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FOREWORD

THIS volume begins with a theoretical review of bimolecular reactions which includes an original discussion of some of the more obscure points of rate theory such as, for example, the relation between free energy and potential energy surfaces. There are two articles on atom reactions, one on hydrogen atoms, the other on hot atom chemistry, which, together with previous reports on oxygen, halogen and excited mercury atom reactions and a projected article on nitrogen atoms, give a rather complete coverage of atom reactions in the gas phase. Gas kinetics are also represented by a review of the fundamental physical process of vibrational relaxation and of the present situation in the long and complex story of the inhibition of radical chain reactions.

Perhaps the most powerful new experimental technique in the field of kinetics is pulse radiolysis which is reviewed by two authors who have been in the vanguard of its development. Their article includes a wealth of kinetic data obtained by this method during the last year or two. More conventional radiation-chemical studies are represented by a discussion of linear energy transfer in radiation processes. Kinetic studies of free radicals by modern direct methods are almost wholly dependent on a knowledge of electronic spectra and the review of recent work on the spectra and kinetics of aromatic radicals provides a useful summary of this field. There are two reviews of the kinetics of polymerization processes in solution; the first deals with polymerization by lithium alkyls and the second with the kinetics of radical polymerization processes.

The reaction index covers the first three volumes of the series. This is now quite extensive and, although it is undoubtedly a valuable feature, its preparation seriously delays publication; future volumes will therefore contain an index of reactions reviewed in that volume only and cumulative indexes will be prepared at regular intervals, probably for every third volume.

<div align="right">GEORGE PORTER</div>

CONTENTS

v

16998

CONTENTS

1

THEORIES OF THE KINETICS OF BIMOLECULAR REACTIONS

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CONTENTS

INTRODUCTION

The theoretical calculation of the absolute rates of chemical reactions is one of the most important, and at the same time one of the most difficult, problems in chemistry today. The problem has still by no means been solved, even for the simplest of reactions. It has proved necessary to employ highly approximate methods, and a considerable number of approaches have been made, involving various kinds of approximations.

This review deals in a general way with the various attacks that have been made on this problem of calculating reaction rates and is concerned particularly with bimolecular reactions. The subject is conveniently divided into two general aspects as a result of Arrhenius's formulation[1] of the rate constant as given by

$$k = Ae^{-E_a/RT} \tag{1}$$

where A, the frequency factor, and E_a, the energy of activation, are approximately independent of temperature. It was first pointed out by Marcelin[2] that the activation energy is conveniently treated from the point of view of the passage of a system over a potential-energy surface, and Section I of this review deals with the various methods that have been used for constructing such surfaces. It will be seen in Section I, A that the purely quantum-mechanical methods are still, despite the advent of high-speed computers, not sufficiently refined to give a reasonably satisfactory solution even for the simplest of reactions. Much greater success is achieved if some degree of empiricism is permitted, as is shown in subsections B and C of Section I.

The ideas of Arrhenius and Marcelin represent the first two important milestones in the development of the theoretical understanding of reaction rates. A third one was the suggestion of W. C. McC. Lewis[3] that the frequency factor A can be identified with a "collision number", and that this can be calculated, using the kinetic theory of gases, in terms of molecular diameters. This theory was certainly along the right lines, but it was soon realized that the calculation of collision frequencies on the assumption that reacting molecules are hard spheres is too crude, and leads to serious numerical errors for many kinds of reactions. An alternative formulation, due to Eyring[4] and independently to Evans and Polanyi,[5] represents essentially a more satisfactory way of dealing with molecular collisions, the detailed structures of the reacting molecules being taken into account. Prior to this treatment Pelzer and Wigner[6] had calculated the rate of the reaction

$$H + H_2 \rightarrow H_2 + H$$
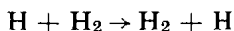
by considering the movement of the system over the potential-energy surface. The formulations of Eyring and of Evans and Polanyi were similar to this, but

3

achieved a great simplification by introducing the approximation that the "activated complexes", or species that are passing over the top of the potential-energy barrier, are in complete equilibrium with the reactant species. For most reactions this is close to the truth, and the result is that the rate can in principle be calculated as easily as an equilibrium constant, by the methods of statistical mechanics. This formulation, now usually known as "absolute rate theory", undoubtedly represents one of the most important developments in the field, and is dealt with at some length in Section II.

