One of the most important meetings in chemical kinetics was a discussion meeting of the Faraday Society, held at the University of Manchester in September 1937. All the stalwarts involved in the development of the Transition State Theory presented papers at this meeting. The proceedings were published as Faraday Transactions, Vol.34, 1938. Morris Travers (who has an Indian connection: he had served as the Chairman of the Department of Inorganic and Physical Chemistry at the Indian Institute of Science, and later on as the Director of the Institute) presided over the meeting and remarked: “The subject before the meeting is of very great general importance in chemistry. After making a certain amount of progress in the study of chemical kinetics we have arrived virtually at an impasse. There are certain obstacles to further progress, and with a view to overcoming them new methods of exploration are suggested. …we may proceed to apply a practical test to them, and try and discover whether they enable us to relate known phenomena, and to extend our knowledge.” 

History shows that the activated complex theory overcame all obstacles and is presently the most successful theory for chemical reactions. The Classic in this issue is the paper by Eyring, presented at this meeting. It summarizes the contributions of his group till that date, and is one of the most important papers in the theory of chemical reactions.

K L Sebastian

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THE THEORY OF ABSOLUTE REACTION RATES.

By Henry Eyring.

Received 26th July, 1937.

In the present paper we review the point of view on reaction rates developed in this laboratory. Other points of view will be found in the other contributions to this meeting. Whether we clothe the theory in the usual language of thermo-dynamics or statistical mechanics is purely a formal matter. The most convenient procedure, and the one we shall follow, is to regard thermodynamics as a branch of statistical mechanics and to use whichever formulation seems most appropriate for a given

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General Theory.

The average value of any property, \( \overline{X} \), of a system has long been known to be expressible in the following form:

\[
\overline{X} = \frac{\sum_{i} X_{i} \omega_{i} \exp \left( \frac{-E_{i}}{kT} \right)}{\sum_{i} \omega_{i} \exp \left( \frac{-E_{i}}{kT} \right)} \quad (1)
\]

and Tolman\(^1\) pointed out that this equation was applicable to the specific reaction rate in the same way as it was to any other property. In equation (1) \( X_{i} \) is the value of the property in state \( i \) which has the energy \( E_{i} \) and statistical weight \( \omega_{i} \), \( k \) and \( T \) are of course the Boltzmann constant and absolute temperature respectively.

This equation can be modified in an important way for reactions which proceed adiabatically in the Ehrenfest sense postulated by London\(^2\) and also for non-adiabatic reactions proceeding by mechanisms such as that considered by Stearn and Eyring\(^3\) for \( N_{2}O \).

A chemical reaction always involves a change in the equilibrium distance between atoms. Conversely it is always possible and frequently convenient to treat even such changes as occur in viscous or plastic flow \(^4\) as chemical reactions. A chemical reaction may proceed by a series of steps or mechanisms. Only the slow step (or steps) can be studied by measuring the rate of reaction. Even in chain reactions where a number of mechanisms are rate determining, the natural procedure is to analyse the overall process into the separate reactions, one for each mechanism, and to characterise each by a specific reaction rate constant, \( k_{r} \). Now it is these separate steps to which we can apply the statistical mechanical (or thermodynamic) method. Such a step reaction is characterized by an initial configuration which passes over by continuous changes of co-ordinates into the final configuration. There is always some intermediate configuration which is critical for the process in the sense that if the system has once attained it there is a comparatively high probability that the reaction will continue to completion.

This critical configuration, we call the activated complex, and (at the absolute zero) it is in general the configuration of highest potential energy through which the system must pass in the process of reaction. The metastable activated complex like the reactants or products of reaction has an average energy which increases with the temperature and as a matter of fact can be characterised by all the usual thermodynamic properties in spite of its fleeting existence.

