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Reactions Involving Hydrogen Molecules and Atoms

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The criticisms of Coolidge and James of activation energy calculations are discussed. It is pointed out that their criticisms of the original London proposal do not apply to the semi-empirical method which in its present form has little more than a formal resemblance to the original scheme. Until a satisfactory quantum-mechanical derivation of the semi-empirical method is provided, it must depend for acceptance on its usefulness and the fact that it is a reasonable interpolation formula for calculating the energies of polyatomic molecules from diatomic ones. The best surface for three hydrogen atoms is constructed and from it the rates of all the possible hydrogen-deuterium reactions are calculated by means of the general theory of absolute rates, these rates are found to be in excellent agreement with the experimental values. The transmission coefficient for reactions on this surface is investigated. Diagrams showing the angular dependence of the potential energy for an H and for a Cl atom approaching a hydrogen molecule are given.

I. INTRODUCTION

IN this paper the absolute rates of all the reactions involving hydrogen and deuterium are calculated theoretically using the best available potential energy surface. The results are compared with the experimental values.[1]

It is advantageous to consider the methods for calculating suitable potential energy surfaces for use in the interpretation of reaction rates. Since the early work of Arrhenius,[2] chemists have realized that the intermediate in a reaction was a state of high energy. In many reactions, this was interpreted as a state of high potential energy which could be reached only by the collision of two molecules having unusually great relative kinetic energy.[3] Thus it was clear that energy surfaces were required. However, there was no theoretical way of supplying this need before the advent of quantum mechanics. In 1928, London[4] proposed that a large body of reactions might be considered as proceeding adiabatically in the Ehrenfest sense and that a single eigenfunction be used to represent the electronic state throughout the course of the chemical reaction, i.e., no electron jumps are involved and just one potential energy surface is required. Villars[5] also proposed a rather specialized procedure of calculating the potential energy for the reaction $H_2+I_2\rightarrow 2HI$. London's suggestion included a first-order perturbation theory formula for constructing the necessary potential surface for three and four-atom reactions. These formulae were derived from first-order perturbation theory when the following assumptions were made:

1. Certain complicated types of electronic interactions known as multiple exchange integrals were neglected.
2. The nonorthogonality of the electronic charge distributions, i.e., overlap integrals, was considered to be negligibly small.
3. The remaining integrals were idealized to the point where they could be calculated from knowledge of corresponding diatomic integrals, and they were expressed in terms of the simplest atomic eigenfunctions.

This last assumption made the energy of the polyatomic configuration a function of diatomic energies only. Eyring and Polanyi[6] first applied this method unmodified to the triatomic hydrogen system using the exchange and coulombic integrals calculated by Heitler and London[7] and by Sugiura.[8] They obtained the activation energy of 29 kcal./mole for the reaction H_2+H

[1a] A. Farkas and L. Farkas, Proc. Roy. Soc. **A152**, 124 (1935).

[1b] L. Farkas and E. Wigner, Proc. Faraday Soc. in press. We wish to thank the authors for the opportunity of seeing their manuscript in advance of publication. They consider some of the questions treated in this paper but from the point of view of going from the experimental rates to a potential surface. Here all of our results are calculated from the surface considered best *a priori*.

[2] Arrhenius, Zeits. f. physik. Chemie **4**, 226 (1889).

[3] M. Polanyi, Zeits. f. Physik **1**, 90 (1920); Zeits. f. Elektrochemie **62**, 228 (1920); and Tolman, *Statistical Mechanics* (Chemical Catalog Co., 1927).

[4] London, *Probleme der Moderne Physik* (Sommerfeld-Festschrift); (S. Hirzel, Leipzig, 1928), page 104; Zeits. f. Elektrochemie **35**, 552 (1929).

[5] Villars, Phys. Rev. **34**, 1063 (1929).

[6] Eyring and Polanyi, Zeits. f. physik. Chemie **B12**, 279 (1931).

[7] Heitler and London, Zeits. f. Physik **44**, 455 (1927).

[8] Sugiura, Zeits. f. Physik **45**, 484 (1927).

