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Founded by Wilder D. Bancroft

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Symposium on Bond Strengths

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Founded by Wilder D. Bancroft

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THE PROBLEM OF BOND ENERGIES[1]

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The bond energy of a chemical bond is defined to include three kinds of terms: The first one describes the reorganization energy needed to change the length of the bond from its state in the corresponding free radical to its length in the molecule under consideration. The second term is the heat of dissociation of the diatomic free radical and the third term takes into account the changes in bond energy due to the presence of the other atoms. The first and the third term together are called the reorganization energy of the bond.

Introduction

In an interesting paper Szwarc and Evans[2] discuss the meaning of the *average bond energy* and the *bond dissociation energy* and the relation of these quantities to each other and to the force constants of the molecule. Their remarks clarify these concepts and they bring out their difference. It is believed that a somewhat different approach will further aid in the elucidation of these basic ideas concerning bond energies and that the proposed definition will help toward a still better understanding of the problem. Three terms are considered to be involved in the definition of bond energies. The first two terms describe the energy of separation of the two atoms of the bond from the distance they have in the molecule to infinity or the pure stretching of the bond. The heat of dissociation of the corresponding free radical is included in this term. The third term concerns the changes in bond energy due to the presence of other atoms. Such a *near-atom*-influence or *near-group-effect* has been mentioned by several authors.[3-6] If the molecule has m atoms and n bonds, there will be $m - 2$ atoms affecting a given bond and altogether $n(m - 2)$ such effects must be considered. Atoms at some distance from a given bond may have only a slight effect on the bond energy. Atoms belonging to a given group as for example the carbon and hydrogen atoms of a methyl group may be considered together and are said to exert a near-group-effect on the bond energy.

The *near-bond-effect* is another way by which the influence of neighboring *bonds* may be described. Again the bonds of a group of atoms may be considered together in their influence on the energy of a given bond. In a molecule of n bonds there would be $n - 1$ such near-bond-effects. The influence of a bond rather far removed from a given bond would be expected to be small.

A third point of view is based on the central force field and it is supposed that the interactions of nonbonded atoms may be invoked in the description of bond energies. This method does not seem to be adequate to describe the large changes which sometimes occur in the energy of a given bond as another atom is added to the molecule. For example when the free hydroxyl radical is placed in the environment of a water molecule, a large modification in the average hydrogen-oxygen bond energy takes place. This variation is rather to be considered on the basis discussed by Heath and Linnett[7] for the water molecule, where they visualize a change in hybridization of the OH bond due to the presence of the other hydrogen atom. In general it is a question of hyperconjugation as proposed by

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[1] Financial support for this work has been received from ONR under contract N-8 onr 79400.

[2] M. Szwarc and M. G. Evans, *J. Chem. Phys.*, **18**, 618 (1950).

[3] E. J. R. Prosen and F. D. Rossini, *J. Research Natl. Bur. Standards*, **27**, 519 (1941).

[4] W. J. Taylor, J. M. Pignocco and F. D. Rossini, *ibid.*, **34**, 413 (1945).

[5] J. R. Platt, *J. Chem. Phys.*, **15**, 419 (1947).

[6] G. Glockler, *ibid.*, **17**, 748 (1949).

[7] D. F. Heath and J. W. Linnett, *Trans. Faraday Soc.*, **44**, 556 (1948).

Mulliken,[8] and all other features of interaction such as van der Waals, London dispersion, dipole and induction effects. These fundamental concepts have been discussed by Pauling.[9] Walsh[10] mentions five factors affecting bond energies. The problem of the detailed nature of this influence on a bond caused by another atom need not be answered for the present purpose, which is to show that *average bond energies can be defined so that their simple sum will equal the heat of atomization and that this definition involves the heat of dissociation of the corresponding free diatomic radical and a reorganization energy.* It is important to devise a satisfactory definition for bond energies as they are needed to calculate resonance energies. Since the latter concept is certainly fashionable and useful in chemistry, the problem of defining bond energy deserves attention. Obviously the arbitrariness inherent in the definition of bond energies will also be involved in the calculated values of the resonance energies.

Notation.—The following symbols are used:

$B(AB;m,\infty)$ = average bond energy of the bond AB in the m-atomic molecule; so defined that $\Sigma B = Q(a,m)$. The numbers m and ∞ in B indicate limits of summation
$B_0(AB;m,\infty)$ = average bond stretching energy of the bond AB in the m-atomic molecule
$D(AB;2,\infty)$ = heat of dissociation of the diatomic free radical AB
$D(AB\text{–}C)$ = bond dissociation energy of the molecule ABC when atom C is removed
E = energy of the molecule
$\Delta E_i(S)$ = the ith addition of energy to the molecule along the path S causing changes in all the coördinates
$\Delta E_i(R_j)$ = the ith increment in the energy of the molecule causing a change in the bond length R_j
$\Delta E_i(r_k)$ = the kth increment of the energy of the molecule due to a change in the coordinate r_j
f = number of "near-atom-influences" on n bonds by $m - 2$ atoms $= n(m - 2)$
$I(AB,C;m,\infty)$ = portion of bond energy of the bond AB due to the influence of the neighboring atom C in the m-atomic molecule
m = number of atoms in the molecule
n = $m - 1, \ldots {}_mC_{2-1}, {}_mC_2$ = number of chemical bonds in the molecule
$Q(a,m)$ = heat of atomization of the m-atomic molecule or radical (in a specified state) to the m free atoms (in specified states) at infinity
$R(AB;m)$ = internuclear distance of bond AB in the m-atomic molecule
$r(AB,C;m)$ = representative distance from the bond AB to the atom C which influences the bond, in the m-atomic molecule
$RE_0(AB;m,m-1)$ = reorganization energy involving a change in bond length from $R(AB;m)$ to $R(AB;\ m-1)$
$RE(AB;m,m-1)$ = reorganization energy of the bond AB when it changes its locale from the m-atomic to the $(m - 1)$-atomic molecule
S,S′ = paths of summation of energy increments

Bond Energies.—The potential energy (E) of a molecule is given by Szwarc and Evans[2] as a function of the n internuclear distances of chemically bonded atoms and $3m$-6-n angles. In order to be able to write the total heat of atomization, $Q(a,m)$ as a sum of terms representing bond energies, they define a particular path of integration L which amounts to an expansion of the molecule while it retains its shape. They state that this process is physically not realizable. However, it does not seem impossible to imagine that energy can be imparted to a molecule to cause its explosion in such a way that all the atoms move away from the center of gravity so as to retain their relative distances in the ratios that existed in the original structure. It is equally conceivable that a multiple collision will cause the separated atoms to collect together to form the molecule. Both processes will be very rare occurrences but not physically impossible. In order to discuss the removal of an atom from a molecule they define another reaction path P which is physically realizable. In the case of the triatomic molecule ABC these two processes lead to the following expressions of the total heat of atomization, $Q(a, 3)$

$$Q(a,3) = \int_{R(AB,3)L}^{\infty} \frac{\partial E}{\partial R(AB)} \times dR(AB) + \int_{R(BC,3)L}^{\infty} \frac{\partial E}{\partial R(BC)} \times dR(BC); \qquad \alpha = \alpha_0 \quad (1)$$

or

$$Q(a,3) = B(AB;3,\infty) + B(BC;3,\infty);\ \text{(Path L)}$$

and the total heat of atomization is represented by a *sum* of bond energies. Considering the removal of atom C from the molecule along the path P

$$Q(a,3) = \int_{R(BC,3)P}^{\infty} \frac{\partial E}{\partial R(AB)} \times \frac{dR(AB)}{dR(BC)} \times dR(BC) + \int_{R(BC,3)P}^{\infty} \frac{\partial E}{\partial R(BC)} \times dR(BC) + \int_{R(BC,3)P}^{\infty} \frac{\partial E}{\partial \alpha} \times \frac{d\alpha}{dR(BC)} \times dR(BC) + \int_{R(BC,2)P}^{\infty} \frac{\partial E}{\partial R(BC)} \times dR(BC) \quad (2)$$

or

$$Q(a,3) = D(AB\text{–}C) + D(AB;\ 2,\infty);\ \text{(Path P)}$$

where

$$D(AB;2,\infty) = \int_{R(BC,2)P}^{\infty} \frac{\partial E}{\partial R(BC)} \times dR(BC)$$

or the heat of dissociation of the diatomic free radical AB. These two expressions of the heat of atomization of the triatomic molecule are well defined. They differ markedly in concept so that any relation between bond energies and bond dissociation energies is not brought out as clearly as is desirable. A more graphic description is presented by the attack of the problem as discussed below. Of special interest seems to be the fact that the definition of a bond energy (B) can involve the heat of dissociation (D) of the corresponding free radical. It means that the latter quantity may be considered as a norm or reference state for the measurement of bond energy values.

In a molecule of m atoms, each bond is acted on by $m - 2$ neighboring atoms. If the molecule has n bonds, n can have the values $m - 1, m, \ldots {}_mC_2$

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(8) R. S. Mulliken, C. A. Rieke and W. G. Brown, *J. Am. Chem. Soc.*, **63**, 41 (1941).

(9) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940.

(10) A. D. Walsh, *J. Chem. Soc.*, 398 (1948).

$- 1$, ${}_mC_2$. The total number of atomic influences is $f = n(m - 2)$ and $n + f = n(m - 1)$. The potential energy of the molecule *may* therefore be described by $n(m - 1)$ coördinates. This number is greater than $3m - 6$ except when $m = 2$ (where $3m - 5 = n(m - 1) = 1$). Some of these coördinates are redundant in the sense that $n(m - 1) - 3m + 6$ of them could be described by the $3m - 6$ elements needed for the geometrical description of the molecule. The numbers n of them are the bond lengths and $n(m - 2)$ of them pertain to some average distances from the bond to the atoms which affect it (Fig. 1 and Table I). The energy of the molecule is represented in this $(n + f)$-fold coördinate space in order to include the atomic influences considered here very important.

The process of atomization is carried out along the path S. It is immaterial whether or not the latter is physically realizable or imaginary as far as its use is concerned for the purpose of defining bond energies. A series of additions of small energy increments, $\Delta E_i(\mathrm{S})$, to the molecule is visualized so that each one of them causes a small change in *each* of the $(n + f)$ coördinates, *i.e.*, the bond lengths $(\Delta E_i(R_j))$, and the influences of neighboring atoms $(\Delta E_i(r_k))$. The ith increment is

$$\Delta E_i(\mathrm{S}) = \sum_{j=1}^{n} \Delta E_i(R_j) + \sum_{k=1}^{f} \Delta E_i(r_k) \qquad (3)$$

The distribution of this energy increment over the various changes of bond length and atomic influences with neighboring atoms is considered to take place by a definite physical pattern. Conceivably this addition of energy may be controlled by quantum condition. Since however all types of interactions between atoms are included, as mentioned earlier, these energy increments may be very small. The totality of these additions is

$$E(\mathrm{S}) = \sum_{1}^{\infty} \Delta E_i(\mathrm{S}) = \sum_{i=1}^{\infty} \sum_{j=1}^{n} \Delta E_i(R_j) + \sum_{i=1}^{\infty} \sum_{k=1}^{f} \Delta E_i(r_k) \qquad (4)$$

TABLE I

NUMBER OF BONDS AND ATOMIC INFLUENCES

m	n	f	$n + f$	$B = B_0 + \sum_{1}^{m-2} I$	$Q = nB_0 + \sum_{1}^{f} I$
2	1	0	1	B_0	B_0
3	2	2	4	$B_0 + I$	$2B_0 + 2I$
	3	3	6	$B_0 + I$	$3B_0 + 3I$
4	3	6	9	$B_0 + 2I$	$3B_0 + 6I$
	4	8	12	$B_0 + 2I$	$4B_0 + 8I$
	5	10	15	$B_0 + 2I$	$5B_0 + 10I$
	6	12	18	$B_0 + 2I$	$6B_0 + 12I$
5	4	12	16	$B_0 + 3I$	$4B_0 + 12I$
	↓	↓	↓	↓	↓
	10	30	40	$B_0 + 3I$	$10B_0 + 30I$
6	5	20	25	$B_0 + 4I$	$5B_0 + 20I$
	↓	↓	↓	↓	↓
	15	60	75	$B_0 + 4I$	$15B_0 + 60I$
↓	↓	↓	↓	↓	↓

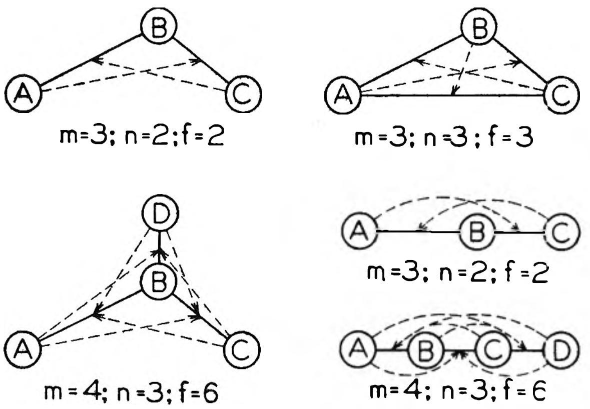

Fig. 1.—The tri- and tetratomic molecules: chemical bonds (full lines); atomic influences (dotted lines).

The process S is physically possible. Reversing the order of summation, yields

$$E(\mathrm{S}') = \sum_{1}^{\infty} \Delta E_i(\mathrm{S}') = \sum_{j=1}^{n} \sum_{i=1}^{\infty} \Delta E_i(R_j) + \sum_{k=1}^{f} \sum_{i=1}^{\infty} \Delta E_i(r_k) \qquad (5)$$

When this change is made from S to S′ and groups of energy increments are added together in the manner indicated, then the realm of physical possibility is left behind. The process S′ is mathematically feasible but it is not physically possible to impart energy to the molecule by selecting for example *only* those increments of energy $(\Delta E_i(R_j))$ which will lengthen the jth bond and cause *no* other disturbance in the molecule. However such an imaginary process is necessary if it is desirable to ascribe some definite energy quantity to a given bond and call it the "bond energy."

In order to define bond energies, *one* of the n sums *and* $(m-2)$ of the f sums are ascribed to *one* given bond. This sum is the bond energy

$$B_{jk} = \sum_{i=1}^{\infty} \Delta E_i(R_j) + \sum_{k=1}^{m-2} \sum_{i=1}^{\infty} \Delta E_i(r_k) \qquad (6)$$

If

$$B_{0j} = \sum_{i=1}^{\infty} \Delta E_i(R_j) \text{ and } I = \sum_{i=1}^{\infty} \Delta E_i(r_k) \qquad (7)$$

then the general relations exist

$$B = B_0 + \Sigma I \qquad (8)$$

and

$$Q = \Sigma B = \Sigma B_0 + \Sigma\Sigma I \qquad (9)$$

Each bond energy term (B) includes a factor B_0 referring to the pure stretching of the bond and factors I representing the influence of neighboring atoms. In this manner every type of bond has a somewhat different value of its bond energy depending on the environment in different molecules.

The Quantity RE_0.—However another definition of bond energy may be written by dividing the quantity B_0 into two portions. The first one is the energy (RE_0) needed to change the bond distance (R) from its value in the molecule to the internuclear distance in the free diatomic radical. This term is called the reorganization energy involving a change in bond length. It is of interest because it refers to the observable internuclear distances of the bond in the molecule and in the free diatomic radical. The second factor is the heat of dissociation of the free diatomic radical related to the bond in question

$$B_{0j} = \sum_{i=1}^{\infty} \Delta E_i(R_j) = \sum_{i=1}^{l} \Delta E_i(R_j) + \sum_{i=l}^{\infty} \Delta E_i(R_j) \quad (10)$$

The lth increment is just sufficient to change the bond length from the value in the molecule to its value in the free diatomic radical. For example the bond energy of the bond AB in the m atomic molecule is

$$B_0(\mathrm{AB};m,\infty) = RE_0(\mathrm{AB};m,2) + D(\mathrm{AB};2,\infty) \quad (11)$$

The Reorganization Energy.—The bond energy of bond AB in an m-atomic molecule may now be written

$$B(\mathrm{AB};m,\infty) = RE_0(\mathrm{AB};m,2) + D(\mathrm{AB};2,\infty) + \sum_{\mathrm{X}} I(\mathrm{AB,X};m,\infty) \quad (12)$$

where the summation extends over $m - 2$ atoms of the molecule excluding atoms A and B which form the bond in question. The reorganization energy is now defined as the sum of the first and third term of the above equation

$$RE(\mathrm{AB};m,2) = RE_0(\mathrm{AB};m,2) + \sum_{\mathrm{X}} I(\mathrm{AB,X};m,\infty) \quad (13)$$

so that the bond energy now appears as the sum of two terms

$$B(\mathrm{AB};m,\infty) = RE(\mathrm{AB};m,2) + D(\mathrm{AB};2,\infty) \quad (14)$$

the quantities "RE" contain all the influences which affect the bond energy except the heat of dissociation of the related free diatomic radical (D). Hence the latter quantity may be considered the norm of the bond energy values. When a chemical bond is changed from its situation in the free diatomic radical to the environment in a given molecule, its bond energy changes from D to B by the amount RE. The following relations may now be written

$$\begin{aligned} Q(a,m) &= \Sigma B \\ &= \Sigma B_0 + \Sigma\Sigma I \\ &= \Sigma RE_0 + \Sigma D + \Sigma\Sigma I \\ &= \Sigma RE + \Sigma D \end{aligned} \quad (15)$$

The reorganization energy (RE) may be defined in a more general manner as the differences in bond energy of a given bond as it occurs in two molecules.[11] For the bond AB in the molecules containing l and m atoms ($m > l$)

$$B(\mathrm{AB};m,\infty) = RE_0(\mathrm{AB};m,2) + D(\mathrm{AB};2,\infty) + \sum_{\mathrm{U}}{}' I(\mathrm{AB,U};m,\infty) \quad (16)$$

and

$$B(\mathrm{AB};l,\infty) = RE_0(\mathrm{AB};l,2) + D(\mathrm{AB};2,\infty) + \sum_{\mathrm{V}}{}' I(\mathrm{AB,V};l,\infty) \quad (17)$$

The summations extend over all of the atoms in these molecules except A and B which form the bond AB. The difference $B(\mathrm{AB};m,\infty) - B(\mathrm{AB};l,\infty)$ is

$$RE(\mathrm{AB};m,l) = RE_0(\mathrm{AB};m,l) + \sum_{\mathrm{X}}{}' I(\mathrm{AB,X};m,l) + \sum_{\mathrm{Y}}{}' I(\mathrm{AB,Y};m,\infty) \quad (18)$$

where the summation over X includes the atoms of the l-atomic molecule except A and B. The summation over Y refers to the atoms in the m-atomic molecule which however are not part of the l-atomic molecule. For example the reorganization energy of the bond AB when it changes its locale from the triatomic molecule ABC to the four atomic molecule ABCD is

$$RE(\mathrm{AB};4,3) = RE_0(\mathrm{AB};4,3) + I(\mathrm{AB,C};4,3) + I(\mathrm{AB,D};4,\infty) \quad (19)$$

This relation may also be obtained by subtracting the second one of equations (21) from the first line of equation (27).

It is of interest that these considerations lead to the notion of an ideal carbon–carbon single bond (C–C). It consists of two carbon atoms with only one valency link and altogether six free valences. Similarly an ideal carbon–carbon double bond must be defined. It need not be the $\mathrm{C_2}(\mathrm{X}\ {}^3\pi_u)$ molecule. In many instances the known diatomic free radical will serve as the reference structure.[6,8]

The Triatomic Molecule A–B–C (*m* = 3; *n* = *2*; *f* = *2*).—The total energy of the structure is

$$E = f(R(\mathrm{AB};3),\ R(\mathrm{BC};3),\ r(\mathrm{AB,C};3),\ r(\mathrm{BC,A};3)) \quad (20)$$

On the principles mentioned above the pertinent quantities are

$$\begin{aligned} B(\mathrm{AB};3,\infty) &= B_0(\mathrm{AB};3,\infty) + I(\mathrm{AB,C};3,\infty) \\ &= RE_0(\mathrm{AB};3,2) + D(\mathrm{AB};2,\infty) + I(\mathrm{AB,C};3,\infty) \quad (21) \\ &= RE(\mathrm{AB};3,2) + D(\mathrm{AB};2,\infty) \end{aligned}$$

and similar expressions for the bond BC. The total heat of atomization, $Q(a, 3)$, can be written as a sum of the two bond energies $B(\mathrm{AB};3,\infty)$ and $B(\mathrm{BC};3,\infty)$ in three forms in accordance with the above expressions. The relations given here are the same for the linear or the bent model of the triatomic molecule (Fig. 1 and Table I).

Bond Dissociation Energy.—An important quantity which has the great advantage of being susceptible of actual physical measurement is the energy needed to sever *one* bond of the molecule. Szwarc and Evans[2] emphasize the significance of this energy value. For the triatomic molecule ABC it is the change in energy, $D(\mathrm{AB{-}C})$, for the reaction removing the atom C

$$\mathrm{ABC} \longrightarrow \mathrm{AB} + \mathrm{C};\ D(\mathrm{AB{-}C})$$

The process involves the stretching of the bond BC from $R(\mathrm{BC};3)$ to infinity, the removal of both influence factors $I(\mathrm{AB,C};3,\infty)$ and $I(\mathrm{BC,A};3,\infty)$ and the reorganization of bond AB from $R(\mathrm{AB};3)$ to $R(\mathrm{AB};2)$. Hence

$$D(\mathrm{AB{-}C}) = RE_0(\mathrm{AB};3,2) + I(\mathrm{AB,C};3,\infty) + RE_0(\mathrm{BC};3,2) + D(\mathrm{BC};2,\infty) + I(\mathrm{BC,A};3,\infty) \quad (22)$$

or

$$D(\mathrm{AB{-}C}) = RE(\mathrm{AB};3,2) + D(\mathrm{BC};2,\infty) + RE(\mathrm{BC};3,2) \quad (23)$$

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[11] L. H. Long and R. G. W. Norrish, *Proc. Roy. Soc. (London)*, **187A**, 337 (1946).

Adding the dissociation energy $D(\mathrm{AB};2,\infty)$ yields $Q(a,3)$ as expected. Similarly for the reaction

$$\mathrm{ABC} \longrightarrow \mathrm{A} + \mathrm{BC};\ D(\mathrm{A{-}BC})$$

$$D(\mathrm{A{-}BC}) = RE(\mathrm{AB};3,2) + D(\mathrm{AB};2,\infty) + RE(\mathrm{BC};3,2) \quad (24)$$

From equations (23) and (24) the difference $D(\mathrm{AB{-}C}) - D(\mathrm{A{-}BC})$ is found to be $D(\mathrm{BC}) - D(\mathrm{AB})$. For example

$$\begin{array}{l} \mathrm{HCN} \longrightarrow \mathrm{HC} + \mathrm{N} - D(\mathrm{HC{-}N}) \\ \mathrm{H} + \mathrm{CN} \longrightarrow \mathrm{HCN} + D(\mathrm{NC{-}H}) \\ \hline \mathrm{H} + \mathrm{CN} \longrightarrow \mathrm{HC} + \mathrm{N} + D(\mathrm{NC{-}H}) - D(\mathrm{HC{-}N}) \end{array}$$

and

$$\begin{array}{l} \mathrm{CN} \longrightarrow \mathrm{C} + \mathrm{N} - D(\mathrm{CN}) \\ \mathrm{H} + \mathrm{C} \longrightarrow \mathrm{CN} + D(\mathrm{CH}) \\ \hline \mathrm{H} + \mathrm{CN} \longrightarrow \mathrm{HC} + \mathrm{N} + D(\mathrm{CH}) - D(\mathrm{CN}) \end{array}$$

If the expressions $D(\mathrm{AB{-}C})$ and $D(\mathrm{A{-}BC})$ from equations (1) and (2) obtained by Szwarc and Evans[2] are subtracted it is difficult to arrive at this simple result.

The dissociation paths described in equations (23) and (24) are artificial in the sense that the energies $D(\mathrm{AB{-}C})$ and $D(\mathrm{A{-}BC})$ cannot be supplied to the molecule one term at a time as expressed on the right side of these equations. It is not possible to cause the reorganization of the bond AB, *i.e.*, supplying the necessary energy $RE(\mathrm{AB};3,2)$ only. The energies represented by all three terms of (23) and (24) must be supplied simultaneously in order to cause the dissociation of the corresponding bonds. These paths of integration lead to the same result as do the paths P and P′ of Szwarc and Evans.[2]

The Triangular Molecule ABC ($m = 3$; $n = 3$; $f = 3$).—The atoms of this molecule are all united by chemical bonds (Fig. 1 and Table I). The above treatment yields

$$\begin{aligned} Q(a,3) = {} & RE(\mathrm{AB};3,2) + D(\mathrm{AB};2,\infty) \\ & + RE(\mathrm{BC};3,2) + D(\mathrm{BC};2,\infty) \\ & + RE(\mathrm{AC};3,2) + D(\mathrm{AC};2,\infty)' \end{aligned} \quad (25)$$

or

$$Q(a,3) = B(\mathrm{AB};3,\infty) + B(\mathrm{BC};3,\infty) + B(\mathrm{AC};3,\infty)$$

and the bond dissociation energy for the removal of atom C or the energy for the reaction

$$\mathrm{ABC} \longrightarrow \mathrm{AB} + \mathrm{C};\ D((\mathrm{AB}) = \mathrm{C})$$

is given by the relation

$$\begin{aligned} D((\mathrm{AB}) = \mathrm{C}) = {} & RE(\mathrm{AB};3,2) \\ & + RE(\mathrm{BC};3,2) + D(\mathrm{BC};2,\infty) \\ & + RE(\mathrm{AC};3,2) + D(\mathrm{AC};2,\infty) \end{aligned} \quad (26)$$

Adding $D(\mathrm{AB};2,\infty)$ yields $Q(a,3)$.

The Tetratomic Molecule ABCD ($m = 4$; $n = 3$; $f = 6$).—The particular model considered has another atom (D) attached to the atom B of the molecule A–B–C by a chemical bond, as shown in Fig. 1. Some of the relevant quantities are

$$\begin{aligned} Q(a,4) = {} & RE_0(\mathrm{AB};4,2) + D(\mathrm{AB};2,\infty) + I(\mathrm{AB,C};4,\infty) + I(\mathrm{AB,C};4,\infty) \\ & + RE_0(\mathrm{BC};4,2) + D(\mathrm{BC};2,\infty) + I(\mathrm{BC,A};4,\infty) + I(\mathrm{BC,D};4,\infty) \\ & + RE_0(\mathrm{BD};4,2) + D(\mathrm{BD};2,\infty) + I(\mathrm{BD,A};4,\infty) + I(\mathrm{BD,C};4,\infty) \end{aligned} \quad (27)$$

If

$$RE(\mathrm{AB};4,2) = RE_0(\mathrm{AB};4,2) + I(\mathrm{AB,C};4,\infty), + I(\mathrm{AB,D};4,\infty), \text{ etc.} \quad (28)$$

then

$$\begin{aligned} Q(a,4) = {} & RE(\mathrm{AB};4,2) + D(\mathrm{AB};2,\infty) \\ & + RE(\mathrm{BC};4,2) + D(\mathrm{BC};2,\infty) \\ & + RE(\mathrm{BD};4,2) + D(\mathrm{BD};2,\infty) \end{aligned} \quad (29)$$

or

$$Q(a,4) = B(\mathrm{AB};4,\infty) + B(\mathrm{BC};4,\infty) + B(\mathrm{BD};4,\infty)$$

The heat of atomization $Q(a,3)$ of the related triatomic molecule or radical ABC can be written in accordance with equation (21). Subtracting this quantity from equation 27 yields $D(\mathrm{ABC{-}D})$

$$\begin{aligned} D(\mathrm{ABC{-}D}) = {} & RE_0(\mathrm{AB};4,3) + I(\mathrm{AB,C};4,3) + I(\mathrm{AB,D};4,\infty) \\ & + RE_0(\mathrm{BC};4,3) + I(\mathrm{BC,A};4,3) + I(\mathrm{BC,D};4,\infty) \\ & + RE_0(\mathrm{BD};4,2) + I(\mathrm{BD,A};4,\infty) + I(\mathrm{BD,C};4,\infty) \\ & + D(\mathrm{BD};2,\infty) \end{aligned} \quad (30)$$

If

$$RE(\mathrm{AB};4,3) = RE_0(\mathrm{AB};4,3) + I(\mathrm{AB,C};4,3) + I(\mathrm{AB,D};4,\infty) \text{ etc.} \quad (31)$$

then $D(\mathrm{ABC{-}D})$ can be written

$$\begin{aligned} D(\mathrm{ABC{-}D}) = {} & RE(\mathrm{AB};4,3) + RE(\mathrm{BC};4,3) \\ & + RE(\mathrm{BD};4,2) + D(\mathrm{BD};4,2) \end{aligned} \quad (32)$$

If another chemical bond existed between the atoms A and D in the molecule ABCD ($m = 4$; $n = 4$; $f = 8$), the total heat of atomization is

$$\begin{aligned} Q(a,4)' = {} & RE'(\mathrm{AB};4,2) + D(\mathrm{AB};2,\infty) \\ & + RE'(\mathrm{BC};4,2) + D(\mathrm{BC};2,\infty) \\ & + RE'(\mathrm{BD};4,2) + D(\mathrm{BD};2,\infty) \\ & + RE'(\mathrm{AD};4,2) + D(\mathrm{AD};2,\infty) \end{aligned} \quad (33)$$

The energy necessary to open the bond AD is obtained by subtracting $Q(a,4)$ (Eq. 29) from $Q(a,4)'$ (Eq. 33)

$$Q(a,4)' - Q(a,4) = \Sigma B' - \Sigma B \doteq B'(\mathrm{AD};4,\infty) \quad (34)$$

in case the differences $(B'-B)$ of the three bonds are small. In the four atomic molecule n can have the values 3 to 6 inclusive and hence four different kinds of the 4-atomic molecule can be discussed.

Separation into Radicals.—As an example the linear four atomic molecule A–B–C–D may be considered to decompose into the two free radicals AB and CD by breaking the bond BC. The heat of atomization is given in equation (29) after replacing BD by CD. The energy of dissociation is

$$\begin{aligned} D(\mathrm{AB{-}CD}) = {} & RE(\mathrm{AB};4,2) \\ & + RE(\mathrm{BC};4,2) + D(\mathrm{BC};2,\infty) \\ & + RE(\mathrm{CD};4,2) \end{aligned} \quad (35)$$

Methane and its Radicals.—The bond energies of the CH– bonds, assumed to be identical in any one structure, are

$$B(\mathrm{CH};m,\infty) = RE(\mathrm{CH};m,2) + D(\mathrm{CH};2,\infty) \quad (36)$$

where $m = 5, 4, 3, 2$ for methane, methyl, methylene and CH radicals, respectively. The corresponding heats of atomization are

$$Q(a,m) = (m-1)\,RE(\mathrm{CH};m,2) + (m-1)\,D(\mathrm{CH};2,\infty) \quad (37)$$

and the bond dissociation energies are $Q(a,m) - Q(a,m-1)$ or

$$D(\mathrm{CH}_{m-2}\text{-H}) = RE(\mathrm{CH};m,2) + (m-2)RE(\mathrm{CH};m,m-1) + D(\mathrm{CH};2,\infty) \quad (38)$$

The removal of the first hydrogen atom for example requires the bond dissociation energy $Q(a,5) - Q(a,4)$ or

$$D(\mathrm{CH}_3\text{-H}) = RE_0(\mathrm{CH};5,2) + 6I(\mathrm{CH,H};5,\infty) + D(\mathrm{CH};2,\infty) \quad (39)$$
$$+ 3RE_0(\mathrm{CH};5,4) + 6I(\mathrm{CH,H};5,4)$$

There are several other ways of writing these expressions.

Ethylene ($m = 6$; $n = 5$; $f = 20$).—The bond energies are

$$B(\mathrm{C{=}C};6,\infty) = RE(\mathrm{C{=}C};6,2) + D(\mathrm{C{=}C};2,\infty) \quad (40)$$

and

$$B(\mathrm{CH};6,\infty) = RE(\mathrm{CH};6,2) + D(\mathrm{CH};2,\infty)$$

assuming the four CH bonds to be identical. The heat of atomization can be written as

$$Q(a,6) = B(\mathrm{C{=}C};6,\infty) + 4B(\mathrm{CH};6,\infty) \quad (41)$$

or

$$\begin{aligned} Q(a,6) = {} & B_0(\mathrm{C{=}C};6,\infty) + 4I(\mathrm{C{=}C,H};6,\infty) \\ & + 4B_0(\mathrm{CH};6,\infty) + 4I(\mathrm{CH,C};6,\infty) \\ & + 4I_1(\mathrm{CH,H};6,\infty) + 4I_2(\mathrm{CH,H};6,\infty) \\ & + 4I_3(\mathrm{CH,H};6,\infty) \end{aligned}$$

The I_i refer to the influence of the three hydrogen atoms located at different distances from the particular CH bond under discussion. Nine different bond dissociation energies can be written on the principles and the notation given above.

Benzene ($m = 12$; $n = 12$; $f = 120$).—If it is assumed that the six carbon–carbon bonds are identical and similarily the six carbon–hydrogen bonds, then

$$B(\mathrm{C}\dot{-}\mathrm{C};12,\infty) = B_0(\mathrm{C}\dot{-}\mathrm{C};12,\infty) + 4I(\mathrm{C}\dot{-}\mathrm{C,C};12,\infty) + 6I(\mathrm{C}\dot{-}\mathrm{C,H};12,\infty) \quad (42)$$

and

$$B(\mathrm{CH};12,\infty) = B_0(\mathrm{CH};12,\infty) + 5I(\mathrm{CH,C};12,\infty) + 5I(\mathrm{CH,H};12,\infty)$$

and the heat of atomization and a considerable number of bond dissociation energies can be written in the formal manner indicated above.

Isomers.—As an example *cis*- and *trans*-dichloroethylene have been studied. The two isomers give quite similar expression for their respective heats of atomization. However the atomic influence factors (I) are different in the two cases and hence the bond energies are different and the corresponding heats of atomizations $Q(a,6,cis)$ and $Q(a,6,trans)$ will not have the same numerical values. Their difference will give the energy of isomerization. The present notation is therefore satisfactory to this extent.

Conclusion

It appears possible to define bond energies and relate them to bond dissociation energies by a consistent scheme. The ideas involve reorganization energies and near-atom-influences and the heat of dissociation of the free radical which is related to a given bond. Attempts have already been made to apply these principles in practice and to obtain numerical values for these atomic-influence factors and near-group effects.[6] The present treatment appears to be flexible enough to describe all molecules and radicals in the manner indicated in the examples. However some very important information, such as the heat of sublimation of carbon, the heat of dissociation of nitrogen and of fluorine and many other energy values of this kind will have to be known definitely before a complete body of knowledge regarding bond energies can be developed. Evidently the first problem is to devise a proper definition of the term bond energy and it is hoped that the present remarks contribute toward this end.

MAGIC FORMULA, STRUCTURE OF BOND ENERGIES AND ISOVALENT HYBRIDIZATION[1,2]

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In order to give approximate quantitative form to the Slater–Pauling "criterion of maximum overlapping," a "magic formula" is presented. It gives the energy of atomization D_0 of any molecule as a sum of terms of which the principal ones are functions of overlap integrals (theoretical), of atomic ionization potentials (experimental), and also of degree of hybridization where the latter can occur without change of valence (*isovalent hybridization*). A preliminary fitting to three molecules whose D_0 values are sufficiently well known yields a magic formula suitable for molecules containing first-row atoms and hydrogen, and which fits the molecules CH, N_2, O_2, F_2, CH_4, C_2H_6, C_2H_4, C_2H_2, H_2^+, He_2^+, within about ±0.3 e.v. per bond. For molecules with isovalent hybridization, the actual degree of hybridization is obtained as a by-product. Especially interesting is what the magic formula says about the *structure* of bond energies; that is, about the way in which the numerous theoretical terms, some bonding, some repulsive, add to give D_0. As compared with VB theory analyses by Van Vleck, Penney and others, it indicates much larger bonding and repulsive exchange terms. It indicates strikingly large exchange repulsions by inner shells, here in agreement with earlier conclusions of James and of Pitzer. The magic formula indicates that the π bonding terms in multiple bonds are much larger than is generally believed. Another striking conclusion is that isovalent hybridization is often very important for molecular stability. This conclusion, agreeing with indications from several other types of evidence for molecules such as CH, OH, HCl, H_2O, O_2 and N_2, is also in harmony with recent theoretical work of Moffitt and of Kotani, using conventional VB methods. The terms in the magic formula for D_0 can be collected into groups, one for each bond, corresponding to the usual concept of *bond energies*. Gross bond energies (a category introduced by Van Vleck in terms of VB theory) and net bond energies are tabulated for several molecules. Section IV includes an analysis and classification of types of hybridization and promotion which occur for atoms in valence states. Suggestions for extension, further applications, and (Section XIII) improvement of the magic formula are given.

