

The Development of Transition-State Theory

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Transition-state theory, as developed in 1935 by Eyring and by Evans and Polanyi, is the culmination of a series of investigations that are conveniently classified under three headings: (1) thermodynamic treatments, (2) kinetic-theory treatments, and (3) statistical-mechanical treatments. In tracing the evolution of these lines of attack some important landmarks stand out: van't Hoff's thermodynamic approach involving enthalpy changes followed by Marcelin's treatment in terms of affinity and subsequent developments by Kohnstamm, Scheffer, and others; Trautz's and Lewis's hard-sphere collision theories; Marcelin's statistical-mechanical treatment, made more precise by Rice, and later treatments of Herzfeld, Eyring, Polanyi, and Pelzer and Wigner. Transition-state theory, by focusing attention on the activated complexes which are assumed to be in "quasi-equilibrium" with reactants, provides a simple way of formulating reaction rates and gives a unique insight into how processes occur. It has survived considerable criticisms and after almost 50 years has not been replaced by any general treatment comparable in simplicity and accuracy.

Introduction

Henry Eyring's formulation,¹ in 1935, of transition-state theory is probably, of his many important scientific contributions, the one that has had the most far-reaching influence and lasting value. His famous equations²

$$k = \kappa \frac{kT}{h} \frac{Q^\ddagger}{Q_A Q_B} e^{-E/RT} \quad (1)$$

$$k = \kappa \frac{kT}{h} e^{\Delta^\ddagger S/R} e^{-\Delta^\ddagger H/RT} \quad (2)$$

have been applied with considerable success to a wide variety of rate processes. An important factor in their favor, in comparison with other treatments of rates, is their relative ease of application; attempts to use improved treatments require much more labor and require an amount of time larger by several orders of magnitude. A second important factor is that the transition-state-theory approach leads to a better understanding of how even very complicated reactions take place.

Nearly 50 years have elapsed since transition-state theory was developed in its present form, but so far only brief commentaries on its origins have appeared.^{3,4} The occasion of this issue in memory of Henry Eyring, to whom all physical chemists and many others owe so much, provides us with an opportunity to make a serious start on putting the theory into some perspective. We hope to elaborate the historical development at a later stage; in the present paper we emphasize more scientific matters.

Beginnings of Kinetics

The way in which chemical kinetics developed in its early days has been dealt with elsewhere,⁵⁻⁸ and here we

mention only some relevant points. The problem of temperature dependence, so crucial to rate theories, was first studied quantitatively by Wilhelmy⁹ in 1850, and for the next 50 years a number of other equations were proposed. There was much confusion, and even at the turn of the century the matter was by no means settled.^{7,8} However, by about 1910 the Arrhenius equation¹⁰

$$k = Ae^{-E/RT} \quad (3)$$

was generally accepted. Further development then required a more detailed consideration of the significance of the activation energy E and the preexponential ("frequency") factor A . The first of these factors was dealt with successfully by Eyring and Polanyi,¹¹ who combined quantum-mechanical principles with a good deal of empiricism. In more recent years, with the aid of new computing techniques, a number of other calculations of activation energies have been made, but except for some fairly simple reactions it is still difficult to calculate values that are in close agreement with experimental ones.¹² This aspect is outside the scope of the present article.

The second important problem in chemical kinetics is the magnitude of the preexponential factor A in the Arrhenius equation. This is the problem that was dealt with so successfully by transition-state theory,¹³ developed almost simultaneously in 1935 by Eyring,¹ then at Princeton University, and by Evans and Polanyi,¹⁴ of the University of Manchester. The theories of these workers follow very similar lines, and the rate equations that they arrived at are equivalent to one another. There are, however, some differences of derivation and of emphasis; Evans and Polanyi, for example, were concerned in particular with applying their equation to the influence of pressure on reaction rates. Eyring's first paper was followed very closely

(1) H. Eyring, *J. Chem. Phys.*, **3**, 107 (1935).

(2) In this paper we will for consistency follow the latest IUPAC recommendations for symbolism and terminology in chemical kinetics (K. J. Laidler, *Pure Appl. Chem.*, **53**, 753 (1981)). To save space, symbols included in that report will not be defined; in eq 1 and 2 κ is the transmission coefficient, which allows for the possibility that activated complexes do not give rise to products. The latest IUPAC recommendation (*Pure Appl. Chem.*, **54**, 1239 (1982) and reprinted in *J. Chem. Thermodyn.* **14**, 805 (1982)) is that the symbol ‡ be placed before H , S , or G .

(3) S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes", McGraw-Hill, New York, 1941.

(4) H. Eyring, *Chem. Rev.*, **17**, 65 (1935).

(5) M. C. King, *Ambix*, **28**, 70 (1981).

(6) M. C. King, *Ambix*, **29**, 49 (1982).

(7) S. R. Logan, *J. Chem. Educ.*, **59**, 269 (1982).

(8) K. J. Laidler, *J. Chem. Educ.*, in press.

(9) L. Wilhelmy, *Pogg. Ann.*, **81**, 422, 499 (1850).

(10) S. Arrhenius, *J. Phys. Chem.*, **4**, 226 (1889).

(11) H. Eyring and M. Polanyi, *Z. Phys. Chem., Abt. B*, **12**, 279 (1931).

(12) For a review see K. J. Laidler, "Theories of Chemical Reaction Rates", McGraw-Hill, New York, 1969, Chapter 3. There have been some important advances in the last few years; for a very recent account, with references to previous work, see W. J. Bouma, J. M. Dawes, and L. Radom, *Org. Mass Spectrom.*, **18**, 12 (1983).

(13) "Transition-state theory" is the expression now favored by IUPAC (V. Gold, *Pure Appl. Chem.*, **51**, 1725 (1979); K. J. Laidler, *ibid.*, **53**, 753 (1981)). Several alternative names have been used, including "theory of absolute reaction rates" and "activated-complex theory".

(14) M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **31**, 875 (1935).