II \( N \) atoms come together in a non-linear configuration to form the activated complex, then three of the \( 3N \) degrees of freedom can be associated with translation of the centre of gravity of the activated complex and except for an interaction term which is frequently small,
three other co-ordinates can be associated with rotation of the system about its centre of gravity. This leaves $3N - 6$ internal co-ordinates whose specification together with the electronic state of the system fixes its potential energy. The potential energy can then be plotted normal to the configurational co-ordinates in a $3n - 5$ dimensional space. The resulting surface will show low valleys or basins which correspond to chemical compounds separated by mountain ranges. Through these ranges there are passes and these configurations are the activated complexes. Because the valleys and basins and the passes all correspond to stationary points in the potential energy, for any change in configuration, we can use the theory of small vibrations to obtain the frequencies that are required in calculating the probability of these critical configurations.

The partition function for complexes lying within a distance $\delta q/2$ on either side of the top of the pass and moving in both directions at equilibrium is then

$$F_n \delta q = \frac{(2mkT)^{\nu_2}}{\hbar^3} \frac{8\pi^2(\sqrt{\pi}m^\nu ABC)^{\nu_2}}{\sigma^2h^3} \prod_{i=1}^{2n-7} \frac{1}{1 - \exp \left( - \frac{\hbar \nu_i}{kT} \right)} \times$$

$$\int_{-\delta q/2}^{\delta q/2} \exp \left( - \frac{p^2}{2m^*kT} \right) dp = \frac{(2mkT)^{\nu_2}}{\hbar^3} \frac{8\pi^2(\sqrt{\pi}m^\nu ABC)^{\nu_2}}{\sigma^2h^3} \prod_{i=1}^{2n-7} \frac{1}{1 - \exp \left( - \frac{\hbar \nu_i}{kT} \right)} \times$$

Here we are neglecting temporarily the usually small quantum mechanical effect of curvature of surface normal to the pass. $F$ is of course the partition function for activated complexes per unit length normal to the pass. $m$ and $m^*$ are the mass of the activated complex and the reduced mass for the degree of freedom normal to the barrier respectively. $A$, $B$ and $C$ are the three moments of inertia of the complex. $h$ and $p$ are Planck’s constant, and the momentum normal to the barrier respectively. $\nu$ is the symmetry number of the activated complex. The ratio of activated complexes (lying in the length $\delta q$) to reactant systems is then

$$K = \frac{F_n \delta q}{F_n}$$

where $F_n$ is the partition function for normal molecules and is readily written down in any particular case. The specific rate of reaction is then obtained by multiplying $K_n \delta q$ (the number of activated complexes in the length $\delta q$ when the reactants are at unit concentration by the frequency with which the half moving in the forward direction pass over the barrier $\frac{\nu}{m^* \delta q}$, and the transmission coefficient $\kappa$. $\kappa$ is the chance that having once crossed the barrier the activated complex does not return. This gives for the specific reaction rate constant.

* Wigner, ibid., 19, 203.
\[ k' = \kappa K a \delta q_{m} \frac{\hat{p}}{\hbar} = \frac{\kappa (2\pi m k T)^{3/2}}{\hbar^{3}} \frac{8\pi^{2}(8\pi^{2}ABC)^{1/2}}{a^{2}h^{3}} (kT)^{3/2} \times \]
\[ \prod_{i=1}^{3n-7} \frac{1}{1 - \exp\left(-\frac{\hbar\nu_{i}}{kT}\right)} \]
\[ = \kappa \frac{F_{a}}{F_{m}} \sqrt{\frac{kT}{2\pi m^{*}}} = \kappa \frac{F_{a}^{+} kT}{F_{m}} = \kappa K a \sqrt{\frac{kT}{2\pi m^{*}}} = \kappa K a \frac{kT}{h} \] (4)

The identities in (4) serve to define \( F^{*} \) and \( K^{*} \). If the activated complex is linear
\[ \frac{8\pi^{2}(8\pi^{2}ABC)^{1/2} kT}{\hbar^{3}} \]

is simply replaced by
\[ \frac{8\pi^{2} kT}{\hbar^{2}} \]

It is of course neither necessary nor desirable to use the normal coordinate frequencies in the partition functions in (4) if we know the exact energy levels and their statistical weights.

