

### Summary

1. Measurements of the e. m. f. of the cell, Ag(s), AgBr(l), PbBr<sub>2</sub>(l), Br<sub>2</sub>(g) have been made at mole fractions of silver bromide varying from 1.00 to 0.10 between the temperatures 425 and 575°.

2. Densities of a 0.5 mole fraction solution of lead bromide in silver bromide are given by the relation  $d^t = 6.243 - 0.00146t$  between the temperatures 490 and 580°.

3. The relations between composition and free energy, heat of formation, entropy change and activity coefficient of the solvent, fused silver bromide, have been calculated for 450, 500 and 550°.

4. The relations between composition and free energy and activity coefficient of the solute, fused lead bromide, have been calculated at 500 and 550°.

5. The activities of both solvent and solute agree very well with that predicted by Raoult's law throughout the entire range of temperature studied.

CAMBRIDGE, MASSACHUSETTS

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

## QUANTUM MECHANICS OF ACTIVATED ADSORPTION

BY ALBERT SHERMAN AND HENRY EYRING

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The experiments of Taylor and Sherman<sup>1</sup> showed that activated adsorption is involved in the ortho-para hydrogen conversion at a variety of surfaces. On charcoal the activation energy must be small—approximately 2 kg. cal.—since the conversion occurs at liquid hydrogen temperatures.<sup>2</sup> The conversion on a given charcoal surface was shown by Taylor and Sherman to be bimolecular at room temperatures, and the surface action exhibited a temperature coefficient less than unity between liquid air temperatures and 0°. It becomes a matter of considerable interest to apply the methods used by Eyring and Polanyi<sup>3</sup> for calculation of activation energies to determine the necessary conditions for so low an activation energy. The calculations presented in the following pages seem sufficiently accurate to indicate clearly the process by which the reaction proceeds, although, of course, the exact numerical results are subject to revision.

The mechanism for the conversion of ortho to para hydrogen on charcoal probably involves three steps: (1) activated adsorption; (2) collision

<sup>1</sup> Taylor and Sherman, *Trans. Faraday Soc.*, Symposium on Adsorption (1932).

<sup>2</sup> Bonhoeffer and Harteck, *Z. physik. Chem.*, **B4**, 113 (1929).

<sup>3</sup> Eyring and Polanyi, *ibid.*, **B12**, 279 (1931).

and reaction of two adjacently adsorbed hydrogen molecules; (3) desorption. At very low temperatures step 3, a zero order evaporation process, is undoubtedly the rate determining step. We should thus expect at intermediate temperatures a transition between second and zero order reactions. As the temperature increases, the rate of desorption increases until finally the collision of two adjacently adsorbed molecules is the slow process. With increasing temperature the chance of two hydrogen molecules being adsorbed in adjacent positions approaches zero and simultaneously the conversion of para to ortho hydrogen drops to zero, in keeping with the results of Taylor and Sherman. It is obvious, therefore, that the rate must go through a maximum when the specific reaction rate  $k$  is plotted against the absolute temperature  $T$ .

Such a temperature variation is probably general for any catalytic reaction involving a collision between adsorbed molecules. The negative slope portion of the curve may not be realizable experimentally in many cases because the temperature at which the maximum occurs may be such as to destroy the catalyst. The part with positive slope may not be realizable because it may correspond to temperatures below the melting point of the reactants. The known experiments of the conversion of ortho to para hydrogen on charcoal correspond only to the part for higher temperatures than that for which the maximum occurs. In the case of a particular sample of a copper catalyst for this same reaction results lying on both sides of the maximum have been found. In the case of ZnO only that portion of the curve with positive slope was realized.

**Adsorption Process.**—It has already been pointed out that the activation energy  $E_a$  of adsorption of hydrogen on charcoal must be very small.

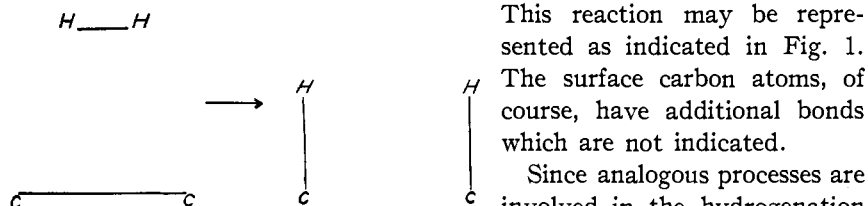


Fig. 1.—Adsorption process.

This reaction may be represented as indicated in Fig. 1.

The surface carbon atoms, of course, have additional bonds which are not indicated.

Since analogous processes are involved in the hydrogenation of ethylene and acetylene we

shall first calculate an approximate activation energy for these reactions. For the purposes of these calculations the C—C distances in ethylene and acetylene were taken equal to that in ethane, 1.54 Å. The effective strength of the C—C bond broken was taken as the difference between the strengths of a double and single bond, 123 — 73.5 = 49.5 kg. cal., in the first case and in the second case as the difference between the strength of a triple and double bond, 162 — 123 = 39 kg. cal. The data used for constructing the Morse potential energy curves for C—H and H—H are given in Table I.

TABLE I

Bond	$\omega$ , cm. <sup>-1</sup>	$r_0$ (Å.)	D (kg. cal.)
C—H	2920 <sup>a</sup>	1.13 <sup>d</sup>	92 <sup>c</sup>
H—H	4262 <sup>d</sup>	0.76 <sup>d</sup>	101.5 <sup>d</sup>
C=C	1623 <sup>b</sup>	1.54	123 <sup>c</sup>
C≡C	1960 <sup>b</sup>	1.54	162 <sup>c</sup>

<sup>a</sup> Andrews, *Phys. Rev.*, **36**, 538 (1930).

<sup>b</sup> Kettering, Shutts and Andrews, *ibid.*, **36**, 531 (1930).

<sup>c</sup> Eucken, "Handbuch der Experimental Physik."

<sup>d</sup> "International Critical Tables," Vol. V.

<sup>e</sup> Taylor, "Treatise on Physical Chemistry," 1931, p. 328.