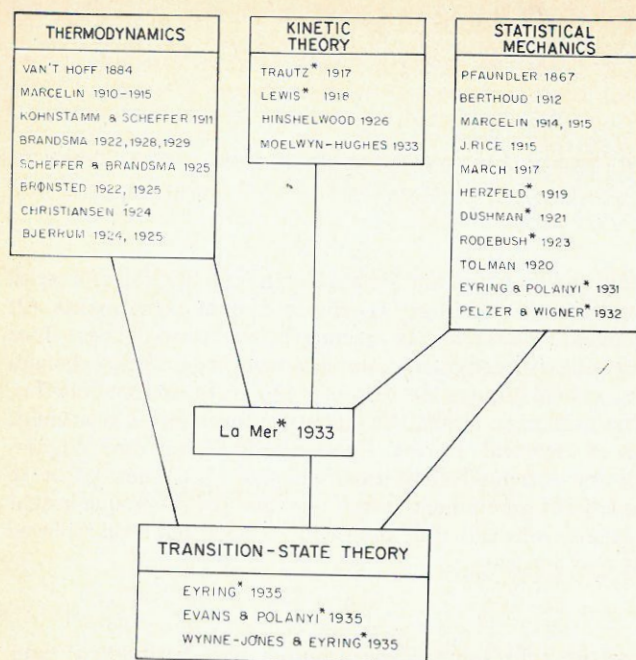


Figure 1. The three main lines of development of transition-state theory. An asterisk denotes those theories that, given an activation energy or a potential energy surface, provide an absolute magnitude for the preexponential factor and the rate constant.

by one with Wynne-Jones,¹⁵ which dealt with reactions in solution, and which formulated the rate equation in terms of thermodynamic quantities such as the enthalpy of activation Δ^*H and the entropy of activation Δ^*S (eq 2).

In considering the evolution of transition-state theory one can discern three lines of development, which are summarized in Figure 1: (1) thermodynamic treatments, (2) kinetic-theory treatments, based on the assumption that molecules behave as hard spheres, and (3) treatments based on statistical mechanics, some later versions of which involved quantum mechanics. Some treatments do not fall squarely into any one of these categories, and some have features of two or three of them. Transition-state theory combined all of these approaches in a very successful way.

Thermodynamic Treatments

The thermodynamic approaches to rate theory all stem from the famous contribution of van't Hoff¹⁶ in 1884, which directly inspired Arrhenius¹⁰ to propose his equation (eq 3). In modern terminology and notation van't Hoff's proposal was as follows. The concentration equilibrium constant K_c for a reaction varies with temperature according to the equation

$$\frac{d \ln K_c}{dT} = \frac{\Delta U^\circ}{RT^2} \quad (4)$$

where ΔU° is the standard change in internal energy. For any reaction at equilibrium, the equilibrium constant is the ratio of the rate constants k_1 and k_{-1} in forward and reverse directions, and therefore

$$\frac{d \ln k_1}{dT} - \frac{d \ln k_{-1}}{dT} = \frac{\Delta U^\circ}{RT^2} \quad (5)$$

In order for eq 5 to apply, the rate constants must vary with temperature according to the same type of equation as eq 4, and van't Hoff therefore split eq 5 into two equations

$$\frac{d \ln k_1}{dT} = \frac{E}{RT^2} - I \quad (6)$$

$$\frac{d \ln k_{-1}}{dT} = \frac{E_{-1}}{RT^2} - I \quad (7)$$

where $E_1 - E_{-1} = \Delta U$. Experimentally it is found that to a good approximation I can be set equal to zero, so that a rate constant is related to temperature by the equation

$$\frac{d \ln k}{dT} = \frac{E}{RT^2} \quad (8)$$

With E temperature independent this equation reduces to what is now called the Arrhenius equation; various types of temperature dependence of E were, however, also considered by van't Hoff.¹⁶

The next important contribution was that of Marcelin,¹⁷ who in a paper presented in 1910 to the Académie des Sciences proposed rate equations involving the concept of affinity, a quantity used by earlier workers in different senses, and now discarded. Marcelin's affinity A can be interpreted as the negative of the partial molar Gibbs energy change Δ^*G in going from the initial to the activated state, although his introduction of the concept of the activated state did not come until a few years later. Marcelin gave an equation which we can write as

$$v = (\text{constant})(e^{A_1/RT} - e^{A_{-1}/RT}) \quad (9)$$

or as

$$v = (\text{constant})(e^{-\Delta^*G_1/RT} - e^{-\Delta^*G_{-1}/RT}) \quad (10)$$

where the subscript 1 refers to the forward reaction and -1 refers to the reverse reaction. This equation is compatible with that given in 1935 by Eyring and Wynne-Jones,¹⁵ although Marcelin gave no interpretation of the preexponential constant. These ideas were followed up by Marcelin in a number of subsequent publications.¹⁸⁻²²

In 1911, quite independently, Kohnstamm and Scheffer²³ published very similar, and rather more explicit, ideas which were further developed in later publications by Kohnstamm, Scheffer, and Brandsma.²⁴⁻²⁷ In modern notation their ideas may be summarized as follows. The equilibrium constant K_c for a reaction may be expressed as

$$\ln K_c = -\Delta G^\circ/RT \quad (11)$$

where ΔG° is the standard Gibbs energy change. As was done by van't Hoff, they split this equation into

$$\ln k_1 - \ln k_{-1} = -\Delta G^\circ/RT \quad (12)$$

(17) R. Marcelin, *C. R. Hebd. Seances Acad. Sci.*, **151**, 1052 (1910).

(18) R. Marcelin, *J. Chim. Phys. Phys.-Chim. Biol.*, **9**, 399 (1911).

(19) R. Marcelin, *C. R. Hebd. Seances Acad. Sci.*, **157**, 1419 (1913).

(20) R. Marcelin, *J. Chim. Phys. Phys.-Chim. Biol.*, **12**, 451 (1914).

(21) R. Marcelin, *C. R. Hebd. Seances Acad. Sci.*, **158**, 116 (1914).

(22) R. Marcelin, *Ann. Phys.*, **3**, 120 (1915).

(23) P. Kohnstamm and F. E. C. Scheffer, *Proc. K. Ned. Akad. Wet.*, **13**, 789 (1911).

(24) W. F. Brandsma, *Chem. Weekbl.*, **19**, 318 (1922).

(25) F. E. C. Scheffer and W. F. Brandsma, *Recl. Trav. Chim. Pays-Bas*, **45**, 522 (1926).

(26) W. F. Brandsma, *Chem. Weekbl.*, **47**, 94 (1928).

(27) W. F. Brandsma, *Chem. Weekbl.*, **48**, 1205 (1929).

(15) H. Eyring and W. F. K. Wynne-Jones, *J. Chem. Phys.*, **3**, 492 (1935).

