SOME ACCOMPLISHMENTS AND LIMITATIONS
OF REACTION RATE THEORY

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*Professor Eyring, of the Graduate School, University of Utah, received the Annual
Thousand Dollar AAAS Prize in 1932.*

THERE are two extreme types of reaction rates. One kind is typified by ordinary radioactive decay where the rate is unaffected by ordinary changes in temperature and pressure. The second is ordinary chemical reactions dependent on both temperature and pressure. For both types of reaction, the rate can be represented as

$$rate = \Sigma_i n_i v_i \gamma_i \qquad (1),$$

where n_i is the number of reacting systems in the ith state, v_i is the number of times per second that the system in the ith state vibrates in the direction normal to the reaction barrier, and γ_i is the chance on each assault that the system successfully traverses the barrier.

If the rate is not affected by temperature or pressure, the values of n_i are in general known from the chemical analysis of the material. For equilibrium systems sensitive to temperature and pressure, the appropriate statistical mechanical calculation is required. This calculation, as well as the calculation of v_i and γ_i, depends on adequate knowledge of the potential energy surface, especially in the neighborhood of the minimum and the barrier saddle point. In principle, it is possible to calculate all such surfaces for molecular complexes. For nuclei, potential surfaces are only known in the region where Coulomb's law holds. For distances closer than about 3×10^{-12} Angstroms (depending somewhat on the atom), the unknown nuclear forces determine the shape of the surface. However, Condon and Gurney and Gamow showed how barrier leakage could explain the radioactive decay of the elements and the capture of a swiftly moving particle colliding with the nucleus.

The fraction of molecules decaying per second radioactively was found to be approximately

$$k = \frac{1}{a}(2\mu E)^{\frac{1}{2}} e - \frac{4\Pi}{h} \int (2\mu(V-E)^{\frac{1}{2}} dx \quad (2).$$

Here a is the width of the interior of the atom. E is the energy of the escaping particle, μ is the corresponding reduced mass, and V is the potential energy of the barrier. The integral is to be taken

* Owing to lack of space, references have been omitted.

from the point of entering the barrier to where it emerges. This treatment is satisfactory in so far as it can be tested without a better knowledge of the nature of the nuclear forces.

Before the above treatment was applied to the nucleus, an analogous treatment of molecular isomerization was made by Hund. Actually, the integral for barrier penetration in equation (2) is roughly the same magnitude for molecules as for the nucleus. This is because, although the barriers are about a million times as high for the nucleus, they are also usually over a thousand times thinner. The result is that chemical reactants almost invariably find it easier at ordinary temperatures to surmount the barrier rather than to tunnel through it. The most notable exception is the case where the three hydrogen atoms in ammonia first form a pyramid with the hydrogen base on one side of the nitrogen apex and then on the other. This turning wrong side out happens about 10^{10} times per second and is a true tunneling very much like radioactive decay. Examples of this kind are extremely rare, however. Most reactions involve the surmounting of the barrier. In 1928 London showed how the quantum mechanics could be used to construct potential barriers and pointed out that, in general, the surmounting of the barrier usually proceeded without electronic reorganizations of the kind occurring in electronic transitions.

Polanyi and Eyring devised means of constructing potential surfaces from London's approximate formula. These were sufficiently accurate to show that tunneling is in general negligible in chemistry and to form the basis for a quantitative statistical theory of reaction rates. In principle, we can presumably calculate the rate of any chemical change. In practice, it has only been possible so far to show from first principles that, for the simplest of reactions, $H + H_{2\ para} = H_{2\ ortho} + H$, the activation energy is less than 19 K calories, whereas experimentally it is found to be about 7 K calories. Nevertheless, we now have a detailed theory of reaction rates. Our only really serious limitation in predicting reaction rates a priori is the lack of workable methods for calculating barrier heights. This is a difficult problem, but it is of sufficient importance that it will surely be solved eventually.