The expression for the binding energy of four atoms is

$$E = A_1 + A_2 + B_1 + B_2 + C_1 + C_2 + \sqrt{1/2[(\alpha_1 + \alpha_2 - \beta_1 - \beta_2)^2 + (\alpha_1 + \alpha_2 - \gamma_1 - \gamma_2)^2 + (\beta_1 + \beta_2 - \gamma_1 - \gamma_2)^2]} \quad (1a)$$

where the italic letters are the coulombic potentials corresponding to the six possible distances between four atoms and the Greek letters are the interchange potentials for these same distances. The method of calculation was to construct a potential energy surface for configurations in which the C—C distance was kept at 1.54 Å., the four atoms were kept in a plane, and only configurations symmetrical about the perpendicular bisector of the line joining the two carbon nuclei were considered. Certain of these assumptions have already been discussed<sup>4</sup> and they are considered in greater detail in a forthcoming paper by Kimball and Eyring.

The activation energies for the hydrogenation of ethylene and acetylene were calculated to be 51.5 and 46.4 kg. cal., respectively, at 0°K. The former value is to be compared with 43.2 kg. cal. recently obtained by Pease.<sup>5</sup> The discrepancy is probably due to the operation of several factors. The experimentally measured value is for a temperature of approximately 700°K.,<sup>6</sup> while the calculated value is of course for 0°K. The effect of directed valence will also be to lower the activation energy but we have not attempted a precise evaluation of the magnitude of this lowering. The choice of 10% for the coulombic energy is only approximately correct, although it is probably not greatly in error.

We now consider the analogous process of the reduction of two carbon atoms on a catalytic surface by hydrogen. This is essentially what happens when we have activated adsorption of hydrogen on a charcoal surface. The adsorption process replaces a single bond of 101.5 kg. cal. between the hydrogen atoms and a weaker one between the carbon atoms by two C—H bonds whose combined strength does not exceed by more than approximately two kilogram calories the strength of the two bonds

<sup>4</sup> Eyring, *THIS JOURNAL*, **53**, 2537 (1931).

<sup>5</sup> Pease, *ibid.*, **54**, 1876 (1932).

<sup>6</sup> Tolman, "Statistical Mechanics," Chemical Catalog Company, New York, 1927, Chap. 21.

broken. If the same potential energy curves are used for this calculation as are used for the hydrogenation of ethylene and acetylene, the upper curve in Fig. 2 is obtained, showing how the activation energy of adsorption changes with the distance between the two carbon atoms. The carbon to carbon bond broken was taken as the difference between a triple and double bond at the appropriate distance. The minimum is not shifted if the carbon to carbon bond broken is assumed instead to be a single bond. On the extreme left where the change would be most marked the curve would be raised by 5 kg. cal. Thus the exact nature of this carbon to carbon bond is not significant for our considerations. The curve shows that

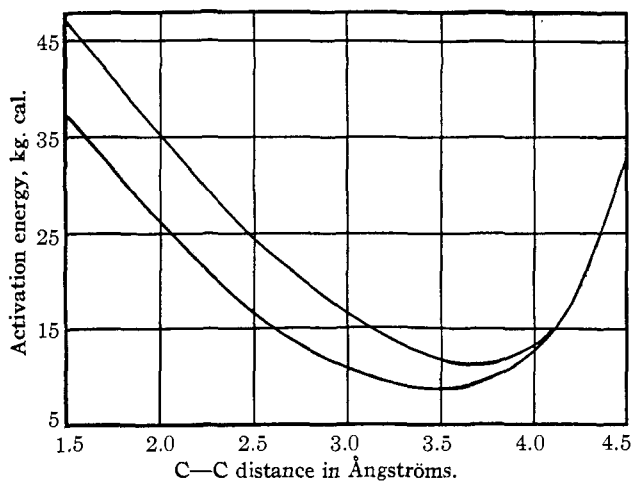


Fig. 2.—The dependence of the activation energy for adsorption of  $H_2$  on charcoal as a function of the distance between surface carbon atoms.

the reaction proceeds with the lowest activation energy for carbon atoms held at a distance of 3.6 Å. The calculated potential surface for the carbon-carbon distance of 3.6 Å. has a minimum which represents the hydrogenation of the carbon atoms with an evolution of 90.5 kg. cal. Actually, as stated previously, hydrogen is adsorbed on charcoal with the liberation of but two kilogram calories, so that there must be forces in the surface preventing the formation of C—H bonds of 96 kg. cal. Since the calculations indicate the adsorption obtained is the so-called atomic adsorption—that is, adsorption in which the hydrogen-hydrogen distance becomes very large—the C—H bonds must have strengths of 51.8 kg. cal. in order that the final bonds will have strengths of only two kg. cal. more than the initial hydrogen bond. We then have the problem of calculating the activation energy for C—H bonds of 51.8 kg. cal. The remaining constants used in the Morse curve are the same as those previously used. Proceeding exactly

as before we obtain the lower curve in Fig. 2. Surprisingly enough, in this case also we find that a carbon-carbon distance of approximately 3.6 Å. is most favorable. This is particularly satisfactory in that it indicates the existence of a most favorable carbon-carbon distance which is practically independent of our choice of the strength of the C—H bond.

That a most favorable carbon-carbon distance is to be expected may be seen from the following qualitative argument. Consider the following two extreme distances between surface atoms. In one case suppose the distance between surface atoms A—A is equal to that of the approaching hydrogen molecule, as illustrated in Fig. 3. In Fig. 3 the subscripts preceding the atomic symbols are used to distinguish the various atoms. In this case there is a large interaction between  ${}_3A$  and  ${}_2H$  and also between  ${}_4A$  and  ${}_1H$ . As can be seen from Equation (1a), making the smallest interchange integrals (those between diagonal atoms) larger decreases the total binding energy, thus making the activation energy larger.

