VALENCE FORCES AS CALCULATED FROM SPECIFIC HEATS AND ABSORPTION SPECTRA

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Chemistry is concerned with the force of valence chiefly when the force is at the point of breaking down and permitting chemical action. It is therefore not to chemical but to physical properties that we must turn in order to get an idea of the nature of valence force when the chemical bond is in its really stable state. For example, in our concept of the thermal energy of a crystal as the vibration of the atoms restrained by elastic forces acting between them, there is illustrated one of the most important features of the stable chemical bond, namely its spring-like nature. Because of this relation between the chemical bond and thermal energy, crystals of organic molecules make an exceptionally good medium in which to study the bond in its normal state, for in these crystals practically the only forces which restrain the thermal motions of the atoms are the non-polar chemical bonds, those being many times stronger than the intermolecular forces. The exact nature of this relation can be most simply seen in the crystal lattice of diamond.

THE VALENCE FORCE IN DIAMOND

Diamond is believed to be made up of carbon atoms in a lattice such that each one is surrounded by four others so placed that lines drawn from the nucleus of an atom to those of its four neighbors pass through the corners of a tetrahedron. A carbon atom vibrating with thermal energy will oscillate about some mean position, restrained by these forces. Now it has been found by Einstein and Debye (1) that to account for the thermal energy of such a crystal lattice we must assume that each atom acts as a harmonic oscillator. This means that the force acting on it must be such that when it is displaced from its mean position by a distance x, the force tending to restore it will be proportional to x, so that the value of the force can be expressed as

$$F = -kx \tag{1}$$

Thus if we measure distance in Ångstrom units (10^{-8} cm.), k will be the force in dynes acting on the atom when it is displaced one Å from its mean position of equilibrium. The distances through which the atoms move under the influence of thermal energy are about 0.2 Å so that this law of force should hold over distances of this order of magnitude.

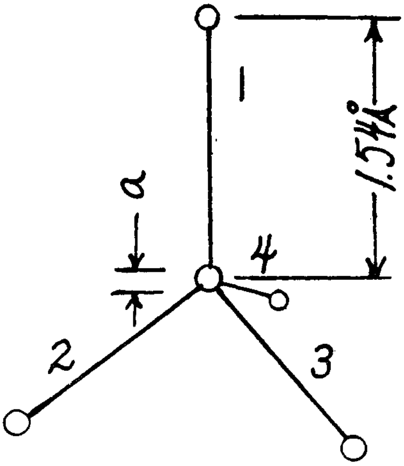

Fig. 1. Forces on Carbon Atom in Diamond
a = approximate amplitude of thermal motion at 700°C.

We believe this restraining force to be actually the sum of the forces of valence acting on the atom. To produce a restraining force of a spring-like nature each valence force must therefore act like a spring. Moreover we find *diatomic* gas molecules also acting as harmonic oscillators, and from this it appears that a *single* valence force is like a spring such as pictured in figure 2. It is in equilibrium in a position such as shown in A. When the atoms are pushed together through a distance c then the force repelling them is *kc;* when they are pulled apart through a distance *b*, then the force attracting them together is $-kb$.

In diamond the force tending to restore a displaced atom to its equilibrium position is the vector sum of the four valence forces. Thus for a small displacement along the line of force 1, figure 1,

$$F = -\left(k_1 + \tfrac{1}{3}k_2 + \tfrac{1}{3}k_3 + \tfrac{1}{3}k_4\right)x \qquad (2)$$

because *force 1* will act in full, but the components of forces 2, 3, and 4 along the direction of *force 1* are only $\frac{1}{3}kx$ since the cosine of the angle between them, 70° 32′ is one-third.

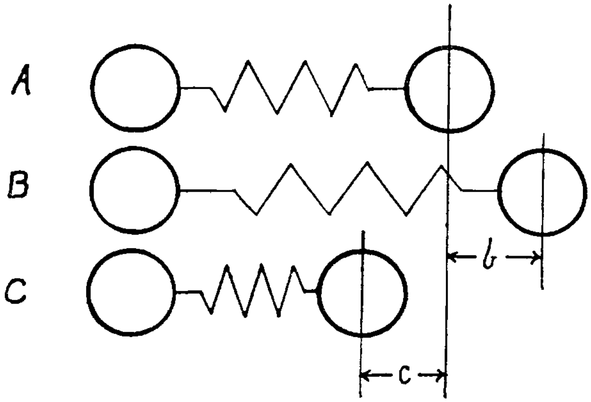

FIG. 2. SPRING-LIKE NATURE OF VALENCE FORCE

An atom oscillating under restoring forces of this kind will vibrate with a definite frequency. This frequency is related to the force constant *k* and the mass as follows:

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}} \qquad (3)$$

Thus if we know the mass of the atom *m* and the nature of the crystal structure in which it is located, together with the actual position of the valence forces acting upon it we can calculate the values of the forces from the frequency (ν).

