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Applications of power-law transition state theory to the reaction of a hydroxyl radical with molecular hydrogen and the respiration in Camellia Japonica

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HIGHLIGHTS

- Two examples are taken into the power-law transition state theory.
- This theory allows accordance with experimental values by a power-law parameter.
- The power-law TST shows a good agreement with experiments.

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ABSTRACT

The reaction of a hydroxyl radical with molecular hydrogen and the respiration in Camellia Japonica are used as examples for studying chemical reaction rate constants by the power-law transition state theory. In the first example, the rate constants are numerically obtained at different temperature and activation energies based on the Morse potential at the potential well and improved potential energy surface 5 (I5B) at the saddle point respectively, and the relationship between the rate constants and the power-law parameter is plotted as well. In the second one, especially, the power-law parameter presents an abrupt change at temperature 290 K around, which may be explained that the Camellia Japonica is the ombrophyte, and the activity of biological enzyme reaches the maximum at this temperature. This theory allows accordance with experimental values by a power-law parameter. It is found that the values of the power-law parameter in both examples deviate from 1 but not too much and lie in the 0–1 range and proved that power-law transition state theory shows a good agreement with experiments.

1. Introduction

The father of reaction rate theory is Arrhenius who in his famous 1889 paper investigated the temperature dependence of the rates and postulated the existence of the activated intermediate [1]. His idea of an activated intermediate was amplified upon by a number of authors during the next 35 years. The collision theory raised by Lewis built on the Arrhenius empirical formula, the transition state theory (TST) introduced by Winger and Eyring based on the canonical ensemble theory, and the Kramers escape rate provided by Kramers from the kinetic theory of gas [2]. The successes and challenges of above rate theories coexist. Now, what is the most challenging problem in the rate theory is the key equilibrium assumption. It is said that there exists quasi-equilibrium in the system and the transition state in which reacting species pass only once

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from the reactants to the products, the thermodynamic equilibrium (obeying Maxwell–Boltzmann distribution) must be available throughout the whole system, and any disturbance to the Maxwell–Boltzmann distribution is almost negligible at all times [3]. However, this key assumption could not be reached in real systems, such as chemical systems and dissipative biological systems [1–3]. Thereby the traditional rate theories must be generalized to the nonequilibrium systems. Recently, studies [4–6] have demonstrated that a system far away from equilibrium does not have to relax to a thermal equilibrium state with Maxwell–Boltzmann distribution, but asymptotically approaches a nonequilibrium stationary state with a power-law distribution. What is more, this power-law distribution has been observed in astrophysics, chemistry etc. [7–10]. The typical forms of such power-law distribution include the κ-distribution or the generalized Lorentzian distributions observed in the solar winds and space plasmas [11–16], the q-distributions within nonextensive statistical mechanics [4], and the α-distribution, just like $P(E) \sim E^{-\alpha}$ [12,17,18]. These power-law distributions may lead to processes different from those in the realm governed by classical statistics with Maxwell–Boltzmann distribution. Particularly it is worth mentioning that the q-distributions within nonextensive statistical mechanics have been successfully applied into interpreting some physical properties of nonequilibrium systems [4]. Nonextensivity (herein refer to the power-law parameter $q \neq 1$) has presented some properties in the real physical systems, so it is reasonable to use this theory to study the systems far away from equilibrium. The power-law TST (transition state theory in systems with power-law distributions) reaction rate coefficients for the elementary bimolecular reactions with [19] or without [20] tunneling correction, and the unimolecular reactions [21], the collision theory power-law rate coefficients [22], and the Kramers escape rate with power distribution [23–25] have been established respectively, next step is then to apply them to the real systems. In this paper, we mainly focus on the application with power-law TST.

Considering the reaction processes in an open system far away from equilibrium can be described as the following form,

$$A \xrightarrow{k_{AB}} B, \tag{1}$$

where k_{AB} is a rate constant of the reaction process changing the reactant A into the product B. In the previous work, the formula of power-law reaction rate constant in one-dimension system, which is deduced and discussed by Du, is [5],

$$k = \frac{\sqrt{(1-v)/2m\beta}}{vB\left(\frac{1}{2}, \frac{1}{1-v} - \frac{1}{2}\right)} \cdot \frac{[1-(v-1)\beta V_s(0)]_+^{1/v-1}}{\int_0^\infty \mathrm{d}x\,[1-(v-1)\beta V_a(x)]_+^{1/v-1}}, \quad (0 < v < 1), \tag{2}$$

and

$$k = \frac{\sqrt{(v-1)/2m\beta}}{vB\left(\frac{1}{2}, \frac{1}{v-1} + 1\right)} \cdot \frac{[1-(v-1)\beta V_s(0)]_+^{1/v-1}}{\int_0^{x_a} \mathrm{d}x\,[1-(v-1)\beta V_a(x)]_+^{1/v-1}}, \quad (v > 1) \tag{3}$$

with m is the mass, $\beta = 1/k_BT$, k_B is the Boltzmann constant, T is the temperature, and v is the power-law parameter, $B(a, b)$ is the beta function, V_s and V_a are the potential energies at the saddle point and reactant well respectively, and $V_s(0)$ means the value of the saddle point.

In this paper, our purpose is applying the power-law TST into practice. In Section 2, two examples, which are the $OH + H_2 \to H + H_2O$ reaction and the respiration in Camellia Japonica, are introduced in detail. In the first one, based on the experimental values and the method of numerical integration, relevant values of parameter v at different temperature and activation energies are got, and they are listed in Table 2. In addition, the connection between the rate constants and values of v is presented in Fig. 3. In the second one, we adopt the expression of power-law *Arrhenius* rate constants (see Ref. [5], Eq. (63)) and calculate the values of v at different temperature listed in Table 3. Also the relationship of temperature T and rate constants k_R is plotted in Fig. 4. In Section 3, the conclusion is given.

2. Applications of two examples, results and discussions

2.1. $OH + H_2 \to H + H_2O$

This reaction is the foundation for studying the combustion reaction [26], and it is also the basic for the atmospheric chemistry [27,28]. The process can be described as,

$$\mathrm{OH} + \mathrm{H}_2 \to \mathrm{H} + \mathrm{H}_2\mathrm{O}. \tag{4}$$

It is obvious that the potential functions in Eqs. (2) and (3) at the reactant region and transition state region need to know if we want to get the rate constants k. In this paper, Morse potential and improved potential energy surface 5(I5B) [29,30] are used at the reactant region and transition state region respectively. At the reactant region, the potential function is described as Morse function,

$$V_a = D_e\left(1 - \exp\left[-a\left(R - R_e\right)\right]\right)^2, \tag{5}$$

where D_e is the depth of the well, R is the distance of two atoms, R_e is the equilibrium bond distances (obtained from experiment data), $a = \omega_e\sqrt{m/2D_e}$, ω_e is the frequency of the atom, m is the mass of the atom. The experimental values are all listed in Table 1.