The methods of perturbation theory lead to the London-type formula, which gives the energy for a system of atoms in terms of the binding energy between pairs. The binding energy between atom pairs is considered to be of two types: a classical "coulombic" binding, which is about 14 percent of the total and is simply additive; and the "exchange," or valence, binding which constitutes the remainder.

The well-known approximate London formula for the energy E for four monovalent atoms is

$$E = Q - \{\tfrac{1}{2}(\alpha-\beta)^2(\alpha-\gamma)^2(\beta-\gamma)^2\}^{\frac{1}{2}} \quad (3).$$

Here the total coulombic binding is included in Q, α may be taken as the sum of the exchange part of the two initial bonds before reaction, and β is the sum of the two bonds formed after the reaction; γ is the sum of the two bonds which are present only in the activated state along with α and β.

The radical in (3) may be shown to be equal to the length of a vector found by adding β onto the end of α at an angle of 60° and γ onto the end of β, making the 60° angle which will make the vector sum smallest. A chemical reaction starts with α large and with β and γ zero and ends with β large and α and γ zero. The activated state will thus come approximately when $\alpha = \beta$ and the total binding will be less than α or β because of γ. For three monovalent atoms, equation (3) still applies with the same meaning except that α, β, and γ now stand for a single bond in each case. Equation (3) and its analogues for more electrons provide a useful basis for constructing approximate potential surfaces in general.

It is of interest to compare the molecular orbital calculation of energy with the results of equation (3), which is based on the method of bond eigenfunctions. The approximate calculated energy for the system taking the state of the separated atoms as nq, where n is the number of atoms, is for two hydrogen atoms $E = 2q + 2\beta$; for three hydrogen atoms on a line, two equispaced from a central atom, $E = 3q + 2.82\beta$; for three hydrogen atoms forming an equilateral triangle, $E = 3q + 3\beta$; and for four hydrogen atoms forming a square, $E = 4q + 4\beta$.

To make the results for the molecular orbital method agree with experiment, we must assume that the repulsion between nuclei and between electrons, which has so far been neglected, will act to change E for three atoms on a line from 2.82β to about 1.8β, with correspondingly bigger corrections for a triangle and a square. Qualitatively, the results would then seem sensible. A systematic application of the molecular orbital method to ac-

tivated complexes should be carried out. A beginning has been made by Sherman and Van Vleck and more recently by Pearson.

The statistical theory for reaction rates takes the form

$$= (A)(B) \ldots K^{\ddagger} \frac{kT}{h} K \quad (4).$$

where (A), (B), etc., are the concentration of reactants. $K^{\ddagger}$ is the equilibrium constant between the normal and activated state and is readily calculable in terms of partition function when the quantum mechanical calculation of barrier shape has been carried through; $\frac{kT}{h}$ is the frequency at the absolute temperature T. At room temperature, it has the value 5.6×10^{12}. The transmission coefficient K is calculable from quantum mechanics when the barrier shape is known, but can usually be taken as unity.

The specific reaction rate constant k' can thus be written as

$$
\begin{aligned}
k' &\equiv K \frac{kT}{h} K^{\ddagger} = K \frac{kT}{h} e^{-\frac{\Delta F^{\ddagger}}{RT}} \\
&= K \frac{kT}{h} e^{-\frac{\Delta H^{\ddagger}}{RT}} e^{-\frac{\Delta S^{\ddagger}}{R}} \\
&= K \frac{kT}{h} e^{-\frac{\Delta E^{\ddagger} + p\Delta V^{\ddagger} - T\Delta S^{\ddagger}}{RT}} \\
&= K \frac{kT}{h} e^{-\frac{\Delta F_o^{\ddagger} + \int \Delta V^{\ddagger} dp}{RT}} \\
&\quad \frac{kT}{h} e^{-\frac{\Delta F_o^{\ddagger} + \overline{\Delta V^{\ddagger}} p}{RT}}
\end{aligned}
\quad (5).
$$