The frequency is related to a number of other physical properties. In certain substances, light of the same frequency as the vibration of the atom will be strongly reflected so that we can get the frequency from the so-called *rest strahlen* or residual rays of Rubens (2). Again in the infra-red absorption spectra there will generally be strong absorption of light of the frequency with which the atom is vibrating. These are *optical* methods of determining frequency.

The frequency is also related to the melting point in a manner first pointed out by Lindemann (3),

$$\nu = 3.08 \times 10^{12} \sqrt{\frac{T_m}{M V^{\frac{2}{3}}}} \tag{4}$$

where ν is the frequency, T_m the melting point, M the gram molecular weight, and V the molecular volume. This relation is based on the idea that at the melting point of a monatomic crystal the atom must possess the energy just sufficient to make its amplitude of vibration equal to the average distance between the atoms. An amplitude greater than this disrupts the crystal and causes melting.

Finally the frequency is related to the heat capacity. Einstein (1) showed that the heat capacity C_v of N harmonic oscillators (N = Avogadro's number) is expressed by

$$C_v = R \frac{\left(\frac{\Theta}{T}\right)^2 e^{\frac{\Theta}{T}}}{(1 - e^{(\Theta/T)})^2} = R\, F_E\left(\frac{\Theta}{T}\right) \tag{5}$$

where R is the gas constant, T absolute temperature and Θ what may be called the converted frequency, i.e. the real frequency multiplied by the constant[1] β, so that it has the dimensions of temperature. This expression which we may call the Einstein function, F_E, has been modified by Debye (4) to take into account the elastic waves in a crystal lattice. His function we will write as

$$C_v = R\, F_D\left(\frac{\Theta}{T}\right) \tag{6}$$

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[1] β is Planck's constant, h, divided by the gas constant per atom, k and is taken equal to 4.778×10^{-4} in the following calculations.

Since both these functions depend only on $\left(\frac{\Theta}{T}\right)$ it is possible to make tables similar to logarithm tables in which values of C_v are given for corresponding values of Θ/T. Such tables (5) have been used in making the calculations which follow.

For diamond it is found that with $\Theta = 1860$, equation 6 reproduces very closely the experimental values for the heat capacity. Dividing this Θ by β gives a value for the frequency ν of 3.89×10^{13} vibrations per second. Putting this in Equation 3 we find that the force constant is 1.17×10^{-2} dynes per Å. Since the force due to a single valence is one-half the total force according to equation 2, we can say that a carbon-carbon bond stretched one-tenth of an Ångstrom unit exerts a force of 5.8×10^{-4} dynes, the actual mechanical force of the chemical bond. The law of force, from which we have derived this value, will probably be quite closely applicable up to a stretching of 0.2 Å, but beyond that other considerations enter in to change it, as will be shown later.

THE VALENCE FORCES IN BENZENE

The problem of calculating the values of the valence forces in an organic molecule is much more complicated than in diamond. It is a question of getting the space arrangement of the atoms in the molecule, and of the molecules in the crystal, then analyzing the motions of the atoms into characteristic types, and finally ascertaining the frequency of each type of motion. To do this precisely involves the solution of some very difficult dynamical problems and requires more intimate knowledge of the mechanics of the molecule than we possess at present. It is, however, possible to make an approximate solution, giving values for the frequencies which should be fairly accurate, and from these the values of the different valence forces can be calculated with the help of equation 3, as was done in the case of diamond. The way in which this is carried out may perhaps best be illustrated by giving in detail the calculation for benzene.

From the analyses of the crystal structure of aromatic organic compounds with the help of x-rays, we believe the carbon atoms in the benzene molecule to be arranged in a hexagon as is postulated by the customary organic chemistry formula. These hexagons are probably stacked together like plates into the crystal lattice, each ring being surrounded by neighboring rings somewhat as shown in figure 3.

