QUANTUM MECHANICS AND CHEMICAL REACTIONS

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TYPES OF CHEMICAL REACTIONS

Chemical reactions proceed by a great variety of mechanisms. In many reactions there is light emission of a kind undoubtedly associated with electron transitions. The overwhelming majority of reactions go faster with a rise in temperature. Of necessity endothermic and exothermic reactions are equal in number, although the latter are more apt to proceed spontaneously. Reactions in the solid phase are rare but very many examples of reactions in solutions, in the gas phase, and on surfaces can be cited. Reactions in solution are frequently instantaneous. These are generally known to involve the combination of ions. Reactions in solution involving the breaking of an electron pair bond are generally slow and proceed more rapidly with a rise in temperature. Such bonds belong to a class known as homopolar and will be the chief concern of this paper. Many bonds which have all the properties of the homopolar bond in the gas phase are polar in solution. Two atoms are really linked by a chain of electrons. If the weak link is the electron pair bond we speak of it as being homopolar. If it is between the positive nucleus and an electron we say it is polar. Naturally the latter link, which is an electrostatic one, is much weakened by solution in a substance of high dielectric constant. In the gas phase the weak link is probably always the homopolar bond.

A large class of reactions proceeds without involving radiation at any step. The energy necessary to permit the breaking and reforming of homopolar bonds comes from violent collisions.

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Since the energy known to be used in reactions is often insufficient to break either bond outright, the bonds must weaken each other as they approach.   Thus upon collision certain bonds go over into new ones by a gradual or adiabatic process.   It is this very general type of reaction that has been most satisfactorily treated by the quantum mechanics and that will be discussed here.

If the bond between two atoms depended only on the distance between them and not on the location of other atoms, valence and activation energy would play a far less prominent rôle than they do.   Actually an atom attracts other unsaturated atoms until its valences are satisfied, after which it repels all others.   If with three atoms of equal valence we want the reaction

$$Y + XZ = YX + Z \tag{1}$$

to occur we must somehow force Y to come so close to X that X becomes undecided to which atom it belongs.   This state of indecision is the activated state.   The energy expended in forcing the atom Y to approach X is the activation energy.

Molecules (or atoms) in the liquid or gaseous state are moving with random velocities.   A fraction of the molecules, increasing with temperature, travel with enormous velocities.   When two of these fast groups collide, head on, the atoms in the different molecules get as near to each other as they are to their former partners, with the result that there may be a change of partners and a bimolecular reaction.   A unimolecular reaction is a violent internal collision with a consequent change in the partners that are bound together.   In some cases the change is a dissociation occurring as soon as the energy concentrates in the right bond. Rice (1) has considered unimolecular reactions in connection with predissociation.

NATURE OF CHEMICAL BONDS

The forces holding atoms together all arise from the fact that they are composed of positive and negative charges and, in fact, roughly one-tenth of the binding energy in a homopolar bond may be calculated simply by using the inverse square law between charges.   The electrons, to be sure, must be assumed to have the

cloudlike probability of distribution given by quantum mechanics. This coulombic binding, or the coulombic integral, is evaluated by integrating the coulombic potentials over the electron clouds. The assumption that a group of atoms with their positive nuclei and electrons must satisfy a Schrödinger equation and the Pauli exclusion principle introduces in addition an entirely new sort of potential energy between atoms, called the interchange binding or interchange integral.   To understand more clearly the nature of this interchange integral we shall digress somewhat at this point.

For a hydrogen atom we have the Schrödinger equation:

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 \mu}{h^2}(E - V)\psi = 0 \tag{1}$$

The potential energy V has the form $V = -\dfrac{e^2}{r}$. x, y and z are ordinary rectangular coördinates. μ is the electron mass and h is Planck's constant.   Equation 1 has only physically interpretable solutions, ψ, for particular values of the energy E. ψ is called the characteristic function or eigenfunction, and E the characteristic value, or eigenvalue.   The values of E are, of course, the energy levels of hydrogen.   The ψ's are functions of the coördinates of the electron x, y, z and certain integers n, l, m. E, on the other hand, does not depend on the coördinates of the electron but does depend on the quantum numbers n, l, m.   Thus, for each particular set of values for the quantum numbers we have a particular ψ and a particular E. n, the principal quantum number, goes from 1 through the positive integers.   The quantum number l is always less than n. $l = 0$ for s electrons, 1 for p electrons, 2 for d, etc.   For a particular value of n and m we can have the $2l + 1$ values of m going from $-l$ to $+l$.   These $2l + 1$ values for m are all the permitted projections of the angular momentum vector, l, along the axis of an applied magnetic field.

