[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE ENERGY OF ACTIVATION FOR BIMOLECULAR REACTIONS INVOLVING HYDROGEN AND THE HALOGENS, ACCORDING TO THE QUANTUM MECHANICS

BY HENRY EYRING[1]

RECEIVED APRIL 23, 1931 PUBLISHED JULY 8, 1931

Experiment shows that in homogeneous bimolecular reactions the specific reaction rate constant, k, is approximately

$$k = Se^{-A/RT} \tag{1}$$

A is the energy of activation and the proportionality factor, S, is equal to the number of collisions at unit concentration of the colliding substances. An *a priori* method of determining A, therefore, would make possible the prediction of rates of reactions.

Heitler and London,[2] using the quantum theory, were able to account satisfactorily for the binding of two hydrogen atoms. The so-called zeroth approximation as evaluated by Sugiura[3] gave a binding energy equal to three-fourths of the experimental value. The term "binding energy" will be used to indicate the energy which must be supplied to break the bonds in question. It is, therefore, the negative of the potential energy of the system referred to the dissociated state as the state of zero energy.

The perturbation theory yields expressions for the binding energy of three and four atoms. Agreement between theory and experiment for some typical cases involving three atoms has been reported elsewhere by Polanyi and the author.[4] They made the calculations for the reactions $H_{2para} + H = H_{2ortho} + H$; $Br + H_2 = HBr + H$ and $Br_2 + H = HBr + Br$ and have also considered the dynamics of such reactions. Many details of calculation were also given which it has not been deemed necessary to repeat here. Certain bimolecular reactions involving three and four atoms are considered below.

London[5] gives for the binding energy, E, holding three monovalent atoms together the expression

$$E = Q + \left[\frac{1}{2}((\alpha - \beta)^2 + (\alpha - \gamma)^2 + (\beta - \gamma)^2)\right]^{1/2} \tag{2}$$

The limitations on this formula will be discussed later. In equation (2) Q is the coulombic binding between three atoms, *i. e.*, the binding energy that one would calculate using classical electrodynamics if one assumed the

[1] Presented March 31, 1931, as part of the Symposium on "Applications of Quantum Theory to Chemistry," Indianapolis Meeting of the American Chemical Society.

[2] W. Heitler and F. London, *Z. Physik*, **44**, 455 (1927).

[3] V. Sugiura, *ibid.*, **45**, 484 (1927).

[4] Eyring and Polanyi, *Z. physik Chem.*, [B] **12**, 279 (1931).

[5] (a) London, *Z. Electrochem.*, **35**, 552 (1929); (b) Sommerfeld Festschrift, S. Hirzel, p. 104.

electrons to be the diffuse clouds of quantum mechanics. The coulombic energy is really the sum of three terms: $Q = A' + B + C$. The A is primed to distinguish it from the activation energy. To define these quantities further, consider the three atoms W, X, Y, which form the triangle of Fig. 1. The energy required to make the distances r_1, r_2, r_3 simultaneously very large is E of Equation 2. The binding between the atoms W and X when Y is far away is $E_1 = A' + \alpha$, and depends only on the distance r_1. Similarly the binding between X and Y with W far away is $E_2 = B + \beta$ and depends only on r_2; and between W and Y with X far away, the energy is $E_3 = C + \gamma$. The energy $E_1 = A' + \alpha$ plotted as a function of r_1 is just the familiar Franck curve for the diatomic molecule, WX. Such curves may be readily constructed using spectroscopic data; it is thus possible to calculate E of Equation 2 if either the coulombic or the interchange binding is known.[6]

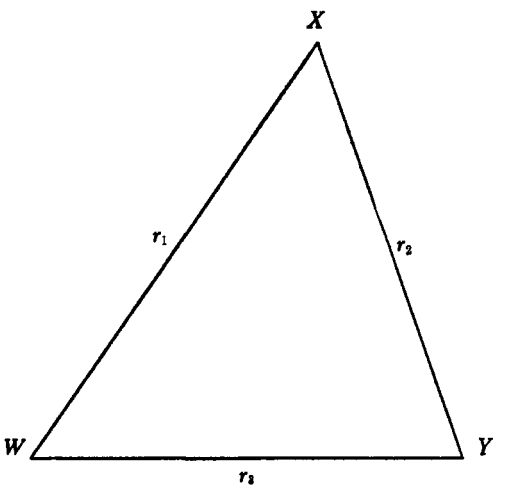

Fig. 1.