Now consider the case in which the surface atoms are very far apart. In this case all the terms in Equation (1a) except those between the two hydrogen atoms are small and this distance must also become very large in order that the hydrogen atoms can be adsorbed. This process, then, is essentially a dissociation of a hydrogen molecule and necessitates an activation energy of approximately 100 kg. cal. Thus, somewhere between these two extremes a most favorable distance of A—A is to be expected. We see that there are no reasons for the assumption sometimes made that it is favorable for the distance between surface atoms to be equal to that of the molecule being adsorbed.

The potential energy surface for the adsorption of hydrogen on two carbon atoms at 3.6 Å. is given in Fig. 4.

Similar surfaces were obtained for other C—C distances used in constructing Fig. 2. These resemble those shown in Fig. 4 and so are not reproduced.

The height of the pass in Fig. 4 separating the valley (corresponding to a hydrogen molecule and two unoccupied carbon atoms) and the basin (corresponding to the two carbon hydrides) is seen to be 8.8 kg. cal. The position of the pass is for an abscissa of 0.77 Å. and an ordinate of 0.80 Å. The course of the hydrogen molecule in the adsorption process is indicated by the arrows in Fig. 4. The activation energy for the desorption of hydrogen will be greater than this by the heat of adsorption, which we have taken to be 2 kg. cal. To agree with experiment we should have obtained 0 kg. cal. for the activation energy instead of 8.8 kg. cal. Thus



Fig. 3.—If the distance A—A is equal to that between the atoms adsorbed, the activation energy will be high.

again, as in the case of the hydrogenation of ethylene, the value obtained for the activation energy is approximately 9 kg. cal. too high. The arbitrary assumption in our calculation is the choice of 10% for the coulombic energy. A slightly higher value for the coulombic energy would have brought closer agreement in both hydrogenation cases as well as for the adsorption process. Taking into account directed valence also tends to lower the activation energy.

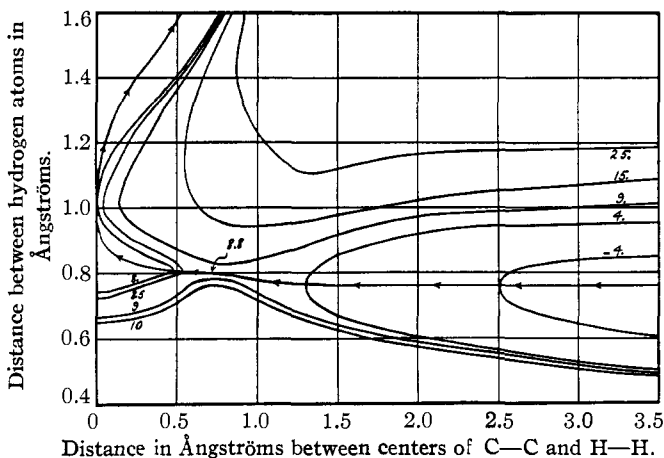


Fig. 4.—Energy contour lines in kg. cal. for the activated adsorption of  $H_2$  on two carbon atoms 3.6 Ångströms apart.

The coulombic energy is known by calculation for the following three cases:  $H_2$ , 10% of the total binding;<sup>7</sup>  $Li_2$ , 22%;<sup>8</sup>  $Na_2$ , 28.3%.<sup>9</sup> If we determine the percentage of coulombic binding for C-H and C-C (14%) by the condition that the calculated value of the activation energy shall agree with the value found experimentally by Pease for the hydrogenation of ethylene, the adsorption of hydrogen on charcoal may be re-determined. Instead of the value of 8.8 kg. cal., we now obtain 5.6 kg. cal., in better agreement with experiment.

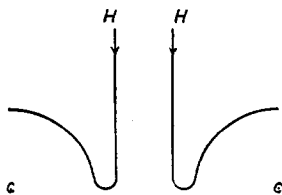


Fig. 5.—Path followed by  $H_2$  when becoming adsorbed on charcoal.

An examination of Fig. 4 shows that the path of the hydrogen atoms as they approach the carbon atoms is of the kind schematically represented in Fig. 5. It is interesting to note that  $H_2$  approaches the carbon-carbon axis before expanding appreciably.

For desorption the path will be just the reverse of that of adsorption.

<sup>7</sup> Sugiura, *Z. physik*, **45**, 484 (1927).

<sup>8</sup> Bartlett and Furry, *Phys. Rev.*, **37**, 1712 (1931).

<sup>9</sup> Rosen, *ibid.*, **38**, 255 (1931).

It might be supposed that it would require a greater activation energy for a second hydrogen molecule to be adsorbed on two carbon atoms adjacent to the pair on which the first hydrogen molecule is adsorbed because of the repulsion of the first two hydrogen atoms already adsorbed. This is not so, however, because of the large distance between the carbon atoms. Thus the activation energy for the successive adsorption of two adjacent hydrogen molecules is just that for the individual processes in this case where the four carbon atoms form a square.

It may be assumed that the actual mechanism for the catalytic conversion of para to ortho hydrogen is not the one just considered but one in which a hydrogen molecule from the gas phase collides with an adsorbed hydrogen molecule. A consideration of this involves solving the six electron problem, one from each of the four hydrogen atoms and one from each of the two carbon atoms, and will be discussed in connection with Table II. The fifth degree equation (4) for the binding energy of six electrons must be used for calculating the potential energy. The value for the elements of this determinant are given in (20) below.

We shall now discuss the evaluation of the activation energy for any configuration such as is indicated in Fig. 6.

At the corners of the quadrilateral *cdef* are four hydrogen atoms having the four eigenfunctions *c*, *d*, *e*, *f*. For the two carbon atoms we have the two eigenfunctions *a* and *b*. The energies corresponding to the fifteen distances between the six atoms are evaluated from the same curves used in the previous calculations. We have assumed as before that the coulombic binding energy is 10% of the total binding energy for each pair of atoms. This enables us to evaluate each of the elements in (4) without further difficulty. We then try values for *E* until we find the numerically largest negative number which satisfies (4). This corresponds to the singlet state of lowest potential energy. In Table II are given the data and resulting binding energies for three configurations.

In Table II, *E* is the potential energy required to break completely all the bonds between the six atoms.