The probability of an electron being at some point in space is proportional to the value of ψ^2 at that point, so that two electrons with any of their quantum numbers different will not have the same probability of being at all points in space.   The same system

of quantum numbers that serves to describe hydrogen enters automatically through the Schrödinger equation into the description of every atom. For atoms with more than one electron the potential energy is simply the sum of all the attractive terms between the nucleus and the electrons plus all the repulsive terms between the electrons. The other modification made in equation 1 is that a Laplacian,

$$\frac{\partial^2 u}{\partial x_i^2} + \frac{\partial^2 u}{\partial y_i^2} + \frac{\partial^2 u}{\partial z_i^2}$$

for the coördinates of each new electron is added. The eigenfunction for the new equation will be approximately a product of hydrogen-like eigenfunctions

$$U = \psi_1 \psi_2 \ldots \psi_n$$

where for each ψ we can specify a set of integral quantum numbers n, l, m just as in hydrogen. It might be supposed that all the electrons would choose the same lowest set of quantum numbers. On the contrary the Pauli principle states that not more than two electrons in one atom can have the same set of quantum numbers n, l, m. In order to explain the Zeeman effect for large atoms it was necessary to assign to all electrons a fourth quantum number, S. The spin quantum number, S, can have only values of $\frac{1}{2}$ or $-\frac{1}{2}$. If two electrons in an atom have the same quantum numbers n, l, m, the spin quantum numbers must have opposite signs. Thus, no two electrons in an atom can have all four quantum numbers equal. Two electrons in separate atoms, however, may have all four quantum numbers equal. The general statement of the Pauli principle then is that no two electrons can have the same eigenfunction, ψS, where S is the spin part of the eigenfunction.

Zener and Slater (2) have shown how one can write down an approximate eigenfunction for an electron in any atom for which the four quantum numbers are given. For our purpose it will not be necessary to write them down. But evidently if one specifies the quantum numbers and the atom to which each electron be-

longs, an enterprising person can write down the eigenfunction for the system as long as the atoms are far apart. It will be merely the product of the separate eigenfunctions for each electron. But, even if one keeps the same set of quantum numbers, still by interchanging the positions of the electrons we get many different eigenfunctions, all corresponding to the same energy and all equally good solutions of Schrödinger's equation. Now, wherever two electronic eigenfunctions overlap, either inside a single atom or between two atoms, the electrons trade around in every possible way not in violation of the Pauli exclusion principle. This is a phenomenon we neglected entirely when we considered the coulombic binding and prepares us to expect a modified binding energy. This trading may be done in different ways. If the electrons are simultaneously in the same neighborhood oftener than they would be if each moved at random, there is increased attraction. If they occupy the same neighborhood less frequently than they would if moving at random, we get a diminished binding. This additional potential energy is called the interchange integral. In order for two equivalent electrons to occupy the same neighborhood, they must, by the Pauli exclusion principle, have oppositely directed spins, since the other part of their eigenfunctions are identical. Thus for oppositely directed spins the interchange integral increases the binding, since the binding electrons can spend more of their time between the atoms.

Heitler and London (3) first discovered the interchange binding for molecules and made the calculation for H_2.

ACTIVATION ENERGY FOR REACTIONS IN WHICH THREE ELECTRONS
CHANGE PARTNERS

If two monovalent atoms have the spins of their electrons oppositely directed (antiparallel), giving an attractive interchange binding (the coulombic attraction does not depend on the direction of the spin), it is evident that a third atom cannot possibly have its spin antiparallel to the other two. The third atom will be repelled by at least one of the other atoms. London (4), using

perturbation theory, gave the following approximate expression for the energy of three monovalent atoms:

$$E_3 = A + B + C + (1/2(\alpha - \beta)^2 + (\alpha - \gamma)^2 + (\beta - \gamma)^2)^{\frac{1}{2}} \qquad (2)$$

Figure 1 represents three monovalent atoms Y, X and Z at the corners of a triangle. The quantities written on the connecting lines between pairs of atoms are the energies which would be required to separate the pair if the third atom were not present. The important point is that although the energy, E_3, is not the sum of the three bond energies, still it is given in terms of the bonds between atom pairs. The potential energy curve for many diatomic molecules can be constructed using well-known
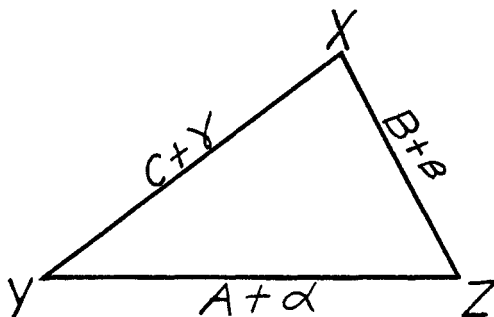