Morse[7] has obtained a convenient function which gives the dependence of the binding energy, E, on the distance, r, between the atoms for a diatomic molecule. In this equation

$$E = D'(2e^{-a(r-r_0)} - e^{-2a(r-r_0)}) \tag{3}$$

a is defined by the equality $a = 0.1227\ \omega_0(M/D')^{1/2}$. D' is the heat of dissociation of the molecule plus the half quantum of vibrational energy it has in the lowest level. ω_0 is the vibration frequency in the lowest level and M, the reduced mass, is defined by the expression

$$M = \frac{M_1 \cdot M_2}{M_1 + M_2}$$

where M_1 and M_2 are the atomic weights of the two elements. D' and ω_0 are to be taken in wave numbers.

E_1 can thus be obtained from optical data and A', the coulombic part of the potential energy, can be calculated from the approximate wave functions of Zener[8] and Slater.[9] The interchange binding α is then given by

[6] H. Eyring, *Naturwissen.*, **44**, 915 (1930).
[7] Morse, *Phys. Rev.*, **34**, 57 (1929).
[8] Clarence Zener, *ibid.*, **36**, 51 (1930).
[9] J. C. Slater, *ibid.*, **36**, 57 (1930).

the relationship $\alpha = E_1 - A'$ with similar expressions for β and γ. The direct calculation of the interchange binding is not feasible both because of the difficulty of such a calculation and because of the approximate nature of the eigenfunctions.

In what follows, however, the coulombic binding will be taken as 10% of the total binding for all values of r, *i. e.*, the theoretical value for H_2. It was shown in a previous paper[4] that in the case of H_2, for all values of r important in determining the energy of activation, the theoretical coulombic binding energy is about 10% of the total theoretical binding energy and about 8% of the empirically found binding energy. This assumption for other gases, while not strictly correct, will make possible a comparison of the theory with experiment and leads to some striking qualitative predictions which depend only on the coulombic binding being approximately 10% of the total.

Consider the reaction

$$WX + Y = W + XY \tag{3a}$$

To begin with, the distance r_1 may be supposed to have the normal value r_0 for the molecule WX while r_2 and r_3 are very large. The total binding energy is thus equal to $A' + \alpha$. If the atom Y is made to approach the molecule WX in such a way as to keep $\beta = \gamma$, the radical in Equation 2 will decrease continuously, becoming zero when $\alpha = \beta = \gamma$; *i. e.*, three identical monovalent atoms at the corner of an equilateral triangle have no interchange binding.

Examination of Equation 2 shows that Y may approach WX with the smallest increase of potential energy of the system if all the atoms remain on a straight line. In this case two distances, say r_1 and r_2, will fix the third, r_3, and so determine the energy of the configuration. If r_1 and r_2 be plotted at right angles to each other and lines of equal energy be drawn, a contour map results which gives the potential energy of the system. Such a map for three hydrogen atoms is given (Fig. 2).

In Fig. 2 the course of the reaction $H_{2\text{para}} + H = H_{2\text{ortho}} + H$ is indicated by the broken line and the arrows. To begin with, r_2 is very large and $r_1 = 0.76$ Ångström ($A' + \alpha = 107.6$ Calories, *i. e.*, the heat of dissociation plus a half quantum of vibration), then as the H atom approaches the para hydrogen molecule the potential energy increases adiabatically until the distance $r_1 = r_2 = 0.93$ Ångström when 11.4 Calories of potential energy have been stored up. This is the activation energy for the reaction. The reaction can now go to completion or the system may return to its former configuration. If r_1 increases the reaction goes to completion. The 11.4 Calories is the minimum value of the energy along the line $r_1 = r_2$, *i. e.*, $\alpha = \beta$, but it is the maximum value along the line with arrows which represents the course of the system during the reaction. It is thus a saddle value and may be calculated from Equation 2 by setting

$\alpha = \beta$, finding the minimum, and subtracting this value from the heat of dissociation of the hydrogen molecule. For reactions with unlike atoms the saddle value will not occur along the line $r_1 = r_2$ but will still be along the curve $\alpha = \beta$. Thus the energy of activation, A, for the reaction

$$WX + Y = W + XY \tag{3a}$$

is $A = D - (Q + \alpha - \gamma)_{\text{min.}}$. Here D is the heat of dissociation of the molecule WX and $(Q + \alpha - \gamma)_{\text{min.}}$ is the minimum value for this quantity

