The Foundations of Reaction Rate Theory
and Some Recent Applications

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Henry Eyring was born in Chihuahua, Mexico, in 1901. He obtained degrees in Mining Engineering and Metallurgical Engineering in 1923–24 from the University of Arizona. In 1924–25 he was an instructor in chemistry at the University of Arizona. He then attended the University of California at Berkeley, where he received a Ph.D. in chemistry in 1927. At the University of Wisconsin he was instructor of chemistry from 1927–28 and research associate from 1928–29. In 1929–30 he attended the Kaiser-Wilhelm Institute in Berlin as a National Research Fellow. He then lectured in chemistry at the University of California. In 1931 he joined the Department of Chemistry at Princeton University, where he remained until August, 1946. From 1944 to 1946 he was Director of the Textile Foundation. During World War II he did research work for the Army, Navy and OSRD on the theory of smokes and the theory of high explosives. In September, 1946, he became Dean of the Graduate School and Professor of Chemistry at the University of Utah.

Dr. Eyring's fields of specialization include radioactivity, the application of quantum mechanics to chemistry, the theory of reaction rates, and the theory of liquids. He has published about 150 papers and various chapters in chemistry books, and is co-author with Glasstone and Laidler of "The Theory of Rate Processes" (1941) and with Walter and Kimball of "Quantum Chemistry" (1944). Dr. Eyring has held numerous offices in national scientific societies. He is a member of the National Academy of Sciences, the New York Academy of Sciences, the American Philosophical Society, The American Association for the Advancement of Science, the Textile Research Institute, Sigma Xi, and the Utah Academy of Sciences, Arts and Letters.

The Foundations of Reaction Rate Theory and Some Recent Applications

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THOUGH philosophers for centuries were conscious of the importance of the universal variable time in the interpretation of nature, it was barely a century ago that this factor was properly taken into consideration in a series of physical measurements on a reacting system, thus marking the birth of the field of chemical kinetics. Forty years passed by without any very significant contributions to the development of kinetics. This period came to a close in 1889, when Arrhenius (1) laid the foundation for the collision theory of chemical reactions, and set the scene for the modern development of rate theory. He proposed that an equilibrium existed between normal and activated molecules, and the variation of the specific rate of reaction with temperature could be expressed by the formula

$$k = Ae^{-E/RT} \qquad (1)$$

This equation correctly represents the temperature dependence not only of most chemical reactions, but also of certain physical processes.

McC. Lewis (2), Hinshelwood (3) and others set the constant A in Arrhenius' reaction isochore for bimolecular reactions equal to the number of collisions. This served as an excellent guide in correlating and furthering our knowledge of chemical changes. Wherever it was found possible to consider the reacting molecules as hard spherical particles the collision theory admirably interpreted the experimental data. As

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further data were accumulated on reacting systems involving more complex molecules it was found necessary to introduce empirical probability or steric factors into the collision-theory expressions for the specific rate of reaction to obtain agreement with experiment. All efforts expended on improving the collision theory only further emphasized its limitations and the need that existed for a new approach to the problem of reaction rates.

A new attack on the problem of the calculation of rates of chemical reactions from first principles utilizing the fundamental properties and molecular constants of the reacting molecules was afforded by the development of quantum mechanics. In 1928, F. London (4) indicated how the methods of quantum mechanics could be employed in calculating the energy of activation of chemical reactions which are termed "adiabatic," in the sense that they do not involve electronic transitions and occur on the same potential energy surface. He developed an equation based on certain approximations showing how the potential energy of a system of three or four atoms with s electrons varied with interatomic distances. This theoretical treatment of the fundamental quantity, the energy of activation, provided new impetus to an attack on the rates of chemical changes. The usefulness of this equation in constructing potential energy surfaces for the interpretation of chemical reactions was developed and extended by H. Eyring and M. Polanyi (5). Since

the London equation even in its approximate form involves quantities which can be completely evaluated only for the simplest system consisting of hydrogen atoms, they considered approximate solutions which led to the "semi-empirical" method for the calculation of the energy of activation. Fundamental contributions came from many sources on the calculation of the absolute reaction rates which are summarized in a recent text (6). A general formulation of the theory of absolute rates of reaction dealing with the calculation of the frequency factor and applicable to any rate process was given by H. Eyring in 1935 (7). A similar treatment was presented by M. Polanyi and M. G. Evans (8) which is sometimes referred to as the transition state method. Both extended an earlier paper of Pelzer and Wigner (9). Briefly, we present the essential points and assumptions of the theory of absolute rates of reaction.

A chemical reaction and many physical changes with time are characterized by an initial configuration which by a continuous change of coördinates passes into a final configuration. For each process, there is an intermediate or critical configuration called the "activated complex" or "transition state," situated at the highest point of the most favorable reaction path on the potential energy surface. If a molecule reaches this critical point in a certain region of phase space, there is a high probability that a reaction will occur. The activated configuration is like an ordinary molecule with the usual thermodynamic properties except that it possesses an extra degree of translational freedom along the direction of the reaction coördinate. By assuming an equilib-

rium to exist between the initial and the activated state, the specific rate of a reaction can be determined by calculating the concentration of the activated complexes and their rate of passage across the potential barrier or saddle point of the potential energy surface, by using statistical methods.

