been measured in the interval -82 to $0°$; the equation is $\log_{10} p = -127_5$ $(1/T) + 7.61_5$. (p in mm.); m. p. $= -105°$; b. p. $-4°$.

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THE FIVE-ELECTRON PROBLEM IN QUANTUM MECHANICS AND ITS APPLICATION TO THE HYDROGEN–CHLORINE REACTION

BY G. E. KIMBALL AND H. EYRING

Calculations of Rollefson and Eyring[1] point to the probable formation of Cl_3 molecules when chlorine atoms collide with chlorine molecules. To determine from perturbation theory whether such triatomic molecules react more rapidly with hydrogen molecules than do chlorine atoms requires a knowledge of at least the five-electron problem, since five valence electrons change partners in the process. It has been suggested recently by Franck and Rabinowitz[2] and more explicitly by Bodenstein[3] that the reaction $H + Cl_2 + H_2 = 2HCl + H$ might be an essential step in the photochemical combination of hydrogen and chlorine. To treat this reaction we again require a knowledge of the five-electron problem.

In the first part of the present paper we have used Slater's[4] method to solve the problem of five electrons with spin degeneracy and have given the rules for finding the eigenfunction corresponding to an arbitrary number of valence bonds between designated atoms. The energy levels can of course be found for more than five or six electrons but the labor becomes extremely great. In the second part of this paper we examine the reactions which might be expected to play important roles in the hydrogen–chlorine reaction.

The Five-Electron Problem.—We shall assume that the reader is familiar with Slater's treatment of the three- and four-electron problems, and shall use the same notation. We refer those desiring a fuller treatment than that given here to the thesis by one of us (G. E. K.).

If the eigenfunctions of the five electrons are $a(1)$, $b(2)$, $c(3)$, $d(4)$, $e(5)$, then the product $a(1)\,b(2)\,c(3)\,d(4)\,e(5)$ is a solution of Schrödinger's equation when the atoms are far apart. Any one of the 120 eigenfunctions obtained by permuting the electrons will likewise be a solution. As the atoms approach one another certain linear combinations of these eigenfunctions will form the "zero order" approximation to the solution.

[1] Rollefson and Eyring, THIS JOURNAL, **54**, 170 (1932).

[2] Franck and Rabinowitz, *Z. Elektrochem.*, **36**, 794 (1930).

[3] Bodenstein, *Trans. Faraday Soc.*, **27**, 413 (1931).

[4] Slater, *Phys. Rev.*, **38**, 1109 (1931).

Although the form of the eigenfunctions a to e will not appear explicitly in the solution, they may be thought of as those linear combinations of the available atomic eigenfunctions which lead to the lowest energy for the system. The evaluation of the resulting integrals from spectroscopic data avoids the difficult application of a variation method and the resulting computation.

Our problem is essentially simplified by introducing the Pauli principle at this point. Each of the electron eigenfunctions a to e is multiplied by a spin eigenfunction α or β, α representing a spin of $+^1/_2$, β a spin of $-^1/_2$. The total number of eigenfunctions resulting is $2^5 \times 120 = 3840$, but Pauli's principle immediately limits us to the 32 possible antisymmetric combinations of the form

$$\psi = \frac{1}{\sqrt{5!}} \sum \pm P(a\alpha(1)b\alpha(2)c\beta(3)d\beta(4)e\alpha(5)) \tag{1}$$

the sum being taken over all possible permutations P of the indices 1, 2, ... 5 each multiplied by $+1$ or -1 as the permutation P is even or odd. The factor $1/\sqrt{5!}$ approximately normalizes ψ. The summation in (1) is frequently written as a determinant.