Both the hard-sphere theory of Lewis and the absolute rate theory have the feature in common that they assume the collision complexes or activated complexes to be in equilibrium with the reactants. As will be discussed in Section II, C this assumption corresponds to the truth when the whole system is in equilibrium, and under these conditions absolute rate theory gives a reliable interpretation of the rates in the two directions. When the whole system is not at equilibrium, however, there may be some error, especially if the reaction is so fast as to cause a depletion of the more active reactant molecules. Various attempts have therefore been made to treat reaction rates without the assumption of equilibrium, and these methods are described in Section III. Most of these treatments consist of a classical or quantum-mechanical formulation of the passage of the system over the potential-energy barrier. These theories of reaction rates are considerably more difficult to formulate than is absolute rate theory, and the rate calculations depend more critically on the precise form of the potential-energy surface—a matter that, as has been seen, is itself of considerable difficulty. For this reason the non-equilibrium theories have all been either very formal, so that numerical values cannot be obtained from them for comparison with experiment, or have involved approximations that may be as serious as the equilibrium assumption itself. Such work that has been done along these lines has made it seem likely that under ordinary circumstances the assumption of equilibrium introduces errors that are quite small, and are within the usual experimental error. Another important result that has come from some of the non-equilibrium formulations relates to the question of the way in which the energy of reaction is distributed between the product molecules, a matter that is susceptible to experimental test. This question is considered in particular in Section III.

In this review, the main emphasis will be on the assumptions of the various theories, on the extent to which they interpret the experimental results, and on certain points that do not appear to have been explicitly reviewed. Among the latter may be mentioned the question of the significance of free-energy as opposed to potential-energy surfaces (II, H), and that of multiple reaction paths (II, E).

I. POTENTIAL-ENERGY SURFACES

A. *Quantum-mechanical Treatments*

Provided that electronic energy can be separated from nuclear energy (the

Born–Oppenheimer approximation), and provided also that the electrons remain in one state (the "adiabatic" assumption), a single potential-energy hyper-surface will give the potential-energy E for all internuclear separations of an assembly of atoms. Since any chemical reaction leading to stable products must involve at least three atoms, the simplest potential-energy surface that can fully describe the changes in potential during the course of a reaction is a four-dimensional hyper-surface. For the reaction,

$$A + BC \rightarrow AB + C$$
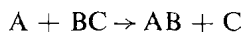
this surface would be designated $E(r_1, r_2, r_3)$, where r_1 is the A–B separation, r_2 the B–C separation and r_3 the A–C separation.

The three-electron system is exemplified by the orthopara hydrogen conversion reaction, $H + H_2 \rightarrow H_2 + H$. All of the many calculations, quantum-mechanical and semi-empirical, that have been made on this system agree in one regard: energetically the most favourable line of approach for the attacking H atom is along the axis of the H_2 molecule. It is therefore not only very convenient, but also useful, to plot three-dimensional potential-energy surfaces, $E(r_1, r_2)$, in which the three atoms are constrained to move in a single line $(r_3 = r_1 + r_2)$.

1. *The London Equation*—The year following Schrödinger's first paper setting out the new wave mechanics, Heitler and London[7] accounted approximately for the electronic energy of H_2 using the wave function,

$$\psi = \psi_A(1)\psi_B(2) \pm \psi_B(1)\psi_A(2) \tag{2}$$

with eigenvalues,

$$E(r) = \frac{Q_A \mp J_A}{1 \mp S_A{}^2} \tag{3}$$

where Q_A, J_A and S_A are the Coulomb, exchange and overlap integrals respectively (each a function of internuclear separation, r). The lower sign refers to the bound state, $^1\Sigma$, the upper to the repulsive state, $^3\Sigma$. $E(r)$ is reckoned relative to the energy of the separated atoms. With overlap included, the Heitler–London treatment accounted for 66 per cent of the bonding in H_2.