In a crystal lattice like this if we analyze the possible different motions into certain characterstic types we may say as a first approximation that the heat capacity of the crystal will be equal to the sum of the heat capacities of each of the different modes of motion. Moreover, the heat capacity of each mode of motion, or more technically speaking, each degree of freedom will at any temperature depend only on the frequency of that motion and its value can be calculated from the frequency by means of equations (5) or (6). Thus if we find values for the frequency for the different types of motion and calculate the heat capacities, the sum of these should equal the experimentally observed heat capacity of the crystal. If this is the case, it is evidence that the analysis of the motion is correct and we can calculate the valence forces by means of equation 3 with a fair degree of confidence.

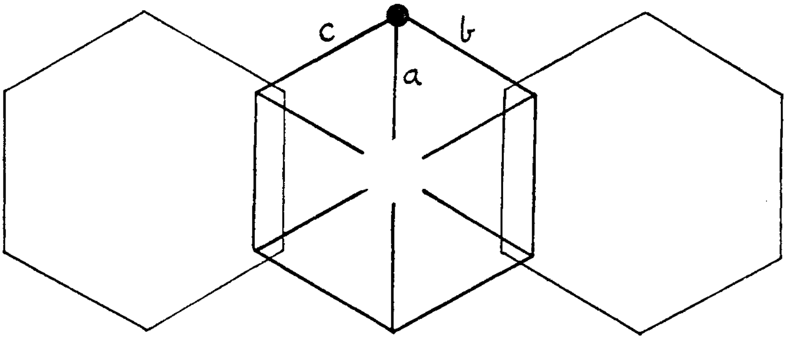

FIG. 3. VALENCE FORCES IN BENZENE

The first type of motion we consider is that of a single molecule in the lattice, moving as a unit, or as it will be termed hereafter, motion of the molecule as a whole. This type of motion occurs because the interatomic forces, i.e., valence forces, are, as will presently be shown, about sixty times as strong as the intermolecular forces. It will have 6 degrees of freedom, three of translational and three of rotational vibration, and as a first approximation we can consider the frequency in them all to be the same.[2]

TABLE 1

The heat capacity of benzene, in calories per degree per mole

The observed values are from W. Nernst, Ann. Physik. (4), **36**, 395 (1911).

TYPE OF MOTION	MOLECULAR	CH GROUPS			EXPANSION	TOTAL	
$T°K$	$6\,F_D\,\frac{(159)}{T}$	1 $6\,F_E\,\frac{(511)}{T}$	2 $6\,F_E\,\frac{(1258)}{T}$	3 $6\,F_E\,\frac{(2080)}{T}$		Calculated	Observed
10	0.2					0.2	0.3
20	1.7					1.7	1.7
30	4.0				0.0	4.0	4.5
40	6.1				0.1	6.2	6.6
50	7.5	0.0			0.2	7.7	8.0
60	8.7	0.2			0.4	9.3	9.4
80	9.9	0.8			0.7	11.4	11.1
100	10.5	1.9			0.9	13.2	12.9
120	11.0	3.1	0.0		1.1	15.2	14.4
140	11.2	4.3	0.1		1.4	17.0	16.0
160	11.4	5.4	0.3		1.6	18.7	17.4
180	11.5	6.3	0.5		1.8	20.1	19.0
200	11.6	7.1	0.9	0.0	2.1	21.7	20.5
220	11.6	7.7	1.2	0.1	2.3	22.9	22.7
240	11.7	8.2	1.7	0.2	2.5	24.3	24.8
260	11.7	8.7	2.2	0.3	2.7	25.6	27.0

To secure a value for these frequencies we can make use of equation 4 as explained above.[3] Then using this value of the frequency in Debye's equation we can calculate the heat capacity

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[2] The detailed reasoning for this analysis is given in a preliminary report on the specific heats of organic compounds by the author in the Proceedings of the Royal Academy of Amsterdam **29**, 744 (1926). See also Communications from the Physical Laboratory, Leiden, Suppl. **56**, 16 (1926). It may be stated very briefly as follows: A single atom in a crystal lattice-like diamond can move in three directions that is, in the three dimensions of space, and is said to have three degrees of freedom because its position can be described by the three space coordinates. On the other hand, a molecule like benzene, which has a moment of inertia not possessed by an individual atom, can have energy of rotation. Its

due to the motion of the molecule as a whole. The values for this are given in the first column of table 1. Moreover by using these values of Θ we can with the help of equation 3 calculate the values of k, the intermolecular force. For a whole benzene ring this has the value of 5.5×10^{-5} dynes for a displacement of 0.1 Å. The force acting on a single CH group will be 0.92×10^{-5} dynes, so that it can be seen that it is very small compared with the C – C bond which is 58×10^{-5} dynes.

