THE ACTIVATED COMPLEX AND THE ABSOLUTE RATE OF CHEMICAL REACTIONS

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Since the first measurement of the rate of a chemical reaction by Wilhelmy (32) in 1850 chemists have been struggling with the question of mechanism. Table 1 indicates the progress of this search for guiding principles and gives the names of some of the individuals who contributed, the concepts they proposed, the rate equation if one was suggested, and the year the work was done. The list is of necessity incomplete, and the contributions recorded differ greatly in importance; in certain cases they are only slightly or perhaps even less important than contributions that have been omitted. The field of chain reactions is treated in this symposium by F. O. Rice and so is not considered here.

The thermodynamic-like considerations of van't Hoff (30) were followed by Arrhenius's concept of an activated molecule. Then in 1911 Scheffer and Kohnstamm suggested the idea of an entropy of activation; this was followed in 1918 by the calculations of W. C. McC. Lewis, which equate the rate of a bimolecular reaction to the number of activated collisions. In 1922 Lindemann suggested delayed decomposition in unimolecular reactions as an alternative to the radiation hypothesis. Brönsted in 1923 gave a theory of the effect of the solvent on reaction rates in terms of a rate for the infinitely dilute solution multiplied by the activity coefficients of the reactants over that for an intermediate complex. Beginning in 1926 Lindemann's suggestion bore fruit in the works of Hinshelwood, Rice and Ramsperger, and Kassel, who developed the theory for the decrease of unimolecular rates with pressure. Polanyi and Wigner then treated reaction rates from the point of view of mechanics, with interesting results.

Then came a development in quite a different direction. London's suggestion that many reactions proceed by an adiabatic process was followed by the actual construction of potential surfaces for reactions by Eyring and Polanyi. These surfaces, although approximate, made it possible for the first time to estimate activation energies and so to answer many questions regarding mechanism, such as the relative rates of competing reactions. These surfaces also provided the means for forming a clear picture of the

TABLE 1

Development of theory of absolute reaction rates

NAME AND DATE	REFERENCE	CONCEPT STRESSED AND EQUATION SUGGESTED
Arrhenius (1889)	(1)	Activated molecules $\ln k = B - \frac{A}{T}$
Trautz (1909)	(29)	Activated molecules
Scheffer and Kohnstamm (1911)	(27)	Entropy of activation
W. C. McC. Lewis (1918)	(15)	Molecules reacting = molecules colliding $\times\, e^{-\frac{E_0}{kT}}$
Polanyi (1920)	(33)	The statistical probability of the collided state substituted for collision number
Rideal (1920)	(24)	Quantization $k_u = \frac{E}{h} e^{-\frac{E}{kT}}$
Dushman (1921)	(4)	
Brönsted (1922)	(3)	Thermodynamic theory of solvents $k = H \frac{f_1 f_2 \cdots}{f^*}$
Rodebush (1923)	(25)	Vibration frequency likened to a collision $k_u = \nu e^{-\frac{E}{kT}}$
Herzfeld (1925)	(9)	Mechanics of decomposition of diatomic molecule $k_u = \nu e^{-\frac{E}{kT}}$

Lindemann Lewis and Smith Hinshelwood Rice and Ramsperger Kassel (1922)	(16) (14) (10) (22) (11)	Delay in decomposition of activated molecules $k_u = e^{-\frac{E}{kT}}\left(\frac{E}{kT}\right)^{s-1}\frac{1}{(s-1)!}$
Tolman (1927)	(28)	Applicability of statistical mechanics to rates $k_u = \frac{\sum\limits_a k_a p_a e^{-\frac{E_a}{kT}}}{\sum\limits_i p_i e^{-\frac{E_i}{kT}}}$
Polanyi and Wigner (1928)	(20)	Mechanical considerations of unimolecular reactions $k_u = \nu e^{-\frac{E}{kT}}$
London (1928)	(17)	Reaction frequently an adiabatic process
Eyring and Polanyi (1930)	(8)	Potential surfaces for activated complexes
Pelzer and Wigner (1931)	(19)	The absolute rate of a simple reaction is calculated for the first time $k_u = 2.1 \times 10^6\, T^{\frac{3}{2}} e^{-\frac{W_0}{kT}}$
Wigner (1932)	(31)	Corrections for barrier leakage given $K_u = \frac{4m^{\left(\frac{n+1}{2}\right)}\pi^{n-1}e^{-\beta V_0}}{2\beta^{n+1}(A_2A_3\cdots A_n)^{-\frac{1}{2}}}\left\{1 - \frac{h^2\beta^2}{24m}(A_1 + \cdots + A_n)\right\}$
La Mer (1933)	(12)	Entropy and free energy of activation. Theory of change of activation energy with temperature $k = (\text{number of collisions})\, e^{\frac{S_{\text{act}}}{R}} e^{-\frac{H_{\text{act}}}{kT}}$

