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Author(s)	CHRISTOV, S. G.
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THE EXACT TRANSITION-STATE THEORY AND ITS RELATIONS TO COLLISION THEORY^{*)}

By

S. G. CHRISTOV^{**)}

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Abstract

An overview is made of the recent development of reaction rate theory on the basis of the exact quantum collision theory. Several equivalent rate expressions representing generalizations of the simple collision theory, the usual and the adiabatic-thermodynamic transition-state theory, are compared. All these expressions have a similar mathematical form but involve different partition functions and different "transmission coefficients" which are generally defined in a similar way as exact corrections to the corresponding classical or semiclassical rate equations. The formulations presented provide insight into the relations between the familiar simplest theories of chemical kinetics and can serve as a basis for determination of the relevant dynamical approximations involved.

1. Introduction

The transition-state (or activated-complex) theory is certainly the most useful formulation of the statistical theory of chemical reaction rates¹⁾. Its relation to collision theory is a central problem of chemical kinetics which has been widely discussed in recent time.²⁾

Several years ago, an "exact transition-state theory" has been developed in a general form on the basis of collision theory.^{3,4)} Starting from an accurate rate equation two equivalent expressions were derived that correspond to the usual formulations of the simple collision theory and the transition-state theory, respectively, but involve the exact corrections to these formulations never defined before. Applications of these rate expressions to both gas-phase and dense-phase reactions have been made in a series of papers during the last years.⁵⁻¹¹⁾ A detailed treatment of chemical kinetics

^{*)} This paper is essentially based on a review lecture at the "All-Union Conference of Quantum Chemistry", Novosibirsk (SSSR), June 28-July 1, 1978. The same lecture was presented later at the Research Institute for Catalysis, Hokkaido University, in Memoriam Professor JURO HORIUTI (October 12, 1979). Here it is complemented with some more detailed comments in the Discussion (Section 4).

^{**)} Institute of Physical Chemistry, Bulgarian Academy of Sciences, Sofia 1000, Bulgaria.

from this general point of view is presented in a recent book²⁾ which provides an insight into the relations between the collision and statistical theories and yields the familiar approximations to these theories as particular cases at well defined conditions.

Quite recently, Kuppermann¹²⁾ presented a similar formal generalization of transition-state theory that involves an exact quantum correction to the semiclassical rate equation for bimolecular gas reactions. The starting point of this derivation is the collision-theory formulation of the rate constant, developed by Eliason and Hirschfelder¹³⁾ in the framework of a general treatment of bimolecular reactions, including an adiabatic justification of transition-state theory.

In the following sections we consider and compare several equivalent formulations of the exact reaction rate theory: the collisional (section 1), the statistical (section 2) and two adiabatic formulations (section 3) that are appropriate for a clear discussion of the different kinds of approximations usually introduced. Finally (section 4), a consideration is made of some important consequences of these formulations and their relations to other work, in particular, to some misinterpretations existing in literature.

2. Collision-Theory Formulation of Reaction Rates

It is presumed that in the initial state of the system, *i. e.* in reactants region of configuration space, the classical reaction coordinate can be separated from the non-reactive modes. This is always possible when this coordinate describes either a relative translation or a vibration of reactants. In the first case, assuming a thermal equilibrium for reactants, the rate constant can be written as^{3,4)}

$$v = \frac{\kappa T}{hZ} \sum_n \sum_{n'} \int_0^\infty \kappa_{nn'}(E_x) e^{-(E_x + E_n)/\kappa T} dE_x / \kappa T \quad (1)$$

where Z is the full partition function of reactants, $\kappa_{nn'}$ is the probability of transition from the quantum state n of reactants to the quantum state n' of products as a function of the initial energy E_x for motion along the reaction coordinate x , E_n is the energy of the non-reactive motions (n being a set of quantum numbers for the electronic and vibration-rotation states) of reactants. If the motion along x corresponds to a vibration, then the rate equation becomes^{*})

^{*}) The possibility of a replacement of the integral in eq. (1) by a sum over n_x in eq. (1') has been first noted in Ref. (5) (footnote 2 on p. 358) and Ref. (7) (footnote 7 on p. 496). See also Ref. (10), p. 515. A detailed derivation of equation (1') is given in Ref. (2).

The Exact Transition-State Theory and its Relations to Collision Theory

$$v = \frac{\kappa T}{hZ} \sum_n \sum_{n'} \sum_{n_x} \kappa_{nn'}(E_{n_x}) e^{-(E_{n_x} + E_n)/\kappa T} \Delta E_{n_x} / \kappa T \quad (1')$$

where n_x is the quantum number of the x -vibration and $\Delta E_{n_x} = E_{n_x+1} - E_{n_x}$.

We can now introduce the statistical average

$$\kappa(\varepsilon_x) \equiv \bar{\kappa}_n(\varepsilon_x) = \sum_n \kappa_n(\varepsilon_x) f(E_n, T) \quad (2)$$

of the total transition probability $\kappa_n = \sum_{n'} \kappa_{nn'}$ over the quantum states n of reactants as a function of the energy variable $\varepsilon_x = E_x - E_c$, where E_c is the maximum of the potential $V(x)$ along the reaction coordinate x , and

$$f(E_n, T) = \frac{g_n e^{-E_n/\kappa T}}{Z^\ddagger}, \quad Z^\ddagger = \sum_n g_n e^{-E_n/\kappa T} \quad (3)$$

is the occupation probability of a quantum state n of reactants, Z^\ddagger being the corresponding partition function.