The first order energy levels are given by the 32 roots of the secular equation formed from these 32 eigenfunctions, but since eigenfunctions corresponding to different total spins do not combine, the secular determinant is already factored into the product of six determinants of orders, 1, 5, 10, 10, 5 and 1, corresponding to total spins of $5/2$, $3/2$, $1/2$, $-1/2$, $-3/2$ and $-5/2$. The energies of the five doublet states (one of which corresponds to the lowest energy) are five of the ten roots of the tenth order determinant corresponding to a total spin of $1/2$. The ten eigenfunctions forming the basis of this determinant are indicated as follows

	a	b	c	d	e		a	b	c	d	e	
ψ_1	α	α	α	β	β	ψ_6	α	β	α	β	α	
ψ_2	α	α	β	α	β	ψ_7	β	α	α	β	α	
ψ_3	α	β	α	α	β	ψ_8	α	β	β	α	α	(2)
ψ_4	β	α	α	α	β	ψ_9	β	α	β	α	α	
ψ_5	α	α	β	β	α	ψ_{10}	β	β	α	α	α	

Each ψ_i corresponds to an eigenfunction of the type (1) in which the electronic eigenfunction at the top of the column is multiplied by the spin eigenfunction indicated. For example, eigenfunction ψ_5 is the particular eigenfunction given in (1).

By taking linear combinations of the ten eigenfunctions (2) the secular equation can be reduced even further. The three sets of linear combinations may be regarded as representing the system of five atoms with two valence bonds, one valence bond and no valence bond. In order to find these linear combinations we define a function δ_{mn} (K) for each eigen-

function ψ_K, and each pair of electron eigenfunctions ab, ac, etc., as follows: δ_{mn} (K) is $+1$ if the spin of m is α and the spin of n is β in ψ_K, -1 if the spin of m is β and that of n is α, and 0 if the spins of m and n are the same. Then if we wish a linear combination of the eigenfunctions representing the system with bonds between a and b, and c and d, the desired eigen-function is $\sum_{K=1}^{10} \delta_{ab}$ (K) δ_{cd} (K) ψ_K. There are fifteen such eigen-functions representing two valence bonds, but only five are linearly inde-pendent. We choose the following

$$\varphi_1 = {}^1/_2(\psi_6 - \psi_8 + \psi_9 - \psi_7)$$
$$\varphi_2 = {}^1/_2(\psi_8 - \psi_9 + \psi_4 - \psi_2)$$
$$\varphi_3 = {}^1/_2(\psi_8 - \psi_{10} + \psi_7 - \psi_5) \qquad (3)$$
$$\varphi_4 = {}^1/_2(\psi_2 - \psi_3 + \psi_{10} - \psi_4)$$
$$\varphi_5 = {}^1/_2(\psi_6 - \psi_{10} + \psi_4 - \psi_1)$$

There are four linearly independent eigenfunctions of the type $\sum_K \delta_{mn}$ (K) ψ_K corresponding to the system with one valence bond. Those we have chosen are

$$\varphi_6 = \frac{1}{\sqrt{6}} (\psi_3 - \psi_4 + \psi_6 - \psi_7 + \psi_8 - \psi_9)$$

$$\varphi_7 = \frac{1}{\sqrt{6}} (\psi_2 - \psi_4 + \psi_5 - \psi_7 + \psi_8 - \psi_{10})$$

$$\varphi_8 = \frac{1}{\sqrt{6}} (\psi_1 - \psi_4 + \psi_2 - \psi_4 + \psi_3 - \psi_{10}) \qquad (3)$$

$$\varphi_9 = \frac{1}{\sqrt{6}} (\psi_1 - \psi_7 + \psi_2 - \psi_9 + \psi_3 - \psi_{10})$$

Finally, corresponding to the system with no bonds, there is

$$\varphi_{10} = \frac{1}{\sqrt{10}} (\psi_1 + \psi_2 + \psi_3 + \psi_4 + \psi_5 + \psi_6 + \psi_7 + \psi_8 + \psi_9 + \psi_{10}) \qquad (3)$$