I. Introduction

Quantum mechanics gives a satisfactory qualitative explanation of the major facts of chemical valence, and is capable "in principle" of predicting all energy relations quantitatively. But because of mathematical difficulties, no such quantitative accounting has yet been attained. Slater and Pauling, in 1931, proposed as a rough measure of the strength of any covalent bond, formed by two electrons on adjacent atoms, the quantum-mechanical *criterion of maximum overlapping* of the orbitals (one-electron wave functions) occupied by these electrons. With the idea of implementing this criterion somewhat quantitatively, C. A. Rieke and the writer before the war sought semi-empirical relations between overlap integrals and bond energies.[3] Recently the writer proposed a preliminary equation for this purpose.[4] An improved "magic formula"[5] is described below.

In the history of valence theory, two main quantum-mechanical methods for describing molecular electronic structures have proved useful, namely, the VB (valence-bond) method, and the MO (molecular orbital) method in its LCAO form. The magic formula has been built in a general pattern indicated by the VB method, and in this respect is by no means entirely novel, but the specific forms of its details have been suggested largely by LCAO MO theory. The structure of the formula and the numerical values of the terms which appear in it are such, it is believed, as to afford increased insights into the nature of chemical binding and to provide helpful suggestions for further work.

It should be emphasized that the magic formula in its present form and with the present values of its coefficients is still preliminary. And further, as compared with the hoped-for future development of really quantitative calculations of chemical binding energies, the attempt to construct a magic formula may probably be looked on as a stop-gap effort.

II. LCAO MO Background of Magic Formula

It is instructive to begin with a survey of LCAO MO energy expressions for the simple molecules H_2^+, H_2, He_2^+, He_2, for states involving occupation of the lowest-energy MO's $1\sigma_g$ and $1\sigma_u$; in LCAO approximation

$$1\sigma_g \approx (1s_a + 1s_b)/(2 + 2S)^{\frac{1}{2}};\quad 1\sigma_u \approx (1s_a - 1s_b)/(2 - 2S)^{\frac{1}{2}}$$

Here $1s_a$ and $1s_b$ are $1s$ AO's (atomic orbitals) on the two atoms a and b, and S is their overlap integral

$$S \equiv \int 1s_a 1s_b\, dv$$

For H_2^+, the energies of the ground state (one electron in $1\sigma_g$) and the first excited state (one electron in $1\sigma_u$) can be, respectively, expressed in the forms

$$E = E_H - (C^+ + E') \pm \beta/(1 \pm S) \qquad (1)$$

Here E_H is the energy of a normal hydrogen atom. Further

$$\left.\begin{aligned} C^+ &= -e^2/R - \omega \\ \beta &= \tau - S\omega \\ \omega = \int u_b 1s_a^2 dv;&\quad \tau = \int u_b 1s_a 1s_b\, dv \end{aligned}\right\} \qquad (2)$$

R is the internuclear distance, and u_b is the potential due to nucleus b. It should be noted that ω, τ and β are all negative quantities. $-E'$ (which is included merely for bookkeeping purposes) is whatever energy is needed to correct the error of the LCAO approximation so as to make Eq. (1) exact. Resonance energy expressions of the type β are of central importance in ordinary LCAO theory.[6]

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[1] This work was assisted by the ONR under Task Order IX of Contract N6ori with The University of Chicago.

[2] Presented at Symposium on Bond Energies of Division of Physical and Inorganic Chemistry, American Chemical Society Meeting at New York, September 6, 1951.

[3] Some of the material in Sections II and III below was presented at a symposium in 1942, but only an Abstract was published: R. S. Mulliken and C. A. Rieke, *Rev. Modern Phys.*, **14**, 159 (1942).

[4] R. S. Mulliken, *J. Am. Chem. Soc.*, **72**, 4493 (1950), in particular Eq. (8) and (9), footnote 14a, and Table X.

[5] *J. Chem. Phys.*, **19**, 900 (1951). Note added in proof.

[6] Combinations of the form of β of Eq. (2a) were introduced with the symbol Y by Mulliken, *J. Chem. Phys.*, **3**, 573 (1935), Eq. (15), and identified with Hückel's semi-empirical LCAO quantity β by Mulliken and Rieke, *J. Am. Chem. Soc.*, **63**, 44, 1770 (1941).

Equation (1) is obtained as follows.[7] As is well known,

$$E = e^2/R - E' + (\alpha \pm \gamma)/(1 \pm S)$$

where

$$\alpha \equiv \int 1s_a h 1s_a \, dv, \quad \gamma \equiv \int 1s_b h 1s_a \, dv$$

h being the electronic Hamiltonian. On substituting

$$\beta \equiv \gamma - S\alpha \tag{2a}$$

and

$$h = h_a + u_b$$

h_a being the Hamiltonian for atom a alone, one readily obtains

$$\alpha = E_H + \omega, \beta = \tau - S\omega,$$

and Eq. (1)

For the ground state of H_2^+, Eq. (1) gives for the dissociation energy D_e, equal to $E_H - E$

$$D_e = (C^+ + E') - \beta/(1 + S) \tag{3}$$

Now it would be very pleasant if $C^+ + E'$ in Eq. (3) could be neglected and D_e put equal to the dominant resonance term $-\beta/(1 + S)$ alone. Actually, this procedure gives rather good results ($D_e = 2.79$ e.v., $-\beta/(1 + S) = 2.22$ e.v., by direct theoretical computation).[8,9]

Similarly for H_2, where[7]

$$D_e = (C + E') - 2\beta/(1 + S) \tag{4}$$

the theoretically computed resonance term $-2\beta/(1 + S)$ agrees rather well (4.07 e.v.) with the observed D_e (4.76 e.v.).[8,10] The results on H_2 and H_2^+, reinforced by similar (though less reliable) evidence on π bonds in C_2H_2 and C_2H_4,[7] suggest that the resonance terms of LCAO theory may be used as a basis for a semi-empirical systematics of bond energies. One might now try to use D expressions of the form $A\beta/(1 + S)$, computing β theoretically for each type of bond. However, a different path will be followed here, on which the next step is to replace β by a function of S.

The simplest reasonable choice is to put

$$-2\beta = ASI \tag{5}$$

where I is the ionization energy for the appropriate valence AO. A is then a factor to be determined empirically so as to satisfy equations like (3) and (4) omitting terms like $C + E'$, as well as may be possible for a number of molecules simultaneously. This procedure gives for a one-electron bond and an electron-pair bond, respectively

$$D = \tfrac{1}{2}AIS/(1 + S) \tag{6}$$

$$D = AIS/(1 + S) \tag{7}$$

Rough proportionality of β to S is seen to be plausible if one studies the forms of τ, ω and β in Eq. (2). Among other things, the rough relation

$$\tau \approx \tfrac{1}{2}S(\omega + \int u_a 1s_a^2 \, dv)$$

is involved. Also by direct computation in two instances, β has been found approximately proportional to S. Namely, for $1s$–$1s$ binding in H_2^+ or H_2, in e.v., $-\beta \approx 7S$ for $R > 1$ Å. (but at the equilibrium distance for H_2, $-\beta \approx 4.7S$); and for $2p\pi$–$2p\pi$ binding as in C_2H_2 or C_2H_4, $-\beta \approx 10S$ (this is valid over a range of R extending to both sides of the equilibrium distances for these molecules).[11] These results suggest the following conclusions, confirmed later in this paper: (1) $-\beta$ may usually be taken proportional to S, but with a larger proportionality constant for π than for σ bonds; (2) but if R is unusually small (relative to AO size), $-\beta$ may become smaller (*cf.* ref. 56 below).

Another instructive approach to Eq. (6) and (7) is the following. Consider the *charge density* ρ for an electron in the MO $1\sigma_g$ in H_2^+. In LCAO approximation (*cf.* Eq. (1)), this is (in units of $-e$)

$$\rho = (1\sigma_g)^2 \approx \tfrac{1}{2}(1s_a^2 + 1s_b^2)/(1 + S) + (1s_a \, 1s_b)/(1 + S)$$

As compared with the charge distribution $\frac{1}{2}(1s_a^2 + 1s_b)^2$, which would exist if the electron were distributed with equal probability between $1s$ AO's on the two nuclei, the above distribution represents a shift of a fraction $\int 1s_a \, 1s_b \, dv/(1 + S) = S/(1 + S)$ of the charge into the region of overlap between the two nuclei. Since, aside from the Coulomb term, which would correspond to the unshifted distribution $\frac{1}{2}(1s_a^2 + 1s_b^2)$, it is precisely this partial shift into the increased field in the overlap region which is primarily responsible for the stability of H_2^+, it is to be expected that D_e for the latter should be approximately proportional to $S/(1 + S)$.

The assumption of approximate proportionality of $-\beta$ to I is made plausible by the following reasoning. Molecule-formation viewed according to the VB method is a phenomenon which causes perturbations in the energies of the valence electrons of the participating atoms. Bond energy is then a measure of the extent of these perturbations. Other things being equal, the perturbation energy should be more or less proportional to (perhaps a nearly constant fraction of) the original energy of the valence electrons, for any one of which its binding energy $-I$ is a measure. (See also ref. 39 below.)

In the ground states of He_2^+ and He_2, there are two $1\sigma_g$, and, respectively, one or two $1\sigma_u$ electrons. The resonance contributions to D are $-\beta/(1 + S)$ for each $1\sigma_g$ and $+\beta/(1 - S)$ for each $1\sigma_u$ electron (*cf.* Eq. (1), (4), (5)). Putting $-2\beta = ASI$, one obtains for He_2^+ and He_2, respectively

$$D = -\beta\left(\frac{2}{1 + S} - \frac{1}{1 - S}\right) = AI\left(\frac{S}{1 + S} - \frac{S}{1 - S}\right) = \tfrac{1}{2}AIS(1 - 3S) \tag{8}$$

$$D = -2\beta\left(\frac{1}{1 + S} - \frac{1}{1 - S}\right) = AI\left(\frac{S}{1 + S} - \frac{S}{1 - S}\right) = -2AIS^2/(1 - S^2) \tag{9}$$

Equation (9) predicts *repulsion* for two He atoms, in agreement with VB theory. Equation (8) for the three-electron bond indicates weaker bonding than for the one-electron bond.

In the process of generalizing Eq. (7)–(9) to obtain a magic formula, as described later in this paper, it was found necessary empirically to introduce (*cf.* Eq. (23)) a correction factor ν to temper somewhat repulsions like those of Eq. (9). Because of the largely empirical character of the final formulas, Eq. (9) may as well also be simpli-

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[7] For further details, see R. S. Mulliken, *J. chim. phys.*, **46**, 497 (1949). For H_2^+, see Eqs. (38)–(40) for τ, ω and β; Eq. (43) and Table II for dissociation energy equation and data. For H_2, see Eqs. (65) and (69) for ω and β (β is slightly different for H_2 than for H_2^+, but this is neglected in Eq. (5)); Eq. (77) and Table III for dissociation energy equation and data. For similar material on C_2H_2 and C_2H_4, see Tables V and VI.

[8] The D_e value given is the experimental value corrected to no zero-point energy. Later in the paper, uncorrected D values (D_0 values) will be used. For H_2, $D_0 = 4.48$ e.v.

[9] The theoretical C^+ is -0.74 e.v., requiring $E' = 1.31$ e.v. It is seen that a much better result is obtained by ignoring the Coulomb term C^+ of LCAO theory than by including it.

[10] In Eq. (4)

$$C = -e^2/R - 2\omega - \tfrac{1}{2}(J_{aa} + J_{ab})$$

where J_{aa} and J_{ab} are as in Eq. (18). Here, just as for H_2^+, inclusion of C (computed value -1.55 e.v.) would only have worsened the agreement ($E' = 2.24$ e.v).

[11] For further details, see R. S. Mulliken, *J. chim. phys.*, **46**, 675 (1949), Section 28.

fied by dropping the factor $1/(1 - S^2)$, which usually is not far from 1.[12] The result is

$$\text{He}_2\text{:}\quad D = AI\left(\frac{S}{1+S} - \frac{\mu S}{1-S}\right) = -2\nu AIS^2 \quad (10)$$

with ν near 0.7 (see later in this paper). Introduction of the factor μ into the antibonding term in the first form of Eq. (10) makes the two forms of Eq. (10) agree if

$$\left.\begin{aligned}\mu &= [(1 - S)/(1 + S)] + 2\nu S(1 - S)\\ &= 1 - 2S(1 - S)(1 - \nu) + \ldots\end{aligned}\right\} \quad (11)$$

If this factor μ is empirically needed in (10), use of the same factor in the antibonding term in (8) is indicated. Equation (8) then becomes

$$\text{He}_2{}^+\text{:}\quad D = AI\left(\frac{S}{1+S} - \frac{\frac{1}{2}\mu S}{1-S}\right) = \tfrac{1}{2}AIS\,[(2 - \mu) - (2 + \mu)S] \quad (12)$$

This predicts a somewhat stronger three-electron bond than Eq. (8) does.

Although Eq. (6)–(9) above have been obtained by LCAO MO theory, it is well known that VB theory gives identically the same wave functions as LCAO theory for $H_2{}^+$, $He_2{}^+$ and He_2 in their ground states, the two theories differing only for H_2.[13] Hence, Eq. (6), Eq. (8) or (12), and Eq. (9) or (10), may be considered to be based on *either* the VB or the LCAO approximation, only (7) being LCAO only. Since VB theory is tolerable for all values of R, all the equations but (7) should likewise be acceptable for all R values. Although the LCAO formula (7) will be used below as a basis for dealing with bonded attractions by the magic formula, it must be recognized that Eq. (7) cannot be valid outside a limited range of smaller R values near equilibrium. For larger R values, the corresponding VB formula must be given preference.

As has been shown previously,[4] Eq. (9) with A = 0.65 fits the curve of repulsion between two He atoms over a broad range of R. Eq. (10) with $\nu = 0.7$ and an increased A also gives a good fit.

In using Eq. (6)–(12), the necessary S values can be looked up in existing tables.[14]

III. Valence-Bond Theory Background of Magic Formula

In the VB method, each electron is first assigned to an AO on one atom. Electrons with unpaired opposite spins on adjacent atoms may then form electron-pair bonds. In the simplest example, H_2, the approximate energy of the $^1\Sigma^+{}_g$ ground state according to VB theory[15] is usually given in the form

$$E \approx (H_{11} + H_{12})/(1 + S^2) \quad (13)$$

In Eq. (13), H_{11} and H_{12} can be written in the form

$$H_{ij} = H_{ji} = \int \psi_j(H_{a1} + H_{b2} + H_{int})\psi_i \, dv_1 \, dv_2$$

where

$$\psi_1 \equiv 1s_a\,(1)\,1s_b\,(2);\quad \psi_2 \equiv 1s_b\,(1)\,1s_a\,(2)$$

$$H_{a1} \equiv -h^2\nabla_1{}^2/8\pi^2m - e^2/r_{a1};\quad H_{b2} \equiv -h^2\Delta_2{}^2/8\pi^2m - e^2/r_{b2}$$

and the *interaction operator* H_{int} is

$$H_{int} \equiv e^2/R + e^2/r_{12} - e^2/r_{b1} - e^2/r_{a2}$$

Equation (13) can be recast[16, 17] to

$$\left.\begin{aligned}E &\approx H_{11} + \eta/(1 + S^2)\\ \text{where}\quad \eta &\equiv H_{12} - S^2H_{11}\end{aligned}\right\} \quad (14)$$

If a bookkeeping term $-E'$ is now added to the right of the first Eq. (14), such as to convert it from an approximate to an exact equality, and if then E is subtracted from $2E_H$, one obtains for the dissociation or bond energy

$$\left.\begin{aligned}D_e &= (C + E') - \eta/(1 + S^2)\\ \text{where}\quad C &\equiv 2E_H - H_{11} = -\int \psi_1 \, H_{int}\psi_1 \, dv\end{aligned}\right\} \quad (15)$$

is the relatively small[15] "Coulomb" term.[18] Equation (15) may conveniently be written

$$D_e = (C + E') + X;\quad X = -\eta/(1 + S^2) \quad (16)$$

the exchange term[18] X being the main term responsible for bonding.

It is instructive to compare the VB expression (16) for D_e of H_2 with the corresponding LCAO expression of Eq. (4). Quantitative theoretical computations have of course been made[15] by both equations, with the result that (omitting the bookkeeping terms E') the VB expression gives a somewhat better computed D_e than does the LCAO expression. However, if the primary bonding terms alone are used, that is, $-2\beta/(1 + S)$ of Eq. (4) and $X = -\eta/(1 + S^2)$ of Eq. (16), the former gives a surprisingly good D value, but the latter of a poor D value.[19] This points toward adoption of the procedure proposed in Section II, of approximating D semi-empirically by $-2\beta/(1 + S)$ with -2β replaced by ASI (*cf.* Eq. (5), (7)).

In view of the strongly empirical character of the search for a magic formula, a definite decision to use expressions of the LCAO-suggested form $ASI/(1 + S)$ for the energies of the bonding electrons of electron-pair bonds seems justified, and will now be made, for the case of molecules with the distances

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[12] At first, a different empirical modification of Eq. (9) was tried, consisting in replacing the terms $S/(1 + S)$ and $S/(1 - S)$ by $S/(1 + aS)$ and $S/(1 - bS)$, respectively, and trying to determine a and b to give as good fits as possible to observed D values for $H_2{}^+$, H_2, $He_2{}^+$, He_2. A number of trial values of a and b were tested, mostly with $a > b > 0$, but finally it was concluded that the use of a form like Eq. (10) has better possibilities for fitting observed D's, besides being simpler.

[13] This is readily verified by setting up the complete antisymmetrized VB and LCAO wave functions for each case in detail, including spins, and comparing. The statement is true, of course, only if 1s hydrogenic AO's with a single Z value are used in each case.

[14] (a) R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949); (b) R. S. Mulliken, *ibid.*, **19**, 900 (1951). The symbolism and notation of ref. 14b has been used in the present paper.

[15] See for example L. Pauling and E. Bright Wilson, Jr., "Introduction to Quantum Mechanics," McGraw-Hill Book Co., Inc., New York, N. Y., 1935, Section 42a.

[16] The definition of η is constructed in analogy to that of the LCAO MO parameter β (*cf.* footnote 6). The quantity here called η (earlier—see footnote 3—called α) has also been used recently by van Dranen and Ketelaar, *J. Chem. Phys.*, **18**, 1125L (1950)—their α'.

[17] The energy of the $^3\Sigma^+{}_u$ repulsive state is also given by Eq. (13) and (14) if the plus signs are changed to minus signs.

[18] In the customary terminology of atomic structure theory, intratomic repulsion integrals analogous in form to the interatomic (two-center) integrals J_{ab} and K_{ab} of Eq. (18) are called Coulomb and exchange integrals, respectively, and it seems appropriate to use the same terminology for J_{ab} and K_{ab} In VB theory, on the other hand, integrals $\int \psi_i H_{int} \psi_i \, dv$ and $\int \psi_i H_{int} \psi_j \, dv$ are commonly called Coulomb and exchange integrals. In the following, expressions of the type $\eta/(1 + S^2)$ will be called "exchange terms" to signalize the fact that their dominant components are "exchange integrals" in the VB sense.

[19] This happens because of the terms C, which have opposite effects in the two cases, making the computed D_e somewhat better in Eq. (16), but much worse (*cf.* footnote 10) in Eq. (4). See sentence containing Eq. (4) for actual values of D_e and $-2\beta/(1 + S)$.

between bonded atoms near their equilibrium values.

A study of the detailed structure[15] of X of Eq. (16) shows that it can be written in the form

$$X = -[2S\beta + (K_{ab} - S^2J_{ab})]/(1 + S^2) \quad (17)$$

Here β is the familiar resonance energy quantity of LCAO theory (*cf.* Eq. (2), (2a)), and[18] K_{ab} and J_{ab} are

$$\left.\begin{aligned} K_{ab} &\equiv \int\int 1s_a^{(1)}1s_b^{(1)}e^2/r_{12}\ 1s_a^{(2)}1s_b^{(2)}dv_1\ dv_2 \\ J_{ab} &\equiv \int\int 1s_a^{(1)}1s_a^{(1)}e^2/r_{12}1s_b^{(2)}1s_b^{(2)}\ dv_1\ dv_2 \end{aligned}\right\} \quad (18)$$

The convenient and rather accurate approximation[20]

$$K_{ab} \approx \tfrac{1}{2}S^2(J_{aa} + J_{ab})$$

where J_{aa} is an intratomic Coulomb integral defined analogously to J_{ab} in Eq. (18), may now be introduced into Eq. (17). One then has

$$X \approx -[2S\beta + \tfrac{1}{2}S^2(J_{aa} - J_{ab})]/(1 + S^2) \quad (19)$$

Usually[21] $\mathbf{H} > 0$, as a result of strong predominance of the positive term $-2S\beta$ (*cf.* Section II) over the negative term $-\frac{1}{2}S^2(J_{aa} - J_{ab})$. (Note that $J_{aa} > J_{ab}$ for $R > 0$.)

It is of interest to compare the primary bonding terms of LCAO and VB theory as given in Eq. (4) and (19). It is seen that these both take the form of a *resonance energy expression*[22] -2β, modified by a *factor* which is somewhat different in the two cases—and plus an added term in the case of Eq. (19). In Eq. (4), the factor is $1/(1 + S)$; in Eq. (19) it is $S/(1 + S^2)$. For a strong bond as in H_2, the difference is not great (for H_2, $1/(1 + S) = 0.57$, $S/(1 + S^2) = 0.48$), but for bonds with smaller S the VB factor leads to the prediction of much weaker bonding than does the LCAO factor; in the VB case, the added term $\frac{1}{2}S^2(J_{aa} - J_{ab})$ acts to cut down the predicted D somewhat further. All in all, the slower variation of D with S indicated by LCAO theory seems to be in much better general agreement with observed bond energies than the more rapid variation suggested by VB theory.[23]

The preceding discussion must now be generalized to the many-electron, polyatomic, case. Here no exact general VB theory expression is available, but for molecules with all electrons paired, at least in rough approximation,[24] conventional VB theory yields

$$D = (C + E') + \underset{\text{bonds}}{\Sigma X_{ij}} - \underset{\substack{\text{non-bonded}\\ \text{pairs}}}{\tfrac{1}{2}\Sigma X_{kl}} - P + RE \quad (20)$$

In Eq. (20), each exchange term X is defined as in Eq. (16), P denotes promotion energy (see below), and RE refers to resonance energy if present. D is now the total energy required to dissociate the molecule (devoid of thermal energy, as at 0°K.) completely into atoms in their ground states (*energy of atomization*).

Equation (20) contains one term of the type X_{ij} for each electron-pair bond in the predominant VB structure, and one term $-\frac{1}{2}X_{kl}$ for *every pair* of electrons *not on the same atom* and *not bonded to each other.* For X_{ij}'s, generalizing from the case of H_2, expressions of the form $ASI/(1 + S)$ will be adopted for the magic formula. The X_{kl}'s may be classified in various ways. For present purposes, they may first be divided into the following two types: (1) *homogeneous:* those involving (as do also the X_{ij}'s) two AO's of the same kind (both σ, or both π); (2) *heterogeneous:* those involving orbitals of different kinds (one σ, one π; or one π^+, one π^-, or one π_x, one π_y).[25] For type (2) X_{kl}'s, $S = 0$, and Eq. (17) shows that these reduce to the relatively simple exchange integrals K_{kl} (*cf.* Eq. (18)); the notation K_{kl} will therefore be used hereafter for the type (2) X_{kl}'s.

The type (1) $\mathbf{H}_{kl}$'s, on the other hand, should according to VB theory be of the same structure (*cf.* Eq. (17)) as the X_{ij}'s. However, comparison with LCAO MO theory suggests a *different* structure for the X_{ij}'s and X_{kl}'s, as can be seen by considering the cases of H_2 and He_2 as special cases of Eq. (21), and comparing with Eq. (4) and (9), respectively:

H_2(VB): $D = (C + E')_{VB} + X_{1s,1s}$;
H_2(LCAO): $D = (C + E')_{LCAO} - 2\beta/(1 + S)$
He_2(VB): $D = (C + E')_{VB} - 2X_{1s,1s}$;
He_2(LCAO): $D = (C + E')_{LCAO} + 4\beta S$

If the terms $C + E'$ are dropped, then in the one case, X corresponds to $-2\beta/(1 + S)$, in the other to $-2\beta S$, a difference of a factor $S(1 + S)$. Since it has already been decided to follow the lead of LCAO theory for the X_{ij}'s, it will make for clarity to adopt at this point a distinctive notation for the two kinds of X's. Accordingly, the X_{ij}'s will still be called X_{ij}'s but the X_{kl}'s will hereafter be called Y_{kl}'s.

IV. Magic Formula

Equation (20) is now ready to be recast to form a basis for the magic formula. For this purpose, (a) the term $(C + E')$ will be considered as absorbed into the other terms (primarily into the X_{ij}'s); (b) the homogeneous X_{kl}'s will be called Y_{kl}'s; (c) the heterogeneous X_{kl}'s, *times* -1, will be called K_{mn}'s; (d) for D, the value D_0 uncorrected for zero-point vibrational energy will be used, since this will be more convenient than a corrected value D_e, and in view of the rough and largely empirical character of the magic formula[26]; (e) the X's and Y's will from here on be considered as semi-empirical functions of the S's, to be so adjusted as to reproduce as nearly as possible the exact D_0 values of actual molecules. Equation (20) now takes the form

$$D_0 = \underset{\text{bonds}}{\Sigma X_{ij}} - \underset{\text{non-bonded pairs}}{\tfrac{1}{2}\Sigma Y_{kl} + \tfrac{1}{2}\Sigma K_{mn}} - P + RE \quad (21)$$

The quantities on the right of Eq. (21) have been so defined that *every letter symbol now stands for an*

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[20] R. S. Mulliken, ref. 7, Eq. (63).

[21] Heisenberg's theory of ferromagnetism assumes $X < 0$ for $3d$–$3d$ bonds between iron or similar atoms at metallic R values. Eq. (19) shows how $X < 0$ might be possible in special cases.

[22] By this is here meant (although the terminology is not very satisfactory) a term such as occurs for H_2^+, where removal of (electron-exchange) degeneracy is not involved. The fact that the "exchange energy" of VB theory owes its negative sign to a predominant term of "resonance" character was pointed out by the writer some time ago (*Chem. Revs.*, **9**, 354 (1931)), but probably is not generally realized.

[23] By reasoning similar to that used in Section II, the VB equation (19) with -2β put equal to cSI suggests the use of a semi-empirical form $AS^2I/(1 + S^2)$ for bond energies. Indeed, this fits the observed D values on the series H_2, Li_2, Na_2, ...better than the form $ASI/(1 + S)$—but not very well. In other cases, the fit is not good. For example, it appears impossible with this form to escape from a computed $D < 0$ for F_2, after necessary antibonding terms are included as described below (Eq. (20) *et seq.*).

[24] *Cf.*, *e.g.*, ref. 15, p. 376, recast in terms of quantities η and X instead of H_{12}. In Eq. (20), multiple exchange integrals and certain other complications have been ignored. It is here assumed that their effects can be taken care of sufficiently well, along with those of the terms $C + E'$, by empirical adjustment of the coefficients in Eq. (21).

[25] Among σ orbitals are ns, $np\sigma$, $nd\sigma$, and hybrids of these. The most usual π orbitals, and the only ones considered in the present paper, are $np\pi$.

[26] Fitted to D_0 values, Eq. (21) can of course reproduce D_0 for only one isotope of a molecule, but the variations of D_0 between isotopes are always less than the uncertainty involved in the roughness of the formula as at present constituted.

intrinsically positive quantity, with possible rare exceptions for the X's.[21]

For molecules in their ground states with all electrons paired, Eq. (21), taken *together with* semi-empirical "magic" expressions for the X and Y terms, now constitutes the magic formula. For the X_{ij}'s as already decided above, LCAO-based expressions

$$X_{ij} = A_j S_{ij} \bar{I}_{ij}/(1 + S_{ij}) \qquad (22)$$

of the form of Eq. (7), are to be used. Here the A's are coefficients to be adjusted empirically, and the $\bar{I}$'s are suitable mean ionization energies (see below). The S_{ij}'s are to be computed theoretically.

Before deciding on a magic form for the Y_{kl}'s, it may be noted that they are of three kinds: (a) lone-pair:lone-pair Y_{kl}'s; (b) lone-pair:bonded-electron Y_{kl}'s; (c) Y_{kl}'s between electrons in different bonds.[27] For the first of these kinds, at least for like lone pairs in the homopolar case,[28] LCAO and VB theory coincide (*cf.* Section II), and the LCAO Eq. (9) may reasonably be adopted as prototype for a suitable magic form. *It will now be assumed,* this time following VB theory, that the same type of expression is equally valid for *all* kinds of Y_{kl}'s.[29]

However, trial and error studies suggest one modification (already discussed in connection with Eq. (9)-(12) in Section II), leading to the magic form

$$Y_{kl} = \nu A_k S_{kl}^2 \bar{I}_{kl} \qquad (23)$$

This form will be adopted and used from here on.[12] The effect of the factor ν, for which values somewhat less than 1 were found to give the best fit to observed D_0's, is to diminish somewhat the importance of the non-bonded repulsions.[30]

Further explanation is now needed as to how to obtain values for certain quantities appearing in Eq. (21)-(23). The K's (*cf.* Eq. (18)) of Eq. (21) are to be obtained theoretically. Fortunately, they are relatively small, so that rough estimates are adequate for the present discussion.[31]

The promotion energy P in Eq. (21) occurs because without it Eq. (21) would in general be valid only for dissociation into certain hypothetical atomic states, with the valence-electron spins completely unpaired, called "valence states."[32] Since valence states in general have higher energies than atomic ground states, the quantity P, equal to the sum ΣP_n of the valence-state promotional energies taken over all the atoms involved, must be subtracted in Eq. (21) in order to give the desired D_0, which has been defined to correspond to dissociation into atoms in their ground states. For the special case of s-univalent atoms (H, Li, *etc.*), ground and valence states are identical ($P_n = 0$).

Often P_n may involve no *configurational* excitation. For example, to obtain trivalent nitrogen, one must "promote" the atom from its s^2p^3, ^4S_u ground state, where the spins of the three p electrons are all parallel, to a trivalent valence state V_3 of the same s^2p^3 configuration. There is required a promotion energy of 1.70 e.v. This kind of promotion might be called *advalent* promotion, that is, *intraconfigurational* promotion from ground state to a valence state.

Trivalent nitrogen gives stronger bonding, however, if there is partial *further* promotion toward the trivalent valence state of the configuration sp^4; that is, s^2p^3, $^4S_u \rightarrow s^2p^3$, $V_3 \rightarrow$ (partially) sp^4, V_3. This second kind of promotion, *extraconfigurational* but without change of valence, and only *partial,* corresponds to a kind of s,p hybridization which Moffitt[33] has called second-order hybridization. These effects might more descriptively be called *isovalent* promotion and *isovalent* hybridization.

Other cases occur in which extraconfigurational and *complete* promotion is accompanied by increase in valence: say, *pluvalent* promotion and *pluvalent* hybridization. Thus for carbon, only advalent promotion (s^2p^2, ^3P_g to s^2p^2, V_2) is required for bivalency, but for tetravalent carbon, pluvalent promotion to sp^3, V_4 or to a related hybrid V_4 state is required (these tetravalent valence states, incidentally, are very considerably higher in energy than the lowest state, ^5S_u, of sp^3). Similarly for bivalent beryllium, pluvalent promotion is required from nullvalent s^2, V_0 (same as s^2, ^1S_g) to sp, V_2 (lying between sp, ^3P_u and sp, ^1P_u).

Valence-state promotion energies are obtainable from spectroscopic data on atoms.[34] Table VIII in Appendix I contains illustrative values for several first-row atoms in valence states suitable for use in

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(27) It may be noted in passing that the K_{mn}'s can be classified in the same way into three kinds.

(28) With reference to *heteropolar* lone-pair:lone-pair repulsions in LCAO theory, if one sets up an LCAO wave function for the artificial case of the interaction of a $1s)^2$ shell on one atom with a $2s)^2$ shell on another, one finds an expression for the interaction energy which is roughly proportional to S^2, just as (*cf.* Eq. (19)) by VB theory.

(29) In general, non-bonded repulsions appear in a very different guise in LCAO theory from that in VB theory: see R. S. Mulliken, *J. Chem. Phys.*, **19**, 912 (1951), where it is pointed out that direct antibonding effects and "forced hybridization" effects in LCAO theory apparently constitute the respective analogs of the lone-pair: lone-pair and the other kinds of non-bonded repulsions of VB theory.

(30) This seems not unreasonable. The flexibility introduced by the adjustable A's takes care roughly of the various errors involved in the use of the simple approximation (22) for the bonding terms; in particular, the effect of the bonding parts of the omitted terms $C + E'$ of Eq. (20). The factor ν then gives in the simplest way some further flexibility in representing the non-bonded repulsions. Earlier workers (*cf., e.g.,* H. M. James, *J. Chem. Phys.*, **2**, 794 (1934)) have also felt that VB theory predicts somewhat too large non-bonded repulsions as well as too small bonded attractions.

(31) Formulas for computing the K's involving $1s$, $2s$, and $2p$ Slater-type A0's are given in a paper by K. Rüdenberg, *ibid.*, **19**, 1459 (1951). For the present paper, a rough procedure was used, whereby SCF-AO K's for N_2, O_2, F_2, and CH were estimated from related Slater-AO K's given for C=O bonds in CO_2 by J. F. Mulligan, *ibid.*, **19**, 347 (1951). Taking $K_{\pi O s C}$ and $K_{\pi C s O}$ as an example, their average (0.37 e.v.) may be taken as characteristic for C=O and used as a basis to estimate $K_{\pi s}$ for N_2, O_2 and F_2. In a similar way, values for $K_{\pi\sigma}$ (0.56 e.v.) and $K_{\pi\pi'}$ (0.041 e.v.) for C=O were obtained, whereas $K_{\pi,1s}$ was found negligible. To estimate K values for N_2, O_2 and F_2, it was assumed that they differ from those for C=O in the ratios of the squares of the overlap integrals S_{ss}, $S_{s\sigma}$ and $S_{\pi\pi}$ for $K_{\pi s}$, $K_{\pi\sigma}$ and $K_{\pi\pi'}$, respectively. The integral $K_{s\pi,\sigma\pi}$ was treated similarly. Since in the present paper, X's, Y's and K's corresponding to SCF-AO's are desired, the squares of ratios of estimated (*cf.* footnote 42) SCF-AO S's for N_2, O_2 and F_2 to Slater-AO S's for C=O were used. The same sort of procedure was used also for C—C, C=C and C≡C bonds. To estimate the CH integral $K_{\pi h}$ (between $2p\pi_C$ and $1s_H$), the Mulligan $K_{\pi s}$ for C=O (0.37 e.v.) was multiplied by the square of the ratio of $S^{SCF}_{(2s_C,1s_H)}$, to $S^{Slater}_{(2s_C,2s_O)}$, giving 0.68 e.v.

(32) See footnote 14 of reference given in footnote 4.

(33) W. Moffitt, *Proc. Roy. Soc.* (*London*), **202A**, 534 (1950); and further reference to Moffitt in Appendix II below.

(34) R. S. Mulliken, *J. Chem. Phys.*, **2**, 782 (1934).

linear molecules.[35] Table IX in Appendix I contains additional valence-state promotion energies, suitable for tetravalent carbon in molecules of several types of symmetry. Use will be made of Tables VIII and IX later in this paper.

The resonance energy *RE* in Eq. (21) refers first of all to resonance energy in the usual sense, as for example in benzene.[36] But it may sometimes include further terms. In particular, when one uses Eq. (21) for carbon compounds in which tetravalent carbon is assumed, with P_n values from Table IX, one underestimates *D*. As Voge has shown,[37] methane is about 1.3 e.v. more stable because the carbon is very considerably more in the s^2p^2 condition than if it were purely tetravalent with tetrahedral AO's. This difference may be regarded with Eq. (21) as *demotional* resonance energy, to be added as part of the *RE* term after the bond energy has been obtained for pure tetrahedral valence.

