the formulas on the experience that they are to explain. Mathematical reasoning about experience must include, beside the antecedent non-mathematical finding and shaping of experience, the equally non-mathematical relating of mathematics to such experience and the eventual, also non-mathematical, understanding of experience elucidated by mathematical theory. It must also include ourselves, carrying out and committing ourselves to these non-mathematical acts of knowing. Hence a mathematical theory of the universe claiming to include its own bearing on experience would be selfcontradictory in the same sense as the conception of a tool would be if the tool were described as including its own user and the things to which it was to be applied.

Knowing is a process in two stages, the subsidiary and the focal, and these two can be defined only within the tacit act, which relies on the first for attending to the second. But again, why should this fact have been overlooked and a false ideal of science been perpetuated for centuries? Because the moment we admit that all knowing is rooted in an act of personal judgment, knowledge seems to lose all claim to objectivity. I have hinted at a way out of this difficulty by my definition of reality, and a substantial treatment of it has been given elsewhere. But the answer will yet have to be worked out fully in the future.

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The Transmission Coefficient in Reaction Rate Theory

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ALTHOUGH an equilibrium constant is defined when the particular reaction is specified, this is not true for either the forward or backward specific rates. Only the ratio is fixed and this equals the equilibrium constant. The mechanism leading to equilibrium often shifts with the conditions. Astronomy provides many examples of the effect of dilution on relaxation times. In our solar system the orbits of the planets, after billions of years, still cluster about the ecliptic. This is eloquent testimony of the rarity of collisions with other heavenly bodies. This example points up the fact that any useful statement of the ergodic hypothesis that strives to attach equal statistical weight to positions in phase space, having equal energies, must recognize a hierarchy of relaxation times. Regions of phase space connected by frequent transitions may be considered in equilibrium only when calculating much less frequent transitions. The rarity of collisions that disturb our solar system contrasts with the 10^{10} collisions per second which a molecule undergoes near atmospheric pressure. Almost every thousandth encounter at atmospheric pressure is a triple collision. This is important for the rate of recombination of atoms and radicals, since roughly a tenth of the triple collisions involving three hydrogen atoms abstract enough energy from a pair to leave it a stabilized molecule.[1,2]

In such a recombination, one of the three atoms may be replaced by any other molecule or by the wall, often with enhanced efficiency. If a molecule, or the wall, forms a complex with an atom, the percentage of collision between atoms involving a third body is increased proportionately. This speeds up the association reaction. At the very low hydrogen pressures of interstellar space, however, where radiation dissociates the hydrogen molecules, recombination of the atoms by a third-body collision is so infrequent that even stabilization by the emission of quadrupole radiation is faster. Whereas about one in 10^{13} collisions between pairs of hydrogen atoms is stabilized by quadrupole radiation, only one out of 10^{22} collisions will involve a third atom, at hydrogen concentrations of one atom per centimeter. Finally, of such three-body collisions, only about one in ten leads to molecule formation.

Catalysts likewise alter the course of reaction. Mixtures of hydrogen and oxygen, although thermodynamically unstable with respect to water, will

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[1] H. Eyring, H. Gershinowitz, and C. E. Sun, J. Chem. Phys. 3, 786 (1935).

[2] E. Wigner, J. Chem. Phys. 3, 720 (1937).

remain unreacted almost forever in a clean vessel, only to explode if a small amount of spongy platinum is added. Similarly, hydrogen and chlorine, while quite stable in the dark, will explode in sunlight because of reaction chains set up by chlorine atoms liberated in the photodecomposition of chlorine.

Marcellin[3] pointed out long ago that chemical reactions are transitions from the part of phase space corresponding to reactants to the part corresponding to products. It is simple enough, in principle, to separate out from all trajectories originating from reactants those leading to products. A summation over the number of successful trajectories per second is then the rate of reaction.

