NOTES

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A Thermodynamic Formulation of Reaction Rates

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The purpose of this note is to show a thermodynamical method to formulate a correct expression for the reaction rate proposed by Horiuti *et al.*[1]

In the current theory of rate processes,[2] except for that of Horiuti, the reaction rate is assumed to be c_*/τ, where c_*=concentration of activated complex and τ=lifetime. By equating this rate to that of the kinetic expression kc_Ac_B we obtain

$$k=\frac{1}{\tau}\cdot\frac{c_*}{c_Ac_B}=\frac{K^*}{\tau}, \tag{1}$$

where k=rate constant, and c_A, c_B=concentration of reactant. K^* is interpreted as an equilibrium constant for the formation of an activated complex M* from A and B. However, if we formulate K^* according to the equilibrium theory, we should have

$$K^*=\frac{c_*^{(e)}}{c_A^{(e)}c_B^{(e)}} \tag{2}$$

and

$$\text{reaction rate}=\left\{\frac{1}{\tau}\cdot\frac{c_*^{(e)}}{c_A^{(e)}c_B^{(e)}}\right\}c_Ac_B, \tag{3}$$

where the concentration of each species in an equilibrium state is distinguished from that in a non-equilibrium state by a superscript (e). The difference between the concentrations of a reactant in equilibrium and non-equilibrium states should be reasonably taken into account.

Let us take a reversible reaction

$$\nu_AA+\nu_BB\rightleftarrows\nu_CC+\nu_DD, \tag{4}$$

where ν_x is the stoichiometric coefficient of a species X.

Reactants are supposed to be immersed in a large heat bath of temperature T which stays in equilibrium irrespective of energy exchange with the reactants. Considering the processes of the formation of an activated complex

$$\nu_AA+\nu_BB\rightarrow M^*\quad\text{(in initial state)} \tag{5.a}$$

and

$$\nu_CC+\nu_DD\rightarrow M^*\quad\text{(in final state)}, \tag{5.b}$$

we introduce the corresponding variables of progress by means of a unilateral variation

$$\vec{\delta}\xi_I=\vec{\delta}c_*=-\nu_A^{-1}\vec{\delta}c_A=-\nu_B^{-1}\vec{\delta}c_B \tag{6.a}$$

and

$$\vec{\delta}\xi_F=\vec{\delta}c_*=-\nu_C^{-1}\vec{\delta}c_C=-\nu_D^{-1}\vec{\delta}c_D, \tag{6.b}$$

where the arrow on the variation notation denotes the unilaterality.

We should mention that the ordinary progress variable for reaction (4) is

$$\begin{aligned}\delta\xi&=-\nu_A^{-1}\delta c_A=-\nu_B^{-1}\delta c_B\\&=\nu_C^{-1}\delta c_C=\nu_D^{-1}\delta c_D(\gtrless0),\end{aligned} \tag{7}$$

whose bilaterality comes from

$$\delta\xi=\vec{\delta}\xi_I-\vec{\delta}\xi_F. \tag{8}$$

With respect to the rate of reaction (5.a) or (5.b), we have to express a unidirectional rate of reaction in terms of chemically observable entities restricted to the reactants in (5.a) or (5.b). So, even from phenomenological consideration, we cannot neglect the probability factor for activation multiplied by the term c_*/τ. The activation probability will be obtained by applying Boltzmann's entropy principle as follows.

When we designate the initial or final state by α=I or α=F, and the occupation probabilities that the system under consideration exists in the unactivated and activated states in an α state by W° and W^*, respectively, the activation probability can be written in the form

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[1] G. Okamoto, J. Horiuti and K. Hirota, *Sci. Papers Inst. Phys. Chem. Res.*, **29**, 223 (1936); J. Horiuti, "Chemistry of Catalysis," (in Japanese), Asakura Book Co., Tokyo (1953).

The author would like to express his sincere thanks to the referee, who kindly informed him that a presupposition in Horiuti's theory was in line with the present result, but was more general. The present treatment seems to enlighten the thermodynamical background of the presupposition on a very elementary level.

[2] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York (1941), pp. 13, 187, 286, 348, 402.

$$\left(\frac{W^*}{W^\circ}\right)_\alpha = \exp\left(\frac{\Delta_\alpha S}{\boldsymbol{R}}\right), \tag{9}$$

where $\Delta_\alpha S$ is total entropy change in the activation of (5.a) or (5.b) which may be calculated by

$$\Delta_\alpha S \equiv \left\{\left(\frac{\partial S}{\partial \xi_\alpha}\right)\Delta\xi_\alpha\right\}_{\Delta\xi_\alpha=+1} = \frac{\partial S}{\partial \xi_\alpha}. \tag{10}$$

Here the total entropy S is expressed by

$$S = S_b(T) + \sum_{\mathrm{X}} n_{\mathrm{X}}\left(s_{\mathrm{X}}{}^\circ - \frac{u_{\mathrm{X}}{}^\circ}{T} - \boldsymbol{R}\ln c_{\mathrm{X}}\right)$$
$$+ n_*\left(s_*{}^\circ - \frac{u_*{}^\circ}{T} - \boldsymbol{R}\ln c_*\right), \tag{11}$$

where $S_b(T)$ is a part in the entropy of heat bath invariant against energy exchange with reactants under energy conservation, whose influence upon the entropy is expressed in terms of $-(\sum_{\mathrm{X}} n_{\mathrm{X}} u_{\mathrm{X}}{}^\circ/T + n_* u^\circ{}_*/T)$, where n_{X} is the number of moles of a reactant X(=A, B, C and D), n_* is the number of moles of M*, and s° and u° are the standard entropy and internal energy per mole of each species. Here the activity of a species to be used in logarithmic term is approximated by concentration.