London[8] attempted to apply this simplest zero-order approximation valence-bond treatment to H_3. He proposed that,

$$E(r_1, r_2, r_3) = Q_A + Q_B + Q_C \pm \{\tfrac{1}{2}[(J_A - J_B)^2 + (J_B - J_C)^2 + (J_A - J_C)^2]\}^{1/2} \tag{4}$$

where Q_A, Q_B, Q_C are Coulomb integrals, and J_A, J_B, J_C exchange integrals, between the pairs of atoms AB, BC and AC respectively. Once again the lower sign refers to the more stable state, and the energy is reckoned relative to the separated atoms. This equation was originally presented without proof; Slater[9] gave the first derivation, which, however, was criticized and amended by Coolidge and James.[10]

It was evident from the outset that the London equation could not be expected to yield good values for E. For one reason, (i), it was based on the Heitler–London approximation which results in a binding energy of 72·4 kcal for H_2, in place of the actual 109·4 kcal; this 37 kcal error is over four times as large as the (classical) activation energy that the London equation is designed to predict. Secondly, (ii), inspection of the London equation shows that for $r_2 = r_3 = \infty$ it reduces to,

$$E(r) = Q_A \mp J_A, \tag{5}$$

which means that S^2 has been neglected. S^2 plays a far from negligible role in the Heitler–London theory. At equilibrium internuclear separation $S^2 = 0·57$.[11, 12] Neglect of S^2 will alter the predicted binding by at least $0·57/1·57 = 36$ per cent.†
The fact that by chance this brings the binding energy closer to the experimental value ($-107·5$ kcal predicted by (5), compared with $-109·4$ from experiment) is, of course, not a theoretical justification for omitting S^2.

Further approximations[10] are (iii) the neglect of terms arising from permutations of more than two electrons, and (iv) the assumption that terms which arise from the exchange of two electrons are the same as if these two electrons and their two nuclei are the only electrons and nuclei present. (J_A, J_B and J_C in (3) should more properly be exchange integrals involving the full three-atom Hamiltonian.)

Nonetheless it appeared possible that E'_c, the *difference* in binding energy between H_3 and $H + H_2$, both calculated by the London equation, might approximate the (classical) activation energy derived from experiment. The experimental activation energy, $E_a = 7·5$ kcal mole^{-1}, must be corrected (i.a.) for difference in zero-point vibrational energy as between the initial and activated states, in order to obtain an approximate value for E_c. This leads to $E_c = 8$–9 kcal mole^{-1},[14] listed as experimental in Table 1.

Eyring and Polanyi[22] considered the possibility of putting this to the test by calculating a potential-energy surface for linear H_3 from the London equation using the Coulomb and exchange integrals, as a function of internuclear separation, computed by Sugiura.[11] However, they did not actually perform the calculation‡ since they felt that the inaccuracies would be too great. (They proceeded, instead, to apply semi-empirical methods—see Section I, B.) There is no record in the literature of the London equation having been solved theoretically, to calculate a potential-energy surface. Figure 1 presents the results of such a calculation, using Sugiura's integrals.[22a] Energies are expressed relative to $E(H + H_2) = 0$. Coolidge and James[10] independently evaluated the integrals and

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† The increase in binding energy is somewhat greater than this, at the new predicted equilibrium separation.

‡ Note that superposition of Eyring and Polanyi's Figs. 12 and 13 would not (as they appear to suggest) give rise to the rigorous London surface, since in calculating these figures they used not Q and J but $Q/(1 + S^2)$ and $J/(1 + S^2)$.

performed the calculation for the single configuration $r_1 = r_2 = 0.9$ Å. They obtained a binding energy of -103.5 kcal relative to 3H. This gives an energy of $+4.0$ relative to $H + H_2$. The 0.7 kcal discrepancy with Fig. 1 (3.3 kcal at $r_1 = r_2 = 0.9$Å) is not significant; it could have arisen from approximations in evaluating the integrals.