Consider a process in which the rate is determined by the passage over a potential barrier and quantum-mechanical tunneling effects can be disregarded, then

$$\text{Rate of reaction } v = \kappa C'^{\pm} \frac{\bar{v}}{\delta} \qquad (2)$$

where $C'^{\pm}$ is the concentration of activated complexes per unit volume and the ratio $\bar{v}/\delta$ is the mean velocity of crossing in one direction divided by a length δ of the activated state. Thus $\bar{v}/\delta$ represents the frequency of emptying the length of path δ of activated complexes. The factor κ, the transmission coefficient, is the factor introduced to take care of the possibility that not all the activated complexes reach the final state. For most reactions it is sensibly equal to unity. Treating the activated complexes as normal molecules by replacing the metastable degrees of vibrational freedom by translational motion along the reaction coördinate, we find

$$C'^{\pm} = C^{\pm} \frac{(2\pi m^{\pm} kT)^{1/2}}{h} \delta.$$

In addition, the mean velocity $\bar{v} = (kT/2\pi m^{\pm})^{1/2}$, so that Eq. (2) becomes

$$v = \kappa C^{\pm} \frac{kT}{h}. \qquad (3)$$

Accepting the hypothesis of an equilibrium between the initial reactants A and B and the activated state, we have for the velocity of a bimolecular reaction

$$\kappa C_A C_B \frac{kT}{h} K^{\ddagger},$$

and in general we obtain for the specific reaction rate of any order:

$$k' = \kappa \frac{kT}{h} K^{\ddagger}. \tag{4}$$

Applying a thermodynamic formulation, by relating the constant $K^{\ddagger}$ to $\Delta F^{\ddagger}$, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, the standard free-energy, heat-content and entropy changes for formation of the activated state, we may express Eq. (4)

$$k' = \kappa \frac{kT}{h} e^{-\Delta F^{\ddagger}/RT}$$

$$= \kappa \frac{kT}{h} e^{\Delta S^{\ddagger}/R} e^{-\Delta H^{\ddagger}/RT}. \tag{5}$$

In terms of partition functions, Eq. (4) reads

$$k' = \kappa \frac{kT}{h} \frac{F^{\ddagger}}{F_A F_B} e^{-E_0/RT}, \tag{6}$$

where E_0 is the energy of activation at the absolute zero temperature.

If we are concerned with non-conservative systems, the Eq. (6) is readily extended to include the effect of an applied external force. Consider an applied force to have a component f along the reaction path. If this force acts across a symmetrical barrier through a distance $\lambda/2$ from the normal to the activated state, the free energy of activation $\Delta F^{\ddagger}$ in the absence of the external force will be decreased by an amount $(\lambda/2)$. The specific rate of the forward reaction in the presence of the applied force will be

$$k_f' = \kappa \frac{kT}{h} e^{-\frac{\Delta F^{\ddagger} - \frac{Nf\lambda}{2}}{RT}}$$

$$= k_0 e^{f\lambda/2kT}, \tag{7}$$

where k_0 is the specific rate in the absence of the external force and N

is Avogadro's number. Similarly for the reverse process, we have

$$k_b' = k_0 e^{-f\lambda/2kT}, \tag{8}$$

giving for the net rate

$$k' = k_f' - k_b' = k_0 (e^{f\lambda/2kT} - e^{-f\lambda/2kT}) =$$
$$2k_0 \sin h \frac{f\lambda}{2kT} \tag{9}$$

A wide variety of physical processes including viscosity, plasticity, diffusion, electrochemical phenomena, creep in metals and high polymeric substances are readily interpreted by modifications of Eq. (9) (6).

The Non-Equilibrium Theory of Absolute Rates of Reaction

In the above formulation of a rate theory which is applicable to any process in which the rearrangement of matter involves surmounting a potential barrier, the tunneling effect was disregarded. Though for the majority of chemical reactions which do not involve a transfer of electrons this effect is negligible, we have to take the barrier penetration into consideration when dealing with the decomposition of N_2O or the inversion of ammonia (10). If the potential barrier is nearly flat, the velocity of reaction is corrected for penetration or tunneling effects by multiplying the specific rate constant by the factor due to Wigner (11), $\left(1 - \frac{1}{24}\left(\frac{h\nu_n}{kT}\right)^2\right)$, where ν_n is the imaginary value of the stretching vibration along the coördinate of decomposition. The leakage effect is generally small and can usually be neglected without serious error. The other point which requires further consideration is the appearance of the probability factor $e^{-E_0/RT}$ in the rate expressions, where E_0 is the difference in the residual or zero-point energies of the

initial and the activated state. It arises from our basic assumption that an equilibrium exists between the normal and the activated states which is not disturbed to any extent during the course of the rate process. The validity of this assumption will now be examined as tantamount to a complete formulation of the theory of absolute rates of reaction.

The applicability of equilibrium theory to chemical reactions was first suggested by Arrhenius. This hypothesis was discussed by Marcelin (12), who expressed the opinion that for measurable reactions occurring under normal conditions of temperature and pressure the assumption is correct. Further discussions of this matter were given by Wynne-Jones and Eyring (13) and also by Guggenheim and Weiss (14). The equilibrium postulate underlies every proposed theory of reaction rates. The success of the crude collision theory and more so of the theory of absolute rates, which closely interprets many diversified physical phenomena, is strong evidence for the correctness of the equilibrium hypothesis. All this, however, is *a posteriori* evidence that an adequate supply of energetic or activated molecules is maintained during all stages of the reaction, and more direct quantitative reasoning is desired. Our present knowledge of chemical dynamics is not sufficiently advanced to investigate in detail the individual collision processes which give rise to an infinite variety of energetic molecules and to determine what fraction of these fortuitously propitious collisions determines the concentration of the activated state. An ingenious approach to this complex problem was made by H. A. Kramers (15). To elucidate the applicability of the absolute

rate theory for calculating the velocity of chemical reactions he considered the effect of Brownian motion on the probability of escape of a particle (caught in a potential well) over a potential barrier. Kramers' results indicated that the theory of absolute rates of reaction gives results correct within 10% over a wide range of viscosity values. In his method of investigation the classical mechanical diffusion theory was employed, so it is of interest to take into account the quantized nature of molecular levels. This has been done in a recent investigation (16) of the non-equilibrium theory of absolute rates of reaction, wherein results were obtained essentially in agreement with Kramers' calculations.

Consider reactants passing by a series of propitious molecular collisions from a set of energy levels to a subsequent set of levels corresponding to the final states of the products. It will be assumed that values for the specific rates of transition k_{ij} from level i to level j are known, which in principle at least are calculable from the quantum-mechanical theory of collisions (17). Restricting ourselves to reactions in which we can neglect the concentration changes in all species except A and designating the number in the ith level by A_i, we have the following set of n rate equations

$$\frac{dA_i}{dt} = \sum_{j \neq i} (k_{ji} A_j - k_{ij} A_i) \quad (10)$$

corresponding to the n possible energy levels of the reactants and products taken as one. Degenerate levels, like other levels, each carry a separate subscript. In each equation of the set (10), the summation

extends over all n values except i. The solution is readily obtained for the set of linear differential equations with constant coefficients.

