'_{\mathrm{i}} = U'_0 + D'T \tag{22}$$

However, Eqs. (21) and (22) have been derived assuming that $E^{\#} = \Sigma U_{\mathrm{i}} + E_{\mathrm{a}}$ and $E^{\#} = \Sigma U'_{\mathrm{i}} + E'_{\mathrm{a}}$. In the present paper it has been shown that it is not true. It has to be supposed that

$$\Sigma U_{\mathrm{i}} + E_{\mathrm{a}} = E^{*} \neq E^{\#} \tag{23}$$

and

$$\Sigma U'_{\mathrm{i}} + E'_{\mathrm{a}} = E^{*\prime} \neq E^{\#} \tag{24}$$

For the case of simplicity, $E^{*} = E^{*\prime}$. From Eqs. (23) and (24) it is possible to derive Eqs. (17) and (18) as well as (21) and (22) in the same way as they were derived from Eqs. (14) and (15).

If Eq. (21) is substituted into Eq. (10), one obtains

$$E^{\#} = E_0^{\#} + DT - RT \tag{25}$$

Analogously,

$$E^{\#} = E_0^{\#} + D'T - RT \tag{26}$$

It can be seen that the energy of the transition state varies linearly with the temperature.

Subtracting Eq. (26) from Eq. (25), Eq. (27) is obtained.

$$D - D' = 0 \tag{27}$$

This is a contradiction because $D - D' = B' - B$ [5]. The reason may be an imperfection of Eq. (25) and, therefore Eq. (3) or a difference in the energy of the transition state for the forward and backward reaction. The author does not think that they obligatory must be equal.

If D and D' are not equal,

$$(D - D')T = E^{\#} - E_0^{\#} - E^{\#\prime} + E_0^{\#\prime} = (B' - B)T \tag{28}$$

and therefore

$$E_0^{\#} = E_0^{\#\prime} \tag{29}$$

If the main equation of the *Eyring* theory (Eq. (3)) is correct, the following conclusions may be drawn.

1. The energy of the transition state is less or higher than $\Sigma U_i + E_a$; most probably, it is much less.
2. The energy of the transition state for the forward reaction is not equal to that of the reverse reaction.
3. The energy of the transition state varies linearly with the temperature.
4. The internal energies of the reactants and products vary linearly with the temperature: $\Sigma U_i = U_0 + DT$, $\Sigma U_i' = U_0' + D'T$.

A final judgement about the validity of Eq. (3) has to be gained from a comparison of the theoretical results with experimental ones.

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