(16) J. H. van't Hoff, "Etudes de Dynamique Chimique", F. Muller, Amsterdam, 1884; "Studies in Chemical Dynamics" (translation by T. Ewan), London, 1896; see also J. H. van't Hoff, "Lectures on Theoretical and Physical Chemistry, Part I, Chemical Dynamics", Edward Arnold, London, 1898.

and then proposed that the expressions for the individual rate constants k_1 and k_{-1} should be

$$\ln k_1 = -\Delta^*G_1/RT + \text{constant} \quad (13)$$

$$\ln k_{-1} = -\Delta^*G_{-1}/RT + \text{constant} \quad (14)$$

This splitting involves the assumption that reaction in the forward direction depends only on the change Δ^*G_1 in Gibbs energy in going from the initial state to some intermediate state represented by the symbol $\ddagger$; similarly for the back-reaction there is a change Δ^*G_{-1} in going from the product state to the intermediate state. For any reaction, we can therefore write

$$k = \nu^* e^{-\Delta^*G/RT} \quad (15)$$

where ν^* is a factor which is the same for all reactions. This at once leads to

$$k = \nu^* e^{\Delta^*S/R} e^{-\Delta^*H/RT} \quad (16)$$

where Δ^*S is the entropy change, and Δ^*H the enthalpy change, in going from the initial to the intermediate state.

By employing arguments of this kind, Kohnstamm and Scheffer²³ were led to the concepts of Gibbs energy of activation and entropy of activation, concepts that play a key role in transition-state theory. These workers were not able, however, to interpret the multiplying factor ν^* , which in transition-state theory is kT/h .

Other important thermodynamic approaches to reaction rates were later made by Bronsted,^{28,29} Bjerrum,^{30,31} Christiansen,³² and Scatchard.³³ Their work was mainly directed toward understanding the effects of ionic strength on the rates of reaction in solution. Their treatments did not involve the assumption of an activated complex but were applied to any intermediate formed between two reactant molecules; by regarding this intermediate as being in equilibrium with reactants, introducing activity coefficients, and applying Debye-Hückel theory, Bronsted²⁸ gave the first interpretation of ionic-strength effects, and his original treatment was developed in later publications.²⁸⁻³³ A very significant consequence of all of this work is that a reaction rate must be proportional to the concentration, not the activity, of a reaction intermediate. These early treatments did not envisage an activated complex, as understood today, but an essential feature of transition-state theory is that the rate is proportional to the concentration of activated complexes.

Kinetic-Theory Treatments

Entirely different attacks on the problem of the preexponential factor were made in 1916-18 by Trautz³⁴ and by Lewis³⁵ on the basis of the collision theory of gases. Because of the First World War, Trautz and Lewis were not aware of one another's work. Their treatments are very similar, but Lewis's is much more explicit and easier to follow.

Trautz and Lewis were both strong proponents of the radiation hypothesis, which was quite popular at the time but was soon to be abandoned. According to this hypothesis, chemical reaction is brought about by the absorption of infrared radiation. This idea was originally proposed in 1906 by Trautz³⁶ in a somewhat obscure form, and it was later developed much more clearly, with additional supporting evidence, by Lewis³⁷⁻⁴⁰ and by Perrin.^{41,42} This theory explained the temperature dependence of reaction rates satisfactorily, because according to Planck's theory⁴³ the energy of radiation varies to a good approximation as $\exp(-h\nu/kT)$ where ν is the frequency; $h\nu$ is thus the critical energy. For the radiation hypothesis to be valid there must be absorption bands in the appropriate spectral region, and the radiation absorbed must provide sufficient energy for reaction to occur. In addition, irradiation with light of the right frequency should lead to an increase in reaction rate.

The radiation hypothesis was short-lived, to be discredited partly through the efforts of Langmuir,^{44,45} who showed for a number of reaction systems that these conditions were not satisfied; he summarized his conclusions by saying that the radiation hypothesis "had all the characteristics of an unsuccessful hypothesis".⁴⁵ Lewis and others remained unconvinced for some time, but by the middle twenties the hypothesis had been largely discarded. Paradoxically, both Trautz and Lewis regarded the success of their kinetic theory equations as giving support to the radiation hypothesis, their idea being that collisions simply bring the reacting molecules together, the critical energy being provided by the absorption of radiation. The usefulness of their treatment was not affected by the realization that the collisions themselves provide the energy required for reaction to occur.

According to simple kinetic theory, for a gas containing molecules regarded as hard spheres, A and B, the collision number Z_{AB} (i.e., the total number of collisions per unit time per unit volume) is

$$Z_{AB} = N_A N_B d_{AB}^2 \left(8\pi kT \frac{m_A + m_B}{m_A m_B} \right)^{1/2} \quad (17)$$

Here N_A and N_B are the numbers of molecules per unit volume, d_{AB} is the sum of their radii, m_A and m_B are their masses, k is the Boltzmann constant, and T is the absolute temperature. According to the theory Z_{AB} multiplied by the Arrhenius factor $e^{-E/RT}$ gives the rate of reaction between A and B; division by $N_A N_B$ and multiplication by the Avogadro constant L then gives a rate constant in molar units (SI unit: $\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$):

$$k = L d_{AB}^2 \left(8\pi kT \frac{m_A + m_B}{m_A m_B} \right)^{1/2} e^{-E/RT} \quad (18)$$

The preexponential factor in this expression is now called

- (28) J. N. Bronsted, *Z. Phys. Chem.*, **102**, 169 (1922).
 (29) J. N. Bronsted, *Z. Phys. Chem.*, **115**, 337 (1925).
 (30) N. Bjerrum, *Z. Phys. Chem.*, **108**, 82 (1924).
 (31) M. Bjerrum, *Z. Phys. Chem.*, **118**, 251 (1925).
 (32) J. A. Christiansen, *Z. Phys. Chem.*, **113**, 35 (1924).
 (33) G. Scatchard, *Chem. Rev.*, **16**, 229 (1932).
 (34) M. Trautz, *Z. Phys. Chem.*, **96**, 1 (1916).
 (35) W. C. McC. Lewis, *J. Chem. Soc.*, **113**, 47 (1918).