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$\rightarrow H+H_2$ and this is to be compared with the experimental value of 7 kcal./mole. This discrepancy is not surprising since the energy of the normal H_2 molecule calculated from these integrals is only -72.2 kcal./mole instead of the experimental value of -108.6. This activation energy agrees as regards order of magnitude but is far from the accuracy which is necessary for the quantitative calculation of reaction rates. In more complicated reactions, the required integrals were not available. Clearly some improvements were required if the method was to be more than suggestive in the treatment of reactions. The suggestion for the improvement and extension made by Eyring and Polanyi was that the small coulombic energy could be calculated and the exchange energy could then be obtained by subtracting this coulombic energy from the spectroscopically known total binding of the diatomic molecules. In later treatments, the coulombic energy was assumed to be a certain constant percentage of the total binding. This assumption is born out by the Heitler-London-Sugiura integrals for hydrogen and what is more important it is justified empirically by the fact that the same constant percentage gives very nearly the experimental activation energy for a wide variety of cases. It will be shown elsewhere that the constant percentage assumption for three like atoms really leads to the conclusion that the activation energy is directly proportional to the energy of binding of the diatomic molecule. When the spectroscopic and other experimental data are used in the London formulae in place of the integrals which are supposed to be calculated with approximate charge distributions, the assumptions involved lose their original significance but the formulae themselves remain at least an interpolation mechanism for going from diatomic to polyatomic knowledge. When the atoms are widely separated, the London assumptions and the semi-empirical method are equally valid. When only pairs of univalent atoms are together, although the London scheme is inaccurate, the semi-empirical method is still correct. Since the percentage of additive energy is chosen to give the right activation energy and the potential energy goes smoothly into the correct values as the atoms separate into individuals or into pairs, the semi-empirical method must be nearly accurate in its important features. The details of the surface which are necessary to calculate the rate of chemical reactions are:

1. The activation energy.
2. The vibration frequencies.
3. The position of the activated state.
4. The probability that the system having once passed through the activated state will not return.

For each of these, the semi-empirical surface cannot be far wrong. When sufficient accurate data become available so that a precise empirical analysis of these features may be obtained, an improved interpolation formula may be indicated. In the meantime, these semi-empirical surfaces represent our best information as to the nature of interatomic forces and provide a very practical tool for investigating the nature of chemical problems.

Coolidge and James[9] have analyzed the London assumptions and find no way of justifying them in their original form. Since no adequate theoretical derivation of the semi-empirical scheme has ever been proposed it is impossible at the present time to say how rigorously it can be derived from quantum mechanics for the interesting intermediate configurations. The London treatment and the semi-empirical one are sufficiently different to make it impossible to base a criticism of the latter on the basis of the former. An accurate quantum-mechanical surface would be very desirable and we are making some progress in this direction. In a recent paper Rosen and two of the present authors[10] derive the energy of the triatomic hydrogen molecule to the Wang plus polar states approximation by the variation method but the calculated activation energy is 25 kcal. On the basis of these calculations which include and go considerably beyond the calculations of Coolidge and James we find that, for the present at least, the only surfaces adequate for the treatment of chemical reactions are the semi-empirical ones.

The Potential Energy Surface for H_3

The semi-empirical potential energy surface of constant percentage additive energy is given

[9] Coolidge and James, J. Chem. Phys. **2**, 811 (1934).
[10] Hirschfelder, Eyring and Rosen, J. Chem. Phys. **4**, 121ff (1936).

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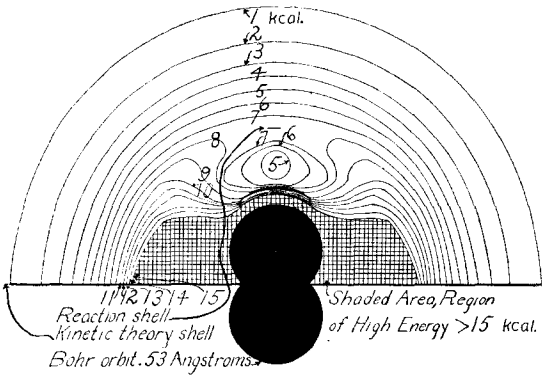

FIG. 1. Potential for an H atom approaching an H_2 molecule.