FIG. 1. THREE ATOMS AND THE POTENTIAL ENERGIES WHICH DETERMINE THE TOTAL POTENTIALS

spectroscopic data in a Morse (5) curve and these may be used for evaluating the binding between atom pairs. To calculate E_3, it is not enough, however, to know $A + \alpha$, $B + \beta$ and $C + \gamma$, which the Morse curves give us. In addition we must know A, B and C, the coulombic part of the binding energy. α, β and γ are the interchange binding. In the case of hydrogen the coulombic part of the binding energy is approximately 10 per cent of the total, as shown by Suguira's (6) evaluation of the integrals of Heitler and London (3).

Farkas (7) found for the reaction

$$H_{2para} + H = H_{2equil.} + H \qquad (3)$$

an activation energy of from 4 to 11 kg-cal.   Eyring and Polanyi
(8) using equation 3 with a Morse curve for H_2 found 13 kg-cal.
If a different Morse curve is used (i.e., one which fits on to the
theoretical curve at great distances, where the theoretical curve is
known to be correct) the calculated activation energy falls inside
the experimental limits.

We will now consider how such a calculation of the activation
energy is made.   The problem is to find how an H atom can be

FIG. 2. POSITION OF THREE ATOMS FOR THE POTENTIAL SURFACE GIVEN IN
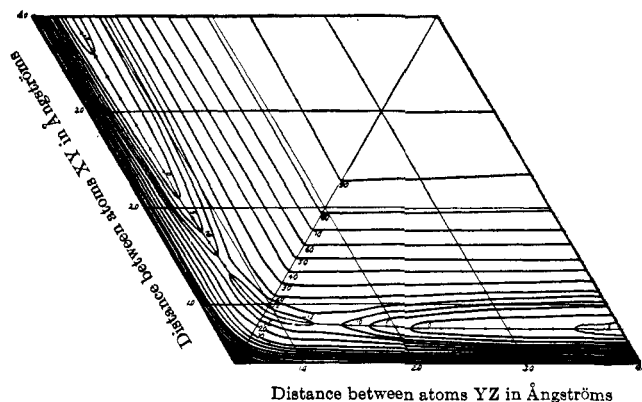FIGURE 3

Distance between atoms YZ in Ångströms

FIG. 3. ENERGY CONTOURS FOR THREE HYDROGEN ATOMS IN A LINE

brought so near an H_2 molecule that the central atom, being as
near one neighbor as the other, is as apt to take the new partner
as to retain the old one.   From equation 2 and a potential energy
curve for H_2 one can calculate the potential for every configuration
so that the problem is certainly soluble.   An examination of E_3
shows that less energy will be required if the three atoms are kept
on a straight line; so we need not consider other configurations.
If the distances r_1 and r_2 of figure 2 be plotted at 120° to each
other and the energy, E_3, be indicated by contour lines we get
figure 3.   It was shown in the paper last quoted that a ball made

to roll on the surface corresponding to figure 3 will show exactly how r_1 and r_2 will change in the H_3 complex. This surface, then, solves our problem. The surface resembles two long valleys stretching away to infinity parallel to the axes. As one travels up either valley toward the origin one climbs slowly to 13 kg-cal. Here one passes into a shallow basin 1.6 kg-cal. deep. Passing through this basin one reaches again, in the symmetrical position, a gap in the basin rim 13 kg-cal. high and then descends slowly into the second valley. The valleys on their sides nearest the borders of the map rise steeply, corresponding to the repulsion between two hydrogen atoms forced closer together than .76 Ångströms. On the inner side the valleys rise less steeply toward a high central plateau, 101.5 kg-cal. high, corresponding to dissociation of the H_3 complex into three separate H atoms. Sea level, or 0 kg-cal., corresponds to the lowest attainable energy for an H_2 molecule with the third H atom infinitely far away. The sea itself descends to a maximum depth of 6.1 kg-cal. This is potential energy corresponding to the half quantum of vibration of the H_2 molecule which it cannot give up as long as it remains an H_2 molecule. It does become available in reducing the activation energy in reaction 3, however. Reaction 3 is represented on our contour map by the broken line with arrows proceeding along the bottom of one valley through the basin into the adjoining valley, i.e., from large r_1 to large r_2. The activation energy is, of course, the least energy which permits passage from one valley to the other. A ball rolling along the valley so that r_1 increases and r_2 remains constant, represents pure translational energy of separation of an H_2 molecule from an H atom. A periodic motion back and forth across the valley corresponds to vibration of the H_2 molecule. The significance of these motions is immediately understood by considering what the corresponding changes in r_1 and r_2 signify from figure 2. To find out whether reaction 3 will require its activation energy in the form of vibration or translation, a ball is placed in the gap between the basin and the valley and allowed to descend into the valley. It is then determined how much of the kinetic energy is motion along the axis of the valley and how much is transverse to it. This will determine how the

