

# Lecture Notes in Chemistry

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Stefan G. Christov

## Collision Theory and Statistical Theory of Chemical Reactions



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IN MEMORIAM  
MY PARENTS



## PREFACE

Since the discovery of quantum mechanics, more than fifty years ago, the theory of chemical reactivity has taken the first steps of its development. The knowledge of the electronic structure and the properties of atoms and molecules is the basis for an understanding of their interactions in the elementary act of any chemical process. The increasing information in this field during the last decades has stimulated the elaboration of the methods for evaluating the potential energy of the reacting systems as well as the creation of new methods for calculation of reaction probabilities (or cross sections) and rate constants. An exact solution to these fundamental problems of theoretical chemistry based on quantum mechanics and statistical physics, however, is still impossible even for the simplest chemical reactions. Therefore, different approximations have to be used in order to simplify one or the other side of the problem.

At present, the basic approach in the theory of chemical reactivity consists in separating the motions of electrons and nuclei by making use of the Born-Oppenheimer adiabatic approximation to obtain electronic energy as an effective potential for nuclear motion. If the potential energy surface is known, one can calculate, in principle, the reaction probability for any given initial state of the system. The reaction rate is then obtained as an average of the reaction probabilities over all possible initial states of the reacting particles. In the different stages of this calculational scheme additional approximations are usually introduced. They concern first of all the evaluation of the potential energy surfaces, which is certainly the most difficult problem. To calculate the reaction probabilities, classical or quantum mechanics may be used in treating the nuclear motions and, correspondingly, classical or quantum statistics is applied for the evaluation of the rate constants. Very often a simplification of the problem is achieved by a semiclassical approach in treating some degrees of freedom of the molecular motions classically and others quantum-mechanically.

Sufficiently accurate complete potential energy surfaces based on half-empirical or ab initio methods are now available only for the simplest gas phase reactions such as the collinear three-

atomic reaction  $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$ . The reaction probabilities can also be calculated exactly or approximately, using the classical or quantum collision theory, for only a few simple reactions. For more complicated reactions these calculations become extremely difficult or even impossible, especially for reactions in solution. This has been the reason for the development of the statistical theories of chemical reaction rates in which the dynamic problem is simplified or completely avoided by introducing some suitable hypotheses. For most reactions which occur via a short-living complex, such a theory is the well-known transition-state (or activated complex) theory which played, and still plays a fundamental role in chemical kinetics. Between the various versions of this theory the EYRING formulation is certainly the most simple and successful one. The more recent statistical theory of some reactions proceeding via a long-living complex is essentially an extension of activated complex theory. It is, therefore, a very important problem to prove the approximation involved in the basic assumptions of that theory in order to determine the limits of applicability of its different formulations. This problem reduces to a general consideration of the relations between collision theory and statistical theory which permits a comparison between their results at least for the simplest bimolecular and unimolecular reactions.

It is not the aim of this book to give a full account of the present stage of the collision and statistical theory by considering all various approaches to the solution of the dynamic problems involved. Instead, it attempts to present a detailed discussion of the relations between both theories from a unified point of view. Therefore, attention is paid not so much to computational techniques as to the fundamental aspects of the problem. Their complete elucidation is possible only by means of exact definitions of the concepts and by accurate formulations of the theories. Computational approaches are certainly of great importance for the practical application of any physical theory. In particular, the physical chemist is much interested in how to calculate the reaction velocities, which requires an estimation of various parameters entering the rate equations. Very often, however, we ask about the procedure of evaluating some quantities which are not well defined, for instance, the quantum correction to a classical (or semiclassical) collision or statistical theory. As a consequence, large discrepancies between the results of different approaches arise mainly

because of the lack of precise definitions of the relevant corrections.

On the other hand, the exact formulation of a theory usually represents an untractable expression which is often not useful from a practical point of view. This is the reason for preference of a simpler formulation even when its results are not very accurate. A way out of this situation is to elaborate a theory as simple as possible and estimate its accuracy through a comparison with the results of the exact theory, if possible, at least in some particular cases. Another and more practical possibility is to find simple criteria permitting the determination of the limits of validity of the approximate theory considered. This is especially desirable in the theoretical study of the chemical reactivity which is the subject of this book.