It is now found that the φ's corresponding to different numbers of bonds do not combine. The energies we wish are those of the system with two valence bonds. These are the five roots of the secular equation

$$| H_{ij} - W d_{ij} | = 0 \qquad (4)$$

where

$$H_{ij} = \int \varphi_i^* H \varphi_j \, d\tau$$
$$\qquad\qquad (i,j = 1,2,3,4,5)$$
$$d_{ij} = \int \varphi_i^* \varphi_j \, d\tau$$

and

$$H_{ij} = H_{ji}$$

If we denote the integral called by Slater $(abcde \,|\, H \,|\, abcde)$ by Q, and the integrals of the type $(abcde \,|\, H \,|\, bacde)$ by ab, and neglect the small integrals involving more than one interchange, and, moreover, assume that the eigen-functions $a, b, \ldots e$ are orthogonal, the elements H_{ij} are

$$H_{11} = Q + ab + cd - \frac{1}{2}(ac + ad + ae + bc + bd + be + ce + de)$$
$$H_{22} = Q + ab + ce - \frac{1}{2}(ac + ad + ae + bc + bd + be + cd + de)$$
$$H_{33} = Q + ac + bd - \frac{1}{2}(ab + ad + ae + bc + be + cd + ce + de)$$
$$H_{44} = Q + ac + be - \frac{1}{2}(ab + ad + ae + bc + bd + cd + ce + de)$$
$$H_{55} = Q + ad + be - \frac{1}{2}(ab + ac + ae + bc + bd + cd + ce + de)$$
$$H_{12} = -\frac{1}{2}Q + de + \frac{1}{4}(ad + ac + ae + bc + bd + be) - \frac{1}{2}(ab + cd + ce)$$
$$H_{13} = -\frac{1}{2}Q + ad + bc + \frac{1}{4}(ae + be + ce + de) - \frac{1}{2}(ab + ac + bd + cd)$$
$$H_{14} = \frac{1}{4}Q + \frac{1}{4}(ab + ac + bd + be + cd + ce) - \frac{1}{2}(ad + ae + bc + de) \quad (5)$$
$$H_{15} = \frac{1}{4}Q + \frac{1}{4}(ab + ad + bc + be + cd + de) - \frac{1}{2}(ac + ae + bd + ce)$$
$$H_{23} = \frac{1}{4}Q + \frac{1}{4}(ab + ac + bd + be + cd + ce) - \frac{1}{2}(ad + ae + bc + de)$$
$$H_{24} = -\frac{1}{2}Q + ae + bc + \frac{1}{4}(ad + bd + cd + de) - \frac{1}{2}(ab + ac + be + ce)$$
$$H_{25} = \frac{1}{4}Q + \frac{1}{4}(ab + ac + ad + be + ce + de) - \frac{1}{2}(ae + bc + bd + cd)$$
$$H_{34} = -\frac{1}{2}Q + de + \frac{1}{4}(ab + ad + ae + bc + cd + ce) - \frac{1}{2}(ac + bd + be)$$
$$H_{35} = \frac{1}{4}Q + \frac{1}{4}(ac + ad + ae + bc + bd + be) - \frac{1}{2}(ab + cd + ce + de)$$
$$H_{45} = -\frac{1}{2}Q + cd + \frac{1}{4}(ab + ae + bc + bd + ce + de) - \frac{1}{2}(ac + ad + be)$$

while the d_{ij} are simply the coefficients of Q in the H_{ij}. These integrals may be found from the spectroscopically determined potential energy curves for diatomic molecules if the eigenfunctions are on different atoms. If two eigenfunctions are on the same atom the integrals may be obtained from the atomic spectrum. This manner of evaluating the integrals probably partially compensates for the approximation involved in neglecting the lack of orthogonality of the eigenfunctions.

In this way we can assign definite numerical values to all the quantities occurring in equation (4) for any configuration of five univalent atoms. By constructing a graph of the determinant on the left side of equation (5) against W, the roots may be obtained to any desired degree of approximation. The lowest root is the desired energy of the configuration. Such calculations have been carried out in certain interesting cases.