It appears that the London equation, without adjustable parameters, yields $E'_c \approx 8.8$ kcal,† compared with the experimental figure of 8–9 kcal. This
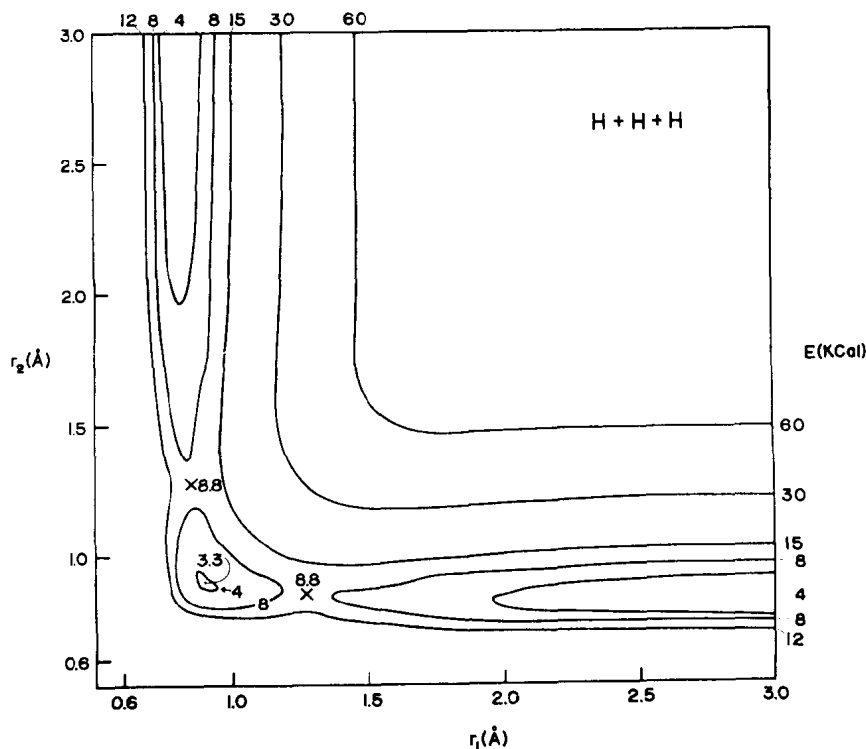
FIG. 1. Potential-energy surface for collinear reaction $H + H_2 \rightarrow H_2 + H$, calculated directly from the London equation using Sugiura's integrals, without empiricism. Energies expressed relative to $E(H + H_2) = 0$. Ref. 22a.

agreement must be regarded as fortuitous in the light of the serious approximations ((i) to (iv) above) which have been made. As will be seen, the terms that have been ignored are greater in magnitude than the quantity to be calculated.

Any doubt as to the accidental nature of the result was removed by Coolidge and James's calculations in which they tested the effect on the energy at $r_1 = r_2 =$

† Ref. No. 23 states that E'_c on this approximation is ~ 30 kcal^{-1} $(E_a)_{calc} = 29$ kcal); this appears to be incorrect.

TABLE 1. VARIATIONAL CALCULATIONS OF THE H_3 ACTIVATED COMPLEX CONFIGURATION AND ENERGY, RELATIVE TO $H + H_2$

	(a) Heitler–London[15]	(b) H.L. plus Polar[15]	(c) H.L. plus Z_{eff}[15]	(d) H.L. Polar plus Z_{eff}[15]	(e) H.L. Polar plus two Z_{eff}[16]	(f) 3-A.O.–M.O.–C.I.[17]	(g) 3-A.O.–M.O.–C.I. plus Z_{eff}[18]	(h) 5-A.O.–M.O.–C.I. plus Z_{eff}[19]	(i) 6-A.O.–M.O.–C.I. plus Z_{eff}[20,21]	Expt.
Z(a.u.)	1	1	1·06	1·09	$\begin{cases} Z_0 = 1·00 \\ Z_m = 1·08 \end{cases}$	1	1·10	1·10	$\begin{cases} Z_1 = 1·245 \\ Z_2 = 0·83 \end{cases}$	
r(Å)	1·06	1·06	1·00	0·975	0·95	~1·0	1·00₅	1·02	0·943	
E_c(kcal mole^{-1})	56·3	49·0	53·2	42·3	~37	48·7	41·1	37·0	29·2	
E'_c(kcal mole^{-1})	19·07	13·63	30·68	25·15	~20	13·3	24	19·9	15·4	8–9

0·9 Å of removing the approximations listed above as (ii), (iii) and (iv). The energy $E(0·9 \text{ Å})$, rose from $+4·0$ to $32·7$ kcal above the energy of $H + H_2$. (The best Heitler–London non-polar variational treatment, column (a) of Table 1, which should give a similar result, gives a 30 per cent lower barrier height, but the lowest point on the barrier is at $1·06$ Å.) The salient point here is that a much more precise formulation, that of Heitler and London, leads to poorer agreement with experiment, indicating that the good agreement using the London equation was fortuitous.