- (36) M. Trautz, *Z. Wiss. Photograph., Photophys. Photochem.*, **4**, 166 (1906).
 (37) W. C. McC. Lewis, *J. Chem. Soc.*, **109**, 796 (1916).
 (38) W. C. McC. Lewis, *J. Chem. Soc.*, **111**, 457 (1917).
 (39) W. C. McC. Lewis, *J. Chem. Soc.*, **113**, 471 (1918).
 (40) W. C. McC. Lewis, *Trans. Faraday Soc.*, **17**, 573 (1922).
 (41) J. Perrin, *Ann. Phys.*, **11**, 9 (1919).
 (42) J. Perrin, *Trans. Faraday Soc.*, **17**, 546 (1922).
 (43) M. Planck, *Ann. Phys.*, **4**, 553 (1901).
 (44) I. Langmuir, *J. Am. Chem. Soc.*, **42**, 2190 (1920).
 (45) I. Langmuir, *Trans. Faraday Soc.*, **17**, 600 (1922).
 (46) C. N. Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems", 1st ed., Clarendon Press, Oxford, 1926.
 (47) E. A. Moelwyn-Hughes, "The Kinetics and Reactions in Solution", 1st ed., Clarendon Press, Oxford, 1933; 2nd ed., 1947.

the collision frequency factor and given the symbol z_{AB} (or z_{AA} if there is only one kind of molecule); thus

$$k = z_{AB} e^{-E/RT} \quad (19)$$

Lewis applied his treatment to the reaction $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$ and obtained remarkably good agreement with experiment.

It was later realized that there are many reactions for which there are large discrepancies between observed rates and those calculated by using the collision formula. A collision theory in which molecules are regarded as hard spheres is inadequate to interpret reaction rates, and refinements are needed. As one approach, Hinshelwood⁴⁶ and others⁴⁷ introduced a steric factor P that was supposed to represent the fraction of the collisions that are effective as far as the mutual orientation of the molecules is concerned; this procedure, however, is somewhat arbitrary, and in no way did it account for the abnormally large preexponential factors that are found for some reactions.

Statistical-Mechanical Treatments

The application of statistical mechanics to reaction rates, so important a feature of transition-state theory, developed rather slowly and spasmodically. This is somewhat surprising, since as early as 1867 Pfaundler⁴⁸ had given a qualitative discussion of chemical equilibrium and reaction rates in terms of molecular motions and the statistical distribution of molecular speeds, a concept that had only just previously (in 1860) been treated by Maxwell and Boltzmann. Pfaundler took as his starting point the work of Williamson,⁴⁹⁻⁵¹ who in 1850 had first suggested that chemical equilibrium is dynamic. Pfaundler proposed that only those molecules that possess a critical energy are capable of undergoing reaction.

In spite of this early qualitative beginning, it was not until 1912 that a quantitative application of the Maxwell-Boltzmann distribution law was given. This was done by Berthoud,⁵² who arrived at an equation of the form

$$\frac{d \ln k}{dT} = \frac{a - bT}{RT^2} \quad (20)$$

where a and b are constants related to energy terms. Two years later Marcelin⁵³ made a very important contribution by representing chemical reaction by the motion of a point in phase space. He suggested that the state of a molecular system can be expressed in terms of Lagrange generalized coordinates: $q_1, q_2, \dots, q_n$ for distance and $p_1, p_2, \dots, p_n$ for momentum. The course of the reaction can therefore be regarded as the motion of a point in $2n$ -dimensional phase space. He applied the statistical-mechanical methods of Gibbs to obtain an expression for the concentration of species present at a critical surface in this phase space and arrived at an equation of the form of eq 9 which he had obtained earlier from thermodynamic considerations. His treatment did not lead to any estimate of the magnitude of the preexponential factor. In a later paper, Marcelin⁵⁴ showed that his equation led to temperature dependence consistent with the Arrhenius equation.

Marcelin developed both his thermodynamic and statistical ideas in two subsequent publications,^{55,56} one of

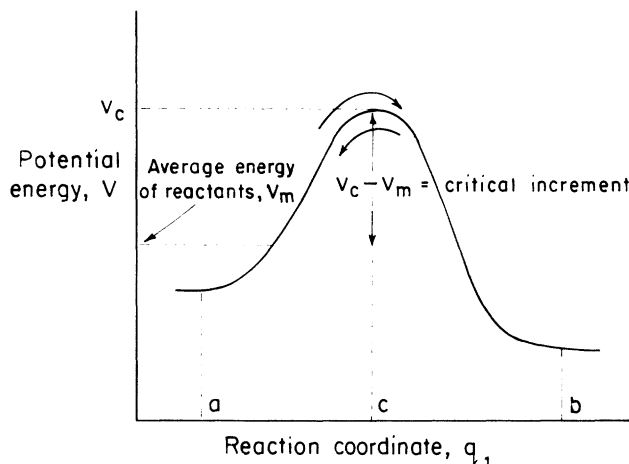


Figure 2. An interpretation of Rice's extension of Marcelin's treatment. Rice's discussion is very cryptic, and he gave no diagrams, but this figure probably represents what he had in mind.

them posthumous. His statistical-mechanical procedures were later sharply criticized by Tolman,⁵⁷ defended by Adams,⁵⁸ and again attacked by Tolman.⁵⁹ Ironically, Tolman was in 1920 very critical of the fact that Marcelin's ideas did not take into account the radiation hypothesis, which had still not been discredited; Adams, however, correctly pointed out that Marcelin's theory was valid whether the radiation hypothesis was true or false. In any case, there is no doubt that Marcelin's theories were of considerable importance and contributed greatly to the development of theoretical chemical kinetics. Unhappily, Marcelin's promising career was cut short; he was killed in action in the early days of the First World War.

An interesting extension of Marcelin's ideas was made by Rice⁶⁰ in 1915. Rice's contribution was made at a meeting in Liverpool of the British Association for the Advancement of Science, and only a brief report is available, so that it is difficult to know exactly what procedure he followed. Rice pointed out that Marcelin's definition of the critical (activated) state for a reaction was somewhat vague and that the critical condition can be defined more precisely. He chose $2n$ generalized coordinates $q_1, q_2, \dots, q_n$ and the derivatives with respect to time, $\dot{q}_1, \dot{q}_2, \dot{q}_3, \dots, \dot{q}_n$. He supposed that one can choose the coordinates in such a way that the potential energy V depends on one position coordinate only; this is taken to be q_1 . The critical state is taken to be when q_1 has a particular value c (see Figure 2); V then has a maximum value V_c . The total range of values of q_1 is from a to b ; when q_1 lies between a and c , the system is in one chemical condition (we should say the reactant state); for $c \rightarrow b$ the state corresponds to products.