ball must be sent in the reverse direction so that it will just reach the top of the pass without any excess energy. For the para-hydrogen reaction only translational energy is used. This is clear when it is remembered that vibrational energy can be absorbed only in lumps of around 12 kg-cal., whereas the surface shows that not more than one or two of the 13 kg-cal. for activation can be efficiently used in the form of vibrational energy.

A ball projected in the most efficient way from one valley passes very slowly through the first pass and into the shallow basin where it zigzags back and forth before finding its way out through the second gap. The three atoms thus form a quasi-molecule or sticky collision. If during the time the ball is in the basin a collision from the outside carries off its energy, it must remain in the basin until it recovers the energy. If the basin were 25 kg-cal. instead of 1.6 kg-cal. deep, H_3 would be stable at room temperatures and the recovery of the energy with the subsequent escape of the ball would constitute a unimolecular decomposition.

It is instructive to consider as simple an example as H_3, since Volmer (9) and his collaborators have demonstrated that the decomposition of nitrous oxide is unimolecular with a peculiarly low specific reaction rate

$$k = 10^{10} \, e^{-\frac{E}{RT}} \tag{4}$$

Ordinarily the proportionality factor is of the order 10^{13}, as Polanyi and Wigner (10) were able to show should be the case for a somewhat specialized molecule with many atoms. Their factor 10^{13} is the most rapid characteristic vibration frequency for the molecule. Their method, which depended on there being many atoms and many characteristic vibration frequencies, is not accurate for so simple a molecule as N_2O, but it is just these simple molecules for which it is possible to construct potential energy surfaces and roll the ball on them. For a unimolecular reaction the activation energy E of equation 4 is the depth of the potential energy basin measured from the bottom to the lowest point in the rim of the basin through which the ball can escape to the outside. The half quanta of vibration must be allowed for. For the ball to

escape from the basin it not only must have the energy E but it must be vibrating in a direction to escape through the low point or points in the rim.   In general, when it first gets the energy E it will not be doing this.   Depending on the shape of the surface, it may require one or many vibrations before it makes its escape. It is thus easy to see that this life of an activated molecule will be a specific thing for each molecule.   For the specific reaction rate constant k we should write an expression analogous to

$$k = \frac{\overline{S}\, e^{-\frac{E}{RT}} \left(\frac{E}{RT}\right)^{1/2\, n\, -\, 1}}{(1/2\, n\, -\, 1)!}$$

since we are supposing the energy distributed among all the internal degrees of freedom. $\overline{S}$ is the average reciprocal of the time required for the ball to escape from the basin after it has at least the energy E (depth of the basin) distributed through its n squared terms.   One interesting proposition follows immediately from this picture of a unimolecular decomposition.   The ball when it has the smallest E enabling it to escape can escape only at the very lowest points of the rim of the basin.   As the energy is increased it can escape over a larger fraction of the rim.   We can then state the proposition: S increases with the excess of E over the minimum activation energy required for decomposition.   For small enough excess of E over the minimum required, this proportionality will of course be linear.   Rice and Ramsperger (11a) and Kassel (11b) were led to this assumption to explain observed unimolecular reaction rates.

The rate of decomposition of activated N_2O molecules, approximately 1/1000th the usual rate, differs more from Polanyi and Wigner's theoretical result than is to be expected from mechanical considerations, so that one naturally looks for a non-mechanical reason.   Wigner (12) has pointed out that when the sum of the electron spins of the resultant molecules in a reaction cannot be added up algebraically to equal a possible algebraic sum of the spins of the initial molecules, the chance of reaction is small (roughly 1/1000th the normal rate) even for molecules which have the necessary activation energy.   Normal N_2O is in a singlet state,

i.e., has no resultant spin.   It is diamagnetic.   The resultant N_2 is certainly in a singlet state, whereas the O atom is certainly in a triplet state, giving a total spin of one unit for the products. Thus the initial and final total spins are different, and we expect an unusually slow reaction.   This slowness of reactions because of changes in the total multiplicity applies also to the following cases if reactants and products are in the normal state: $CO + O = CO_2$; $H_2 + O = H_2O$; $H_2 + O_2 = H_2O_2$.   This is the reason why O_2 with its unpaired electrons does not behave more often like a free radical.

