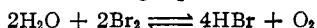


temperature which is possible in the mixtures considered because the experiments were not carried out adiabatically, but is indicative of the temperature at which the equilibria found were frozen out.

Summary

The influence of hydrogen on the thermal decomposition of ozone sensitized by bromine vapor has been investigated. In the non-explosive reaction it is found that hydrogen behaves only as an inert gas retarding the reaction to about the same degree as other inert gases do. No water is formed, indicating that hydrogen does not react readily at room temperature with the oxygen atoms and energy-rich oxygen molecules assumed to play a role in the decomposition of ozone. The explosion pressure limit of ozone is greatly increased by hydrogen, which fits well into the order in which inert gases increase the explosion limit—namely, argon, oxygen, nitrogen, helium and hydrogen. During the explosion the hydrogen is burned to water and the following equilibrium is established



The concentrations of the products are determined and the equilibrium constants calculated. These are compared with the equilibrium constants at different temperatures derived from two independent sources. The temperature at which the equilibria are established is found to be $1600 \pm 100^\circ$ Absolute.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

STERIC HINDRANCE AND COLLISION DIAMETERS¹

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Introduction

A large part of chemistry is interpretable in terms of potential energy diagrams. Stable compounds are configurations of low potential energy which are separated from configurations of still lower energy by energy ridges of approximately 20 kg. cal. or more per mole. If the ridge is much lower than this the rate at which molecules accumulate sufficient energy to pass over the barrier, even at ordinary temperatures, make it impossible to isolate any but the molecular species of lowest energy. Energy barriers are sometimes lowered by two molecules colliding, making a complex from which a new species emerges—a bimolecular reaction. A rearrangement or splitting inside a single molecule is a unimolecular

¹ Presented except for minor changes September 2, 1931, as part of the symposium on the Kinetics of Chemical Reactions at the Buffalo meeting of the American Chemical Society, by Henry Eyring and J. C. Slater.

reaction. Every bimolecular reaction has a unimolecular stage, *i. e.*, the rearrangement inside the complex.

Spectroscopy gives the information from which potential energy curves for diatomic molecules can be constructed. A convenient way of doing this is to use Morse curves.²

Quantum mechanics and the Pauli principle give approximate values for the potential energy of a complex configuration of atoms in terms of the potential energies that would exist between pairs of electrons if the other electrons were not present. Thus for reactions involving three and four valence electrons it is possible to construct potential energy functions such that the minimum energy which permits molecules to approach near enough to exchange partners can be calculated.³

Calculation of Potential Energy of Molecules.—In a recent paper by Slater,⁴ the method of calculating energy terms in complex atomic spectra has been extended to molecules. For a definite way of drawing the valence bonds in molecules perturbation theory gives

$$E = Q + \Sigma\alpha_p - \frac{1}{2}\Sigma\alpha_u \quad (1)$$

Here Q is the sum of all coulombic interactions plus the sum of the energies due to mutual polarization of atom pairs (van der Waals forces) plus terms arising from permanent dipoles. $\Sigma\alpha_p$ is the sum of the resonance attraction between the pairs forming shared electron bonds. $\frac{1}{2}\Sigma\alpha_u$ is the sum of the resonance repulsions between all pairs where there is not a bond and can be evaluated in exactly the same way as the terms, α_p , that is, as half the interchange bond that exists between the electrons when paired. In these considerations it is immaterial how the valence electrons are distributed among the various atoms, that is, whether we are considering monovalent or polyvalent atoms. Electron pair bonds within atoms are the same things as closed shells, and are formed inside all atoms showing less than the highest spin valence. For purposes of calculations these bonds need not be considered different in kind from those between neighboring atoms. The interchange integrals for these internal bonds correspond to half the difference between definite terms of successive multiplicities in the atom, and are known from atomic spectra.

Equation (1) is a general result, as may be seen in the following way. Consider any system of molecules, such that all valence electrons are bound in definite electron pairs. Then an approximate wave function can be set up, corresponding to this way of drawing the electron bonds. And the energy value connected with this wave function is just analogous to the expression (1).

² Morse, *Phys. Rev.*, **34**, 57 (1929).