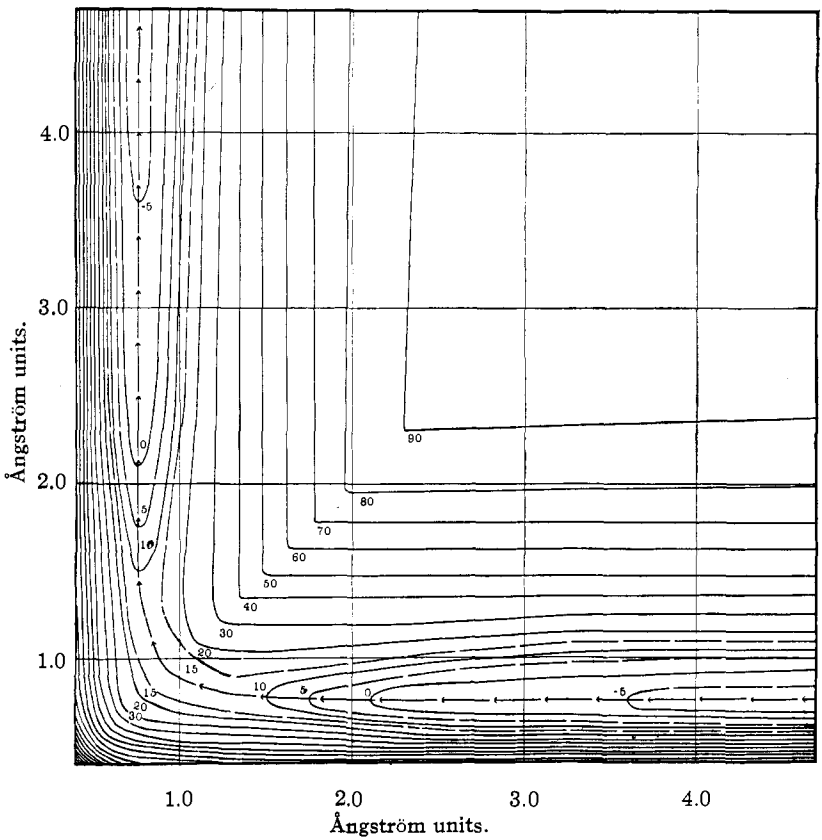

Fig. 2.

along the curve $\alpha = \beta$. It is important to remember that all binding energies are taken, like the heat of dissociation itself, as the negative of the potential energy, referred to complete dissociation as the zero of energy.

This reaction may thus be visualized as the motion of a mass point under the impetus of its kinetic energy moving up a valley until the lowest place in the divide between this valley and a neighboring valley is reached. Here the point may either return or pass over into the adjoining valley. The quantum mechanics provides still another alternative. The point

may pass through the energy mountain without bothering to go over the divide. Langer[10] discusses this possibility for chemical reactions. The chance of this happening falls off exponentially with the square root of the area enclosed between the line through the mountain and the one over the divide. This process becomes very improbable for the gentle slopes met in this type of reactions. The probability of going over the top of the mountain falls off exponentially with the height and does not depend on the slope.

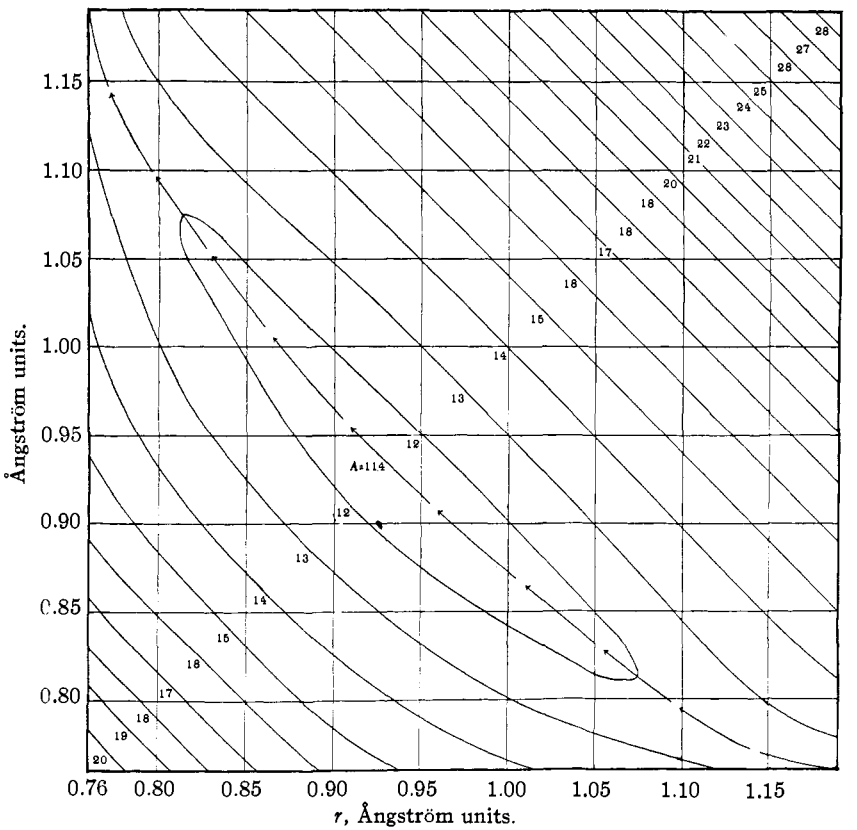

Fig. 3.