The perturbation theory as ordinarily formulated (16) neglects the possibility of a change in multiplicity.   When magnetic forces are considered this probability is found to be small, but not zero.   The analogous forbidden transitions in spectra give us a way of estimating this probability of change in multiplicity (13).

It is helpful in discussing potential energy surfaces to use a terminology adopted earlier (8).   We shall call β activation energy that energy which one calculates from equation 2 if it be assumed that all the binding energy is interchange ($A = B = C = 0$) and also that the bond, $A + \alpha$, between the outer atoms of the three on a line is zero.   The β activation energy for reaction 3 is 14.4 kg-cal.   The agreement of β activation energy with the activation energy calculated from the unmodified equation 2 is accidental.   The increase in the β activation energy when α is not neglected is called the α activation energy.   The α activation energy is sometimes small but is always positive.   The coulombic activation energy is the difference between the sum of α and β activation energy and that calculated from equation 2.   It is due to the coulombic forces and is always negative.   In calculating activation energy we figure not from the lowest part of the surface but from a half quantum higher.   Thus we assume the activation energy is lessened by the half quantum.   This is, in general, not quite true, since the half quanta of the activated state are generally not quite negligible.

If one calculates the β activation energy for reaction 3 and constructs the surface it is found that an H_3 complex has a lower energy by 10 kg-cal. than $H_2 + H$ and that an activation of 24

kg-cal. would be required for the decomposition of the H_3, making it a stable compound at room temperature. This is of course not true, and it shows that equation 2 must be used to get reasonable results. London, in the example he gave, considered only β activation energy.

Three similar halogen atoms actually do have a small α activation energy for reactions of the type $X_2 + X = X + X_2$. If the coulombic binding is as much as 10 per cent of the total, as it is in H_2, then complexes of the type F_3, Cl_3, Br_3 and I_3 are more stable at room temperature than the diatomic molecule and an atom. Rollefson and Eyring (14) have pointed out the significance of such complexes in photochemical reactions. The assumption that a reaction will be excessively slow because it involves three molecules is certainly open to question, in view of the stickiness of many collisions.

It is interesting to consider an extension of Eyring and Polanyi's treatment of the reaction

$$H_{2_{para}} + H = H_{2_{equil.}} + H \tag{3}$$
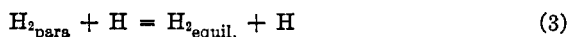
They found that if the three atoms collided on a line the activation energy was 13 kg-cal.; for collisions not on a line the activation energy is of course higher. Now the fraction of collisions exactly on a line is negligible, so that one must really include with the appropriate probability factor collisions in which the approaching atom makes an angle with the molecular axis. By doing this one can obtain not only the activation energy but the absolute rate of reaction 3.

Pelzer and Wigner (15) by doing this have found a reaction rate based entirely on theory in excellent agreement with Farkas' measurements. They also consider the probability of electron transitions being involved in this reaction and conclude that the reaction must proceed by the adiabatic process previously assumed. Thus any modifications in treating this reaction must be in the technique of calculating the activation energy, and not in the conception that it is an adiabatic process.

ACTIVATION ENERGY FOR REACTIONS IN WHICH FOUR ELECTRONS CHANGE PARTNERS

The equation for the potential energy for any configuration of four monovalent atoms is

$$E_4 = A_1 + A_2 + B_1 + B_2 + C_1 + C_2 + [1/2\,((\alpha_1 + \alpha_2 - \beta_1 - \beta_2)^2 +$$

$$(\alpha_1 + \alpha_2 - \gamma_1 - \gamma_2)^2 + (\beta_1 + \beta_2 - \gamma_1 - \gamma_2)^2)]^{\frac{1}{2}} \qquad (4)$$