³ Eyring and Polanyi, *Z. physik. Chem.*, **B12**, 279 (1931); Eyring, *THIS JOURNAL*, **53**, 2537 (1931).

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

The way of setting up a wave function corresponding to definite bonds is interesting. Suppose the $2n$ valence electrons are distributed among $2n$ states whose wave functions have the dependence on coordinates given by a, b, c, d, \dots , and suppose the bonds are situated between states as indicated by the lines, $a-b, c-d, e-f, \dots$, etc., where more than one electronic function can belong to the same atom. Now to specify a state of the system completely we must give not only the dependence on coordinates but also on spin. Thus if α represents a spin directed along a fixed axis, β a spin in the opposite direction, such a state is given by assigning to each function a, b, \dots , a definite spin, as is given by the symbol $(a\alpha) (b\beta) (c\alpha) (d\beta) (e\alpha) \dots$. To get the actual wave function, we must form an antisymmetric function of the electrons, in a manner which has been described elsewhere. This state which we have symbolized above does not correspond to valence binding; we require rather a linear combination of such states. This linear combination is of the following nature. In each state concerned in it, the two electrons in a pair, as a and b , have opposite spins, but in some the spins are arranged $\alpha\beta$, in others $\beta\alpha$. There are, in other words, just 2^n different states consistent with this condition, and all of them are added together to get the required linear combination. The coefficient multiplying the functions for each state is $+1$ if an even number of interchanges of spins is required to get back to the original function and -1 if an odd number of interchanges is required.

We should consider the relation of this procedure to the case of a chemical reaction. Suppose after a reaction the eigenfunction a is paired with c instead of b , and that b simultaneously becomes paired with d . Then a different function representing the new arrangement of bonds is easily found. If by a reaction the bonds change adiabatically from the one state to the other, the perturbation theory gives us a two-rowed secular determinant the lowest root of which gives the energy during reaction. This equation for the energy has the form

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

The quantities not under the radical sign have the significance given the same symbols in equation (1). These quantities outside of the radical do not include the bonds between the four electrons which interchange partners during the reaction. α_1 and α_2 are the bonds between these latter electrons before reaction, β_1 and β_2 the bonds after the reaction and γ_1 and γ_2 bonds which have an appreciable value for configurations intermediate between the initial and final states. These quantities are explained in more detail for equation (3) which is a special case of (2). Equation (2) should be used for reactions involving steric hindrance. Let us now consider the potential arising from the collision of two molecules.

Kinetic Theory Diameters

We shall content ourselves here with an illustrative example. For four monovalent atoms we have the expression for the potential energy

$$E = A_1 + A_2 + B_1 + B_2 + C_1 + C_2 + \sqrt{1/2((\alpha_1 + \alpha_2 - \beta_1 - \beta_2)^2 + (\alpha_1 + \alpha_2 - \gamma_1 - \gamma_2)^2 + (\beta_1 + \beta_2 - \gamma_1 - \gamma_2)^2)} \quad (3)$$

Greek letters are for interchange binding. The italic letters are for the types of binding which are independent of spin, coulombic plus van der Waals, etc. Figure 1 represents molecule WX colliding with molecule ZY. The sum written on the line joining the symbols for two atoms is the total energy required to separate these atoms if the other two atoms were far away. If WX is at a considerable distance from YZ the radical in (3) can be expanded considering

$\alpha_1 + \alpha_2$ large compared with $\beta_1 + \beta_2$ and $\gamma_1 + \gamma_2$.

This gives

$$E = A_1 + A_2 + B_1 + B_2 + C_1 + C_2 + \alpha_1 + \alpha_2 - 1/2(\beta_1 + \beta_2 + \gamma_1 + \gamma_2) \quad (4)$$

i. e., interchange attraction between the electrons whose spins are anti-parallel and a repulsive interchange potential with a coefficient of $1/2$ between all other pairs where there is no chemical bond. Equation (4) may equally well be regarded as a special case of (1). In an ordinary collision there is practically no distortion of the two molecules so that $(A_1 + A_2 + \alpha_1 + \alpha_2)$ stays constant throughout the process. The collision potential is thus

$$E = B_1 + B_2 + C_1 + C_2 - 1/2(\beta_1 + \beta_2 + \gamma_1 + \gamma_2) \quad (5)$$