It is this exponential dependence on kinetic energy which makes it improbable that the mass point will arrive at the top of the divide with much excess kinetic energy. Thus the height of the divide measured from the bottom of the first valley can be identified with the energy of activation for the forward reaction, whereas for the reverse reaction the height of the divide must be measured from the second valley. The difference in the height of the two valleys is the heat of reaction. Having reached the top

[10] R. M. Langer, *Phys. Rev.*, **34**, 92 (1929).

of the divide, if P_1 represents the chance that the mass point will return to the first valley and P_2 the chance that it will continue on into the second, the entropy of the reaction is $\Delta S = R \ln (P_2/P_1)$.

A closer examination of the potential energy surface for three hydrogen atoms as shown in Fig. 3 reveals a slightly more complex surface than Fig. 2 would lead one to suspect. The configuration of lowest potential energy for which both of the outer hydrogen atoms are symmetrically placed with respect to the central atom is 11.4 Calories higher than the configuration in which the hydrogen atom is far away from the hydrogen

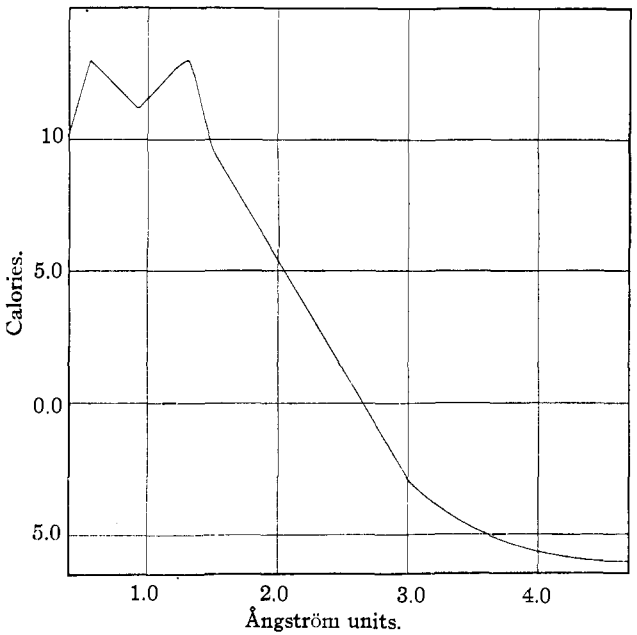

Fig. 4.

molecule but this symmetrical configuration, instead of corresponding to a saddle value, is really the floor of a shallow basin with a rim 1.6 Calories higher in the direction of the two valleys. However, since it is rather difficult to calculate the exact position and height of the rim of the basin and since in the reactions with which we are concerned the difference between the height of the rim and the floor of the basin will be about a Calorie and a half the values included in Table II are for the floor of the basin.

In Fig. 4 one simply sees in elevation the section through the contour map 2 traversed by the arrows. Because of the complete symmetry the section is only carried a little way beyond the symmetrical basin.

In Fig. 4 the smallest possible potential energy of the three atoms in a straight line is plotted as ordinate while as abscissa the distance between

the nearest atom in the molecule and the approaching free atom is plotted until the symmetrical position is reached at 0.93 Ångström. From here on the distance between the receding atom and the nearest atom of the new molecule is plotted as abscissa. The profile shows that an H_3 molecule is so unstable (heat of dissociation 1.6 Calories) that even if the heat of formation were carried away it would survive only a very few collisions and consequently has no existence in the ordinary chemical sense.

For reactions involving more atoms the potential energy surface will depend on more than two positional coördinates but with this single exception the discussion just given applies without essential change.

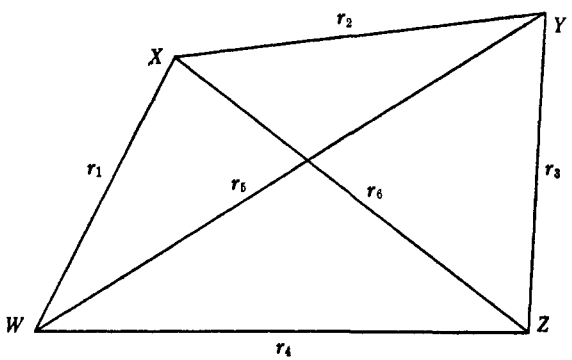

Fig. 5.