Rice then applied a statistical analysis and arrived at the result that the rate constant is given by

$$k = e^{-V_c/RT} / \left\{ 2(\pi RT)^{1/2} \int_a^c e^{-V/RT} dq \right\} \quad (21)$$

From this it follows that

$$\frac{d \ln k}{dT} = \frac{V_c - V_m - \frac{1}{2}RT}{RT^2} \quad (22)$$

where V_m , the mean energy of a molecular group, corresponds to points between a and c and is equal to

(48) L. Pfaundler, *Ann. Phys. Chem.*, **131**, 55 (1867).

(49) A. W. Williamson, *Br. Assoc. Adv. Sci., Rep.*, ii, 65 (1850).

(50) A. W. Williamson, *Philos. Mag.*, **37**, 350 (1850).

(51) A. W. Williamson, *J. Chem. Soc.*, **4**, 229 (1852).

(52) A. Berthoud, *J. Chim. Phys. Phys.-Chim. Biol.*, **10**, 573 (1912).

(53) R. Marcelin, *C. R. Hebd. Seances Acad. Sci.*, **158**, 116 (1914).

(54) R. Marcelin, *C. R. Hebd. Seances Acad. Sci.*, **158**, 407 (1914).

(55) R. Marcelin, *J. Chim. Phys. Phys.-Chim. Biol.*, **12**, 451 (1914).

(56) R. Marcelin, *Ann. Phys.*, **3**, 120 (1915).

(57) R. C. Tolman, *J. Am. Chem. Soc.*, **42**, 2506 (1920).

(58) E. P. Adams, *J. Am. Chem. Soc.*, **43**, 1251 (1921).

(59) R. C. Tolman, *J. Am. Chem. Soc.*, **44**, 75 (1922).

(60) J. Rice, *Br. Assoc. Adv. Sci. Rep.*, 399 (1915).

$$V_m = \int_a^c V e^{-V/RT} dq / \int_a^c e^{-V/RT} dq \quad (23)$$

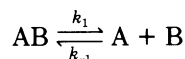
Rice called the quantity $V_c - V_m$ the "critical increment".

Unfortunately, Rice did not clarify the basis of his derivation of eq 21 or, indeed, state how his rate constant k is defined; any conventional rate constant has (time)⁻¹ in its dimensions, but Rice's k has the dimensions of (mass)^{-1/2} (mol)^{1/2} (length)⁻² (time). Rice's treatment is nevertheless of considerable interest in that it led to the important result, later proved more rigorously by Tolman,⁵⁹ that the critical increment is the energy at the activated state minus the mean energy of the reactants. Rice would have been more on the right track if he had multiplied

$$e^{-V_c/RT} / \int_a^c e^{-V/RT} dq$$

by the velocity of passage through the critical state. It is curious and disappointing that, in his excellent text on statistical mechanics published 15 years later,⁶¹ Rice made no mention of Marcelin or of his own extension of Marcelin's ideas. In that text he included a careful treatment of reaction rates in terms of kinetic theory and gave a detailed discussion of the validity of the equilibrium assumption that is inherent in it, but no reference is made to the equations that he developed in 1915, which perhaps he had discarded as unsatisfactory.

In 1917, Marsh⁶² further developed some ideas about phase space, and 2 years later a particularly interesting and important attack on the problem was made by Herzfeld.⁶³ For the dissociation of a diatomic molecule AB



Herzfeld first expressed the equilibrium constant K_c in terms of partition functions, his final expression reducing to

$$K_c = \frac{1}{d_{AB}^2 h} \left(\frac{kT}{8\pi} \right)^{1/2} \left(\frac{m_A m_B}{m_A + m_B} \right)^{1/2} (1 - e^{-h\nu/kT}) e^{-Q/RT} \quad (24)$$

where Q is the energy difference between initial and final states, m_A and m_B are the atomic masses, d_{AB} is the interatomic distance in the molecule AB, and ν is its vibrational frequency. He then used the kinetic theory expression, eq 18, for the rate constant k_{-1} for the reverse reaction. If the assumption is made that the collision interatomic distance d_{AB} is the same as the interatomic distance in the molecule AB, the resulting expression for the first-order rate constant k_1 is

$$k_1 = (kT/h)(1 - e^{-h\nu/kT}) e^{-Q/RT} \quad (25)$$

This expression is particularly significant since it is the first time that the factor kT/h , so essential a feature of transition-state theory, has appeared in a rate equation. Moreover, for the dissociation of a diatomic molecule, eq 25 is the expression to which transition-state theory leads. The fact that Herzfeld obtained eq 25 from a combination of equilibrium and kinetic theory is of interest in view of Hinshelwood's later demonstration^{64,65} that for a bimole-

cular reaction between two atoms transition-state theory reduces to hard-sphere kinetic theory.

Later, Herzfeld and Smallwood⁶⁶ attacked the problem of the dissociation of a diatomic molecule from a different point of view. They used statistical mechanics to calculate the density of points in phase space corresponding to a particular interatomic separation at which reaction was supposed to occur. The rate of reaction was then taken to be this density multiplied by the velocity of crossing and integrated with respect to $\dot{x}$ from zero to infinity. In this way they found the rate constant to be

$$k = \nu e^{-Q/RT} \quad (26)$$

where ν is the frequency of vibration.

Somewhat similar approaches to the problem were made by Rideal,⁶⁷ Dushman,⁶⁸ and Rodebush,⁶⁹ with special reference to unimolecular reactions, and by Topley⁷⁰ for surface reactions. However, these approaches were really interesting inspired guesses rather than formal treatments.