Magee[24] calculated potential-energy surfaces for the reactions $X + H_2$ and $H + HX$ (X is a halogen atom) using the full Heitler–London treatment with the exception of triple exchange integrals. The calculation yielded a low barrier, and predicted a stable triangular complex. The result is probably, as he puts it, "closer to the Heitler–London prediction than the latter is to reality".

The great importance of these early calculations of $E(r_1, r_2)$ was that they provided a framework within which it was possible to understand the low energy barriers often associated with reactions in which, nonetheless, strong bonds were being broken. The London equation constituted the first quantum-mechanical statement of the possibility of bond breaking under the influence of new-bond formation.

2. *The Variation Method*—The only hope at present for a precise solution to. even the three-electron problem lies in the variation method.

The first attempt to calculate a potential-energy surface, $E(r_1, r_2)$, by this method was made in a series of papers by Hirschfelder, Eyring and coworkers.[15, 25-28] (a) In their initial calculations they looked for the best linear symmetric configuration based on homopolar wave functions. They then essayed in turn (b) the best linear combination of polar as well as homopolar functions, (c) the best homopolar wave function with variable effective nuclear charge, Z_{eff}, (sometimes referred to as "screening" or simply as the "scale factor" in the exponent of the exponential term of the wave function), and (d) the best wave-function with simultaneous variation in both the polarity and effective charge. It should be noted that in every case, (a) to (d), the "best" wavefunction was constructed from three $1s$ hydrogen-like atomic orbitals. The reason that Z_{eff} was so ineffective a variable in these calculations (cf. H_2) may be that the central H atom is forced, in this approximation, to assume the same screening constant as the two outer ones (see below).

Columns (a) to (d) of Table 1 give the activated complex configurations $(r_1 = r_2 = r)$ and the barrier heights, E_c and E'_c, from these calculations. The barrier height E'_c was computed relative to the potential energy of $H + H_2$, *calculated* according to the same approximation; it was hoped that this might bring about a cancellation of errors. If the *experimental* figure for the $H + H_2$ energy (relative to 3H) is used, then the barrier height E_c was obtained; this is a more satisfactory test of the accuracy of the calculated H_3 binding energy.

Throughout this calculation[15] only linear symmetrical configurations of H_3

were considered. However, a few years later Hirschfelder[27, 28] was able, with the aid of an early computer, to evaluate the difficult three-centre integrals for non-linear symmetrical configurations. He showed that linear H_3 is about 80 kcal more stable than the equilateral triangular configuration.

For some fifteen years little attempt was made to improve on the variational calculations of the H_3 energy, described above. However, more recently, with the availability of high-speed computers, there has been a resurgence of interest in the problem. Walsh and Matsen[29] calculated the binding energy of H_3 using several molecular-orbital approximations, but appear to have made an error in setting up their wavefunction.[21] Their most complete treatment, with configuration interaction (C.I.), was repeated by Ransil.[17] Ransil's value for E_c is recorded in Table 1, column (f). Ransil's M.O.–C.I. treatment should give the same result as the valence-bond treatment with polar structures included;[30] the discrepancy between E_c from columns (b) and (f) of Table 1 (0·3 kcal) is surely within the computational error. Similarly Griffing, Jackson and Ransil's M.O.–C.I. treatment[18] with variation in Z_{eff} recorded in column (g), should give the same result as the valence-bond treatment of column (d); in fact the correspondence is fairly close.

Neither Walsh et al.[24] nor Ransil[17] quote the exact r for their best calculation, but both authors make it clear that r (ca. 1·0 Å) is quite insensitive to the approximation used. A similar marked insensitivity of predicted equilibrium separation to crudities in the model has been noted in stable molecules.[31] It has been suggested that this insensitivity of r might be put to good use in the following way. Approximate integrals could be employed in a relatively quick calculation of the best activated-state configuration, and then exact integrals need only be applied to this single configuration.[32] Barker and Eyring[16] used this method to choose $r = 0·95$ Å for the activated configuration, and then proceeded to explore the effect on the binding energy in this configuration of a "mixed orbital-charge treatment" in which the effective charge on the middle atom (Z_m) is varied independently of that on the outer atom (Z_0). With $Z_0 = 1$ and $Z_m = 1·08$, they estimated a 5-kcal increase in the H_3 binding energy, as compared with the best Heitler–London calculation including ionic terms but employing only one screening constant (cf. columns (d) and (e) of Table 1).