The usual way of developing an approximate theory, such as the classical kinetic collision theory or the semiclassical transition state theory, is to postulate some assumptions which greatly simplify the corresponding rate equation derived and to introduce additionally corrections such as a "probability factor" or a "transmission coefficient", which are, in general, not well defined. From a logical point of view it is more satisfying, however, to deduce an approximate theory from an accurate one under certain restrictive conditions. We, therefore, prefer to start from a general collision theory expression which can be brought in several equivalent forms corresponding to the familiar equations of the classical (or semiclassical) collision and statistical theories. This approach allows one, first, to rigorously define the corrections to both types of theories and, second, to derive the criteria at which the approximations involved are valid.

The purpose of a theory is, however, not only to compute the observable parameters of the phenomena, such as the cross section or the rate constant of a chemical reaction, but also to clarify the actual sense of any concept used, which may have a real physical meaning or may be simply introduced in a quite artificial way in the course of the mathematical derivations.

There exists, of course, a type of physical theory which rests on some postulates, such as the Newton equations of motion or

the Schrödinger equation; hence, the theory is reduced to solving a pure mathematical problem in order to calculate the observable quantities (for instance, the radiation-frequencies) without being interested in the inner nature of the phenomenon. There is, however, another theoretical approach in which one is interested at some stages of the derivation in the physical sense of the ideas used. According to MAXWELL<sup>x</sup>, this approach is preferred because it reveals in a clear way the essence of the phenomena investigated. This means that the mathematical description, which yields solely numerical results for measurable quantities, cannot be the unique purpose of the theoretical research which requires, moreover, an *interpretation* of these results. This requirement is valid in our century to the same extent as in Maxwell's time. It does not contradict the contemporary development of computer techniques which permits, for example, solving numerically the Schrödinger equation for a large molecule to obtain the electronic spectrum in agreement with the experiment. However, as WIGNER<sup>xx</sup> said on such an occasion, "not much would be learned from the calculation."

In the spirit of Maxwell's philosophy, our trend is to combine as much as possible the conceptual and computational aspects of the theory of chemical reactivity.

In order to achieve this goal, after an historical introduction, we treat the basic concepts in the contemporary theory of interatomic interactions and the dynamics of molecular collisions to the extent which is necessary for the theory of chemical reaction rates as developed from our point of view, and for some illustrative applications of this theory.

For our purposes it is not necessary to make a complete review of the extended literature devoted to the evaluation of the electronic energy of various reacting systems and to the calcula-

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<sup>x</sup> J.C. MAXWELL, On the Faraday Force Lines, Moscow, 1907 (Russian translation of the German edition with notes of L. Boltzmann).

<sup>xx</sup> E.P. WIGNER, Proc.Int.Conf.Theor.Phys., Tokyo, 1954 (p.650)



tion of the reaction probabilities (or cross sections). Therefore, in the first chapter we consider briefly the fundamental methods for computation of the potential energy surfaces with emphasis on their general properties and, in particular, on the relation between electronic structure and chemical reactivity. For the same reason, in the second, more extended chapter we restrict ourselves mainly to the basic methods for calculations of the reaction probabilities of electronically adiabatic and non-adiabatic reactions, but discuss also some details of several approaches we consider to be very useful from a practical point of view.

In the third, most extensive chapter, which occupies the central place in this book, we deal with the theory of reaction rates, making an effort for a unified treatment of the most important versions of this theory. The reader will judge whether our attempt is successful or not. The practical usefulness of this treatment is demonstrated in the fourth chapter by some applications of the new formulations proposed.

## ACKNOWLEDGEMENTS

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## NOTE

Somewhat before and after the completion of this work two books appeared in the series LECTURE NOTES IN CHEMISTRY:

The first one, SELECTED TOPICS OF THE THEORY OF CHEMICAL ELEMENTARY PROCESSES by E.E. NIKITIN and L.ZÜLICHE, Springer-Verlag, 1978, is closely related to Chapter II of the present article which considers the molecular dynamics.

The second one, CHARGE TRANSFER PROCESSES IN CONDENSED MEDIA by J.ULSTRUP, Springer-Verlag, 1979, apparently has a relation to some applications of the general reaction rate theory considered in Chapter IV of this book.