In configurations 1, 2 and 3 all the atoms lie in a plane and there is symmetry about the perpendicular bisector of the C—C bond. First

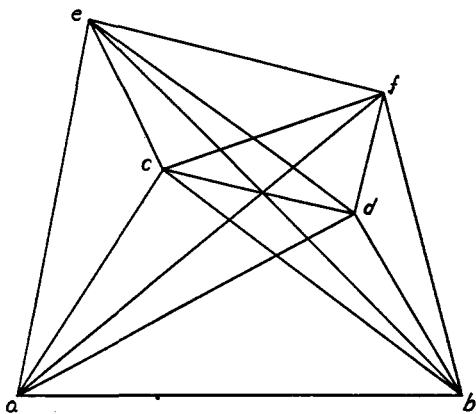


Fig. 6.—The potential curves for pairs of atoms connected by lines determine the potential for the whole configuration.

TABLE II

Configura- tion	1			2			3		
	Dist.	Coul.	Inter.	Dist.	Coul.	Inter.	Dist.	Coul.	Inter.
ab	2.60	0.4	3.1	3.26	0.0	0.0	3.26	0.0	0.0
ac	1.13	5.4	48.8	1.13	5.4	48.8	1.24	5.1	45.6
ad	1.97	1.3	11.2	2.25	0.7	6.6	2.28	0.7	5.8
ae	1.97	1.3	11.2	1.51	3.4	30.8	1.24	5.1	45.6
af	2.54	0.3	3.0	2.44	0.4	3.9	2.28	0.7	5.8
bc	1.97	1.3	11.2	2.23	0.7	6.6	2.28	0.7	5.8
bd	1.13	5.4	48.8	1.13	5.4	48.8	1.24	5.1	45.6
be	2.54	0.3	3.0	2.44	0.4	3.9	2.28	0.7	5.8
bf	1.97	1.3	11.2	1.51	3.4	30.8	1.24	5.1	45.6
cd	1.00	9.3	83.5	1.00	9.3	83.5	1.00	9.3	83.5
ce	1.00	9.3	83.5	1.00	9.3	83.5	1.00	9.3	83.5
cf	1.41	5.5	49.3	1.41	5.5	49.3	1.41	5.5	49.3
de	1.41	5.5	49.3	1.41	5.5	49.3	1.41	5.5	49.3
df	1.00	9.3	83.5	1.00	9.3	83.5	1.00	9.3	83.5
ef	1.00	9.3	83.5	1.00	9.3	83.5	1.00	9.3	83.5
E	89.6 kg. cal.			73.0 kg. cal.			65.0 kg. cal.		

we may consider the activation energy to bring four hydrogen atoms into a square of 1 Å. on a side, when the carbon atoms are not present. This is 84.2 kg. cal. A square configuration for four atoms of hydrogen is clearly one in which any hydrogen atom is equally apt to depart with either of two neighbors as a partner, so that the square corresponding to the least potential energy is the activated state for the homogeneous ortho-para conversion between two diatomic hydrogen molecules.

Let us now consider the decrease in potential energy for our three configurations of six atoms resulting when we remove the two hydrogen atoms with eigenfunctions e and f to a great distance from the other four atoms but to the normal distance of 0.76 Å. from each other. The other four atoms are held fixed. The decreases in energy are 96.5, 119.8 and 124.5 kg. cal., respectively, for the three configurations. The activation energy for the reverse process will clearly be given by these same figures. Thus it is highly improbable for a second hydrogen molecule to approach an adsorbed hydrogen molecule without the aid of two additional carbon atoms.

Let us next consider the activation energy of four hydrogen atoms in the absence and in the presence of two surface atoms. The activation energy without the surface atoms, as already stated, is 84.2 kg. cal. Instead of being lowered, our calculations for configurations 1, 2 and 3 show that the surface carbon atoms raise this activation energy to the values  $2 \times 101.5 - 89.6 = 113.4$ , 130.0 and 138.0 kg. cal., respectively.

The process we considered in our first adsorption calculations thus appears to be the true catalytic process. The ortho-para hydrogen conversion has also been discussed recently by Ekstein and Polanyi.<sup>10</sup>

<sup>10</sup> Ekstein and Polanyi, *Z. physik. Chem.*, B15, 334 (1932).



The five independent eigenfunctions that we have used in calculating the energy for the six electron problem correspond to five different ways of drawing three bonds, indicated as

$\psi'_1$	a - b	c - d	e - f
$\psi'_2$	a - b	c - e	d - f
$\psi'_3$	a - c	b - d	e - f
$\psi'_4$	a - c	b - e	d - f
$\psi'_5$	a - d	b - e	c - f

For a particular set of six monovalent atoms the configuration determines the eigenfunctions associated with each of the energy values which are roots of the secular equation. Thus, if the lowest root of the secular equation is the sum of the heats of dissociation of the three molecular bonds a—b, c—d, e—f, and the three corresponding molecules are remote from each other, the eigenfunction going with this energy is just  $\psi'_2$ . As the six monovalent atoms approach each other the binding can no longer be represented simply by three fixed bonds. Thus for the three configurations in Table II we have instead of some one of the eigenfunctions  $\psi'_1$  to  $\psi'_5$  the following linear combinations

$$\text{Configuration 1: } 0.406\psi'_1 + 0.568\psi'_2 + 0.694\psi'_3 + 0.130\psi'_4 + 0.122\psi'_5.$$

$$2: 0.524\psi'_1 + 0.432\psi'_2 + 0.698\psi'_3 + 0.224\psi'_4 + 0.019\psi'_5.$$

$$3: 0.757\psi'_1 + 0.200\psi'_2 + 0.366\psi'_3 + 0.355\psi'_4 + 0.355\psi'_5.$$

The squares of the coefficients of the eigenfunction for each configuration must, of course add up to one. As is well known, the binding energies for most compounds correspond closely to what one calculates if a definite set of bonds is assumed. A chemical reaction consists in passing from a potential minimum corresponding to a single set of bonds such as is represented by  $\psi'_1$  or  $\psi'_2$ , etc., through states of mixed bonds for which the potential energy is higher, such as those corresponding to those of our configurations 1, 2, 3, to a new potential minimum where there is again a single set of bonds.