Reactions involving three hydrogen atoms are particularly useful illustrations of reaction kinetics both for their simplicity and for their historical interest. The actual construction of potential energy surfaces by Eyring and Polanyi,[4] using the approximate equation of London,[5] started a new cycle of development in reaction kinetics. Pelzer and Wigner[6] using this potential surface calculated the absolute rate of ortho–para conversion. Eyring[7] generalized the result to any system traversing a barrier, treating the activated complex as a normal molecule in its passage through the transition state except for a fourth translational degree of freedom. Polanyi and Evans[8] emphasized the thermodynamic properties of the transition state with special emphasis on the effect of pressure. Wynne-Jones and Eyring,[9] following Eyring's[7] earlier formulation, wrote the specific rate constant as

$$k' = \kappa(kT/h)K^{\ddagger}\,. \tag{1}$$

Here k' is a product of three factors: (1) an equilibrium constant $K^{\ddagger}$ between the reactants and the activated complex, (2) a recripocal lifetime kT/h of the activated complex, and (3) the transmission coefficient κ. Amusingly enough, the widely used symbol‡, designating the activated state, started as a star in the manuscript, became a plus-minus sign in the typescript, and ended as a double dagger in the published paper—a warning to slipping stars. The particular way of factoring the specific rate constant is a matter of convenience since only the specific rate constant itself is a fixed quantity. For certain reactions κ is the factor which corrects a classical calculation for the fact that trajectories traversing the transition state should be treated as wave packets rather than as particles. It is more useful to operationally define κ as the factor which corrects the model calculation of k' to the experimental value. With this definition, κ may be less than one if reflection at the barrier top is most important, or greater than one if barrier leakage is important. The importance of Eq. (1) is that in many cases κ is very close to unity, and even when this is not true, it is usually clear what has been neglected in the calculation.

Equation (1) applies to an elementary process for which crossing a single barrier is rate determining. The theory of chain reactions treats the complicated cases involving interconnected elementary steps. If the resistance to reaction is due to a series of steps, the over-all rate constant k' takes the form[10]

$$k' = (\textstyle\sum_i k_i^{-1})^{-1}\,. \tag{2}$$

Here each k_i is to be calculated as though the passage of reactants over the ith barrier were the only obstacle to reaction, i.e., as though the other barriers were not there. If k' is thought of as an over-all conductance with k_i being the conductance of the ith step in the series, then k_i^{-1} is the ith resistance. The resistances are seen to be additive, as is common for resistances in series. Equation (2) shows that n barriers of equal height, in series, will cut the rate down by a factor of n. The steps in the series considered in Eq. (2) may equally well be the successive quantum states in the activation and deactivation of a system passing over a potential barrier or the steps in any other random walk problem for that matter. If activation of a molecule occurs in steps, with the slowest step k_m at the top of the barrier, and with the activation free energy dropping off by an amount kT for each successive step in each direction, then from Eq. (2) one obtains

$$\begin{aligned} k' &= k_m[1 + 2(e^{-1} + e^{-2} + \cdots)]^{-1} \\ &= k_m[2(1 - e^{-1}) - 1]^{-1} = 0.46k_m\,. \end{aligned} \tag{3}$$

The factor 0.46 may be thought of as a transmission coefficient for this case. Multiple jumps complicate the situation and are discussed elsewhere.

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[3] A. Marcellin, Ann. Phys. **3**, 158 (1915).

[4] H. Eyring and M. Polanyi, Z. physik. Chem. **B12**, 279 (1931).

[5] F. London, *Sommerfeld Festshrift* (S. Hirzel, Liepzig, Germany 1928), p. 104.

[6] H. Pelzer and E. Wigner, Z. physik. Chem. **B15**, 445 (1932).

[7] H. Eyring, J. Chem. Phys. **3**, 107 (1935).

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

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

[10] R. B. Parlin and H. Eyring, in *Ion Transport Across Membranes*, edited by H. T. Clarke (Academic Press Inc., New York 1954), p. 103.