From eqs. (1 to 3) one obtains the rate equation^{3,4)}

$$v = \mathcal{X} \frac{\kappa T}{h} \frac{Z^\ddagger}{Z} e^{-E_c/\kappa T} \quad (4)$$

where the factor $\mathcal{X} \geq 1$ is defined by either of the expressions

$$\mathcal{X} = \int_{-\infty}^{\infty} \kappa(\varepsilon_x) e^{-\varepsilon_x/\kappa T} d\varepsilon_x / \kappa T \quad (5)$$

or

$$\mathcal{X} = \sum_{n_x} \kappa(\varepsilon_{n_x}) e^{-\varepsilon_{n_x}/\kappa T} \Delta \varepsilon_{n_x} / \kappa T \quad (5')$$

corresponding to a translation or a vibration of reactants along the reaction coordinate ($\varepsilon_{n_x} = E_{n_x} - E_c$ and $\Delta \varepsilon_{n_x} = \Delta E_{n_x} = E_{n_x+1} - E_{n_x}$).

Equation (4) is equivalent to the accurate collision theory expression (1) since it is derived without introducing any approximations.⁹⁾ From computational point of view, in the general case, it has the advantage that requires the numerical evaluation of a single integral (5), instead of evaluating a set of integrals corresponding to different values of n in eq. (1).

For a bimolecular gas reaction eq. (4) yields⁷⁾

$$v = \mathcal{X} Z_0 e^{-E_c/\kappa T}, \quad Z_0 = \pi d_0^2 (8\kappa T / \pi \mu_x)^{1/2} \quad (6)$$

where Z_0 is the collision number (per unit concentration), d_0 being the collision diameter and μ_x the reduced mass, while \mathcal{X} is the exact correction to the simple collision theory defined by the integral (5). For a unimolecular reaction one gets, instead⁷⁾,

S. G. CHRISTOV

$$v = 2\mathcal{A} \frac{\kappa T}{h} \sinh\left(\frac{h\nu_x}{2\kappa T}\right) e^{-E_c/\kappa T} \quad (7)$$

by assuming a harmonic vibration with frequency ν_x along the reaction coordinate x , the factor \mathcal{A} being defined accurately by the sum (5') (if $\Delta\varepsilon_{n_x}/\kappa T = h\nu_x/\kappa T \ll 1$ it turns into the integral (5)).

3. Statistical Formulation of Reaction Rates

The rate equation (4) is quite general and is valid for any reaction described by an arbitrary many-dimensional potential energy surface. If, however, there is a col on the ground-state electronic surface, then, one can define a transition state (or "activated complex"), as a possible stationary state in the limiting conditions of a very slow classical motion along the reaction coordinate, by the equations⁴

$$E = E_x + E_n = \varepsilon_x^+ + \varepsilon_n^+ + E_c \quad (8)$$

and

$$f(\varepsilon_n^+, T) = \frac{g_n e^{-\varepsilon_n^+/\kappa T}}{Z_{ac}^\ddagger}, \quad Z_{ac}^\ddagger = \sum_n g_n e^{-\varepsilon_n^+/\kappa T} \quad (9)$$

where ε_x^+ is the translation and ε_n^+ the vibration-rotation energy at the saddle-point ($x=x^+$). Eq. (8) is an expression of the total energy conservation and eq. (9) gives the occupation probability of a quantum state n of the "activated complex" under the assumption that during the (slow) x -motion the quantum state n is conserved from *reactants* to *transition* region of configuration space.

Using this definition of the activated complex as a "virtual state", we can introduce the statistical average

$$\kappa(\varepsilon_x^+) \equiv \bar{\kappa}_n(\varepsilon_x^+) = \sum_n \kappa_n(\varepsilon_x^+) f(\varepsilon_n^+, T) \quad (10)$$

of the exact total transition probability $\kappa_n = \sum_{n'} \kappa_{nn'}$ over the quantum states of the activated complexes. Then, with eqs. (8 to 10), the collision-theory expression (1) can be transformed into^{2,4}

$$v = \mathcal{A}_{ac} \frac{\kappa T}{h} \frac{Z_{ac}^\ddagger}{Z} e^{-E_c/\kappa T} \quad (11)$$

where the factor $\mathcal{A}_{ac} \geq 1$ is given by either of the equations

$$\mathcal{A}_{ac} = \int_{-\infty}^{\infty} \kappa(\varepsilon_x^+) e^{-\varepsilon_x^+/\kappa T} d\varepsilon_x^+/\kappa T \quad (12)$$

or

The Exact Transition-State Theory and its Relations to Collision Theory

$$\mathcal{X}_{ac} = \sum_{n_x} \kappa(\varepsilon_{n_x}^+) e^{-\varepsilon_{n_x}^+/kT} \Delta\varepsilon_{n_x}^+ / \kappa T \quad (12')$$

corresponding again to a translation or a vibration of reactants along the reaction coordinate ($\varepsilon_{n_x}^+ = E_{n_x}^+ - E_c$, $\Delta\varepsilon_{n_x}^+ = \Delta E_{n_x}^+ = E_{n_x+1}^+ - E_{n_x}^+$).

Expression (11) differs from the familiar Eyring formulation of activated-complex theory¹⁾ by the presence of an exact correction \mathcal{X}_{ac} defined by eq. (12) or (12')*).