Let us try the solutions $A_i = B_i e^{bt}$ where B_i is a constant, b is the characteristic parameter, and t is the time. Substituting in Eq. (10), we obtain the simultaneous set of homogeneous algebraic equations

$$\sum_{j \neq i} [k_{ji}B_j - (k_{ij} + b)B_i] = 0. \quad (11)$$

Solving for the B_i's, we have specifically for the constant B_1,

$$B_1 = \frac{\begin{vmatrix} 0 \, k_{21}k_{31} \cdots\cdots\cdots\cdots k_{n1} \\ \cdots\cdots\cdots\cdots\cdots\cdots \\ 0 \, k_{2n}k_{3n} \qquad -\sum_{i \neq j}(k_{ni} + b) \\ \end{vmatrix}}{\begin{vmatrix} -\sum_{i \neq j}(k_{ji} + b)k_{21}\cdots\cdots k_{n1} \\ \cdots\cdots\cdots\cdots\cdots\cdots \\ k_{1n}k_{2n} \qquad -\sum_{i \neq j}(k_{ni} + b) \\ \end{vmatrix}} \quad (12)$$

Aside from the trivial solution $B_1 = B_2 = \ldots = B_n = 0$, a solution for non-zero values of the B_i's exists only if the characteristic determinant, that is, the denominator of (12), is set equal to zero. With this equal to zero, the n values of the characteristic parameter b may be found by substituting values for the transition constants k_{ij} and solving the nth order determinant. By substituting the determined value of the kth root b_k into Eq. (11) in the usual way, one is led to the solutions $B_{jk} = G_k C_{jk}$, where for each j and k one obtains a numerical value for C_{jk}, and G_k is the same arbitrary constant for all j's. Summing all the particular integrals, the general solution of (10) is

$$A_i = \sum_{k=1}^{n} B_{ik}e^{b_k t} = \sum_{k=1}^{n} G_k C_{ik}e^{b_k t} \quad (13)$$

In (13) the values of C_{ik} and b_k are known, and by putting $t = 0$ and the A_i's equal to their initial concentrations, the arbitrary constants are readily calculated. Each A_i thus becomes a completely determined function of time.

The applicability of the general procedure outlined above will be shown in a specific case. The following simple model was chosen in which the initial state was considered to consist of levels 1 and 2 and the final state of levels 3 and 4, with 4 designated as the level of lowest energy. This case corresponds to $n = 4$ in the general expressions given above. The rate equations are

$$\frac{dA_1}{dt} = -\sum_{j \neq 1}^{4} k_{1j}A_1 + k_{21}A_2 + k_{31}A_3 + k_{41}A_4$$

$$\frac{dA_2}{dt} = k_{12}A_1 - \sum_{j \neq 2}^{4} k_{2j}A_2 + k_{32}A_3 + k_{42}A_4$$

$$\frac{dA_3}{dt} = k_{13}A_1 + k_{23}A_2 - \sum_{j \neq 3}^{4} k_{3j}A_3 + k_{43}A_4$$

$$\frac{dA_4}{dt} = k_{14}A_1 + k_{24}A_2 + k_{34}A_3 - \sum_{j \neq 4}^{4} k_{4j}A_4. \quad (14)$$

Proceeding according to the general method outlined for the case of n levels, the particular solutions are assumed to take the form

$$A_i = B_i e^{bt} \quad (i = 1, \ldots, 4). \quad (15)$$

To make possible a solution of the characteristic 4th order determinant for the parameter b and, subsequently, to obtain values for the

constants $B_1, \ldots, B_4$, certain assumptions have to be made with reference to the $n(n-1) = 12$ reaction rate constants and proper values chosen to represent their magnitudes. If we assume that a molecule in the activated state has the same probability for decomposition along the reaction coördinate to any level of the final state, then for the forward process $k_{13} = k_{14}$ and $k_{23} = k_{24}$. Similarly for the reverse process, $k_{41} = k_{42}$ and $k_{32} = k_{31}$. If in addition we limit ourselves to reacting systems of small heats of reaction, so that the energies of the respective molecular levels in the initial and final state are approximately the same, and combine the resulting relations between the k_{ij}'s with those based on the first assumption, the following set of relations is found to exist between the twelve specific reaction rate constants of the system:

$$k_{13} = k_{14} = k_{41} = k_{42}$$
$$k_{23} = k_{32} = k_{24} = k_{31}$$
$$k_{12} = k_{43}; \quad k_{21} = k_{34}$$

The second assumption implies further that the transmission coefficients of the specific rate constants with reference to a similar pair of transitions, as, for example, k_{23} or k_{32} or k_{12} and k_{43}, are approximately equal. On the basis of the above assumptions for the k_{ij}'s, the characteristic 4th order determinant is readily diagonalized to yield expressions for the parameter b in terms of the four determining rate constants k_{12}, k_{13}, k_{21} and k_{23}. Choosing the following plausible values for the k_{ij}'s,

$$k_{12} = 0.01 \quad k_{23} = 0.1$$
$$k_{21} = 1 \quad k_{13} = 0.001$$

the quantities b_k and C_{jk} have been calculated and are given in Table 1. With the particular integrals of Eq. (15) fully determined, it is only

TABLE 1

k	C_{1k}	C_{2k}	C_{3k}	C_{4k}
0	1	0.01	0.01	1
-1.306	-1	1.437	-1.437	1
-1.111	1	-1	-1	1
-6.737 $\times 10^{-3}$	-1	-6.959 $\times 10^{-3}$	6.959 $\times 10^{-3}$	1

necessary to specify the supplementary conditions when $t = 0$, and evaluate the arbitrary constants $G_1, \ldots, G_4$ to permit us to obtain the explicit expressions as to how the population in the four levels varies with time of reaction. We will then be able to compare the rates of reaction under equilibrium and non-equilibrium conditions.