Molecules involving polyvalent atoms may not reach the ideal state of a single set of bonds because of the mutual interaction of two groups attached to the same atom. This manifests itself as steric hindrance and the eigenfunctions will be of the mixed type just described. Organic molecules never quite have the simple set of bonds ordinarily assigned them.

Bonhoeffer and Farkas<sup>11</sup> suggested that the conversion they observed on platinum could be attributed to the pulling apart of the atoms of hydrogen with a subsequent reunion of these same two atoms upon desorption to form a molecule with a changed resultant nuclear spin. Quantum mechanics indicates that such a process will not occur except as catalyzed by radiation or by other hydrogen atoms. Even if the atoms are separated

<sup>11</sup> Bonhoeffer and Farkas, *Trans. Faraday Soc.*, Symposium on Adsorption (1932).

to great distances by electrostatic forces, they always return with the same resultant nuclear spin they had initially. Only magnetic perturbations can hasten a change in nuclear spin. The following picture illustrates the situation. Suppose one thinks of the two atoms as two ships, each carrying a gyroscopic compass corresponding to nuclear spins. If the compasses point in the same direction when the ships are each proceeding in a given direction and parallel to each other and if the ships then separate to any distance, it will still be found that upon returning to their original relative positions the gyroscopic needles will be parallel. The needles, of course, may have any relative positions to begin with, which is conserved no matter what forces are applied to the ships so long as these forces do not act directly on the compasses.

Bonhoeffer and Harteck in one of their early papers<sup>2</sup> on the ortho-para hydrogen conversion include a discussion by Wigner on the rate at which black body radiation affects the conversion and we have had the opportunity of discussing this question in some detail with Professor Wigner. At ordinary temperatures a half life of approximately 300 years is found for the atoms in *s* states. If they are in *p* states the half life is shown to be about twelve hours. Thus to the extent to which a catalytic surface changes the quantum state of the atoms we obtain a greatly increased effect of radiation on the rate of conversion. One can only estimate the magnitude of this change in quantization but it would be surprising if the catalyst raises the binding electrons more than 10% into *p* states, which would still give us a rate far too low to account for the observed rates of conversion at surfaces. In fact a half life of twelve hours, that for atoms in *p* states, is too slow to account for the experimental observations on catalytic surfaces.

Because of the apparent success of the present method of attack we are extending our calculations to other surfaces.

We now give the solution of the six electron problem.

To secure the utmost brevity we shall assume familiarity on the part of the reader with a recent paper by Slater<sup>12</sup> in which the problem of spin degeneracy is solved for three and four electrons. We use his notation. The reader desiring a simple and detailed treatment of this problem may be referred to the thesis of one of us on file in the Princeton Library.

The Schrödinger equation for six electrons is approximately satisfied by the product of the six electronic eigenfunctions  $a_1 b_2 c_3 d_4 e_5 f_6$ , where the numbers specify the electrons and the letters the available eigenfunctions. The 720 different products obtained by permutation of the numbers are all equally good solutions of the Schrödinger equation. Any linear combination of them is also a solution. Taking account of electron spins we write for electron 1 having the positional eigenfunction *a* and

<sup>12</sup> J. C. Slater, *Phys. Rev.*, **38**, 1109 (1931).

spin  $+1/2$ ,  $(a\alpha)_1$  and for a spin of  $-1/2$  the expression  $(a\beta)_1$ . Now when we use the Pauli principle instead of 720 eigenfunctions in our secular equation we need consider only the 64 antisymmetric eigenfunctions

$$\psi_i = \Sigma \pm p (a\alpha)_1(b\alpha)_2(c\beta)_3(d\beta)_4(e\alpha)_5(f\beta)_6 \tag{1}$$

where  $\Sigma \pm p$  signifies the sum of the 720 possible quantities obtained by permutation of the subscripts, using the positive sign if the product may be obtained from the initial product by an even number of interchanges of pairs of subscripts, and otherwise the negative sign (1) may also be written as a determinant. There are just  $2^6 = 64$  eigenfunctions of the type (1) since in each of the six parentheses we can insert either an  $\alpha$  or  $\beta$ . Terms  $\int \psi_i H \psi_j d\tau$  in the secular equation are zero if the sum of the spins in  $\psi_i$  is not the same as in  $\psi_j$ , where  $H$  is the well-known operator for six electrons and the integration is over all the coordinates of the six electrons. This is true because a term of the form

$$\int (a\alpha)_1(b\beta)_2(c\alpha)_3 \dots (f\alpha)_6 H (a\alpha)_1(b\beta)_2(c\alpha)_3 \dots (f\alpha)_6 d\tau$$

for which the spin eigenfunctions of every electron before and after  $H$  is the same, is equal to  $\int a_1 b_2 c_3 d_4 e_5 f_6 H a_1 b_2 c_3 d_4 e_5 f_6 d\tau$ , and if for any single electron the spin eigenfunctions are not the same, the integral is identically zero. This causes our 64 rowed secular determinant to break up into the product of seven determinants corresponding to the integral spin values from 3 to  $-3$ .