An important contribution was made in 1920 by Tolman,⁵⁷ who made a detailed application of statistical mechanics to rate processes, and showed rigorously that the activation energy is equal to the difference between the energy of the activated state and the average energy of the reactant molecules; this conclusion had previously been reached, although on the basis of obscure reasoning, by Rice.⁶¹

Just 2 years before the papers of Eyring and of Evans and Polanyi appeared, La Mer⁷¹ published a very significant article that came close to transition-state theory. La Mer discussed the rate problem on the basis of thermodynamics, kinetic theory, and statistical mechanics and suggested that the rate constant could be expressed as

$$k = Z e^{-\Delta^*G/RT} \quad (27)$$

where Z is the collision frequency factor and Δ^*G the Gibbs energy of activation. However, a flaw in this equation became evident when we consider the expressions for forward and reverse reactions: $k_1 = Z_1 \exp(-\Delta^*G_1/RT)$ and $k_{-1} = Z_{-1} \exp(-\Delta^*G_{-1}/RT)$. The equilibrium constant is then $K = k_1/k_{-1} = (Z_1/Z_{-1}) \exp(-\Delta G^\circ/RT)$, whereas it should be simply $\exp(-\Delta G^\circ/RT)$; Z_1 and Z_{-1} are not the same. Also, as Hinshelwood^{64,65} was later to show, the collision frequency factor Z is already taken care of in the transition-state formulations, so that La Mer had really introduced this factor twice in his equation. Nevertheless, his equation is of great interest and no doubt was helpful in leading to transition-state theory.

In addition, there were a number of treatments of reaction rates based on statistical mechanics which were also concerned with molecular dynamics. The first of these was that of Eyring and Polanyi,¹¹ having constructed the first potential energy surface for a reaction, they carried out some dynamical calculations of the motion of a mass point on their surface. Similar calculations were later carried out by Eyring, Gerschinowitz, and Sun⁷² and by Hirschfelder, Eyring and Topley.⁷³ A serious difficulty with these

(65) C. N. Hinshelwood, *Trans. Faraday Soc.*, **34**, 74 (1938).

(66) K. F. Herzfeld and H. M. Smallwood in H. S. Taylor's "Physical Chemistry", Macmillan, 1931, pp 151-2.

(67) F. K. Rideal, *Philos. Mag.*, **40**, 461 (1920).

(68) S. Dushman, *J. Am. Chem. Soc.*, **43**, 397 (1921).

(69) W. H. Rodebush, *J. Am. Chem. Soc.*, **45**, 606 (1923).

(70) B. Topley, *Nature (London)*, **128**, 115 (1931).

(71) V. K. La Mer, *J. Chem. Phys.*, **1**, 289 (1933).

(72) H. Eyring, H. Gerschinowitz, and C. E. Sun, *J. Chem. Phys.*, **3**, 786 (1935).

(73) J. O. Hirschfelder, H. Eyring, and B. Topley, *J. Chem. Phys.*, **4**, 170 (1936).

(61) J. Rice, "Introduction to Statistical Mechanics for Students of Physics and Physical Chemistry", Constable and Co., London, 1930.

(62) A. Marsh, *Phys. Z.*, **18**, 53 (1917).

(63) K. F. Herzfeld, *Ann. Phys.*, **59**, 635 (1919).

(64) C. N. Hinshelwood, *J. Chem. Soc.*, 635 (1937).

early dynamical calculations is that they involved an enormous amount of labor. A trajectory over a surface had to be calculated point by point, with the help of simple calculators. A single trajectory took a very considerable time, and, to obtain a meaningful rate constant, one must obtain a large number of trajectories, corresponding to a range of starting conditions. Even with the help of modern computers, such dynamical calculations are still very time-consuming.

A very important treatment of reaction rates, made by Pelzer and Wigner,⁷⁴ appeared in 1932. Much of their paper is concerned with a general treatment of the problem in terms of the time-dependent Schrödinger equation, but it also contains a very interesting discussion of the situation at the col or saddle point of the potential energy surface. Pelzer and Wigner obtained an expression for the rate by considering the passage of systems through the col. Their treatment is not as general as the later formulations of Eyring and of Evans and Polanyi, but their paper is important as being the first to focus attention on the potential energy surface. There is no doubt that it contributed significantly to the more general treatments given in 1935. Quantum corrections to the Pelzer-Wigner treatment were later given by Wigner.⁷⁵

Transition-State Theory

Eyring, with characteristic generosity, freely admitted that his formulation of transition-state theory owed much to collaboration and cooperation with others. During the years prior to 1935 he had a number of first-rate graduate students, including George E. Kimball, Joseph O. Hirschfelder, and John F. Kincaid, all of whom did distinguished work then and later. Also, a number of scientists from the United Kingdom spent various periods of time working with Eyring: these include Bryan Topley, who spent 1933–1934 at Princeton, and W. F. K. Wynne-Jones, who spent 1934–1935 there. M. G. Evans was also at Princeton in 1933–1934, but worked with H. S. Taylor. In his 1935 paper¹ Eyring acknowledged in particular the discussions he had held with Topley “as it was with him that the present calculations of absolute rates were begun”. He also acknowledged helpful discussions with H. S. Taylor and T. J. Webb.

It was always Eyring's practice to discuss his ideas freely with anyone willing to listen; he kept nothing to himself and always generously acknowledged the help he had received from others. Many of his early collaborators have commented that Eyring was constantly producing new ideas and that one of the important functions of his students and colleagues was to sift the good ideas from the bad, of which there were a substantial proportion. Polanyi also received much inspiration from others, in particular, from Eugene Wigner, discussions with whom are acknowledged in the Evans-Polanyi paper.¹⁴

It is not our intention in this article to outline transition-state theory.⁷⁶ We should, however, comment on the essential features of the theory:

(1) Rates can be calculated by focusing attention on the activated complexes, which lie at the col or saddle point of the potential energy surface; the details of what happens before the transition state is reached are irrelevant if one is content with obtaining an expression for the overall rate.

(2) The activated complexes are in a state of “quasi-equilibrium” with the reactants. By this is meant simply that, since for a system at complete equilibrium the complexes are also at equilibrium, and since the concentration of complexes passing from reactants to products will be unchanged by removing products, that concentration can be calculated by using equilibrium theory.

(3) The motion of the systems at the col, along a particular “reaction coordinate”, can be treated as a free translational motion and expressed by using kinetic theory.

It is of particular interest to note that not one of these three features was completely new. The first feature was explicit in the work of Marcelin,^{53–56} Rice,⁶⁰ and Herzfeld.⁶⁶ The second was implicit in many of the earlier thermodynamic, kinetic-theory, and statistical treatments, although the subtlety about quasi-equilibrium had not been appreciated. Treating the motion through the transition state as free motion is explicit in the Herzfeld⁶⁶ and Pelzer-Wigner⁷⁴ theories. The genius of the 1935 work was in putting these three features together and arriving at a simple but general rate equation. In addition, Eyring made a very important and novel contribution in appreciating the great significance of the reaction coordinate.