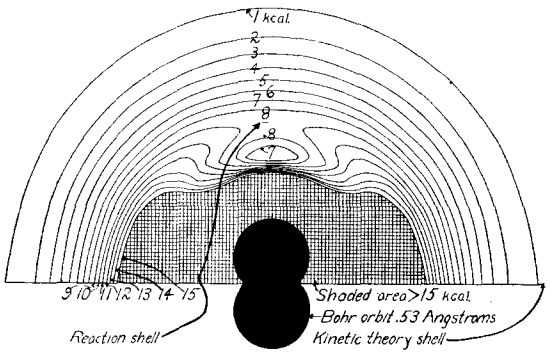

FIG. 2. Potential for a Cl atom approaching an H_2 molecule.

by the lowest root:

$$E = D' + n(w_{ab} + w_{bc} + w_{ac}) \mp (1-n)(w_{ab}^2 + w_{bc}^2 + w_{ac}^2 - w_{ab}w_{bc} - w_{ab}w_{ac} - w_{bc}w_{ac})^{\frac{1}{2}} \quad (1)$$

where D' is the heat of dissociation of H_2 minus the half-quanta of zero-point energy,

w_{ab} is the energy of H_2 for the internuclear separation r_{ab} and similarly for w_{bc} and w_{ac},

n is the fraction of the total binding energy of H_2 which is taken to be additive.

w_{ab}, w_{bc}, w_{ac} are taken from the spectroscopically determined Morse[11] curve for H_2.

Certain features of the surface are exhibited in Fig. 1. In this case two atoms of a hydrogen molecule are held at the normal internuclear distance. The contour lines are the lines of constant potential energy for the various positions of the third atom. The third atom approaching in any direction is first attracted by weak van der Waals forces. Coming closer, the attraction changes to repulsion. An atom of only average thermal velocity (at room temperatures) will be repelled before it reaches the first contour line. At large distances the equipotential surfaces are very nearly spherical. A colliding atom with very high energy penetrates into the interior where it becomes easier to advance parallel to the line of nuclei than perpendicular to this line. If the atom approaches along the line of nuclei and has sufficient energy, it will cross over the energy pass marked, "reaction shell." From this point, it is now attracted for a short distance as previously stated. In Fig. 1 we have kept the two atoms of the original hydrogen molecule at a fixed distance apart. If left to itself the molecule expands slightly as the atom approaches, and after the atom has reached the reaction shell all three atoms vibrate violently. One of the outer atoms departs. If the departing atom belonged to the original molecule a chemical reaction has taken place. The similarity between surfaces of this type is seen by a comparison of Figs. 1 and 2. In the latter the equipotentials for a hydrogen molecule and a chlorine atom are given. As before, the energy pass lies along the molecular axis but at a somewhat greater interatomic separation.

The more nearly the atom approaches along the molecular axis the less the energy required for reaction. For this reason, it is desirable to examine the motion of the three atoms in a line in greater detail; the angular motion is treated by the method of small vibrations and so to this approximation the two motions are separable. The equipotential energy surface for three atoms colliding along a straight line is given in Fig. 3. Only the portion of the surface in the neighborhood of the activated state is shown here. This is the important region for this reaction. The initial state for the system is far to the right and the final state is correspondingly far above the figure as drawn. This surface is drawn so that a mass point having the potential energy indicated by the contour lines and moving in the plane faithfully describes the behavior of a three H atom system. The significance of the

[11] P. Morse, Phys. Rev. **34**, 57 (1929).

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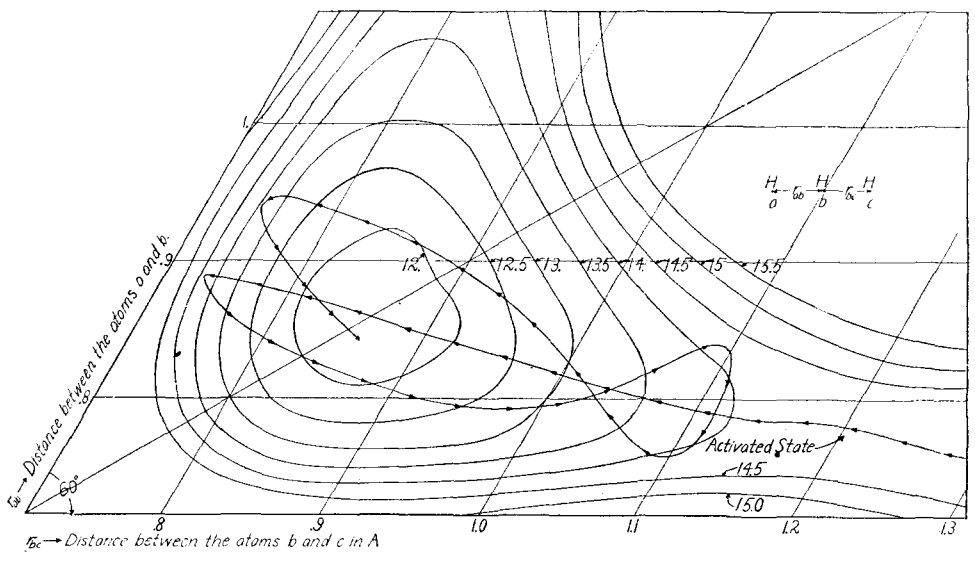