TABLE 1—*Concluded*

NAME AND DATE	REFERENCE	CONCEPT STRESSED AND EQUATION SUGGESTED
Rodebush (1933)	(26)	Thermodynamics and the kinetics of gaseous reactions $\ln K = -\frac{Q_1}{RT} + \ln\left[2^{\frac{3}{2}}\pi^{-\frac{1}{2}}\left(\frac{m_1+m_2}{m_1m_2}\right)^{\frac{1}{2}} r^2(kT)^{\frac{1}{2}}\right]$
Rice and Gershinowitz (1934)	(21)	For molecules to react they must lie in a certain fraction of the total phase space
Eyring (1935)	(6)	For a reaction in any phase of any order (in which the slow process is passage over an energy barrier) there is an activated complex much like an ordinary molecule except for a fourth translation $K = \kappa \frac{F_0 e^{-\frac{E_0}{kT}}}{F_n}\left(\frac{kT}{2\pi m}\right)^{\frac{1}{2}} = \frac{\kappa F_0^*}{F_n} e^{-\frac{E_0}{kT}} \frac{kT}{h}$

detailed mechanical behavior of a reacting system; how the activation energy is distributed between translation and vibration and the precise nature of the activated complex. The surface for three hydrogen atoms was used by Pelzer and Wigner as the basis for the first successful calculation of the absolute rate of a chemical reaction.

Next a calculation of the temperature dependence of the activation energy was made by La Mer, based on the earlier work of Tolman. This was very soon followed by the work of Rodebush, in which he extended an earlier paper and pointed out the usefulness of the conception of an entropy as well as a heat of activation. Neither of the latter authors gave a general theory of the absolute rate of chemical reaction. Rice and Gershinowitz set out to remedy this situation for bimolecular association reactions. They assumed, correctly, that for a reaction to take place the system must lie in a certain fraction of phase space. This led them to some very interesting results. Because of their method of approach, however, they failed to realize the full significance of the potential surface in defining the precise nature of the activated complex, and so did not give a general equation for the rate of a reaction. All the equations given which are correct, including the very interesting one of Brönsted, arise as specializations of a general theory.

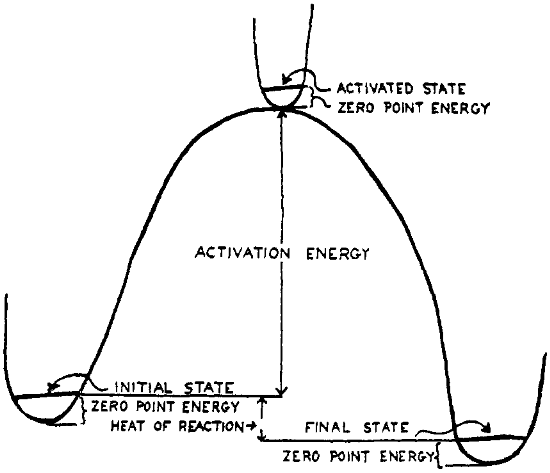

FIG. 1. Energy profile of path of reacting system on many dimensional surface

We will now give the general theory for the rate of any reaction in any phase for which the slow process is the passage over a potential energy barrier. The basic conceptions gained from a consideration of the potential surfaces are the following. The activated complex has very nearly the properties of an ordinary molecule except that instead of having only the three regular translational degrees of freedom it has a fourth, along which it first approaches the barrier, crosses it, and then flies to pieces. Since the activated complex when represented as a point on a potential surface is at a minimum for all the internal degrees of freedom except the one degree of translation for which it is a maximum, we can apply the theory of small vibrations in the same way used for stable compounds. Figure 1 shows in section the path of a point representing our reacting system moving along the many dimensional potential energy surface. The rate of a reaction is given by the equilibrium number of activated complexes per unit of length normal to and near the top of the potential barrier multiplied by the average velocity of crossing the barrier. Thus we have for the rate constant k_i for a reaction of any order in any phase

$$k_i = \kappa K^* \frac{(2\pi mkT)^{\frac{1}{2}}}{h} \sqrt{\frac{kT}{2\pi m}} = \kappa K^* \frac{kT}{h} \tag{1}$$