As an example we will consider the collision of two H_2 molecules. Sugiura's⁵ evaluation of Heitler and London's⁶ potential energy for an H_2 molecule is used for evaluating the quantities in (5). The curve $f(r)$ in Fig. 2 gives the interchange potential between two H atoms as a function of the distance. This serves to determine β_1 , β_2 , γ_1 and γ_2 . The coulombic parts of B_1 , B_2 , C_1 and C_2 are determined similarly from the curve $F(r)$. The polarization or van der Waals potential is likewise independent of the spin and can be calculated as the sum of four parts to be added to the coulombic terms. We use $101/r^6$ in kg. cal. for the van der Waals potential between each pair of atoms. r is to be expressed in Ångströms. This is the value London selects.⁷ Eisenschitz and London's⁸ theoretical value is $91.5/r^6$. This latter value for the van der Waals poten-

⁵ Sugiura, *Z. Physik*, **45**, 484 (1927).

⁶ Heitler and London, *ibid.*, **44**, 455 (1927).

⁷ London, *Z. physik. Chem.*, [B] **11**, 222 (1930).

⁸ Eisenschitz and London, *ibid.*, **60**, 491 (1930).

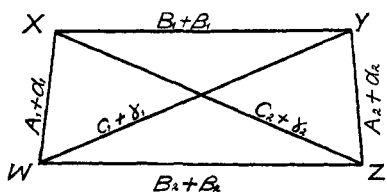


Fig. 1.—Potential terms which determine the total potential of colliding molecules.

tial would make the theoretical curve agree more closely with the Lennard-Jones curve for large distances between hydrogen molecules but also makes the difference slightly larger when the molecules come closer together.

The resulting total potential energies for various orientations of the H_2 molecules are given as curves I and III of Fig. 3. These are to be compared with the Lennard-Jones⁹ empirical potential energy curve II for the collision of two hydrogen molecules. His curve was obtained by choosing the constants A and B and the powers of r in the equation for the potential $E = Ar^{-13} - Br^{-4}$ so as to lead to the experimental second virial

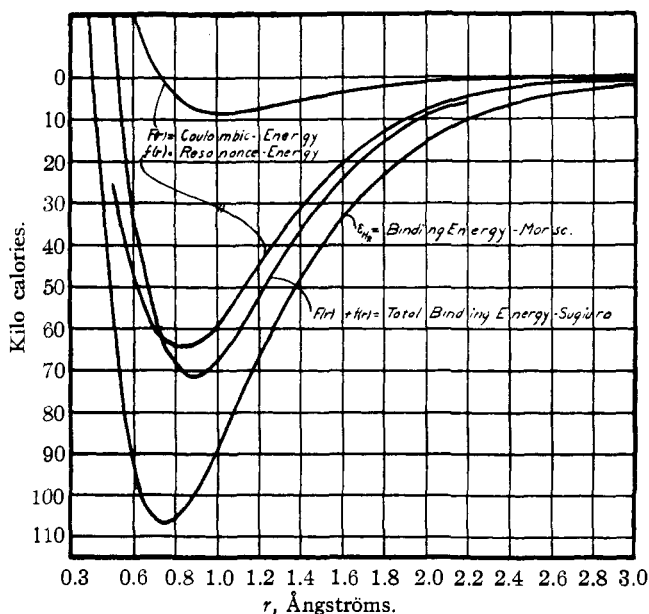


Fig. 2.—Potential energy of the H_2 molecule.

coefficient. The values given are $A = 2.473 \times 10^6$ and $B = 5.65$. In all three curves the abscissa is the distance between the centers of gravity of the colliding molecules. The ordinate is the potential energy referred to zero energy for infinite abscissas. Curve I is for a collision between two molecules colliding with axes parallel to each other but perpendicular to the line joining the centers of gravity of the molecules. As long as the two molecular axes remain perpendicular to the line joining centers of gravity the energy does not change perceptibly (at these large distances) with rotation of one of the molecules about this line. Curve III, however, gives the potential energy for the extreme case in which both molecular axes have turned in such a way that they coincide with the line joining molecular centers of gravity. This gives a much greater repulsion for a