FIG. 3. A detailed vibrational trajectory for linear H_3 is indicated by the line with arrows.

coordinates are made clear in Fig. 3. The line with the arrows represents a trajectory calculated point by point from the classical equations of motion. It is interesting to note that although the system has 300 cal. more energy than is required for reaction (i.e., to pass up beyond the top of the diagram) it wanders about in the potential basin a considerable time. Eventually the system will either react or pass back into the valley from which it came. Which it will do is a mechanically determined problem if we use classical theory. Using classical theory approximately half of a group of such particles entering at various angles will react and half will return to the initial state. Although this problem has not been treated quantum mechanically (and it is not easy to do so) it seems safe to anticipate this same result. If the true surface instead of having the basin shown in Fig. 3 should have the activated state on the symmetrical line this probability of reaction will be considerably increased over one-half but the factor cannot exceed one. However, we will find that when the two outer atoms are identical the symmetry now possessed by the activated complex introduces a statistical factor acting to slow down the rate by a factor of two so that there will be very little net change. We shall therefore restrict our considerations to the surface of Fig. 3. At present it is impossible to say whether the existence of this basin is a virtue or defect of the semi-empirical method of calculating surfaces.

One of the most interesting applications of a potential energy surface is in the determination of the rates of a chemical reaction. The specific reaction rate, k', i.e., the rate at which a reaction takes place when the concentrations of the reacting substances are each equal to unity, has usually been expressed in the form:

$$k' = cZe^{-E/kT}, \tag{2}$$

where Z is the number of collisions which the molecules make in unit time. E is the activation energy of the reaction. The c is the collision efficiency or the ratio of the number of chemical reactions to the number of collisions between the desired molecules which have a kinetic energy relative to its center of mass of more than the energy E. The objections to the form (5) are that c is not defined in terms of molecular properties, it varies from unity to 10^{-8} in magnitude,[12] and it is often found experimentally to be a function of the temperature. Pelzer and

[12] Moelwyn-Hughes, *Kinetics of Reactions in Solutions* (Oxford Press, 1933); L. Kassel, *Kinetics of Reactions* (Chemical Catalog Co., 1932), p. 16; Gershinowitz and Eyring, J. Am. Chem. Soc. **57**, 985 (1935).

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Wigner[13] considered explicitly the reaction $H+H_2$ (*ortho*) $\rightarrow H_2$ (*para*) $+H$. They used classical statistical mechanics to determine the density of systems in phase space within prescribed velocity ranges and in the vicinity of the activated state. With this information, they were able to determine the specific reaction rate as the number of systems crossing the activated state from right to left in unit time multiplied by the fraction of these reactions which lead to H_2 (para). They treated the vibrations of the activated complex as classical simple harmonic motion and have given a justification of treating the motion of the atoms as adiabatic. In a subsequent paper Wigner[14] has given a correction to the classical calculation of the rate of crossing the barrier which we discuss below. Eyring[15] generalized the statistical treatment of reaction rates by considering:

$$k' = \kappa \frac{F_a^*}{F_n} \frac{kT}{h} \exp(-E_0/kT), \qquad (3)$$

where F_a and F_n are the partition functions for the activated and the initial configurations of the system. The zero of energy for F_a^* is the lowest state at the top of the barrier while the energy for F_n is the lowest initial state. These states differ by E_0. κ is the transmission coefficient or the fraction of the systems which having reached the activated state leads to a chemical reaction. F_a^* is the product of translational, rotational, and vibrational functions for all except the degree of freedom in the direction in which the complex is decomposing. The partition function for this degree of freedom multiplied by the velocity of crossing the barrier is included in the frequency factor kT/h if we treat crossing the barrier as a pure translation. To take into account the curvature of the barrier we must introduce the additional factor $1-(1/24)(h\nu_t/kT)^2$ which is a quantum-mechanical correction. ν_t^2 is negative and is the square of the imaginary frequency which the theory of small vibrations give for the degree of freedom normal to the barrier. This correction is due to Wigner.[14] It becomes negligible at high temperatures or for small curvatures. When barriers of sufficiently high curvature are encountered the correction should be carried to higher powers of h to give the tunnel effect. Such calculations have been made exactly by Eckart[16] for a special potential surface of one degree of freedom and have been considered approximately by a number of people.[17] The rotations and vibrations are treated as sharply quantized states, which is probably a very good approximation. The transmission coefficient, κ, is a constant of the order of unity. For the reaction $H+H_2 \rightarrow H_2+H$, we have seen that κ is nearly one-half. However, if we distinguished a chemical reaction only when a particular form of H_2, *ortho* as an example, is converted into another particular form (*para*), this value for k' must be multiplied by an *a priori* probability of the conversion occurring. These *a priori* probabilities may be easily computed from a consideration of nuclear spin coupling; for the *ortho-para* conversion of hydrogen this factor is one-fourth. It is therefore possible to use the semi-empirical energy surfaces to calculate the rate of a simple chemical reaction.

The specific rate of reaction of a hydrogen or deuterium atom with a hydrogen, deuterium or mixed molecule is given by the expression:

$$\begin{matrix} a & b & c \\ \cdot & \cdot & \cdot \end{matrix} \qquad a+bc \rightarrow ab+c$$

$$k' = \kappa i \left(\frac{h^2}{4(2\pi)^{\frac{3}{2}}k^{\frac{1}{2}}}\right) \frac{g_{abc}\sigma_{bc}}{g_{bc}\sigma_{abc}} \left(\frac{m_a+m_b+m_c}{m_a(m_b+m_c)}\right)^{\frac{3}{2}} \frac{I_{abc}}{I_{bc}} \frac{\sinh \frac{1}{2}(h\nu_{bc}/kT)}{\sinh \frac{1}{2}(h\nu_s/kT) \sinh^2 \frac{1}{2}(h\nu_\varphi/kT)}$$

$$\times \left(1-\frac{1}{24}\left(\frac{h\nu_t}{kT}\right)^2\right) T^{-\frac{1}{2}} \exp(-E_c/kT). \qquad (4)$$

[13] Pelzer and Wigner, Zeits. f. physik. Chemie **B15**, 445 (1932).
[14] E. Wigner, Zeits. f. physik. Chemie **B19**, 203 (1932).
[15] H. Eyring, J. Chem. Phys. **3**, 107 (1935).
[16] C. Eckart, Phys. Rev. **35**, 1303 (1930).
[17] Bell, Proc. Roy. Soc. **A139**, 466 (1933); Cremer and Polyani, Zeits. f. physik. Chemie **B19**, 443 (1932); Baun and Ogden, Proc. Faraday Soc. **30**, 432 (1935).

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This is the expanded form of Eq. (3) for this particular case in the units cc molecules^{-1} sec.$^{-1}$. To obtain it in the units liters moles^{-1} sec.$^{-1}$ we must multiply (7) by $N^{5/2}\ 10^{-3}$ where now the masses are to be taken in atomic weight units and N is Avogadros number. Here: i=the *a priori* probability of the reaction occurring on the basis of the nuclear spin interactions. It is one except for the *ortho-para* hydrogen and the singlet-triplet to doublet (nuclear spin) deuterium conversion.

1. $H+H_2$ (*ortho*) $\rightarrow H_2$ (*para*)$+H$, $i=1/4$
2. $H+H_2$ (*para*) $\rightarrow H_2$ (*ortho*)$+H$, $i=3/4$
3. $D+D_2$ (sing.-trip.)$\rightarrow D_2$ (doub.)$+D$, $i=1/3$
4. $D+D_2$ (doub.) $\rightarrow D_2$ (sing.-trip.)$+D$, $i=2/3$

In general, i seems to be equal to the ratio of the number of nuclear states of the resultants to the sum of the initial and final states.

g_{abc} is the number of electronic states of the activated complex and this is equal to two for all of the states that we consider and is equal to g_{bc} the number of electronic states for the initial molecule plus atom.