Introducing the arbitrary constants, the general solution of our simple four-level system is

$$A_1 = G_1 e^{b_1 t} - G_2 e^{b_2 t} + G_3 e^{b_3 t} - G_4 e^{b_4 t}$$
$$A_2 = G_1 \times 10^{-2} e^{b_1 t} + 1.437 G_2 e^{b_2 t} - G_3 e^{b_3 t} - 6.959 G_4 \times 10^{-3} e^{b_4 t}$$
$$A_3 = G_1 \times 10^{-2} e^{b_1 t} - 1.437 G_2 e^{b_2 t} - G_3 e^{b_3 t} + 6.595 G_4 \times 10^{-3} e^{b_4 t}$$
$$A_4 = G_1 e^{b_1 t} + G_2 e^{b_2 t} + G_3 e^{b_3 t} + G_4 e^{b_4 t}$$
$$(16)$$

where: $b_1 = 0$, $b_2 = -1.306$, $b_3 = -1.111$, $b_4 = -6.737 \times 10^{-3}$. By specifying the supplementary initial conditions (i. e., when $t = 0$) for the cases of equilibrium and non-equilibrium, the arbitrary constants of the respective general solutions are calculable. Under equilibrium conditions, the equilibrium concentrations of the various species A_i defined as $n_1, \ldots, n_4$ are

$$n_i = \frac{D e^{-\epsilon_i / kT}}{\sum\limits_{j=1}^{4} e^{-\epsilon_j / kT}} \quad (17)$$

where D is the total concentration of the molecules A in the system and

the statistical weights w_i for all levels are taken to be equal. From the principle of detailed balance, we may write that $k_{ij} = k_{ji}e^{-\epsilon_{ji}/kT}$ where $\epsilon_{ji} = \epsilon_j - \epsilon_i$, so that Eq. (17) is equally well written:

$$n_i = \frac{D}{\sum\limits_{j=1}^{4} \dfrac{k_{ij}}{k_{ji}}} \quad (i = 1, \ldots, 4). \quad (18)$$

This represents the supplementary conditions for the equilibrium case. For the non-equilibrium case, it is assumed that the concentration in the lowest level of the initial state (level 1) is at its equilibrium value and the concentrations of the species A in all the remaining levels of the initial and final states are zero; thus the supplementary conditions for the chosen non-equilibrium case when $t=0$ are that $A_1=D/2.02$ and $A_2=A_3=A_4=0$. The value for A_1 was obtained by substituting the chosen values for the rate constants k_{ij} into Eq. (18), the expression for the equilibrium concentration. The respective arbitrary constants for the two cases considered have been calculated and are summarized in Table 2. Substituting these

<center>TABLE 2</center>

G_k	Equilibrium	Non-Equilibrium
G_1	$D/2.02$	$0.2451D$
G_2	0	$-1.193 \times 10^{-3}D$
G_3	0	$0.2451 \times 10^{-2}D$
G_4	0	$-0.2463D$

values into the general expression given in Eq. (16), the general solution for the case of equilibrium is simply

$$A_1 = \frac{1}{2.02} D$$

$$A_2 = \frac{1}{2.02} \times 10^{-2}D$$

$$A_3 = \frac{1}{2.02} \times 10^{-2}D$$

$$A_4 = \frac{1}{2.02} D, \quad (19)$$

where the concentrations in the various levels are constant. Proceeding similarly for the case of non-equilibrium, the general solution is,

$$A_1 = D[0.2451e^{b_1t} + 1.193 \times 10^{-3}e^{b_2t} + 2.451 \times 10^{-3}e^{b_3t} + 0.2463e^{b_4t}]$$
$$A_2 = D \times 10^{-2}[0.2451e^{b_1t} - 0.1714e^{b_2t} - 0.2451e^{b_3t} + 0.1714e^{b_4t}]$$
$$A_3 = D \times 10^{-2}[0.2451e^{b_1t} + 0.1714e^{b_2t} - 0.2451e^{b_3t} - 0.1714e^{b_4t}]$$
$$A_4 = D[0.2451e^{b_1t} - 1.193 \times 10^{-3}e^{b_2t} + 2.451 \times 10^{-3}e^{b_3t} - 0.2463e^{b_4t}]$$
$$(20)$$

where: $b_1 = 0$, $b_2 = -1.306$, $b_3 = -1.111$, $b_4 = -6.737 \times 10^{-3}$.

To test the soundness of the equilibrium postulate of the activated complex theory of rate processes, it is required to show to what extent the equilibrium between initial levels is disturbed, as molecules from the activated state rearrange or decompose into the products of the final state. This is best demonstrated by formulating an expression for the ratio of the actual rate to the equilibrium rate for the process, and calculating the variation of this ratio Γ with the amount of the substance that has reacted. The effect of transitions between levels of the initial state is taken into consideration in our expressions for the concentrations A_1 and A_2 as given by Eq. (20). The actual velocity of the forward reaction is then

$$v_a = (k_{13} + k_{14})A_1 + (k_{23} + k_{24})A_2. \quad (21)$$

To calculate the rate of reaction by the theory of absolute rates of reaction, the basic assumption is made that the population of the levels in the initial state for the reacting species A is determined by the

Maxwell-Boltzmann distribution function. Referring to this velocity as the "equilibrium" rate v_e for the forward process, we have

$$v_e = (k_{13} + k_{14})(A_1 + A_2)\frac{e^{-\epsilon_1/kT}}{\sum\limits_{i=1}^{2} e^{-\epsilon_i/kT}} +$$

$$(k_{23} + k_{24})(A_1 + A_2)\frac{e^{-\epsilon_2/kT}}{\sum\limits_{i=1}^{2'}e^{-\epsilon_i/kT}}, \quad (22)$$

where (A_1+A_2) is the total concentration of the substance A in the initial state. Hence, from Eqs. (21) and (22) the ratio Γ of the actual rate to the equilibrium rate is

$$\Gamma = \frac{v_a}{v_e} = \frac{(k_{13} + k_{14})N_1 + (k_{23} + k_{24})N_2}{(k_{13} + k_{14})\dfrac{e^{-\epsilon_1/kT}}{\sum\limits_{i=1}^{2} e^{-\epsilon_i/kT}} + (k_{23} + k_{24})\dfrac{e^{-\epsilon_2/kT}}{\sum\limits_{i=1}^{2} e^{-\epsilon_i/kT}}}, \quad (23)$$

where $N_1 = A_1/A_1 + A_2$ and $N_2 = A_2/A_1 + A_2$ are the mole fractions with reference to the initial state.