For any molecule with polar bonds, a *polar RE* term must also be included in Eq. (21). These polar *RE* values would presumably be of the same orders of magnitude as the observed deviations from additivity of bond energies for heteropolar bonds, used by Pauling in setting up his electronegativity scale.[38]

A procedure is now needed for obtaining the mean *I* values in Eq. (22) and (23). On the basis of rough theoretical considerations[39,40] and of simplicity and empirical acceptability, each $\bar{I}$ is to be obtained by averaging (1) intratomically, for each AO, over (*valence-state*) *I* values, obtained from spectroscopic data,[34] for all electrons in the same valence shell as the given AO; (2) then interatomically.[40,41]

The *S*'s in Eq. (22)–(23) may be taken from theoretically computed tables.[14] Extensive trials were made first using *S*'s based on Slater AO's, and then on SCF AO's. The latter should of course be more accurate, and after numerous trials it was tentatively concluded that they must be used, and they have been used below,[42] although it had been hoped at first that the much simpler Slater *S*'s would give acceptable results.

Since most of the terms in Eq. (21), likewise the *S*'s in Eq. (22)–(23), depend on *R* values, it needs to be emphasized that Eq. (21)–(23) are intended here to be used primarily for molecules with their bonds at equilibrium lengths; and the *S* values are to be computed, and the *A* values and ν determined, to fit this situation. However, the possibility that Eq. (21)–(23) can be extended or adapted to reproduce interatomic potential curves over considerable ranges of bond distances may well deserve exploration.[43,44]

Moreover, it is to be noted that the *non-bonded* repulsion (Eq. (23)) and attraction terms, the *Y*'s and *K*'s, are not limited in their validity to any particular range of *R* values. Thus they should be capable as they stand of representing closed-shell interactions and the repulsion potentials of steric hindrance for varying configurations of non-bonded atoms (here see last paragraphs of Section II, and ref. 4).[45]

V. Magic Formula for Special Cases

The magic formula Eq. (21)–(23) is applicable for molecules in their ground states with all electrons paired. It can, however, easily be modified to include several other cases.

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[35] See also footnote 33.

[36] If the term "resonance energy" is used in a strict sense, some resonance energy is present for nearly all molecules, since in general numerous "excited" and "ionic" VB structures mix to some extent into the usual single predominant ground-state structure. However, the corresponding numerous small "normal" resonance terms are covered (as part of the E' term in Eq. (20)) in the empirical adjustment of the *A*'s and perhaps especially ν in Eq. (22) and (23). Hence, *RE* in Eq. (21) corresponds only to "excess" resonance energy above normal, which is really what is usually meant by the term "resonance energy."[74]

[37] H. H. Voge, *J. Chem. Phys.*, **4**, 581 (1936); **16**, 984 (1948). See also Kotani and Siga, *Proc. Phys. Math. Soc. Japan*, **19**, 471 (1937).

[38] See, *e.g.*, L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940.

[39] Referring to Eq. (2) for the case of homopolar bonding, it is seen that insofar as τ is its major term, the quantity β is the potential energy of a charge of magnitude *S*, located in the overlap region, in a field of potential u_b. If then -2β is put equal to *ASI* (Eq. (5)), the *I* used should be so chosen as to be a measure of the magnitude of u_b in the overlap region. But since u_b in this region depends on *all* the electrons in the outer shell, an *I* averaged over the latter is suitable (Rule (1) for $\bar{I}$). A similar analysis for the heteropolar case (*cf.* Ref. 7, Sections 15–16), leads again to Rule (1), *plus* Rule (2). The foregoing arguments are directly applicable to the bonding terms X_{ij} in Eq. (21) and to Y_{kl} repulsions between like lone pairs (*cf.* Eq. (8), (9)). It is here *assumed* that the same kind of argument based on the form of β in Eq. (2) can be extended to *all* Y_{kl} terms.

[40] The application of Rule (2) to AO pairs differing greatly in *I* deserves further discussion beyond that in footnote 39. Consider for example $Y_{1s,2s}$ between the 1*s* lone pair of carbon and the 2*s* lone pair of fluorine in CF_4. The overlap integral is small but not negligible. Most of the overlap occurs in the region where 1*s* of carbon is strong. The potential in which the overlap charge finds itself is then nearly the same as for a 1s carbon AO, suggesting that *I* for 1*s* carbon should be used. Rule (2), which calls for the arithmetic mean of this and *I* of the outer shell of fluorine, is a compromise between this and the use of a smaller *I* such as for example a geometric mean. Considerable support for Rule (2) for inner-shell:outer-shell Y_{kl}'s is afforded by the magnitudes of K_{mn}'s as estimated theoretically (*cf.* J. F. Mulligan, *J. Chem. Phys.*, **19**, 347 (1951)). That inner-shell:outer-shell repulsions are very large is shown also by the work of H. M. James, *ibid.*, **2**, 794 (1934), on Li_2. Also, a direct estimate by the writer of $Y_{1s,2s}$ for Li_2 gives a result in close agreement with the magic formula expression Eq. (23) with $A = 1.16$, $\nu = 0.7$.

[41] What is meant by Rule (1) should be clear from footnotes *d* of Table VIII and *b* of Table IX. As an example of Rule (2), $\bar{I}_{1s_a2s_b}$ would be $\frac{1}{2}(I_{1s_a} + \bar{I}_{(n=2)b})$.

[42] Actually, SCF *S*'s have been published only for C–C and C–H bonds (*cf.* footnote 14b). In the work below, they were estimated in the following way for N≡N, O=O and F—F bonds. From the Slater μ value for N, O or F, together with the equilibrium *R* value, a Slater ρ value (*cf.* ref. 14a, Table I and Eq. (12)) was determined. The *S* value corresponding to this ρ was then looked up in a table of SCF *S*'s *for carbon–carbon bonds*. This was done for $S(1s,2p\sigma)$ using Table IX of ref. 14b, and for $S(2s,2p\sigma)$, $S(2p\sigma,2p\sigma)$ and $S(2p\pi,2p\pi)$ using Table VI of ref. 14b. *Hybrid S*'s, $S(1s,\beta)$, $S(\beta,\beta)$ and $S(\beta,o\beta)$ were then computed using Eqs. (2), (4), (6) of ref. 14b. [Accurate analytical expressions for 1*s*, 2s, and 2*p* SCF AO's of C, N, O, and (by extrapolation) F have recently been determined by Dr. P.-O. Löwdin, and will soon be published. Direct computation of *S*'s for N_2 and O_2 using these expressions, by Mr. C. W. Scherr in this Laboratory, gives values in satisfactory agreement with those obtained in the manner described above. Details will be published later.]

[43] Note that in general Eq. (21)–(23) are capable of giving a minimum of energy (maximum D_0) as a function of the bond distances, though only if important Y_{kl} terms are present—*not*, for example, for H_2. To make the single term $ASI/(1 + S)$ give a maximum *D* for H_2, one would have to make *A* a suitable function of distance.

[44] In fact, calculations with a preliminary form of the magic formula, as applied to N≡N, N=N, N—N, *etc.*, show that it gives maximum values for *D*, calculated and plotted as a function of *R*, at *R* values very roughly equal to the observed equilibrium values.

[45] Related computations on the variations of exchange energies with bond angle, and their effect on bending vibration frequencies, have been made by various authors using VB theory: *e.g.*, J. H. Van Vleck and P. C. Cross, *J. Chem. Phys.*, **1**, 357 (1934); references in footnote 55 of the present paper; and other more recent articles.

Odd-electron molecules involving what Pauling calls one-electron or three-electron bonds are easily included by using Eq. (6) for the former and Eq. (11)–(12) for the latter instead of Eq. (22), just as in the prototype cases of H_2^+ and He_2^+ for which these equations were developed. Various molecule-ions (*e.g.*, N_2^+, O_2^+) fall under this case.

For radicals containing unused valence electrons, *e.g.*, CH or NH, Eq. (21)–(23) can be used directly, although some care may be needed in determining what valence states and P values are required.

The case of O_2 is somewhat special, but is most easily treated by computing D_0 for the first excited ($^1\Delta_g$) state, to which Eq. (21)–(23) are directly applicable, then correcting to the $^3\Sigma^-_g$ ground state.

For excited states, LCAO theory (Section II) may often be used as a guide in setting up a magic formula.

VI. Determination of A's and ν in Magic Formula; and of Degrees of Hybridization

In order to give empirical reality to the magic formula, Eq. (21)–(23), values of A and ν must first be determined so as to make it fit a few molecules whose D_0 values are reliably known. Predicted D_0 values obtained from the resulting formula can then be checked against empirical D_0 values for additional molecules.

After considerable preliminary exploration, the following plan was adopted for the first step in this procedure. First it was decided to try to get along with only three empirical parameters: A_σ (for all σ bonds and σ–σ non-bonded repulsions), A_π (for all π bonds and π–π non-bonded repulsions), and ν.[25] This plan required a fitting to at least three representative molecules whose D_0 values are reliably known. For this purpose, the molecules CH, O_2, N_2 and F_2 were selected, the first two to be fitted exactly, the last two as well as possible.

For the CH radical, the value D_0 = 3.47 e.v. is known with a high degree of probability, although there may be a very slight possibility that it is 0.1–0.3 e.v. higher (not more).[46] For O_2, the value D_0 = 5.08 e.v. (within about 0.01 e.v.) is certain.[47]

For F_2, there has been some uncertainty about D_0, but there is scarcely any doubt that it is in or close to the range 1.6 ± 0.3 e.v.[48] For N_2, there is perhaps some doubt as to whether D_0 is 7.37 or 9.76 e.v., but the evidence is decidedly in favor of the second of these values, and all other values seem to be definitely excluded.[49]

The magic formula for CH involves only A_σ and ν; for the other three molecules, it also involves A_π. It is convenient then to begin with CH, determining A_σ for each of several assumed ν values; that is, A_σ as a function of ν. Then assuming the same $A_\sigma(\nu)$ for O_2, $A_\pi(\nu)$ is determined. Using $A_\sigma(\nu)$ and $A_\pi(\nu)$, D_0 is computed as a function of ν for N_2 and for F_2,[23] and compared with the empirical D_0 values to obtain a best-compromise ν.

A very interesting by-product of the process of determining A_σ, A_π, and ν is that at the same time the degree of $s,p\sigma$ hybridization α^2 in each of the molecules used must and (to the extent that the magic formula is correct in structure) can be determined (see Sections VII–IX, in particular, Fig. 1 for CH, and its caption).

VII. The Fitting for the CH Radical

The VB electron configuration for CH may be written[14b]

$$k)^2\, h_{0\beta})^2 h_\beta{\cdot}h)\ \pi)$$

where all the AO's but h are carbon atom AO's; h_β and $h_{0\beta}$ are mutually orthogonal $2s,2p\sigma$ hybrids of the forms

$$h_\beta = \alpha s + \beta p\sigma;\quad h_{0\beta} = \beta s - \alpha p\sigma \qquad (24)$$

where $\alpha > 0$, $\beta > 0$ (thus making h_β overlap h more strongly than if $\beta = 0$), with $\alpha^2 + \beta^2 = 1$. The magic formula Eq. (21) becomes

$$D_0 = X_{\beta\mathrm{h}} - Y_{\mathrm{kh}} - Y_{0\beta,\mathrm{h}} + \tfrac{1}{2}K_{\pi\mathrm{h}} - P \qquad (25)$$

if RE is assumed negligible.[50] In each subscript, the first symbol refers to the carbon AO, the second to $1s_\mathrm{H}$. It can be shown (see Appendix II) that P is given by $P_0 + \alpha^2\Delta P$, with P_0 and ΔP having the meaning and numerical values given in Table VIII. Next making use of Eq. (22)–(23), Eq. (25) becomes

$$\begin{aligned}3.47 = D_0 = A_\sigma\{&14.24\, S_{\beta h}/(1 + S_{\beta\mathrm{h}}) - 151\nu S^2{}_{\mathrm{kh}} - \\ &14.24\nu\, S^2{}_{0\beta,\mathrm{h}}\} - \alpha^2\Delta P + \tfrac{1}{2}(K_{\pi\mathrm{h}} - P_0) \qquad (26)\end{aligned}$$

The numbers 14.24 and 151 are average I values as required, being, respectively, $\frac{1}{2}(\bar{I}_\mathrm{L} + I_\mathrm{H})$ and $\frac{1}{2}(I_\mathrm{K} + I_\mathrm{H})$, where $\bar{I}_\mathrm{L}$ and I_K refer to carbon and are taken from Table VIII, and I_H = 13.60 e.v.

Since ν cannot yet be determined, trials were made for each of the four assumed ν values 1.0, 0.85, 0.70 and 0.55. The right side of Eq. (26) is a sum of three groups of terms: first, $A_\sigma\{\cdots\}$, which, with ν assumed fixed, depends on two adjustable quantities, namely, A_σ and α^2; second, $-\alpha^2\Delta P$, which is a constant times α^2; third, $(\frac{1}{2}K_{\pi\mathrm{h}} - P_0)$, a constant. For each assumed value of ν, values of A_σ and α satisfying Eq. (26) were simultaneously determined by a graphical procedure described in the caption of Fig. 1.

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(46) The value 3.47 e.v. for the $^2\Pi$ ground state of CH (and 3.52 e.v. for CD) was determined from predissociation in the v = 0 and 1 levels of the $^2\Sigma^-$ excited state by T. Shidei, *Jap. J. Phys.*, **11**, 23 (1936), and confirmed by others. This value is accepted by Herzberg (*cf.* footnote 47) and by Gaydon. On the other hand, by a Birge–Sponer extrapolation of the vibrational levels of the $^2\Sigma^-$ state, one obtains 3.70 e.v. as a probable upper limit to D_0. (That the $^2\Pi$ is the ground state is shown by the occurrence of absorption from it in interstellar space.)

(47) *Cf.* G. Herzberg, "Spectra of Diatomic Molecules," Second Edition, D. Van Nostrand Co., Inc., New York, N. Y., 1950.

(48) R. N. Doescher, *J. Chem. Phys.*, **19**, 1070 (1951), and references given there. Evans, Warhurst and Whittle, *J. Chem. Soc.*, 1524 (1950). H. J. Schumacher, *C. A.*, **45**, 2300^4 (1951).

(49) *Cf.* G. B. Kistiakowsky, *J. Am. Chem. Soc.*, **73**, 2972 (1951); A. E. Douglas and G. Herzberg, *Can. J. Phys.*, **29**, 294 (1951). The latter work definitely eliminates all values but 7.38 and 9.76 e.v.; the former work seems to be incompatible with the smaller value. Considerations on the nature of active nitrogen advanced by G. Cario and L. H. Reinecke, *Abh. Braunschw. Wiss. Gesell.*, **1**, 8–13 (1949), also strongly favor 9.76 e.v. But in favor of 7.38 e.v., see H. D. Hagstrum, *Rev. Modern Phys.*, **23**, 185 (1951).

(50) If the C–H bond were strongly polar, there would be an appreciable RE. To estimate the polarity, one needs the relative electronegativity of C and H for an $h\beta$–$1s$ bond. As was pointed out some time ago (*cf.* footnote 34), the electronegativity of carbon depends strongly on the degree of s,p hybridization α^2 in the carbon bond orbital. As it happens, α^2 as deduced below for $h\beta$ in CH (*cf.* Table I) is such that carbon $h\beta$ and hydrogen $1s$ are almost equally electronegative. Thus the assumption $RE = 0$ is justified.

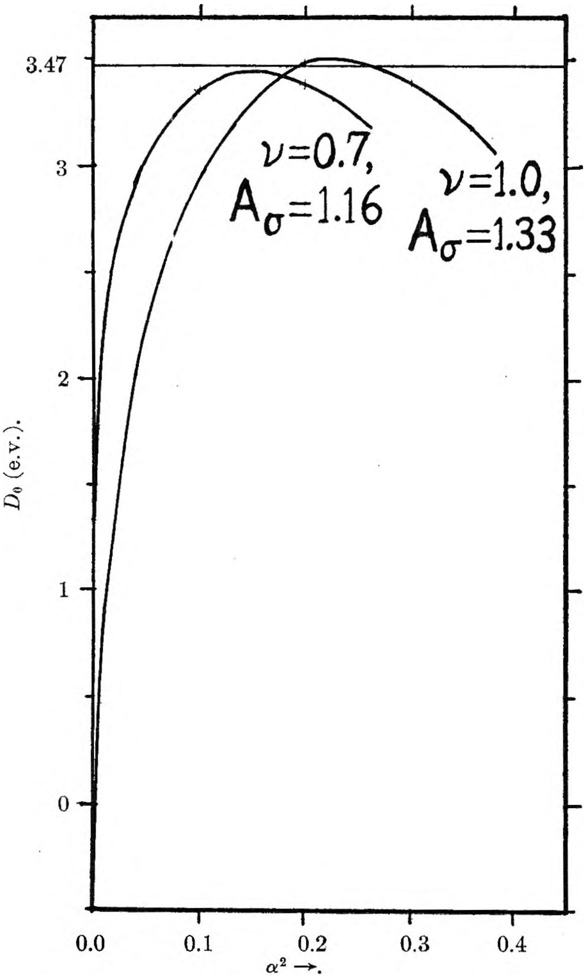

Fig. 1.—D_0 for CH computed using the right side of Eq. (26), and plotted as function of degree of hybridization α^2 in the carbon bonding AO h_β (*cf.* Eq. (24)), for each of two assumed values of ν (0.7 and 1.0). For each graph, the ordinate scale has been adjusted (by adjusting the value of A_σ) until the maximum ordinate of the graph is equal to the empirical D_0 of 3.47 e.v. (left side of Eq. (26)). In this way, for any assumed value of ν, a simultaneous determination is made of those values of A_σ and α^2 which can reproduce the empirical D_0. In this procedure, the final α^2 has the character of an eigenvalue. For the *correct* value of ν, the α^2 value so determined should be the actual degree of hybridization, if the magic formula is essentially correct in form. (To make the curves have their maxima exactly at 3.47 e.v., A_σ should be slightly increased for ν = 0.7, slightly decreased for ν = 1.0; but there is no point in determining A_σ to more than two decimals.)

The necessary S values, for any α value, were first looked up in published tables,[51] P_0 and ΔP were taken from Table VIII, and $K_{\pi h}$ was taken as 0.8 e.v.[52]

The graphical eigenvalue procedure used in Fig. 1 needs justification. First of all, it should be noted that it is not necessary that the procedure be valid except near the correct value of ν (which, moreover, need not at first be known), and the following reasoning is to be understood as applying only to that value of ν. Suppose, then, that one is working with a magic formula, including correct values of ν and A_σ, such that when the degree of hybridization existing in the true molecular wave function is assumed, the formula will correctly reproduce the true bond energy. Under these circumstances, an *exact* formula for the energy of the true wave function and of others differing from it only in degree of hybridization would show a maximum D_0 (minimum total energy) for the true degree of hybridization. If the structure of the magic formula represents approximately correctly the various elements which combine to give the final D_0, it should show essentially the same property. If the magic formula were really bad, it might give no maximum at all for D_0 as function of α, and the fact that it actually gives well-defined maxima (*cf.* Fig. 1) is reassuring. The writer feels that if coefficients for the magic formula can be obtained by the procedure described, such that observed D_0 values for a reasonably large and varied group of molecules can subsequently be reproduced, then both the formula *and* the procedure are probably valid to a reasonable degree of approximation.

The results obtained for CH are summarized in Table I. In Table II, details of the individual terms in Eq. (25) and (26) for D_0 of CH are given, for the parameter values (ν = 0.7, A_σ = 1.16) later adjudged to be about correct. This tabulation gives a vivid picture of how the various bonding, repulsive, and promotion terms combine to give the final resultant D_0.

TABLE I

VALUES OF A_σ AND α^2 FOR CH AS FUNCTION OF ASSUMED VALUE OF ν

ν	1.0	0.85	0.70	0.55
A_σ	1.33	1.25	1.16	1.07
α^2	0.22	0.20	0.155	0.10

TABLE II

STRUCTURE OF D_0 FOR CH IF ν = 0.7, A_σ = 1.16[a]

	$\alpha = 0$	$\alpha^2 = 0.155$
$S_{\beta h}$	0.509	0.686
S_{kh}	0.071	0.071
$S_{0\beta, h}$	0.553	0.308
$X_{\beta h}$ (ev.)	5.57	6.73
$-Y_{kh}$	−0.62	−0.62
$-Y_{0\beta, h}$	−3.54	−1.09
$-\alpha^2\Delta P$	0.00	−1.46
$\frac{1}{2}K_{\pi h}$	0.40	0.40
$-P_0$	−0.49	−0.49
D_0	1.32	3.47

[a] See Table VIII for P_0 and ΔP, ref. 51 for S values, ref. 52 for $K_{\pi h}$, Eq. (25)–(26) for magic formula.

A comparison, for ν = 0.7, between the results computed for the case of no hybridization (α = 0) and for the probable actual hybridization (α^2 =

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(51) *L.c.*, ref. 14b, Table XI (SCF values) for $S_{\beta h}$ and $S_{0\beta, h}$ (positive hybrids for $S_{\beta h}$, negative hybrids for $S_{0\beta, h}$); ref. 14a, Table IV, for S_{kh} values.

(52) J. R. Stehn, *J. Chem. Phys.*, **5**, 186 (1937), and G. W. King, *ibid.*, **6**, 378 (1938), applied VB theory in instructive studies of CH, NH, OH and FH. Using atomic and molecular spectroscopic data, they obtained empirical values for various exchange and Coulomb energies. However, they made assumptions (including neglect of inner-shell non-bonded repulsions, and *no hybridization*), which in the light of the present work render very questionable the meanings of the numerical values they obtained. However, their value of 0.8 e.v. for $K_{\pi h}$ (J_π in their notation) appears free from serious objection. It agrees well with the value 0.68 e.v. estimated semi-theoretically at the end of footnote 31 above.

0.155) likewise shows vividly the importance of the relatively small amount of isovalent hybridization in stabilizing the molecule (see Fig. 1 and Table II). Moffitt,[33] using VB theory with semi-empirical values of the necessary exchange integrals (instead of Eq. (22) and (23)), and maximizing the bond energy with respect to degree of hybridization in essentially the same way as here, has obtained similar results (α^2 about 0.1 for CH; he has also discussed NH and OH). Noteworthy in Table II is the fact that hybridization is effective in two ways, namely, by *increasing* the size of bonding term $X_{\beta \mathrm{h}}$ and by *decreasing* the magnitude of the non-bonded repulsion term $-Y_{0\beta,\mathrm{h}}$.

VIII. The Fitting for O_2

Since the $^3\Sigma^-{}_g$ ground state of O_2 is a somewhat special case in terms of VB theory, it will be more convenient to make a fitting to the first excited, $^1\Delta_g$, electronic state, whose VB electron configuration[14b] is

$$k)^2\ k)^2\ h_{0\beta})^2\ h_{0\beta})^2\ h_\beta{\cdot}h_\beta)\ \pi{\cdot}\pi)\ \pi')^2\ \pi')^2 \qquad (27)$$

with one h_β–h_β bond and one π–π bond[53]; h_β and $h_{0\beta}$ are as defined in Eq. (24). For the $^1\Delta_g$ state, D_0 is less by its known excitation-energy (0.98 e.v.)[47] than D_0 (5.08 e.v.) of the $^3\Sigma^-{}_g$ state. Eq. (21) now takes the form

$$\left.\begin{aligned} 4.10 = D_0 = (X_{\beta\beta} + X_{\pi\pi}) - (2Y_{\beta,0\beta} +{}& \\ 2Y_{0\beta,0\beta} + 2Y_{k\beta} + 4Y_{k,0\beta} + 2Y_{\pi\pi}) + (3K_{\beta\pi} +{}& \\ 6K_{0\beta,\pi} + 6K_{k\pi} + 2K_{\pi\pi'}) - 2(P_0 + \alpha^2\Delta P)& \end{aligned}\right\} \qquad (28)$$

with P_0 and ΔP as given for the V_2 valence states of the oxygen atom listed in Table VIII.[54]

In Eq. (28), $K_{k\pi}$ is negligible and can be dropped. Further, it is convenient to rewrite some of the other terms as follows (the relations stated are easily proved)

$$2(Y_{k\beta} + Y_{k,0\beta}) = 2(Y_{ks} + Y_{k\sigma});\ 3(K_{\beta\pi} + K_{0\beta,\pi}) = 3(K_{s\pi} + K_{\sigma\pi}) \qquad (29)$$

The terms in Eq. (28) can then be usefully regrouped as

$$4.10 = D_0 = C + E(\nu) + F(\alpha) + G(\alpha,\nu) + H(A_\pi,\nu) \qquad (30)$$

where

$$\left.\begin{aligned} C &= -2P_0 + (3K_{s\pi} + 3K_{\sigma\pi} + 2K_{\pi\pi}) \\ E(\nu) &= -2(Y_{ks} + Y_{k\sigma}) \\ F(\alpha) &= -2\alpha^2\Delta P + X_{\beta\beta} + 3K_{0\beta,\pi} \\ &= -2\alpha^2\Delta P + X_{\beta\beta} + \alpha^2K_{\sigma\pi} + \beta^2K_{s\pi} - 2\alpha\beta K_{s\pi,\sigma\pi} \\ G(\alpha,\nu) &= -2(Y_{\beta,0\beta} + Y_{0\beta,0\beta} + Y_{k,0\beta}) \\ H(A_\pi,\nu) &= X_{\pi\pi} - 2Y_{\pi\pi} = A_\pi\bar{I}_L[S_\pi/(1 + S_\pi) - 2\nu S^2{}_\pi] \end{aligned}\right\} \qquad (31)$$

Using Eq. (23) for the Y's and the method of ref. 31 for the K's, C becomes a known constant and $E(\nu)$ a known function of ν. Similarly, $F(\alpha)$ becomes a known function of α. G is an expression which (using Eq. (22) and (23)) is seen to be proportional to A_σ, and also to depend on α and ν, but after inserting the value of A_σ (as determined in Section VIII for CH) corresponding to any one of the ν values 1.0, 0.85, 0.7, 0.55, G becomes a quantity which depends only on α and ν. To obtain the hybrid SCF S's required in computing the Y's by Eq. (23), in C and G, the method of ref. 42 and 51 was used. Finally H, after inserting $\bar{I}_L$ for the oxygen atom from Table VIII, depends only on ν and on the as yet undetermined $A\pi$.

For any assumed value of ν, the complete expression on the right of Eq. (30) now depends (aside from known constants) only on A_π and α. It is then possible, for any particular assumed ν value, to determine A_π and α^2 by the method that was used to determine A_σ and α^2 for CH. The results are included in Table IV.

IX. Definite Determination of Empirical Parameters for the Magic Formula

Determination of Degrees of Hybridization

For the final determination of A_σ, A_π and ν, it is convenient next to compute D_0 for several molecules by the magic formula, for each of the ν values 1.0, 0.85, 0.70, 0.55, using the corresponding appropriate values of A_σ and A_π as determined in Sections VII and VIII. By comparing these computed $D_0(\nu)$ values with empirical D_0 values, one can determine what ν value gives the best average fit. With ν thus fixed, the values of A_σ, A_π, and of α^2 for the molecules considered are determined.

Selecting first the ground states of N_2 and F_2, it may be noted that their electron configurations are formally identical with (27) for the $^1\Delta_g$ state of O_2, except for the π electrons. The respective π partial configurations are

$$\left.\begin{aligned} N_2\!:&\quad \pi{\cdot}\pi)\ \pi'{\cdot}\pi') \\ O_2\!:&\quad \pi{\cdot}\pi)\ \pi')^2\ \pi')^2 \\ F_2\!:&\quad \pi)^2\ \pi)^2\ \pi')^2\ \pi')^2 \end{aligned}\right\} \qquad (32)$$

Equations for N_2 and F_2 corresponding to Eq. (28)–(31) are easily written; values of P_0, ΔP, I_K and $\bar{I}_L$ for use in connection with these equations are found in Table VIII, and the necessary S's and K's are obtained in the manner described for O_2 following Eq. (31). Regarding A_σ and A_π now as known (for any given ν), and D_0 as a quantity to be computed as a function of ν, the analog of Eq. (30) is

$$D_0(\alpha,\nu) = C + F(\alpha) + G(\alpha,\nu) + H(\nu) \qquad (33)$$

with

$$\left.\begin{aligned} C &= (2\text{ or }0)X_{\pi\pi} - 2P_0 + (2\text{ or }4)(K_{s\pi} + K_{\sigma\pi}) + (1\text{ or }4)K_{\pi\pi'} \\ E(\nu) &= -2(Y_{ks} + Y_{k\sigma}) + (0\text{ or }-4)Y_{\pi\pi} \\ F(\alpha) &= 2\alpha^2\Delta P + X_{\beta\beta} + (2\text{ or }-4)K_{O\beta,\pi}; \\ &\qquad \text{for reduction of } K_{O\beta,\pi}\text{, see Eq. (31)} \\ G(\alpha,\nu) &= -2\,(Y_{\beta,O\beta} + Y_{O\beta,O\beta} + Y_{k,O\beta}) \end{aligned}\right\} \qquad (34)$$

Where a choice is given in Eq. (34), the first alternative refers to N_2, the second to F_2. The next step, for either N_2 or F_2, for each assumed ν value, is to plot the computed D_0 against α^2, as in Fig. 1. The *maximum* of each such curve then gives the desired value of D_0 (also of α^2) for the given ν value.

If the electron configuration of CH_4 is written using tetrahedral carbon orbitals[14b,55]

$$k)^2\ te_a{\cdot}h_a)\ te_b{\cdot}h_b) te_c{\cdot}h_c)\ te_d{\cdot}h_d)$$

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[53] One has either $\pi^+{\cdot}\pi^+)\ \pi^-)^2\ \pi^-)^2$ or $\pi^-{\cdot}\pi^-)\ \pi^+)^2\ \pi^+)^2$, the two cases corresponding to the $M_L = -2$ and $+2$ sub-states of the doubly degenerate electronic state $^1\Delta_g$.

[54] For $\alpha = 0$, $\beta = 1$ in Eq. (24), the state of each oxygen atom would be $s^2\sigma\pi\pi'^2$, V_2; for $\alpha = 1$, $\beta = 0$, it would be $s\sigma^2\pi\pi'^2$, V_2. The proof that P for each oxygen atom is $P_0 + \alpha^2\Delta P$ is indicated in Appendix II. A factor two is then required in Eq. (28) since *both* oxygen atoms are promoted.

[55] For some discussions of hydrocarbons using VB methods, see for example, J. H. Van Vleck and A. Sherman, *Rev. Modern Phys.*, **7**, 167 (1935), and references there cited; R. Serber, *J. Chem. Phys.*, **17**, 1022 (1935); W. G. Penney, *Trans. Faraday Soc.*, **31**, 734 (1935)

TABLE III

COEFFICIENTS OF TERMS IN D_0 FORMULAS (EQ. (21)) FOR C_2H_n[a]

	$X_{\beta h}$	$X_{\beta\beta}$	$X_{\pi\pi}$	$-Y_{ss}$	$-Y_{s\sigma}$	$-Y_{\sigma\sigma}$	$+Y_{\beta\beta}$	$-Y_{\pi\pi}$	$-Y_{ks}$	$-Y_{k\sigma}$
$n = 2$	2	1	2	$\frac{1}{2}$	1	$\frac{1}{2}$	$\frac{1}{2}$	0	2	2
$n = 4$	4	1	1	$\frac{1}{2}$	1	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	2	2
$n = 6$	6	1	0	$\frac{1}{2}$	1	$\frac{1}{2}$	$\frac{1}{2}$	1	2	2

	$-Y_{o\beta,h}$	$-Y'_{sh}$	$-Y'_{\sigma h}$	$-Y_{kh}$	$-Y'_{kh}$	$-Y_{hh}$	$-Y'_{hh}$	$-Y''_{hh}$
$n = 2$	1	1	1	2	2	0	0	$\frac{1}{2}$
$n = 4$	2	2	2	4	4	1	1	1
$n = 6$	3	3	3	6	6	3	3/2	3

	$-P_t$[b]	V[c]	$K_{s\pi}$	$K_{\sigma\pi}$	$K_{\pi\pi'}$	$K_{k\pi}$[d]	$K_{\pi h}$	$K'_{\pi h}$
$n = 2$	2	2	2	2	1	4	2	2
$n = 4$	2	2	2	2	1	4	4	4
$n = 6$	2	2	2	2	1	4	6	6

[a] Unprimed exchange terms refer to AO pairs on nearest, singly primed to those on more distant, and doubly primed to pairs on most distant neighbor atoms. The subscripts β refer to *di*, *tr*, *te* for $n = 2, 4, 6$, respectively, $o\beta$ to the corresponding orthohybrids (*cf.* footnote 14b). For C_2H_6, the coefficients given above were worked out on the basis of the *opposed* form (symmetry D_{3h}). [b] See Table IX for the P_t values (cases B', C, D for $n = 2, 4, 6$, respectively). [c] For the computations of Table IV, it is *assumed* that the *RE* correction analogous to the Voge demotional *RE* correction (*cf.* footnote 37) for CH_4 ($V = 1.28$ e.v.) is the same *per carbon atom* in C_2H_n. This must be considered a guesstimate. *Polar RE* corrections for the C–H bonds have been neglected. [d] Negligible.

the magic formula becomes

$$D_0 = 4X_{te,h} - 4Y_{kh} - 2Yo_{te,h} + 4K_{\pi h} - 3Y_{hh} - P(te_4, V_4) + V \quad (35)$$

The terms $-2Yo_{te,h} - 4K_{\pi h}$ come from transformation of a term $-6Y_{te'h}$ corresponding to the 12 non-bonded exchange terms between H atoms and the *te* AO's to which they are not bonded; $K_{\pi h}$ is taken as in ref. 52, except for a slight correction for the smaller C–H distance. P is Voge's value for case D of Table IX and V is Voge's demotional *RE* correction[37] (see Section IV). A *polar RE* term, though probably appreciable, has been neglected in Eq. (35). In computing X and the Y's using Eq. (22)–(23), the S values are obtained as for CH,[51] the I values are $I_H = 13.60$ e.v., $I_K = 288$ (Table VIII), and $\bar{I}_L = 13.68$ (Table IX).

For C_2H_n ($n = 2, 4,$ or 6), the non-bonded exchange terms are very numerous, and the D_0 formulas are best presented in tabular form (Table III).[55] The electron configurations[14b] are

$$\left.\begin{array}{ll} C_2H_6: & k)^2\,k)^2\,te_a{\cdot}h_a)\,te_b{\cdot}h_b)\,te_c{\cdot}h_c)\,te_d{\cdot}te_d^*) \\ & \qquad te_e^*{\cdot}h_c^*)\,te_b^*{\cdot}h_b^*)\,te_a^*{\cdot}h_a^*) \\ C_2H_4: & k)^2\,k)^2\,tr_a{\cdot}h_a)\,tr_b{\cdot}h_b)\,tr_c{\cdot}tr_c^*)\,tr_b^*{\cdot}h_b^*) \\ & \qquad tr_a^*{\cdot}h_a^*)\,\pi_x{\cdot}\pi_x^*) \\ C_2H_2: & k)^2\,k)^2\,di'{\cdot}h)\,di{\cdot}di^*)\,di'^*{\cdot}h^*)\,\pi{\cdot}\pi^*)\,\pi'{\cdot}\pi'^*) \end{array}\right| \quad (36)$$

Many of the non-bonded exchange integrals involving hybrid AO's occur in groups which (by using relations similar to Eq. (29) above) can conveniently and rigorously be transformed into Y's and K's which are largely non-hybrid, and this transformation has been done in preparing Table III.

For H_2 and He_2, Eq. (21)–(23) reduce to Eq. (7) and (10), respectively. For H_2^+ and He_2^+, Eq. (6) and (11)–(12) are respectively applicable.

The results of computations on all the molecules mentioned above, carried out in accordance with the first paragraph of this Section, are presented in Table IV. As will be seen from this Table, the computed D_0 varies rapidly, and in opposite ways for N_2 and F_2, with ν, so that the best ν is rather sharply determined. On the whole, agreement of observed and computed D_0 values is best for about $\nu = 0.7$, with $A_\sigma = 1.16$, $A_\pi = 1.53$. The fact that a compromise ν can be determined at all to fit (even though roughly) such different molecules as N_2 and F_2 gives important support to the *validity of the general structure* of the magic formula.

Excluding H_2 and Li_2 as exceptional,[56] the average difference *per electron-pair bond* between observed and computed D_0 values for $\nu = 0.7$ is about ±0.3 e.v.[57] In view of the presence of only three adjustable parameters in the magic formula, the agreement found is all that one could reasonably hope for, and much too good to be reasonably attributable to accident. As a corollary, this argument indicates that the hybridization coefficients in the $\nu = 0.7$ column in Table IV are probably fairly near the truth.

The following further point is worth emphasizing. Although the specific values for the coefficients in the magic formula were obtained by procedures which some readers may question, the formula with these coefficients now stands on its own merits, independent of these procedures. Its degree of quantitative validity should be judged by its empirical success in representing observed bond energies. One should also bear in mind that the present magic formula is a *first edition*, in need of further test by application to more molecules, and undoubtedly capable of further improvement in various ways (see Section XIII).