The rate equations (4) and (11) show a remarkable formal similarity, however, the partition functions Z^\ddagger and Z_{ac}^\ddagger in eq. (3) and eq. (9) refer to different states of the system (the non-reactive modes of reactants and activated complexes, respectively), whence the difference between the factors \mathcal{X} and \mathcal{X}_{ac} , defined by eq. (5) and eq. (12), which are related by the equation

$$\frac{\mathcal{X}}{\mathcal{X}_{ac}} = \frac{Z_{ac}^\ddagger}{Z^\ddagger}. \quad (13)$$

It is easily seen that the "exact transition-state theory" expression (11), with \mathcal{X}_{ac} given by eq. (12) or (12'), can be directly obtained from the exact collision-theory expression (4), with \mathcal{X} defined by eq. (5) or (5'), by a simple replacement of energy variables ($\varepsilon_x \rightarrow \varepsilon_x^+$ or $\varepsilon_{n_x} \rightarrow \varepsilon_{n_x}^+$) with a simultaneous replacement of partition functions ($Z^\ddagger \rightarrow Z_{ac}^\ddagger$) corresponding to reactants and activated complexes. This possibility demonstrates in a clear way the relation between the accurate formulations of the collision and statistical theories, which is expressed by the simple equation (13). These exact formulations are appropriate for a discussion of the conditions under which the well known approximations to both theories are allowed.^{2,4,7)}

It should be emphasized that, in principle, both \mathcal{X} and \mathcal{X}_{ac} may be greater or less than unity, even in the case of a classical (or semiclassical) treatment of the nuclear motion. That is because the averaged reaction probabilities, defined by eqs. (2) and (10), take into account through $\kappa_n = \sum_{n'} \kappa_{nn'}$ the nonseparability of the reaction coordinate and the sudden changes of the electronic state as well.^{3,4)} This situation is demonstrated by concrete calculations.^{2,9)} In the framework of the classical (semiclassical) approximation one obtains the high temperature limit $\mathcal{X} \leq 1$ if the motion along the reaction coordinate is very *fast* compared to the non-reactive (vibration-rotation)

*) The definition (12) of \mathcal{X}_{ac} is equivalent to $\mathcal{X}_{ac} \equiv v/v_{ac}$ where v is given by the exact collision theory expression (1) and v_{ac} by Eyring equation¹⁾. An expression for \mathcal{X}_{ac} has been derived in this way by Mortensen^{14a)} for a bimolecular reaction of the type $H+H_2 \rightarrow H_2+H$. The above derivation of the exact rate equation (11) yields automatically a more general definition of \mathcal{X}_{ac} given by either eq. (12) or (12').

S. G. CHRISTOV

motions. In particular, for a bimolecular reaction eq. (6) then yields the rate constant expression of the simple collision theory⁷ (with $\mathcal{X} \leq 1$). In contrast to this from eq. (11) we get $\mathcal{X}_{ac} \leq 1$ if in the high temperature limit the classical motion along the reaction path is so *slow* that the vibrations and rotations of the system change adiabatically from reactants to transition state.⁴ This is the necessary and sufficient condition for the validity of Eyring formulation¹ of activated complex theory (with $\mathcal{X}_{ac} \leq 1$).

The above consideration implies the *dynamic nonseparability* of the reaction coordinate from the non-reactive coordinates, *i. e.* the presence of a nonnegligible coupling between reactive and non-reactive modes. Only then a comparison between the extreme conditions of a very slow and a very fast classical motion along the reaction coordinate x is meaningful. Indeed, the Eyring transition-state theory is valid if the x -motion from reactants to transition region of configuration space is so slow that the inequality²

$$\left| \frac{d\nu}{dt} \right| = \left| \frac{d\nu}{dx} \frac{dx}{dt} \right| \ll \nu^2$$

is fulfilled, where ν is the frequency of any of the non-reactive vibrations and rotations. The factor $d\nu/dx$ represents the coupling between the reactive and non-reactive motions and the factor dx/dt is the velocity of x -motion. The above condition for an *adiabatic separation* of the reaction coordinate can be obviously satisfied for any value of dx/dt , if $d\nu/dx$ is sufficiently small. If, however, $d\nu/dx=0$ (or $d\nu/dx \simeq 0$) the reaction coordinate is actually dynamically separable (or almost separable), hence the motion along it is not influenced by the non-reactive modes. In this particular case, the partition function Z^\ddagger remains unchanged from reactants to transition state, *i. e.* $Z^\ddagger = Z_{ac}^\ddagger$; therefore, from eq. (13) it follows that $\mathcal{X}_{ac} = \mathcal{X}$ which means that the transition-state theory equation (11) becomes identical to the collision theory formulation (4) of reaction rates^{4,7}. It is seen that a distinction between the conditions at which either $\mathcal{X} \leq 1$ (simple collision theory) or $\mathcal{X}_{ac} \leq 1$ (activated-complex theory) is possible only if the coupling between reactive and non-reactive modes is significant; then, the velocity of motion along the classical reaction path becomes important for determining the conditions of validity of both theories.

In a complete quantum-mechanical treatment the factors \mathcal{X} and \mathcal{X}_{ac} incorporate through the reaction probabilities κ_{nn} , both the nuclear tunneling and the non-adiabatic transitions from the ground to the excited electronic states. For an electronically adiabatic reaction the "tunneling correction" can be defined by either of the equations⁹

The Exact Transition-State Theory and its Relations to Collision Theory

$$\mathcal{X}_t = \frac{\mathcal{X}}{\mathcal{X}^{cl}} = \frac{\mathcal{X}_{ac}}{\mathcal{X}_{ac}^{cl}} \quad (14)$$

where \mathcal{X}^{cl} and \mathcal{X}_{ac}^{cl} have to be calculated by eqs. (5) and (12), respectively, using the classical (or semiclassical) transition probabilities. The two equivalent definitions (14) show, indeed, that the value of the tunneling factor \mathcal{X}_t is independent of the calculation procedure (averaging of the total reaction probabilities $\kappa_n = \sum_{n'} \kappa_{nn'}$ over the quantum states of reactants or over those of activated complexes).