σ_{abc} is the symmetry number of the activated state. Since the potential surface which we are considering, makes the activated complex unsymmetrical with respect to a and c, this number is equal to unity.

σ_{bc} is the symmetry number of the initial molecule bc. It is equal to two if bc is either H_2 or D_2 and unity if bc is HD.

E_c is the difference of the potential energy of the initial molecule bc from that of the activated complex abc where the zero-point energies for both states have been absorbed in the various hyperbolic sines. For the potential surface which we shall consider (20 percent additive energy), $E_c=7.63$.

I_{bc} is the moment of inertia of the initial molecule bc. It may be expressed in terms of the atomic masses and the equilibrium separation $(r_0)_{bc}$:

$$I_{bc}=\frac{m_b m_c}{m_b+m_c}(r_0)_{bc}^2.$$

I_{abc} is the moment of inertia of the activated complex. In terms of the masses of the constituents and the separations in this configuration, r_{ab}, r_{bc}:

$$I_{abc}=\frac{1}{m_a+m_b+m_c}(m_a(m_b+m_c)r_{ab}^2+2m_a m_c r_{ab}r_{bc}+m_c(m_b+m_a)r_{bc}^2).$$

ν_{bc} is the vibration frequency of the diatomic molecule bc. It varies inversely as the square root of the reduced mass of the molecule.

ν_ϕ= the bending frequency of the activated complex and it is doubly degenerate since the molecule can bend in two perpendicular planes with the same frequency.

ν_s is that frequency of the normal linear mode of vibration of the activated complex whose square is positive. ν_t is the other linear frequency.

The internal kinetic energy for the linear triatomic molecule in the neighborhood of the activated complex separates into two independent parts. The first part T_L is due to two independent linear modes of motion for which we shall use the coordinates r_{ab} and r_{bc} already defined by reference to Fig. 3. Here

$$T_L=(1/2M)[m_a(m_b+m_c)\dot{r}_{ab}^2+2m_a m_c\dot{r}_{ab}\dot{r}_{bc}+m_c(m_b+m_a)\dot{r}_{bc}^2],$$

where $M=(m_a+m_b+m_c)$ and the other m's have been defined. The second part of T_ϕ is due to a doubly degenerate bending vibration having the kinetic energy

$$T_\phi=\frac{r_{ab}^2 r_{bc}^2 m_a m_b m_c\dot{\phi}^2}{2MI_{abc}}$$ associated with each mode.

Here ϕ is the angle between r_{ab} and r_{bc}. Now the linear potential energy in the neighborhood of the activated state for 20 percent additive binding is

$$v_L=7.63+\tfrac{1}{2}f_1(r_{bc}-1.354)^2+f_{12}(r_{bc}-1.354)(r_{ab}-0.753)+\tfrac{1}{2}f_2(r_{ab}-0.753)^2.$$

Where the r's are subtracted from the corresponding coordinate of the activated state. Angstrom units are used for the lengths. The force constants have the values

$$f_1=-14.15;\quad f_{12}=62.70\quad f_2=624.4,$$

where the units are kcal. mole^{-1} A^{-2}. Finally $\nu_\phi=\frac{1}{2}f_\phi\phi^2$ where $f_\phi=5.80$ kcal. mole^{-1} radians^{-2}.

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By the usual method for small vibrations[18] we find for

$$\nu_s=(1/2\pi)(2m_am_bm_c)^{-\frac{1}{2}}\times[\alpha+(\alpha^2-4m_am_bm_cM(f_1f_2-f_{12}))^{\frac{1}{2}}]^{\frac{1}{2}},$$

$$\nu_t=(1/2\pi)(2m_am_bm_c)^{-\frac{1}{2}}\times[\alpha-(\alpha^2-4m_am_bm_cM(f_1f_2-f_{12}))^{\frac{1}{2}}]^{\frac{1}{2}},$$

where

$$\alpha\equiv m_a(m_b+m_c)f_1+m_c(m_b+m_a)f_2-2m_am_cf_{12}.$$

Here of course ν_s, ν_t and ν_0 are the linear symmetrical vibration, the imaginary frequency across the barrier and the bending frequency, respectively. We get Table I for the frequencies and for the zero-point energies and moments of inertia for the different reactions.