The significance of these quantities is apparent from a consideration of figure 4, where the binding which would exist between
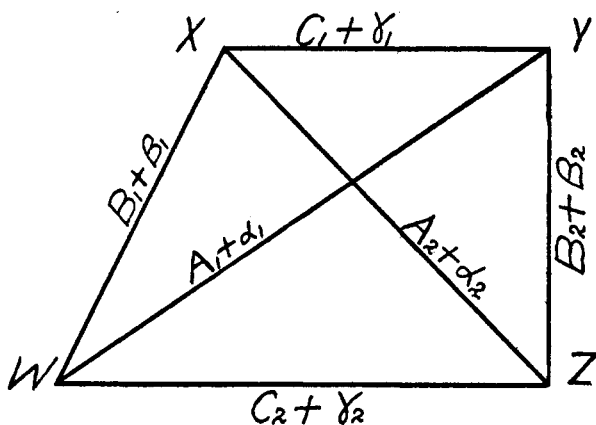

FIG. 4. FOUR ATOMS AND THE POTENTIAL ENERGIES WHICH DETERMINE THE TOTAL POTENTIAL

atom pairs in the absence of other atoms is written along the connecting lines and is a function of this distance only if the electrons are in S states. For directed valences the eigenfunctions will point in a direction to make E_4 as large numerically as possible. It was stated in an earlier paper that equations 2 and 4 could be obtained by using Slater's method for complex atoms. Zener, Gibson and the author did not publish these results, but the reader may be referred to the recent comprehensive treatment of molecular problems by Slater (16), which includes these two cases along with many other interesting results important to chemists.

The activation energy for six reactions of the type

$$WX + YZ = XY + WZ \qquad (5)$$

have been calculated (17) and compared with the activation energy for the same net reaction where the intermediate reactions involved atoms. It is found, in agreement with experiment, that reactions of halogens with hydrogen will proceed by way of the atoms, except in the case of I_2 which will involve molecules only. It is also shown that the homogeneous change of para-hydrogen to the equilibrium mixture will definitely go by way of the atoms as Farkas showed.

STERIC HINDRANCE AND KINETIC THEORY DIAMETERS

Some of the reactions which invove the breaking of two bonds and the formation of two new ones (essentially a reaction involving but four electrons) involve forcing other atoms to approach each other to distances at which there is repulsion. This is steric hindrance, and the increase in the activation energy is readily calculated by using the following consequence of Slater's method for molecules. The added repulsive potential is the sum of one-half of the interchange energy between all possible pairs of electrons, one from each of the molecules (other than the four involved in the reaction proper). The interchange energy, as before, is estimated from the appropriate Morse curves. The accompanying coulombic potentials always act to lessen the repulsion. These two quantities added to equation 4 enable one to calculate the activation energy for a reaction involving steric hindrance. Where there are permanent dipoles, the potential arising from this source must also be included. The mutual polarization of molecules, or van der Waals' forces, gives rise to a further small attractive potential varying inversely as the 6th power of the distance. London (18) and Slater and Kirkwood (19) have each given relationships for calculating this quantity, so that it is now possible to calculate the activation energy in the first approximation for reactions involving three and four electrons, taking account of the steric hindrance due to atoms not themselves involved in the reaction. Such a calculation involves

a detailed knowledge of the position of the atoms in the molecule supplied in many cases by x-ray data. Steric effects due to permanent dipoles must be considered in addition.

Ordinary collisions are of course simply a special case of steric hindrance, and one for which the distance of approach should be calculable by just the methods outlined above. In fact, Slater and Kirkwood (19) have calculated the constants of van der Waals' equation for helium with excellent agreement with experiment. Kirkwood and Keyes (20) have investigated other physi-
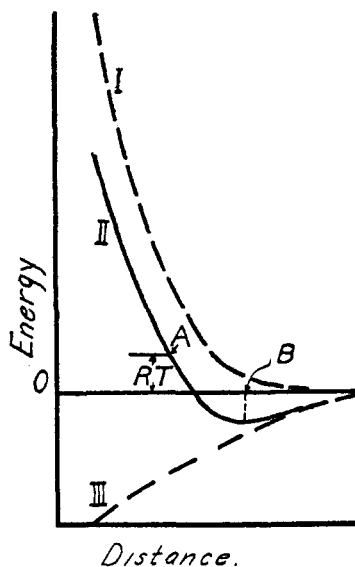

FIG. 5. POTENTIAL CURVES BETWEEN TWO COLLIDING MOLECULES

cal properties, also with satisfactory agreement with experiment. The collision process of two H_2 molecules has likewise been calculated theoretically (21). The agreement with experiment is good. Figure 5 shows schematically the potential energy between two molecules at a distance approximately that of their kinetic theory diameters.