Here $\Delta F^{\ddagger}$ is the Gibbs free energy of activation at pressure p, and $\Delta F_o^{\ddagger}$ is this value at $p = o$. $\Delta H^{\ddagger}$ is the heat of activation; $\Delta S^{\ddagger}$ is the entropy of activation; $\Delta V^{\ddagger}$ is the increase in volume between the normal and the activated state. This equilibrium theory is applicable to all rate processes, both physical and chemical, where the activated state does not involve excessive barrier leakage. Where there is leakage, the corresponding contribution can be added to the contribution (5) for passing over the barrier. The only serious difficulty in estimating reaction rates a priori is the estimation of $\Delta E^{\ddagger}$.

a) Association reactions involving the breaking of no bonds ordinarily have $\Delta E^{\ddagger} = 0$.

b) Substitution reactions of the type $A + B - C \rightarrow A - B + C$ have $\Delta E^{\ddagger}$ equal to 5 percent of the

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bond $B - C$ if A is an atom and if the bond $A - B$ is stronger than $B - C$. This defines the activation energy for the reverse reaction since it must be greater by the energy of reaction.

c) The reaction $A - B + C - D \rightarrow A - C + B - D$ has a $\Delta E^{\ddagger}$ about 28 percent of the two bonds broken if it is proceeding in the exothermal direction. The reaction $A - B + C - D \rightarrow A - D + B - C$ is likewise possible. Presumably that process will be most rapid which is most exothermal. This would be an interesting point to investigate.

d) In viscous flow, the free energy of activation is equal to the heat of vaporization of the flowing unit (usually a molecule) divided by 2.8. Diffusion very frequently proceeds by the same mechanism with the same activation-free energy.

e) In many organic reactions, the energy of activation is the energy of ionization of one of the reactants. Thus, if one nitrates solutions of benzene or of toluene in sulfuric acid, they go at the same rate, but if a benzene-toluene mixture is nitrated, the toluene is 29 times as apt to nitrate as benzene. This proves the critical complex does not contain benzene or toluene, but when formed it reacts with one or the other rather than decomposes spontaneously—reacting 29 times faster with the toluene molecule. This is in line with the usual situation in organic reactions. Thus, frequently, reactive complexes are formed which may react alternatively in a variety of ways.

f) Optically active synthesis, so common in biological systems, is certain proof of the existence of an optically active enzyme which acts as a templet, making better secondary bonds with the favored optically activated complex than with the other. This of course does not preclude simultaneous enzyme action on primary bonds. Such action, however, does not favor one optical isomer over the other.

g) Solvents with high dielectric constant, such as water, are such effective catalysts of intercombination between ionic crystals that there is no measurable slowness of solution and reaction.

THERE are many other general influences affecting individual reaction rates, but we turn now to another type of question. As we consider the natural rate processes occurring around us, they usually turn out to be a complex of the elementary processes for which the general theory has been outlined. This complex of elementary processes can often be thought of as being in fact a machine. We consider as a first example, very briefly, the process of growing old. Children from young or from old parents do not necessarily reveal the difference in the age of their parents. It thus is not individual cells that are growing old. Actually, in a certain sense, each individual is as old as the race; and, under favorable circumstances, the race might continue forever. Each individual is a sort of backwater along the stream of life. In the individual, certain cells have become specialized to form organs, and failure or unbalance between these organs sooner or later must spell disaster for the individual. This may be brought about by a series of elementary chemical processes or by physical damage. In any case, the interesting problem involves a whole complex of processes which will require reaction rate theory as a chief tool in its solution. Considerable progress has already been made in applying rate theory to living cells.

The weathering of a building or a rock on a mountain is another complicated series of events. Here chemical processes of solution proceed along cracks, started by unequal heating and cooling, that are then enlarged by freezing and thawing. Again, we require our theory of elementary rate processes if we are to bring order out of chaos.