The most stable chemical state will correspond to a state for which the sum of the spins for the six electrons is zero; so that we are only concerned with solving the corresponding twenty rowed determinant. The 20 eigenfunctions may be indicated in the following symbolic fashion

	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>f</i>		<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>f</i>		<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	
$\psi_{23}$	$\alpha$	$\alpha$	$\alpha$	$\beta$	$\beta$	$\beta$	$\psi_{30}$	$\alpha$	$\beta$	$\beta$	$\alpha$	$\alpha$	$\beta$	$\psi_{37}$	$\beta$	$\alpha$	$\beta$	$\alpha$	$\beta$	$\alpha$
$\psi_{24}$	$\alpha$	$\alpha$	$\beta$	$\alpha$	$\beta$	$\beta$	$\psi_{31}$	$\beta$	$\alpha$	$\beta$	$\alpha$	$\alpha$	$\beta$	$\psi_{38}$	$\beta$	$\beta$	$\alpha$	$\alpha$	$\beta$	$\alpha$
$\psi_{25}$	$\alpha$	$\beta$	$\alpha$	$\alpha$	$\beta$	$\beta$	$\psi_{32}$	$\beta$	$\beta$	$\alpha$	$\alpha$	$\alpha$	$\beta$	$\psi_{39}$	$\alpha$	$\beta$	$\beta$	$\beta$	$\alpha$	$\alpha$
$\psi_{26}$	$\beta$	$\alpha$	$\alpha$	$\alpha$	$\beta$	$\beta$	$\psi_{33}$	$\alpha$	$\alpha$	$\beta$	$\beta$	$\beta$	$\alpha$	$\psi_{40}$	$\beta$	$\alpha$	$\beta$	$\beta$	$\alpha$	$\alpha$
$\psi_{27}$	$\alpha$	$\alpha$	$\beta$	$\beta$	$\alpha$	$\beta$	$\psi_{34}$	$\alpha$	$\beta$	$\alpha$	$\beta$	$\beta$	$\alpha$	$\psi_{41}$	$\beta$	$\beta$	$\alpha$	$\beta$	$\alpha$	$\alpha$
$\psi_{28}$	$\alpha$	$\beta$	$\alpha$	$\beta$	$\alpha$	$\beta$	$\psi_{35}$	$\beta$	$\alpha$	$\alpha$	$\beta$	$\beta$	$\alpha$	$\psi_{42}$	$\beta$	$\beta$	$\beta$	$\alpha$	$\alpha$	$\alpha$
$\psi_{29}$	$\beta$	$\alpha$	$\alpha$	$\beta$	$\alpha$	$\beta$	$\psi_{36}$	$\alpha$	$\beta$	$\beta$	$\alpha$	$\beta$	$\alpha$							

Here the table indicates with which italic letters in (1) an  $\alpha$  or  $\beta$  should be associated. Actually  $\psi_i$  of (1) is  $\psi_{27}$ .

If now instead of using the 20 eigenfunctions of (2) we had used the 20 given below, which are a linear combination of them, our 20th order determinant now factors into four sub-determinants of orders 5, 9, 5, 1.

$$\psi'_1 = \frac{1}{\sqrt{8}} (\psi_{28} - \psi_{29} - \psi_{30} + \psi_{31} - \psi_{34} + \psi_{36} + \psi_{38} - \psi_{37})$$

$$\psi'_2 = \frac{1}{\sqrt{8}} (\psi_{25} - \psi_{26} - \psi_{30} + \psi_{31} - \psi_{34} + \psi_{36} + \psi_{39} - \psi_{40})$$

$$\psi'_3 = \frac{1}{\sqrt{8}} (\psi_{27} - \psi_{29} - \psi_{30} + \psi_{32} - \psi_{38} + \psi_{35} + \psi_{36} - \psi_{38})$$

$$\begin{aligned}
\psi'_4 &= \frac{1}{\sqrt{8}} (\psi_{24} - \psi_{26} - \psi_{30} + \psi_{32} - \psi_{33} + \psi_{35} + \psi_{39} - \psi_{41}) \\
\psi'_5 &= \frac{1}{\sqrt{8}} (\psi_{23} - \psi_{26} - \psi_{28} + \psi_{32} - \psi_{33} + \psi_{37} + \psi_{39} - \psi_{42}) \\
\psi'_6 &= \frac{1}{\sqrt{8}} (\psi_{28} - \psi_{29} - \psi_{30} + \psi_{31} + \psi_{34} - \psi_{35} - \psi_{36} + \psi_{37}) \\
\psi'_7 &= \frac{1}{\sqrt{8}} (\psi_{27} - \psi_{29} + \psi_{30} - \psi_{32} - \psi_{33} + \psi_{35} - \psi_{36} + \psi_{38}) \\
\psi'_8 &= \frac{1}{\sqrt{8}} (\psi_{23} - \psi_{24} - \psi_{28} + \psi_{30} + \psi_{35} - \psi_{37} - \psi_{41} + \psi_{42}) \\
\psi'_9 &= \frac{1}{\sqrt{8}} (\psi_{25} - \psi_{26} - \psi_{30} + \psi_{31} + \psi_{34} - \psi_{35} - \psi_{39} + \psi_{40}) \\
\psi'_{10} &= \frac{1}{\sqrt{8}} (\psi_{28} - \psi_{29} + \psi_{30} - \psi_{31} - \psi_{34} + \psi_{35} - \psi_{36} + \psi_{37}) \\
\psi'_{11} &= \frac{1}{\sqrt{8}} (\psi_{24} - \psi_{26} + \psi_{30} - \psi_{32} - \psi_{33} + \psi_{35} - \psi_{39} + \psi_{41}) \\
\psi'_{12} &= \frac{1}{\sqrt{8}} (\psi_{23} - \psi_{26} + \psi_{28} - \psi_{32} - \psi_{33} + \psi_{37} - \psi_{39} + \psi_{42}) \\
\psi'_{13} &= \frac{1}{\sqrt{8}} (\psi_{24} - \psi_{26} - \psi_{30} + \psi_{32} + \psi_{33} - \psi_{35} - \psi_{39} + \psi_{41}) \\
\psi'_{14} &= \frac{1}{\sqrt{8}} (\psi_{24} - \psi_{25} - \psi_{31} + \psi_{32} + \psi_{33} - \psi_{34} - \psi_{40} + \psi_{41}) \\
\psi'_{15} &= \frac{1}{\sqrt{12}} (\psi_{25} - \psi_{26} + \psi_{28} - \psi_{29} + \psi_{30} - \psi_{31} + \psi_{34} - \psi_{35} + \psi_{36} - \psi_{37} + \psi_{39} - \psi_{40}) \\
\psi'_{16} &= \frac{1}{\sqrt{12}} (\psi_{24} - \psi_{26} + \psi_{27} - \psi_{29} + \psi_{30} - \psi_{32} + \psi_{33} - \psi_{35} + \psi_{36} - \psi_{38} + \psi_{39} - \psi_{41}) \\
\psi'_{17} &= \frac{1}{\sqrt{12}} (\psi_{23} - \psi_{26} + \psi_{27} + \psi_{28} - \psi_{31} - \psi_{32} + \psi_{33} + \psi_{34} - \psi_{37} - \psi_{38} + \psi_{39} - \psi_{42}) \\
\psi'_{18} &= \frac{1}{\sqrt{12}} (\psi_{23} + \psi_{24} + \psi_{25} - \psi_{29} - \psi_{31} - \psi_{32} + \psi_{33} + \psi_{34} + \psi_{36} - \psi_{40} - \psi_{41} - \psi_{42}) \\
\psi'_{19} &= \frac{1}{\sqrt{12}} (\psi_{23} + \psi_{24} + \psi_{25} + \psi_{27} + \psi_{28} + \psi_{30} - \psi_{35} - \psi_{37} - \psi_{38} - \psi_{40} - \psi_{41} - \psi_{42}) \\
\psi'_{20} &= (1/\sqrt{20}) \sum_{i=23}^{42} \psi_i
\end{aligned} \tag{3}$$