For the binding energy, E, of four atoms London[5a] has given the value

$$E = Q + \sqrt{\frac{1}{2}\left((\alpha_1 + \alpha_2 - \beta_1 - \beta_2)^2 + (\alpha_1 + \alpha_2 - \gamma_1 - \gamma_2)^2 + (\beta_1 + \beta_2 - \gamma_1 - \gamma_2)^2\right)} \tag{4}$$

The coulombic energy, Q, has the value $Q = A_1 + A_2 + B_1 + B_2 + C_1 + C_2$. In this equation, α_1 and A_1 depend only on r_1 of Fig. 5; and the dependence of the other quantities may be indicated by writing $\alpha_2(r_3)$, $\beta_1(r_2)$, $B_1(r_2)$, $B_3(r_4)$, $B_2(r_4)$, $\gamma_1(r_5)$, $C_1(r_5)$, $\gamma_2(r_6)$, $C_2(r_6)$. Each of these quantities has the same meaning as in the three atom case and may be determined in the same way from the binding of diatomic molecules.

The reaction may be written

$$WX + YZ = WZ + XY \tag{5}$$

Reaction 5 consists in passing from a configuration in which only r_1 and r_3 are small to a final one in which only r_2 and r_4 are small. The system will necessarily pass through an intermediate configuration for which $\alpha_1 + \alpha_2 = \beta_1 + \beta_2$. A simple argument shows that this is the smallest value E is forced to take in the reaction (*i. e.*, the largest potential energy the system must take) and so is the one to use in calculating the activation energy.

First it may be shown that the reaction will take place with the four atoms in a plane. For suppose any configuration in a plane has been

reached, such, for example, as that shown in Fig. 5. Keep all distances except r_5 fixed and make it smaller. Since $(\gamma_1 + \gamma_2) < (\alpha_1 + \alpha_2)$ and also $(\gamma_1 + \gamma_2) < (\beta_1 + \beta_2)$, this change in r_5 which increases γ_5 will decrease the radical in Equation 4. Q will increase but by a smaller amount so that the total binding will be diminished. Since changes occurring in reaction can all take place in a plane and since every departure from a plane decreases the binding energy, it follows that in the activated state all the atoms will lie in a plane. Four identical atoms at the corners of a symmetrical tetrahedron have no interchange binding.

Next consider the change in E for $(\alpha_1 + \alpha_2) = (\beta_1 + \beta_2)$ and $\delta(\alpha_1 + \alpha_2) = -\delta(\beta_1 + \beta_2)$. Then the change in $(\gamma_1 + \gamma_2)$, *i. e.*, $\delta(\gamma_1 + \gamma_2)$ will be negative since this change can be carried out in such a way as to increase the length of r_5 and r_6, and the change in the total binding energy, E, is

$$\delta E = \delta Q + \frac{1}{2}\frac{(\alpha_1+\alpha_2-\gamma_1-\gamma_2)(\delta(\alpha_1+\alpha_2)-\delta(\gamma_1+\gamma_2))+(\beta_1+\beta_2-\gamma_1-\gamma_2)(\delta(\beta_1+\beta_2)-\delta(\gamma_1+\gamma_2))}{\sqrt{\frac{1}{2}((\alpha_1+\alpha_2-\beta_1-\beta_2)^2+(\alpha_1+\alpha_2-\gamma_1-\gamma_2)^2+(\beta_1+\beta_2-\gamma_1-\gamma_2)^2)}}$$

$$= \delta Q - \frac{(\alpha_1+\alpha_2-\gamma_1-\gamma_2)\delta(\gamma_1+\gamma_2)}{\sqrt{\frac{1}{2}((\alpha_1+\alpha_2-\beta_1-\beta_2)^2+(\alpha_1+\alpha_2-\gamma_1-\gamma_2)^2+(\beta_1+\beta_2-\gamma_1-\gamma_2)^2)}}$$

but $(\alpha_1 + \alpha_2 - \gamma_1 - \gamma_2) > 0$ and $\delta(\gamma_1 + \gamma_2) < 0$ so that for δQ small, which is true for reactions with large activation energies, δE is positive, or becomes positive after emerging from the very shallow coulombic basin (depth of the order of a Calorie and a half), which we can ignore as in the case of three atoms. This shows that the reaction $WX + YZ = WZ + XY$ reaches a configuration when $\alpha_1 + \alpha_2 = \beta_1 + \beta_2$ such that the reaction can proceed in either direction with a decrease in the potential energy. Thus to find the activation energy one finds the minimum value of Equation 4 subject to the condition

$$\alpha_1 + \alpha_2 = \beta_1 + \beta_2 \tag{6}$$

which is just the minimum value of $E' = Q + \alpha_1 + \alpha_2 - \gamma_1 - \gamma_2$. This quantity subtracted from the sum of the heats of dissociation of WX and YZ gives the energy of activation.