⁹ Fowler, "Statistical Mechanics," Cambridge Univ. Press, 1929, Chapt. X.

fixed distance between centers of gravity since it brings two of the colliding atoms much closer together. For comparison with II a weighted average of all configurations should be taken. Both geometrical and energy considerations tend to weight the low lying configurations. The weighted curve of course varies with the temperature but would not differ greatly from I at the temperature for which II represents experiment. The theoretical minimum is 0.05 kg. cal. deeper than the minimum of curve II calculated from experiment. The fact that an oscillator always has a half quanta of energy decreases the discrepancy. Even if the value $91.5/r^6$ is used for calculating van der Waals forces the theoretical minimum is still 0.038 deeper than the minimum of the Lennard-Jones curve. The general agreement is fairly satisfactory and it is probably too early to decide which method of obtaining the potential curve is the better.

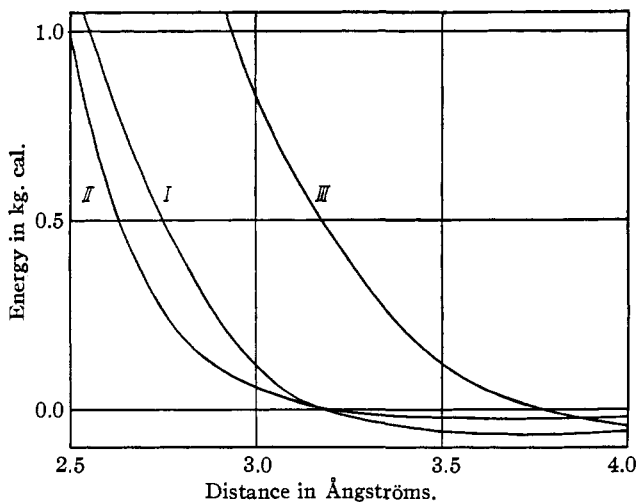


Fig. 3.--Potential energy curve for the collision of two hydrogen molecules.

Cremer and Polanyi¹⁰ have calculated the equilibrium distance between H_2 molecules in the crystal lattice using essentially the method used here for the liquid. They were interested in ascertaining the applicability of the Morse curve for this purpose and so used ϵ_{H_2} of Fig. 2 rather than $f(r)$ for calculating β_1 , β_2 , γ_1 and γ_2 . They neglected coulombic binding. This led to a calculated equilibrium distance between H_2 molecules of 5 Ångströms as compared with an experimental 4 Ångströms. Using the same assumptions in the case of HCl, HBr and HI the agreement was much better, probably indicating that the Morse curve is more satisfactory in these cases. Since the Morse curves are correct in the

¹⁰ Cremer and Polanyi, *Z. physik. Chem.*, [A] Bodenstein Festband, 720 (1931).

neighborhood of the minimum they are probably better for calculating activation energies than for calculating kinetic theory diameters.

Eisenschitz and London⁸ have given potential energy curves at large distances for the attraction of two hydrogen atoms in a singlet state and the repulsion in a triplet state. It is of considerable interest in addition to know how two hydrogen atoms interact when they are each bound to another atom since it is this interaction which largely determines the physical properties of the hydrocarbons as well as the properties of hydrogen itself. In Fig. 4 we have drawn the corresponding experimental and theoretical curves. The ordinate of curve I is the van der Waals force,

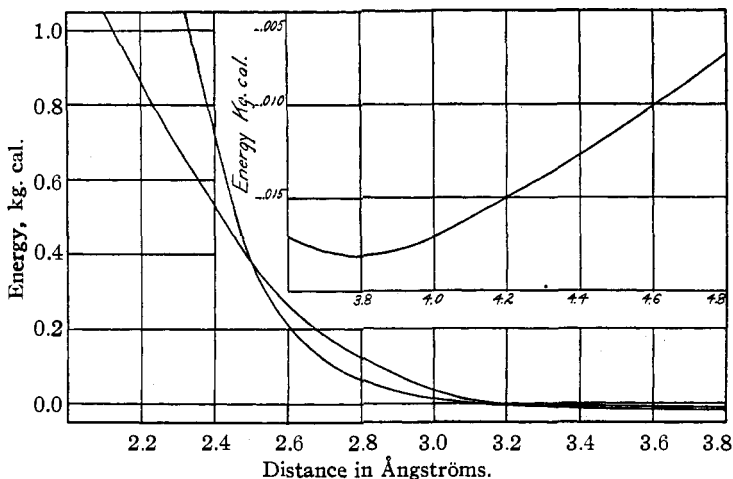


Fig. 4.—Potential energy between widely separated saturated hydrogen atoms.