where $K^* \frac{(2\pi mkT)^{\frac{1}{2}}}{h}$ is the equilibrium constant between the activated complex (having four translational degrees of freedom) and the reactants; this multiplied by the velocity of crossing the barrier $\sqrt{\frac{kT}{2\pi m}}$ and by the probability κ of not returning gives the specific reaction rate k_i. Here K^* is the equilibrium constant for a hypothetical molecule exactly like the activated complex, except that for convenience we think of the fourth translation as replaced by a stiff vibration. We now define an entropy of activation S^* and a heat of activation H^* by the equation

$$K^* = e^{\frac{\Delta S^*}{R}} e^{-\frac{\Delta H^*}{RT}} \tag{3}$$

Introducing equation 3 in equation 1 gives

$$k_i = \kappa e^{\frac{\Delta S^*}{R}} e^{-\frac{\Delta H^*}{RT}} \frac{kT}{h} \tag{4}$$

The theory for a rate process involving a change of phase such as adsorption, vaporization, or sublimation is contained in the first form of equation 1, for which cases κ is to be identified with the accomodation coefficient. The equilibrium constant K^* can be written also as the ratio of a partition function for the activated complex divided by a partition function for the reacting molecules (6) and the theoretical methods available for any equilibrium apply and are sufficient for calculating K^* providing we know our potential surface fairly well. In general, because a part of the systems cross the barrier only to collide with the surface and recross in the reverse direction, we must introduce the proper fraction κ. The transmission coefficient κ is just the ratio of systems crossing the barrier to systems reacting, and for many simple reactions has approximately the value unity. κ is particularly interesting in that it is the one factor under consideration not deducible from straightforward statistical mechanics. To obtain it theoretically we must solve a problem in mechanics. Fortunately, as stated for many reactions we make a negligible error by taking it as unity.

That the theory does in fact agree precisely with experiment for simple gas reactions is shown by the calculations of Pelzer and Wigner (19) for the ortho-para conversion, and by the calculations with Wheeler and Topley, not yet published, for this reaction and for the reactions $Br + H_2$ and $H_2 + I_2$. The general theory outlined here differs from that of Pelzer and Wigner and of Wigner (31) in a number of ways, but perhaps the most important is in the explicit account it takes of the rotations of the system. In many problems this is of fundamental importance. How successfully this theory resolves the problem of trimolecular reactions is shown in a paper by the author and Gershinowitz, so that this point need not be discussed further now. Instead the adaptation of the theory to reactions in condensed phases will be considered.

We will, in fact, be largely concerned with a thermodynamic discussion of the equilibrium constant K^* for the activated complex.

As in ordinary equilibria, in order that the equilibrium constant K^* be really a constant we must define it as belonging to some standard state. The particular state chosen as standard is not very important, and we shall in fact use different standard states as convenience may dictate, being, however, careful to designate in each case what the standard state is. The dilute gas has one very great advantage as a primary standard if we propose to use statistical mechanics to calculate K^*. This is because we can then restrict our considerations to the internal coördinates and the distances between the molecules actually reacting, which in the present condition of the theory of condensed phases is important. Choosing this standard we then define the activity a_i of the molecule A_i as equal to its concentration at low pressures. For high pressures or condensed phases we introduce an activity coefficient α_i such that $c_i\alpha_i = a_i$. For the activated complex these quantities are starred thus a^*, c^*, α^*. Now

$$\text{the rate of any reaction} = \kappa c^* \frac{kT}{h} \tag{5}$$

But

$$K^* = \frac{a^*}{a_1 a_2 \cdots} = \frac{\alpha^* c^*}{\alpha_1 c_1 \alpha_2 c_2 \cdots}$$

whence

$$c^* = K^* \frac{\alpha_1\alpha_2 \cdots}{\alpha^*} c_1c_2 \cdots$$

Substituting in equation 5 we get

$$\left(\kappa K^* \frac{\alpha_1\alpha_2 \cdots}{\alpha^*}\right) c_1c_2 \cdots$$

Dividing by the concentration of reactants we have for the specific reaction rate

$$k_i = \kappa \left(K^* \frac{\alpha_1\alpha_2 \cdots}{\alpha^*} \frac{kT}{h}\right) \tag{6}$$

If now we want to introduce as a secondary standard state that of the infinitely dilute solution, we next write

$$\alpha_i = \beta_i f_i$$

where $\beta_i c_i$ is the concentration of the vapor of the molecule A_i over its dilute solution of concentration c_i, and f_i is the usual activity coefficient referred to dilute solution. Then

$$k_i = \left(K^* \kappa \frac{\beta_1\beta_2 \cdots}{\beta^*} \frac{kT}{h}\right) \frac{f_1f_2 \cdots}{f^*} \tag{7}$$

which is Brönsted's equation, except that now we have a complete theory for the quantity in parenthesis.