The relation (13) has been first used to compute the values of \mathcal{X}^4 from those of $\mathcal{X}_{ac} \equiv v/v_{ac}$ calculated by Mortensen^{14a)} for the colinear H+H₂ and D+D₂ reactions on the basis of Weston's potential energy surface (including a correction for non-linear collisions). Direct calculations of both \mathcal{X} and \mathcal{X}_{ac} , using the definitions (5) and (12), have been recently⁹⁾ performed with the exact numerical data of Mortensen^{14a,b)} for the quantum-mechanical and semiclassical transition probabilities $\kappa_{nn'}(\epsilon_x)$ and $\kappa_{nn'}(\epsilon_x^+)$ for four isotopic reactions (H+H₂, D+D₂, H+D₂, D+H₂). Use is made also⁹⁾ of the accurate quantal results of Truhlar and Kuppermann^{15,16)} for $\kappa_{nn'}$, based on the SSMK (*Shavitt-Stevens-Minn-Karplus*) potential surface for the collinear H+H₂ and the related isotopic reactions. The values of \mathcal{X}_{ac} obtained from those of \mathcal{X} using eq. (13) agree very well with the corresponding results of Truhlar, Kuppermann and Adams¹⁶⁾ for the ratio v/v_{ac} of the exact rate constant v and the activated-complex theory rate constant v_{ac} ¹⁾. Quite recently²⁾, the exact numerical data of Schatz and Kuppermann¹⁷⁾ for $\kappa_{nn'}$ for the reaction in the three-dimensional physical space (based on the Porter-Karplus potential surface) have been used for an evaluation of both \mathcal{X} and \mathcal{X}_{ac} . Calculations of the proper tunneling correction \mathcal{X}_t defined by eqs. (14) were also made²⁾.

In the frame-work of the above treatment^{4,7)} the Eyring rate equation¹⁾ follows directly from the collision theory expression (11), which represents only a *formal* generalization of Eyring theory, since the concept of the "activated complex" is introduced by means of eqs. (8) and (9) in a quite artificial way as a "virtual" state⁴⁾, *i. e.* a state which may be realized only at certain extreme conditions. Indeed, in the general case, the activated complex is *not* a real transition state in the sense of Eyring definition: at very high temperatures, because of its short life-time, it does not correspond to a set of stationary quantum states for which eqs. (8) and (9) are valid and at very low temperatures, because of the nuclear tunneling, the most probable reaction path considerably deviates from the saddle-point of the potential energy surface^{2,4)}.

The Eyring equation can be derived in a pure deductive way from eq. (11) at certain well defined dynamical conditions⁴⁾ at which $\mathcal{X}_{ac} \leq 1$. This derivation has the great advantage of being free of some conceptual difficulties²⁾ of the usual derivation¹⁾ (in which, for instance, an imaginary one-dimensional box in the saddle-point region of the potential-energy surface is introduced).

The analysis of the extreme conditions of a very fast and a very slow motion along the classical reaction coordinate shows^{4,7)} that the simple collision theory ($\mathcal{X}=1$) and the transition state theory ($\mathcal{X}_{ac}=1$) are incompatible, except in the special case of a completely separable reaction coordinate in which the notion of the activated complex is no longer useful.

4. Adiabatic Formulations of Reaction Rates

The adiabatic justification of the semiclassical transition state theory, first suggested by Hirschfelder and Wigner¹⁸⁾, has been widely discussed in literature.^{4,13,19)} Therefore, it is of particular interest to consider the situation in which the vibration-rotation motions change adiabatically from *reactants* to *products* region of configuration space, hence the quantum number n remains constant throughout the reaction. Then, the (slow) classical motion along the reaction coordinate is governed by an effective potential energy¹³⁾

$$V_n(x) = V(x) + \varepsilon_n(x) \quad (15)$$

where $V(x)$ is the electronic energy along x and $\varepsilon_n(x)$ is the vibration-rotation energy as a function of x . The position $x = x_n^+$ of the maximum $E_c^{(n)} = V(x_n^+)$ of $V_n(x)$ determines the transition state which generally depends on the quantum state of the system.¹³⁾ At this situation we can introduce, instead of eqs. (8) and (9), the equations^{2,8)}

$$E = \varepsilon_x^+ + \varepsilon_n^+ + E_c = E_c^{(n)} + \varepsilon_x^{(n+)} \quad (16)$$

and

$$f(E_c^{(n)}, T) = \frac{g_n e^{-E_c^{(n)}/\kappa T}}{Z_{ac}^+}, \quad Z_{ac}^+ = \sum_n g_n e^{-E_c^{(n)}/\kappa T} \quad (17)$$

corresponding to an alternative definition of the "activated complex" where $\varepsilon_x^{(n+)}$ is the local kinetic translation energy along x at $x = x_n^+$. The statistical average of κ_n over the quantum states of the activated complex (though again as a "virtual state") is then given by

$$\kappa(\varepsilon_x^{(n+)}) \equiv \bar{\kappa}_n(\varepsilon_x^{(n+)}) \equiv \sum_n \kappa_n(\varepsilon_x^{(n+)}) f(E_c^{(n)}, T).$$