$101/r^6$, plus the theoretical coulombic integral minus one-half the interchange integral. The ordinate of curve II is one quarter the Lennard-Jones potential between two H_2 molecules plotted, however, against an abscissa which instead of being the distance between centers of gravity of the molecules is the corresponding distance between two H atoms one from each molecule for configurations in which all four such distances are equal. This way of choosing the abscissa is justified by the remarks previously made in connection with Curve I, Fig. 3, that as long as the two molecular axes remain perpendicular to the line joining centers of gravity the energy does not change perceptibly with rotation of one of the molecules about this line. Thus, the statistical curve given by Lennard-Jones gives substantially the potential energy for the configuration assumed. The upper right-hand corner of Fig. 4 simply gives a continuation of Curve I on a larger scale. We shall find such a curve useful in discussing the physical and chemical properties of the hydrocarbons.

All the physical properties of a gas such as the kinetic theory diameter heat of vaporization, compressibility, coefficient of expansion, Sutherland constant and specific heats are deducible from a correct potential energy surface. Conversely these physical properties may be used for determining constants in an equation for the potential energy which in turn gives the activation energy. This fact is of importance in the many cases where the complete quantum mechanical calculations of the energy integrals are excessively difficult to obtain.

The method used for considering the collision of H_2 molecules may be extended to collisions between polyatomic molecules using Morse curves for the energy between atom pairs, x-ray data for the position of the atoms inside the molecules and substituting in Equation 1. The repulsive potential is simply the sum of one-half the interchange integrals between all pairs of atoms one from each molecule. The coulombic and van der Waals forces are all attractive. The van der Waals forces are calculable either by the method of Slater and Kirkwood¹¹ or of London.⁷

Steric Hindrance

We may now consider another application of Equations (1) and (2). Since all the interchange integrals are presumably negative the potential energy terms, $-\frac{1}{2}\sum\alpha u$, increase as unpaired electrons approach each other and are largely responsible for steric hindrance. This repulsion becomes appreciable at kinetic theory diameters as we have just seen and increases exponentially upon closer approach. Permanent dipoles localized in bonds give additional steric effects. The electric moments are known in many cases so that this term is roughly calculable. The other source of attractive potential, van der Waals potential and the coulombic energy are readily calculable.

That the interchange forces are an important factor in steric hindrance is shown in a recent paper by Stuart.¹² He examined the experimental data for heats of combustion of substituted benzene isomers differing only in the relative position of certain radicals. After theoretically calculating the polarization and dipole potentials there is left in many cases a positive potential energy which must be attributed to the repulsive interchange energy between neighboring unpaired electrons. To calculate the energy from potential energy curves for diatomic molecules one must know what fraction of the total energy is coulombic. The coulombic part is 10% of the total in the case of H_2 ,¹³ for Li_2 it is 22%¹⁴ and for Na_2 ¹⁵ it is 28.3%. It must be estimated in other cases. The rest of the potential energy is

¹¹ Slater and Kirkwood, *Phys. Rev.*, **37**, 682 (1931).

¹² Stuart, *ibid.*, **38**, 1372 (1931).

¹³ Sugiura, *Z. physik. Chem.*, **45**, 484 (1927).

¹⁴ Bartlett and Furry, *Phys. Rev.*, **37**, 1712 (1931).

¹⁵ Rosen, *ibid.*, **38**, 255 (1931).

interchange binding except for the small fraction due to polarization. The percentage of coulombic binding for a particular molecule from the minimum out to almost complete dissociation is constant to about 1% in the cases where it is known.