We are now in a position to define more closely the intermediate complex to which Brönsted's equation refers. It is a molecular aggregate which is first forming and then exploding at a velocity of about 10^{-5} cm. per second along a particular internal normal coördinate. The potential surface properties only stay approximately constant for a distance of a few tenths of an Ångström unit, giving our activated complex a mean life of 10^{-14} to 10^{-13} second. If there is appreciable interaction between the normal coördinates of the activated complex such a short life will give, instead of sharp energy levels, the fuzzy quantization observed in predissociation. For sharp quantization we should use in our statistics the energy levels of quantum mechanics, while for unsharp levels we can do this or use classical theory. The isotopes provide the best available tool for determining how big the half-quanta of the activated state are, and this will vary from case to case. Degrees of freedom but slightly altered in a reaction will have their normal half-quanta in the activated complex. The results of Bach, Bonhoeffer, and Moelwyn-Hughes (2) for $Br + H_2$ and $Br + D_2$ seem to indicate not very sharp quantization for such simple activated complexes. This is a problem in which Kassel is much interested, as he informed me privately. It is a problem which was carefully considered during the writing of a previous paper, but still requires consideration. This problem is closely connected with quantum mechanical leakage through a potential energy barrier which has the effect of adding a term to the equation we are using for the rate, as the equation given by Wigner (31) shows. The theoretical potential surfaces and the experiments both indicate this is in general a very small effect. Finally a change in multiplicity may occur as in the famous unimolecular decomposition of nitrous oxide, which introduces another type of chemical inertia. For the great majority of reactions these latter effects are either non-existent or of decidedly secondary importance. They do, however, possess a very great theoretical interest. If we know the α's of equation 6 we have a complete theory for the number of collisions in solution in terms of the theory for collisions in the gas phase.

We now consider certain applications of our equations to solutions. From Langmuir's (13) considerations on vapor pressure it can be shown that for any substance forming a perfect solution α, which is equal to the concentration in the gas divided by the concentration in the pure liquid, is approximately equal to

$$5T^{\frac{1}{2}}e^{-\frac{\Delta H}{RT}}$$

This same value of α holds for a perfect solution. For a unimolecular reaction our general equation takes the form

$$k_i = \kappa K^* \frac{kT}{h} \frac{\alpha}{\alpha^*}$$

By our definition of the standard state $\alpha/\alpha^* = 1$ for the gas. Applying this equation to the decomposition of saturated solutions of nitrogen pentoxide in nitromethane, carbon tetrachloride, and nitrogen tetroxide the results of Eyring and Daniels (7) give $\alpha/\alpha^* = 1.71$, 2.32, and 2.01, respectively, at 15°C. The concentration of nitrogen pentoxide in nitromethane is 740 and in carbon tetrachloride 1108 times the concentration in the vapor. These large numbers are therefore the values we must take for α with α^* only slightly smaller. These solvents thus shift the equilibrium K^*, so that it favors the activated complex by a small amount. Nitrogen pentoxide does not decompose inside a crystal, so that $\alpha/\alpha^* = 0$. Since α is not very different than for a saturated liquid it follows that the activity coefficient α^* of the activated complex is very large. This is just another way of saying that the activated complex is not isomorphous with the normal molecules and so cannot be formed without disrupting the crystal, which would involve a prohibitive activation energy. Thus in general the neighboring molecules inside a crystal are very effective negative catalysts.

We now consider a different point. Knowing the experimental rate and the heat of activation, our theoretical equation enables us to solve for the entropy of activation. The transmission coefficient is set equal to unity, as it can hardly differ materially from this value in the reactions to be considered. The experimental equation for the decomposition of nitrogen pentoxide is