Using eqs. (16) and (17) the general collision theory expression (1) or

The Exact Transition-State Theory and its Relations to Collision Theory

(1') yields^{2,8)}

$$v = \mathcal{X}_{ac}^+ \frac{\kappa T}{h} \frac{Z_{ac}^+}{Z} \quad (18)$$

where the factor \mathcal{X}_{ac}^+ is defined by the expression

$$\mathcal{X}_{ac}^+ \equiv \overline{\mathcal{X}}_n = \sum_n \mathcal{X}_n f(E_c^n, T) \quad (19)$$

with

$$\mathcal{X}_n = \int_{-\infty}^{\infty} \kappa_n(\varepsilon_x^{(n+)}) e^{-\varepsilon_x^{(n+)}/\kappa T} d\varepsilon_x^{(n+)}/\kappa T \quad (20)$$

or

$$\mathcal{X}_n = \sum_{n_x} \kappa_n(\varepsilon_{n_x}^{(n+)}) e^{-\varepsilon_{n_x}^{(n+)}/\kappa T} \Delta\varepsilon_{n_x}^{(n+)}/\kappa T \quad (20')$$

depending on whether in the initial state of the system the reaction coordinate describes a relative translation or a vibration of reactants.

An equivalent exact formulation of the adiabatic theory of reaction rates is possible on the basis of another definition of the "activated complex" as a "virtual" transition state corresponding to the maximum of free energy¹⁸⁾

$$F(x, T) = V(x) - \kappa T \ln Z(x, T) \quad (21)$$

of the system as a function of the reaction coordinate x , where

$$Z(x, T) = \sum_n g_n e^{-\varepsilon_n(x)/\kappa T} \quad (21')$$

is the partition function of the non-reactive modes at a fixed value of x . The maximum of $F(x, T)$, defined by the conditions

$$\begin{aligned} \frac{dV}{dx} &= \kappa T \frac{\partial \ln Z(x, T)}{\partial x}, \\ \frac{d^2V}{dx^2} &< \kappa T \left(\frac{\partial^2 \ln Z(x, T)}{\partial x^2} \right)_{x=x^*}, \end{aligned} \quad (22)$$

lies at the point $x=x^*$ which is independent of the quantum state of the system. According to this definition of the activated complex, we can use the relations²⁾

$$E = E_c^{(n)} + \varepsilon_x^{(n+)} = V_n(x^*) + \varepsilon_x^* \quad (23)$$

and

$$f[V_n(x^*), T] = \frac{g_n e^{-V_n(x^*)/\kappa T}}{Z_{ac}^*}, \quad Z_{ac}^* = \sum_n g_n e^{-V_n(x^*)/\kappa T} \quad (24)$$

where ε_x^* is the local kinetic energy of x -motion at $x=x^*$, in order to make a change of energy variables ($\varepsilon_x^{(n+)} \rightarrow \varepsilon_x^*$) and introduce the partition function

S. G. CHRISTOV

Z_{ac}^* instead of Z_{ac}^+ .

Introducing the statistical average of κ_n ,

$$\kappa(\varepsilon_x^*) \equiv \bar{\kappa}_n(\varepsilon_x^*) = \sum_n \kappa_n(\varepsilon_x^*) f[V_n(x^*), T], \quad (25)$$

over the quantum states of the "activated complex" and using eqs. (23) and (24) one gets the rate equation²⁾

$$v = \mathcal{X}_{ac}^* \frac{\kappa T}{h} \frac{Z_{ac}^*}{Z} \quad (26)$$

where

$$\mathcal{X}_{ac}^* = \int_{-\infty}^{\infty} \kappa(\varepsilon_x^*) e^{-\varepsilon_x^*/\kappa T} d\varepsilon_x^*/\kappa T \quad (27)$$

or

$$\mathcal{X}_{ac}^* = \sum_{n_x} \kappa(\varepsilon_{n_x}^*) e^{-\varepsilon_{n_x}^*/\kappa T} \Delta\varepsilon_{n_x}^*/\kappa T. \quad (27')$$

A comparison between the two equivalent "adiabatic" rate equations (18) and (26) yields the relation²⁾

$$\frac{\mathcal{X}_{ac}^+}{\mathcal{X}_{ac}^*} = \frac{Z_{ac}^*}{Z_{ac}^+} \leq 1. \quad (28)$$

At the assumption of vibrational-rotational adiabaticity throughout the reaction course the transition probabilities obey the conditions⁸⁾

$$\kappa_{nn'} = 0 \text{ for } n \neq n'; \quad \kappa_{nn'} = \kappa_{nn} \text{ for } n = n' \quad (29)$$

so that the statistical averages become

$$\kappa(\varepsilon_x^{(n+)}) \equiv \bar{\kappa}_{nn}(\varepsilon_x^{(n+)}) = \sum_n \kappa_{nn}(\varepsilon_x^{(n+)}) f(E_c^{(n)}, T) \quad (30)$$

and

$$\kappa(\varepsilon_x^*) \equiv \bar{\kappa}_{nn}(\varepsilon_x^*) = \sum_n \kappa_{nn}(\varepsilon_x^*) f[V_n(x^*), T]. \quad (31)$$

Introducing these expressions in eq. (20) or (20') and (27) or (27') respectively, we obtain an *actual* generalization of the adiabatic rate theory^{2,8)} in two equivalent forms, given by eqs. (18) and (26) in which, however, the "activated complex" is a real and not a virtual state.