The next type of motion to be considered is that of the CH groups. In order to analyse this it is necessary to choose some arrangement of the valence forces in benzene and, as the double bond is still an uncertain quantity, it is assumed that each carbon atom has a bond similar to that in diamond, joining it to its neighboring carbon atoms and a third bond directed toward the center of the ring. The nature of this third centric bond is decidedly uncertain but there are some considerations which indicate that it is similar to the normal bond. For example, the heat of formation of benzene appears to be almost exactly the sum of six C – H heats of linkage and nine normal aliphatic C – C heats of linkage.[4] With regard to the space arrangement of the

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motion will have to be described by six coördinates like any rigid body, and it is therefore said to have six degrees of freedom.

Applying Equation 6 to an "atomic" crystal lattice we get

$$C_v = 3\,RF_D\left(\frac{\Theta}{T}\right)$$

since each atom has three degrees of freedom and will be equivalent to three harmonic oscillators. For a "molecular" crystal lattice

$$C_v = 6\,RF_D\left(\frac{\Theta}{T}\right)$$

since there will be both translational and rotational vibration. This implies tortional elastic waves, in addition to translational waves. This assumption is justifiable according to the best authorities on the subject.

[3] The application of this equation to molecules will be described in a paper to be published soon in the J. Am. Chem. Soc. It was presented at the St. Louis meeting of the American Chemical Society by J. C. Southard and D. H. Andrews.

[4] Values taken from Eucken, Jette and LaMer: Fundamentals of Physical Chemistry, N. Y., McGraw Hill (1925), p. 637 are as follows:

C – H	87 calories per mol.
C – C	70 calories per mol.
Calculated value for benzene will be 6(C – H) + 9(C – C)	1152 calories
Observed heat of formation	1155 calories

CH groups, it is doubtful whether the atoms are in a plane or in a puckered hexagon, but since the difference between these two arrangements is less than the probable error of the calculation, we assume a plane hexagon. The motion characteristic of a CH group will probably be made up of *two* types of motion in the plane of the ring which will stretch directly some of the bonds, and, a *third* type of motion perpendicular to the plane of the ring which will not directly stretch any of them.

Considering the first type of motion for the CH group at the top of the ring in figure 3, motion along the line of the valence directed toward the center will have a force constant as shown in the following equation

$$k_a = k_1 + (k_2 + k_3) \cos 30°$$

Taking all the valences the same as those in diamond, that is $k_1 = k_2 = k_3 = k_D$ then $k_a = 16.0 \times 10^{-4}$ dynes. Then, from equation 3, $\Theta = 2080$.

In a system as small as the benzene ring we will not expect elastic waves to enter into the heat capacity to an appreciable extent so that the Einstein equation should be applicable. Employing Θ with this equation, number 5, we find values for the heat capacity of this motion as shown in column 5, table 1.

In a similar way we find k_b for motion in the plane, perpendicular to the first type.

$$k_b = (k_2 + k_3) \cos 60° = 5.85 \times 10^{-4}$$

From equation 3, $\Theta = 1258$, and employing this in equation 4 the values of the heat capacity given in column 4 of table 1 are computed. There is no special reason for calculating the heat capacity for motion in these two particular directions, but they are representative of any direction on the plane and the choice of any others will not appreciably affect the result.

Motion perpendicular to the ring plane will, however, be opposed by much weaker forces. It will not stretch directly any of the bonds and, as has been seen, the intermolecular force opposing this type of motion is only $\frac{1}{60}$th of the force of a C – C bond. There is no evident means of calculating the frequency of this motion which, in a way, depends on the ease of bending of the bonds, a topic on which there has been much discussion, but little evidence. We have, however, one possible source of help. In the infra-red absorption spectra Ellis (6) has found a series of bands which seem to be quite definitely associated with the carbon-carbon bond. There are some grounds for believing that the frequency of the initial band of this series is that of