Wigner and Farkas[19] find from an examination of the experimental data of Farkas and Farkas for the rates of the various types of hydrogen-deuterium reactions, that for $H+H_2$

$$1/2h\nu_s=5.3 \text{ kcal. mole}^{-1},$$
$$1/2h\nu_\phi=0.75,$$

which is in very good agreement with our values given in Table I. They find that the difference of the potential energy at the activated state and the initial states, i.e., our E_c is 7.2 kcal./mole as compared with our calculated value of 7.63 using 20 percent additive energy. The reinterpretation of the results of Farkas and Farkas by Wigner and Farkas changes the activation energy from 5.5 to 7.8 kcal./mole which is now in agreement with the low temperature measurements of Geib and Harteck[20] and is to be compared with the value of 8.5 which we are using. The important features of our surface all lie well within the probable error of the best available experiments. For this reason it is of considerable interest to present our theoretical values for all the reactions over a considerable range of temperature. The calculated values were obtained before the experimental results of Farkas and Farkas and the reinterpretation of Farkas and Wigner were available and the agreement came as something of a surprise particularly since it was felt that for the zero-point energy of the activated state to be actually larger than the initial state would probably lead to wrong relative rates for some of the reactions.

Table I.

	Reaction	I_{abc} (g cm²)	$-i/2h\nu_t$ (kcal./mole)	$\frac{1}{2}h\nu_\phi$ (kcal./mole)	$\frac{1}{2}h\nu_s$ (kcal./mole)	Zero-Point Energy Activated State (kcal./mole)	Zero-Point Energy Initial State (kcal./mole)
1	$H+H_2$	3.79×10^{-40}	0.90	0.95	5.18	7.08	6.21
2	$D+D_2$	7.58	.64	.67	3.66	5.00	4.39
3	$H+DH$	4.69	.83	.86	4.57	6.29	5.38
4	$D+HD$	7.50	.68	.86	4.38	6.10	5.38
5	$H+HD$	4.92	.83	.88	4.40	6.16	5.38
6	$D+H_2$	5.45	.73	.93	5.17	7.03	6.21
7	$D+DH$	5.77	.66	.76	4.56	6.08	5.38
8	$H+D_2$	4.92	.82	.70	3.67	5.07	4.39

$\kappa=\frac{1}{2}$ for the reactions 1. $H+H_2\rightarrow H_2+H$, 2. $D+D_2\rightarrow D_2+D$, 3. $H+DH\rightarrow HD+H$, 4. $D+HD\rightarrow DH+D$. The absolute rates of these reactions are therefore calculated from Eq. (4). See Table II. Eqs. (1) and (2) are for the total reaction rates. If one is interested in the *ortho-para* conversions these rates must be multiplied by the appropriate values of i already discussed.

In reactions (4) to (8) where the zero-point energies are different in the two passes on either side of the central basin, it is more difficult to calculate the transmission coefficient. However, this factor may be evaluated if we assume that when a system passes through the nearest pass and into the basin, its chances of decomposing in the two different manners is independent of the initial state of the system. This assumption is equivalent to the relation: $\kappa_f+\kappa_r=1$. Let G_f and G_r be the reaction rates of the forward and reverse reactions except for the transmission coefficients:

$$k_f'=\kappa_fG_f \quad k_r'=\kappa_rG_r.$$

But the equilibrium constant for the reaction, K, is defined as the ratio of the rates of the forward and the reverse reactions. Therefore:

$$K=k_f'/k_r'=G_f\kappa_f/G_r\kappa_r$$

and $\kappa_f=G_rK(G_f+G_rK)^{-1}$, $\kappa_r=G_f(G_f+G_rK)^{-1}$.

Now since κ_f and κ_r separately can never exceed

[18] Whittaker, *Analytical Dynamics* (Cambridge Press, 1927), p. 127.

[19] Farkas and Wigner (reference 1b) obtained the results for $\frac{1}{2}h\nu_s$, $\frac{1}{2}h\nu_\phi$, and E_0' quoted here by using a combination of the low and high temperature measurements. The use of high temperature measurements alone would, in their opinion, indicate a somewhat different set of constants.