The current density of diffusing matter Q can be written as

$$Q = (\lambda_0 a_0 - \lambda_n a_n)\left(\sum_{i=0}^{n-1} k_i^{-1}\right)^{-1} . \tag{4}$$

Here the λ's are the distances between successive barriers, while the a's give the activities. Thus, $\lambda_0 a_0$ is the effective number of molecules per square centimeter of cross sections lying between the barriers in front of and behind the zeroth position, with a similar significance for the final state $\lambda_n a_n$. In writing Eqs. (2) and (4), it has been tacitly assumed that the activated complex, in flowing systems, is a function of position but not of the direction of crossing the barrier. Such an assumption is implicit in irreversible thermodynamics that takes no explicit account of the activated state. Further investigation of this point might well proceed from Eq. (7) of a paper by Parlin and Eyring.[10] This latter paper applies transition state theory to nerve conductance.

The effect of all sorts of gradients, such as temperature gradients in the Soret effect, electrical potentials in electrode processes, and in nerve conduction, etc., can be treated by using Eq. (4) if one introduces the appropriate local properties, in the expressions for the normal and activated states as they occur in the rate constant and activities.

Smelting, which reverses corrosion, is somewhat less obviously an electrolytic process than is corrosion.[11,12] At around 1500°C, where molten slag overlies molten iron, the oxygen ions in the slag diffuse across the interface to react with the carbon dissolved in the iron, liberating CO gas and electrons, which attach themselves to the metal. The resulting steady-state potential is superposed on other interfacial gradients to drive various ions into or out of the metal bath as conditions are varied. Using Eq. (4) for the various ion currents across the interface, striking agreement with experiment is obtained.[12]

The evaporation and condensation of liquids are processes which may be thought of as unimolecular decompositions and association reactions, respectively. When a vapor molecule condenses on its own liquid surface a vapor molecule disappears and one more bulk liquid molecule appears. There is accordingly substantially no increase in the number of surface molecules since as one molecule condenses on the surface the molecule just beneath it which was previously a surface molecule is now buried and becomes a bulk molecule. The number of vapor molecules hitting a square centimeter of liquid per second is $p/(2\pi mkT)^{1/2}$ and if the fraction s stick, the rate of condensation in molecules per cm^2 per second $\dot{n}$ is

$$\dot{n} = sp(2\pi mkT)^{1/2} . \tag{5}$$

If one supposes that the activated complex must have the rotational partition function of the bulk liquid in order to be able to stick we have

$$s = f_{rl}/f_{rv} . \tag{6}$$

Here f_{rl} and f_{rv} are the rotational partition functions of liquid and vapor, respectively. Equation (6) gives general agreement with experiment for liquids in all known cases.[13–15] For normal liquids obeying Trouton's rule, $s = 1$, and for hydrogen-bonded liquids s may drop to the order of hundredths. On the other hand, nearly every nitrogen molecule striking a tungsten wire loses enough energy to become weakly adsorbed, temporarily. Afterwards, there is a competition between desorption and getting molecularly or atomically adsorbed.[16–17] In this case, the weak temporary compound formed may allow the molecule to continue rotating, even though these weakly adsorbed molecules may eventually pass over into more tightly bound states. In association reactions involving the combination of two methyl radicals, for example, association occurs while both radicals are still rotating freely, whereas for two NO_2 groups to combine, the rotation of the separate groups must be considerably restricted.[18] Even though it would be difficult to anticipate the exact degree of restriction on the rotation of radicals in activated complexes for association reactions, there are reactions for which the rotational properties of the radicals approach the freedom of the dissociated state and others where the restrictions approach those for the associated state.[18] The more polar the reactants, the more severe are the restrictions on free rotation in the activated complex, paralleling the disappearance of free rotation in hydrogen-bonded liquids. In the example discussed, as well as in many others, it has been possible to calculate specific reaction rate con-

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[11] T. B. King and S. Ramachandran, in *The Physical Chemistry of Steel Making*, edited by J. F. Elliott, (John Wiley & Sons, Inc., New York 1958), p. 125.