It is noteworthy, that, in general, an exponential factor involving the classical activation energy E_c does not enter the exact adiabatic expressions (18) and (26)²⁾. We can, however, bring eq. (18) in the usual exponential form by writing¹²⁾

$$E_c^{(n)} = E_c^0 + E_c^{(n)} \quad (32)$$

The Exact Transition-State Theory and its Relations to Collision Theory

where $E_c'^{(n)}$ is the maximum of the adiabatic potential $V_n(x)$, defined by eq. (15), measured relative to the maximum E_c^0 of the zero-point energy potential $V_0(x)$. Introducing eq. (32) in eq. (16 to 20) yields

$$v = \mathcal{X}_{ac}^+ \frac{\kappa T}{h} \frac{Z_{ac}^+}{Z} e^{-E_c^0/\kappa T} \quad (33)$$

where

$$Z_{ac}^+ = \sum_n g_n e^{-E_c'^{(n)}/\kappa T}.$$

Equation (33) is identical with the exact "adiabatic" rate expression derived by Kupprenmann¹²⁾ (his eq. (20)) for the special case of bimolecular reactions.

Equation (26) can be conveniently transformed by introducing the standard free energies

$$F = -\kappa T \ln Z, \quad F_{ac}^* = -\kappa T \ln Z_{ac}^*$$

of reactants and activated complexes to obtain the exact "thermodynamic" formulation²⁾

$$v = \mathcal{X}_{ac}^* \frac{\kappa T}{h} e^{-\Delta F_{ac}^*/\kappa T} \quad (34)$$

of the rate constant, where $\Delta F_{ac}^* = F_{ac}^* - F$ is the "free energy of activation". Introducing the adiabatic conditions (29) through (31) into the definitions (27) and (27') of \mathcal{X}_{ac}^* one obtains the situation of an actual thermodynamic formulation in which the "activated complex", defined by eqs. (22 to 24), may be considered as a real stationary transition state. The additional conditions at which $\mathcal{X}_{ac}^* \leq 1$ can be well defined on the basis of a dynamical consideration²⁾. Thus, one gets as a special case the semiclassical rate equation first derived by Eliason and Hirschfelder¹³⁾ (with $\mathcal{X}_{ac} = 1$) for bimolecular gas reactions.

5. Discussion

The overview of our previous work²⁻¹⁰⁾, made in sections 2, 3 and 4, shows that the exact collision theory of reaction rates can be formulated in different equivalent ways by means of a simple general procedure of substitution of energy variables and corresponding partition functions. These formulations represent appropriate generalizations of the most important classical or semiclassical reaction rate theories such as the simple collision theory, the Eyring activated-complex theory and the adiabatic-thermodynamic rate theory. All these generalizations have a similar mathematical form and

include corresponding dynamical factors which are generally defined also in a similar way*).

On the basis of these formulations the necessary and sufficient conditions for the validity of the simplest approximate theories can be determined in a rigorous and unique way. They allow us also to estimate the approximations involved in the correction factors, usually introduced on the basis of simplified dynamical calculations, by a comparison with the corresponding exact quantum or classical corrections, sometimes called "transmission coefficients".

The exact definition of the correction factors involved in the different formulations of reaction rate theory are particularly important as a means of preventing any confusion between them. There exist, especially, large discrepancies in the various definitions^{15,20)} of the correction to Eyring rate equation. Thus, for instance, Truhlar and Kuppermann¹⁵⁾ have calculated exactly several kinds of "transmission coefficients" in the usual transition state theory. The definition of one of them given by their eq. (14) is, however, a special case of the definition (5) of \mathcal{X}^{st} which is actually the exact correction to the simple collision theory equation (6), hence it does not correspond to the relevant correction \mathcal{X}_{ac} , defined by eq. (12), of activated complex theory**).

There are also misinterpretations concerning some well known treatments of the theory of reaction rates. Thus, Eyring, Walter and Kimball²¹⁾ have derived an expression (their eq. (16, 17)) which they incorrectly⁴⁾ consider as a rate equation of transition-state theory. In fact, the notion of the "activated complex" has not been introduced in the course of this derivation, which involves only partition functions of reactants. It is based on a collisional expression (their eq. (16, 15)) which is equivalent to eq. (1). The consistent derivation⁸⁾ along the same line necessarily leads to the accurate rate equation (4) which yields as a special case eq. (6) for bimolecular reactions. Evidently, this is an expression of the simple collision theory, including an exact correction \mathcal{X} defined by eq. (5). The rate equation of Eyring *et al.*²¹⁾ represents actually a semiclassical approximation to the exact collision theory, which results from eq. (4) for $\mathcal{X} \leq 1$, therefore, it has no any relation

*) Except the definition (19) in which the transition state depends on the quantum state n of the system.

***) Eq. (14) in the paper of Truhlar and Kuppermann¹⁵⁾ is considered as an "extended tunneling correction" to transition-state theory, although the authors themselves state that it can be evaluated without any reference to the concepts of that theory. Setting $E_0^{\text{b}} = E_c$ it can be readily shown that their definition is identical with eq. (5) if in the expression (2) for $\kappa(\epsilon_x)$ only the first term ($n=0$) is retained.

The Exact Transition-State Theory and its Relations to Collision Theory

to transition-state theory.

This situation is misunderstood in literature. Thus, for instance, in the recent review of Truhlar and Wyatt²²⁾ the treatment of Eyring *et al.*²¹⁾ as well as our generalization³⁾ are incorrectly referred to the collision-theory justification of transition-state theory using the "vibrational adiabatic model". Obviously, a transition-state theory cannot be derived without introducing in any way the basic concept of the "transition state" as is the case of the above treatments^{3,21)}

This point has been fully clarified in our subsequent work⁴⁾ which presents an accurate formal generalization of Eyring semiclassical reaction rate theory¹⁾. There,⁴⁾ the notion of the "activated complex" as a "virtual state" was defined through eqs. (8) and (9) by assuming vibrational-rotational adiabaticity only from reactants region to transition (saddle-point) region of configuration space. This work⁴⁾ is correctly quoted in the review of Micha²³⁾ in relation with the recent development of activated-complex theory on the basis of collision theory.