X. Validity and Uses of the Magic Formula Procedure

The magic formula has now been implemented with specific values for its coefficients. One may ask: How good is it? What can it be used for?

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(56) The figures on H_2 and Li_2 suggest that a distinct coefficient A_s, with value about 0.7, may be needed for pure s–s bonds, as was proposed in Ref. 4. Or possibly A_σ is anomalous for molecules which have unusually small ξ values, as is true of H_2 and Li_2 (*cf.* second column in Table IV); the fact that proportionality of the theoretically computed LCAO quantity $-\beta$ to S fails when ξ gets small (see Section II: sentence with Ref. 11) suggests this possibility. The discrepancy for F_2 might then possibly be attributed to its exceptionally *large* ξ value. For other possible ways of dealing with H_2, Li_2 and F_2, see also footnote 23 and Section XIII.

(57) If the hydrocarbons, for which both the observed D_0 values and the assumed resonance energies (Table III, footnote *c*) are rather uncertain, were omitted, a somewhat improved fit for the remaining molecules could be obtained with (say) $\nu = 0.75$ (or perhaps 0.85, if A_π is made somewhat smaller than for $\nu = 0.85$ in Table IV, and exact agreement for O_2 is sacrificed).

TABLE IV

COMPUTED D_0 VALUES FROM MAGIC FORMULA

Molecule	ξ[d]	Computed D_0 Values (e.v.)[a,b,c]				Observed D_0 (e.v.)[e]
		ν 1.0	0.85	0.70	0.55	
		A_σ 1.33	1.25	1.16	1.07	
		A_π 3.36	2.28	1.53	0.975	
CH	0.9	3.47	3.47	3.47	3.47	3.47
		(α^2 = 0.22)	(α^2 = 0.20)	(α^2 = 0.155)	(α^2 = 0.10)	
O_2[f]	1.3	4.10	4.10	4.10	4.10	4.10
		(α^2 = 0.14)	(α^2 = 0.12)	(α^2 = 0.09)	(α^2 = 0.06)	
N_2	1.0	27.27	13.70	8.32	4.91	9.76 or 7.37
		(α^2 = 0.31)	(α^2 = 0.26)	(α^2 = 0.21)	(α^2 = 0.15)	
F_2	1.8	−0.46	1.97	3.12	3.82	1.6 ± 0.2
		(α^2 = 0.031)	(α^2 = 0.024)	(α^2 = 0.018)	(α^2 = 0.014)	
H_2^+	1.0	3.32	3.12	2.89	2.66	2.65
H_2	0.7	7.79	7.32	6.78	6.24	4.48
He_2^+	1.7			1.46		2.1 ± 1.0[h]
He_2[g]	1.7	−4.30	−3.66	−3.01	−2.37	(−2.38)[k]
Li_2	0.8			2.06		1.03
CH_4	0.9	17.31	17.64	17.61	17.36	15.02 or 17.30
C_2H_6	1.2	22.05	25.03	26.72	27.62	24.90 or 29.46
C_2H_4	1.0	25.86	24.23	22.79	21.47	19.11 or 23.67
C_2H_2	0.9	31.81	23.83	18.36	14.15	12.90 or 17.46

[a] See text of this Section for methods of computation. [b] The α^2 values given were determined by maximizing the computed D_0 in the manner illustrated in Fig. 1. [c] For the hydrocarbons, α^2 values were *assumed* corresponding to the electron configurations in (36), but demotional *RE* corrections were then included in the computed D_0's to allow for deviations from the assumed states of hybridization. This correction was 1.28 e.v. for CH_4, 2.56 e.v. for all C_2H_n (*cf.* Table III, note *c*). Polar *RE* corrections have been neglected. [d] For definition of ξ, see Eq. (3) of ref. 4. [e] For CH, ref. 46; for F_2 and N_2, ref. 48, 49; for He_2, ref. 4, Table X; for the other diatomic molecules, ref. 47. The values for CH_4 and C_2H_n are based on heats of formation $\Delta H_f°$ for 0°K. taken from the American Petroleum Institute Project No. 47 Tables (15.99 kcal. per mole for CH_4, 16.52 for C_2H_6, −14.52 for C_2H_4, and −54.33 for C_2H_2), combined with D_0 = 4.478 e.v. = 103.2 kcal. for H_2 and, for the heat of sublimation *L* of graphite, either (a) 124 kcal. or (b) 175 kcal. (see footnote 58). 1 e.v. = 23.06 kcal./mole is assumed throughout. [f] $^1\Delta_g$ state. [g] At 1.06 Å. [h] Band-spectrum value, 3.1 e.v., not very reliable (ref. 47); theoretical value, 2.2 e.v. (S. Weinbaum, *J. Chem. Phys.*, **3**, 547 (1935)); electron-impact value, between 1.2 and 2.1 e.v. (J. A. Hornbeck and J. P. Molnar, *Phys. Rev.*, **84**, 621 (1951)). [k] Theoretical.

The first question is discussed at the end of Section IX and in Section XIII.

In answer to the second question: the magic formula, used in connection with the maximizing procedure described above, may be expected to be valuable principally in three ways. They are: (1) as a tool for the approximate computation or estimation of bond energies; (2) as an expression which shows roughly quantitatively how the total energy of atomization results from the addition and subtraction of significant individual terms; (3) in determining approximate degrees of isovalent hybridization. The first of these applications will be considered now, the second in Section XI, and the third in Section XII.

As can be seen from Table IV, the magic formula is not as yet reliable enough to yield conclusive decisions between controversial alternative observed D_0 values, such as occur in several cases (see last column of Table IV). However, it is striking that, no matter what value-pairs A_σ, ν that fit CH are taken, the magic formula always predicts for CH_4 a value of D_0 which agrees closely with the highest of the "observed" D_0 values corresponding to the several competing values[58] for the heat of sublimation of graphite. (Note that A_π is not involved for either CH or CH_4.) In view of the nature of the similarities and differences in the structure of the C–H bond in CH and CH_4 (*cf.* Eq. (25) and Table II; Eq. (35) and Tables III, VI), and in view of the fact that the only possibly needed further corrections to the computed D_0 of CH_4 would probably be polar *RE* corrections which would increase D_0, the definite indication given by the magic formula in favor of the high heat of sublimation of carbon may have real significance.

The magic formula should be applicable to radicals, and so, by the use of differences between heats of atomization for molecules and radicals, should permit the calculation of energies of dissociation *into* radicals.

The magic formula may be helpful also in the prediction of bond energies for excited and ionized molecules.

The formula, either in its present form or after improvement, may also be useful in dealing with non-bonded repulsions (see the last paragraph of Section IV).

XI. The Theoretical Structure of Chemical Bond Energies

Any system of dividing the total energy of atomization of a molecule into a sum of individual terms is more or less arbitrary unless these terms correspond to realizable physical processes—as, for example, if D_0 is expressed as the sum of energies required to remove the atoms one by one in a specified order.[59] Even then, there is no *unique* way of analyzing D_0 into a sum of terms. And even in a

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(58) The extreme values are 124 and 175 kcal. For recent reviews, see H. D. Springall, *Research*, **3**, 260 (1950); H. D. Hagstrum, *Rev. Modern Phys.*, **23**, 185 (1951).

(59) For a recent analysis of these problems, see M. Szwarc and M. G. Evans, *J. Chem. Phys.*, **18**, 618 (1950).

Table V

Terms in Computed N_2 Bond Energy[a] Using the Magic Formula[b]

A1. Constant Terms (Total C)

$2X_{\pi\pi}$	$-2Y_{ks}$	$-2Y_{k\sigma}$	$-2P_0$	$+2K_{s\pi}$	$+2K_{\sigma\pi}$	$+K_{\pi\pi'}$	$=C$
14.97	− 1.04	− 3.24	− 3.40	+ 0.89	+ 1.68	+ 0.10	= 9.96

A2. Terms Including Those Depending on Hybridization

	C	$-2\alpha^2\Delta P$	$+2K_{o\beta,\pi}$	$+X_{\beta\beta}$	$-2Y_{\beta o\beta}$	$-2Y_{o\beta,o\beta}$	$-2Y_{k,o\beta}$	$=D_0$
$\alpha^2 = 0$:	+ 9.96	+ 0.00	+ 0.89	+ 3.26	− 7.15	− 5.96	− 1.04	= −0.04
$\alpha^2 = 0.21$:	+ 9.96	− 5.44	+ 0.03	+ 8.22	− 4.38	− 0.05	− 0.02	= +8.32

B. Distribution of Terms Between σ and π Bonds[c]

		$\alpha^2 = 0$	$\alpha^2 = 0.21$
σ bond:	$X_{\beta\beta} + \frac{1}{2}\Sigma K_{\sigma\pi} - 2P_0/3 - 2\alpha^2\Delta P - \Sigma Y$	−14.57	− 5.78
π bonds:	$2X_{\pi\pi} + K_{\pi\pi'} + \frac{1}{2}\Sigma K_{\sigma\pi} - 4P_0/3$	+14.53	+14.10
Total (D_0)		− 0.04	+ 8.32

[a] *Cf.* Eq. (33)-(34). [b] Eq. (21)-(23) with $A_\sigma = 1.16$, $A_\pi = 1.53$, $\nu = 0.7$ (*cf.* Section IX). [c] For certain terms where the distribution between the σ and π bonds is of necessity rather arbitrary, it has been effected as follows. Of the promotion energy, the amount $2P_0$ is necessary for the trivalent valence state, and it is here assigned one-third to the one σ and two-thirds to the two π bonds. The additional promotion energy $2\alpha^2\Delta P$ is assigned exclusively to the σ bond, since hybridization affects almost exclusively this bond. The mixed terms $K_{\sigma\pi}$ are divided equally between the σ and π bonds.

purely theoretical approach, any attempt to break D_0 down into a sum of terms must ultimately be regarded as merely a matter of convenience for computation or understanding. In spite of all these considerations, everyone recognizes the usefulness of writing D_0 as a sum of terms of more or less theoretical character. Most often, D_0 is calculated as a sum of standard contributions ("bond energies") one for each chemical bond—plus corrections if necessary for "resonance." The standard bond energies are determined empirically to fit observed thermal data.[38]

The present magic formula likewise is a sum of terms, including corrections for "resonance,"[36] and contains coefficients adjusted to make it fit observed thermal data. However, it has (like the VB theory formulas[55] from which it is adapted) a much richer structure than the ordinary additive bond energy formula, and, if soundly based, should afford a much deeper and more detailed theoretical insight into the various factors which determine the total energies of chemical binding, and greater possibilities of prediction. The possibilities of the magic formula for steric hindrance effects have already been mentioned.

Finally, whereas the use of a table of bond energies involves a different empirical bond energy for each kind of bond, the magic formula has a more universal character in that, for all molecules built from first-row atoms, or first-row atoms and hydrogen, it contains only three empirical coefficients. (To cover the whole periodic system, more will doubtless be needed.) To be sure, the magic formula involves also certain other quantities which must be determined: the overlap integrals S, theoretically; the ionization and promotion energies, best from empirical spectroscopic data on atoms.

The way in which the magic formula gives insight into the structure of chemical bond energies can best be appreciated in terms of examples. For this purpose, reference may be made to Table II and Figure I above, for the CH radical, to Table V below, for the N_2 molecule, and to Table VI. Table VB indicates, contrary to the usual idea that π bonds are weak, that the π contribution to the bonding is very large, the sum of the σ contributions actually being strongly *negative*.[60] Comparing the calculated results for $\alpha^2 = 0$ and $\alpha^2 = 0.21$, it further indicates that without isovalent hybridization (which is equivalent—see Table VIII—to partial promotion from s^2p^3 to sp^4 without change of the formal valence three), the bond strength would be very small.

A notable feature of Tables V and VI is the large size of the non-bonded repulsion terms Y_{ks}, $Y_{k\sigma}$, $Y_{k,o\beta}$, etc., involving the inner-shell (1s) electrons.[40] The valence-shell repulsion terms $Y_{\beta,o\beta}$ and $Y_{o\beta,\beta}$ would be large if there were no hybridization ($\alpha^2 = 0$), but are made much smaller by hybridization. Another point of interest is the very considerable positive contributions made by the non-bonded attractions (K terms).

The breakdowns of the total energies of atomization into individual terms in Tables II, V and VI are similar to those presented by Van Vleck, Penney and others some years ago,[61] guided by theoretical computations and by spectroscopic and other empirical data. However, the individual terms are now in many cases much larger. There are two main reasons for this difference: (1) the terms corresponding to inner-shell:outer-shell repulsions earlier were almost always neglected, whereas actually they are probably fairly large[40]; (2) the possibility of hybridization was usually neglected earlier except for CH_4 and C_2H_n, and except for CH, NH and OH in a recent paper by Moffitt.[22] When these two effects are considered, one arrives at much larger bonding terms than when they are ignored.

By making suitable combinations of individual terms in the magic formula, theoretical expressions

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(60) This can be understood as follows. As two nitrogen atoms approach each other, σ bonding first sets in, with little hybridization and only moderate non-bonded repulsions; π bonding is weak because the π overlap integral is small. At closer approach, both hybridization and non-bonded σ repulsions increase. Meantime the π bonding increases so rapidly with increasing π overlap that equilibrium is not established until long after the σ interaction sum has turned negative.

(61) See J. H. Van Vleck and A. Sherman, *Rev. Modern Phys.*, **7**, 167 (1935), for a review; also ref. 37, 52, 55. Reference should also be made to the important work of M. Kotani and collaborators in Japanese journals.

TABLE VI

STRUCTURE OF ATOMIZATION ENERGIES[a]

A. HOMOPOLAR DIATOMIC MOLECULES

Terms in Atomization Energy (e.v.)[b]

		σ,σ Terms			σ,π Terms	π,π and π,π' Terms			Bond energies[c]	
	$-P^d$	X	$(\Sigma_k)^e$	ΣY	ΣK	X	ΣY	ΣK	Gross	Net
F_2	−0.80	6.25	(−0.25)	−1.91	0.83	...	−1.29	0.04	3.92	3.12
O_2	−4.31	7.95	(−1.60)	−5.50	2.21	6.29	−2.62	.08	9.39[b]	5.08[f]
N_2	−8.84	8.22	(−4.30)	−8.73	2.60	14.97	....	.10	17.16	8.32

B. HYDROCARBON MOLECULES[g]

1. CH_m Intragroup Terms (e.v. per C-H Bond)

	σ,h Terms			h,h	π,h
	X	$(\Sigma Y_k)^e$	ΣY	ΣY	ΣK
CH	6.73	(−0.62)	−1.71	....	0.40
CH_4	6.66	(− .70)	−1.00	−0.65	.82
C_2H_6	6.63	(− .68)	−0.97	− .44	.83
C_2H_4	6.77	(− .74)	− .90	− .18	.86
C_2H_2	6.91	(− .79)	− .80	....	.89

2. Intergroup Terms (e.v. per Molecule)

	H-H and C-H Terms				C-C Terms						
	h,h	σ,h		π,h	σ,σ Terms			σ,π	π,π and π,π'		
	ΣY	$(\Sigma Y_k)^e$	ΣY	ΣK	X	$(\Sigma Y_k)^e$	ΣY	ΣK	X	ΣY	ΣK
C_2H_6	−0.56	(−0.07)	−2.86	0.36	6.20	(−1.38)	−2.16	1.86	...	−1.20	0.06
C_2H_4	− .21	(− .07)	−2.26	.30	6.72	(−2.54)	−3.43	2.48	5.56	−0.96	.09
C_2H_2	− .01	(− .02)	−0.67	.09	7.22	(−4.23)	−4.80	2.96	12.45	...	.13

C. HYDROCARBON BOND ENERGIES (EV.)[h]

		C—H Bonds		C—C, C═C, or C≡C	
	$-P + RE^k$	Gross	Net	Gross	Net
CH	−1.95	5.42	3.47		
CH_4	−1.42	5.82	4.40		
C_2H_6	−1.42	5.75	4.33		
	−2.845			3.51	0.67
C_2H_4	−1.465	6.25	4.79		
	−5.86			9.48	3.62
C_2H_2	−1.63	6.85	5.22		
	−9.765			17.67	7.91

[a] Computed by magic formula with coefficients as in $\nu = 0.7$ column of Table IV. The terms are grouped by type (X, Y, K, P) and by category (σ,σ; σ,π; *etc.*), in a way which will be made clear by comparison with the detailed table of terms for N_2 (Table V, with $\alpha^2 = 0.21$). [b] The nature of the terms in detail can be seen in Eq. (28)–(31) for O_2, Eq. (33)–(34) for N_2 and F_2 (also Table V for N_2). [c] The *net* bond energy is the sum of *all* the terms listed (except the Y_k's (*cf.* footnote *e*), which are included in the ΣY's). The *gross* bond energy is the sum obtained excluding $-P$ and so corresponds to the energy of formation from the promoted valence state. [d] P is $2P_0 + 2\alpha^2\Delta P$ with P_0 and ΔP from Table VIII and α^2 from Table IV ($\nu = 0.7$ column). [e] These sums represent *those portions of* the immediately-following ΣY's which result from non-bonded repulsions between the inner shell (K shell, $1s^2$ or k^2) electrons of one atom and the valence electrons of its neighbor. They are separately listed to show their frequently large magnitude. [f] Here for the $^3\Sigma^-_g$ ground state of O_2, an additional term +0.98 e.v. (determined empirically from the molecular spectrum) has been included, equal to the extra bond energy of the $^3\Sigma^-_g$ state as compared with the $^1\Delta_g$ state for which the magic formula computation was made. [g] In CH_4, and within each CH_m group in C_2H_n ($m = n/2$), there are C—H terms (intragroup σ,h and π,h in Table VIB) and H—H terms (intragroup h,h in Table VIB). In addition, there are in C_2H_n also intergroup terms of three kinds: H—H terms, between one H_m group and the other; C—H terms (σ,h and π,h) between H_m in one group and carbon atom electrons of the other; and carbon–carbon terms of various categories. (See Eq. (25) and Table II for CH, Eq. (35) for CH_4, and Table III for C_2H_n, for a complete listing of all these terms; *cf.* also footnote 55.) [h] Each C—H bond energy is taken (*cf.* footnote 55) as one m^{th} of the sum of the following terms: (a) all intragroup C—H and H—H terms in CH_m; (b) all intergroup H—H terms; (c) one-half the sum of the intergroup C—H terms. Each C—C or C═C or C≡C bond energy is taken (*cf.* also footnote 55) as the sum of (a) one-half the sum of the intergroup C—H terms; (b) the total of all C—C terms. For each *net* bond energy, a term (*cf.* footnote *k* below) $-P + RE$ from the second column is included; for the *gross* bond energies, these promotion terms are omitted. [k] The values in this column are all *per bond* (C—H or C—C or C═C or C≡C). For CH, $RE = 0$ and $-P = -P_0 - \alpha^2\Delta P$, with P_0 and ΔP as in Table VIII, and $\alpha^2 = 0.155$ (*cf.* Table I). For CH_4, $-P + RE$ is *one-fourth* of $(-6.97 + 1.28)$, where 6.97 e.v. is the tetrahedral promotion energy P_t of carbon (Table IX, case *D*), and 1.28 e.v. is the Voge resonance energy (RE) correction V (see Section IV and Ref. 37). Similarly for C_2H_n (somewhat arbitrarily), the amount $-(P_t - V)/4$ is assigned to each individual *electron-pair-bond terminus* ending on carbon; hence $-(P_t - V)/4$ to each C—H bond and $-(a/2)(P_t - V)$ to the carbon–carbon bond, with $a = 1, 2, 3$ for C_2H_6, C_2H_4, and C_2H_2, respectively; note that P_t differs somewhat in the three molecules (see Table III, especially footnotes *b*, *c*); *cf.* also footnote 55.

or numerical values can be obtained which are counterparts of the ordinary "bond energies." In the case of diatomic molecules, the bond energy is the same as the atomization energy, hence is the sum of all terms in the magic formula. For polyatomic molecules, as illustrated by the hydrocarbons C_2H_n in Table VIC, there is some arbitrariness (especially for the promotion energy corrections) in dividing the total atomization energy among the carbon–hydrogen and carbon–carbon bonds.[62]

The ordinary assumptions[38] of approximate constancy and additivity of standard bond energies

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(62) For earlier VB theory discussions of the division of D_0 among bond energies, see ref. 55, especially the paper by Serber.

have been criticized by Serber[62] and others.[59] It will be noted that the magic formula yields definite bond energies which are not necessarily constant or additive; but in particular cases where they actually *are so*—as for example in a series of molecules such as the normal paraffins—it should be able to show the reasons why; and in cases where they *are not*, it should make clear the reasons. Here the magic formula (preferably in a future improved edition, including if possible a systematic formulation of the RE term) should give interesting insights. As an example, using the present magic formula—and probably significant in spite of the latter's limitations—Table VIC shows approximate equality of C–H bond strengths for CH_4 and C_2H_6—a relation which presumably would extend also to the higher paraffins—but somewhat varying C–H bond strengths for other types of hydrocarbons.

As Van Vleck clearly pointed out in the case of hybrid carbon bonds,[63] it is useful to distinguish between *gross* bond energies, referred to atoms in suitable valence states, and *net* bond energies, representing what is left after promotion energy deductions have been made.[62] Gross bond energies are truer measures of real or *intrinsic* bond strengths, and it is with these rather than with net bond energies that equilibrium distances and force constants should tend to be correlated. (This idea should, however, be applied with caution, since degrees of hybridization or promotion may often vary appreciably with interatomic distances even near equilibrium; for sufficiently *large* distances, of course, they *must* change.)

Table VI lists both gross and net bond energies for a number of bonds, as computed using the magic formula based on the $\nu = 0.7$ column of Table IV. Interesting, and probably significant in spite of the preliminary character of the present magic formula, is the slowly increasing C–H bond strength from CH to CH_4, C_2H_6, C_2H_4 and C_2H_2, in spite of a nearly constant primary bonding term $X_{h\beta}$.[64] For the carbon–carbon bonds,[62] the computed variation from C—C to C=C to C≡C in Table VIC seems to be too rapid, and this impression is confirmed by reference to Table IV, where the computed atomization energy (for $\nu = 0.7$) is relatively too small for C_2H_6 and too large for C_2H_2, as compared with the observed values.[65]

An interesting problem is the possible resolution of the (net or gross) bond energy of a double or triple bond into a σ bond energy plus a π bond energy or bond energies. Unfortunately there is no uniquely justifiable logical basis for doing so. Nevertheless, it can be done in one or another way if one is willing to accept a considerable degree of arbitrariness (particularly so for net bond energies) in making fractional assignments of some of the terms in D_0 partly to the σ and partly to the π bonds. The terms in question include the promotion energy, the σ,π K terms, and in C_2H_n the H-H and C-H intergroup terms of Table VIB.[62] One way of making such a division is illustrated by Table VB for the nitrogen molecule. This makes the σ net bond energy *negative* in the N_2 triple bond, and the π net bond energy very large and positive.[60] Applying the same method also to other molecules listed in Table VI, one would obtain as a general result that σ net bond energies are positive for single bonds, near zero in double bonds, negative in triple bonds. The σ gross bond energies appear to be always positive.

A very arbitrary but simple way to obtain separate σ and π bond energies is to use the assumption of constancy of bond energies, including equality of energies of σ bonds in single and multiple bonds. Although this procedure cannot be logically justified, and is seriously at variance with the results of the magic formula approach, a few results obtained by it may be of interest for comparative purposes (see Table VII; the assumption of constancy of σ bond energies is embodied in footnote *b* of the Table).

TABLE VII

σ AND π BOND ENERGIES

Assuming Constancy of C–H and C–C σ Bond Energies[a]

Bond	Type	Bond energies B (e.v.) Net[b]	Gross[c]
H—H in H_2	σ	4.48	4.48
C—H in CH_4	σ	3.78 or 4.35	5.20 or 5.77
C—C in C_2H_6	σ	2.41 or 3.55	5.26 or 6.40
C=C in C_2H_4	σ	[2.41 or 3.55][d]	
	π	1.69 or 2.83	4.62 or 5.76
C≡C in C_2H_2	σ	[2.41 or 3.55][d]	
	π	1.48 or 2.62	4.74 or 5.88

[a] This material was first presented at a meeting in 1942 (footnote 3), and was later published in part in Ref. 7 (see footnotes** to Tables V and VII there). See also footnote 62. [b] Obtained as follows (and see Table IV), footnote *e*):

$B(C_mH_n) = \Delta H_f^\circ(C_mH_n) + mL + \frac{1}{2}nD_0(H_2)$

$B(C—H) = \frac{1}{4}D_0(CH_4)$; $B(C—C) = D_0(C_2H_6) - 6B(C—H)$

$B_\pi(C{=}C) = D_0(C_2H_4) - 4B(C—H) - B(C—C)$

$B_\pi(C{\equiv}C) = \frac{1}{2}[D_0(C_2H_2) - 2B(C—H) - B(C—C)]$

[c] $B(\text{gross}) = B(\text{net}) + \frac{1}{4}m(P_t - V)$, with $m = 1$ for CH_4, 2 for C_2H_n, and $V \equiv 1.28$ e.v. (*cf.* Table VI, footnote *k*), with P_t values from Table IX. [d] Assumed.

XII. Degrees of Hybridization and Bond Properties

Recently evidence has appeared from a number of sources indicating the essential importance of isovalent hybridization (*i.e.*, partial hybridization without increase of formal valence—see Section IV) for the energy and other properties of many molecules. One of the most interesting aspects of the magic formula, taken in connection with the procedure for maximizing D_0 as a function of degree of isovalent hybridization, is its ability to yield information about the latter quantity (see Table IV, $\nu = 0.7$ column, for results on CH, N_2, O_2 and F_2). Moffitt[33] has already applied a similar procedure to CH, NH and OH, using a conventional VB formula with smaller values than here for the X's and Y's, and neglecting the Y_k's;[61] he obtained calculated

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(63) *Cf.* ref. 61, p. 195; also ref. 37.

(64) For an earlier VB calculation, based on similar consideration of varying hybrid character in the carbon bonding AO in the C–H bond, and in the bond energy of the latter, see T. Förster, *Z. physik. Chem.*, **43B**, 58 (1939), in particular the Fig. In a recent semi-empirical analysis relating bond energies to bond distances, G. Glockler (*J. Chem. Phys.*, **16**, 842 (1948)) also obtains similar results.

(65) Possibly hyperconjugation (R. S. Mulliken, C. A. Rieke and W. G. Brown, *J. Am. Chem. Soc.*, **63**, 41 (1941)) is partly responsible. However, the authors mentioned estimated the hyperconjugation energy per mole as 2.5 kcal. for C_2H_6, and 5.5 kcal. for C_2H_4, not nearly large enough to account for the discrepancies under discussion. It seems not impossible that a revision of the calculations (*cf.* footnote 30 of ref. 74) might give considerably larger computed hyperconjugation energies.

degrees of isovalent hybridization somewhat smaller than here.

The interpretation of information on the following properties of molecules has also yielded rough values for degrees of isovalent hybridization: molecular dipole moments,[66,67] atomic electronegativities,[67,68] molecular quadrupole moments,[69] coupling constants of molecular force-fields with nuclear quadrupole moments,[70] absolute intensities of molecular electronic spectra.[71] The degrees of isovalent hybridization indicated by all these methods agree roughly with those by the present method.

A brief discussion will be given here only of the effect of isovalent hybridization on dipole moments and on electronegativities. Robinson[66] has shown that if HCl were covalent, it would have, according to a VB theory calculation, a considerable dipole moment of polarity H^-Cl^+ if there were no s,p hybridization, while about 12% s,p hybridization in the chlorine bonding AO would give a dipole moment of the observed magnitude and with sign H^+Cl^-. Actually, there is no reasonable doubt that HCl has primary heteropolar character of polarity H^+Cl^-, so that *less* than 12% hybridization would be sufficient to account for the observed moment. However, the VB calculation is not reliable enough to permit quantitative conclusions. The main point to be emphasized here is that dipole moments are extremely sensitive to small amounts of isovalent hybridization.

In a rough LCAO calculation,[67] the writer concluded that as much as 20% s,p hybridization in the bonding AO of Cl in HCl would be needed to explain: (a) the observed dipole moment; (b) a sufficient electronegativity of the chlorine atom to account for the latter. The second point is quite distinct from the first, and is also of interest for itself. Some time ago,[34] in setting up a semi-theoretical scale of electronegativities, the writer pointed out that the electronegativity of an atom should vary greatly with the type of bonding AO it was using, and in the case of a hybrid AO should depend strongly on the degree of hybridization. As applied to the chlorine atom, the writer's conclusion[67] was that, for it to have the degree of electronegativity necessary to account for a strong enough H^+Cl^- heteropolarity in the H–Cl bond to reproduce the observed HCl dipole moment, there must be a considerable amount of s,p hybridization in the bonding AO. Regardless of the quantitative soundness of the conclusion in this particular case, it is clear that isovalent hybridization must be of essential importance in determining the actual electronegativities of atoms like N, O and Cl.[68]

The effect, on electronegativities, bond strengths, bond lengths and dipole moments, of varying degrees of $s,p\sigma$ hybridization in σ bonds formed by carbon atoms with pluvalent hybridization—in particular, of C–H bonds in CH_4 and C_2H_6, C_2H_4, C_2H_2—has been discussed by various authors.[72]

XIII. Criticisms and Possible Improvements on the Magic Formula

As has been emphasized above, the present magic formula (*cf.* Section IV, in particular ref. 30), both as to its precise form and as to the choice of numerical values of its coefficients, is still preliminary. In this Section some criticisms of its possible shortcomings and some possible leads for its future improvement will be sketched.

First of all, it may be an oversimplification to lump the "Coulomb" terms C of VB theory into the other terms (compare Eq. (21) with Eq. (19), (20)). This procedure was adopted because in the VB theory for H_2, the theoretically computed Coulomb term C is relatively small, especially at the equilibrium R; also because in LCAO theory for H_2—which was used as a basis for the adopted form of the X's (Eq. (22)) in the magic formula—it was found empirically that the sum of Coulomb plus error terms ($C + E'$ in Eq. (4)) is small. However, theoretically computed Coulomb energies indicate[37,65] that in C–H bonds (and in general whenever $p\sigma$ and hybrid σ bonds are present) the Coulomb terms of VB theory are much larger than in H_2.[73] If so, the fact that the magic formula, using Eq. (22) for the primary bonding terms X of VB theory, works as well as it does may be a result of the likely possibility that in general the Coulomb terms, if actually important, may be more or less proportional to the overlap integral S. The fact that the value of A_σ, determined by fitting CH and other molecules involving $p\sigma$ and hybrid-AO bonds, is too large to fit H_2 and Li_2 might then be explainable as a result of the presence of much larger Coulomb terms in the former. However, all this is as yet hypothetical.

Another rather uncertain feature in the magic formula lies in the method of calculating the non-bonded repulsions between inner (here 1s) and outer electrons. As computed using Eq. (23) with $\bar{I}$ values taken as averages of 1s and outer-electron I values, these particular non-bonded repulsions are often rather large (*cf.* ΣY_k columns in Table VI). Although there are rather good reasons[39] for giving credence to these large values, a more thorough study—theoretical or empirical—would be desirable. (It seems possible even that such a study might point to somewhat *larger* rather than smaller values.)

When a study of the effect of Coulomb terms is made, possible effects corresponding to the "multiple exchange integrals" of VB theory[24] should also be looked into.

With explicit inclusion of Coulomb terms in the magic formula (and possibly smaller Y_k terms), leading to smaller A_σ and revised A_π and ν values, the resulting revised Table IV might perhaps show improved agreements between computed and observed D_0 values, in particular for H_2, Li_2 and F_2,[56] and for the molecules C_2H_n. (For CH_4 and C_2H_n, polar RE corrections for the CH bonds, neglected in Table IV, should be included.) With smaller A_σ values, the X's and Y's would become smaller, and thereby closer to the much smaller effective exchange integrals indicated by the earlier work of Van Vleck and others.[61]

The magic formula should of course be tested and adjusted by fitting to more molecules, including molecules containing atoms higher in the periodic system. For this purpose, it will be necessary to obtain self-consistent-field S

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[66] D. Z. Robinson, *J. Chem. Phys.*, **17**, 1022 (1949), theoretical calculations on HCl.

[67] Reference 7, p. 541.

[68] The effect of isovalent hybridization on the electronegativities of N and O was discussed in ref. 34 (p. 787 and Table I), and it was pointed out there that the observed (Pauling) electronegativities of N and O could be explained (aside from an improbable explanation using "second-stage electronegativities") only by assuming fairly large amounts of isovalent s,p hybridization. For the trivalent N atom, the result was 44%, which, however, now seems rather too large to be credible. In the same discussion, Pauling's electronegativity for the carbon atom was found to agree fairly well with that calculated by the writer for a tetrahedral hybrid carbon AO.

[69] C. Greenhow and W. V. Smith, *J. Chem. Phys.*, **19**, 1298 (1951), explanation of molecular quadrupole moments deduced from microwave line-broadening. Theoretical computations indicated that 20% s,p hybridization in the σ bond of N_2, and 5–10% in that of O_2, could explain the magnitudes of these quadrupole moments.

[70] C. H. Townes and B. P. Dailey, *ibid.*, **17**, 782 (1949): "Hybridization of the normal covalent bonds of N, Cl, and As with at least 15% s character is clearly shown."

[71] H. Shull: intensities in C_2 and N_2^+ spectra (to be published soon).

[72] Reference 64; ref. 4 (Fig. 2 and p. 4500, and references in footnote 24 there); A. Maccoll, *Trans. Faraday Soc.*, **46**, 359 (1950); and see Table VI above.

[73] Also in Li_2, the Coulomb energy seems to be relatively somewhat larger than in H_2 (*cf.* H. M. James, *J. Chem. Phys.*, **2**, 794 (1934)).

values for overlaps between such atoms. The hybridization situation will also be more complicated.

The usefulness of the present magic formula is to some degree limited by the fact that corrections under the general heading of resonance energy are often needed (*cf.* Section IV); these corrections, although usually of moderate size, must be obtained by outside considerations. They are needed in the following situations: (1) where strongly polar bonds are present; (2) where there is unusual stabilization by conjugation or aromatic resonance[74]; (3) where atoms are present in a partially demoted valence state.

With regard to polar bonds, reference may be made to Section V above. In extreme *ionic* bonds, the procedure indicated there fails, but the magic formula should now be valid with the molecular structural units taken as ions instead of atoms, and an ionic attraction term added.

In addition to *RE* terms like those used in VB theory for aromatic or conjugated molecules, a small second-order hyperconjugation *RE* term[65,74] is probably needed in the magic formula for C_2H_4, C_2H_6, and higher olefins and paraffins.

The magic formula is particularly good in cases where there is only *isovalent* hybridization (*cf.* Section IV). Here the use of hybrid-AO S values, together with a subtractive correction for the corresponding excess promotion energy, completely takes care of the effect of hybridization on D_0. But when, as in CH_4 and C_2H_n (*cf.* Section IV), *pluvalent* hybridization is modified by partial demotion, no simple way is apparent for taking care of the demotion energy except by an *RE* correction like the Voge correction in Tables III and VI. Like other *RE* terms, this one must be computed or estimated by special methods.

Finally, it may be recalled that the use of the magic formula is at present limited to molecules with bond lengths at their equilibrium values, except with respect to non-bonded interactions (see last paragraph of Section IV). It seems possible that, when perfected, the magic formula may be capable of reproducing D as a function of all the interatomic coördinates for large ranges of these. In relation to this possibility, the magic formula, taken in connection with the standard procedure adopted above of always maximizing the computed D_0 with respect to degree of hybridization, has the very good property that it permits needed adjustment of hybridization with varying R without extra complications.