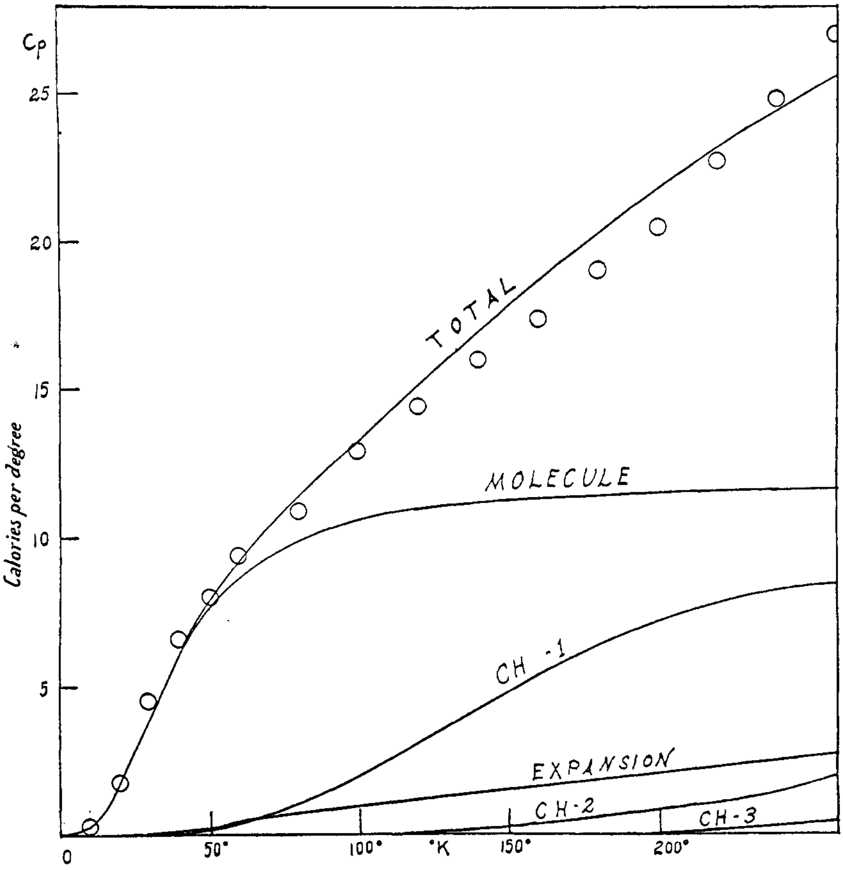

FIG. 4. THE HEAT CAPACITY OF BENZENE
Circles are values observed by Nernst

motion of CH groups perpendicular to the bonds rather than along them, from considerations of the electric moment of a carbon chain. If we employ the frequency of the bond $\Theta = 511$ in the Einstein equation we get values for the heat capacity of this type of motion which are given in column 4, table 1. This will give the force for bending a bond as 0.32×10^{-4} dynes when the CH is moved 0.1 Å. These three types of motion thus make up the three translational degrees of freedom for each CH group. The rotational degrees of freedom will probably be connected with motion of the H atom under the influence of the CH bond, the next topic to be considered.

The value of the force constant for the CH bond can be most easily secured from infra-red absorption spectra. There is a series of bands definitely associated with this bond with the initial band located at about 3μ. This gives a frequency of $\Theta = 4280$ and a force of 4.78×10^{-4} dynes for a stretching of the bond of 0.1 Å. Calculations from the Einstein Equation with this frequency show that motions of the hydrogen atom will not appreciably affect the heat capacity of crystalline benzene at any temperature.

The sum of the terms we have calculated should therefore give values of C_v for benzene. In order to compare these with the experimental values of C_p we have used an adaptation (7) of Nernst's equation for the heat absorbed due to the expansion of the crystal.

$$(C_p - C_v) = (C_v)^2_{\text{mole.}} \frac{T}{T_m} \times 0.0214$$

where $(C_v)_{\text{molecule}}$ is used because in view of the difference in the magnitude of the interatomic and intermolecular forces it appears that expansion of the molecule itself is negligible.