In the recent paper of Kuppermann¹²⁾ there is a statement that "Eyring, Walter and Kimball presented a derivation of the usual TST" but it is further noted that the "crucial transition" to eq. (33) (Kuppermann's equation (20) through eq. (16) (his equation (14) is *not* made by Eyring *et al.*²¹⁾ in order to obtain explicit expressions for the partition function Z_{ac}^+ (his f_{b*}^+) and the factor \mathcal{L}_{ac}^+ (his κ^{ex}). The fact that a relation like eq. (16) is not used actually means that the concept of "transition state" is not introduced at all, neither explicitly nor implicitly. Therefore, the rate equation derived by Eyring *et al.*²¹⁾ is directly related to the simple collision theory and *not* to transition-state theory.^{2,4)}

A consistent adiabatic justification of the semiclassical transition-state theory of bimolecular reactions has been first done by Eliason and Hirschfelder¹³⁾ who combined the collisional approach of Eyring, Walter and Kimball²¹⁾ with the assumption that the quantum state of the system does not change during the collision (*i. e.* from reactants to products region of configuration space). This assumption leads, however, to an alternative definition of the "activated complex", corresponding to eqs. (16) and (17), which differs in the general case from Eyring definition based on eqs. (8) and (9). As a consequence an exact or approximate rate equation like Eyring expression (11) with $\mathcal{L}_{ac} \geq 1$, which involves the classical activation energy E_c , cannot be obtained in this way, except in special cases^{2,8)}.

An extension of the adiabatic rate theory to unimolecular-type reactions in dense media has been first made⁸⁾, using a particular two-frequency har-

monic oscillator model, on the basis of eq. (4) which in this case is identical with eq. (11). In this way a rate expression related to eq. (18), which includes the exact quantum corrections (20') at the conditions (29) of vibrational adiabaticity, was derived.

In our subsequent work²⁾ a full generalization of the adiabatic theory of unimolecular and bimolecular reactions is presented^{*)}. There, the accurate expression (18) with \mathcal{K}_n defined by either eq. (20) or (20') was derived. The "thermodynamic" version of the "exact adiabatic rate theory", based on the definitions (22) of the "activated complex", was also developed, thus obtaining the equivalent equations (26) and (34).

In the work of Kuppermann¹²⁾ an "exact quantum-mechanical transition-state theory" of bimolecular reactions is derived in a somewhat different, more detailed way^{**)}. As already mentioned, his equation (20) is identical with eq. (33) which directly follows from the adiabatic formulation (18) of the rate theory. His definition of the exact "transmission coefficient" (his eq. (21) or (47) is equivalent to the definition (19) of \mathcal{K}_{ac} .

The "thermodynamic" version (26) of the adiabatic formulation of rate theory is superior from conceptual point of view as far as the transition configuration is independent of the quantum state of the system. As a consequence, the definition (27) of \mathcal{K}_{ac}^* has the computational advantage of being simpler than that of \mathcal{K}_{ac}^+ since the numerical evaluation of a single integral is needed, while the definition (19) of \mathcal{K}_{ac}^+ requires, in the general case, the evaluation of a set of integrals \mathcal{K}_n for the different quantum states of the system.

In our previous calculation^{2,4,9)}, based on quantal and semiclassical data for the reaction probabilities of the isotopic H+H₂ reactions, a comparison was made between the corrections \mathcal{K} and \mathcal{K}_{ac} to the simple collision and Eyring activated-complex theories, which are the most widely used approximations to the exact reaction rate theory. It is, of course, of particular interest to make similar calculations of the corrections \mathcal{K}_{ac}^+ and \mathcal{K}_{ac}^* which

*) These results were first presented at the "All-Union Conference of Quantum Chemistry", Novosibirsk (SSSR), June 28-July 1, 1978. (See footnote on p. 1).

***) The details in Kuppermann's treatment concern the derivation of his starting collision-theory expression (8) or (45) for bimolecular reactions, which is closely related to our eq. (1)^{3,4)} and the similar equations derived earlier by Eyring *et al.*²¹⁾ (their eq. (16. 15)) and Marcus²⁴⁾ (his eq. (A 19)). (See Ref. 4, footnote 3 on p. 539). The transition to eq. (18) or (33) (his eq. (20) or (47)) by using relation (16) (his eq. (14)) is made by Kuppermann¹²⁾ in the same way as the transition from eq. (1) to eq. (11) through the use of relation (8) (his eq. (24)) (See Ref. 4). The same approach has been used before by Marcus²⁴⁾ to obtain the usual activated-complex theory expression (his eq. (A 21)) with $\mathcal{K}_{ac}=1$.

The Exact Transition-State Theory and its Relations to Collision Theory

enter the exact "adiabatic" formulations (18) and (26), respectively.