APPENDIX I. VALENCE-STATE ENERGY DATA

TABLE VIII

SOME VALENCE-STATE ENERGY DATA APPLICABLE TO FIRST-ROW ATOMS WHEN IN LINEAR MOLECULES[a]

Atom	Ground state	Promotion energies[b]				Ionization energies (e.v.)	
		State[c]	P_0 (e.v.)	State[b]	ΔP(e.v.)	I_K[d]	$\bar{I}_L$[e]
Li	s, ^2S	s, V_1	0.00	......	.....	(66)	5.39
C	s^2p^2, $^3P_0$	$s^2\sigma\pi$, V_2	0.49	$s\sigma^2\pi$, V_2	9.45	288	14.88
N	s^2p^3, ^4S	$s^2\sigma\pi\pi'$, V_3	1.70	$s\sigma^2\pi\pi'$, V_3	(12.60)	(398)	18.11
O	s^2p^4, $^3P_2$	$s^2\sigma\pi\pi'^2$, V_2	0.67	$s\sigma^2\pi\pi'^2$, V_2	16.49	530	21.22
F	s^2p^5, $^2P_{3/2}$	$s^2\sigma\pi^2\pi'^2$, V_1	0.02	$s\sigma^2\pi^2\pi'^2$, V_1	[20.92]	686	[24.88]

[a] All energies are in e.v., assuming 13.60 e.v. as the ionization energy of the H atom. [b] P_0 denotes energy above the ground state, ΔP the *additional* promotion energy to reach the state listed. The P_0 values are from Ref. 34, and the ΔP values (estimated uncertainties a few tenths e.v.) are from data in ref. 34, except the value for fluorine which is extrapolated. (The values for carbon are slightly inconsistent with Voge's G_1, G_2 and P_t values in Table IX, but since the present values had already been used in the later computations, it did not seem worth while to readjust them. Voge's parameters would lead to $P_0 = 0.32$ and $P_0 + \Delta P = 10.04$ e.v.) [c] The detailed configurations given correspond to quantization in a force-field of cylindric symmetry, as in diatomic or other linear molecules; the symbols s, σ, π, π', respectively, mean $2s$, $2p\sigma$, $2p\pi^+$ and $2p\pi^-$. [d] The I_K values are $1s$ I's of Holweck quoted by Dauvillier, *J. phys. radium,* [6] **8**, 1 (1927) (see also J. Thibaud, *ibid.*, **8**, 447 (1927)), corrected slightly to agree with footnote *a*. (Actually, slightly higher estimated values—291, 401, 542, 696, for C, N, O, F—were used in the calculations in this paper.) [e] The $\bar{I}_L$ values are L shell valence-state values from footnote 34 or from data given there, obtained by averaging over the $3 + m$ electrons in the $s^2\sigma\pi^m$ valence states above. For example, $\bar{I}_L$ for nitrogen is one-fifth of

$$2I_s(s^2\sigma\pi\pi',V_3 \longrightarrow s\sigma\pi\pi',V_4) + I_\sigma(s^2\sigma\pi\pi',V_3 \longrightarrow s^2\sigma\pi,V_2) + 2I_\pi(s^2\sigma\pi\pi',V_3 \longrightarrow s^2\sigma\pi, V_2)$$

TABLE IX

VALENCE-STATE ENERGY DATA FOR TETRAVALENT CARBON[a]

Case	State	P_t(e.v.)	$\bar{I}_L$(e.u.)[b]
A	$s\sigma\pi_x\pi_y$, V_4	8.47	13.68
A′	$s\sigma\pi\pi'$, V_4	8.78	
B′	didi′$\pi\pi'$, V_4	7.79	
C	trtr′tr″σ, V_4	7.14	
D	tete′te″te‴, V_4	6.97	

[a] The AO symbols are in part as in Table VII, note *c;* in addition, *di*, *tr*, *te* refer to digonal, trigonal and tetrahedral $2s$,$2p$ hybrids, respectively. P_t denotes promotion energy to a tetravalent valence state. The value 6.97 e.v. for Case D is from H. H. Voge, *J. Chem. Phys.*, **4**, 581 (1936); **16**, 984 (1948). The values for the other unprimed cases are obtained from this by using Voge's 1948 values of G_2 (0.21 e.v.) and G_1 (2.24 e.v.) and a formula of J. H. Van Vleck, *J. Chem. Phys.*, **2**, 20 (1934), Eq. (7), noting that Cases D, C, B (didi′$\pi_x\pi_y$), A, correspond to $\mu = \frac{1}{4}$, $^1/_3$, $\frac{1}{2}$, and 1, respectively, in Van Vleck's formula. The cases A′, B′, are obtained from A and B, respectively, by adding $1\frac{1}{2}G_2$ (*cf.* Tables in ref. 34). [b] One-fourth of $2s$ plus three-fourths of $2p$ ionization energy for State *A*. Since the whole magic formula procedure is rough, this I for State *A* can serve for all tetravalent states.

Appendix II. Energies of Isovalent Hybrid Valence States

For the carbon atom in the state $k)^2\ h_{0\beta})^2\ h_\beta)\ \pi)$, V_2, first consider the antisymmetrized wave function written in determinant form, $(6!)^{-\frac{1}{2}}$ Det $k(1)\ k'(2)\ h_{0\beta}(3)\ h_{0\beta}'(4)\ h_\beta(5)\ \pi(6)$, where the unprimed symbols refer to AO's with positive spin ($m_s = +\frac{1}{2}$), the primed ones to AO's with negative spin ($m_s = -\frac{1}{2}$). Writing out $h_{0\beta}$ and h_β as per Eqs. (24), the determinant may be expanded (*cf.*, *e.g.*, Margenau and Murphy, "The Mathematics of Physics and Chemistry," D. Van Nostrand Co., Inc., 1943, p. 289) into a linear combination of eight determinants of which four vanish, and the remaining four combine (using $\alpha^2 + \beta^2 = 1$) to give the result

$$\psi(k^2h_{0\beta}{}^2h_\beta\pi) = \alpha\psi(k^2sp\sigma^2\pi) + \beta\psi(k^2s^2p\sigma\pi) \quad (37)$$

This derivation is for the case of a carbon atom with $m_s = +^1/_2$ for the spins of h_β and π. An analogous derivation evidently holds for each of the other three possible combinations of m_s values for these two AO's, hence also for the $k^2h_{0\beta}{}^2h_\beta\pi$, V_2 *valence state*, since each V_2 valence state wave function is a linear combination, of like form in all cases, of wave functions for the four different m_s combinations mentioned.

W. Moffitt,[75] in a similar discussion of hybrid valence states, arrives at a relation the same as Eq. (37) except that, apparently erroneously, he gives α^2 and β^2 as coefficients instead of α and β. In a later paper,[33] he makes computations whose results, when graphed (his Fig. 1), are in agree-

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[74] For a theoretical analysis and some theoretical computations of conjugation and resonance energies, see R. S. Mulliken and R. G. Parr, *J. Chem. Phys.*, **19**, 1271 (1951). Serber (*cf.* footnote 55) has also discussed the problem. Mulliken and Parr also give some analysis of hyperconjugation energies.

[75] W. Moffitt, *Proc. Roy. Soc. (London)*, **96A**, 524 (1948), top of p. 527.

ment with Eq. (38) and Table VIII of the present paper.

By computing $E = \int \psi^* H \psi dv$ with ψ taken as a V_2 valence-state function given by an equation corresponding to Eq. (37), one obtains, after noting that the two terms on the right of Eq. (37) are mutually orthogonal if orthogonal AO's are used or in general if true exact ψ's are used

$$\left.\begin{aligned} E(k^2 h_{0\beta}{}^2 h_\beta \pi, V_2) &= \beta^2 E(k^2 s^2 p\sigma\pi,\ V_2) + \ \alpha^2 E(k^2 sp\sigma^2\pi,\ V_2) \\ &= E(k^2 s^2 p^2,\ {}^3P) + P_0 + \alpha^2 \Delta P \end{aligned}\right\} \quad (38)$$

where P_0 and ΔP have the meanings and the numerical values given in the carbon atom entry in Table VIII. (The derivation of Eq. (38) based on determinant wave functions, though strictly not exactly valid for true exact wave functions, should be very nearly so, and entirely satisfactory for present purposes. The values of P_0 and ΔP listed in Table VIII, being based on spectroscopic data, corresponding to *accurate* wave functions.)

For hybrid valence states of other atoms, like that of carbon in having the configuration $k)^2\, h_{0\beta})^2\, h_\beta) \ldots$, but containing additional π electrons, equations analogous to (37) and (38) can be proved by the same kind of procedure.

Acknowledgment.—The author is greatly indebted to Mr. Tracy J. Kinyon for extensive assistance in carrying out the numerical computations for this paper.

FACTORS AFFECTING THE BOND LENGTHS IN CONJUGATED AND AROMATIC MOLECULES

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A critical discussion is given of some of the factors which influence the bond lengths of conjugated and aromatic molecules. The three quantities (1) bond order, (2) hybridization type and (3) formal charge distribution are particularly important, usually, though not always, in the sequence (1) more than (2) more than (3). A critical survey of published bond lengths in aromatic hydrocarbons vindicates the concept of fractional bond order, by which bond lengths may be estimated to within about 0.015 Å. When hetero-atoms such as N and O are present the accuracy is much less.

Recent very accurate three-dimensional Fourier analyses of the crystal structure of organic molecules such as naphthalene[1] or the pyrimidines[2] make it desirable that we should consider as carefully as possible the accuracy with which theoretical predictions of the bond lengths in these molecules may be made. In many cases the experimental uncertainty is no more than 0.015 A. and with more refined electrical methods for measuring the intensity of the various scattered rays in a Laue diagram, it may even improve. We are led, therefore, to ask first, what factors affect these bond lengths, and second, how closely may we reasonably hope to calculate them?

We are not concerned here with simple molecules, for which, as Warhurst[3] and others have shown, a wider variety of technique is available. Our concern is with large molecules where some simplifying assumptions have to be made. The most important of these is the assumption that resonating bonds can be described in terms of a fractional bond order, and that this bond order effectively determines the corresponding bond length. There are however other factors of importance, as we shall see. The present account will be concerned with (1) bond order, (2) hybridization type and (3) formal charges, all of which are significant in this connection.

(1) **Bond Order.**—Ever since the pioneer work of Pauling, efforts have been made to improve and refine the definition of fractional bond order.[4] The crucial question is this: is there a genuine correlation between calculated order and observed length? Thanks to the greatly improved accuracy of recent experimental work it is possible to answer this question unambiguously. Figure 1 shows the conventional curve for C–C bonds, drawn to pass through the basic points corresponding to diamond (C–C), ethylene (C═C) and acetylene (C≡C). These all have integral bond orders, 1, 2 and 3, respectively. If the concept of bond order is to be useful, then the points for other molecules where the orders are no longer integral, should lie on or near this curve. Figure 2[5] shows all the presently available data. The legend underneath defines the molecules to which the various points apply. The solid curve represents about the best curve through the points. This curve follows extremely closely the shape predicted theoretically by the writer,[6] of the form

$$x = s - (s - d) \Big/ \left\{ 1 + K \left(\frac{2 - p}{p - 1} \right) \right\} \quad (1)$$

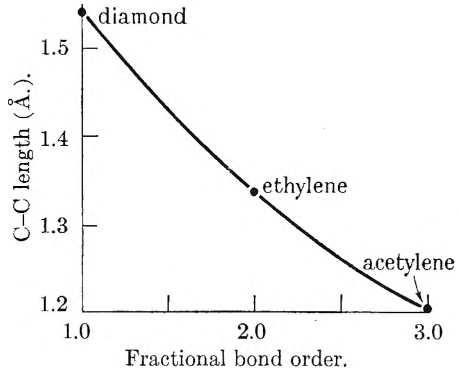

Fig. 1.—An order length curve for carbon–carbon bonds.

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[1] S. C. Abrahams, J. M. Robertson and J. G. White, *Acta Crystall.* **2**, 233, 238 (1949).

[2] W. Cochran, *ibid.*, **4**, 81 (1951).

[3] E. Warhurst, *Proc. Roy. Soc.* (*London*), **A207**, 32 (1951), and earlier papers.

[4] For a review see C. A. Coulson, *ibid.*, **A207**, 91 (1951), and C. A. Coulson, R. Daudel and J. M. Robertson, *ibid.*, **A207**, 306 (1951).

[5] Taken, by permission, from ref. (4a).

[6] C. A. Coulson, *Proc. Roy. Soc.* (*London*), **A169**, 413 (1939).

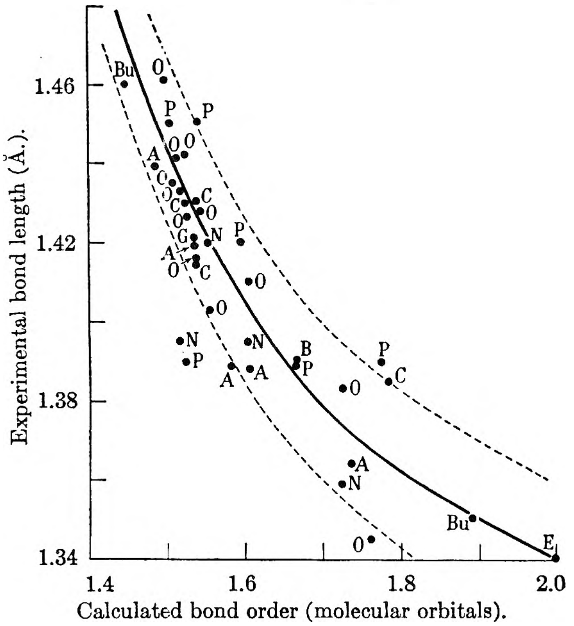

Fig. 2.—Curve showing relation between calculated bond order (by use of molecular orbital approximation) and observed bond length in conjugated hydrocarbons: A, anthracene; Be, benzene; Bu, butadiene; C, coronene; E, ethylene; G, graphite; N, naphthalene; O, ovalene; P, pyrene.

where x is the length appropriate to bond order p; s and d denote single and double bond lengths and K is some constant. The two dotted curves on either side are drawn parallel to the solid curve, a distance 0.02 Å. from it. There is no possible doubt, from a study of this curve, but that bond lengths are, in fact, closely correlated with bond orders; and that an error exceeding 0.02 Å. in predicting the bond length in aromatic and conjugated hydrocarbons of this class, is exceedingly rare. The points in Fig. 2 were calculated by using the molecular-orbital approximation. A similar curve, with similar spread of points, can be obtained (though with more difficulty; see later) with the valence-bond approximation. The two curves are not quite identical, since the definitions of bond order are not identical. It is important, therefore, always to specify what method of calculation is being used. In the case of naphthalene, for which Coulson, Daudel and Robertson[4b] have made a detailed study of the accuracy, the root-mean-square deviation of the calculated and experimental bond lengths is almost the same for the two methods, with a value 0.018 Å. This is scarcely greater than the precision claimed for the experimental values themselves.

When dealing with large molecules in this way, the molecular-orbital method seems to have considerable advantages over the valence-bond method. For in this latter, as Mme. Pullman[7] has shown, the choice of canonical structures is made very complicated by the fact that, the larger the molecule, the more important are the more highly-excited structures. A similar difficulty is experienced in the alternative "spin-states" treatment of Vroelant and Daudel.[8] The odd conclusion is reached with the molecular-orbital method, that the validity increases with the size of the molecule. This is well brought out in Fig. 3, which relates to the twelve distinct bonds in ovalene ($C_{32}H_{14}$). This is the largest molecule for which a detailed comparison can be made; but as Miss Buzeman's calculations[9] show, the relative distribution of length agrees quite astonishingly well with the observed distribution. It is true that the calculated spread of lengths is rather smaller than the observed spread—this appears to be fairly generally true—but the sequence is correct, to the degree of significance of the measurements themselves.

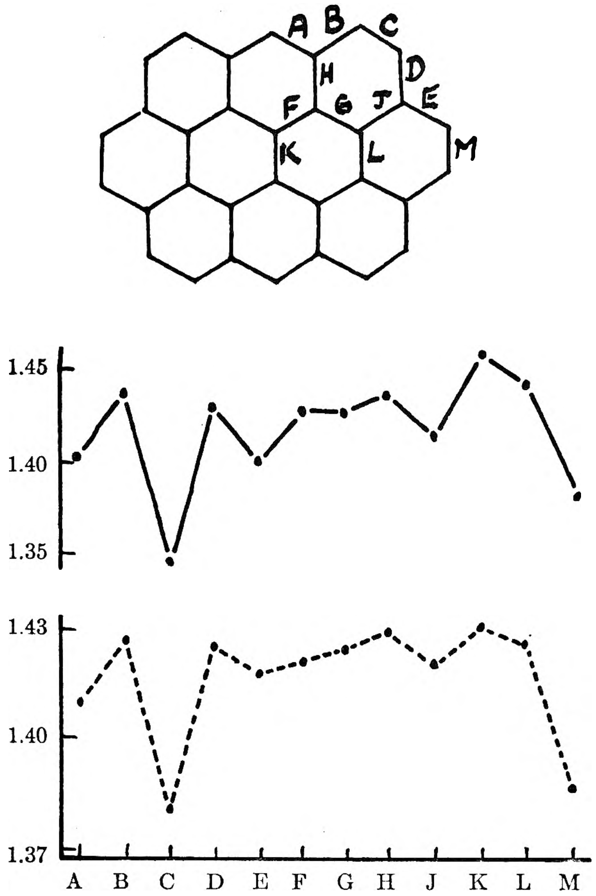

Fig. 3.—Bond lengths in ovalene: ——, X-ray measurements (Robertson); ------, m.o. calculations (Buzeman).

The situation with heteromolecules is far less satisfactory. The presence of other atoms than carbon in the resonating framework leads to charge migrations and a resonance moment. These migrations cannot yet be calculated adequately since the theory is still insufficiently developed. Furthermore, as Cox and Jeffrey[10] have pointed out, the standard bond distances are not known sufficiently well for a curve similar to that of Fig. 1 to be drawn for other bonds than those between carbon atoms. Nor is there a theoretical form available, similar to that represented by (1) for carbon–carbon bonds. In section 3 we shall have something to say about the changes in bond length which are in-

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(7) A. Pullman, *Ann. chim.*, **2**, 5 (1947).

(8) C. Vroelant and R. Daudel, *Bull. soc. chim.*, **16**, 36, 217 (1949).

(9) A. J. Buzeman, *Proc. Phys. Soc.*, **A63**, 827 (1950).

(10) E. G. Cox and G. B. Jeffrey, *Proc. Roy. Soc.* (*London*), **A207**, 110 (1951).

duced by the uneven charge distribution. There are, however, one or two general results which can be inferred, even without a precise knowledge of the order-length curve. One such result is illustrated for aniline[11] in Fig. 4. On the left is the diagram of bond orders in the ground state: on the right is the corresponding diagram in the excited state reached by absorption of ultraviolet light. It is immediately clear that certain bonds acquire a greater, and others a smaller, bond order corresponding to a more nearly quinonoid character. In an exactly analogous way there are different charge migrations in the excited state and ground states, showing, as has been pointed out by various workers, that the chemical reactivity of a molecule of this kind may be quite different in an excited state from what it is in its unexcited state. If, as sometimes happens, the excited state is metastable, with a fairly long lifetime, this might be susceptible of experimental verification. The only experimental verification of such calculations of excited molecular states which has so far been made concerns benzene, where in one of the excited states the hexagon length increases from 1.39 to 1.43 Å., in excellent agreement with what was predicted.

The case of a chain molecule, such as butadiene, is interesting. Here electronic excitation should increase the bond order of the central bond to such an extent that instead of writing the molecule as = — =, we may then represent it more nearly as — = — with two large free valences at the ends. Much the same situation will occur with styrene and similar molecules. The relation of all this to the question of photo-polymerization is at once obvious.

Before concluding this section there are two comments that must be made. First, evidence is accumulating that when using the molecular-orbital technique, we ought to introduce a greater measure of electron-correlation than is found in the simple treatment usually given.[12,13] This may be achieved by the device, already familiar from studies of atomic spectra, of configuration interaction. A careful analysis[4b] for the case of naphthalene suggests that its inclusion has the result of increasing all the bonds, approximately by the same amount. [For naphthalene this is 0.007 Å.] There is no reason for supposing that the situation would be greatly different in other molecules of this type. If so, we conclude that the introduction of configuration interaction in the ground state is a refinement with which we need not concern ourselves until experimental techniques are much improved beyond their present power. In this connection it may be worth mentioning[14] that this is comparable with the root-mean-square amplitude of vibration of the atoms, even in their zero-point vibrational level, so that not much significance attaches to closer measures of bond length than this.

The second comment is that there are several other minor improvements in the simple molecular-orbital method, which may be introduced. It is shown in reference (4) that these are not all of the same sign, and individually they can cause bond length changes of the order of magnitude of ±0.005 Å. The final conclusion therefore is that the limit of reliable prediction is about 0.015 Å., and that an inordinate amount of work would be necessary to improve on this degree of precision. Fortunately even this is sufficient to bring out the most interesting features of these molecules: it is doubtful whether any greater precision is worthwhile.

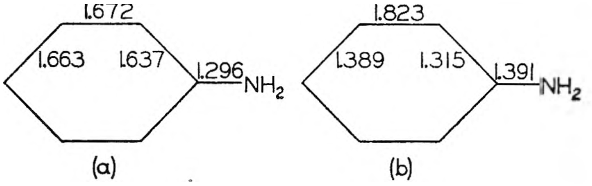

Fig. 4.—Aniline: (a) ground state; (b) excited state.

(2) **Hybridization.**—The second factor which is of importance in determining bond lengths is the type of hybridization of the atoms in the resonating framework. In all the aromatic and condensed molecules so far referred to, the bond angles are either exactly or approximately 120°; the hybridization is therefore trigonal, and no effect of this kind arises. But if the angles differ significantly from 120°, or if we have triple bonds, or near-triple bonds, derived from acetylene by conjugation, then the hybridization is no longer trigonal. With acetylene it becomes approximately digonal, and the bond length is thereby altered. Whereas the bond order effects were essentially π-electron effects, these are σ-electron effects. The present writer[15] has shown how the bond angle determines the hybridization of s and p orbitals around each atom, and how this affects the covalent radius r_c of the atom in the direction of the bond formed by this hybrid. A hybrid of s and p may be expressed in the form $s + \lambda p$, where λ is a coefficient of mixing whose value ranges through 0 for pure s bonds to $\sqrt{3}$ for tetrahedral bonds and ∞ for pure p bonds. We may regard r_c as a function of λ. Figure 5 shows how r_c varies with λ for the particular case of a carbon atom. The details of this curve may be found experimentally from a knowledge of the C–H bond lengths in methane, ethylene, acetylene and the CH radical; but the form of the curve is in complete agreement with theoretical calculation.[15] Reference to this curve shows that the bond between two carbon atoms in digonal hybridization

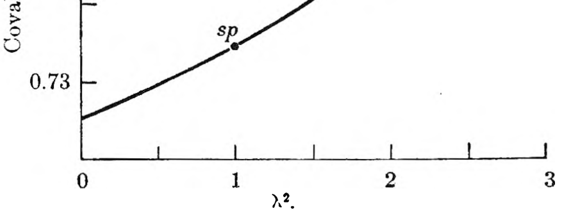

Fig. 5.—Covalent radius of carbon as a function of λ^2 where λ = coefficient of mixing in the hybrid orbital $s + \lambda p$.

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[11] C. A. Coulson and Miss J. Jacobs, *J. Chem. Soc.*, 1983 (1949).

[12] D. P. Craig, *Proc. Roy. Soc.* (*London*), **A200**, 474 (1950).

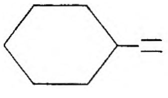
[13] J. Jacobs, *Proc. Phys. Soc.* (*London*), **A62**, 710 (1949).

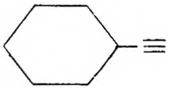
[14] C. A. Coulson, P. W. Higgs and N. H. March, *Nature*, **168**, 1039 (1951).

[15] C. A. Coulson, Victor Henri Memorial Volume, Desoer, Liège, 1948, p. 15.

($\lambda = 1$) may be 0.03 Å. shorter than one between two similar atoms in trigonal hybridization ($\lambda^2 = 2$). This effect is entirely additional to any changes due to bond order differences.

A very clear example of this was provided by Penney and Kynch.[16] If we compare the "single" bond joining the phenyl group to the "double" or "triple" bonds in styrene (I) and tolan (II) we recognize that in (I) the two carbon atoms bonded together are both in trigonal-type hybridization, but in (II) one is in trigonal and the other digonal hybridization. The fractional bond order of this bond is substantially the same in the two molecules. The distinct shortening of the central link in (II) as compared with (I) must largely be attributed to the change in r_c due to change of hybridization type.


(I) Styrene


(II) Tolan

Care must be exercised in using this particular argument. The hybridization ratios are determined by the geometry of the molecule, as in reference (15), only if the bonds are "straight"; that is to say, the hybrids at each particular nucleus are directed straight toward the attached neighbor atoms. Often this will be the case, though there are exceptions, such as molecules with a closed ring of less than six atoms where in the language of Baeyer, we could say that the bonds were strained. The wave-mechanical description of this form of strain is that the bonds are "bent," as a result of the hybrids which are paired together not being pointed directly toward each other. The physical significance of this arises from the fact that bond strength is closely related to the overlap between these orbitals, and the overlapping power of a hybrid varies greatly with the degree of hybridization, being maximum for *sp* digonal hybrids and least for pure *s* or pure *p* orbitals. A compromise is therefore reached whereby the tendency to have *sp* hybrids is balanced by the fact that if we did have them their greater potential overlapping could not be used since they would necessarily have to point at an angle with the line joining the nuclei. Coulson and Moffitt[17] have discussed cyclopropane in some detail. The best description of this molecule in terms of localized electron-pair-bonds is to suppose that the three carbon atoms are hybridized in such a way that the bonding orbitals in the plane of the molecule are directed as shown by the arrows in Fig. 6. They make an angle of 22° with the lines joining the nuclei. One result of this is that the C–C distances are reduced below the normal single bond distance. This is entirely in accord with experimental evidence.

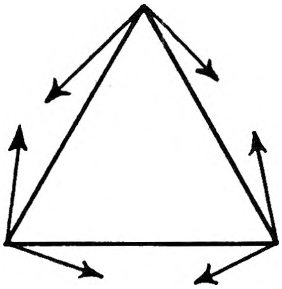


Fig. 6.—Cyclopropane. Arrows denote directions of hybrids at corner C atoms for making bent C–C bonds.

It would be wrong to give the impression that such hybridization effects on bond length are easy to deal with. They are not. Partly this is because the actual determination of the hybrids in cases of strain is a tedious computation, only practicable when, as in cyclopropane, there is considerable symmetry to help. Partly also it results from the recent discovery[14,18] that the distinction between σ- and π-electrons is nothing like so sharp as was formerly believed, and that, as a consequence, there is a species of σ–π resonance. Such resonance mixes together the influence of bond order and hybridization. Other difficulties arise from our present ignorance of all the effects of changes in hybridization ratios. Thus in 1,2,3,4-tetraphenylcyclobutane studied by Dunitz,[19] the C–C bonds in the cyclobutane ring are increased in length from the conventional 1.54 Å. to an average of 1.57 Å. Dunitz gives reasons why we might expect these bonds to have more *p*-character than a normal tetrahedral bond. If so, it remains hard to see why an increase in *p*-character decreases the C–C distance in cyclopropane, but increases it in this phenylcyclobutane. The only likely explanation seems to lie in the fact established by Coulson and Moffitt[17] that in cyclopropane the bonds are notably bent, whereas in cyclobutane the degree of bending is very much smaller (9° instead of 22°). Further analysis of this phenomenon is desirable.

(3) **Formal Charge Distribution.**—The last factor which we shall consider is the formal charge distribution. When heteroatoms are present within the conjugated framework there will be resonance charge migrations away from certain atoms on to others. If we associate formal charges with each atom, some will carry a net positive charge, others a net negative one. Now in almost all of the methods used to calculate these charges, no allowance is made for their mutual interaction. Since charges of similar sign repel, they will tend to increase the bond length if they are adjacent. Similarly, if the charges are of opposite sign they will tend to shorten the bond. A rough estimate of this additional effect may be made as follows.

Let q_1 and q_2 be the net charges, in units of e, on the atoms of a bond. Then the force between them may be written $q_1q_2e^2/Kr^2$, where K is some effective dielectric constant for the medium around the bond. A conventional value $K = 2$ is often taken in other somewhat similar circumstances. Let us suppose that, in the absence of this force, the bond length would be r, and in the presence of it, there is a change to $r + \Delta r$. Then we may equate the Coulomb repulsive force between the charges to the restoring force $\kappa\Delta r$ where κ is the force constant of the bond. Thus

$$\kappa\Delta r = q_1q_2e^2/K(r + \Delta r)^2$$

Approximately, therefore

$$\Delta r = q_1q_2e^2/K\kappa r^2 \tag{2}$$

It is a little surprising at first to see how small this bond change is. For if we take the rather extreme case of $q_1 = q_2 = 1$, $K = 1$, and suppose that $r = 1.5$ Å., $\kappa = 6 \times 10^5$ dynes/cm., we find that $r = 0.2$ Å. As a general rule the charges will be much less than unity, and Δr will be correspondingly reduced.

If our heteromolecule is derived from an alternant hydrocarbon (*i.e.*, one with an even number of carbon atoms in each ring) we may anticipate that this effect will be particularly small (except for the bonds from the heteroatom itself). This is because atoms in the meta position to the heteroatom or substituent have their charge only very slightly altered. It is the atoms in ortho and para positions that give or receive most of the charge migration. Thus in each bond either q_1 or q_2 is small, and no large bond contraction will be expected. If two heteroatoms or substituents are in positions ortho or para to each other, we may anticipate greater effects,

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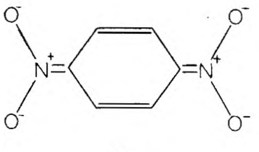
[16] W. G. Penney and G. J. Kynch, *Proc. Roy. Soc.* (*London*), **A164**, 409 (1938).

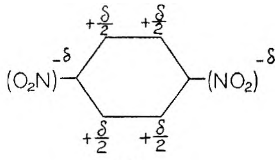
[17] C. A. Coulson and W. E. Moffitt, *Phil. Mag.*, **40**, 1 (1949).

[18] S. L. Altmann, *Proc. Roy. Soc.* (*London*), **A210**, 327, 343 (1951).

[19] J. D. Dunitz, *Acta. Crystall.*, **2**, 1 (1949).

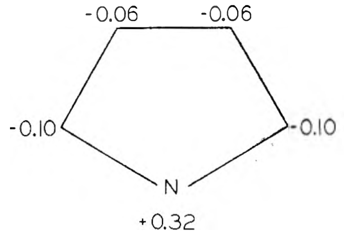
Such occurs in *p*-dinitrobenzene where, in fact,[20] the quinonoid bonds have a rather longer length than would be anticipated on the basis of a single structure such as (I). If, however, we realize that the formal charges on the nitro-groups would require that these be charges of the type represented by (II) on the ring atom, it becomes clear that we have here one possible explanation of the somewhat anomalous lengths in the ring.


(I)



(II)

When we have to deal with non-alternant molecules the situation is rather different, and measurable effects are just possible with only one heteroatom. An example is pyrrole for which the net charges[21] are given in the figure. Application of formula (2), with reasonable values for κ, leads to a shortening of the bond N–C_1 by about 0.007 A. The changes in the other bonds are somewhat smaller. This change, however, is just about within the range of being significant.



The situation becomes clearer when we pass to charged molecules, particularly the ionic groups found in crystals. Two examples will serve to illustrate this. If we may treat the carbonate ion as if it were purely ionic, with charge distribution

$$\begin{matrix} O^- \; O^- \\ C^+ \\ O^- \end{matrix}$$

then the formal charges give rise to a bond contraction of about 0.02 Å. This system of charges almost certainly exaggerates the effect, but it may still be appreciable. Our second example is the azide ion N_3^-. A conventional molecular-orbital treatment, in which the Coulomb terms of the N atoms are all taken to be the same, yields the rather surprising result that the bond orders are both exactly double, and the charge distribution is again exactly integral. The ion could thus be represented as $N^-{=}N^+{=}N^-$. This diagram exaggerates the unevenness of the charge distribution, since the migration of charge alters the Coulomb terms in such a way as to attract more electrons back to the central atom. A calculation by Mme. Bonnemay and Daudel[22] gives a charge $-0.83e$ on the end atoms instead of our $-1.0e$. But this is partly compensated by an increased bond order (2.37 instead of our 2.00), so that the charge and the bond order effects are to some extent complementary. What is lost by a decrease in the one seems to be compensated by an increase in the other. Several other molecules, including the carbonate ion and nitrate ion, have been investigated with so nearly identical a conclusion that one suspects it to be quite general. In the case of N_3^- the formal charge distribution -1, $+1$, -1 leads to a bond contraction of the order of 0.10 to 0.15 Å. depending on the appropriate value of K. This shows how dangerous it is to estimate the interatomic distances solely by reference to fractional bond order.

In this particular molecule there is a further matter of some importance. The central N atom must almost certainly be hybridized in a digonal manner, in order to give equivalent bonds in a straight line. But the end N atoms will almost equally certainly be hybridized so that the bonding σ-type orbital is more nearly p. The discussion in section (2) shows that the difference in the two hybridizations may affect the bond length by an additional 0.02 or 0.03 Å. Such changes would be relevant to any comparison such as that attempted in reference (22), between N_3^- and CH_3N_3.

There is still one further way in which ionic charges may affect bond lengths. It was suggested by the fact, reported in reference (4b), that the central bond (9–10) in naphthalene was predicted to be about 0.025 Å. too long by all the simple types of approximation: and also by the conclusion of Mulliken[23] that the Coulomb term appropriate to an "internal" carbon atom may differ appreciably from that appropriate to an "external" one. This would mean, in conventional language, that α_9 and α_{10} for naphthalene differed from, and were numerically smaller than, the other α's. A careful analysis of the resulting bond changes[4a,4b] reveals that individually they are unlikely to exceed 0.005 Å., and are not of the same sign. These are the matters referred to at the end of section 1, and which appear, at present, to limit the accuracy of the bond order factor.

Conclusion

The preceding discussion has shown that all the three factors, *viz.*, bond order, hybridization type and formal charge distribution, are important, and that their importance is often, though not always, in the sequence (1) > (2) > (3). It is not possible at this stage to sort out these effects separately, since normally they all occur simultaneously. In order to improve on the analysis referred to in this account, it would be necessary to undertake an exextremely heavy amount of computation, which would be applicable only to one particular molecule. Perhaps what is most important is that we do have solid ground for believing that we understand the chief factors which are effective, and are able to estimate their influence with a precision comparable with that attainable experimentally.

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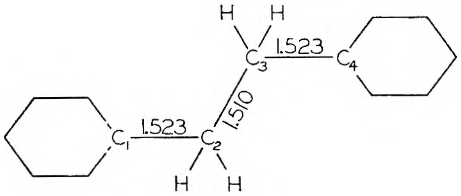
[20] F. J. Llewellyn, *J. Chem. Soc.*, 884 (1947); S. C. Abrahams and J. M. Robertson, *Acta Crystall.*, **1**, 252 (1948); S. C. Abrahams, *ibid.*, **3**, 194 (1950); T. H. Goodwin, M. Przybylska and J. M. Robertson, *ibid.*, **3**, 279 (1950).

[21] See *e.g.*, H. C. Longuet-Higgins and C. A. Coulson, *Trans. Faraday Soc.*, **43**, 87 (1947).

[22] A. Bonnemay and R. Daudel, *Compt. rend.*, **230**, 2300 (1950).

[23] R. S. Mulliken, *Phys. Rev.*, **74**, 736 (1948); *J. chim. phys.*, **46**, 497 (1949).

There are still one or two peculiar features, not fully comprehended. We shall conclude by reference to one of them. It has recently been shown by Cruickshank,[24] who refined some earlier experimental work of Jeffrey, that in dibenzyl the bond lengths of the C–C bonds which connect the two rings have values 1.523 and 1.510 Å. as in the figure. These are both distinctly less than the normal paraffinic value 1.544 Å. It has been suggested that hyperconjugation is responsible for this shortening. But if by this it is implied that structures symbolically represented by $H_2{=}C_2{-}C_3{=}H_2$ are effective, then the explanation can hardly be correct, since such structures occur in every paraffin chain, where the standard C–C length is 1.54 A. The explanation of the shortening of the bond C_1C_2 seems to be that C_1 is a trigonal atom and C_2 a tetrahedral one, so that the analysis of section (2) applies. The shortening is of the right order of magnitude. The explanation of the shortening of the central bond C_2–C_3 is a little more complicated. Partly it arises from the angle $C_1C_2C_3$ which is larger than tetrahedral (for steric reasons, presumably); and this affects the hybridization ratios and leads to a small shortening of C_2C_3 and C_2C_1 at the expense of the CH bonds. (These latter should correspondingly be a little weaker.) Partly also it may be related to the fact that if we regard dibenzyl as derived from a paraffin chain by replacing the alkyl groups at C_1 and C_4 by phenyl groups, then the greater electron affinity of the phenyl groups will remove σ-electrons from C_2 and C_3 toward C_1 and C_4. This, in turn, will increase the electron affinity of C_2 and C_3, and so strengthen the bond; it will also remove electrons which are not paired with each other away from C_2 and C_3 and therefore reduce the repulsive forces in C_2-C_3 which always exist between non-paired electrons.[25] It seems as if the best that we can say at the moment is that all three effects cooperate in reducing the length of C_2-C_3. But further study of this and other similar systems is clearly desirable.



(24) D. W. J. Cruickshank, *Acta Crystall.*, **2**, 65 (1949).

(25) A. D. Walsh, *Trans. Faraday Soc.*, **43**, 60 (1947); K. S. Pitzer, *J. Am. Chem. Soc.*, **70**, 2140 (1948).