Adding the values calculated with the help of this equation to the sum of the other heat capacity terms we get values of C_p which we can compare with experiment. As shown in table 1 and in figure 4 the agreement is as good as could be expected in view of the approximate nature of the calculation. It appears that the choice of frequency for the molecular motion, and for the motion of the CH group perpendicular to the plane of the ring, is at least qualitatively correct. About all it shows concerning the other frequencies is that they are so high that they do not affect the heat capacity appreciably. On the whole it seems to justify the choice of frequencies and the location of the

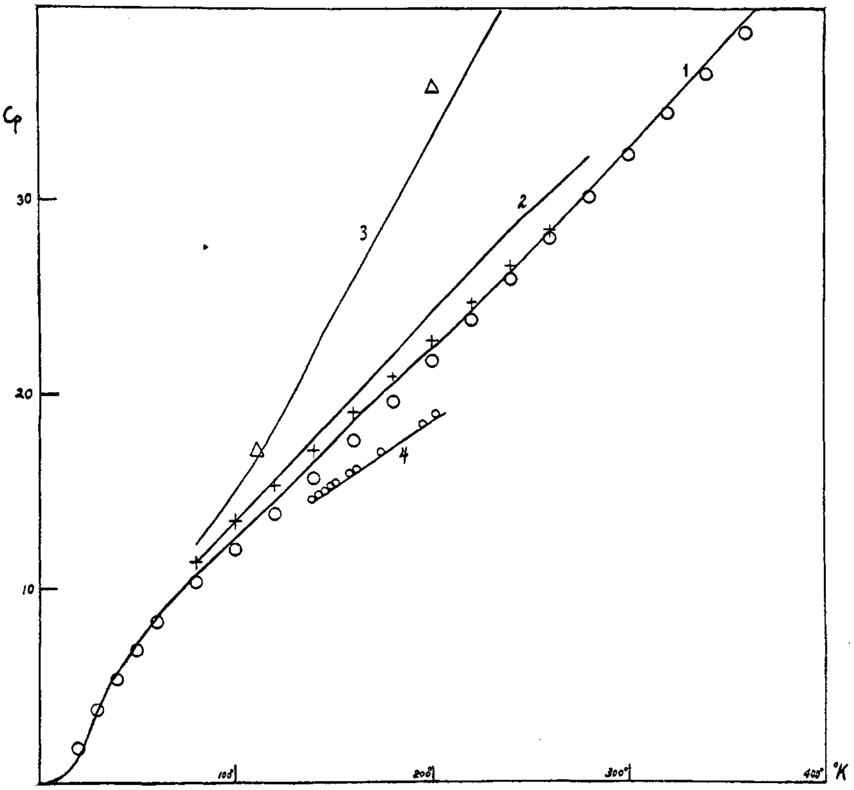

Fig. 5. Heat Capacities for: ⊙, 1, Hydroquinone; +, 2, Glycerol; △, 3, Dextrose; ◦, 4, Methyl Alcohol

The lines represent the calculated values. The symbols show the observed values taken from the data of (1) F. Lange, Z. physik. Chem. **110**, 351 (1924), Andrews, Lynn, and Johnston, J. Am. Chem. Soc. **48**, 1274 (1926), D. H. Andrews, J. Am. Chem. Soc. **48**, 1293 (1926); (2) Gibson and Giauque, J. Am. Chem. Soc. **45**, 93 (1923); (3) Simon, Ann. Physik. (4) **68**, 241 (1922); (4) Parks, J. Am. Chem. Soc. **47**, 338 (1925).

bonds, and shows that this is a fairly correct picture of the mechanics of the benzene molecule.

In a similar way the heat capacities of a number of other organic molecules have been calculated[5] and the comparison with experimentally measured values is shown in figure 5. The same values for the force of the different normal bonds were used as in the case of benzene. It has not been possible up to the present time to extend the study far enough to include the more abnormal bonds such as the tertiary C − H, and C = C, but it is hoped that studies of heat capacity and absorption spectra which are now being carried on will make these methods of use in solving the problems of chemical activity.

TABLE 2

The force of valence

BOND	DYNES FOR STRETCHING 0.1 Å.	OBSERVED HEAT OF LINKAGE	x_D
		kgm. cal./mole	*Å units*
C − C			
Stretching	5.85×10^{-4}	81.6	0.44
Bending	0.32		
Intermolecular force per CH group in benzene	0.092		
H − H	4.60	101.0	0.55
H − N	5.62	98.0	0.48
H − C	4.78	90.0	0.51
C − Cl	1.88	81.0	0.77
C − Br	1.89	39.7	0.54
C − I	2.08	40.0	0.52
Cl − Cl	3.30	58.5	0.49
Cl − I	2.36	49.6	0.54
Br − Br	2.48	45.2	0.50
I − I	1.68	35.2	0.54

Note: For the sources of most of the above values see Bates and Andrews, loc. cit. Certain values have been revised somewhat since first published.