We have so far neglected the effect of tunnelling. If the potential barrier is nearly flat it is sufficient to introduce the correction factor due to Wigner \(^8\) \[ \left( 1 + \frac{1}{2\pi \hbar^{2}} \right) \], where \( \nu_{n} \) is the imaginary frequency \[ \nu_{n} = \left( \frac{1}{2\pi} \right) \left( \frac{f_{n}}{m^{*}} \right) \] in which \( f_{n} \) and \( m^{*} \) are the force constant and reduced mass normal to the barrier. For thin barriers Wigner's calculations must be extended. Approximate results are also obtained by applying the Eckart \(^9\) equation in the way Baw and Ogdin \(^10\) have done for atomic reactions involving hydrogen and deuterium. For unimolecular reactions such as the decomposition of \( N_{2}O \) or the inversion of ammonia we can take account of the tunnelling effect by adding a term \(^{11}\) to (4).

\[ k' = \kappa k^{+} \frac{kT}{h} + \frac{1}{F_{a}} \sum_{i} \kappa_{v_{n,\omega_{n}}} \exp\left(-E_{i}/kT\right) \] (5)

Here \( \kappa, \nu_{n}, \omega_{n} \) and \( E_{i} \) are the transmission coefficient, vibration frequency, degree of degeneracy, and energy of the \( i \)th state. So far the particular partition functions we have written down are for a dilute gas but the theory is completely general and can be applied to any process in which material particles move with respect to each other.

**Thermodynamic Treatment.**

Consider the reaction:
\[ A_{1} + A_{2} + \ldots A_{n} \rightarrow A^{*} \rightarrow B_{1} + B_{2} + \ldots B_{m} \] (6)

\(^{8}\) Eckart, Phys. Rev., 1934, 45, 746.
\(^{10}\) Stearn and Eyring, J. Chem. Physics, 1937, 5, 113.
where certain of the A’s or the B’s may be alike and where $A^*$ is the activated complex. Then we define the concentration of the activated complex by the following equations,

$$k^* = \frac{(A^*)}{(A_1) \cdots (A_n)} \gamma_1 \cdots \gamma_n \frac{kT}{h} = k^* \left( \frac{kT}{h} \right) = \frac{k_{obs}}{\gamma_1 \cdots \gamma_n}$$

(7)

Here the parentheses around a species signifies the concentration of that species and the $\gamma$’s are the corresponding activity coefficients and have the value unity for the standard state and in general $(A_i)\gamma_i = a_i$ the activity of the species $i$. $k_{obs}$ is the observed specific reaction rate constant in terms of the concentrations $(A_1) \cdots (A_n)$ and $k^*$ the specific reaction rate constant at the standard state, i.e., in terms of activities. Since $k^*$, $k_{obs}$ and $\gamma_1$ to $\gamma_n$ can all be separately observed it is possible to calculate $\gamma^*$ and so get an insight into the effect of the changed environment on the activated complex. This information is a powerful aid in deducing the mechanism of the reaction, i.e., the nature of the activated complex. The vapour pressures of a reactant above two solutions, or a distribution ratio between two phases provides a well-understood method of comparing the activities of the reactants, and this with the observed rates provides a method of detecting any change in mechanism in the two phases.

We use $K^*$ rather than $K_a$ in the capacity of an equilibrium constant between the activated complex and reactants because (1) it has the usual dimensions of an equilibrium constant whereas $K_a$ does not; (2) in calculating it from $k^*$ or $k_{obs}$ we always know the universal frequency $\frac{kT}{h}$ whereas the velocity $\sqrt{\frac{kT}{2\pi m}}$ involves the reduced mass normal to the barrier which we very frequently do not know. These reasons are important and there are not any more fundamental reasons for preferring one quantity over the other. As Wynne-Jones and Eyring have pointed out the ultimate choice is a matter of convenience.