The potential energy depends, of course, not only on the distance between the center of gravity of the two molecules, but on the relative orientation of their axes. Two colliding H_2 molecules at

these large distances behave almost like two spheres. Curve I
for H_2 was calculated using equation 4. If equation 4 is expanded
by the binomial theorem for configurations where α_1, α_2, A_1,
and A_2 are large and the other quantities small we get

$$E_4 = Q + \alpha_1 + \alpha_2 - [1/2\,(\beta_1 + \beta_2 + \gamma_1 + \gamma_2)] \tag{6}$$

We have already stated the manner in which equation 6 is to be
modified for more complicated molecules colliding. During an
ordinary collision $\alpha_1 + \alpha_2$ stays practically constant as do the
attractive potentials A_1 and A_2 in Q. The other terms increase
exponentially with the distance as the two molecules approach,
giving us a net repulsion indicated by curve I in figure 5. The
individual terms are evaluated from potential energy curves for
atom pairs. Thus, no matter how complicated the colliding mole-
cules, to construct curve I one needs only to know the relative
position of atoms in the separate molecules and the potential
energy curve for pairs of atoms, one from each molecule. The
potential energy will ordinarily depend on the relative orientations
of the molecules as well as the distances between centers of
gravity. The repulsive potential between molecules (without
permanent dipoles) arises entirely from interchange forces which
would give attraction if the electron spins were antiparallel. The
van der Waals' forces indicated by curve III are calculable using
the relationships suggested by London (18) or by Slater and Kirk-
wood (19). The sum of the two curves gives us II, which repre-
sents the actual potential energy between two molecules plotted
against the distance between them (for a definite relative orienta-
tion). It is interesting to consider how much information is given
by such a curve. We shall leave out of account for the moment
the difference in the energies with which pairs of molecules collide
at the same temperature. Two molecules then approach with an
energy RT so that the abscissa at A is the kinetic theory diameter.
The decrease of the diameter with temperature depends on the
slope at A and can be compared with the Sutherland constant.
The abscissa at B is the diameter of the molecules in the liquid
state at zero degrees. The ordinate at B is the heat of sublima-

tion at zero degrees.   As the temperature rises, molecules of the liquid vibrate about the minimum.   This reduces the heat of sublimation and also causes an expansion of the liquid.   The expansion arises from the unsymmetrical nature of the curve, since the vibrating molecules spend more time traversing the less steep portions of the curve.   Thus the coefficient of expansion measures the dissymmetry of curve II.   The slope of II to the left of B determines the compressibility.   The curvature at the minimum determines the frequency of vibration which enters into the specific heat of the liquid.   Thus we see that we have these additional experimental checks on the accuracy of our calculation of the valence forces which determine activation energy.

An obvious way to calculate the repulsive potential at kinetic theory distances is to consider that some definite fraction of the Morse potential curve gives the interchange binding.   It is too much to expect that such a procedure would lead to accurate results, although the results are generally not greatly in error. The Morse potential energy for H_2 does not fall off as rapidly with distance between the H atoms as the theoretical curve.   A consideration of the way in which the potential energy of other diatomic molecules, calculated from Slater's eigenfunctions, falls off with distance indicates that this may be a fairly general difficulty of Morse curves.   This defect leads to activation energies and kinetic theory diameters a little bit too large.   The whole question should be more carefully considered.

THE RATIO OF INTERCHANGE TO COULOMBIC BINDING

In previous calculations of activation energy the interchange binding has been taken as 10 per cent of the total binding, the value calculated for H_2.   Rosen (22) has recently calculated the potential energy binding for Na_2 using Slater eigenfunctions. He finds very good agreement with experiment for the heat of dissociation, distance between atoms and the vibration frequency of the lowest state.   His value for the ratio of coulombic to total binding in the neighborhood of the minimum is 28.3 per cent. Bartlet and Furry (23) have carried out a similar calculation

for Li_2, which is likewise in excellent agreement with experiment. Their value for the ratio of coulombic to total binding is 22 per cent. This percentage is constant to within 1 per cent from the minimum out to distances for which the binding energy has dropped to one-fifth of its greatest value. This is additional evidence for the assumption that the ratio of coulombic to interchange binding is approximately independent of the distance between atoms in the region important for calculating activation energies. However, it also shows that this ratio depends very much on the molecule. We need, therefore, some criterion for estimating when the coulombic fractions will be large.