## CONTENTS

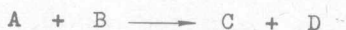
Preface	
Historical Introduction	1
CHAPTER I	
THE POTENTIAL ENERGY OF REACTIVE SYSTEMS	
1. The Adiabatic Approximation	8
2. Corrections to the Adiabatic Approximation	12
3. Potential Energy Surfaces	18
3.1. Calculation of the Electronic Surfaces	18
3.2. Correlation between Chemical Reactivity and Electronic Structure (or Electronic State)	31
CHAPTER II	
DYNAMICS OF MOLECULAR COLLISIONS	
1. General Considerations	37
1.1. Separation of Nuclear Motions	37
1.2. Time-Dependent and Time-Independent Collision Theory	44
2. Transition Probability and Cross Section	49
3. Classical Trajectory Calculations	54
4. Quantum-Mechanical Calculations	61
4.1. One-Dimensional Consideration	61
4.2. Many-Dimensional Consideration	73
5. Quasi-Classical Calculations	90
6. Non-Adiabatic Transitions in Chemical Reactions	95
6.1. Semiclassical Consideration	95
6.2. Quantum-Mechanical Consideration	99
CHAPTER III	
GENERAL THEORY OF REACTION RATES	
1. Basic Assumptions	122
2. Collision Theory Formulation of Reaction Rates	130
3. "Statistical" Formulation of Reaction Rates	139
4. Classical and Semiclassical Approximations to the Rate Equations	145
4.1. Collision Theory Treatment	145
4.2. Statistical Theory Treatment	150
5. Adiabatic Statistical Theory of Reaction Rates	158
5.1. Exact Formulation of the Adiabatic Theory	158
5.2. Approximate Equations of the Adiabatic Theory	168
6. Evaluation of the Transmission Coefficient and the Tunneling Correction	174
6.1. General Remarks	174

6.2. Evaluation of the Transmission Coefficient	176
6.3. Evaluation of the Tunneling Correction	183
6.3.1. One-Dimensional Treatment	183
6.3.2. Many-Dimensional Treatment	191
7. General Consequences from the Rate Equations	199
7.1. Basic Relations	199
7.2. Effective Activation Energy and Collision (Frequency) Factor	200
7.3. Effective Activation Energy, Rate Constant and Reaction Heat	206
7.4. Kinetic Isotope Effects	215
CHAPTER IV	
APPLICATIONS OF REACTION RATE THEORY	
1. General Considerations	227
2. Gas Phase Reactions	230
2.1. Unimolecular Reactions	230
2.1.1. General Remarks	230
2.1.2. Collision Theory Treatment	232
2.1.3. Statistical Treatment	237
2.2. Bimolecular Reactions	242
2.2.1. General Remarks	242
2.2.2. Collision Theory Treatment	243
2.2.3. Statistical Treatment	250
2.2.4. Calculations of the Correction Factors $\alpha$ and $\alpha_{ac}$ for the Isotopic H + H <sub>2</sub> Reactions	256
2.2.5. Calculations of the Rate Constants and Arrhenius Parameters of the Isotopic H <sub>2</sub> + H Reactions	266
3. Dense Phase Reactions	271
3.1. General Remarks	271
3.2. Redox Reactions	271
3.3. Proton-Transfer Reactions in Solution	282
3.4. Electrode Reactions	294
3.5. Biochemical Reactions	303
CONCLUDING REMARKS	314
REFERENCES	316



## A. HISTORICAL INTRODUCTION

The simplest version of the theory of chemical reactions rates is the kinetic collision theory of gas reactions /1/ which has been developed several decades ago by LEWIS (1918), HERZFELD (1919), POLANYI (1920), HINSHELWOOD (1937) a.o./2/. For a simple bimolecular reaction of the type



this theory admits that the reaction occurs if the kinetic energy of the relative translation of the colliding molecules (or atoms) A and B is greater than some critical value  $E_c$  called "activation energy". Assuming further a statistical velocity distribution among the reacting molecules, which obeys Maxwell's law, the kinetic theory yields a known expression for the rate constant

$$(1A) \quad v = z_0 \exp(-E_c/kT)$$

where  $z_0$  is the collision number per unit time and unit volume (the concentrations of A and B assumed to be one molecule per unit volume), T is the absolute temperature and k is the Boltzmann constant. This expression has the form of the empirical Arrhenius equation

$$(2A) \quad v = K \exp(-E_a/kT)$$

where K and  $E_a$  are constants which can be determined experimentally in a relatively restricted temperature range. If  $E_a$  is identified with the activation energy ( $E_c$ ), the prefactor K is to be interpreted as the collision number  $z_0$  in equation (1A). For a number of reactions (such as  $H_2 + J_2 \longrightarrow 2HJ$ ) the values of K are really close to that of  $z_0$ , however, there are many reactions for which  $K \ll z_0$ , therefore, a factor  $P < 1$  has been introduced in (1A) in writing

$$(3A) \quad v = Pz_0 \exp(-E_c/kT).$$

The correction factor P in (3A), called "probability" (or "steric") factor, is supposed to take into account that the reaction probability for a collision between two "activated" molecules A and B may be less than unity (for a large number of reactions P has a value between  $10^{-1}$  and  $10^{-8}$ ), however, for some reactions  $P > 1$ .