This new choice is of course permissible since any linear combination of solutions of a Schrödinger equation is still a solution of the equation. The new sub-determinant of order one corresponds to one component of the septet—that is, to no electron pair bonds. The last mentioned 5th order determinant corresponds to the five independent eigenfunctions arising from having one bond among the six electrons. (There are actually fifteen ways of drawing one bond, giving rise to fifteen eigenfunctions, of which not more than five are linearly independent.) Similarly, the 9th and the other 5th order determinants are associated with the independent eigenfunctions arising from drawing two and three bonds, respectively.

The twenty eigenfunctions of (3) thus fall into four non-combining sets—

$\psi'_1$  to  $\psi'_6$ ,  $\psi'_6$  to  $\psi'_{14}$ ,  $\psi'_{15}$  to  $\psi'_{19}$ ,  $\psi'_{20}$ . That is,  $\int \psi'_i H \psi'_{20} d\tau = 0$  for  $i$  running from 1 to 19. The eigenfunctions  $\psi'_{15}$  to  $\psi'_{19}$  combine among themselves but not with those outside the group. The same may be said of the groups  $\psi'_1$  to  $\psi'_6$  and  $\psi'_6$  to  $\psi'_{14}$ .

Since we are only interested in the energy corresponding to three bonds we need consider only the determinant arising from the eigenfunctions  $\psi'_1$  to  $\psi'_6$ . It is interesting to remark that there are actually fifteen ways of drawing three bonds and therefore 15 eigenfunctions, of which not more than five are linearly independent. Any linearly independent set of five would have served our purpose as well as the set we chose.

Actually the way of forming the eigenfunctions (3) from the set given in (2) is important; for no bonds one simply takes a sum of the twenty eigenfunctions. An eigenfunction for six electrons corresponding to a bond between  $a$  and  $b$  is obtained by taking a linear combination of the twelve eigenfunctions in the set (2) for which the spins of  $a$  and  $b$  are opposite. Those for which  $a$  is associated with  $\alpha$  are taken with a plus sign and those for which  $a$  is associated with  $\beta$  are taken with a minus sign. For convenience in calculation we divide by a normalizing factor  $\sqrt{12}$ . The eigenfunction corresponding to a bond between  $a$  and  $b$  is  $\psi'_{15}$  of (3).

To obtain an eigenfunction with two bonds, say one between  $a$  and  $b$  and one between  $c$  and  $d$ , we select a linear combination of the eigenfunctions from (2) which have different spins for  $a$  and  $b$  and at the same time different spins for  $c$  and  $d$ . If a particular eigenfunction is taken as positive, *e. g.*,  $\psi_{28}$ , then the sign of any other is positive if the spins associated with  $a$ ,  $b$ ,  $c$  and  $d$  may be made the same as those in  $\psi_{28}$  by interchanging the spin eigenfunctions of  $a$  and  $b$  and simultaneously those of  $c$  and  $d$ . If it is obtained by only one of these interchanges, it is negative. In this case we divide by a normalizing factor  $\sqrt{8}$ . The eigenfunction just described is  $\psi'_6$ . There are 45 eigenfunctions corresponding to drawing two bonds, of which not more than 9 are linearly independent.

For the case of three bonds connecting the eigenfunctions  $a$  to  $b$ ,  $c$  to  $d$ , and  $e$  to  $f$  a linear combination of all eigenfunctions from (2) is chosen in which the spin associated with each atom of these three pairs is different from its partner. If for an arbitrary one,  $\psi_{28}$ , a plus sign is taken, the sign of any other one of the 8 is positive if it may be obtained from  $\psi_{28}$  by an even number of spin interchanges between atom pairs, and negative if by an odd number. The eigenfunction here described is  $\psi'_1$ .

With more than six electrons exactly the same scheme as outlined above can be used for obtaining an eigenfunction corresponding to an arbitrary number of bonds.

In evaluating our determinant for the singlet state we shall make certain approximations. We shall neglect energy integrals corresponding to more than two electrons jumping simultaneously. When all the atoms

are far apart the electronic eigenfunctions are strictly orthogonal. We shall neglect the fact that this is no longer true as the atoms approach each other. A partial correction for this results automatically from the fact that we use spectroscopic potential curves for evaluating the energy integrals.

The 5th order determinant for the singlet state can be written symbolically as follows

$$\begin{vmatrix} H'_{11} - Ed'_{11} & H'_{12} - Ed'_{12} & H'_{13} - Ed'_{13} & H'_{14} - Ed'_{14} & H'_{15} - Ed'_{15} \\ H'_{12} - Ed'_{12} & H'_{22} - Ed'_{22} & H'_{23} - Ed'_{23} & H'_{24} - Ed'_{24} & H'_{25} - Ed'_{25} \\ H'_{13} - Ed'_{13} & H'_{23} - Ed'_{23} & H'_{33} - Ed'_{33} & H'_{34} - Ed'_{34} & H'_{35} - Ed'_{35} \\ H'_{14} - Ed'_{14} & H'_{24} - Ed'_{24} & H'_{34} - Ed'_{34} & H'_{44} - Ed'_{44} & H'_{45} - Ed'_{45} \\ H'_{15} - Ed'_{15} & H'_{25} - Ed'_{25} & H'_{35} - Ed'_{35} & H'_{45} - Ed'_{45} & H'_{55} - Ed'_{55} \end{vmatrix} = 0 \quad (4)$$

where  $H'_{ij} = \int \psi'_i H \psi'_j d\tau$  and  $d'_{ij} = \int \psi'_i \psi'_j d\tau$ .