The following scheme was used in calculating the activation energies given below. First, potential energy curves were constructed for all molecules entering into the reactions. The necessary constants were taken for the most part from the "International Critical Tables" and from Landolt-Börnstein.

r_0 for bromine was calculated from Morse's relation $r_0^3\omega_0 = 3000$. The constants in Table I for hydrogen, bromine and hydrogen bromide are slightly different than those used by Eyring and Polanyi.[4] The difference arises from taking the constants from different sources, and represents a slight uncertainty rather than an improvement. The effects on the calcu-

TABLE I

CONSTANTS USED IN DETERMINING THE MORSE EQUATION

Gas	D	D'	r_0	a	ω_0
H_2	101.5	107.6	0.76	1.85	4262
F_2	63.5	65	1.4	2.39	1071.5
Cl_2	58	58.8	1.74	2.22	570
Br_2	45.7	46.2	2.09	2.00	326.6
I_2	34.5	34.8	2.66	1.50	213.9
HI	69	72.2	1.62	2.28	2272
HBr	82.1	85.8	1.42	1.83	2603
HCl	101.5	105.7	1.28	1.77	2940.8
HF	146.5	152.2	0.923	2.00	3987
ICl	50.7	51.2	1.99	1.84	382

lated activation energies are very small, as a comparison of the results shows.

D in the table is the heat of dissociation in large calories and D' is the heat of dissociation plus a half quantum of vibrational energy. The other quantities have been defined. Consider for example the reaction

$$I + H_2 = HI + I$$

The maximum value of $(A + B + C + \alpha - \gamma)$ was calculated for the case of the three atoms on a line where in addition $\alpha = \beta$. This maximum value was then subtracted from the heat of dissociation of hydrogen, giving the energy of activation.

Two series of activation energies were calculated: one in which A, B and C were taken as 10% of the corresponding bonds, and the second for which they were taken as 3.5%.

For reactions of the type

$$H_2 + I_2 = 2HI$$

the maximum value of

$$(A_1 + A_2 + B_1 + B_2 + C_1 + C_2 + \alpha_1 + \alpha_2 - \gamma_1 - \gamma_2) \qquad (7)$$

was calculated subject to the conditions $(\alpha_1 + \alpha_2) = (\beta_1 + \beta_2)$. By considering (4) it can be shown that for the saddle value $r_2 = r_4$ and $r_5 = r_6$. Using these conditions, the maximum value of (7) is soon found. This maximum value is subtracted from the sum of the heats of dissociation of hydrogen and iodine to give the energy of activation. In Table II the results of the calculations are tabulated.

The first column in Table II gives the letter which will be used in referring to the reaction in the second column. The third to sixth columns give the distances between the atoms in the activated state. For three atom reactions the distances to which the r values refer will be clear from considering the general expression (3a) for a reaction in connection with Fig. 1. For four atom reactions the same information is obtained by considering equation (5) in conjunction with Fig. 5. Columns 7 and 8 give the calculated energy of activation when the coulombic binding

TABLE II

ENERGIES OF ACTIVATION IN K. CAL.

	Reaction	r_1	$r_2 = r_4$	r_3	$r_5 = r_6$	A_{10}	$A_{3.5}$	$A_{exp.}$	References
a	$H_2 + I_2 = 2HI$	0.86	1.78	3.17	2.43	28	40	40	11, 12
b	$H + I_2 = HI + I$					0	0		
c	$H_2 + I = HI + H$	1.23	1.67		2.90	29	41	>23	
d	$H_2 + Cl_2 = 2HCl$	0.93	1.70	1.87	2.15	54	75	>39	
e	$H + Cl_2 = HCl + Cl$					0	0	<10	13
f	$H_2 + Cl = HCl + H$	0.93	1.43		2.36	14	25	>10	14, 15, 16, 20
g	$H_2 + Br_2 = 2HBr$	0.94	1.72	2.28	2.26	45	62	>43	
h	$H + Br_2 = HBr + Br$					0	0	<10	13
i	$H_2 + Br = HBr + H$	1.13	1.53		2.66	26	32	19 to 30	13
j	$H_2 + F_2 = 2HF$	0.93	1.50	1.50	1.90	50	71	>25	17
k	$H + F_2 = HF + H$					0	0		
l	$H_2 + F = HF + H$	0.84	1.33		2.17	5	15	> 0	17
m	$I_2 + Cl_2 = 2ICl$	2.83	2.25	1.85	3.20	12	20	>15	18
n	$Cl_2 + I = ICl + Cl$	1.96	2.10		4.05	5	7		
o	$I_2 + Cl = ICl + I$					0	0		
p	$2H_{2para} = 2H_{2ortho}$	1.20	1.20	1.20	1.70	96	115	>55	
q	$H_{2para} + H = H_{2ortho} + H$	0.93	0.93		1.86	11	21	4 to 11	19

is taken as 10 and 3.5%, respectively. Column 9 gives the available experimental information on energies of activations. Activation energies are in kilocalories and distances in Ångströms.