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[5] A slightly different method of calculation has been proposed by E. O. Salant, Proc. Nat. Acad. Sci. **12**, 334, 370 (1926). For further details of the above method of calculation see the paper by the writer in the Proceedings of the Royal Academy of Amsterdam, loc. cit.

THE CHANGE OF VALENCE FORCE WITH STRETCHING OF THE BOND

It is interesting to compare with each other the various values of the force of valence which can be secured. The values calculated above, together with a number calculated by Bates and Andrews (8) are shown in table 2. As these authors have pointed out, it is remarkable how close together the values lie for the different non-polar bonds. It seems to indicate a common mechanism which is very nearly the same in all the bonds.

There is other striking evidence of similarity in the behavior of the bond when stretched to distances greater than atomic diameters. We know from the heat of linkage the value of the work done in pulling two atoms apart and severing the bond completely. Now if the law of force $F = -kx$, which holds for a stretching of 0.2 Å, should continue to hold for greater distances, we could calculate the amount of stretching which would just perform the amount of work equal to the heat of linkage. Values for this distance, x_D, as calculated by Bates and Andrews are given as x_D in table 2, column 3. If this were the case we would expect that the force would suddenly cease at this point, and the atoms would fly apart without further restraint. In all probability this is not the case. We have evidence from the term

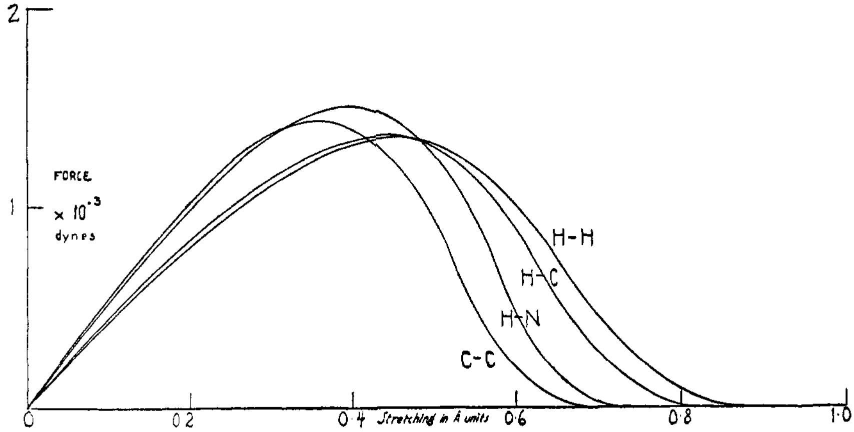

FIG. 6. VALUES OF THE VALENCE FORCE WHEN THE BOND IS STRETCHED

values of absorption spectra that even at distances of 0.3 Å in H – H and C – H the force is considerably less than that required by Equation I, and it probably begins to decrease as the bond is stretched over 0.4 Å. But in the fact that on the basis of Table 2 in all cases about the same amount of stretching is required to perform the work equal to the heat of linkage, we have evidence of the great similarity of all non-polar bonds.

This same relation is shown graphically in figure 6. Following the general shape of the force curve for H – H as calculated from spectral term values,[6] the force curves for the different bonds have been drawn so that the area under each one is equal to the heat of linkage. The portions of the curves beyond 0.4 Å. have little more than qualitative significance because we do not know whether atoms pulled apart may not even be repelled after a certain distance is reached. This does show, however, that it is quite probable that a stretching of something a little less than 1 Å is involved in most chemical processes. If a chemical reaction involved performing work against the force of the bond for distances greater than this, the heat of activation would be so large that action under most conditions would be impossible.

A study of the chemical bond from facts of this sort shows what the mechanical nature of the bond probably is, though it does not explain the mechanism, electrical or magnetic, producing the mechanical force. We hope, nevertheless, that it may serve as a basis for inquiring further into the problems more closely related to chemical activity and to the thermal decomposition of molecules.

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[6] This was calculated with the help of the equation for an anharmonic oscillator given in Max Born: Vorlesungen über Atommechanik, Berlin, Springer (1925), p. 78. A treatment of this problem with the help of the new quantum mechanics has just been published by Sugiura: Z. Physik. **45,** 491 (1927).

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