Transition-state theory met a good deal of opposition in its early stages, and we can now see several reasons for this. One reason is that the first papers of Eyring, and of Evans and Polanyi,¹⁴ were by no means easy to follow; some of their later publications were more readable.^{3,15} Also, Eyring's expression “the theory of absolute reaction rate” was probably unfortunate, and became ambiguous when abbreviated, as it often was, to “absolute rate theory”; what he meant was that the theory predicted an absolute magnitude for the preexponential factor, so that together with a calculated potential energy surface one could calculate the rate. However, some critics thought that Eyring was claiming that his theory was definitive, and they sometimes distorted his title into “the absolute theory of reaction rates”. Finally, in developing their treatment, Eyring, and Evans and Polanyi, had to take very bold—some would say reckless—steps, and it was predictable that many would fail to understand their arguments.

Trouble began even before the theory was born. Eyring submitted his paper to the *Journal of Chemical Physics*, and it was first rejected by its editor, Harold C. Urey. A referee had written a detailed report on the paper⁷⁷ and summarized his conclusions with these words: “I have given considerable thought to the problems involved, and although I have not been able to resolve my uncertainties I have nevertheless become convinced that the method of treatment is unsound and the result incorrect”. However, Taylor and Wigner intervened with Urey, and the paper was published. It is an interesting commentary on the speed of publication at that time that, in spite of the initial rejection, the paper, received by the journal on November 3, 1934, still appeared in the February 1935 issue!

Over the years comments on the theory have ranged from complimentary to acrimonious. In 1936 Eyring presented his theory at a seminar at Oxford, and one of us (K.J.L.) well remembers that F. A. Lindemann (later Lord Cherwell) attacked the theory in terms that were offensive to Eyring and embarrassing to the audience and particularly to Hinshelwood, who had invited him; several years later Lindemann's words still rankled with Eyring.

(74) H. Pelzer and E. Wigner, *Z. Phys. Chem., Abt. B*, **15**, 445 (1932).

(75) E. Wigner, *Z. Phys. Chem., Abt. B*, **15**, 203 (1932).

(76) For an account and discussion of the theory see K. J. Laidler, “Theories of Chemical Reaction Rates”, McGraw-Hill, New York, 1969; B. H. Mahan, *J. Chem. Educ.*, **51**, 709 (1974); I. W. M. Smith, “Kinetics and Dynamics of Elementary Gas Reactions”, Butterworths, London, 1980, Chapter 4.

(77) The referee's report is reproduced as Appendix V (pp 209–10) of S. H. Heath, “Henry Eyring, Mormon Scientist”, M. A. Thesis, University of Utah, Salt Lake City, UT, 1980. Note that a few relevant words have been omitted from the first paragraph of this appendix; these are included on p 59 of the thesis.

Early in 1937 the Chemical Society held, in London, a discussion specifically on "The Transition State"; those present included Polanyi, Evans, Wynne-Jones, F. G. Donnan, and R. G. W. Norrish. Judging from the written record, the discussions were largely favorable to the theory. Hinshelwood's comment at the meeting⁷⁸ perhaps reflects the general attitude: "...the great value of the transition-state method is in causing us to think more deeply about the interrelation of thermodynamic and kinetic magnitudes, rather than in providing us with an essentially more accurate calculus. It must certainly be said that sometimes the answer to a problem may be seen more easily from one point of view than from the other: we can then translate the answer into the language which we prefer". In his later writings, Hinshelwood^{79,80} continued to take this moderate and favorable view of the theory, although it is significant that in his research publications he made little application of transition-state theory; perhaps as a result of a natural conservatism he felt more comfortable with the kinetic-theory approach that he had used previously.

Norrish's views at the meetings are not recorded, but he was later to refer to the theory, with characteristic cheerfulness, as "high-falutin stuff";⁸¹ in his own distinguished contributions to kinetics he felt no need to make any use of the theory.

Later in 1937, the Faraday Society held a discussion on "Reaction Kinetics" in Manchester.⁸² Here the atmosphere was not so happy, mainly because of the attitude of Guggenheim. In his paper with Weiss⁸³ he described Eyring's theory as "sterile", and in a later contribution⁸⁴ said, "I was pleased to note in Eyring's paper an admission that 'we very frequently do not know the reduced mass normal to the barrier'. This seems to be a confession that we do not know what the reaction coordinate is and in such a case I do not believe the treatment described can be of any use". Over the years Guggenheim's attitude was oddly inconsistent. In his book with Fowler⁸⁵ the theory was treated much more sympathetically, and in a contribution in 1962 he wrote the following: "It has long seemed to me, and still seems to me, that the essential superiority of Eyring's treatment over the earlier (1915) treatment of Marcelin consists in Eyring's introduction of the reaction coordinate".⁸⁶ This reference to the reaction coordinate contrasts strongly with his comment 25 years earlier.

This last comment by Guggenheim was made at a symposium on "The Transition State" held at Sheffield in 1962. Attitudes were then much more conciliatory than at the 1937 Faraday Society meetings. In the meantime, a number of difficulties with the theory had been clarified; Eyring himself, always conscious of the limitations of his treatment, had made significant further contributions. And by that time the enormous value of the theory in providing an insight into reaction rates had been recog-

nized by a wide range of workers, including organic and inorganic chemists, metallurgists, and nuclear physicists.

One matter that has been a source of considerable discussions and some dissension over the years is the assumption of quasi-equilibrium that is inherent in the theory. Surprisingly, this assumption does not appear to have been raised at the Chemical Society meetings in 1937 and 1962, apart from a reference in a paper by Eyring and co-workers⁸⁷ at the latter meeting. At the 1937 Faraday Society meeting, however, the assumption was attacked by Guggenheim and Weiss⁸³ and the matter has very frequently been raised at other times.

Considerable confusion has existed with regard to this hypothesis. In the first place, it is sometimes supposed that the hypothesis is not inherent in theories other than transition-state theory. In reality, the validity of the hypothesis is also essential to the kinetic theories, as had been clearly recognized by Rice,⁶¹ Fowler and Guggenheim,⁸⁴ and many others. The hypothesis was not specifically considered in the 1935 papers of Eyring and of Evans and Polanyi, but at the 1937 Faraday Society meeting the hypothesis was very clearly defended by Polanyi,⁸⁸ in a contribution that included the following passage: "At equilibrium there can be no lack of any species of molecules appertaining to the Boltzmann distribution. It follows that at equilibrium the rate of reaction (in either direction) is such as corresponds to a fully established Boltzmann equilibrium. However, the rate of each of these reactions...will not change if the products of reaction are eliminated from the system. It follows that the preservation of the Boltzmann equilibrium required for the application of the transition-state method is guaranteed if the reaction obeys any expression of the type $[v_1 = k_1 c_1^{n_1} c_2^{n_2} \dots$ and $v_{-1} = k_{-1} c_1^{*n_1} c_2^{*n_2} \dots]$ ".