Expressions for the mole fractions N_1 and N_2 as completely determined functions of time are readily obtainable from the general solution in Eq. (20). Thermodynamically, the ratio of rate constants is

$$\frac{k_{23} + k_{24}}{k_{13} + k_{14}} = e^{-\epsilon_{21}/kT}, \quad (24)$$

where $\epsilon_{21} = \epsilon_2 - \epsilon_1$, providing that the transmission coefficients of the various rate constants are the same, which is equivalent to the assumption made in solving the secular determinant for the characteristic parameter b. There, the hypothesis was made that the probability for the decomposition of the activated complex into any level of the final state is the same. Making use of the above relation and simplifying the

Maxwell-Boltzmann probability factors, we arrive at the expression

$$\Gamma = \frac{N_1 + N_2 e^{\epsilon_{21}/kT}}{\dfrac{1}{1 + e^{-\epsilon_{21}/kT}} + \dfrac{e^{\epsilon_{21}/kT}}{1 + e^{\epsilon_{21}/kT}}} =$$

$$\tfrac{1}{2}[N_1 + N_2 e^{\epsilon_{21}/kT}](1 + e^{-\epsilon_{21}/kT}). \quad (25)$$

From the principle of detailed balance, we can substitute for $e^{-\epsilon_{21}/kT}$ the ratio of rate constants k_{12}/k_{21} and obtain

$$\Gamma = \frac{1}{2}\left[N_1 + N_2\frac{k_{21}}{k_{12}}\right]\left(1 + \frac{k_{12}}{k_{21}}\right), \quad (26)$$

which on substituting our chosen values for $k_{12}=0.01$ and $k_{21}=1$ reduces to

$$\Gamma = 0.505[N_1 + 100N_2]. \quad (27)$$

Thus, an expression is available for determining the correctness of the equilibrium theory of absolute rates of reaction. Using the analytical expressions for the mole fractions N_1 and N_2 as determined from the general solution in Eq. (20), the complete expression for the ratio of the actual rate of reaction to the equilibrium rate is given by

$$\Gamma = 0.505\frac{[0.4902 - 0.1702e^{-1.306t} - 0.2426e^{-1.111t} + 0.4177e^{-6.737 \times 10^{-3}t}]}{[0.2476 - 5.212 \times 10^{-4}e^{-1.306t} + 0.2480e^{-6.737 \times 10^{-3}t}]}. \quad (28)$$

We considered the case where the four-level system starts with molecules only in state one, all other states being empty. To test the validity of the equilibrium postulate of rate theory on the basis of our simple model, we calculate how the velocity ratio Γ deviates from its theoretical equilibrium value of unity with the extent of reaction as determined in this specific case by
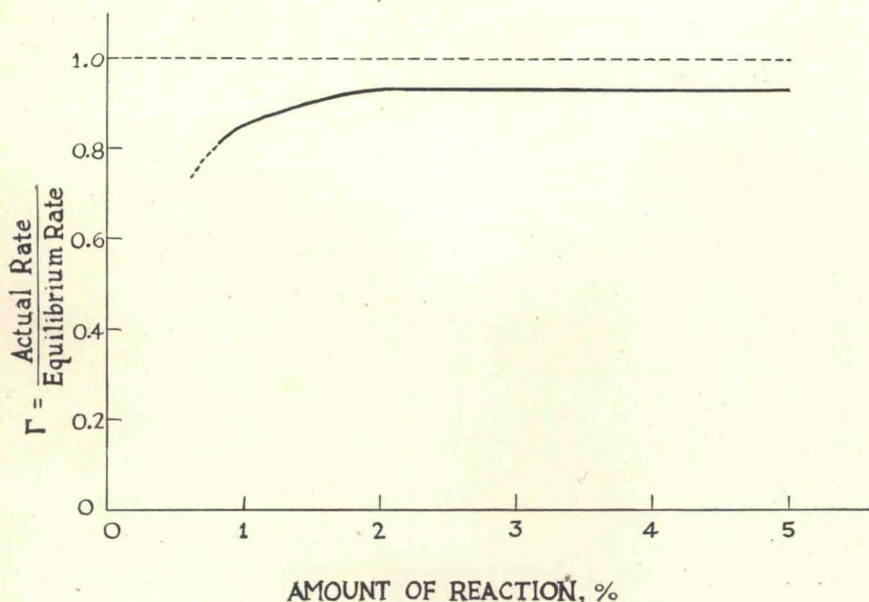
AMOUNT OF REACTION, %

FIGURE 1

the concentration of substance A in level 1 of the initial state. Employing Eq. (28), the variation of the velocity ratio Γ with the concentration A_1 is plotted in Fig. 1. The calculations are summarized in Table 3.

The magnitude of the variation of the function Γ is of extreme interest, even though the calculations are based on an extremely simple model. The maximum deviation of approximately 20% in the velocity ratio at the beginning of the reaction represents the over-all error to be expected in the specific rate constant as determined by the theory of absolute rates of reaction. Inasmuch as the calculations were carried out on a simple four-level system under drastic conditions of nonequilibrium, the results are most gratifying. In practice, the conditions for rapid restoration of equilibrium concentrations in the

activated state will be aided by the multitudinous number of energy levels in any reacting molecular system.