Molecules (independent of the valences of the component atoms) which solidify to give molecular crystals do so because the interchange potentials preponderate largely over the coulombic ones. On the other hand the formation of atomic crystals from atoms having a valence of two or less indicates that interchange binding, associated with antiparallel spins, is of secondary importance to the coulombic binding. This becomes clear when it is realized that two antiparallel electrons repel all others, so that only when the pair is relatively isolated will the total interchange binding help to stabilize the crystal. Since the alkalis form atomic crystals, we expect them to have the coulombic part of the bond relatively large. On the other hand, hydrogen and the halogens form molecular crystals and so have a relatively smaller fraction of coulombic binding. This is the same conclusion to which one is led by considering the activation energies. Of course the way molecules crystallize is a good indication of how they will behave upon colliding in the gas phase. In particular it indicates how much energy is required to make them forget who their former partner was. In a recent paper Cremer and Polanyi (24) consider certain properties of crystals, including their vibration frequencies, in relation to the interchange binding.

With directed valence the relations for calculating the activation energy are the same as for s electrons except that the individual values for bonds depend on the angle θ between the line joining the atoms and the axes of the eigenfunctions. The

bond, D, between a p and s electron depends on the angle, θ, between the atoms in the following way

$$D = A \cos^2 \theta + kA \sin^2 \theta.$$

Slater (16) estimated k for the OH bond to be roughly .2. k may be experimentally determined from the transverse vibration frequency associated with directed valences.

SUMMARY

It is perhaps well to summarize the general point of view. Most of the problems of compound formation (valence) and activation energy may be solved by constructing a potential energy surface the low places of which correspond to compounds stable at ordinary temperatures, provided the barrier separating one minimum from a still lower one is greater than about 20 kg-cal.   The height of the barrier is of course the activation energy. It is then only a problem in mechanics to find how a ball will roll on this surface.   The essence of the theory of adiabatic reaction is that the specification of the relative position of the atoms suffices to determine the energy, the idea being that the electrons because of their more rapid motion adjust to the configuration of lowest energy.   The fact that light is sometimes emitted shows that this is not always true.   A system containing excited atoms is to be thought of as being on a higher potential energy surface. The transition from the higher to the lower surface appears as kinetic energy in some direction which may suffice to carry the ball (representing the system) over a potential barrier.   This constitutes a chemical reaction.

Such a visualization of compounds and reactions would not be particularly helpful if we were unable to construct the potential energy surfaces at least with some approximation.   The relative heights of the potential minima are the material which thermodynamics gives us in the form of heats of reaction.   The position of these minima in terms of the distances between atoms we get from x-ray data and from the illuminating discussions on directed valence by Pauling (25) and by Slater (26).   From the spectroscopic data for diatomic molecules we learn the binding energy

between atom pairs as a function of distance, and finally from perturbation theory we may calculate the energy of complex configurations in terms of the energy between atom pairs, thus enabling us to explore the barriers between minima in our potential surface.

Such a method, which seems general in its applicability, has certain limitations. First, we are using first order perturbation theory, which applied to the H_2 molecule gave a binding energy only three-fourths of the experimental one. However, it has recently been applied to Na_2 and Li_2 with results within a few per cent of the experimental value. Also, the results found for H_3 and other cases seem to be surprisingly near the experimental values. Second, besides knowing the potential curve for a diatomic molecule we must know what fraction of it is coulombic. This is known only in three cases by direct calculation. There are many ways of estimating this quantity so that this cannot be considered a great difficulty. Third, the labor of applying a perturbation method is sometimes great. When only three or four electrons change partners in a reaction, the binding energy for any configuration of the atoms is readily found by methods already described. Steric hindrance, consequent upon non-reacting electrons being forced to approach each other, is also calculable without serious difficulty. When five or six electrons change partners during the reaction, the energy of each configuration can be found by solving a fifth degree equation. Kimball and the author have done this for certain interesting cases. The calculation, is not difficult but tedious. If a reaction involves seven or eight electrons changing partners simultaneously, an equation of the fourteenth degree for each configuration must be solved. Although it is entirely possible to find the roots of such an equation, it is certainly not practical. Fourth, activation energies arising from other sources than spin valence, as for example, l-valences or the inability of charged ions to approach each other must be considered separately. Fifth, Morse curves must be regarded as a temporary expedient to be supplanted by better potential energy curves for atom pairs as they become available. In spite of these limitations we may anticipate that a much more

accurate understanding of chemical reaction will follow from the application of perturbation theory and that it will point the way to something better.   The conception of spin valence bonds going gradually (adiabatically) into new spin bonds without the system ever having sufficient energy to break the bonds outright seems established for certain cases already considered.

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