It is of some interest to estimate the magnitude of steric effects in a typical case. Quantum theoretical considerations¹⁶ lead to the conclusion that the two strongest eigenfunction bonds in an oxygen atom will make an angle of 90° with each other. This angle will be modified by the positive interchange energy $-\alpha/2$ between H atoms, by the negative coulombic energy, the negative van der Waals energy, and the positive energy due to the two dipoles. In addition to these factors there is a new one to consider for directed valences. If one considers the Heitler-London coulombic and interchange integrals for a bond formed from a directed P eigenfunction and a spherically symmetrical one, it is found that the bond energy, E , depends in the following way on the angle, θ , between the axis through the atoms and the axis of the directed eigenfunction.

$$E = L \cos^2 \theta + M \sin^2 \theta$$

Thus for $\theta = 0$ we have $E = L$, the heat of dissociation of the strongest possible bond. Lacking precise information we shall assume $M = L/5$. We can then construct Table I for the energy terms between the two H atoms in H₂O for angles of 90, 110 and 120° between the OH bonds. The distance O to H is taken as 0.98 Ångströms and the value L for an OH bond is taken as 104 kg. cal.

TABLE I

Angle between bonds	Distance H to H	$-\alpha/2$	A	P	$0.8 L \sin^2 \theta$
90°	1.385	16.1	-5.7	-14.3	0
110°	1.606	10.2	-3.6	-5.9	29
120°	1.697	8.2	-2.9	-4.2	43

Column 2 of Table I gives the distance between two H atoms corresponding to the angle between the OH bonds given in Column 1. Column 3 gives the interchange repulsive energy; Column 4 the coulombic attraction; Column 5 the van der Waals attraction; Column 6 the positive potential due to distortion of the valence bond. The potential energies of Columns 3, 4 and 5 are zero when the H atoms are very far apart, whereas Column 6 depends only on the angle between the OH bonds. The van der Waals potential given in Column 5 is certainly much too large. All the energies are in kg. cal. The fact that the two OH bonds are polar will tend to increase the angle between the bonds. In spite of the approximateness of our calculations it is clear that steric effects are not to be neglected in H₂O. Also an angle differing greatly from 90° would be

¹⁶ Slater, *Phys. Rev.*, **37**, 481 (1931); Pauling, *THIS JOURNAL*, **53**, 1367 (1931).

surprising because of the rapidity with which directed valence falls off with θ . Equation 5 is, however, only valid for small values of θ . The methods suggested for calculating the potential energy upon collision of complicated molecules suffice also to calculate steric hindrance in complicated cases. Collision potentials and steric hindrance are really two aspects of the same problem. Kinetic theory diameters are a convenient measure of the distance at which steric hindrance starts to be important.

With alcohols and ethers the angle between the oxygen bonds should be still further increased by the larger steric effects and this is what electric moments indicate.¹⁷ A carbon to oxygen bond involves two directed eigenfunctions. If the axis of the carbon eigenfunction makes an angle, θ_1 , with the line joining the atoms and the axis of the oxygen eigenfunction an angle, θ_2 , with this same line, the bond varies with the angles approximately in the following fashion.

$$L \cos^2 \theta_1 \cos^2 \theta_2 + M (\sin^2 \theta_1 \cos^2 \theta_2 + \cos^2 \theta_1 \sin^2 \theta_2) + N \cos^2 \theta_1 \cos^2 \theta_2 \quad (6)$$

The significance of L , M and N is made clear by substituting the value 0 and $\pi/2$ for θ_1 and θ_2 in various ways. In (6) many terms have been neglected, some of which are probably almost as large as the last term and it is only approximately true for small values of θ_1 and θ_2 . Equation 6 is readily obtained by considering the interchange and coulombic integrals for a bond formed from two directed eigenfunctions. According to the views of Slater¹⁶ and Pauling¹⁶ each of the four valences of the carbon atom in the saturated hydrocarbons is approximately three-quarters a directed P valence, the remaining s valence is spherically symmetric. This introduces no difficulty in applying (6) to the directed part of the eigenfunction.