As a final somewhat complicated example, consider mountain building. Here, besides the wrinkling that is to be expected with the contraction accompanying solidification of a liquid, we require an explanation of why mountain building seems still to be continuing about as briskly as ever. Clearly, some heat engine is at work which requires a continuing supply of heat. We think we know that no chemical reactions could be supplying the amount of heat required, so we turn to radioactivity. The known radioactive decay in granite supplies roughly 5 calories/million years/gram. Since the specific heat is about 1/3 calorie/gram, this would mean a temperature rise of about 15 degrees/million years at depths where the heat loss by conduction is small. In the course of time, such rocks must melt and so expand about 10 percent with an almost irresistible force. Thus, either the overburden will move up or strata will be pushed sideways or invaded, or liquid will pour out onto the surface, whichever process is easiest. With the melting of sufficient rock, heat losses are stepped up owing to convection; such losses are increased also by the foundering of part of the overburden and by the liquid finding its way to the surface. These processes, when they get in full swing, will cool the mass faster than heat is supplied, and a period of solidification and subsidence sets in, only to be followed in time by remelting. Thus, we have almost endless cycles of uplift and subsidence wherever the radioactive "yeast" is present. Especially is this true in the deltas formed at the margins of

continents, which in due course rise to make mountainous continental margins. Thus one confidently anticipates that a great mountain chain will eventually rise from the sediments now depositing at the mouth of the Mississippi.

In the earth, radioactivity is concentrated in the acid crust, which forms the continents. This concentration may be due in part to chemical affinity. However, since radioactive material has the property of becoming heated, its surroundings as a result automatically become lighter and so move upward, to be finally captured with other light materials in the surface crust. Explosions such as those at Krakatoa are the natural result of overheating large volumes of gases, such as water, and the distillates from partially oxidized organic materials, such as CO_2, NH_3, and the hydrocarbons. As radioactivity slowly heats buried sediments, oil distilled from buried organic matter moves upward along porous strata, dissolving material as it goes, to be trapped in appropriately situated domes. In other places where the temperature gets high enough, as around the edges of batholiths, natural smelting occurs and ore deposits form. Joly, especially, has emphasized the role of radioactivity and isostasy in geology. Although his views have been criticized and although the criticisms are probably justified in part, still radioactivity must be the chief fuel in the engine warping the surface of the earth.

Finally, we come to the dilemma that challenges all who would understand the broader aspects of reaction rate theory. The second law of thermodynamics tells us that the entropy of the world always increases, and the result of reactions is to move ever closer to the final equilibrium. In this "heat death," life and all the changes that interest us will have ceased except for possible fluctuations from equilibrium. Reaction rate theory is a theory of the possible fluctuations of reacting molecules from equilibrium. A reaction occurs at a moderate rate if the activated state must acquire 40 times the average energy of an oscillator, as a fluctuation at equilibrium; but if it must acquire 2 or 3 times this energy, one must wait geologic ages for the fluctuation to happen. It thus becomes fantastically improbable to think of a hot sun and a relatively cool earth ever originating by simple fluctuations from a region at constant temperature.

On the other hand, if the expanding universe because of inertia expands too far, only then to reverse itself and contract too far, we have in the expanded state a system with great randomness and relatively low energy density, reverting after some billions of years to a state of great material and energy density, which will of necessity be a state also of great order. During the expanding phase spontaneous processes tend to decrease the order and increase the entropy, whereas during contraction the reverse will be true. In this view, the second law of thermodynamics is a consequence of living in the expanding phase of the cycle. During the contracting phase matter and energy seem to be pouring in toward the center from outer space, spontaneously assuming states of greater order. In this way impossible fluctuations become the comparatively orderly consequences of a cyclic process. In any case, we are much further from a complete understanding of how systems out of equilibrium arise than we are from understanding how they subsequently proceed toward equilibrium.