In adopting $K^*$ as our equilibrium constant (for activated complex with reactants) we are in fact adopting the convention that systems for which the position co-ordinate normal to the potential barrier falls within the distance of one-half of $\frac{2\pi m kT}{(2\pi m kT)^{1/2}}$ on each side of the barrier are to be counted as activated complexes. For three hydrogen atoms reacting at room temperature this is of the order of angstroms and so seems physically sensible. Another way of saying essentially the same thing is that $h$ is the area in the phase space along the co-ordinate normal to the barrier and its conjugate momenta which is to be taken as belonging to the activated complex. Since the choice of a standard state is purely a matter of convenience and since exactly the same considerations are involved for $K^*$ as for any equilibrium constant we propose following in general the conventions and nomenclature of Lewis and Randall. Guggenheim has related Lewis and Randall’s nomenclature to his own and that of other writers.

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15 Evans and Polanyi, ibid., 1937, 33, 448.
16 Guggenheim, ibid., 1937, 33, 607.
18 Guggenheim, Modern Thermodynamics, Methuen & Co., Ltd., 1933.
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From this point on the treatment of $K^*$ proceeds precisely in the same way as any equilibrium constant. We thus have all the usual problems and the customary tools of thermodynamics and statistical mechanics. In the space here available it is neither possible nor desirable to reproduce the thermodynamic theory of equilibria. We shall only very briefly review some of the applications of the present theory to solutions.

We take $p$, $T$ and mole fractions as our independent variables and the activities of our reactants and our activated complex as equal to their molality in an infinitely dilute solution. Our standard state then corresponds to unit activity and for the standard free energy of activation we write (using $?),$

$$\Delta F^{*o} = RT \ln K^* = -RT \ln \left( \frac{\gamma_1 \cdots \gamma_n}{\gamma_1 \cdots \gamma_n} \right)$$

(8)

for the heat of activation

$$\Delta H^* = \frac{\partial \ln K^*}{\partial T}$$

(9)

and for the entropy of activation

$$\Delta S^{*o} = \frac{\Delta H^* - \Delta F^{*o}}{T}$$

(10)

Guggenheim \(^{10}\) (see also Bell and Gatty) \(^{11}\) in a very interesting paper has pointed out certain objections to this nomenclature which must be taken into account in an exact statistical treatment of the subject. These arise from the customary use of an equilibrium constant involving concentrations, which we follow, rather than one involving mole fractions. The result is that $\Delta H^*$ really includes a small term depending on the coefficient of expansion of the solution while the volume change, $\Delta V^* - \frac{\Delta F^{*o}}{2p}$, includes a small term arising from the compressibility of the solution. In the opinion of the author however, equations (8), (9) and (10) should be used in discussions of reaction rates because of the simple way they follow from the data and the word apparent prefixed to the corresponding names of such quantities as $\Delta F^{*o}$, $\Delta H^*$, $\Delta S^{*o}$ and $\Delta V^*$ where this seems necessary. Guggenheim gives the small corrections to these quantities, in certain ideal cases, and other cases can be exactly treated when the necessary data becomes available. When for lack of more precise information $\gamma_1 \cdots \gamma_n$, $\gamma_1$ and $\kappa$ are all taken equal to unity in calculating $K^*$, there is of course a further reason for preferring "apparent" to our calculated thermodynamic properties. For most cases these approximations will not introduce uncertainties which interfere seriously with the use of $\Delta F^{*o}$, $\Delta S^{*o}$, etc., in deducing the mechanism of a reaction.

Applications.

Thus the data of Chick and Martin \(^{20}\) on the denaturation of haemoglobin and egg albumin leads to values of $\Delta S^{*o}$ of about 100 E.U. and 320 E.U. respectively. Stearn and Eyring \(^{11}\) point out that this means that the activated state is one with much greater randomness of motion than the initial state. Thus the mechanism is necessarily one involving the breaking of many weak bonds to form the activated state and any type of mechanism which does not account for this great increase in

\(^{17}\) Bell and Gatty, Phil. Mag., 1935, 10, 75.

\(^{20}\) Chick and Martin, Colloid Chem. Beh., 1933, 5, 49.
randomness inside the activated complex is definitely excluded by our theory.