We shall now consider rotation about a single bond. Using the potential energy between two saturated H atoms given in Curve 2, Fig. 4, we can readily calculate the sum of the nine potentials between the hydrogen atoms on the two methyl groups in ethane. In Fig. 5 the sum of these nine potentials is plotted against angular displacement. Zero angle corresponds to the hydrogen atoms of one methyl group just eclipsing the hydrogen atoms of the other group as viewed along the C-C axis. Such an eclipse occurs three times in a revolution and accounts for the periodic nature of the potential. It is assumed that tetrahedral angles are preserved; that the C-C distance is 1.54 Å., and that the C-H distance in a methyl group is 1.13 Å. The distance between two H atoms on adjacent carbons is then given by the expression $d = (7.53 - 2.27 \cos \varphi)^{1/2}$, where φ measures the angular displacement of the two H atoms viewed along the C-C axis. If Curve II, Fig. 4, instead of I is used for estimating the potential between H atoms the ordinates in Fig. 5 are all approximately

¹⁷ Smyth, *Chem. Rev.*, **6**, 549 (1929).

cut in two. The true potential curve will probably lie between these extremes. A detailed consideration of the physical properties of hydrocarbons will enable us to come to more precise conclusions and this is being done.

If one uses for the potential between saturated hydrogen atoms a repulsion corresponding to 35% of the Morse curve, which amounts to assuming that it is 10% coulombic and 90% interchange, and then adds to this a van der Waals potential, $101/r^6$, a somewhat larger potential is found than those given in Fig. 4. For some other atoms such assumptions lead to fairly good results. A systematic investigation of such potentials is being carried out.

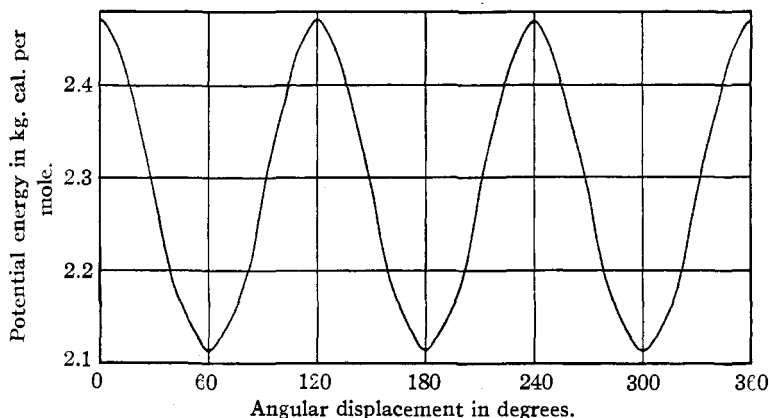


Fig. 5.—The dependence of the potential energy of the ethane molecule on rotation about the C—C bond.

As a final illustration of steric effects we will consider for hydrocarbons how the strength of a C—H bond is affected by successive substitution of CH_3 radicals for the other three hydrogen atoms in methane. Two hydrogen atoms in methane are at a distance from each other of 1.84 Ångströms. From Fig. 2 we find that half the theoretical interchange integral for this distance is -5.8 kg. cal. and the coulombic integral is -1.9 kg. cal. These values are probably each about 10% too low, since the corresponding integrals are about (but not more than) twenty-five per cent. too low when the atoms are 0.76 Ångströms apart and approach the correct values as the distance increases. The van der Waals attraction between hydrogen atoms cannot be satisfactorily estimated at such small distances with an expression of the type $101/r^6$ since this gives a fantastically large figure for the van der Waals attraction at 0.76 Å. for which the upper limit is the difference between the true heat of dissociation and that calculated by Sugiura. The van der Waals attraction is then considerably less than $101/1.84^6 = 2.62$ kg. cal. Ten per cent. of the sum of the interchange

plus coulombic integral, which is -1.4 kg. cal., cannot be far from correct. Using these figures we get for the total potential $5.8 - 1.9 - 1.4 = 2.5$ kg. cal.