The extent to which the specific rate constants between non-adjacent energy levels affect the equilibrium between the normal and activated state has also been determined (16). The same four-level system was considered with the exception that zero values were assigned to all specific rate constants between non-adjacent levels, i. e., $k_{13} = k_{31} = k_{14} = k_{41} = k_{24} = k_{42} = 0$. Similar assumptions were made in relating the rate constants between adjacent levels, and the same values were retained for these rate constants as were chosen in the complete solution of the four-level case considered above. For this simplified treatment of the four-level model, a maximum error of 8.2% in the over-all specific rate constant was found during the

TABLE 3
VARIATION OF THE RATIO OF ACTUAL TO
EQUILIBRIUM RATES WITH AMOUNT OF
REACTION

Time (seconds)	Γ	A_1 in D units	Amount of* reaction % $\left(= \dfrac{[(A_1)_{t=0} - (A_1)_t]}{(A_1)_{t=0}} \times 100 \right)$
1	0.7967	0.4908	0.87
2	0.8858	0.4885	1.33
3	0.9134	0.4865	1.74
4	0.9222	0.4848	2.08
5	0.9251	0.4832	2.40
10	0.9276	0.4754	3.98
100	0.9492	0.3707	25.1
1000	0.9944	0.2480	49.9
∞	0.9998	0.2451	50.5

* $(A_1)_{t=0} = 0.4951D$, where D is the total chosen concentration for the system.

course of the reaction. This indicates that possibly the chosen values for the rate constants between non-adjacent levels were taken slightly too large.

It is now of interest to apply equilibrium reaction rate theory to the problem of spontaneous combustion.

The Critical Temperatures for Combustion of Metals and Their Alloys*

Generally speaking, combustion is a chemical reaction accompanied by heat and light. In a limited sense, the term has been adopted for the rapid union of substances with

* Professor J. R. Lewis and Messrs. L. D. Gulbransen and W. M. Fassell of the Department of Metallurgy at the University of Utah pointed out the value of a theoretical discussion of the published data on ignition temperatures.

oxygen leading to their decomposition to form oxides, the process being accompanied by evolution of light and heat. Similar phenomena are observed when reactive elements such as fluorine or chlorine replace oxygen. All substances, whatever may be the medium for combustion, are characterized by a certain minimum temperature for rapid reaction which leads to combustion. Thermal conductivity of the substance plays a determining rôle in establishing this minimum temperature. For poor conductors such as wood and plastics, the temperature at which they take fire is commonly referred to as the kindling temperature. With reference to combustion of good thermal conductors like metals and alloys, the term employed is the ignition temperature.

The existent data in the literature on combustion of metals and alloys are very meager. Recently, however, an excellent study was made by Leontis and Rhines (18) on the rates of high-temperature oxidation of magnesium and magnesium alloys, in which they report the combustion of some of their samples. The purpose of this section is to show how the problem of ignition temperatures of metals and alloys can be put on a quantitative basis. The above-reported data will be utilized in predicting the ignition temperatures of magnesium and its alloys. By using the formulation given below, it is possible to calculate values for the activation energies of high-temperature corrosion of metals from a knowledge of their ignition temperatures.

Leontis and Rhines have shown how the Theory of Absolute Rates of Reaction readily explains the kinetics of the high-temperature corrosion of magnesium. Before pro-

ceeding to a discussion of ignition temperatures, it may be worth while to present briefly the theory of corrosion of metals which exhibit a linear law of corrosion at high temperatures. This will be applicable to all metals which on corrosion form a non-protective film. According to the Pilling and Bedworth (19) classification, this will include metals whose corrosion films are less voluminous than the base metal; i. e., $\frac{\text{vol. of film}}{\text{vol. of metal}} < 1$. As examples, we may cite the alkali and the alkaline earth metals. At lower temperatures, magnesium corrodes in accordance with the parabolic law, indicating protectivity; however, at temperatures above 450° C., the film becomes non-protective, as indicated by the zero-order kinetics with respect to oxygen.

The following reactions will apply to metals which obey the linear law of corrosion,

$$C_a \rightleftharpoons C^{\pm} \rightarrow \text{products}$$
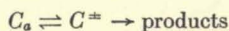
where C_a is the number of adsorbed gas molecules per sq. cm. of metal surface and $C^{\pm}$ is the number of activated complexes per sq. cm. of surface. The rate is assumed to be determined by the number of activated complexes crossing the potential hump, so the number of magnesium atoms reacting per sq. cm. per sec. is given by

$$v = C^{\pm} \frac{kT}{h}. \tag{29}$$

On the basis of the assumed equilibrium between the initial and activated states

$$K^{\pm} = \frac{C^{\pm}}{C_a} = \frac{f^{\pm}/S}{f_a/S} e^{-\epsilon/kT}, \tag{30}$$

where $f^{\pm}$ = partition function of the activated complex, f_a = partition function of adsorbed gas, ϵ = surface activation energy and S = total area of surface, so that on substitution

$$v = C_a \frac{kT}{h} \frac{f^{\pm}}{f_a} e^{-\epsilon/kT}. \tag{31}$$

The concentration of adsorbed gas molecules can also be defined by

$$C_a = \theta C_S,$$

where θ is the fraction of surface covered and C_S is the number of adsorption sites or metal atoms per sq. cm. of surface. For relatively high pressures θ is equal to unity, and since the ratio $f^{\pm}/f_a \sim 1$ our expression for the linear rate of corrosion simplifies to

$$v = C_S \frac{kT}{h} e^{-\epsilon/kT}. \tag{32}$$

The present formulation of the theory of ignition temperatures of metals is applicable to samples such as strips, ribbon, wire or coarse powders which are stable at ordinary temperatures and possess protective oxide films at least of the order of 20 Å. The general principles will apply to fine powder samples, except that refinement of treatment is required to take into consideration factors such as the fine state of subdivision, the higher surface areas with greater activity, i. e., lower energies of activation, and the method of preparation of the sample. The latter point may very likely be of prime importance in explaining the combustion of pyrophoric iron in oxygen at temperatures close to 0° C. as a result of the adsorbed layer of hydrogen.

The ignition of metal samples will occur when the conduction of heat through the oxide film is inadequate for the removal of the heat produced at the metal-film interface as a re-

sult of corrosion. Radiation effects are of minor importance. Consequently, inadequate loss of heat through film conduction will increase the temperature at the metal-film boundary, overheating the metal and increasing the rate of reaction. The progressive acceleration of the rate of corrosion will result in the vaporization of the metal with subsequent ignition of the metal vapor. The heat loss per second through a unit area is equal to the rate of conduction through a unit area of the film, whereas the heat produced per second per unit area is equal to the product of the velocity of surface corrosion and the heat of combustion. Setting up a heat-balance equation, we have

$$\kappa \frac{(T - T_0)}{d} = v \frac{\Delta H}{N}, \qquad (33)$$

where to a first approximation the shape of the sample is neglected by replacing the differential temperature gradient by a ratio. The symbols are defined as

κ = thermal conductivity $\left(\frac{\text{cal.-cm.}}{°C.\ cm.^2\ sec.} \right)$

v = rate of corrosion (no. of metal atoms/cm.²-sec.)