The closing of a ring such as occurs in the formation of a methyl radical and cyclopentone from a hydroxyl radical proceeds by way of an activated complex of much lower apparent entropy, $\Delta S^\circ$, than the original molecule. Statistical mechanics in this case yields a result in good agreement with experiment. Bawn has discussed still other applications of the general theory. Another type of reaction of great interest involves the recombination of atoms. Here there is no critical energy to attain but rather energy to be dissipated. In spite of the fact that there is no activation energy barrier to surmount for the reaction $3\text{H} \rightarrow \text{H}_2 + \text{H}$ it turns out that it is convenient to treat symmetrical configurations as critical configurations and apply our general theory. Kimball has also treated recombination of radicles in an interesting way. When the activation energy is zero or is small compared with the rotational energy it may no longer be reasonable to treat rotational and internal vibrational co-ordinates as separable. In this case the rotational energy for each configuration is added to the potential energy to give a slightly different potential surface for each set of rotational quantum number. The activated complex then corresponds to the slightly different critical configuration on each of these surfaces. Our statistical treatment now proceeds as readily as before except that we must sum over the rotational states.

Evans and Polani whose results will be treated elsewhere in this symposium have also given a valuable treatment of the same general theory, which differs only in detail. They have treated at length a number of the consequences of the thermodynamic theory on reaction rates and in particular the effect of pressure.

Wigner and Farkas, and Hirschfelder, Topley and the present author have shown that the wide variety of isotopic hydrogen atom reactions are in satisfactory accord with experiment. The latter authors find $\kappa$ approximately equal to $\frac{1}{4}$ for the ortho para-convension in contrast with a value of about $2 \times 10^{-4}$ for the non-adiabatic decomposition of $\text{N}_2$ treated also by the present theory. The theory for $\kappa$ in its extrathermodynamic nature is sharply distinguishable from the theory for $K^*$. A more detailed understanding of $\kappa$ on the basis of both theory and experiment is no doubt one of the lines of development in the near future. More complicated four atom reactions have also been treated.

The general statistical theory has been equally fruitful in interpreting ionic reactions in the gas phase and in solutions. In the latter
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Thus a decrease in the heat content of a system by bond formation as in salivation is accompanied by a partially compensating entropy decrease because of the increased order (or decrease in freedom of motion).

Photochemical Reactions.31

Most thermal reactions proceed on the lowest possible potential surface corresponding to unexcited atoms. However, for each excited state of the system we get a new potential energy surface and a new chemistry with activated complexes, exactly as for the normal state. Thus in photochemical reactions according to the Franck-Condon principle, the absorption of a quantum of light corresponds to a vertical transition from the lowest potential surface to some higher one. The mass point representing the system immediately after the absorption of a quantum of light, may thus find itself considerably displaced from equilibrium on the upper surface. (1) If it lies higher than each of several passes leading into surrounding basins or valleys there will be competing reactions and the products will be more or less equally divided among the various possibilities. The products will then proceed by secondary reactions until equilibrium is finally reached. (2) It may lie higher than a single pass in which case there will be a unique set of primary products with their subsequent secondary reactions. (3) The system may have energy lying between 0 and about 4 Kg. cal. below the lower pass. In this case a part of the systems decompose by way of the low pass and a part simply lose their energy in collisions, if the pressure is near atmospheric, or they may fluoresce. (4) If the energy is much more than 4 Kg. cal. below the pass the systems will dissipate their energy without reacting. A knowledge of the excited and normal potential energy surfaces makes possible a complete treatment of photochemical reactions in much the same way as a knowledge of the normal surfaces allows us to treat thermal reactions.

The general reaction rate theory is thus applicable to all material rearrangements and whether one describes it as a kinetic, statistical or thermodynamic theory scarcely matters since when two or more formulations are each adequate they will be found to be identical aside from trivial details of form.

Summary.

The general statistical mechanical theory of reactions rates has been given and its application to a wide variety of examples has been reviewed. The thermodynamic theory has been developed in terms of the equilibrium constant, $K^\circ$, between the activated complex and reactants. $K^\circ$ is the constant which has the correct dimensions for an equilibrium constant, i.e., it is dimensionally equal to the specific rate constant divided by a frequency. The advantages of using this constant are summarised. The manner in which the general theory applies to photochemical reactions is briefly given.

Brick Chemical Laboratory,
Princeton, New Jersey.