The solution of the problem of n electrons may be carried out in the same way. After forming the 2^n antisymmetric eigenfunctions of the type (1), we pick out the set of lowest spin S ($S = 0$ if n is even; $S = \frac{1}{2}$ if n is odd). From this set of $n!/[(n/2 + S)! \, (n/2 - S)!]$ eigenfunctions, ψ_K, we now take the linear combinations $\sum_K \delta_{mn}(K)\ldots\delta_{rs}(K)\,\psi_K$ corresponding to the maximum number of bonds. From these we pick the largest possible set of linearly independent combinations, $\varphi_1 \ldots \varphi_f$, where $f = (2S + 1)n!\Big/\Big(\frac{n}{2} + S + 1\Big)!\,\Big(\frac{n}{2} - S\Big)!$, and set up the secular equation on these f eigenfunctions. In this way the six-electron problem has been carried through.[5] The solutions of the seven- and eight-electron problems involve fourteenth order secular equations even after all of this reduction has been carried out.

Application.—The application of this theory must be treated with some care. Because of the uncertainty in determining the ratio of coulombic

[5] Sherman and Eyring, THIS JOURNAL, 54, 2661 (1932).

to interchange energy, the absolute value of any activation energy is rather unreliable. If the coulombic part of the energy of a diatomic molecule is taken to be 10% of the total, the results will in general be too high. Nevertheless, if all the activation energies are calculated on this basis, it is very improbable that the relative magnitudes will be wrong (except in very close cases). The theory in its present state may be used to greatest effect in deciding which of a number of possible reactions between a given set of reactants is the most likely to take place. For example, Eyring[6] showed that the reaction between H_2 and Cl_2 goes more rapidly through the atoms than by the direct reaction. A similar result holds for the reaction of H_2 and Br_2, but H_2 and I_2 react more easily directly.

In constructing the Morse curves used in the calculation which follows we have used the constants

	r_0	ω_0	D	D'
HCl	1.28	2940.8	101.5	105.7
Cl_2	1.98	565	57.0	57.8
H_2	.74	4375	101.5	107.5
OH	.98	3660	113	118

Here r_0 is the distance between atoms in the normal state; ω_0 the corresponding vibrational frequency in wave numbers; D is the heat of dissociation in kg. cal. and D' is D plus a half quantum of vibrational energy.

The applications we shall make are to some of the reactions which have been proposed to account for the observed phenomena of the photochemical reaction between hydrogen and chlorine. Here the primary process is certainly

$$Cl_2 + h\nu = 2Cl \tag{1}$$

The chlorine atoms are not formed in the same state, for one is in the normal $^2P_{3/2}$ state while the other is in the excited $^2P_{1/2}$ state, the energy of excitation amounting to 2.5 kg. cal. This energy is not enough, however, to change any of our conclusions. Now it has been shown by Rollefson and Eyring[1] that at room temperature most of these chlorine atoms react with chlorine molecules

$$Cl_2 + Cl = Cl_3 \tag{2}$$

The question immediately arises, is the chain carried on by Cl or Cl_3? The reaction

$$Cl + H_2 = HCl + H \tag{3}$$

was one of those studied by Eyring, who found an activation energy of 14 kg. cal. The potential energy surface has been drawn completely, and is shown in Fig. 1. It will be seen that the activation energy is 16 kg. cal. (The difference between this value and that given by Eyring is due to his use of an approximation formula.) In order to compare this activation energy with that of the reaction

$$Cl_3 + H_2 = Cl_2 + HCl + H \tag{4}$$

[6] Eyring, THIS JOURNAL, 53, 2537 (1931).

the energies of two corresponding points on the potential energy surfaces were found.   The Cl_3 molecule has the three Cl atoms in a straight line with a separation practically equal to the distance between Cl atoms in Cl_2. The configurations which were chosen were, therefore, of the form