[20] Geib and Harteck, Zeits. f. physik. Chemie (Bodenstein Volume), 849 (1931).

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TABLE II. *Reaction rates (in liter mole^{-1} sec.$^{-1}$).*

REACTION	k'	283°	300°	600°	900°	1000°
1. $H+H_2 \rightarrow H_2+H$	(H.E.T.)		7.3×10^4	7.3×10^7	9.2×10^8	1.5×10^9
	(F.&F.)				1.5×10^9	2.2×10^9
	(G.&H.)	8.5×10^4				
2. $D+D_2 \rightarrow D_2+D$	(H.E.T.)		3.0×10^4	3.5×10^7	4.4×10^8	7.6×10^8
	(F.&F.)					1.2×10^9
3. $H+DH \rightarrow HD+H$	(H.E.T.)		2.2×10^4	2.6×10^7	3.2×10^8	5.2×10^8
	(F.&F.)					6.8×10^8
4. $D+HD \rightarrow DH+D$	(H.E.T.)		2.4×10^4	2.4×10^7	2.6×10^8	4.4×10^8
	(F.&F.)					1.0×10^9
5. $H+HD \rightarrow H_2+D$	(H.E.T.)		1.1×10^4	1.8×10^7	2.6×10^8	4.5×10^8
	(F.&F.)					9.5×10^8
6. $D+H_2 \rightarrow DH+H$	(H.E.T.)		7.1×10^4	6.2×10^7	7.1×10^8	1.2×10^9
	(F.&F.)					2.5×10^9
7. $D+DH \rightarrow D_2+H$	(H.E.T.)		3.0×10^4	2.5×10^7	3.0×10^8	5.0×10^8
	(F.&F.)					7.9×10^8
8. $H+D_2 \rightarrow HD+D$	(H.E.T.)		1.5×10^4	2.8×10^7	4.3×10^8	7.4×10^8
	(F.&F.)					1.2×10^9

In the above table H.E.T. indicates the present authors, F.&F. Farkas and Farkas[18] and G.&H. Geib and Harteck.[19]

unity their sum cannot exceed 2 so that the true rates cannot exceed the calculated ones by more than a factor two due to the assumed relation $\kappa_f+\kappa_r=1$. That $\kappa_f+\kappa_r$ does not differ much from unity seems reasonably certain from an inspection of the surface. Thus we know the wave packet representing the system will be refracted like a light wave with an index of refraction depending on the total energy minus the potential energy and in this basin this will lead to repeated reflection. The same kind of factors operate to make egress random in quantum mechanics as operate in the classical case. The equilibrium constants can be evaluated independently of κ_f and κ_r from a knowledge of the initial and final states.

$$K_{H+HD}=\frac{k'_{H+HD}}{k'_{D+H_2}}=\frac{g_{H_2}\sigma_{HD}}{g_{HD}\sigma_{H_2}}\times\left(\frac{2m_D}{m_H+m_D}\right)^{\frac{1}{2}}\frac{\sinh\frac{1}{2}(h\nu_{HD}/kT)}{\sinh\frac{1}{2}(h\nu_{H_2}/kT)},$$

$$K_{D+DH}=\frac{k'_{D+DH}}{k'_{H+D_2}}=\frac{g_{D_2}\sigma_{HD}}{g_{HD}\sigma_{D_2}}\times\left(\frac{2m_H}{m_H+m_D}\right)^{\frac{1}{2}}\frac{\sinh\frac{1}{2}(h\nu_{HD}/kT)}{\sinh\frac{1}{2}(h\nu_{D_2}/kT)}.$$

The transmission coefficients are then found from the above relations. They are functions of the temperature since the zero-point energy at the two activated states are different. The transmission factors and the equilibrium constants are:

T	K_{H+HD}	K_{D+DH}	κ_{H+HD}	κ_{D+H_2}	κ_{D+DH}	κ_{H+D_2}
300°	0.144	2.147	0.192	0.808	0.819	0.181
600°	.287	.929	.332	.668	.673	.328
900°	.364	.719	.383	.618	.621	.379
1000°	.378	.677	.396	.604	.621	.379
∞	.577	.408				

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