When a hydrogen atom in methane is replaced by a methyl radical, there is a corresponding change in the repulsion on any one of the remaining hydrogen atoms. The repulsion due to the hydrogens on the methyl group depends on the angular displacement of the methyl group about the C—C bond and is just one-third of the ordinate in Fig. 5. We must still estimate the repulsive potential due to the carbon atom in the methyl radical. For this purpose we shall assume a Morse potential curve with the following constants, $\omega = 2920$; $r_0 = 1.13$; $D = 92$. ω is the vibration frequency in wave numbers for the lowest level; r_0 is the normal distance in Ångströms between atoms and D is the heat of dissociation in kg. cal. If the C—C distance is taken as 1.54 Ångströms, then the distance from a carbon atom to a hydrogen atom on an adjacent carbon is 2.19 Å. The Morse curve gives 24.5 kg. cal. for the potential energy at this distance. If we assume this is eighty per cent. interchange binding and twenty per cent. coulombic plus van der Waals, the net repulsion is $[(0.80/2) - 0.20] 24.5 = 4.9$ kg. cal. This estimate is probably low since proper account has not been taken of the repulsion of three of the electrons on the carbon atom. As a final result then we find for the difference in the repulsive potential of a methyl group and a hydrogen atom on a single hydrogen atom the value $4.9 + (2 \times 1/3) - 2.5 = 3.1$, which is probably low rather than high. If the CH bond is assumed to have a strength of 120 kg. cal. everything else being the same, we obtain instead of 3.1 kg. cal., the value 5.6 kg. cal. We shall use the value 3.1 kg. cal. Thus, if we neglect changes in the bonds themselves, we should expect it to be hardest to remove a hydrogen from a carbon in methane, 3.1 kg. cal. easier to remove a hydrogen from ethane, 6.2 easier to remove a hydrogen atom from the central carbon in propane and 9.3 kg. cal. easier to remove a hydrogen from a carbon in which the other three bonds are methyl radicals.

The experiments of Bonhoeffer and Harteck¹⁸ show that while hydrogen atoms will dehydrogenate other hydrocarbons, the reaction $H + CH_4 = H_2 + CH_3$ does not go. Since during a reaction of hydrogen with ethane the approaching H atom is much farther away from the methyl radical from which it does not remove a hydrogen than is the hydrogen removed, it is necessary to suppose that the principal effect of this methyl group is to weaken the bond of carbon to the attached hydrogen. The repulsion of the methyl group for the approaching hydrogen atom is negligible. The difference in rates observed is thus to be attributed to a stronger C—H bond in methane and not just to a higher activation energy. Ex-

¹⁸ Bonhoeffer and Harteck, *Z. physik. Chem.*, [A] **139**, 64 (1929).

periments of von Hartel and Polanyi¹⁹ show that sodium atoms more readily detach halogen atoms from ethyl than from methyl radicals. Here again we see the effect of the repulsive potential of methyl radicals. From this point of view the heat of combustion might be supposed greater for branched than for the corresponding straight chain hydrocarbons. However, the net heat effect is greatly complicated by attraction between groups slightly farther apart than those we have just found repel.²⁰ Isopentane evolves 5 kg. cal. more heat upon combustion than normal pentane but with some of the longer chains this effect is lessened and even reversed so that for comparison of heats of combustion a more detailed treatment is necessary.

I wish to thank Professor J. C. Slater for many helpful discussions.

Summary

The method of calculating the potentials between saturated molecules or groups of atoms is indicated and the potential energy curve for two colliding H₂ molecules is calculated and compared with experiment. The agreement is good. A potential energy curve for the collision of two saturated hydrogen atoms is given and used in constructing a potential for the rotation of the two methyl groups in ethane about the C—C axis. Viewed along the C—C axis the greatest potential occurs at eclipse of the far hydrogen atom by the near ones. The lowest potential corresponds to a position half way between two eclipses. The calculated change in potential is 0.36 kg. cal. The true value probably lies between 0.36 kg. cal. and half this amount. A similar calculation indicates that a hydrogen in ethane is at a potential at least 3.1 kg. cal. higher than a hydrogen in methane due to the greater repulsion of a methyl group than of a hydrogen atom. This fact explains the increase in reactivity of a hydrogen attached to carbon as the three neighboring hydrogens are replaced by methyl groups.

PRINCETON, NEW JERSEY

¹⁹ Von Hartel and Polanyi, *Z. physik. Chem.*, [B] 11, 97 (1930).

²⁰ "International Critical Tables."