$$Cl{-}{-}{-}Cl{-}{-}{-}Cl{-}{-}{-}H{-}{-}{-}H$$
$$a \qquad b \qquad c \qquad d$$
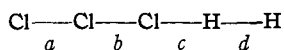
In the first configuration the distances were $a = 1.74$, $b = 1.74$, $c = 1.28$, $d = 0.76$ Å.   The activation energy of this configuration was found to be 31 kg. cal., whereas for the system Cl–H–H with the same distances the activation energy was 22 kg. cal.   The other configuration had $a = 1.74$, $b = 1.74$, $c = 1.45$, $d = 0.90$ Å.   The energy was found to be 20.5 kg. cal., against 16 kg. cal. for Cl–H–H.   These figures indicate that the activation energy of reaction (4) is higher than that of reaction (3) by about 5 kg. cal. The accuracy of this result is probably not high, but the conclusion that reaction (3) is the faster of the two is quite certain.
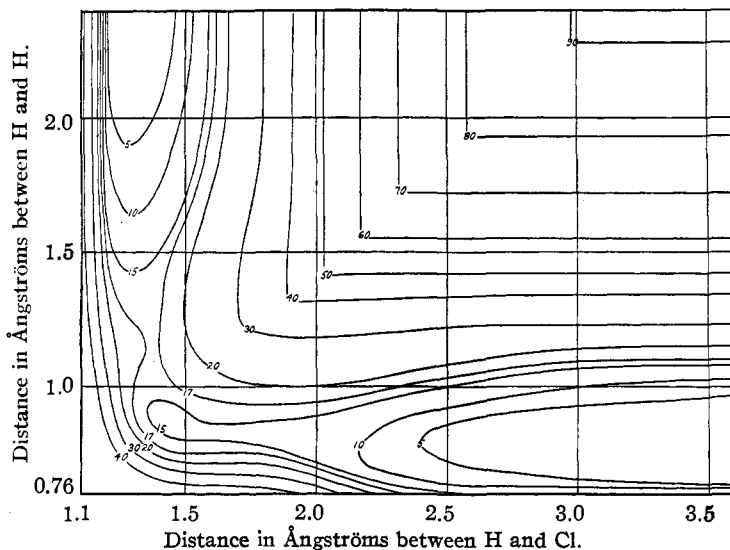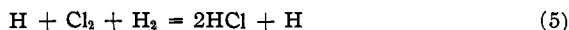

Fig. 1.—Potential energy in kg. cal. of the system H–H–Cl.

The activation energy of reaction (3) seems rather high for such a fast reaction as the hydrogen–chlorine reaction is known to be.   In order to avoid this difficulty a mechanism has been proposed by Franck and Bodenstein[2,3] in which the hydrogen atoms formed at some stage in the chain (either from (3) or some reaction involving H_2O) react by

$$H + Cl_2 + H_2 = 2HCl + H \qquad (5)$$

rather than by

$$H + Cl_2 = HCl + Cl \qquad (6)$$

Now reaction (6) was found by Eyring to have no activation energy, and the complete potential energy surface (Fig. 2) shows an activation energy
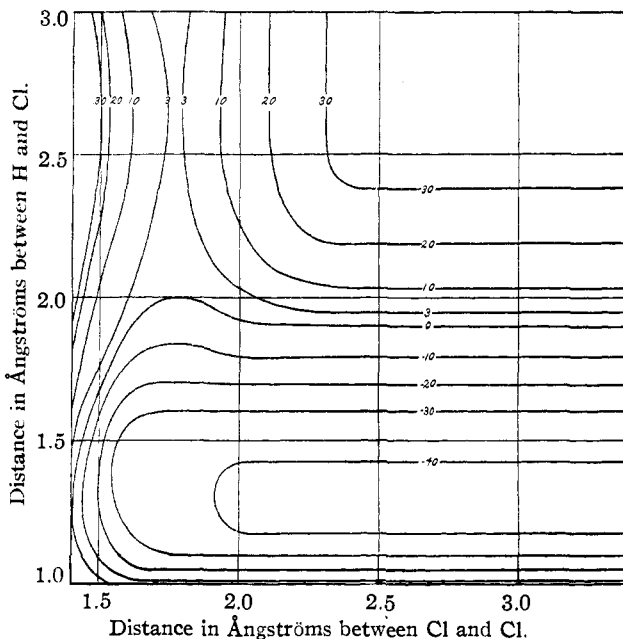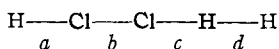

Fig. 2.—Potential energy in kg. cal. for the system H-Cl-Cl.

of only 3 kg. cal. In order to investigate reaction (5) the energies of the configurations of the type

$$\text{H-----Cl-----Cl-----H-----H}$$
$$a \qquad b \qquad c \qquad d$$

were calculated. The zero of energy was taken to be the energy of H, H_2 and Cl_2 at a large distance apart. The results are shown in Table I.