The unidirectional rate of reaction is defined by

$$\frac{\overrightarrow{d\xi_\alpha}}{dt} \equiv \frac{c_*}{\tau}\left(\frac{W^*}{W^\circ}\right)_\alpha = \frac{c_*}{\tau}\exp\left(\frac{\Delta_\alpha S}{\boldsymbol{R}}\right). \tag{12}$$

By means of the relation

$$\Delta_\alpha S = s_*{}^\circ - \frac{u_*{}^\circ}{T} - \boldsymbol{R}\ln c_*$$
$$-\sum_{\mathrm{X}\in\alpha} \nu_{\mathrm{X}}\left(s_{\mathrm{X}}{}^\circ - \frac{u_{\mathrm{X}}{}^\circ}{T} - \boldsymbol{R}\ln c_{\mathrm{X}}\right), \tag{13}$$

it follows that

$$\frac{\overrightarrow{d\xi_\alpha}}{dt} = \frac{1}{\tau}\cdot\exp\left\{\frac{1}{\boldsymbol{R}}(s_*{}^\circ - \sum_{\mathrm{X}\in\alpha}\nu_{\mathrm{X}} s_{\mathrm{X}}{}^\circ)\right\}$$
$$\times\exp\left\{-\frac{1}{\boldsymbol{R}T}(u_*{}^\circ - \sum_{\mathrm{X}\in\alpha}\nu_{\mathrm{X}} u_{\mathrm{X}}{}^\circ)\right\}\prod_{\mathrm{X}\in\alpha} c_{\mathrm{X}}{}^{\nu_{\mathrm{X}}}$$
$$= \frac{1}{\tau}\cdot\exp\left\{-\frac{1}{\boldsymbol{R}T}(f_*{}^\circ - \sum_{\mathrm{X}\in\alpha}\nu_{\mathrm{X}} f_{\mathrm{X}}{}^\circ)\right\}\prod_{\mathrm{X}\in\alpha} c_{\mathrm{X}}{}^{\nu_{\mathrm{X}}}$$
$$= \frac{1}{\tau}\cdot\exp\left\{-\frac{1}{\boldsymbol{R}T}(f_*{}^\circ - \sum_{\mathrm{X}\in\alpha}\nu_{\mathrm{X}} f_{\mathrm{X}})\right\}, \tag{14}$$

where $\sum_{\mathrm{X}\in\alpha}$ and $\prod_{\mathrm{X}\in\alpha}$ show the summation and multiplication referring to the reactants X (=A and B, or C and D) belonging to an α (=I or F) state. $f_{\mathrm{X}}{}^\circ = u_{\mathrm{X}}{}^\circ - Ts_{\mathrm{X}}{}^\circ$ is the standard Helmholtz energy per mole of X, and $f_{\mathrm{X}} = f_{\mathrm{X}}{}^\circ + \boldsymbol{R}T\ln c_{\mathrm{X}}$.

It should be noted that the rate expression of (14) is derived without using explicitly any condition of "activation equilibrium", that is, $c_* \neq c_*{}^{(e)}$, and $c \neq c^{(e)}$ for all of X. However, if we use the condition of the equilibrium of activation given by $\Delta_\alpha S = 0$, or

$$\ln\frac{c_*{}^{(e)}}{\prod_{\mathrm{X}\in\alpha}(c_{\mathrm{X}}{}^{(e)})^{\nu_{\mathrm{X}}}} = \frac{1}{\boldsymbol{R}}(s_*{}^\circ - \sum_{\mathrm{X}\in\alpha}\nu_{\mathrm{X}} s_{\mathrm{X}}{}^\circ)$$
$$-\frac{1}{\boldsymbol{R}T}(u_*{}^\circ - \sum_{\mathrm{X}\in\alpha}\nu_{\mathrm{X}} u_{\mathrm{X}}{}^\circ), \tag{15}$$

the rate expression may be transformed into

$$\frac{\overrightarrow{d\xi_\alpha}}{dt} = \left\{\frac{1}{\tau}\cdot\frac{c^{(e)}}{\prod(c_{\mathrm{X}}{}^{(e)})^{\nu_{\mathrm{X}}}}\right\}\prod_{\mathrm{X}\in\alpha} c_{\mathrm{X}}{}^{\nu_{\mathrm{X}}}. \tag{16}$$

Finally, with the aid of Eq. (8), the net rate of reaction may be expressed in the form

$$\frac{d\xi}{dt} = \frac{\overrightarrow{d\xi_{\mathrm{I}}}}{dt} - \frac{\overrightarrow{d\xi_{\mathrm{F}}}}{dt}$$
$$= \frac{1}{\tau}\cdot\exp\left(-\frac{f_*{}^\circ}{\boldsymbol{R}T}\right)\left\{\exp\left(\frac{\sum_{\mathrm{X}\in\mathrm{I}}\nu_{\mathrm{X}} f_{\mathrm{X}}}{\boldsymbol{R}T}\right)\right.$$
$$\left.-\exp\left(\frac{\sum_{\mathrm{X}\in\mathrm{F}}\nu_{\mathrm{X}} f_{\mathrm{X}}}{\boldsymbol{R}T}\right)\right\}. \tag{17}$$

In conclusion the present formulation gives a thermodynamical basis to the theory of transition state.