THE SPECTRA AND DISSOCIATION ENERGIES OF THE DIATOMIC INTERHALOGEN MOLECULES

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The analyses of the BrF and IF emission band systems, recently observed in the bromine/fluorine and iodine/fluorine flames, has made possible an accurate determination of the dissociation limits at 21190 ± 150 cm.$^{-1}$ for BrF and 23570 ± 300 cm.$^{-1}$ for IF. In each case there are two possible alternative assignments for the dissociation products at these limits, and hence two alternative values for the dissociation energies of BrF and IF to normal atoms. The dissociation energies and force constants for all the diatomic halogen and interhalogen molecules are compared and discussed. The chemical stability of IF is also considered in relation to the two alternative values for its dissociation energy. Available data do not allow a conclusive choice between the alternative values, but slightly favor the lower values, D(BrF) = 2.16 ± 0.02 e. v. and D(IF) = ± 1.98 ± 0.04 e.v.

Introduction

The reaction of fluorine with many substances is accompanied by the appearance of a flame. As part of a program of research on flame spectra we have studied the spectra of a number of these flames given by fluorine.[1] Among these flames are those with iodine and bromine. These are obtained quite simply by impinging a small jet of fluorine gas on the surface of either solid iodine or liquid bromine. The emission spectra of these flames show band systems due to IF and BrF, respectively, and these spectra have been measured and analyzed[2] and the molecular constants have been derived. In the case of IF the spectrum is new. For BrF, the spectrum had been observed in absorption by Brodersen and Schumacher[3], but the observation of the system in emission has enabled many new bands to be obtained and it has been found necessary to make some modification in the vibrational analysis, with a consequent adjustment of molecular constants.

The spectra of all the diatomic halogen molecules (except F_2) and other interhalogen molecules have been known for some time, and the new data for BrF and IF make possible a systematic comparison of their molecular constants. For these interhalogen molecules it is possible in all cases to fix the dissociation limits fairly accurately from the spectroscopic data, but there are two possible alternatives for the assignment of dissociation products at the limits, and hence we may in these cases be in doubt as to which of two values of the dissociation energies are correct. It is our purpose here to discuss this problem of finding the correct dissociation energies.

(1) R. A. Durie, *Proc. Phys. Soc.*, **63A**, 1292 (1950).

(2) R. A. Durie, *Proc. Roy. Soc.* (*London*), **A207**, 388 (1951).

(3) P. H. Brodersen and H. J. Schumacher, *Z. Naturf.*, **2a**, 358 (1947).

The Dissociation Limits for IF and BrF

The vibrational analysis of the spectrum of IF gives us reliable data for vibrational levels of the excited electronic state from $v' = 0$ to $v' = 11$ and we can plot the energy intervals $\Delta G(v' + {}^1/_2)$ against v' to obtain a graphical Birge–Sponer extrapolation for the dissociation energy in the excited state. This curve is shown in Fig. 1a. It will be seen that the rate of convergence of levels increases with v'; the dissociation energy is given by the area beneath the curve, and it will be seen that the extrapolated portion is a small fraction of the total area. We obtain $D' = 4615 \pm 300$ cm.$^{-1}$. If we add to this the value for the energy of the lowest level of the excited state above the ground level, that is, the wave-number for the (0,0) band of the system at 18955 cm.$^{-1}$, we obtain a dissociation limit at 23570 ± 300 cm.$^{-1}$.

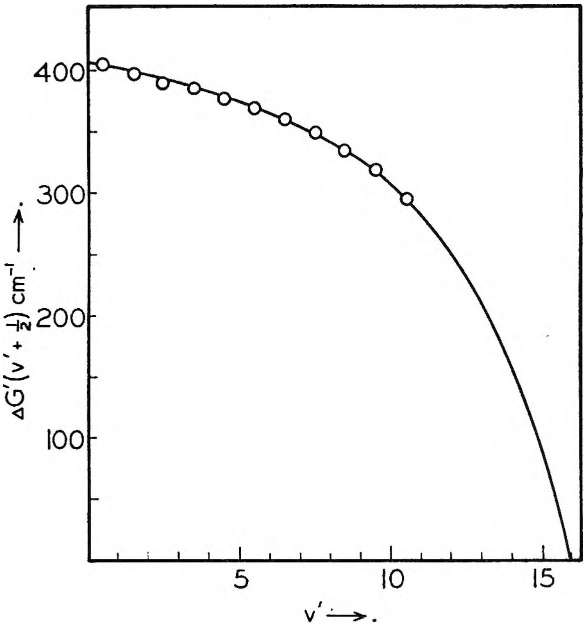

Fig. 1a.—Birge–Sponer extrapolations for the excited state of IF.

Similarly for BrF we have good data for v' from 0 to 8. There is also a rather diffuse band which is probably the (9,0) band. The extrapolation including this slightly doubtful last point is shown in Fig. 1b. Here the extrapolation, although made from fewer points, is shorter and we obtain $D' = 2695 \pm 150$ cm.$^{-1}$. Adding $\nu(0,0) = 18495$, we obtain a dissociation limit at 21190 ± 150 cm.$^{-1}$.

The Nature of the Dissociation Products

For all the halogen atoms, the ground state is ^2P with the $^2P_{3/2}$ component the lower, and the $^2P_{1/2}$ component higher; the separations for F, Cl, Br and I are 404, 881, 3685 and 7598 cm.$^{-1}$, respectively. There are no other low-lying atomic states to interest us. Thus if we denote an excited atom in the $^2P_{1/2}$ state with an asterisk (*), for a molecule XY we have in general four possible pairs of dissociation products, X + Y, X + Y*, X* + Y and X* + Y*.

For I_2, Br_2 and Cl_2 the main band systems have been shown to be due to transitions between an excited $^3\Pi_{0+}$ state and the ground $^1\Sigma^+$ state. For I_2 and Br_2, weak systems from an excited $^3\Pi_1$ state are also known. For the interhalogen molecules the correlations between molecular states and atomic dissociation products will be different, and there is the possibility of other transitions, such as $^1\Sigma^+ \rightarrow {}^1\Sigma^+$, but it has generally been assumed that the upper states of the known systems are again $^3\Pi_{0+}$ and $^3\Pi_1$. For a discussion of the correlations see Mulliken,[4] Brown and Gibson[5] and Gaydon.[6]

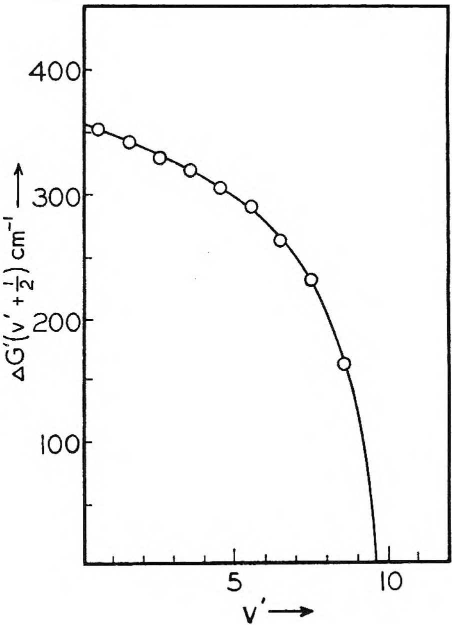

Fig. 1b.—Birge–Sponer extrapolations for the excited state of BrF.

For BrF the rotational structure of the absorption bands has been examined by Brodersen and Schumacher[7]; only single P and R branches are found, and the transition has been assumed to be from $^3\Pi_{0+}$ to the ground state. For IF we have not been able to make a full rotational analysis, but we have examined the structure under fairly large dispersion and again it is clear that there are only P and R branches; the transition is therefore again either $^3\Pi_{0+} \rightarrow {}^1\Sigma^+$ or possibly an ordinary $^1\Sigma^+ \rightarrow {}^1\Sigma^+$ transition.

Now if we compare the band systems of the interhalogen molecules which arise from the presumed $^3\Pi_{0+}$ states, we find that the upper vibrational levels of the excited state of ClF, ICl and IBr are predissociated[5,8,9]. Hence we cannot correlate their convergence limits with unexcited atoms. Similarly the (9,0) band of BrF appears diffuse, and this effect is probably due to predissociation. It therefore seems that we cannot assign the dissociation limits which we have derived for BrF and IF with dissociation to unexcited atoms. Since there are several lower states of 0^+ type, it also seems that we should not correlate these limits with the 0^+ state arising from two excited atoms.

(4) R. S. Mulliken, *Phys. Rev.*, **37**, 1412 (1931).

(5) W. G. Brown and G. E. Gibson, *ibid.*, **40**, 529 (1932).

(6) A. G. Gaydon, "Dissociation Energies," 1947.

(7) P. H. Brodersen and H. J. Schumacher, *Ann. Asoc. quim. argent.*, **38**, 52 (1950).

(8) A. L. Wahrhaftig, *J. Chem Phys.*, **10**, 248 (1942).

(9) W. G. Brown, *Phys. Rev.*, **42**, 355 (1932).

It therefore seems fairly certain that we should correlate the dissociation limits with one excited atom and one normal atom. Thus for IF we have the possibilities I + F* and I* + F. For BrF we may have Br + F* or Br* + F.

For IBr and ICl we also have systems of type $^3\Pi_1 \rightarrow {}^1\Sigma^+$, and these appear to give convergence limits to normal products while the $^3\Pi_{0+}$ states converge to normal I and Cl* or Br*, this being supported by some thermochemical data on the dissociation energies.[10,11] Brodersen and Schumacher[7] assumed a similar type of correlation for BrF, but if we do the same for IF we get a very high dissociation energy of 23570 − 404 cm.$^{-1}$ = 23166 cm.$^{-1}$ or 2.87 e.v. This is very much higher than $D(I_2)$ which is 1.54 e.v. or $D(F_2)$ whose value is still the subject of some controversy but may be 1.8 e.v. and is certainly well below 2.87. We thus feel far from sure that we should take the higher of the values for the dissociation energies for IF and BrF. We propose therefore to make a systematic comparison of force constants and dissociation energies, and then to discuss the chemical stability of IF.

Comparison of Force Constants and Dissociation Energies

For IF we have either 2.87 or 1.98 ± 0.04 e.v. for the dissociation energy, according to whether we assume the products are I + F* or F + I*. For BrF we have either 2.58 or 2.17 according to whether the F or Br atom is excited. For ClF we may use the known convergence limit to give either 2.62 or 2.56 e.v. for the dissociation energy according to whether the F or the Cl atom is excited. In Table I we have collected values of the force constant k for the halogen molecules using data collected by Herzberg[12] and our values for BrF and IF. $k = 4\pi^2c^2\mu\omega_e^2$ where c is the velocity of light, μ the reduced mass in g. and ω_e the vibrational frequency in cm.$^{-1}$ for the ground state. We have also given the dissociation energies, with alternative values where there is doubt, and the ratio of dissociation energy to force constant for both the high and low alternatives for the dissociation energy. Values of dissociation energy followed by T.C. are based on thermochemical data, and may be less precise than the spectroscopic values.

Table I

Dissociation Energies and Force Constants for Halogens and Interhalogen Compounds

	k, dynes × 10^5	D_0, e.v.	D_0/k, high D	D_0/k, low D
F_2	4.46	?1.8	0.40	0.40
ClF	4.56	2.62 or 2.56	.57	.56
BrF	4.10	2.58 or 2.17	.63	.53
IF	3.64	2.87 or 1.98	.79	.54
ClF	4.56	2.62 or 2.56	.57	.56
Cl_2	3.28	2.47	.75	.75
ClBr	2.68	2.26 (T.C.)	.84	.84
ClI	2.38	2.15	.90	.90
BrF	4.10	2.58 or 2.17	.63	.53
BrCl	2.68	2.26 (T.C.)	.84	.84
Br_2	2.46	1.97	.80	.80
BrI	2.19	1.82	.83	.83
IF	3.64	2.87 or 1.98	.79	.54
ICl	2.38	2.15	.90	.90
IBr	2.19	1.82	.83	.83
I_2	1.72	1.54	.90	.90

The comparison of values of D/k may be made in various ways. It seems possible to use the data to argue either for the high or low dissociation energies. The high energies seem to give more nearly constant ratios for the bromides and iodides, but a more smooth trend for the fluorides. The low energies give more constant values throughout, except in all cases for the much lower ratio for the fluoride. For the three heavier members of the bromide and iodide groups D/k seems constant, and if this similarity were to hold for the three heavier members of the fluoride group, this would favor the low dissociation energies. For the three heavier members of the chloride group, however, the ratio is not constant, and if the trend to change smoothly increases as we go to fluorides, then the comparison may favor the high dissociation energies.

The Chemical Stability of IF

All the diatomic interhalogen compounds except IF can be obtained chemically. Davy and Gay Lussac discovered ICl as far back as 1824 and Balard prepared IBr in 1826. The existence of IBr was confirmed by Yost,[13] ClF was isolated by Ruff and Ascher[14] and BrF by Ruff and Braida.[15] There does not, however, appear to be any record of the preparation of IF. Vapor pressure measurements by Ruff and Braida[16] on iodine penta- and heptafluorides mixed with iodine led them to conclude that it was unlikely that any lower compound of iodine and fluorine existed.

If we take the high value of 2.87 e.v. (or 66 kcal./mole) for the dissociation energy of IF, then this molecule should be very stable and despite the existence of IF_5 and IF_7 we should expect it to occur in appreciable concentration in mixtures containing excess iodine. For the lower value of the dissociation energy, 1.98 e.v. or 46 kcal., it seems more reasonable that IF should not be detected chemically. For a full discussion of this aspect it would be necessary to calculate the equilibrium constants, but here it may suffice to point out that from the known data[17] for the heat of formation of IF_5 we obtain the following heats of reaction

$$5I_2 + 5F_2 = 4I_2 + 2IF_5 + 167 \text{ kcal.}$$
$$5I_2 + 5F_2 = 10IF + \text{either } 275 \text{ kcal. or } 70 \text{ kcal.}$$

Obviously if we take the high dissociation energy for IF, giving 275 kcal. for the heat release in the above reaction, we should expect IF to exist in large concentrations, whereas with the low value for the dissociation energy, the reaction would be expected to go to IF_5 rather than to IF. Thus if we are forced to choose between the two values of the dissociation energy of IF, the failure to detect IF in mixtures of

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(10) G. E. Gibson and H. C. Ramsperger, *Phys. Rev.*, **30**, 598 (1927).

(11) J. McMorris and D. M. Yost, *J. Am. Chem. Soc.*, **53**, 2625 (1931).

(12) G. Herzberg, "The Spectra of Diatomic Molecules," 2nd Edit., 1950.

(13) D. M. Yost, *Z. physik. Chem.*, **153**, 143 (1931).

(14) O. Ruff and E. Ascher, *Z. anorg. Chem.*, **176**, 258 (1928).

(15) O. Ruff and A. Braida, *ibid.*, **214**, 81 (1933).

(16) O. Ruff and A. Braida, *ibid.*, **220**, 43 (1934).

(17) A. A. Woolf, *J. Chem. Soc.*, 231 (1951).

iodine with IF_5 and IF_7 must be taken as strong evidence against the high dissociation energy and in favor of 1.98 e.v.

For the two possible values of $D(IF)$, either 2.87 or 1.98 e.v., the systematic comparison of force constants and dissociation energies is not very helpful, perhaps slightly favoring the high value. The chemical evidence that IF does not exist in appreciable concentration is, however, strong evidence in favor of the lower value.

If we accept the lower value for IF, then by analogy we should favor the lower values for BrF and ClF. In the case of ClF the change is not appreciable, but such as it is it would cause a further lowering in the value of $D(F_2)$ if we accept a value for this constant based on $D(ClF)$ and the heat of formation of ClF.

It may be necessary to make some slight reservations to these conclusions. To begin with, the apparent convergence limits of the vibrational levels of the excited states may not coincide exactly with the dissociation limits if there are potential maxima. It seems quite likely from the work of Brown and Gibson[5] that such potential maxima exist. Such maxima are, however, small, at the most a few hundred cm.$^{-1}$ and would not alter the main conclusions and would only affect the result slightly. We must also take into account the possibility of the correlations between the excited electronic states of the molecules and the atomic products varying from molecule to molecule. For the homonuclear molecules, it seems certain that the excited states are $^3\Pi_{0+}$, but for the heteronuclear molecules the excited state might be an ordinary $^1\Sigma^+$; it is possible that for the heavier molecules containing I we are near Hund's case c coupling and that the upper states are 0^+ derived from $^3\Pi$, but that for the lighter molecules nearer Hund's case *b* the transition from $^3\Pi$ to the ground $^1\Sigma^+$ is forbidden and the upper state for these molecules is the $^1\Sigma^+$.

Another possible way of getting at the dissociation energy would be by a Birge–Sponer extrapolation for the ground state. Unfortunately the extrapolation is so long that it carries little weight. For IF a very long linear extrapolation would give $D(IF) = 3.5$ e.v., but it is known[6] that these extrapolations tend to come high, especially for heavy molecules, and while the result probably favors the higher dissociation energy, it carries negligible weight.

Further work to confirm the chemical instability of IF seems the most promising way to settle the dissociation energies of this group of molecules.

RELATIONS BETWEEN LENGTH AND REACTIVITY IN SOME CARBON–HALOGEN BONDS[1]

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In recent discussions of reactivity of carbon–halogen bonds, and in particular of their dissociation energies, emphasis has tended to shift from the unperturbed state to the transition state. It is of interest, therefore, to find that for the methyl halides and acetyl halides there is an inverse linear relation between bond length and dissociation energy; and that an inverse relation between the mean bond energy and the square of the bond length applies to these compounds and several other organic halides.[2] Such relations indicate that the characteristics of the transition state are to some extent shown in the unperturbed state. It is unlikely that so simple a state of affairs holds very widely. Other series of halides are in fact found to give dissociation energy/bond length lines parallel to the original one. An explanation of these facts is offered.

As a result of examining the structures of the acetyl halides by the electron diffraction method for vapors, Allen and Sutton[2] found two relations between the lengths of the carbon–halogen bonds and bond energy quantities.

First, they showed that the mean bond energies, derived using C–C bond energies corrected for bond length by a relation of the type proposed by Gordy,[3] *i.e.*, $H_a(X - Y) = \alpha l^{-2}(X - Y) + \beta$, themselves fall on a curve obeying this relation. The points for the acetyl halides and for a number of fluorides, chlorides, bromides and iodides all fall, in fact, on a common curve

$$H_a(\text{C–Hal}) = 250 \times l^{-2}(\text{C–Hal}) - 4 \qquad (1)$$

H_a being in kcal./mole and l in Å.

This observation shows that there is a simple relation between the length and the energy content assignable to a particular bond in a molecule when this latter is formed by simultaneous coalescence of all the atoms. It is not an obvious inference, however, that there will be any simple relation between the length of a bond in a polyatomic molecule and the energy required to break it, and it alone; because this energy is a function not only of the bond itself but also of the molecule of which it is part, and of the radical which is formed by dissociation.[4] If the molecule as a whole is stabilized, relative to some reference state, *e.g.*, by resonance (*alias* mesomerism or bond delocalization), or is in some way destabilized, then as dissociation proceeds this energy term becomes zero: in the former case it would increase the energy required to break the bond, in the latter case it would decrease it. Furthermore, the radical which is formed may be stabilized, again, *e.g.*, by resonance, or it may be destabilized,

(1) Presented at the Symposium on Bond Strengths, New York, N. Y., September, 1951.

(2) Allen and Sutton, *Trans. Faraday Soc.*, **47**, 236 (1951).

(3) Gordy, *J. Chem. Phys.*, **15**, 305 (1947).

(4) Szwarc, *ibid.*, **18**, 1660 (1950); Long and Norrish, *Proc. Roy. Soc.* (*London*), **A187**, 337 (1946).

in a way that the molecule itself is not, and this energy would reach its limiting value as dissociation proceeds; so in the first case it would decrease the energy required to break the bond and in the latter case it would increase it.

Despite this unfavorable prognostication, Allen and Sutton found that a very simple linear relation holds between the length and the dissociation energies[5] for the carbon–halogen bonds in three methyl halides (that for the fluoride has not been reported) and the four acetyl halides (see Fig. 1), *viz.*

$$D(\text{C–Hal}) = 213 - 76 \times l(\text{C–Hal}) \qquad (2)$$

A relation of the inverse square type used above between H_a and l has also been tried, but the point for acetyl fluoride, which is removed somewhat from the others, fits less well on this than on the linear relation.

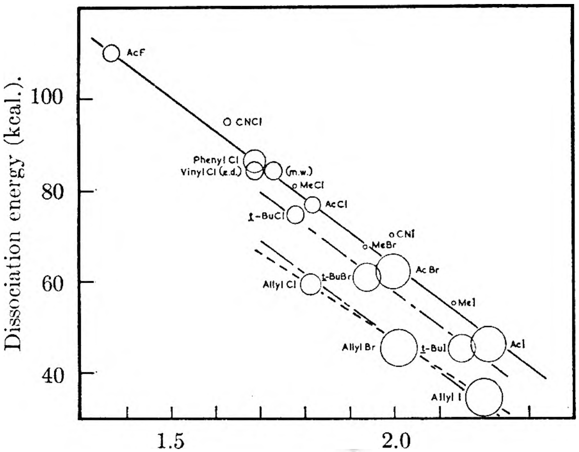

Fig. 1.—Dissociation energy/bond length curves for carbon–halogen bonds. The abbreviations (e.d.) and (m.w.) mean, respectively, from electron diffraction measurements and from micro-wave measurements. The broken line through the points for the allyl compounds is the best one parallel to that for the methyl and acetyl ones, while the dashed line is the best line through them. The circles denote probable error in bond length.

The relations given previously between dissociation energy and other energy quantities may be expressed by the equation

$$D = D_0 - (R_r - R_m) \qquad (3)$$

wherein D is the observed dissociation energy, R_r is the stabilization energy of the radical, R_m that of the molecule *save for* that portion of the stabilization energy which may be regarded as belonging to the bond which is to be broken. D_0 may thus be regarded as the "intrinsic energy" of this bond, *i.e.* as the energy which would be needed to break it if the reorganization energy, $R_r - R_m$, were zero. As defined above, it includes part of the stabilization or destabilization energy of the whole molecule; therefore it is not a constant characteristic only of the type of bond, *e.g.*, it would not be the same for all C–Br bonds; it depends upon its molecular environment. There might therefore be some connection between this quantity which is a characteristic of the unperturbed bond, and the bond length. From equation (3) it follows, however, that D can be put equal to D_0 only if $R_r = R_m$.

It is difficult to imagine a molecule for which this condition actually holds, or to suggest how we should know if it did hold. Szwarc[4] has suggested that the methyl compound might be taken as a standard of reference in such considerations. $R_r - R_m$ need not be zero for the methyl compounds. It is at least likely to be small; and if it is not zero, this means merely that the true zero line is displaced vertically and parallel to that for the methyl compounds (*vide infra*).

Having this in mind, the present authors suggest that the linear relation described above means that the bond length provides a measure of D_0 of the type $D_0 = \kappa - \lambda l$ which is common for the bonds from carbon to all four of the halogens, and that the value of $R_r - R_m$ for acetyl compounds is accidentally the same as that for methyl compounds.[6] The first of these two assumptions embraces the more limited one that D_0 for a particular carbon–halogen bond is composed of a constant term and a variable one which represents the effect of, *e.g.*, resonance stabilization on that bond alone, and which is related to the difference between the actual bond length and that of the reference bond to which the constant energy term also relates.

If these assumptions be granted, it would be predicted that for instances where $R_r > R_m$ the points would fall below the curve to equation (2), and conversely. In general, then, carbon–halogen bonds will not fit equation (2): but it might be expected that $R_r - R_m$ would be roughly constant for the series of halides of any one radical, so that all the points for such a series would be displaced vertically by an equal amount from the line to the equation, *i.e.*, will lie on a line parallel to this latter. This is indeed the case for the allyl halides[7] and the *t*-butyl halides according to determinations of carbon–halogen bond lengths therein by one of the authors and Mr. H. J. M. Bowen (see Fig. 1). The displacements correspond to $R_r - R_m = 16$ and 6 kcal., respectively. The former is somewhat smaller than the radical stabilization ascribed by taking $R_r - R_m = D(\text{CH}_3\text{–Hal}) - D(\text{R–Hal})$; because some allowance has been made in it for the destabilization of the unperturbed carbon–halogen bond in allyl halides relative to methyl halides.

It appears that the point for the carbon–chlorine bond in vinyl chloride lies on or very near to the line to equation (2); so here again $R_r - R_m = 0$ or, more precisely, is the same as for methyl compounds. If this be true, the greater dissociation energy for this compound is to be regarded as a function of the carbon–halogen bond itself in this compound. The same is true of chlorobenzene. These are unexpected results.

The point for cyanogen chloride lies above the line; so in this case $R_m > R_r$, according to these arguments, which is plausible because of the possibility of there being two generalized π-bonds in the

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[5] Roberts and Skinner, *Trans. Faraday Soc.*, **45**, 339 (1949); Carson and Skinner, *J. Chem. Soc.*, 936 (1949).

[6] Allen and Sutton (ref. 2) had reached the same conclusion from a different argument.

[7] The best straight line through the points for the allyl compound is not quite parallel to that for the methyl compounds, but is inclined to it in such a way as to signify that $R_r - R_m$ decreases numerically in the order Cl, Br, I.

molecule which are not possible in the radical. The same is true for cyanogen iodide.

The treatment outlined above may make possible a better assessment of the relative parts played by the bond itself and by effects characteristic of the molecule as a whole or of the radical, in determining dissociation energies.

The simplicity of the relation between D_0 and l is surprising: it is unlikely to be accidental. If we assume, as above, that $R_r - R_m$ is the same for acetyl compounds as for methyl ones, then some such explanation as the following seems to be required.

The potential energy/bond length curve for any bond arises by the superimposition of curves showing, respectively, the variation of attraction energy and of repulsion energy with internuclear distance. The latter generally varies with a much higher inverse power of the distance than does the former.

If now we assume (a) that, over the range of internuclear distance which covers all carbon–halogen bonds, there is one linear attraction curve *common to all four halogens*, and (b) that the repulsion curves between carbon and the several halogens have the same form and differ merely by their lateral displacement, then the observed relation follows; for as may be seen from Fig. 2 the minima lie on a straight line (the broken line) parallel to the attraction curve (the inversion is due merely to the different sign conventions for D and V).

The assumptions are possibly rather more restrictive than is necessary, *e.g.*, it would be sufficient if the repulsion curves were geometrically similar.

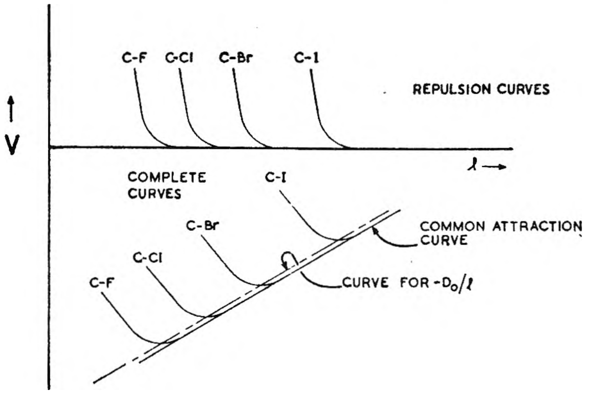

Fig. 2.—Hypothetical potential energy/distance relations for carbon–halogen bonds.

Further, if $R_r - R_m$ were not the same for acetyl compounds as for methyl ones, so that the D_0 values for the carbon–halogen bonds therein really lie off the line for those of the bonds in the methyl compounds, then it might be that the curves of D_0 against l for the individual halogens do not form a common straight line but lie on four parallel straight lines: in this case the attraction curves for the several halogens could also form a set of parallel straight lines, which would have to be such that the lateral displacements between them are in the same ratio as those of the repulsion curves.

In any case, the degree of regularity in the relations between the energy curves for the different halogen–carbon bonds seems surprisingly high.

A METHOD OF DETERMINING THE POTENTIAL BARRIERS RESTRICTING INVERSION IN AMMONIA, PHOSPHINE AND ARSINE FROM VIBRATIONAL FORCE CONSTANTS

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The height of the potential barrier restricting inversion in the ammonia molecule has been determined by several investigators using data on the hyperfine splitting of certain lines in the infrared and micro-wave spectra of that molecule. None of these methods can be applied to phosphine and arsine, since no corresponding experimental data are available. By assuming that the ammonia molecule can be inverted by gradually increasing the amplitude of the symmetrical deformation vibration, the force constants controlling this vibration can be used to plot a parabolic potential of the form $V = A\,(\Delta\alpha)^2$ on either side of the planar configuration. For ammonia, the resulting calculated barrier height agrees very closely with that derived from inversion splittings in the spectrum by the Manning potential function, *viz.*, 2070 cm.$^{-1}$ (5.9 kcal./mole). This indicates that a similar method can be applied to phosphine and arsine and when this is done the corresponding barrier heights are computed to be close to 6000 cm.$^{-1}$ (17.1 kcal./mole) and 11,200 cm.$^{-1}$ (32.1 kcal./mole). Such values are consistent with the absence of inversion splittings in the infrared spectra of phosphine and arsine. The implications of these results in the stereochemistry of trivalent derivatives of ammonia, phosphine and arsine are briefly discussed.

Analyses of the infrared spectra of ammonia, phosphine and arsine prove conclusively that these molecules all possess a pyramidal configuration.[1] In the case of ammonia, the dimensions of the pyramid can be deduced with great accuracy from the observed values of the moments of inertia of NH_3 and ND_3, but in addition a doubling of all the lines in certain of the absorption bands makes it possible to estimate[1,2] the height of the potential barrier restricting inversion as 2100 ± 50 cm.$^{-1}$ or 6000 ± 200 cal./mole. Early analyses of the infrared spectrum of phosphine indicated a similar doubling of the Q branch in an absorption band at 10 μ, from which it was deduced[3] that the height of the barrier in phosphine was approximately the same as that in ammonia. No doubling has been observed in the infrared spectrum of arsine but it can be similarly deduced[3] that if the inversion potential for arsine is also about 6000 cal./mole, the resultant

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(1) G. Herzberg, "Infra Red and Raman Spectra," D. Van Nostrand Co., Inc., New York, N. Y., 1945.

(2) D. M. Dennison and G. E. Uhlenbeck, *Phys. Rev.*, **41**, 313 (1932).

(3) G. B. B. M. Sutherland, E. Lee and C. K. Wu, *Trans. Faraday Soc.*, **35**, 1373 (1939).

splitting of the spectral lines would be much too small to be observed. However it has recently been shown[4] that the apparent doubling of the 10μ Q branch in phosphine is probably spurious, arising from an accidental conglomeration of rotation lines and thus no inversion doubling is observed in either phosphine or arsine. The previous estimates of the barrier heights in phosphine and arsine must therefore be discarded and some other method sought for evaluating the heights of these barriers from spectroscopic data. In the present paper a method is suggested based on vibrational force constants, which is shown to yield excellent results for ammonia and may therefore be assumed to give a reasonable first approximation to the true values in phosphine and arsine.

The basic assumption underlying this method is that the simplest way for a pyramidal XY_3 molecule to invert is through the motion associated with the symmetrical deformation vibration, in which the apical angle of the pyramid opens symmetrically, accompanied by a minor symmetrical change in the XY bond lengths. For such a vibration, the simple valency force field gives as the potential energy

$$V = \frac{3}{2}K_1(\Delta l)^2 + \frac{3}{2}K_\delta(\Delta\alpha)^2 \qquad (1)$$

where Δl is the change in each bond length XY, and $\Delta\alpha$ is the change in each bond angle YXY. The values of the force constants K_1 and K_δ may be deduced from the spectroscopic data. However it is possible to derive a relation between the Δl and $\Delta\alpha$ displacements for this vibration so that the potential energy may then be written formally as

$$V(\alpha) = A(\Delta\alpha)^2 \qquad (2)$$

where A can be computed. As the molecule inverts α passes through a maximum value of 120° in the planar configuration. Thus $(\Delta\alpha)_{\max}$ is known and the height of the potential barrier is taken to be equal to the change in V as α goes from the equilibrium value to 120°. The procedure will now be described in detail for ammonia.

Ammonia.—It is first necessary to obtain values for the force constants K_1 and K_δ. We use the normal frequencies ($\omega_1 = 3589$ cm.$^{-1}$, $\omega_2 = 1055$ cm.$^{-1}$) corrected for anharmonicity[5] instead of the observed fundamentals ($\nu_1 = 3337$ cm.$^{-1}$, $\nu_2 = 950$ cm.$^{-1}$), since the former will give more accurate figures for our assumption of a pure harmonic potential. The equations connecting the frequencies, force constants and molecular constants are well known,[1] *viz.*

$$4\pi^2(\omega_1^2 + \omega_2^2)m = K_1\left(1 + \frac{3m}{M}\cos^2\beta\right) + \frac{k_\delta}{l^2}\frac{12\cos^2\beta}{(1 + 3\cos^2\beta)}\left(1 + \frac{3m}{M}\sin^2\beta\right) \qquad (3)$$

$$16\pi^4\omega_1^2\omega_2^2 = \frac{k_1k_\delta}{l^2}\frac{12\cos^2\beta}{(1 + 3\cos^2\beta)}\left(1 + \frac{3m}{M}\right) \qquad (4)$$

where m and M are, respectively, the masses of the hydrogen and nitrogen atoms, while β is the angle between the symmetry axis and any bond and l is as defined in (1). The values so obtained are $K_1 = 7.21 \times 10^5$ dynes/cm. and $K_\delta/l^2 = 0.474 \times 10^5$ dynes/cm. and equation (1) may be rewritten as

$$V = \frac{3}{2} \times 7.21 \times 10^5(\Delta l)^2 + \frac{3}{2} \times 0.474^2(\Delta\alpha)^2 \qquad (1a)$$

Now we may choose symmetry coördinates[1] S_1, S_2 to describe ω_1 and ω_2 such that

$$\Delta l = pS_1 - sS_2$$

and

$$\Delta\beta = \frac{\sqrt{3}(2r - 1)\cos\beta}{l\cos\frac{\alpha}{2}}S_2 - \frac{\sqrt{3}\cos\beta}{\cos\frac{\alpha}{2}}\frac{s}{l}S_1$$

where

$$p = \frac{3m}{M}\cos^2\beta - 1, \quad r = \frac{3m}{2M}\sin^2\beta + 1$$

$$s = \frac{3m}{M}\sin\beta\cos\beta$$

Furthermore it may be shown[1] that in the vibration ω_2, which we assume governs the inversion

$$S_1:S_2 = 0.1477:1.0$$

in the particular case of NH_3 and this ratio may readily be computed for phosphine and arsine from a similar analysis of their vibration spectra. Assuming the following values for the dimensional constants of the NH_3 molecule[5]

$$l = 1.014 \times 10^{-8}\text{ cm.}, \alpha = 106°46'$$

and remembering that in such a molecule

$$\sin\beta = \frac{2}{\sqrt{3}}\sin\frac{\alpha}{2}$$

we may now rewrite (1a) as

$$V(\alpha) = 3.89 \times 10^4(\Delta\alpha)^2\text{ cm.}^{-1} \qquad (2a)$$

We assume now that this parabolic potential may be used to evaluate the change in energy as α goes from the equilibrium value of 106°46′ to the planar value of 120°, *viz.*, a change of 0.231 radian. The resulting value obtained for the height of the barrier restricting inversion is

$$V = 2077\text{ cm.}^{-1} = 6005\text{ cal./mole}$$

The corresponding values obtained from the doubling phenomenon by various workers are assembled in Table I.

Table I

Inversion Potential Barrier (in cm.$^{-1}$) in Ammonia

Dennison and Uhlenbeck[2]	1770
Morse and Rosen[6]	1950–2100
Wall and Glockler[7]	3314
Manning[8]	2076

The best of these is undoubtedly that given by Manning who had to use no approximations and was able to use eleven experimental values of energy levels to solve the wave equation. The almost exact agreement of our value with that of Manning is of course fortuitous. More important is the fact that if we transform our potential function so that the energy is plotted as a function of the height of the ammonia pyramid (h), the shape of Manning's whole curve is very accurately followed (Fig. 1). Our original function is a double parabola but it should be noted that the oscillations are not

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(4) H. H. Nielsen, *Faraday Society Discussions*, **9**, 85 (1950).

(5) D. M. Dennison, *Rev. Modern Phys.*, **12**, 175 (1940).

(6) N. Rosen and P. M. Morse, *Phys. Rev.*, **42**, 210 (1932).

(7) F. T. Wall and G. Glockler, *J. Chem. Phys.*, **5**, 314 (1937).

(8) M. F. Manning, *ibid.*, **3**, 136 (1935).