Despite the various interpretations proposed, a rigorous definition of the "probability" factor has never been given in the framework of the collision theory.

The statistical theory of chemical reactions /3/ starts with the pioneering work /4/ of MARCELIN (1915), MARCH (1917), TOLMAN (1920), RODEBUSH (1923) a.o. It was further developed /5/ by WIGNER (1932), EYRING (1935) and POLANYI (1935) in the form of the so-called activated complex (or transition state) theory. The basic idea of this theory is that during reaction the system has to overcome a critical region of configuration space (transition state) in order to pass from the initial state (reactants region) to final state (products region). Assuming a thermal equilibrium in both the initial and transition state, MARCELIN /4/ derived on the basis of statistical mechanics the formula

$$(4A) \quad v = \chi \frac{P_t}{P_i} \frac{\bar{u}}{\delta}$$

where  $v$  is the reaction rate,  $P_i$  and  $P_t$  are the probabilities of the system being in the initial and transition state, respectively;  $\bar{u}$  is the mean velocity with which the system crosses a strip of width  $\delta$  in configuration space representing the transition state;  $\chi \leq 1$  is the average probability that a system crossing the transition state will reach the final state. PELZER and WIGNER /5a/ introduced the concept of a potential energy surface in the statistical treatment of chemical kinetics, identifying the transition state with the saddle-point of that surface. This permitted one to define the "reaction path" as the line of minimum potential energy leading from reactants to products valley through the saddle point.

The formula (4A) is an exact expression in which, however, the "transmission coefficient"  $\chi$  is undetermined in the framework of statistical mechanics. WIGNER /5b/ first replaced the probabilities  $P_i$  and  $P_t$  by the corresponding partition functions of quantum theory. As a generalization of these ideas EYRING /5c/ then developed his famous theory in which the transition state, called also "activated complex", is considered as a relatively stable configuration being in thermal equilibrium with reactants, except for motion along the reaction path. This motion is treated classically, hence the Eyring theory is a semiclassical one. The expression for the rate constant is written in the well-known form

$$(5A) \quad v = \chi_{ac} \frac{kT}{h} \frac{Z_{ac}^{\#}}{Z} \exp(-E_c/kT)$$

where  $E_c$  is the classical "activation energy" at  $0^\circ K$ , which is determined by the height of the saddle-point;  $Z$  is the full partition function of reactants and  $Z_{ac}^{\#}$  is that of the activated complex in which the motion along the reaction coordinate (i.e., the line of lowest energy) is excluded;  $h$  is the Planck constant. The transmission coefficient  $\chi_{ac} \leq 1$  remains quantitatively undefined as in the formula (4A).

HIRSCHFELDER and WIGNER /6/ first discussed the validity of activated complex theory from the viewpoint of quantum mechanics. They showed that the notion of an activated complex is compatible with Heisenberg's uncertainty principle only when the potential  $V(x)$  along the reaction path in the saddle-point region is sufficiently flat that the condition

$$(6A) \quad h\nu_x^{\#} \ll kT, \quad \nu_x^{\#} = \frac{1}{2\pi} \left( \frac{f_x^{\#}}{\mu_x} \right)^{1/2}$$

is satisfied, where  $\nu_x^{\#}$  is the frequency of vibration in a virtual parabolic potential well with the same absolute value of curvature  $f_x = -(\partial^2 V / \partial x^2)_{x=x^{\#}}$  as the real potential  $V(x)$  at the saddle point ( $x=x^{\#}$ ),  $\mu_x$  being the effective mass for  $x$ -motion.

The condition (6A) is necessary for the definition of the activated complex in Eyring's theory as far as the translation motion along the classical reaction path is concerned. If this condition is not fulfilled, the quantum-mechanical penetration of the potential barrier, i.e., the nuclear tunnel effect, has to be taken into account. Then, the formula (5A) has to be corrected by an additional factor  $\chi_{ac}^t > 1$  so that the equation

$$(7A) \quad v = \chi_{ac}^t \chi_{ac} \frac{kT}{h} \frac{Z_{ac}^{\#}}{Z} e^{-E_c/kT}$$

is obtained. As shown by WIGNER /5b/, in a first approximation,

$$(8A) \quad \chi_{ac}^t = 1 + \frac{1}{24} \left( \frac{h\nu_x^{\#}}{kT} \right)^2$$

In general, however, the "tunneling correction"  $\chi_{ac}^t$  is not defined in the framework of transition state theory.