The separate terms of the determinant are given below. The following notation is used:  $ac = \int a_i H c_j dx_i dy_i dz_i dx_j dy_j dz_j$ . Thus  $ac$  is the interchange integral between the eigenfunctions  $a$  and  $c$ , with similar definitions for other terms. Also  $Q$  is defined as

$$Q = \int a_1 b_2 c_3 d_4 e_5 f_6 H a_1 b_2 c_3 d_4 e_5 f_6 d\tau \quad (5)$$

Any permutation of the electrons in (5) applied both to the electronic eigenfunctions before and after  $H$  does not change the value of the integral.  $Q$  is really the sum of the 15 Coulombic integrals between pairs of eigenfunctions—that is, between the atoms if all the atoms are monovalent.

The terms are

$$\begin{aligned} d'_{11} &= d'_{22} = d'_{33} = d'_{44} = d'_{55} = 1 \\ d'_{12} &= d'_{13} = d'_{24} = d'_{34} = d'_{45} = 1/2 \\ d'_{14} &= d'_{23} = d'_{25} = d'_{35} = 1/4 \\ d'_{15} &= -1/4 \end{aligned}$$

$$\begin{aligned} H'_{11} &= Q + ab + cd + ef - 1/2[ac + ad + ae + bc + bd + be + bf + cf + ce + de + df + af] \\ H'_{22} &= Q + ab + ce + df - 1/2[ac + ad + cd + be + bf + ef + af + cf + bd + de + ae + bc] \\ H'_{33} &= Q + ac + bd + ef - 1/2[ab + ae + be + cd + cf + df + af + bf + de + ce + ad + bc] \\ H'_{44} &= Q + ac + be + df - 1/2[ab + ad + bd + ce + cf + ef + af + bf + cd + de + ae + bc] \\ H'_{55} &= Q + ad + be + cf - 1/2[ab + ac + bd + ce + df + ef + af + bf + cd + de + ae + bc] \\ H'_{12} &= \frac{Q}{2} - cf - de - 1/2 \left[ \frac{ad + ae + bc + bf + ac + af + bd + be}{2} - df - ce - ef - cd - ab \right] \\ H'_{13} &= \frac{Q}{2} - bc - ad - 1/2 \left[ \frac{af + df + cf + bf + de + be + ce + ae}{2} - cd - ef - ab - bd - ac \right] \\ H'_{24} &= \frac{Q}{2} - bc - ae - 1/2 \left[ \frac{ad + de + bf + cf + af + ef + bd + cd}{2} - be - ac - ce - df - ab \right] \\ H'_{34} &= \frac{Q}{2} - bf - de - 1/2 \left[ \frac{ab + af + cd + ce + ae + bc + cf + ad}{2} - df - be - ef - bd - ac \right] \\ H'_{45} &= \frac{Q}{2} - af - cd - 1/2 \left[ \frac{ab + bf + ce + de + ae + ef + bc + bd}{2} - cf - df - be - ac - ad \right] \\ H'_{14} &= 1/4Q + 1/4[be + af + bd + ef + cd + ac + ab + ce + df - 2(ae + bf + bc + ad + de + cf)] \\ H'_{25} &= 1/4Q + 1/4[bd + af + be + ac + ce + df + ab + ef + cd - 2(bf + ad + bc + ae + de + cf)] \\ H'_{35} &= 1/4Q + 1/4[bf + ad + be + ac + de + cf + ce + df + ab - 2(bd + af + bc + ae + ef + cd)] \\ H'_{45} &= 1/4Q + 1/4[cf + ae + ef + bd + ac + bc + ad + be + df - 2(ce + af + ab + bf + cd + de)] \\ H'_{15} &= -1/4Q - 1/4[be + af + bc + ad + ef + cd + ab + cf + de - 2(ae + bf + bd + ac + ce + df)] \end{aligned} \quad (6)$$

Thus for monovalent atoms all the quantities in (4) are determined if we know the Coulombic and interchange integrals between atom pairs.

We wish to express our thanks to Professor Taylor for helpful suggestions in connection with this paper.

### Summary

1. It is pointed out that in general for bimolecular surface reactions a plot of the specific reaction rate against the temperature will exhibit a maximum.

2. The quantum mechanical calculations of the activation energies for the hydrogenation of ethylene, acetylene and the activated adsorption of hydrogen on charcoal are given. If the Coulombic binding is taken as 10% of the total for all atom pairs the activation energy is approximately 9 kg. cal. too high in all cases. The significance of this result has been discussed.

3. It is shown that a most favorable distance of carbon-carbon atoms in charcoal exists (approx. 3.6 Å.) such that the activation energy for adsorption is a minimum.

4. The calculations indicate a probable mechanism for the ortho-para hydrogen conversion and point to the improbability of the following three possible mechanisms: (a) a conversion resulting from the dissociation of a single molecule of hydrogen by surface carbon atoms (with subsequent recombination), in the absence of a neighboring hydrogen molecule; (b) the lowering of the activation energy of the homogeneous reaction of two hydrogen molecules due to the presence of two surface carbon atoms; (c) a collision of a hydrogen molecule from the gas phase with an adsorbed hydrogen molecule. This case differs from (b) only that in (c) we assume that two of the hydrogen atoms come much closer to the surface than the other two atoms.

5. The problem of spin degeneracy of six electrons is solved and the equation for the potential energy applied to the calculation of activation energies.

PRINCETON, NEW JERSEY