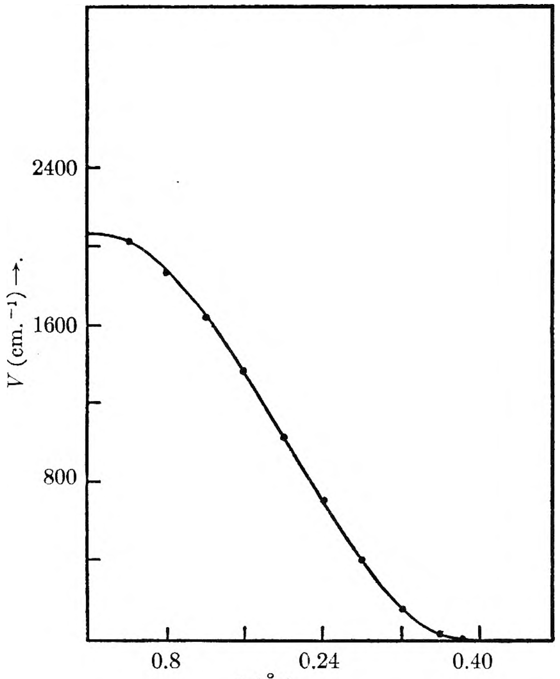

Fig. 1.—Inversion potential for ammonia as a function of the distance, h, of the nitrogen atom from the plane of the hydrogen atoms. Full curve calculated from vibrational data; dots indicate values of Manning's function.

necessarily exactly harmonic since the reduced mass is changing point by point. The transformation of $V(\alpha)$ to $V(h)$ is done by using geometrical relations, *e.g.*

$$\cos^2\frac{\alpha}{2} = \frac{1}{4}(l + 3\cos^2\beta)$$

$$\text{giving}\quad \cos\alpha = \frac{1}{2}(3\cos^2\beta - 1) = \frac{1}{2}\left(\frac{3h^2}{r^2} - 1\right)$$

This may be used directly although a series expansion is more accurate near the planar position.

As the final and possibly most critical test of our potential curve we may compute from it the splittings of the energy levels in the ground and first vibrational states. The results shown in Table II. are the splittings which give rise to the doubling phenomenon.

TABLE II

Splitting, in cm.$^{-1}$	Calcd.	Obsd.	Manning
Ground state, Δ_0	0.789	0.7935	0.83
First vibrational state, Δ_1	36.6	35.8	26.0

Thus using only data from vibration frequencies and ignoring doubling we have obtained a potential function which is comparable to the best derived from the observation of inversion splitting in respect of (a) height of barrier; (b) general shape; (c) prediction of the observed doublet fine structure. We can therefore proceed to apply the method to phosphine and arsine with some degree of confidence that the results must give a reasonably correct picture of the situation there, although one must remember that since the height of the pyramid is now considerably greater than in ammonia, the change in bond angle in going through the planar configuration will be appreciably larger and the assumption of purely harmonic forces will be less justifiable.

Phosphine.—Here the observed frequencies[1] ν_1 = 2327 cm.$^{-1}$ and ν_2 = 991 cm.$^{-1}$ must be used as the normal frequencies have not yet been determined. These yield $K_1 = 3.32 \times 10^5$ dynes/cm. and $K_\delta/l^2 = 0.33 \times 10^5$ dyne/cm. Taking P–H = 1.46 Å. and h = 0.67 Å.[3] the height of the barrier is computed to be 6085 cm.$^{-1}$ or 17,450 cal./mole. The shape of the potential barrier is shown in Fig. 2. The calculated doublet separations in the ground state and the first, fourth and fifth vibrational levels come out as

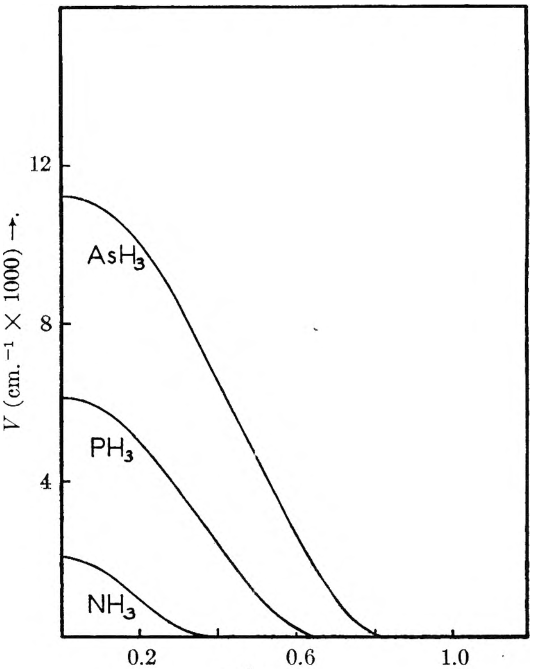

Fig. 2.—Inversion potential for NH_3, PH_3 and AsH_3 as a function of the height of the molecule, h.

$$\Delta_0 = 4.76 \times 10^{-4}\ \text{cm.}^{-1}$$
$$\Delta_1 = 2.38 \times 10^{-4}\ \text{cm.}^{-1}$$
$$\Delta_4 = 9 \times 10^{-1}\ \text{cm.}^{-1}$$
$$\Delta_5 = 33.2\ \text{cm.}^{-1}$$

There might be a possibility of observing Δ_4 at very great path lengths and thus obtaining a confirmation of this method of approach.

Arsine.—Here the values of the normal frequencies are known[9] to be ω_1 = 2209 cm.$^{-1}$ and ω_2 = 973.9 cm.$^{-1}$ giving $K_1 = 2.865 \times 10^{-5}$ dyne/cm. and $\frac{K\alpha}{l^2} = 0.258 \times 10^{-5}$ dyne/cm. Using the values of the moments of inertia of AsH_3 and AsD_3 given by Nielsen and McConaghie[9] we obtain As–H = 1.523 Å. and h = 0.856 Å. These values differ somewhat from the dimensions computed by Nielsen and McConaghie, which appear to be slightly in error. The height of the barrier comes out to be 11,220 cm.$^{-1}$ or 32,090 cal./mole. The shape of the curve is shown in Fig. 2. The doublet splittings are immeasurably small, *e.g.*, $\Delta_0 = 3.7 \times 10^{-18}$ cm.$^{-1}$ and $\Delta_1 = 6.0 \times 10^{-16}$ cm.$^{-1}$, so no experimental confirmation is possible in this case.

(9) V. M. McConaghie and H. H. Nielsen, *Phys. Rev.*, **75**, 633 (1949).

Optically Active Derivatives of Phosphine and Arsine.—The time of inversion τ is very simply related to the splitting in the ground state Δ_0 by the equation $\tau = 1/2\Delta_0 c$, where Δ_0 is in cm.$^{-1}$ and c is the velocity of light. For instance in NH_3 this time is 2.5×10^{-11} sec. and is accepted as the reason that no optically active derivates of trivalent nitrogen have ever been made. The corresponding times for PH_3 and AsH_3 come out to be 2.3×10^{-6} sec. and 1.4 years. For AsD_3 the time is however 3.5×10^7 years, the inversion time being very sensitive to the masses of the atoms attached to the apical atom. Thus one might expect optical activity associated with trivalent arsenic. Evidence for this has been given by Lesslie and Turner[10] and Chatt and Mann[11].

[10] M. J. Lesslie and E. E. Turner, *J. Chem. Soc.*, 1170 (1934); 1051, 1268 (1935); 730 (1936).

[11] J. Chatt and F. G. Mann, *ibid.*, 1184 (1940).

SOME PROBLEMS OF INTERNAL ROTATION

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We have studied by the infrared, Raman, dielectric and electron diffraction investigations the structure of many molecules with regard to the internal rotation about the C–C axis. By comparing the experimental results obtained for molecules with various rotating groups ($XH_2C–CH_2Y$, $XH_2C–COY$, XOC–COX, $X(CH_3)_2C–C(CH_3)_2X$, $X_3C–CX_3$ and $X_3Si–SiX_3$ where X and Y denote Cl, Br, OH and CH_3) we arrived at the following conclusions concerning the nature of the hindering potential for the internal rotation. If there is no appreciable double bond character in C–C bond, the steric force between atoms contained in different movable groups plays the most important role in determining the main feature of the potential curve: *e.g.*, the positions of potential minima, corresponding to the stable configurations and the positions of potential maxima or of the potential barrier. The stable molecular configurations determined by this force would not be greatly changed by other conceivable forces as electrostatic force, hydrogen bond, etc., which would only affect such a quantity as the energy difference between the stable configurations. The intermolecular forces which are responsible for the change in equilibrium ratio of stable configurations cannot also change the main feature determined by the steric force.

Based on the experimental results of Raman effect,[1,2] infrared absorption,[3] dielectric constant[1,4] and electron diffraction[5] we have determined the stable configurations of rotational isomers which differ from one another in azimuthal angle of internal rotation about single bonds as axes. Some of the experimental results so far obtained in our laboratory are summarized in Table I.[6]

We believe that our conclusion for the configurations of these molecules is very sound, since we have applied various experimental methods as stated above. We shall now discuss several problems of internal rotation, especially those concerning the nature of the hindering potential based on these experimental data. Although this potential has been discussed theoretically by several investigators,[7] it is desirable to discuss the experimental material more extensively.

The data shown in Table I confirm our previous conclusion that the most important force in determining stable configurations of rotational isomers is the steric repulsion between two groups rotating against each other about a single bond as axis. For example, the fact that the molecules of the type of $XH_2C–CH_2Y$ have rotational isomers of the same configurations (*i.e.*, the *trans* and the gauche forms[8]) irrespective of the dipole moment values of C–X and C–Y bonds reveals that the steric repulsion is far more important than the electrostatic force. This conclusion is also compatible with the experimental result that the internal rotation of $Cl_3C—CCl_3$ is hindered considerably (the height of the potential barrier amounting to about 10 kcal./mole), while that of $Cl_3Si–SiCl_3$ is almost free. In the eclipse form[9] of $Cl_3C–CCl_3$ corresponding to the potential maximum of the internal rotation, the distance between the two chlorine atoms, one contained in one Cl_3C– group and the other in the other group, is 2.72 Å. while that of $Cl_3Si–SiCl_3$ is 3.20 Å. The fact that such a minor difference in the interatomic distance in these two molecules results in a large difference in internal rotation suggests that the most important force must be the steric repulsion which is

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[1] Mizushima, Morino and Higasi, *Physik. Z.*, **35**, 905 (1934); *Sci. Pap. Inst. Phys. Chem. Res. Tokyo*, **25**, 159 (1934); Mizushima, Morino and Nojiri, *Nature*, **137**, 945 (1936); Mizushima, Morino and Kubo, *Physik. Z.*, **38**, 459 (1937).

[2] Mizushima, Morino, Watanabe, Shimanouchi and others, *Sci. Pap. Inst. Phys. Chem. Res. Tokyo*, **39**, 387, 396 (1942); **40**, 87, 100 (1942); **42**, 1, 5, 27 (1944); *J. Chem. Phys.*, **18**, 754, 1516 (1950); Mizushima, Morino and Takeda, *ibid.*, **9**, 826 (1941); Mizushima, Morino, Watanabe, Shimanouchi and Yamaguchi, *ibid.*, **17**, 591 (1949); Katayama, Shimanouchi, Morino and Mizushima, *ibid.*, **18**, 506 (1950).

[3] Shimanouchi, Tsuruta and Mizushima, *Sci. Pap. Inst. Phys. Chem. Res. Tokyo*, **42**, 51 (1946); Mizushima, Morino, Shimanouchi and Kuratani, *J. Chem. Phys.*, **17**, 838 (1949).

[4] Watanabe, Mizushima and Morino, *Sci. Pap. Inst. Phys. Chem. Res. Tokyo*, **39**, 401 (1942); Watanabe, Mizushima and Mashiko, *ibid.*, **40**, 425 (1943).

[5] Yamaguchi, Morino, Watanabe and Mizushima, *Sci. Pap. Inst. Phys. Chem. Res. Tokyo*, **40**, 417 (1943); Morino, Yamaguchi and Mizushima, *ibid.*, **42**, 5 (1944); Morino and Iwasaki, *J. Chem. Phys.*, **17**, 216 (1949).

[6] Similar studies have also been made by Pitzer, Glockler, Bernstein, Gwinn, Sheppard, Cleveland and others and their results are generally in good agreement with ours.

[7] Glockler, *Rev. Mod. Phys.*, **15**, 112 (1943).

[8] The trans form is the configuration in which X and Y atoms of $XH_2C–CH_2Y$ are at the farthest distance apart and the *gauche* form can be obtained from the *trans* form by an internal rotation of about 120°.

[9] The eclipse form of $Cl_3C–CCl_3$ is the configuration in which all the three Cl atoms of one Cl_3C–group eclipse the three Cl atoms on the other Cl_3C–group when viewed along the C–C axis.

TABLE I

STABLE CONFIGURATIONS OF ROTATIONAL ISOMERS

Figures in parentheses denote the energy difference between the rotational isomers in kcal./mole

Molecule	Solid state	Liquid state	Gaseous state	CCl_4 Solution
ClH_2C-CH_2Cl	*trans*	*trans* *gauche* (*ca* .0)	*trans* *gauche* (1.2)	*trans* *gauche*
BrH_2C-CH_2Br	*trans*	*trans* *gauche* (0.7)	*trans* *gauche* (1.4)	*trans* *gauche*
ClH_2C-CH_2Br	*trans*	*trans* *gauche*		*trans* *gauche*
ClH_2C-CH_2I	*trans*	*trans* *gauche*		*trans* *gauche*
$CH_3CH_2-CH_2CH_3$	*trans*	*trans* *gauche*	*trans* *gauche* (0.8)	
$CH_3CH_2-CH_2Cl$	*trans*	*trans* *gauche*		
HOH_2C-CH_2Cl	*gauche*	*trans* *gauche*	*trans* (0.95) *gauche*	
$ClH_2C-COCl$	*trans*	*trans* *gauche*		
$BrH_2C-COCl$	*trans*	*trans* *gauche*	*trans* *gauche* (1.0)	
$ClOC-COCl$	*trans*			
$Br(CH_3)_2C-C(CH_3)_2Br$				*trans* *gauche* (1.6)
$Cl(CH_3)_2C-C(CH_3)_2Cl$				*trans* *gauche* (1.0)
Cl_3C-CCl_3	Staggered			
$Cl_3Si-SiCl_3$		Almost free rotation	Almost free rotation	

very sensitive to the variation of interatomic distance. (This force is inversely proportional to the 12th power of interatomic distance.)

Concerning the steric repulsion in Cl_3C-CCl_3 we should like to note that in the staggered form[10] (or the stable form) the distance between two nearest chlorine atoms on different movable groups is almost equal to the sum of the van der Waals radii of two chlorine atoms, while in the eclipse form this distance becomes 2.72 Å. at which there must be a considerable repulsion. This is the most important reason why the eclipse form corresponds to the potential maximum of internal rotation.

In the stable configurations, therefore, the repulsive potential tends to take as low value as possible and the repulsive force may become of the same order of magnitude as the electrostatic force, hydrogen bonding, etc. This would be seen, for example, from the value of the energy difference of the rotational isomers of $Br(CH_3)_2C-C(CH_3)_2Br$ (ΔE = 1.6 kcal./mole) which is even greater than that of BrH_2C-CH_2Br (ΔE = 1.4 kcal./mole). As the CH_3-group has almost the same van der Waals radius as the Br-atom, ΔE of $Br(CH_3)_2C-C(CH_3)_2Br$ cannot be so large, if only the steric repulsion would contribute to the energy difference between the rotational isomers. In such a case we have, therefore, to consider an important contribution of the electrostatic force to ΔE.

It is, however, evident that even in stable configurations we cannot neglect the steric repulsion. This will be seen, for example, from the difference of ΔE between ClH_2C-CH_2Cl (ΔE = 1.2 kcal./mole) and BrH_2C-CH_2Br (ΔE = 1.4 kcal./mole) shown in Table I. The contribution of electrostatic force to ΔE in the dichloride must be greater than that in the dibromide, since the bond moment of C–Cl is almost equal to that of C–Br and the induction effect in the dichloride is smaller than that in the dibromide.[11] Therefore, the fact that ΔE of ClH_2C-CH_2Cl is smaller than that of BrH_2C-CH_2Br shows that there is a considerable contribution of the steric repulsion to ΔE of such rotational isomers.

It would be very interesting, if we could determine the ratio of the steric part to the electrostatic part of the hindering potential. The value of ΔE (= 0.8 kcal./mole) of *n*-butane may tell us the approximate magnitude of the steric part of ΔE of BrH_2C-CH_2Br, since *n*-butane is a non-polar substance and the van der Waals radius of the CH_3-group is almost equal to that of the Br-atom as stated above.

In such a substance as ClH_2C-CH_2OH an internal hydrogen bond is formed between the two rotating groups. This bond lowers the energy of the *gauche* form to make it more stable than the *trans* form which otherwise would be always the lower energy form in the case of molecules of the type of XH_2C-CH_2Y (see Table I). However, the internal hydrogen bond is not so strong as to shift the *gauche* position up to the *cis* position.

In the case where the internal rotation axis acquires a double bond character to a considerable amount, the situation may become quite different from what we have stated above. Among the

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[10] The staggered form of Cl_3C-CCl_3 is the configuration in which the projection of one C–Cl bond upon the plane perpendicular to C–C axis is midway between those of two C–Cl bonds in the other half of the molecule.

[11] This would be seen from the difference in the moment value μ_g. of the *gauche* molecule between the dichloride and the dibromide. μ_g. of ClH_2C-CH_2Cl was found to be 2.55 *D*, while μ_g. of BrH_2C-CH_2Br was 2.0 *D*.

substances shown in Table I ClOC–COCl provides us with such an example. For this substance the *trans* form is found to be the stable configuration, which would not be the case, if the steric repulsion is the predominant factor in determining the stable configuration. The stability of the *trans* form in this case is due on one hand to the single bond–double bond resonance of the structure of O═C—C═O and on the other hand to the fact that the steric repulsion between two Cl-atoms is much greater than that between Cl- and O-atoms.

So far we have mainly discussed the molecular configurations and their energy differences in the free state. We have, however, often reported the considerable change of the equilibrium ratio of different configurations with the change of state.[1,2] For example, for $ClH_2C–CH_2Cl$ the *gauche* molecule becomes more abundant in the liquid state than in the gaseous state at the same temperature, while in the solid state this molecule disappears almost completely (see Table I). Such a change in equilibrium ratio must be explained in terms of the intermolecular forces as was already discussed in our previous papers. However, as we can see from Table I, the intermolecular force is not so strong as to change greatly the positions of maxima and minima of the hindering potential which is determined mainly by steric repulsion in case there is no considerable single bond–double bond resonance.

THE CALCULATION OF VIBRATIONAL FREQUENCIES OF MOLECULES WITH MANY ATOMS AND LITTLE SYMMETRY. I. SIMPLE DERIVATIVES OF SYMMETRICAL MOLECULES

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The use of approximate normal coördinates is suggested as a basis for the calculation of vibrational frequencies in the more complicated molecules. Two basically similar methods have been proposed. The first, which takes advantage of the existence of group frequencies, has not been tested sufficiently. The second method, dealing with molecules which may be regarded as simple derivatives of symmetrical molecules, is tested numerically with simple examples.

Introduction

One of the most potent devices in the analysis of vibrational spectra is the calculation of the fundamental modes of vibration of a molecule based on a mechanical model. All of our progress in the correlation of observed frequencies with types of motion of the various component elements of structure of a molecule has its origin in such calculations. Fundamentally the use of infrared and Raman spectra in qualitative structural analysis rests upon this base.

Because of the high order of the matrices and determinants involved in the practical application of the methods so far developed, such calculations have been limited to molecules containing few atoms and of relatively high degree of symmetry. The extension of the methods of theoretical infrared and Raman spectroscopy to complex molecules depends upon the penetration of this barrier. A tremendous wealth of information available in spectra is as yet untapped because we do not recognize its correlation with structure and environment. There is no reason why one should not apply the same methods to penicillin and cortisone as are now applied to methane and ethyl alcohol.

Two fundamentally similar methods of extending vibrational calculations to complex molecules have been outlined recently.[1] They involve perturbation methods based upon the use of normal coördinates as a practical tool in numerical calculations. Such a use of normal coördinates has been neglected except in the application to the isotope effect.[2,3] The first and simpler method applies to molecules which may be considered as a simple derivative of a molecule possessing greater symmetry. Examples would be cyclic C_4F_7Cl considered as a derivative of cyclic C_4F_8 or C_2F_5Cl and CF_2ClCF_2Cl as derivatives of C_2F_6 and C_6H_5Cl as a derivative of C_6H_6. The second method regards a complex molecule as being built up of basic structural units such as methyl and ethyl groups, benzene rings, etc., joined together by coupling links. It puts the concept of group frequencies upon a quantitative basis. While it will be relatively simple in actual application, this method requires considerable ground work including the calculation of numerous tables for its practical use.

The present communication deals with the numerical test of the first method. No loss in generality and considerable savings in labor are involved by restricting the test to simple molecules.

Normal coördinates by definition yield a unit matrix for the kinetic energy matrix and a diagonal potential energy matrix whose elements are the square of the (circular) frequencies of vibration. Unfortunately frequencies of vibration must be calculated first before normal coördinates can be obtained. However it can be predicted that the normal coördinates for a molecule like cyclic C_4F_7Cl will be similar to those for the molecule cyclic C_4F_8. The use of the normal coördinates of the latter or parent molecule in setting up the expressions for the former or derivative molecule will

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[1] Walter F. Edgell, Paper No. 16, Sixty First Session of the Iowa Academy of Science, Inorganic and Physical Chemistry Section, April, 1949.

[2] Walter F. Edgell, *J. Chem. Phys.*, **13**, 306 (1945).

[3] *Ibid.*, **13**, 539 (1945).

result in kinetic and potential energy matrices which are approximately diagonal. This permits the use of perturbation methods for obtaining the frequencies. Thus, for the example just cited, the necessity of expanding and finding the roots of a 16th order secular equation is replaced by the multiplication of matrices of the same size. This is a very much simpler (*and possible*) task and is readily carried out with ordinary calculating machines. Because of the symmetry of the parent molecule (cyclic C_4F_8) the calculation of the basic normal coördinates is a relatively simple matter.

The methods and hence the equations are very similar to those already applied to the isotope effect.[3] The main difference results from the fact that now the potential energy matrix will also contain relatively small off diagonal terms.

Let the transformation to the normal coördinates of the parent molecule be given by the expression

$$R = LQ \qquad (1)$$

The inverse kinetic energy matrix of the derivative molecule based upon the approximate normal coördinates Q is $L^{-1}G\tilde{L}^{-1}$, where G is the corresponding matrix for the coördinates R. The potential energy matrix for Q will be $\tilde{L}FL$ where F is the matrix for R. The square of the (circular) vibrational frequencies of the derivative molecule are the roots of the matrix

$$H = L^{-1}GFL \qquad (2)$$

Because the off diagonal terms of H are small the matrix can be diagonalized by perturbation methods to a sufficient degree of accuracy. Applying an appropriate transformation to H yields the following expression for the i^{th} root of H, correct to the second order

$$\lambda_i = H_{ii} + \sum\nolimits_j' \frac{H_{ij}H_{ji}}{H_{ii} - H_{jj}} \qquad (3)$$

Numerical Test of the Method

As pointed out in the introduction no loss in generality is involved by testing the method with simple molecules. Methyl chloride was taken as the parent molecule for the derivative molecules CH_3Br and CH_3F. Its normal coördinates were calculated and the H matrices for the derivative molecules were obtained from equation 2. The frequencies were calculated by equation 3 and are compared with an exact calculation in Tables I and II.

TABLE I: CH_3Br

Frequency	Exact, cm.$^{-1}$	Eq. (3)	Diff., %
W_1	2953	2953	0
W_2	1302	1302	0
W_3	613	613	0
W_4	3074	3074	0
W_5	1452	1452	0
W_6	953	953	0

TABLE II: CH_3F

Frequency	Exact, cm.$^{-1}$	Eq. (3)	Diff., %
W_1	2860	2860	0
W_2	1500	1500	0
W_3	1037	1037	0
W_4	2978	2978	0
W_5	1484	1487	0.20
W_6	1223	1220	0.25

Further tests are provided by considering bromoform as a derivative of chloroform and CCl_4 as the parent molecule for CF_4 and CBr_4. The results are found in Tables III–V. It should be pointed out that equation 3 must yield exact results for W_1 and W_2 of the last two molecules.

The force constants used in these calculations were taken from the work of Noether, Linnett, and Decius.[4-6]

TABLE III: $CHBr_3$

Frequency	Exact, cm.$^{-1}$	Eq. (3)	Diff., %
W_1	3037	3037	0
W_2	540	540	0
W_3	223	223	0
W_4	1135	1132	0.26
W_5	645	645	0
W_6	154	153	0.65

TABLE IV: CF_4

Frequency	Exact, cm.$^{-1}$	Eq. (3)	Diff., %
W_1	904	904	0
W_2	437	437	0
W_3	1266	1266	0
W_4	630	629	0.16

TABLE V: CBr_4

Frequency	Exact, cm.$^{-1}$	Eq. (3)	Diff., %
W_1	269	269	0
W_2	123	123	0
W_3	672	672	0
W_4	183	183	0

The results are uniformly excellent. It is clear that equation 3 yields the same results as the exact calculation for all practical purposes. This method is being applied to the interpretation of the Raman and infrared spectrum of cyclic C_4F_7Cl and the results will be published in connection with that work.

In some cases where the mass change is large, as for example C_6H_5F as a derivative of C_6H_6, several terms in the inverse kinetic energy matrix, and hence in H, will be relatively large. A modification is required in such cases. The offending terms are collected into a diagonal submatrix by reordering the rows and columns. The roots of this submatrix (of H) are obtained by solution of its secular equation and the results used to transform H to the new basis coördinates so determined. The roots, and hence the vibrational frequencies, are obtained by applying equation 3 to the transformed H matrix. This is analogous to the use of equation 23 of the paper on the isotope effect (3). The restriction of the method to *simple* derivatives ensures that the secular equation of the offending submatrix will never be of high order.

Similar techniques will be required when several roots have nearly the same value.

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(4) H. Noether, *J. Chem. Phys.*, **10**, 667 (1942).

(5) J. W. Linnett, *ibid.*, **8**, 91 (1940).

(6) J. C. Decius, *ibid.*, **16**, 214 (1948).

PREDICTION OF ISOMERIC DIFFERENCES IN PARAFFIN PROPERTIES.[1]

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Parameters proposed for predicting paraffin properties are examined critically. The most important ones are: *f*, the sum of first C–C neighbors of every C–C bond in the molecule; *p*, the number of "steric pairs" or groups on carbon atoms three bonds apart, which is half the sum of second C–C neighbors; and *w*, the Wiener number, the sum of the number of bonds between all pairs of carbon atoms in the skeleton. The variables *f* and *p* determine internal properties such as H_0, the heat of formation of the gas at 0°K., and *R*, the molar refraction; *p* and *w* determine external properties such as *L*, the standard heat of vaporization, *B*, the boiling point, and *V*, the molar volume. The heat of formation of the gas at 25°, H_{25}, requires all three, and the same promises to be true of most other properties at room temperature. Least squares equations are given for H_0 and *R* and for the isomeric variance in H_{25}, *L*, *B* and *V*. The mean deviations are close to the experimental errors, except for the boiling points, where additional or better external parameters are needed. The interaction terms of steric pairs—the *p*-coefficients—in H_0 and *R* can be obtained for different angles of twist about the intermediate single bond, from data on alkyl cyclanes. They follow a $(1 + \cos\theta)$ law within experimental error, showing zero interaction at the 180° angle. The steric barrier height is about 1500 cal./mole at the 0° angle. First-neighbor alkyl substitution on a bond lowers its contribution to H_0, produces a red shift in its first ultraviolet absorption region, and increases *R*. Steric hindrance decreases *R;* a possible explanation is that steric strain causes differential lengthening of a C–C bond in high excited states, producing a shift of the high-frequency absorption to shorter wave lengths.

The hypothesis is proposed that the Wiener number, *w*, is an index of the mean external contact area of the molecule, except for a correction for steric hindrance. This will account for the fact that *w* unstabilizes an isomer in the gas phase (decreases the self-contact area and increases H_{25}) by almost the same amount by which it stabilizes the liquid (increases the external contact area and *L*). The molar volume formula contains a large negative steric term which seems to express the compression of steric pairs.

The isomeric paraffins are remarkably similar in stability, bond energies and force fields. Differences in their properties are largely of geometric origin. As a result they are well suited for the isolation and study of geometric factors which must be of importance for all molecules.

These properties were selected for study:

H_{25}, the heat of formation of the gas at 25°
R, the molecular refraction for the D lines at 20° for the air-saturated hydrocarbon in the liquid state at one atmosphere
V, the molecular volume under the same conditions
B, the boiling point at the same pressure

Later two more were added:

H_0, the heat of formation of the gas at 0°K.
L, the standard heat of vaporization at 25°

The most elaborate, systematic and successful formulations of these properties in the literature seem to be those of Taylor, Pignocco and Rossini,[2] Wiener,[3] and Platt.[4] The Appendix defines the parameters in these formulations and gives the constants and mean deviations of some of the least-squares solutions through the octanes (Tables I and II).

Wiener Formulas

The great success of the Wiener 2-constant equations for all the properties is immediately evident. They are almost as accurate as 5- and 6-constant equations involving other parameters.

Let us consider the Wiener variables.

The importance and physical significance of one of his parameters, *p*, is easy to see. This is the number of pairs of carbon atoms three bonds apart in the hydrocarbon. It accounts alone for 80% of the isomeric variance in *R* and for a large part of the variance in the other properties. It appeared in the TPR analysis as the factor k_1 used to relate their coefficients, and was responsible for the reversals of sign noted by Platt in his a_2 coefficients. It is evidently an index describing the steric interference of the groups on carbon atoms three bonds apart during rotation about the intermediate single bond. Hereafter we shall call such pairs of groups "steric pairs."

Wiener supposed that *p* was due to an alternation in bond or atom interactions along a chain, comparable to the alternations found in conjugated systems. But the coefficients of *p* in the formulas are unreasonably large for such an interpretation, while the simple first-neighbor, second-neighbor, etc., interaction formula[4] shows no further alternation for pairs of carbons four bonds, five bonds, and six bonds apart. The analysis of the data on the cyclanes given below seems to show conclusively that *p* is an index of steric hindrance.

The meaning of Wiener's other parameter, *w*, the "path number," which we might properly call the "Wiener number," is harder to see. It is the sum of the numbers of bonds between all pairs of carbons in the molecular skeleton. It increases for large molecules as N^3, where *N* is the number of carbon atoms in the paraffin. Evidently $\sqrt[3]{w}$ is a sort of mean molecular diameter; and $\Delta w/N^2$, the term in the Wiener formulas, is approximately proportional to the increment in $\sqrt[3]{w + \Delta w}$, and represents the increment in mean diameter for a given isomeric change. The N^2 acts as a normalizing factor so as to make the Δw term for a given type of change almost independent of *N*.

The success of the Wiener formulas for describing internal properties of molecules was at first surprising, because *w* seems physically unreasonable as a factor in such properties. Thus in going from a normal chain to a 3-branched isomer with branch lengths l_1, l_2, l_3, the change in *w* is the product $-l_1l_2l_3$. For a given *N*, this product continues to increase with increased lengths of the shorter branches, no matter how long they are, until all the branch lengths are equal.[5] Dependence on such a parameter in large molecules would imply very long-range forces indeed.

New Formulas

In an attempt to duplicate the success of the Wiener formulas for internal properties without encountering this objection, other parameters were examined which it was hoped would be measures of the molecular compactness, similar to *w*, but which

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[1] Previously given in part at The Ohio State University Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, June 11, 1947.

[2] W. J. Taylor, J. M. Pignocco and F. D. Rossini, *J. Research Natl. Bur. Standard*, **34**, 413 (1945).

[3] H. Wiener, *J. Am. Chem. Soc.*, **69**, 17, 2636 (1947); *J. Chem. Phys.*, **15**, 766 (1947); THIS JOURNAL, **52**, 425, 1082 (1948).

[4] J. R. Platt, *J. Chem. Phys.*, **15**, 419 (1947).

[5] I am indebted to Dr. J. E. Mayer for this observation.

would represent interactions extending for no more than three or four bonds along the skeleton.

By its nature, such a search cannot be straightforward. With the limited types of variations possible in paraffin isomers, every structural parameter is correlated with every other one.[6] A spurious parameter may therefore substitute for a true one, because of this correlation, with no great loss in accuracy. It may even give a slight gain in accuracy if somehow, possibly by a physical connection, possibly by unfavorable random fluctuations, it is highly correlated with experimental errors in a limited set of data. The problem of finding the correct variables resembles the problem of finding the fundamental law of force in a mechanical system whose motions are limited and related by fixed constraints.

Under these circumstances it seems best to choose our formulas by balancing several requirements.

Accuracy.—In predicting the data, the formula should give minimum deviations, or deviations close to the experimental error. A variable is relatively inessential if it does not reduce the deviation when added to other variables.

Simplicity.—The formula should have a minimum number of variables.

Reasonableness.—Their effects should be physically understandable and the magnitudes physically reasonable. There should be no absurdities in the limit of large or small molecules.

Stability.—If the variables are really fundamental, their effects should be independent of N, and their empirical coefficients in least-squares formulas should be almost unaffected by the presence or absence of other variables. This last requirement is peculiar to the examination of correlated parameters.

The obvious variables for representing terminated interactions were tried: the sums of numbers of first-neighbors, second-neighbors, etc.[7]; the sums of squares of numbers of neighbors, etc.; the products of neighbors on one end of a bond with those on the other, etc.; and the number of *gauche* (or *trans*) pairs in rotational isomerism about every C–C bond (called h in the Appendix; both the most stable and the least stable rotational isomers were tried).

The coefficients and mean deviations of some of the better least-squares formulas are shown in the Appendix. Upon balancing the criteria stated above, we find that *none of these formulas is better than the Wiener formula*, except in the case of one property.

The comparison nevertheless led to significant conclusions which could hardly have been obtained otherwise.

The property for which the Wiener formula was not best is H_0. The best variables in this case are the first-neighbor sum, f; and the second-neighbor sum, which is twice the number of steric pairs, p. Call a formula with these variables a two-neighbor sum.

This property, H_0, which is fitted without using the Wiener number, w, is as purely internal as any property could be. This suggested that w is not in fact an internal parameter but an external one. This idea was supported by the fact that w is the principal and essential variable for describing the boiling point—a most external property.

Whenever w is needed to describe presumably internal properties, it must mean that external variables are entering into the measurement of these properties to such an extent that w, which after all is correlated with f (and with the other neighbor sums and products), becomes a good substitute for f in the equations.

Thus if w is involved in H_{25} but not in H_0, "external" effects must contribute to the gaseous heat content in warming up from 0°K. (Any one of the f, p, w coefficients in H_{25} can be adjusted initially over a wide range without causing much loss in accuracy in a least-squares solution for the other two. By taking the f-coefficient the same as for H_0, which is arbitrary but plausible, the isomeric differences in heat content are described by the alteration in the p-coefficient from 0°K. to 25°C., and by the w-coefficient at 25°).

If w enters into R, perhaps there are external influences on R which are not completely represented by the simple density term in the classical formula. Actually in this case, a two-neighbor sum gives about the same accuracy as the Wiener formula and both seem to be pressing the limit of experimental error. Since we expect R to be internal, the f, p description is adopted here.

For the largely external properties, V, L and B, the Wiener formula is best.

The adopted least-squares formulas for the properties are:

$$H_0 = -12.450 - 4.074(N - 1) - 0.499f + 0.688p \pm 0.33 \text{ kcal./mole}$$

$$R = 6.460 + 4.750(N - 1) + 0.0112f - 0.1304p \pm 0.016 \text{ ml./mole}$$

$$\Delta H_{25} = -0.500\ \Delta f + 0.796\ \Delta p + 5.33\ \Delta w/N^2 \pm 0.38 \text{ kcal./mole}$$

$$\Delta L = 0.210\ \Delta p + 5.086\ \Delta w/N^2 \pm 0.052 \text{ kcal./mole}$$

$$\Delta B = 5.640\ \Delta p + 98.36\ \Delta w/N^2 \pm 0.55°$$

$$\Delta V = -2.256\ \Delta p - 10.95\ \Delta w/N^2 \pm 0.21 \text{ ml./mole}$$

The formulas for H_0 and R give the total value of the property, the first two coefficients being determined from the n-C_2 to n-C_8 series for H_0 and from n-C_5 to n-C_8 for R. The other two terms in these formulas, and the terms in the other formulas were determined from least-squares solutions for the isomeric variance in the C_5 through C_8 groups, and the mean deviations given are for these solutions. Formulas for the total value of the other properties must await more precise theoretical definition of w, since its contribution is known only for the isomeric variance. Its contribution to the CH_2 increment in

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[6] That is, skeletal parameters. The skeleton of a hydrocarbon completely defines the structure. No examination of chain isomers can isolate variables which are theoretically more primitive, such as the contributions of H-atoms, of C-atoms, of C–H bonds, of C–C bonds, or their interactions, etc. These contributions are lumped indistinguishably into the coefficients of skeletal parameters. What linear combination of them is involved depends on one's taste in choosing his zero-order theoretical approximation. The correlation of these variables is complete. The correlation of different skeletal parameters is not complete and so a choice among them or an estimate of their independent contributions is still possible.