[12] X. deHemptinne, H. Eyring, and T. Ree, in *Physical Chemistry of Process Metallurgy*, edited by G. R. St. Pierre (Interscience Publishers, Inc., New York, 1961), Part I, Vol. 7, p. 69.

[13] G. Wyllie, Proc. Roy. Soc. (London) **A197**, 383 (1949).

[14] E. M. Mortensen and H. Eyring, J. Phys. Chem. **64**, 846 (1960).

[15] W. J. Heideger and M. Boudart, Chem. Eng. Sci. **17**, 1 (1962).

[16] G. Ehrlich, J. Chem. Phys. **34**, 39 (1960).

[17] F. M. Wanlass, Ph.D. Thesis (1962) University of Utah (unpublished).

[18] T. S. Ree, T. Ree, H. Eyring, and T. Fueno, J. Chem. Phys. **36**, 281 (1962).

stants in close agreement with experiment. The remaining discrepancies may include factors in the neighborhood of 1/2 for activation–deactivation steps. The viscous flow of liquids apparently involves a transmission coefficient of about 0.4, since the calculated fluidity exceeds the observed value by about this factor.[19] The viscosity calculation is based on the significant structure theory of liquids.[20] In this theory the liquid is considered to be a solid in which vacancies in addition to conferring degeneracy on the solid-like molecules move through the liquid in the same way that molecules move in the vapor. This motion of vacancies reflects the gas-like properties of the molecule which jumps into the vacancy. It is then shown[20] that there is the fraction V_s/V of solid-like molecules with the rest gas-like. Here V_s and V are the volume of a mole of solid and of liquid, respectively. The viscosity of the liquid η_l is then

$$\eta_l = (V_s/V)\eta_s + (1 - V_s/V)\eta_g \tag{7}$$

where η_s and η_g are solid-like and gas-like viscosities, respectively. The formula for gas-like viscosity η_g is well known. Solid-like viscosity may be understood in terms of a model. The material above a shear plane can be thought of as an elastic body resting on the molecules that form the upper side of this shear plane, much as if these molecules were the feet of the plastic body. Each foot is nesting in a potential well formed by the molecules below the shear plane. When a shear stress urges the elastic body forward, the feet move slightly more frequently into vacancies in the forward direction than in the backward direction, resulting in shear along the shear plane. The total motion of the system is compounded of all such motions along shear planes. Since the significant structure theory predicts the number of vacancies while transition state theory predicts the frequency of jumps into vacancies the only unknown is the likelihood that a foot when once advanced into a vacancy will be stabilized in this position and not return to the original state. If this likelihood of stabilization is estimated as constant and equal to 0.4 over the liquid range there is excellent agreement between the observed and calculated viscosity.[19]

Transition state theory has been an extremely powerful tool in systemitizing organic reactions and it has been equally useful in interpreting solid state physics as well as biology.[21] Each area poses its own problems as to the exact nature of the mechanism involved. However, the concept of an activated complex in equilibrium with reactants traversing a transition state is an enormous simplification over efforts to find all the successful trajectories between initial and final state afterward counting the number of these occurring per second to get the reaction rate. Both procedures are useful. When the gateway between reactants and products is not a transition state only some version of the method of trajectories is available.

It has been a pleasure to review briefly a few of the developments in a theory which owes so much to Professor Wigner.

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[19] T. S. Ree, T. Ree, and H. Eyring, Proc. Natl. Acad. Sci. U. S. **48**, 501 (1962).

[20] H. Eyring, T. Ree, Proc. Natl. Acad. Sci. U. S. **47**, 526 (1961).

[21] F. H. Johnson, H. Eyring, and M. J. Polissar, *The Kinetic Basis of Molecular Biology* (John Wiley & Sons, Inc., New York 1954).