TABLE I

Configuration	a	Distances, Å. b	c	d	Energy, kg. cal.
1	1.28	1.74	2.30	0.76	−37
2	1.28	1.74	1.90	.76	−16
3	1.28	1.74	1.61	.76	−16
4	1.28	1.74	1.28	.76	− 5
5	1.28	2.04	1.28	.76	−11
6	1.28	2.49	1.28	.76	−15
7	2.50	1.74	1.28	.76	19

In order to interpret these results let us consider a complex H–Cl–Cl with the distances $a = 1.28$, $b = 1.74$. When the complex has reached this configuration, it is easily seen from Fig. 2 that reaction (6) has to all

intents and purposes already taken place. Most of the energy of the reaction has been converted into kinetic energy. If now a hydrogen molecule is brought up to the complex we first reach configuration 1. As the hydrogen molecule comes nearer the system passes through configurations 2, 3 and finally 4. During this process the potential energy of the system is always less than zero, so that it might be thought that configuration 4 could be reached. A closer analysis shows that this is not the case. When the hydrogen molecule first arrives, the rest of the system is not stationary. The kinetic energy of the system consists mainly of translational energy of the Cl atom and HCl molecule separating. Now in order to prevent the system from flying apart, the hydrogen molecule must stop this motion. In order to do this a large momentum is necessary. Since the mass of the chlorine atom is 17.5 times that of the hydrogen molecule, this requires that the velocity of the hydrogen atom be 17.5 times that of the chlorine atom. Since such a velocity would correspond to an energy of some 350 kg. cal., we must conclude that it is practically impossible to reach configuration 4.

Configurations 5 and 6 indicate that conditions are not greatly improved by allowing the Cl to separate a little from the HCl. Since it seems impossible to make reaction (5) proceed after the system has passed the point of activation for reaction (6), the only hope for reaction (5) is that the presence of a hydrogen molecule will lower the energy of the point of activation. But configuration 7 shows that instead of being lowered the energy is raised by some 16 kg. cal., and we must conclude that reaction (5) cannot take place.

In 1927 a series of experiments was carried out by Coehn and Jung[7] which led them to believe that complete desiccation of a hydrogen–chlorine mixture prevented the reaction in visible light. In order to explain this phenomenon many reaction chains were suggested which involved water at some step. Recently attempts to duplicate this result have been made in Bodenstein's laboratory,[8] and have failed to find any such effect. Nevertheless, we have carried out some calculations on the reaction of Cl atoms with water. These calculations are less certain than the others, for the potential energy curve for the molecule Cl–O is not known. However, it was found that a large variation in this curve made little change in the activation energy, since the largest interaction energy amounted to some 4 kg. cal. Since one of the hydrogen atoms of the water molecule remains with the oxygen atom throughout the reaction, its effect, and that of the valence electron of the oxygen binding this hydrogen atom to it, was neglected. The water molecule was, therefore, treated as an hydroxyl molecule. Fig. 3 shows the potential energy of the system Cl–H_2O when the

[7] Coehn and Jung, Z. physik. Chem., 110, 705 (1927).
[8] Private communication.