To the theoretical activation energy of a reaction of the type $H_2 + I = H + HI$ must be added half the heat of dissociation of I_2 in order to obtain the apparent activation energy for the thermal combination of hydrogen and iodine by way of the atoms. This follows from thermodynamic considerations. Thus the theory shows the combination of hydrogen and iodine will not involve the atoms since this would require an activation energy greater by $41 + 17 - 40 = 18$ Calories than if the reaction involved only molecules. This value is arrived at using the figures in Column 9; exactly the same conclusion is reached using Column 8. Column 8 indicates that bromine will react with hydrogen without dissociating into atoms. Column 9 indicates it will involve atoms. Experimentally it is known to go through the atoms. On the other hand, all the other halogens

[11] Bodenstein, *Z. physik. Chem.*, **29**, 295 (1899).

[12] Kistiakowsky, THIS JOURNAL, **50**, 2315 (1928).

[13] E. Boehm and K. F. Bonhoeffer, *Z. physik. Chem.*, **119**, 285 (1926).

[14] Coehn and Jung, *ibid.*, **110**, 705 (1924).

[15] Bodenstein and Dux, *ibid.*, **85**, 297 (1913).

[16] R. G. W. Norrish, *ibid.*, **120**, 205 (1926).

[17] H. N. Wartenberg and J. Taylor, *Nachr. Ges. Wiss. Göttingen. Geschäft. Mitt. Math.-physik. Klasse*, **1**, 119 (1930).

[18] Gibson and Liebhafsky, unpublished.

[19] L. Farkas, *Z. physik. Chem.*, [B] **10**, 419 (1930).

[20] H. v. Hartel, *ibid.*, [B] **11**, 96 (1930).

will react with hydrogen by way of the atoms. This is in agreement with experiment. The theory also shows that the change of para to ortho hydrogen will proceed by way of the atoms. This too is correct, as Farkas'[19] experiments show.

This evidence is particularly cogent since with the exception of bromine it is independent of the fraction of the binding energy taken to be coulombic and so is direct evidence for the correctness of the adiabatic theory of reactions. Another interesting bit of evidence for the theory may be given.

The energy of activation for a three-atom reaction is $A = D - Q - \alpha + \gamma$. The three atoms in the activated state lie on a line thus: WXY and α is the interchange binding which would exist between W and X and also between X and Y if in each case the third atom were removed. γ is the interchange binding which would exist between W and Y if X were removed without altering the distance between W and Y. Since γ falls off with the distance between W and Y, a lower activation energy is to be expected for reactions in which the central atom is large, *i. e.*, for the halogens the activation energy should decrease progressively as the central atom changes through the series from fluorine to iodine. This fact is suggested and beautifully illustrated by some recent experiments of v. Hartel and Polanyi.[21]

Reactions	Activation energy
$CH_3F + Na = CH_3 + NaF$	25
$CH_3Cl + Na = CH_3 + NaCl$	8.8
$CH_3Br + Na = CH_3 + NaBr$	3.2
$CH_3I + Na = CH_3 + NaI$	0

They suggest that a proportionately greater coulombic binding, Q, for the heavier halogens, together with weaker binding, D, may partly account for this trend. There is, however, no indication in Table II that the coulombic part of the binding is greater for the heavier atoms.

Experimental values are not given in Table II for the reaction of hydrogen atoms with the halogens. However, the experiments of Boehm and Bonhoeffer[13] show that the mean life of hydrogen atoms in the presence of Cl_2 and Br_2 is less than a hundredth of a second and Polanyi shows that the ratio of the rates is as seven to one. These facts are at least consistent with the theoretical activation energy of zero Calories for both reactions.

The heat of dissociation of 63.5 kilocalories for fluorine estimated by Wartenberg and Taylor[17] is rather uncertain. If, however, even a value as high as 82.6 kilocalories be assumed, the activation energies for (*j*) are, respectively, 56 and 79 kilocalories; for (*k*) they are zero and zero and for (*l*) are 6 and 13 kilocalories for Columns 8 and 9, respectively. These changes would affect none of our conclusions and the intermediate value of

[21] H. v. Hartel and Polanyi, *Z. physik. Chem.*, [B] **11**, 97 (1930).