$$k = 5.08 \times 10^{13} e^{-\frac{24,700}{RT}}$$

Equating this to the theoretical equation we obtain the result that the activated complex is 4.27 units richer in entropy than the normal molecules. This is a typical result for many unimolecular reactions. We now consider some very different cases. The examples to be used are drawn from a paper with Wynne-Jones, which treats the whole theory of rates in condensed phases in more detail. The decomposition of triethylsulfonium bromide into diethyl sulfide and ethyl bromide, as shown by table 2, proceeds at a normal rate at a temperature of 66°C., in spite of the very high activation energy of 35,000 calories. In the column marked ΔS is given the total increase of entropy for the reaction. ΔS^*, on the other hand, is the entropy of activation calculated from our theory. The agreement is striking. For this unimolecular reaction the activated complex, instead of being like the reactants, has an entropy almost exactly equal to the product molecules. If we measured the reverse bimolecular reaction and interpreted it as a collision process we would be led to ludicrously large collision diameters,—about seven times ordinary diameters. Actually the forces between the molecules do not necessarily extend to larger distances than usual. The large entropy of the activated complex can arise just as well from comparatively free relative vibration and rotation of the constituent diethyl sulfide and ethyl bromide.

We next consider a bimolecular reaction (see table 3) which proceeds many times more slowly than would be expected. This is the combination of dimethylphenylamine with methyl iodide to give the quaternary ammonium salt. Gaseous bimolecular associations under the condition of concentration, etc., which are taken as standard for the specific reaction rate constant, often involve an entropy decrease of about 14 entropy units with a corresponding decrease of about 7 units for forming the intermediate activated complex. For this reaction, however, the one equilibrium measured shows a decrease of 54 entropy units, so that the corresponding decrease of 37 units for the activated complex, although extremely large, might have been anticipated. Predictions for reaction kinetics in the future will probably be largely based on known entropy changes for analogous equilibrium processes rather than on calculations of the number of collisions,—a procedure which ignores all degrees of freedom except those which are initially translations.

As a final example we will use our general theory to calculate the steric factor for one of the elementary processes of chain reactions postulated by F. O. Rice (23). The reaction is the formation of a five-membered ring and a methyl radical from the normal hexyl radical. The activated complex will be an almost closed five-membered ring with a methyl group in the act of leaving the ring. From Parks and Huffman's (18) book on free energy we find that the entropy of cyclopentane is about 21 units less than that for pentane at 25°C. The formation of the ring changes four rotations into vibrations, so that the difference in entropy should increase with temperature approximately as $\frac{4}{2}R \ln T$. This leads us to calculate an entropy decrease from this ring closure of about 25.6 units at 650°C., which corresponds to a steric factor of 2.5×10^{-6} as compared with Rice's estimate of 10^{-6}. Our calculation, although approximate, is right as regards order of magnitude. Thus this point of view leads us to a quantitative theory of the change of the steric factor with temperature, something not possible with the previous ideas for calculating reaction rates.

TABLE 2

Decomposition of triethylsulfonium bromide in benzyl alcohol–glycerol mixtures

T = 353° Absolute

PER CENT ALCOHOL	ΔS	ΔS^*	$\Delta S - \Delta S^*$
100	20.85	20.42	0.43
90.23	17.25	15.86	1.39
80.39	13.14	12.91	0.23
69.39	6.80	11.07	−4.27

From data of Corran (Trans. Faraday Soc. **23**, 605 (1927)) given by Soper in Discussion of the Chemical Society, 1931.

TABLE 3

Reaction of dimethylphenylamine with methyl iodide

T = 333° Absolute

SOLVENT	H*	$-S^*$	$-S$
$C_2H_2Cl_4$	11,680	39.48	54.1
$C_6H_5NO_2$	13,020	37.45	
$C_6H_5CH_2OH$	14,400	27.90	
With C_2H_5I in $(CH_3)_2CO$	13,680	38.83	

Data from Essex and Gelormini (5).

I shall not take time for more examples, but it should be clear that in all chemical reactions we must begin thinking of an activated complex which is very much like an ordinary molecule except that it has a fourth translational degree of freedom. This activated complex is not the old one most of us are in the habit of thinking about, which when formed was equally apt to decompose into reactants or products, but rather it is one for which the rate in the forward direction is entirely unaffected by how many activated complexes are proceeding in the reverse direction. This is because the two processes "happen in different coördinates," much like two trains passing on different tracks. Thus the use of equilibrium statistics to count the number of molecules decomposing is unaffected by how far the system is from equilibrium or how fast the reverse reaction is occurring. To be sure, if there is autocatalysis we have a new elementary process with its particular activated complex to be treated exactly as any other elementary process.

In the brief time available I have outlined a general theory of reaction rates, which includes the earlier theories as special cases. I hope that this discussion will have conveyed some idea of the power of this method of attack and the kind of problems which remain to be solved.

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