Cl, O and the H which takes part in the reaction lie in a straight line. In this case there is a deep hollow, showing that a molecule (ClH_2O) may be
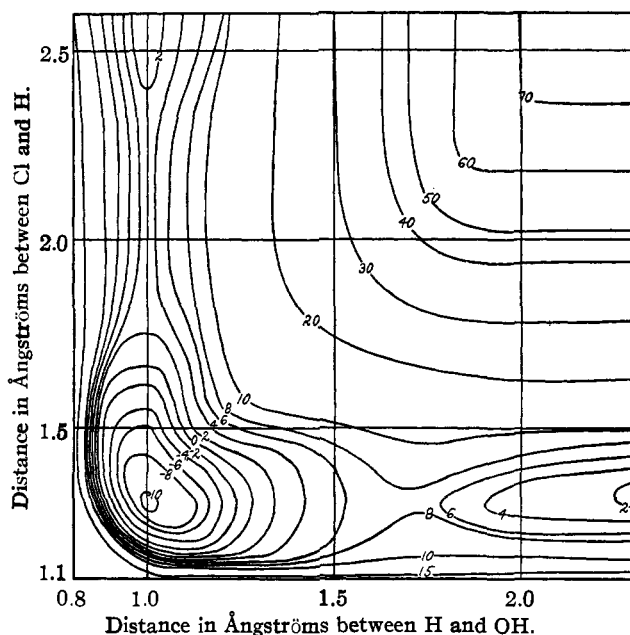

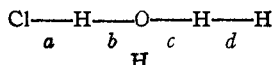Fig. 3.—Potential energy in kg. cal. of the system Cl–H–OH.

formed. The reaction $Cl + H_2O = ClH_2O$ has an activation energy of 4 kg. cal. With an activation energy of 8 kg. cal. the reaction

$$Cl + H_2O = HCl + OH \qquad (7)$$

can take place. The reaction

$$Cl + H_2O + H_2 = HCl + H_2O + H \qquad (8)$$

has also been suggested. In order to estimate its activation energy the energies of the configurations

$$\underset{a \quad b \quad c \quad d}{Cl\text{---}H\text{---}O\text{---}H\text{---}H}$$
$$H$$

were calculated. The energies are shown in Table II.

TABLE II

	Distances, Å.			
a	b	c	d	Energy, kg. cal.
1.28	0.98	0.98	0.76	25
1.28	0.98	1.20	0.76	15
1.28	1.40	0.98	0.76	25

The activation energy must, therefore, be in the neighborhood of 25 kg. cal. (The activation energies of reactions (7) and (8) were calculated

using a value of 104 kg. cal. for the heat of dissociation of the OH bond. The value 113 kg. cal. is probably better.   This would raise the activation energy of each reaction by about 9 kg. cal.)

Since the reaction of OH with H_2 is known to be slow (we find an activation energy of 8 or 17 kg. cal. according to whether the heat of dissociation of OH is taken to be 104 or 113 kg. cal.) it does not seem possible that water can be of any assistance to the hydrogen–chlorine reaction.

If all the activation energies we have obtained were numerically correct, it would appear that it was impossible for hydrogen and chlorine to combine at all at room temperature.   Nevertheless, we do not claim any great accuracy for these figures   A change in the ratio of coulombic energy to interchange energy from 9:1 to 6:1 would lower the activation energy of reaction (3) to the neighborhood of 7 kg. cal., which would agree quite well with experiment.   The other activation energies would also be lowered, but all in approximately the same ratio.   The conclusions that reaction (3) goes faster than reaction (4), and (6) faster than (5), would not be changed. It would, therefore, seem that if the hydrogen–chlorine reaction proceeds through any of the reactions we have considered, it must go by the Nernst chain

$$Cl + H_2 = HCl + H$$
$$H + Cl_2 = HCl + Cl$$
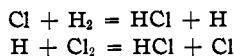
Summary

1.   Slater's method of finding the energy of three and four atoms has been extended to five monovalent atoms, and the general method is outlined.

2.   By means of this result the activation energies of the reactions

$$Cl_2 + H_2 = Cl_2 + HCl + H$$
$$H + Cl_2 + H_2 = 2HCl + H$$
$$Cl + H_2O + H_2 = HCl + H_2O + H$$
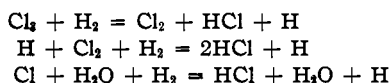
have been calculated.   The results indicate that none of these reactions takes part in the photochemical reaction between hydrogen and chlorine.

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