In the work of Kuppermann¹²⁾ accurate numerical results for \mathcal{X}_{ac}^+ (his κ^{ex}) are presented and compared with different kinds of approximations for the H+H₂ reaction. It should be noticed, however, that for this reaction one expects that the values of \mathcal{X}_{ac}^+ will be close to those of \mathcal{X}_{ac} which is the correction in the Eyring-type equation (11). That is because for symmetric reactions the adiabatic potentials (15) have their maxima at the saddle point, at least for the lowest vibrational levels ($n=0, 1$) which give the major contributions to the reaction rate. This situation is noted by Kuppermann¹²⁾ too (p. 174). As a consequence, his data for \mathcal{X}_{ac}^+ (his κ^{ex}), presented on Fig. 5 for the SSMK potential surface, are quite close to our results⁹⁾ for \mathcal{X}_{ac} based on the definition (12) for the same surface. As already mentioned in Sec. 2, these results agree very well with the earlier numerical data of Truhlar, Kuppermann and Adams¹⁰⁾ for $\mathcal{X}_{ac} \equiv v/v_{ac}$. Therefore, for the H+H₂ reaction there is practically no difference between the generalization \mathcal{X}_{ac} and \mathcal{X}_{ac}^+ of the Eyring equation and the "adiabatic" formulation of transition-state theory, represented by the exact equations (11) and (18) (or (33)), respectively. It would be very interesting to compare for other reactions for which their values may differ considerably. The same concerns the evaluations of \mathcal{X}_{ac}^* which is expected, however, to differ not too much from \mathcal{X}_{ac}^+ as expressed by relation (28).

Apart from the very useful detailed discussion of various possible dynamical approximations to the reaction probabilities which simplify the calculation of $\mathcal{X}_{ac}^+ \simeq \mathcal{X}_{ac}$, Kuppermann¹²⁾ has made some general conclusions which agree with the results of earlier considerations. Thus, it is claimed that \mathcal{X}_{ac}^+ can be greater than unity even in absence of tunnelling. This has been first shown by Mortensen^{14b)} for the H+H₂ reaction on the basis of quasi-classical trajectory calculations, using the definition $\mathcal{X}_{ac} \equiv v/v_{ac}$ which is equivalent to eq. (12). Similar results have been obtained⁹⁾ for the "classical" correction $\mathcal{X} = \mathcal{X}^{cl}$ to the simple collision theory by using either the definition (5) or the relation (13). The fact that \mathcal{X}^{cl} and \mathcal{X}_{ac}^{cl} can be greater than unity was the reason to introduce⁹⁾ the two equivalent definitions (14) for the proper "tunnelling correction" \mathcal{X}_t which has been computed in this way²⁾ for the isotopic H+H₂ reactions.

The statement of Kuppermann¹²⁾ that with increasing temperature ($T \rightarrow \infty$) \mathcal{X}_{ac}^+ (his κ^{ex}) does not necessarily tends to unity is certainly true by dynamical reasons. The same is valid, of course, for \mathcal{X}_{ac} and \mathcal{X} . Therefore, in our treatments^{3,4)} the high temperature limits of both \mathcal{X} and \mathcal{X}_{ac} are generally written as $\mathcal{X} = \chi \leq 1$ and $\mathcal{X}_{ac} = \chi_{ac} \leq 1$ by noting that χ and χ_{ac}

take into account both reflexion effects due to the curvature of the reaction path and sudden changes of the electronic state. For electronically adiabatic reactions the values $\chi=1$ and $\chi_{ac}=1$ are obtained only for a separable reaction coordinate^{2,7}.

An important question raised by Kuppermann¹²⁾ (p. 180) is whether the use of a potential surface for a colinear triatomic complex in calculating \mathcal{Z}_{ac}^+ (his κ^{ex}) is justified when considering non-linear collisions in the three-dimensional physical space. The same problem arise to the same extent when evaluating \mathcal{Z}_{ac} and \mathcal{Z} which are related by eq. (13). This matter was considered in our recent work⁹⁾ where \mathcal{Z} and \mathcal{Z}_{ac} were calculated accurately for both the strictly collinear *ab initio* SSMK potential surface and the half-empirical Weston surface corrected for the bent configurations of the colinear H-H-H collision complex.¹⁴⁾ Using the new collision-theory expression (6) the absolute values of the rate constant v have been computed for four isotopic reactions (H₂+H, D₂+D, H₂+D and D₂+H) in the temperature range 300-1000 K, the effective collision diameter d_0 being estimated from a single experimental value of v (at T=1000 K) only for the H₂+H reaction. This procedure yields an excellent agreement between the theoretical and experimental v -values for the four reactions considered when the modified Weston potential surface is used, while the use of the SSMK surface in the same way leads to a large disagreement between them. It was concluded⁹⁾ that a correction for non-linear collisions is probably more important for an adequate description of the reaction dynamics than an exact (*ab initio*) calculation of a colinear potential surface. This conclusion should be tested by experiment further, making use of other half-empirical or *ab initio* potential-energy surfaces including corrections for the bent configurations.

The different versions of the exact formulation of chemical reaction rates, based on the collision theory, are important first of all from conceptual point of view since they provide insight into the relations between the familiar approximate theories in chemical kinetics. However, they are important also from practical point of view as far as they can serve as a solid basis for a discussion of the different dynamical approximations involved in these approximate theories^{*}). We hope that our work²⁻¹¹⁾ may be useful for a complete elucidation of these fundamental problems of theoretical chemistry.

*) As already mentioned, the conditions of validity of the simple collision theory ($\mathcal{Z}=1$) and Eyring activated-complex theory ($\mathcal{Z}_{ac}=1$) are, in general, essentially different^{3,4,7}). In the general case, such a difference exists between the necessary conditions for deriving the semiclassical adiabatic theory ($\mathcal{Z}_{ac}^+=1$) and the usual transition-state theory ($\mathcal{Z}_{ac}=1$)²⁾ as emphasized by Kuppermann too¹²⁾.

The Exact Transition-State Theory and its Relations to Collision Theory

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