72 kilocalories for D estimated by Mullikan[22] would give intermediate values of the activation energies.

The numerical agreement between the calculated and experimental activation energies in Table II is as good as could be hoped for and indicates the essential correctness of the theory. Better checks must await more accurate experiments as well as the theoretical evaluation of the ratio of coulombic to total binding. The latter, though difficult, is by no means impossible. The above theoretical calculations suffice, however, to decide whether bimolecular reactions will involve single atoms or not and give the actual activation energies as accurately as they are known experimentally in a majority of the cases considered. Taking explicit account of the fact that the valence electron on the halogens is a p-electron would not change the activation energy for three atom reactions but would increase it for four atom reactions. This is in a direction to give better agreement with experiment in every case and to insure that the reaction between bromine and hydrogen will go by way of the atoms. Equations 2 and 4 were first obtained by group theory methods but may be very readily obtained by the method of Slater.[23] The details will not be given here. These equations in the form written are only strictly valid when the atoms are rather far apart. At closer ranges normalizing factors should be introduced. This correction has been approximately achieved in the above calculations by substituting for the quantities $A + \alpha$, etc., the experimental values for diatomic molecules which are automatically normalized.

Certain general remarks can be made regarding the applicability of the method of calculating activation energies that has been used here. It has been assumed that the atoms behave as they would classically in the potential energy fields calculated from quantum mechanics. This is possible because it is permissible to assume eigenfunctions for the atoms which have much greater curvature than the curvature of the potential energy fields in which the atoms move.

Even in reactions where the three and four atoms of the previous calculations are replaced by radicals or even by surfaces, the calculation should give a good approximation for the activation energy provided the bonds made and broken involve only the spins of three or four S electrons. This will include many reactions. The group theory can be used to obtain the potential energy in more complicated cases.

As the fraction of the binding which is coulombic increases, the activation energy decreases, becoming zero, for example, in strong electrolytes.

I have had the advantage of many helpful discussions with Dr. Clarence C. Zener, Professor G. E. Gibson and other members of the Departments of Chemistry and Physics, in the preparation of this paper.

[22] R. S. Mullikan, *Phys. Rev.*, **32**, 186 (1930).

[23] J. C. Slater, *ibid.*, **34**, 1293 (1929).

Summary

The adiabatic (London) theory of reaction rates has been applied, for the first time, to reactions involving four atoms. It shows, unambiguously, that the thermal reaction of hydrogen with iodine will involve only iodine molecules, while the other halogens will react with hydrogen by way of the atoms. It shows further that the conversion of para to ortho hydrogen will involve an atom and a molecule rather than two molecules. It explains the well-known greater reactivity of the heavy halogen compounds over the lighter ones. These checks with experiment are independent of the ratio of coulombic to total binding except in the case of bromine. If the known theoretical ratio of coulombic to total binding for hydrogen is assumed to hold for the other atoms, approximate agreement with experiment is obtained. To obtain exact agreement in the reaction $H_2 + I_2 = 2HI$ the coulombic binding must be assumed to be only three and a half per cent. of the total binding. The theoretical evaluation of the coulombic binding is possible, but difficult, using the approximate eigenfunctions of Zener and Slater.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 283]

THE VAPOR DENSITY OF SELENIUM TETRABROMIDE AND THE EXISTENCE OF SELENIUM DIBROMIDE

BY DON M. YOST AND JOHN B. HATCHER

RECEIVED APRIL 27, 1931 PUBLISHED JULY 8, 1931

Introduction

The results of the few qualitative observations that have been made on selenium tetrabromide[1] show definitely that it decomposes to some extent at room temperature and much more so at higher temperatures, the products of the decomposition being bromine and a lower bromide or bromides of selenium. Since no information of a quantitative nature seems to exist on the chemistry involved in the decomposition, the experiments described in this paper were undertaken.

Experimental Procedure and Preparation of the Materials.—The experiments consisted essentially in determining by the Dumas method the vapor densities of mixtures of selenium and bromine over the temperature range from 250 to 500°. Carefully weighed portions of bromine and elementary selenium were introduced into a cylindrical Pyrex tube

[1] *Cf.* Abegg, Auerbach and Koppel, "Handbuch der anorganischen Chemie," Leipzig, **1927**, IV Band, 1 abt., 1 hälfte, p. 724; Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green, London, **1930**, V. X, p. 899; J. Meyer and V. Wurm, *Z. anorg. Chem.*, **190**, 90 (1930).