T = temperature in °K. at metal-film interface

T_0 = temperature in °K. at outer surface of film

d = thickness of film in cm.

ΔH = heat of formation in kcal./mole

N = Avogadro's number.

For ignition to occur, the heat balance will be destroyed and Eq. (33) is written as an inequality,

$$\kappa \frac{(T - T_0)}{d} < v \frac{\Delta H}{N}. \qquad (34)$$

The blanketing effect of the corrosion film is clearly demonstrated in Fig. 7 of Leontis and Rhines' article (18). The linear rate of corrosion of a Mg-Al alloy (1.78% Al)

is plotted at 548° C. After ten hours the sample ignited on reaching the critical film thickness whose blanketing effect destroyed the heat balance.

Another point has to be taken into consideration, namely, the ratio of the reaction surface (A_M) to the outer area of the corrosion film (A_F) where temperature equilibrium is maintained through gas collisions. Recently, Brown and Uhlig (20) have shown through measurement of ethane adsorption isotherms on chrome-plated nickel strips that the roughness factor (21) (i. e., $f = \frac{\text{true area}}{\text{geometric area}}$) of these samples varied from 9.4 to 53. For corrosion films of the order of several microns, the microscopic irregularity of the metal surface is lost in the formation of the voluminous porous film, so that we can expect the ratio A_M/A_F to have values closely corresponding to the roughness factor values quoted above. Since most surfaces are quite heterogeneous in their activities for corrosion, a certain amount of microscopic pitting is expected, which would increase the above ratio.

Limiting ourselves to the class of metals or alloys which obey the linear law of corrosion, we can substitute expression (32) for the velocity of corrosion into Eq.(34), thus:

$$\kappa \frac{(T - T_0)}{d} \leq C_S \frac{kT}{h} e^{-\epsilon/kT} \frac{\Delta H}{N} \frac{A_M}{A_F}. \qquad (35)$$

Since most metals are characterized by a cubic or hexagonal close-packed system, C_S is approximately 1×10^{15}. The above expression can now be utilized to predict ignition temperatures (T_0) from measured values of the activation energies for corrosion (ϵ) or to calculate activa-
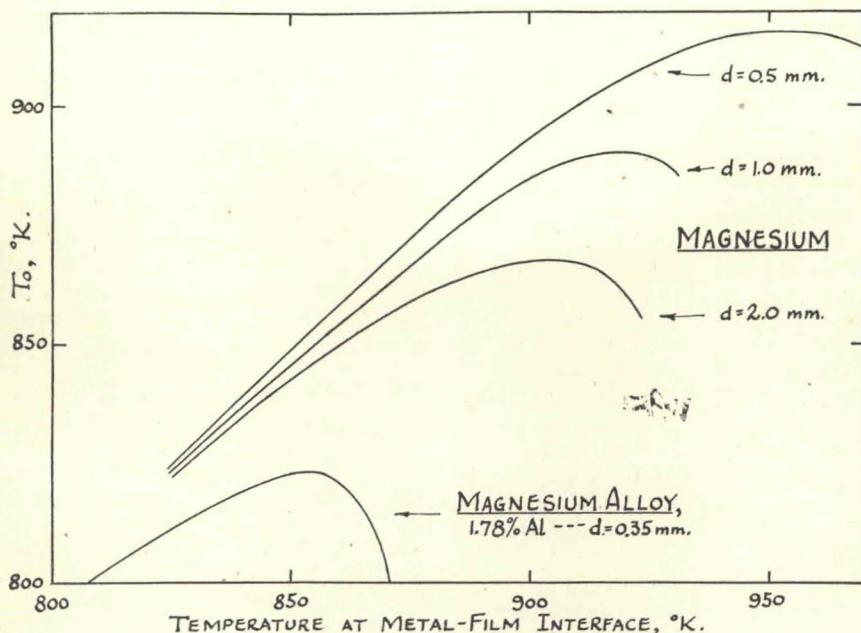
FIGURE 2

tion energies for the rate of corrosion at high temperatures of metals from experimental values of their ignition temperatures. For ease of calculation, Eq. (35) is transformed to read

$$T_0 \leq \left[1 - C_S \frac{kd\,\Delta HF}{h\kappa N}\, e^{-E/RT}\right] T, \tag{36}$$

where $F = A_M/A_F$ and our two variables are d and T. If we use the equality sign in (36) and plot T_0 as ordinate against T as abscissa, we get the set of curves in Fig. 2 showing maxima. These curves are labeled to indicate the thickness of the oxide layer considered. The lowest curve corresponds to an aluminum alloy, and the other three to pure magnesium. Clearly it is impossible to have T_0, the outside temperature, higher than the value

given by the maximum without combustion occurring. Thus the maximum value on the curve for T_0 is the ignition temperature. It should be possible, however, to have the temperature inside higher than corresponds to the ignition temperature if the inside is heated, say by an electric current, being careful always to keep the outside temperature below the ignition temperature.