Secondly, it has not always been realized that there are really two aspects to the quasi-equilibrium hypothesis. Polanyi's comment certainly applies to reactions that are not too fast, but perhaps he did not realize that his argument is not valid for an extremely rapid reaction. For such a process it is no longer true to say that there is a fully established Boltzmann distribution as far as species in the neighborhood of the transition state are concerned. If reactants and products are at equilibrium, but the barrier is low, so that the flows through the transition state are very rapid, there will be a depletion of the more energized reactant and product molecules; the concentration of activated complexes will then be less than corresponds to true equilibrium. This problem has been treated in more recent theories,⁸⁹ and the conclusion is that, if the ratio of the critical energy to kT is greater than about 5, the quasi-equilibrium hypothesis is valid to a good approximation.

In assessments of transition-state theory at the present time it is important to look at it from two different points of view. In the first place, to what extent does the theory allow us to calculate reaction rates and give a quantitative interpretation of other features of chemical reactions? From this point of view it must be admitted that the theory has its difficulties. By its very nature, the theory tells us nothing about the energy states of the reaction products or about the details of the collision process. In addition, the difficulty of obtaining reliable potential energy surfaces for any but the simplest reactions means that we must agree with Guggenheim's 1937 comment⁸³ that

(78) C. N. Hinshelwood, *J. Chem. Soc.*, 638 (1937).

(79) C. N. Hinshelwood, "The Kinetics of Chemical Change", Clarendon Press, Oxford, 1940.

(80) C. N. Hinshelwood, *Nature (London)*, 180, 1233 (1957).

(81) R. G. W. Norrish, personal comment to K.J.L.

(82) *Trans. Faraday Soc.*, 34, 1-268 (1938). The meeting was held in Sept 1937 and was attended by a number of well-known scientists including Eyring, Evans, Polanyi, C. N. Hinshelwood, J. N. Bronsted, J. A. Christiansen, L. P. Hammett, V. K. La Mer, M. Letort, H. S. Taylor, E. A. Guggenheim, and E. Wigner.

(83) E. A. Guggenheim and J. Weiss, *Trans. Faraday Soc.*, 34, 57 (1938).

(84) E. A. Guggenheim, *Trans. Faraday Soc.*, 34, 72 (1938).

(85) R. W. Fowler and E. A. Guggenheim, "Statistical Thermodynamics", Cambridge University Press, 1939, Chapter XII, especially pp 509-19.

(86) E. A. Guggenheim in "The Transition State", The Chemical Society, London, 1962, *Spec. Publ.—Chem. Soc.*, No. 16, p 27.

(87) H. Eyring, T. S. Ree, T. Ree, and F. M. Wanless, ref 86, p 3.

(88) M. Polanyi, *Trans. Faraday Soc.*, 34, 73 (1938).

(89) For a brief review with references see K. J. Laidler, ref 76, Chapter 8.

we cannot properly identify the reaction coordinate; this raises particular problems for the treatment of kinetic-isotope effects. With all of these criticisms Eyring was in full agreement.

The second standpoint from which we must judge transition-state theory is: To what extent does it provide us with a conceptual framework with the aid of which experimental chemists (and others) can gain some insight into how chemical processes occur? On this score the theory must receive the highest marks; for nearly half a century it has been a valuable working tool for those who are not concerned with the calculation of absolute rates but are helped by gaining some insight into chemical and physical processes. The theory provides both a statistical-mechanical and a thermodynamic insight—one can take one's choice or use both formulations. It leads to extremely useful qualitative predictions, without the need

for any calculations, of solvent effects, relative rates of similar processes, kinetic-isotope ratios, pressure influences, and a host of other important effects.

Porter's assessment in 1962⁹⁰ of transition-state theory makes the point very well: "On the credit side, transition-state theory has an indestructable argument in its favour. Since its inception, it has provided the basis of chemical kinetic theory; imperfect as it may be, it is undoubtedly the most useful theory that we possess. During the last twenty-five years its greatest success has been not in the accurate prediction of the rates even of the simplest reactions, but in providing a framework in terms of which even the most complicated reactions can be better understood". Most of us would agree that these comments remain valid today.

(90) G. Porter, ref 86, p 2.

Current Status of Transition-State Theory

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We review the current status of transition-state theory. We focus on the validity of its basic assumptions and of corrections to and improvements of conventional transition-state theory. The review is divided into sections concerned in turn with bimolecular reactions in the gas phase, unimolecular reactions in the gas phase, and isomerizations and atom-transfer reactions in liquid-phase solutions. Some aspects that are emphasized are variational transition-state theory, tunneling, the assumption of an equilibrium distribution of reactants, and the frictional effects of solvent molecules.

1. Introduction

Transition-state theory has achieved widespread acceptance as a tool for the interpretation of chemical reaction rates. The theory has, however, been less successful in its original goal, the calculation of absolute reaction rates. A difficulty with the calculation of absolute reaction rates is that it requires very accurate knowledge of potential energy surfaces. For example, an error of 1 kcal/mol in an activation barrier causes an error of a factor of 5.6 in a rate calculation at room temperature, and an error of 2 kcal/mol causes an error of a factor of 31. Even though very remarkable advances have been made in the calculation of potential energy surfaces, it is still very hard to calculate activation barriers this accurately even for

simple reactions. Furthermore, it may be necessary in many cases to calculate global regions of the potential surface, not just barrier heights, in order, for example, to accurately treat systems with large tunneling effects or systems with temperature-dependent or energy-dependent dynamical bottlenecks.

Despite the difficulties, many workers remain enthusiastic about the value of absolute rate calculations for a variety of reasons. First of all, the methods of electronic structure theory and the capabilities of computers are still improving rapidly. Accurate ab initio prediction of activation barriers for simple reactions and then for increasingly complicated ones may be "just around the corner". However, when ab initio methods are still insufficiently