If condition (6A) is fulfilled, according to (8A) the motion along the reaction coordinate  $x$  is a classical one ( $\chi_{ac}^t = 1$ ). This condition is, however, not sufficient for the definition of the activated complex as a stationary-state configuration in relation to its vibrations and rotations, which are treated quantum-mechanically. It is, moreover, necessary to assume that the lifetime of the activated complex is sufficiently long that many vibrations and rotations occur during the passage of the system-point across the critical portion  $\delta$  of configuration space. According to HIRSCHFELDER and WIGNER /6/, the activated complex theory is justified if the motion along the reaction coordinate is so slow that throughout the course of reaction the vibration-rotation motions change in an adiabatic way so that the quantum state of the system is conserved. This assures both a full quantization of the vibration-rotation energy and thermal equilibrium in the transition state.

The simple collision theory and the activated complex theory have appeared as two alternative treatments of chemical reaction kinetics. It is clear, however, that they represent only two different kinds of approximation to an exact collision theory based either on classical or quantum mechanics. During the past few years considerable progress has been achieved in the collisional treatment of bimolecular reactions /7,8/. For more complicated reactions, however, the collision theory yields untractable expressions so that the activated complex theory provides a unique general method for an estimation of the rates of these reactions. Therefore, it is very important to determine well the limits of its validity.

EYRING, WALTER and KIMBALL /9/ first employed a quantum-mechanical approach to derive a rate equation of the form (5A) which they considered to be identical to Eyring's formula of activated complex theory. Actually, the notion of a "transition state" has not been used in any way in that derivation and, in fact, an essentially different collision theory expression was obtained (See Ref./20b/). ELIASON and HIRSCHFELDER /10/ have used a similar collisional procedure, but under the additional assumption that the quantum state of the system does not change in the course of reaction. In this way they derived a rate expression which is considered as a more general formulation of transition state theory as far as the "activated complex" is defined as a point on the reaction path corresponding to the maximum of free energy, instead of the peak of the potential barrier (sad-



dle-point). This results from an application of the variational method of WIGNER /11/ to a quantum-mechanical treatment of transition state theory. The above adiabatic justification of transition state theory has been widely accepted more recently /12-14/. It should be noted, however, that this approach yields a rate equation which is not identical to the Eyring formula (5A), except in particular cases.

Three basic assumptions are involved in Eyring's transition state theory: I. Statistical equilibrium between reactants and activated complexes. II. Classical motion along the reaction path. III. Separability of the reaction coordinate from the other coordinates in the transition region of configuration space. These assumptions are the basis of a derivation of the Eyring rate equation in which the nonadiabatic transitions, the non-equilibrium effects, the nuclear tunneling, the reflection and the nonseparability of the (curvilinear) reaction coordinate, are completely neglected. As a result of all these approximations, both the "tunneling" factor ( $\chi_{ac}^t$ ) and the "transmission coefficient" ( $\chi_{ac}$ ) in expression (7A) must be taken equal to unity.

The assumptions of the activated complex theory have been questioned for different reasons. KASSEL /15/ first pointed out that the lifetime  $\tau$  of the transition state is too short ( $\tau \sim 10^{-14}$  sec) so that the uncertainty of the energy determination, according to Heisenberg's relation  $\Delta E \sim h/\tau$ , is comparable to the distance between the energy levels.

Recent calculations /16/ for some simple gas reactions show that  $\tau$  is shorter than the periods of vibrations and rotations of the activated complex, therefore, it cannot be considered as a stationary state configuration with a well-defined discrete energy spectrum. This is contrary to the assumption of vibrational-rotational adiabaticity which is related to the equilibrium hypothesis of activated complex theory.

In many cases the sudden changes in the electronic state, i.e., the nonadiabatic transitions from a lower to a higher potential energy surface, have to be taken into account /3/. The reflection in the curvilinear part of the reaction path may also considerably influence the reaction probability. Therefore, the introduction of a transmission coefficient ( $\chi_{ac} < 1$ ) in the rate equation (7A) is necessary for a large number of reactions /3/.

Recent calculations indicate that for reactions with participation of light atoms, such as H and its isotopes, the nuclear tunnel effect is not negligible /17-19/ and the Wigner tunneling cor-