Replacing the constants in Eq. (36) by the values given in Table 4 for the Mg-Al alloy containing 1.78% Al gives

$$T_0 = [1 - 4.33 \times 10^9 \times 10^{-9350/T}]T. \tag{37}$$

A word of explanation is required in reference to the quantities d, κ and F. The thickness of the film (d) was calculated from the total amount of corrosion measured at the point of ignition as given in reference (18)

TABLE 4

C_S = 1.1 × 10^{15} Mg atoms/cm.^{2}
k = 1.38 × 10^{-16} ergs/°K.
d = 1.35 × 10^{-2} cm.
ΔH = heat of formation, MgO = 146 kcal./mole
F = 16
h = 6.62 × 10^{-27} ergs-sec.
κ = 2.8 × 10^{-4} $\left(\dfrac{\text{cal.-cm.}}{\text{°C. cm.}^2 \text{ sec.}} \right)$
N = 6.02 × 10^{23} atoms/mole
E = 42.7 kcal./mole*

* Leontis and Rhines, ref. (18).

using the lower density value of 0.8 of pressed MgO powder in view of the porous nature of the film. The value of 2.8 × 10^{-4} for κ is an extrapolated value at 500° C. from thermal conductivity data on 85% magnesia over the temperature range 20–260° C. This value is used in place of the thermal conductivity of crystal MgO, for the porous oxide film with its adsorbed layer of oxygen will have a smaller conductivity than crystal MgO, whose κ = 3.01 × 10^{-3} at 15° C. The arbitrary value of 16 was chosen for $F = A_M/A_F$ in order to obtain good agreement between the calculated and observed values of the ignition temperature for the Mg-(1.78%)Al alloy. This value for F was also found to be of the right magnitude to predict satisfactory values for the ignition temperatures of pure Mg of varying thicknesses of film. In calculating the ignition temperatures of pure magnesium the same values as given in Table 4 were utilized, with the exception of the activation energy E,

for which the measured value of 50.5 kcal./mole was used [see reference, p. 20 (18)]. For pure Mg, the equation is

$$T_0 = [1 - 2.00 \times 10^{10}d\,10^{-11,000/T}]T. \quad (38)$$

The calculated ignition temperatures are given in Table 5.

The difference between the abscissa and ordinate on any curve gives the corresponding difference between the inside and outside temperatures of the oxide layers.

Flow of Concentrated Solutions of Large Molecules*

If a molecule is so long that at equilibrium it has several possible equilibrium positions for each segment, then when a shear stress is applied (22) as in viscous or plastic flow the stress will be relieved by the segments taking up new positions to release the strain. Suppose a liquid made up of unattached segments of the type which do the moving in flow would have the viscosity (23)

$$\eta_{seg.} = \frac{Nh}{V} e^{\Delta F^{\neq}/RT}. \quad (39)$$

But suppose the segment j can only move if each of the other segments

* The theoretical treatment of Flory's measurements [P. S. Flory, J. Am. Chem. Soc., 62, 1057 (1940)] for large molecules follows the method of Charles Fletcher and Henry Eyring presented at the A.C.S. Chicago meeting, 1946. See also the discussion by W. Kauzmann and H. Eyring, J. Am. Chem. Soc., 62, 3113 (1940).

TABLE 5

Substance	Film Thickness (Cm.)	Ignition Temperatures °C. calc.	°C. obs.	M. P., °C.
Mg-(1.78%)Al	1.35 × 10^{-2}	551	548	∼620
Mg-(3.81%)Al	1.35 × 10^{-2}	460	...	∼588
Mg	5 × 10^{-2}	642	...	651
	1 × 10^{-1}	618	...	...
	2 × 10^{-1}	595	...	...

of this molecule occupies particular ones of the possible positions. The ratio of the positions of the ith segment $(i \neq j)$ which allow the jth segment to move over the total number of positions of the ith segment is p_i^{-1}. The viscosity of a liquid made up of these long molecules will then be

$$\eta = \frac{Nh}{V} e^{\Delta F \pm /RT} \prod_{i \neq j} p_i. \quad (40)$$

The values of p_i will no doubt vary with the nature of the solution. If a molecule is stretched out in the direction of flow, then a segment moving to extend the molecule further in this direction may well be resisted by the net number of segments already stretching in this direction. Consider the case of random distribution of the segments with respect to their projection in the direction of flow. We assume there is an equal chance of each segment having a positive or negative projection, and that a positive extension acts in such a way as to overcome a negative one and make the product of the two factors unity. Remembering further the result of Kendall (24) and its theoretical interpretation that the viscosity of a mixture (6) is the geometrical mean on a volume basis of the viscosity of the components, we have for the viscosity

$$\eta = \prod_i \left(\frac{Nh}{V_i} e^{\Delta F_i \pm /RT} \prod_{r=1}^{n_i} p_i^{|n_i - 2r|} \frac{n_i!}{(n_i - r)!r!2^{n_i}} \right)^{\varphi_i}. \quad (41)$$

Here φ_i is the volume fraction of molecules of chain length n_i and $\frac{n_i!}{(n_i - r)!r!2^{n_i}}$ is the fraction of molecules with chain length n_i which have a net extension of $|n_i - 2r|$ of the

segments in the direction of flow. For long molecules we can write with sufficient approximation

$$\sum_{r=1}^{n_i} |n_i - 2r| \frac{n_i!}{(n_i - r)!r!2^{n_i}} \cong$$

$$\frac{\int_0^\infty x e^{-x^2/2n_i} dx}{\int_0^\infty e^{-x^2/2n_i} dx} = \left(\frac{2n_i}{\pi} \right)^{1/2}. \quad (42)$$

where $x = (n_i - 2r)$.

This then gives:

$$\eta = \prod_i \left(\frac{Nh}{V_i} e^{\Delta F_i \pm /RT} p_i^{\sqrt{2n_i/\pi}} \right)^{\varphi_i} =$$

$$\prod_i \left(\frac{Nh}{V_i} e^{\Delta F_i \pm /RT} a Z_i^{1/2} \right)^{\varphi_i}, \quad (43)$$

where

$$a Z_i^{1/2} \equiv \left(\sqrt{\frac{2}{\pi}} \ln p_i \right) n_i^{1/2} \equiv$$

$$\left(\sqrt{\frac{2}{\pi}} \ln p_i \left(\frac{Z_i}{S} \right)^{1/2} \right)$$

$$\equiv \left(\sqrt{\frac{2}{\pi S}} \ln p_i \right) Z_i^{1/2}. \quad (44)$$

In these equations Z is taken as the number of atoms in the chain and S the number of atoms in the segment. Reasonable values for p_i and S give the values for a found by Flory (25) and Eyring and Powell (26).

From the above we see that probably the equilibrium theory of reaction rates is seldom in appreciable error. A theory of the ignition temperature of combustibles has been given, and finally we have given a framework for discussing the flow of large molecules which is capable of extension and wide application.

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