Kimball and Trulio[19] opened a new chapter in these calculations by increasing the number of atomic orbitals used in the construction of the H_3 molecular orbital, beyond the three used in all previous calculations. An L.C.A.O. M.O. wave function was set up for linear symmetric H_3 (with complete configuration interaction) from five $1s$ hydrogen-like orbitals, with centres equally spaced on the line of nuclei. The effective nuclear charge was the same for all three nuclei. The five orbitals could be moved freely relative to the nuclei, subject to the restriction of equal spacing, and of symmetry. Varying r, Z_{eff}, and orbital positions, they obtained an improvement of 11·7 kcal in H_3 binding, over Ransil's three A.O. M.O. treatment. The improvement, though significant, was small in

comparison with the 40 kcal discrepancy between Ransil's figure and the true H_3 binding of about 101 kcal (i.e. the classical binding energy of H_2, 109·4 kcal, less the classical activation energy for the $H + H_2$ reaction $E_c = 8–9$ kcal). Kimball and Trulio attributed this somewhat disappointing outcome to the fact that the charge distribution, even without the two additional orbitals interposed between atoms A and B, and B and C, is already quite adjustable along the molecular axis. They surmised that, had they been able to pile up charge on the middle nucleus by bringing the two extra orbitals in toward the centre, they would have achieved a substantially greater stabilization (cf. the double screening-constants of Barker and Eyring, described above).

Boys and Shavitt[21] have performed the most complete variational treatment of H_3 to date. They arranged for concentration of charge, not by the differential screening attempted by Barker and Eyring, nor the freely "floating" orbitals proposed by Kimball and Trulio, but by locating a pair of $1s$ atomic orbitals at each nucleus, with different effective nuclear charges for the members of each pair. Thus, at the A nucleus were located a $1s$ orbital with $(Z_{eff})_1$ and another $1s$ orbital with $(Z_{eff})_2$; at the B nucleus a $1s$ with $(Z_{eff})_1$ (as before) and another with $(Z_{eff})_2$, and so on. Since $(Z_{eff})_1/(Z_{eff})_2$ was fixed (arbitrarily at 1·5), and the same at every nucleus, only one scale factor could be varied. The energy of the system, it turned out, was not very sensitive to the values used for Z_{eff}, since the redistribution of charge took place "automatically", through variational optimization of the relative contributions from the two types of orbitals located at each nucleus. This feature probably obviates the need for different sets of Z_{eff} at each nucleus. In the (symmetric) activated configuration the charge on the central atom proved to be about 10 per cent greater than on the outer atoms. Asymmetric and bent configurations were tried and, as in all earlier calculations, the linear configuration was found to be the most stable.

The binding energy was, however, only 7·8 kcal better than that calculated by Kimball and Trulio; there remains today an unbridged gap of 21 kcal between the calculated and the experimental binding energy. Reckoned relative to the calculated binding energy this is a 26 per cent error. Reckoned, however, as an error in E_c, it is a discrepancy of over a factor of three. This can be reduced to a factor of a little less than two if we consider E'_c, the barrier height on a surface for which both the initial and activated states have been calculated by Boys and Shavitt's variational method. This accuracy cannot be regarded as satisfactory, in view of the fact that doubling E has a large effect on the predicted reaction rate, which is the quantity of greatest interest. With today's computers, at least 1000 times faster than that used by Boys and Shavitt, it should be possible to improve on their result by such expedients as varying $(Z_{eff})_1/(Z_{eff})_2$, or adding a third orbital at one or more nuclei (with $(Z_{eff})_3$).

If it were possible to introduce the three interelectronic co-ordinates explicitly into the wave function (as was done for H_2 by James and Coolidge[33]) then it would no longer be necessary to employ these multiple wavefunctions—some expanded