[7] The Wiener number is in fact a particular neighbor-sum (*J. Chem. Phys.*, **15**, 766 (1947)) but with the property that the coefficients of successive orders of neighbors, instead of approaching zero, increase linearly with increasing distance. This is another way of saying that it would correspond to long-range forces if it were an internal property.

the line of homologs is different for several different ways of computing w (which give the same Δw), and its physical meaning needs to be better understood before it can be intelligently used in formulas.

The deviation of H_{25} for methane from the expected value given by linear extrapolation from the line of the higher n-paraffins was successfully predicted earlier by the six-constant formula. The present simpler formula for H_0 gives the ethane deviation accurately, but misses the methane value by about 3 kcal./mole. The quadratic neighbor terms which were dropped from the higher paraffins with no great loss in accuracy may be essential for describing the methane deviation.

All the present formulas, except the one for boiling point, give mean deviations approaching the experimental error. It does not seem that the coefficients of additional parameters could be determined with any confidence. The boiling points are known to perhaps fifty times the accuracy of the formula, and a search for more elaborate external parameters to add to the Wiener formula for this property might be rewarding.

Cyclanes: H_0 and R

Anomalous molecules demand modifications in the equations. They provide an acid test for any physical interpretation of the parameters. The methane and ethane deviations from the linear n-paraffin series are stringent tests of paraffin formulas.

The anomalous cyclane properties are similarly hard to fit. Happily, it appears that the formulas given above for H_0 and R can be adapted easily and plausibly to the C_8-cyclohexane and C_7-cyclopentane isomeric deviations.

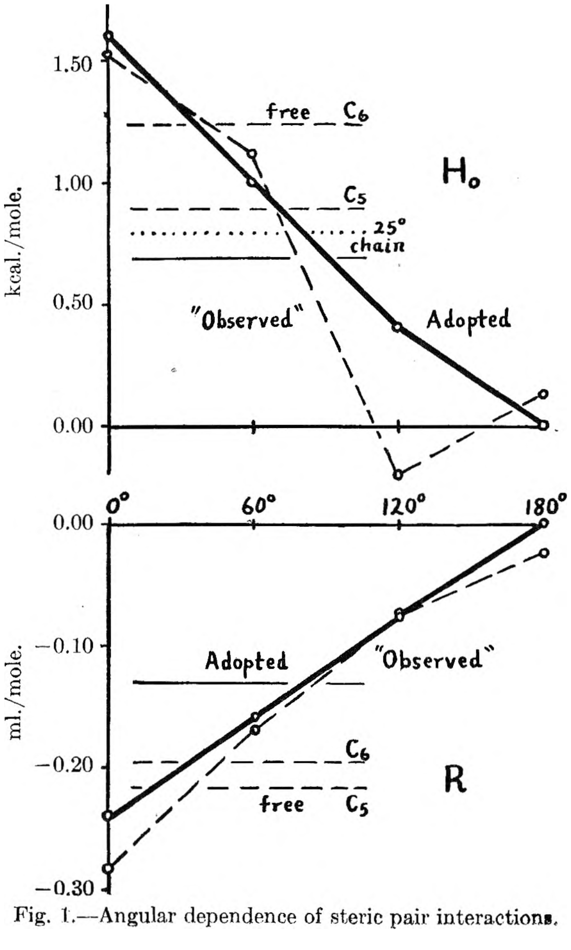

Fig. 1.—Angular dependence of steric pair interactions.

The data may be analyzed in terms of a first-neighbor interaction, like that in the chain paraffins, plus a second-neighbor interaction which is a function of the relative angle of rotation of a steric pair about the middle C–C bond. When the middle C–C bond is a ring bond, the angles are held close to certain equilibrium values, 60 and 180° for puckered cyclohexane with normal tetrahedral valence angles; and close to 0 and 120° on the average for approximately planar cyclopentane. If the intermediate C–C bond is adjacent to the ring, the angles are not fixed and we may have a "free" second-neighbor interaction similar to that in the chain paraffins.

When the intermediate C–C bond is in the ring, examination of the data shows that the steric effect is the same whether the two interacting groups are both outside the ring, or one outside and one in the ring; this is true for both H_0 and R. By examining only isomeric variance for a fixed ring system, we avoid having to evaluate the steric interaction between different groups within the ring.

We thus have three second-neighbor coefficients for the cyclohexanes: $a_2(60)$, $a_2(180)$, and $a_2(\text{free})$; plus a_1. Similarly for the cyclopentanes: $a_2(0)$, $a_2(120)$ and $a_2(\text{free})$; plus a_1. The four constants for each group can be determined independently, as seen in Table III in the Appendix. However, by modifying them slightly as shown in the "Adopted" set, they can be made more consistent with the alkane values with no great loss in accuracy for the cyclane predictions.

The adopted formulas are:

$$\Delta H_0 = -0.500\Delta f + 1.00\Delta p_{\text{free}} \begin{cases} +\ 1.00\ \Delta p_{60} + 0.00\Delta p_{180} \pm 0.07 \text{ kcal./mole for cyC}_6 \\ +1.60\Delta p_0 + 0.40\Delta p_{120} \pm 0.37 \text{ kcal./mole for cyC}_5 \end{cases}$$

$$\Delta R = 0.015\Delta f - 0.130\Delta p_{\text{free}} \begin{cases} -0.160\Delta p_{60} - 0.00\Delta p_{180} \pm 0.016 \text{ ml./mole for cyC}_6 \\ -0.240\Delta p_0 - 0.075 p_{120} \pm 0.035 \text{ ml./mole for cyC}_5 \end{cases}$$

In the R for the cyclopentanes the accuracy is appreciably worse than in the corresponding two-constant sum for the alkanes. This is mostly because the methyl groups seem to have an abnormal interaction in 1,1-dimethylcyclopentane, possibly because of deviations of the ring bond angles from the tetrahedral values; and in *cis*-1,3-dimethylcyclopentane, possibly because they come in contact more than is usual for third-neighbor C–C bonds. Both effects can reasonably be associated with the well-known puckering of the C_5 ring.

The second-neighbor interactions in H_0 and R are plotted as functions of angle in Fig. 1. In both cases they increase smoothly from near zero at 180° to a maximum effect at 0°. The zero at 180° and the absence of dip near 90° show that no appreciable part of the interaction can be due to hyperconjugation, which would give maxima at 0 and 180° and minima at 90°, approximating a $\cos^2\theta$ function. The observed curve can be fitted within its accuracy by a $(1 + \cos\theta)$ function without higher order terms.

The Free Interactions.—The free second-neighbor interaction in the alkanes is close to the mean of the fixed-angle interactions. For properties observed at room temperature, such as R, this can be understood if an angle near 90° is a turning-point of the motion under hindered rotation, so that most of the steric pairs are found a maximum fraction of the time near this position. The free second-neighbor interaction in the ethyl cyclanes corresponds to a turning-point nearer to 45°. This may of course be normal for rotation about a bond which is doubly-substituted at one end.

This behavior of the free interaction is harder to understand for properties measured at absolute zero, such as H_0. One would suppose that a steric pair would have deep potential minima at 60 and 180° from the hydrogen-atom repulsions on the central bond like the well-known minima in ethane and the substituted ethanes; and that at absolute zero the pair would be frozen in one of these positions, preferably at 180° where possible, in view of the higher energy required to reach 60° in Fig. 1.

But such a model leads to three expectations which are not verified experimentally. First, there is no longer any reason for the mean angle of a "free" steric pair at absolute zero to agree with its mean angle at room temperature since the first pair is frozen while the second is really almost free.

But they do agree almost within experimental error as shown in Fig. 1 for H_0 and H_{25} and R. (The small increment in the p-coefficient for H_{25} may be due to a tendency for a steric pair to go higher up the steric barrier at room temperature; or it may be due to an effect discussed for the L coefficients below, the effect of steric hindrance at room temperature in reducing the probability of intramolecular van der Waals attractions.)

Second, the success of a two-neighbor sum formula should be worse at absolute zero than at room temperature if in the first case the second-neighbors are not all alike and if at the higher temperature they are all alike, on the average. But the two-neighbor sum is better at the low temperature (where the experimental errors are worse!) than the three-constant formula for H_{25}. On the other hand this may be due to the inadequacy of w as a variable for describing the heat content.

Finally, if the steric pairs at absolute zero are fixed in the configurations described above as most probable, it should be possible to predict H_0 better by replacing p with a new variable, h, which is the sum of the number of 60° pairs when the most stable configuration is taken about every C–C bond. This would assume that the 180° interaction could be taken to be zero, as found for the cyclanes. But a least-squares formula for H_0 in terms of f and h was found to have a mean deviation of ± 0.46 kcal./mole, 40% worse than the formula with f and p.

The simplest way of accounting for these results is to suppose that the most stable configurations were not in fact obtained in the low-temperature paraffin studies. The steric pairs may be frozen into the 60 and 180° positions, but at random, in a non-equilibrium distribution; so that p, which is indifferent to configuration, is better than the ordered parameter, h. Such situations are familiar in the quenching of alloys, in the freezing-in of dislocations in metals and crystals, and even in solid paraffins themselves, many of which are glasses and crystallize only with great difficulty if at all. A paraffin gas molecule by itself may be a large enough aggregate to show such behavior also.

H.—The height of the curve at 0° in Fig. 1 is about 1500 cal./mole for each steric pair. This is comparable to the heights of free-rotation potential barriers in paraffins and substituted paraffins found by other methods. It is important to remember that the curve for H in Fig. 1 would be only an approximate potential curve even if there were no experimental error in the measurements, since each point on it represents only a time-average value over a zero-point range of rotational configurations. In the alkyl cyclopentanes, because of the zero-point puckering motion of the ring, the angles of a steric pair may range to ± 60° on either side of the average value.

The first-neighbor term in the adopted formulas for H of the alkanes and cyclanes would appear as the stabilization of a C–C bond by about 500 cal./mole on methyl substitution, if we considered the effects as being due simply to perturbation of the C–C skeleton. Such a picture is too simple. This energy term is a sum of differential effects of substitution on C–H and C–C bonds; or on the C and H atoms, for those who prefer that formulation. For the prospective theorist, the best statement of the significance of the first-neighbor term is probably phenomenological: that the whole system at the end of a paraffin chain is "ideally" stabilized by about 1000 cal./mole on rearranging to the 2-methyl form; and that this is probably largely electronic or internal energy with small or negligible contributions from steric effects.

The data on H_{25} for the cyclanes were not analyzed since it was not clear how to compute w or an analog for it in these structures, or even Δw; and since the w term had already shown its importance in the alkane H_{25} formula at these temperatures.

Transmission Limits: *R*

The molar refractivity, R, depends on the wave lengths and intensities of ultraviolet absorption in the molecule. Some observations on the absorptions of paraffins, as shown by their transmission limits, have been made by Klevens and Platt.[8] Regularities found in these limits throw some light on the regularities in R, and were indeed the initial stimulus for the present study.

The transmission limits, which are determined by the lowest-frequency absorption bands, were found to depend principally on the number of first C–C neighbors around the most-substituted C–C bond in the molecule. This same factor seems largely to determine the known first ionization potentials,[9,10] as though the most substituted bond contained the least tightly bound electrons in the molecule. The situation is parallel to that in substituted ethylenes where the spectra and the ionization potential both move to lower frequencies with increasing number of first neighbors of the C=C bond.[10]

The increase in R of the paraffins with increasing values of the variable f corresponds to this shift to longer wave lengths with number of first neighbors. The shift in limit for every additional neighbor on the most substituted bond is about 30 Å., or about 1.5% in wave length. The increase in R per first-neighbor is about 0.2% of the increment for every C–C link. No doubt R is mainly determined by higher-frequency absorption bands which have large excited-state orbitals whose energy is relatively insensitive to local isomeric variations of structure.

The decrease in R with increased number of steric pairs in the molecule represents a mean loss of intensity or shift to higher frequency in the absorption spectrum. The effect is several times larger than the first-neighbor effect. The transmission limit shows no signs of such behavior; in fact, second-neighbors of the most-substituted bond are associated with a small shift to lower frequencies rather than to higher.

One attractive explanation of these effects is as follows. Consider the central C–C bond of a steric pair and the upper states produced by exciting an electron from this bond. We may suppose that the addition of the neighbors to this bond in forming the steric pair lowers the energy of each of these states. Assume the energy reduction would be equal for all angles between the pair in the absence of steric effects. But the steric strain will cause lengthening of the central C–C bond, by approximately the same amount in the ground and first excited states where the excited electron is still nearby; but by much greater amounts in the higher excited states where the excited electron is essentially removed and the bond becomes a weak one-electron bond. Since the Franck–Condon principle requires vertical excitation, differential lengthening of the bond in the upper state will produce a shift of the absorption to shorter wave lengths, which may overshadow the lowering of the upper state potential minimum, and which will cause a steric decrease in the contribution of this bond to R.

Many other explanations could be put forward. This interesting second term in R seems worthy of a careful theoretical examination.

The Wiener Number: *L*, *B* and *V*

Having examined the meaning of the first and second-neighbor parameters, we are in a better

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[8] H. B. Klevens and J. R. Platt, *J. Am. Chem. Soc.*, **69**, 3055 (1947).

[9] W. C. Price, *Chem. Revs.*, **41**, 257 (1947).

[10] R. E. Honig, *J. Chem. Phys.*, **16**, 105 (1948).

position to understand the effects assigned to the mysterious and important external parameter, w.

The behavior of the w coefficients suggests as a working hypothesis: that the quantity $\sqrt[3]{w}$, which is a sort of mean distance between the carbon atoms in a molecule, is an approximate inverse measure of the probability of one part of the molecule being attracted to another part by van der Waals forces, or an inverse measure of the "mean self-contact area." Since the total possible contact area—something like the exposed surface of the hydrogen atoms—is approximately constant in isomers, the sum of the self-contact area and the external contact area must be constant. If w is an inverse measure of the former it must be a direct measure of the latter.

This notion gains support from the near-equality of the w-terms in H_{25} and in L at 25°. Within a set of isomers, a larger mean molecular diameter reduces the internal contact area and decreases the intramolecular van der Waals attractions of the gaseous molecules, by about the same amount by which it increases the external contact area and increases the intermolecular van der Waals attractions in the liquid.

The failure of w to contribute to H_0 can be understood if we suppose that at absolute zero the molecules are frozen in configurations determined by the hindered-rotation potential barriers about each C–C bond, and that these configurations offer little opportunity for contact beyond the second-neighbor contacts already described. The mean area of the random long-range internal contacts described by w must be small or zero.

What then is the role of the p-term in L? For a given w, this steric term increases the intermolecular binding in the liquid. Plausibly we may suppose that steric hindrance makes some of the internal contacts more awkward and improbable, decreases the internal contact area, and increases the external. The increment in the p-term between H_0 and H_{25} may be due to this loss of van der Waals stability in the more sterically hindered isomers. The increment is of the same order as the steric term in L, but smaller. Because of the "surface irregularities" produced by steric effects, there is in this case no reason to expect the loss of internal contact area to balance exactly the external gain.

In brief, it is proposed here that the steric and Wiener terms in the adopted formula for L together describe approximately the isomeric variance in the mean intermolecular contact area of molecules in the liquid phase. The dependence of the intermolecular contact area on w and p may be calculable for molecules with partially-hindered rotation by statistical mechanical methods.

About the boiling-point formula all that need be said is that the coefficients of the two terms in B are roughly proportional to the coefficients in L.

As for V, we see that an increase of intermolecular binding in the liquid as shown by larger L is accompanied by a decrease of molecular volume. A stronger total force between molecules produces a closer average approach. Or we can say that a compact molecule uses its volume inefficiently and contains holes; it will have a small external contact area and small L; while the opposite will be true for an extended molecule. Or both effects may be present.

If the variance in volume were largely external, due to variations in the mean space between molecules, we should expect the V coefficients to be proportional to the L coefficients. If the variance were largely internal, then for a given external contact area as determined by L, we should expect an increase in steric hindrance to produce less efficient packing and more holes "within" the molecule, with a positive contribution to the second-neighbor V-coefficient. Actually, this coefficient is much larger (more negative) than the w-coefficient in V, relative to their values in L.

In short, steric hindrance reduces the internal volume. No doubt this added p-effect is due to the familiar interpenetration of steric pairs to distances of approach smaller than the usual van der Waals radii. This penetration is necessary to account for the mean repulsive potential in Fig. 1. The apparent compression of volume per steric pair is about 1.8 ml./mole, about 12% of the total volume contribution per added CH_2 group.

Indicated Studies

The variables adopted here will undoubtedly be the simplest ones to use in making empirical correlations of other properties of the paraffins. Of especial interest would be further studies on free energy and entropy of formation, surface tension, octane number and so on.

The type of reasoning used here can probably be extended in a straightforward way to alkenes, alkynes and alkyl aromatics; the disappearance of free rotation and the possible appearance of directional intermolecular forces will add interesting but difficult variables to the analysis. The treatment of substituted hydrocarbons will have its own delights and complications.

Of the terms discussed here, the f-terms in H and R and the two terms in L are those which seem most likely to succumb easily to theoretical prediction.

The Wiener number, with its N^2 denominator, especially needs theoretical examination and justification, with both theoretical and empirical attention to the question whether it is itself a fundamental variable or only a good approximation to some more significant quantity.

In the boiling points, the search for an additional or a better external parameter should continue.[11]

Appendix

In Table I are given the values of parameters which seem likely to be useful in future analyses of other properties of

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(11) NOTE ADDED IN PROOF.—Reference should be made to J. K. Brown and N. Sheppard, *J. Chem. Phys.*, **19**, 976 (1951), and to D. W. Scott, J. P. McCullough, K. D. Williamson and Guy Waddington, *J. Am. Chem. Soc.*, **73**, 1707 (1951), on low-temperature rotational disorder in methylbutanes. Also to K. S. Pitzer, *Disc. Far. Soc.*, **10**, 66 (1951), and to J. G. Aston, *ibid.*, **10**, 73 (1951), on the *n*-butane steric barrier. Also to J. L. Lauer, Thesis, University of Pennsylvania, 1947, and *J. Chem. Phys.*, **16**, 612 (1948), on the shift of the "characteristic wave lengths" of methylcyclohexanes to higher frequencies with steric hindrance. Also to A. R. Ubbelohde and J. C. McCoubrey, *Disc. Far. Soc.*, **10**, 94 (1951), on coiling and self-contact of *n*-paraffins.

TABLE I

VALUES OF PARAMETERS

Isomer	N	$\epsilon/\frac{1}{2}\Delta_\epsilon$		$f_2/\frac{1}{2}\Delta f_2$		$f_3/\frac{1}{2}\Delta f_3$		$f_{11}/\frac{1}{2}\Delta f_{11}$		$f_{12}/\frac{1}{2}\Delta f_{12}$		$f_{22}/\frac{1}{2}\Delta f_{22}$		$w\_\ \Delta w/N^2$		h
—1	1															
—2	2													1		
—3	3	2						2						4		
—4	4	4		2				6		2		2		10		
2-m-3	4	6	1		−1			12	3		−1		−1	9	0.06250	
—5	5	6		4		2		10		6		4		20		
2-m-4	5	8	1	4			−1	18	4	6		6	1	18	0.08000	1
22-m-3	5	12	3		−2		−1	36	13		−3		−2	16	0.16000	
—6	6	8		6		4		14		10		8		35		
2-m-5	6	10	1	6		4		22	4	12	1	8		32	0.08333	1
3-m-5	6	10	1	8	1	2	−1	24	5	14	2	14	3	31	0.11111	2
22-m-4	6	14	3	6			−2	44	15	12	1	12	2	28	0.19444	2
23-m-4	6	12	2	8	1		−2	32	9	16	3	16	4	29	0.16666	2
—7	7	10		8		6		18		14		12		56		
2-m-6	7	12	1	8		6		26	4	16	1	14	1	52	0.08163	1
3-m-6	7	12	1	10	1	6		28	5	20	3	18	3	50	0.12245	2
3-e-5	7	12	1	12	2	6		30	6	24	5	24	6	48	0.16326	3
22-m-5	7	16	3	8		6		48	15	20	3	14	1	46	0.20408	2
23-m-5	7	14	2	12	2	4	−1	38	10	26	6	26	7	46	0.20408	3
24-m-5	7	14	2	8		8	1	34	8	20	3	12		48	0.16326	2
33-m-5	7	16	3	12	2	2	−2	52	17	26	6	28	8	44	0.24490	4
223-m-4	7	18	4	12	2		−3	60	21	30	8	30	9	42	0.28571	4
—8	8	12		10		8		22		18		16		84		
2-m-7	8	14	1	10		8		30	4	20	1	18	1	79	0.07812	1
3-m-7	8	14	1	12	1	8		32	5	24	3	24	4	76	0.12500	2
4-m-7	8	14	1	12	1	10	1	32	5	26	4	22	3	75	0.14062	2
3-e-6	8	14	1	14	2	10	1	34	6	30	6	30	7	72	0.18750	3
22-m-6	8	18	3	10		8		52	15	24	3	22	3	71	0.20312	2
23-m-6	8	16	2	14	2	8		42	10	32	7	32	8	70	0.21875	3
24-m-6	8	16	2	12	1	10	1	40	9	28	5	24	4	71	0.20312	3
25-m-6	8	16	2	10		8		38	8	22	2	22	3	74	0.15625	2
33-m-6	8	18	3	14	2	8		56	17	34	8	32	8	67	0.26562	4
34-m-6	8	16	2	16	3	8		44	11	36	9	38	11	68	0.25000	4

TABLE I (*Continued*)

Isomer	N	$f/\frac{1}{2}\Delta f$	$f_2/\frac{1}{2}\Delta f_2$	$f_3/\frac{1}{2}\Delta f_3$	$f_{11}/\frac{1}{2}\Delta f_{11}$	$f_{12}/\frac{1}{2}\Delta f_{12}$	$f_{22}/\frac{1}{2}\Delta f_{22}$	$w - \Delta w/N^2$	h
2-m-3-e-5	8	16	16	10	44	38	38	67	4
		2	3	1	11	10	11	0.26562	
3-m-3-e-5	8	18	18	6	60	42	48	64	6
		3	4	−1	19	12	16	0.31250	
223-m-5	8	20	16	6	66	42	42	63	5
		4	3	−1	22	12	13	0.32812	
224-m-5	8	20	10	12	60	30	18	66	3
		4		2	19	6	1	0.28125	
233-m-5	8	20	18	4	68	46	50	62	6
		4	4	−2	23	14	17	0.34375	
234-m-5	8	18	16	8	52	40	40	65	4
		3	3		15	11	12	0.29687	
2233-m-4	8	24	18		90	54	54	58	6
		6	4	−4	34	18	19	0.40625	

TABLE II

CONSTANTS AND MEAN DEVIATIONS OF LEAST-SQUARES FORMULAS

a_1	a_2	a_3	a_{11}	a_{12}	a_{22}	a_w	M.D.
			H_0, kcal./mole				1.38
	0.544					14.05	0.44
−0.499	.344						.33
−0.505	.342					− .19	.33
						(f and h)	.46
			H_{25}, kcal./mole				2.23
	0.597					19.42	0.37
−0.668	.301						.44
−0.500	.398					5.33	.38
−1.658	− .335		0.165	0.201	0.011		.29
−1.570	− .545	−0.140	.120	.235	.070		.19
−1.118	− .160		.101	.210	.002	7.31	.25
			R, ml./mole				0.163
	−0.0702					−0.325	.015
0.0112	− .0652						.016
.0055	− .0680					−0.170	.015
.0243	− .0749		−0.0036	0.0037	0.0011		.013
.0239	− .0741	− .0015	− .0039	.0070	− .0020		.011[a]
.0285	− .0736		− .0011	.0038	.0010	0.056	.012
						(TPR-6-const)	.013
			L, kcal./mole				0.712
	0.105					5.086	.052
−0.172	.0238						.097
− .0385	.0892					4.001	.043
			B, °C.				11.8
	2.820					98.36	.55
−3.258	1.198						2.38
0.295	2.943					106.76	0.53
−8.476	0.165		−1.112	0.120	−0.139		1.54
−8.23	−2.34	−1.43	0.76	1.03	0.14		0.67
−1.639	2.368		0.304	0.004	0.030	92.51	.42
						(TPR-6-const)	.55
			V, ml./mole				2.14
	−1.128					−10.95	0.21
0.358	−0.943						.38
−0.110	−1.173					−14.063	.21
1.160	−0.797		−0.169	−0.001	−0.004		.28
1.090	−0.505	.160	− .120	− .100	− .035		.22[a]
0.355	−1.056		− .073	− .016	.008	−10.90	.19
						(TPR-6-const)	.16[a]

[a] Fitted to older API data.

TABLE III

ANGULAR DEPENDENCE OF STERIC PAIR INTERACTIONS

A. Parameters

Isomer	$^1/_2\Delta$	$-^1/_2\Delta f_2$					$-\Delta H_0 \times 100$		$\Delta R \times 1000$	
		free	0°	60°	120°	180°	obs.	pred.	obs.	pred.
C_8-Cyclohexanes										
e-*c*6	..	..		..		..	..	..	..	..
11-m-*c*6	2	−2		2			199	200	27	0
12-m-*c*6										
cis(ep)	1	−2		3			1	0	−173	−190
trans(ee)	1	−2		1		2	197	200	106	130
13-m-*c*6										
cis(ee)	1	−2				2	308	300	281	290
trans(ep)	1	−2		2			112	100	−13	−30
14-m-*c*6										
cis(ep)	1	−2		2			114	100	−14	−30
trans(ee)	1	−2				2	305	300	293	290
							M.D. =	7		16
C_7-Cyclopentanes										
e-*c*5	..	..	..		..		..	..	..	..
11-m-*c*5	2	−2			2		261	320	86	170
12-m-*c*5										
cis	1	−2	1		2		58	60	−99	−100
trans	1	−2			3		231	180	108	65
13-m-*c*5										
cis	1	−2			2		157	220	134	140
trans	1	−2			2		211	220	185	140
							M.D. =	37		35

B. Angular Coefficients

Coeff.	H_0, kcal./mole Observed *c*5	*c*6	Adopted	R, ml./mole Observed *c*5	*c*6	Adopted
a_1	−0.20	−0.43	−0.50[a]	−0.049	0.020	0.015[a]
a_2 (free)	0.45	0.62	0.50[b]	−.108	−.098	−.065[b]
a_2 (0°)	.76		.80	−.142		−.120
a_2 (60°)		.56	.50		−.085	−.080
a_2 (120°)	−.10		.20	−.038		−.038
a_2 (180°)		.06	.00[a]		−.012	.000[a]

[a] Assumed. [b] Assumed in C_6's.

hydrocarbons. They are listed for all the alkane isomers through the octanes.

N is the number of carbon atoms.

f_i is $\sum_\alpha f_{\alpha i}$ where $f_{\alpha 1}$ is the number of first-neighbor C–C bonds adjacent to the αth C–C, $f_{\alpha 2}$ is the number of second-neighbor C–C bonds, or bonds one bond removed from the αth C–C, etc.; the sum being taken over all the C–C bonds in the molecule.

f is f_1.

$\frac{1}{2}f_2$ is p, the number of steric pairs in the molecule. When p replaces f_2 in a formula, its coefficient is numerically twice as large.

f_{ij} is $\sum_\alpha f_{\alpha i} f_{\alpha j}$.

The offset columns give half the isomeric increment in each parameter over the value for the n-paraffin of the same N. The offset f_2 column gives Δp.

w is the sum of the numbers of bonds between all pairs of carbon atoms in the molecule. The offset column gives $1/N^2$ times the isomeric increment, which is the quantity actually employed in the Wiener formulas.

h is the total number of steric pairs at an angle of 60° to each other around their central C–C bond, under the condition that each pair is allowed to take only the angles 60 or 180°, with the 180° position around every C–C bond being filled first. This variable is most likely to be useful for describing low-temperature properties.

There are some useful sum rules for the f's. Since

$$\sum_j f_{\alpha j} = N - 2$$

and

$$\sum_j \sum_k f_{\alpha j} f_{\alpha k} = (N - 2)^2$$

it follows that

$$\sum_j f_j = \sum_j \sum_\alpha f_{\alpha j} = (N - 1)(N - 2)$$

and

$$\sum_j \sum_k f_{jk} = \sum_\alpha \sum_j \sum_k f_{\alpha j} f_{\alpha k} = (N - 1)(N - 2)^2$$

The third of these relations is useful for checking the determinations of the f's.

The f's can be expressed in terms of c_3, the number of tertiary carbons; c_4, the number of quaternary carbons; c_{31}, the number of tertiaries next to an end; etc. The first few formulas are

$$f_1 = 2(N - 2 + c_3 + 3c_4)$$

$$f_2 = 2(N - 3 + 2c_3 + 6c_4 - c_{31} - 2c_{41} + c_{33} + 2c_{34} + 4c_{44})$$

$$\begin{aligned} f_{11} &= -10 + 4N + 12c_3 + 42c_4 - 2c_{31} - 4c_{41} + \\ &\qquad 2c_{33} + 4c_{34} + 8c_{44} \\ &= f_1 + f_2 + 6c_3 + 24c_4 \end{aligned}$$

$$\begin{aligned} f_{12} &= 10 - 4N + f_1 + 2f_2 - f_3 + 6c_4 - 2c_{41} + \\ &\qquad 2c_{33} + 6c_{34} + 16c_{44} \end{aligned}$$

The higher f's, f_3 and f_{12} and beyond, cannot be expressed completely in terms of c's with only one or two subscripts.

Wiener showed that w is a neighbor-sum

$$w = {}^1/_2N(N-1) + \tfrac{1}{2}\sum_j jf_j$$

The isomer designations in Table I are obvious simplifications, such that—4 means n-butane; 2-m-3-e-5 means 2-methyl-3-ethylpentane; and 2233-m-4 means 2,2,3,3-tetramethylbutane; etc.

For each property G of Table II, each row gives the coefficients determined for a least-squares fitting of a formula of the type

$$\Delta G = a_1\Delta f_1 + a_2\Delta f_2 + a_3\Delta f_3 + a_{11}\Delta f_{11} + a_{12}\Delta f_{12} + a_{22}\Delta f_{22} + a_w\Delta w/N^2$$

to the observed isomeric deviations, ΔG, obtained from the API Tables. Some terms in this formula were omitted in each solution; the entries in each row correspond to the terms kept.

The last column shows the average deviation (neglecting sign) between the observed values and the values predicted by the resulting formula for the property. The first entry in this column for each property shows the raw isomeric variance, *i.e.*, the mean deviation of the data on this same group of isomers from the formula $\Delta G = 0$. The amount by which this figure is reduced by using the other formulas is a measure of their merit.

All the C_5–C_8 isomer data were used in the analysis, omitting the 2,2-dimethylpropane and 2,2,3,3-tetramethylbutane, since some of the data for these compounds were taken under non-standard conditions. The data used in Tables II and III were from the Selected Values of Properties of Hydrocarbons, American Petroleum Institutre Research Project 44 at the National Bureau of Standards, as follows, by property, table numbers, and latest dates of revision (except as noted in Table II):

H_0: 1*w*, 2/49; 2*w*, 11/46; 3*w*, 10/44; 6*w*, 4/49; 7*w*, 4/47
H_{25}: 1*p*, 4/45; 2*p*, 11/46; 3*p*, 4/45
R and *V*: 1*b*, 6/48; 2*b* and 3*b*, 12/48; 6*b* and 7*b*, 6/49
L: 1*q*, 2*q* and 3*q*, 5/44
B: 1*a*, 6/48; 2*a* and 3*a*, 12/48

The coefficients of the f, h solution for H_0 in Table II were not tabulated since this solution was unsuccessful. Mean deviations are also given for the TPR least-squares solutions for several properties. These authors used different parameters, c_3, c_4, c_{23}, c_{24}, c_{33} and c_{34} to fit essentially the same data used here.

Part A of Table III gives the isomeric deviations in the parameters f_1 and f_2 (angular) and the properties H_0 and R for the C_8-cyclohexanes, taking ethylcyclohexane as reference compound; and for the C_7-cyclopentanes, taking ethylcyclopentane as reference compound.

Part B shows the corresponding coefficients, a_1 and a_2 (angular) necessary to fit the observed values of Part A. The "Observed" columns give the coefficients obtained by simple subtraction among the data in Part A. The "Adopted" columns give the best values of the angular coefficients when some of the others are fixed as indicated so as to be more consistent with the alkane values. The predictions from these "adopted" sets of coefficients are shown in part A, with their mean deviations. The "Observed" and "Adopted" sets are plotted in Fig. 1 as functions of angle, after having been multiplied by two to convert them to p-coefficients.

POSSIBLE MOTIONS OF VIBRATING MOLECULES AND THEIR INTERPRETATION IN TERMS OF MOLECULAR STRUCTURE

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The possible motions of a system of vibrating particles in a normal mode are studied briefly in the general case, and it is indicated how in a given configuration they may be expected to depend on the potential function. The case of the symmetrical vibrations of the symmetrical triatomic molecule is treated in detail, taking water, sulfur dioxide and chlorine monoxide as three typical systems. The problem is reduced to one in a single coördinate, and formulae obtained for the shape of the potential well representing the vibrating system, for all allowed solutions of the force constants. The contours of the potential well are found to be concentric ellipses of the same eccentricity, this latter and the orientation of the well being functions of the force constants. The directions of the vectors representing the two normal modes are related to each other and to the axes of the elliptical contours.

I. Introduction

The study of molecular force fields has been considerably hampered by what perhaps can best be described as a feeling of discouragement which arises at quite an early stage of an investigation. This possibly applies to other fields of work as well, of course, but in the present instance one can at least be quite explicit as to the underlying cause. It is merely that one cannot in general be certain enough that a set of force constants chosen, after the usual fitting with the vibration frequencies, as a best set, is near enough to the real set to justify a complete normal coördinate analysis, with its attendant additional information—atomic displacements and potential energy distributions. After all, the calculation of force constants is not the be-all and end-all of a theoretical spectroscopist's life—he wants to use them to investigate the normal "life" of his molecule—the way it moves in its everyday existence while translating in between reacting. There are two obvious courses of action in proceeding beyond the choosing of a "best set" of force constants, and its interpretation in terms of individual bond strengths, bond angle rigidities, oribital coupling and interatomic repulsions. The first is the direct calculation of the potential function by quantum mechanical methods. Until the exact significance of localised and over-all molecular orbitals[1] is properly understood—why apparently one has to use one set for one type of phenomena, the other for a different type—this appears to be beyond the bounds of possibility even in simple triatomic systems; the problem is rather different from that of obtaining force constants of the correct order of magnitude as a demonstration of quantum-mechanical method. It might be noted in passing that the improvement of the simple Heitler–London treatment of the

(1) Lennard-Jones and Pople, Faraday Soc. Discussion on Hydrocarbons, 1951.

hydrogen molecule by including a scale factor, thus reducing the error in the dissociation energy by fifty per cent, actually *worsens* the vibration frequency, already too high in the simple treatment.[2] In more complex molecules it seems rather unlikely that exact variational wave functions can ever be found, so it is as well to note the above defect. The second course of action is really one that we are forced to adopt while waiting for the first to give results, or because we feel that perhaps it probably cannot. It is to forget (for more than the moment) the initial problem and to treat the vibrational equation as the problem to be solved. It is suggested that we require a rough idea of the ranges of solutions allowed to the force constants, their mutual dependence, and the approximate relation between their values and the normal coordinates; and a more exact knowledge of these quantities and properties, plus the derivatives determining the dependence of the frequencies on the force constants, in the region of the real set. The first study can perhaps be omitted once sufficient simple and one or two more complex cases have been dealt with. It is a necessary one for correlation with subsequent quantum mechanical calculations; and has considerable intrinsic interest and possible application outside the field of molecular vibration theory.

Detailed information over the whole ranges of allowed solutions is now available for triatomic systems[3] having various mass-ratios, and less completely for the pair C_2H_4, C_2D_4,[4] and for C_2Cl_4.[5] For H_2O and D_2O the exact solutions are known, of course,[6] and for C_2H_4, C_2D_4 we can be fairly certain that both the zero-order (anharmonicity-corrected) and "empirical" solutions are satisfactory, with the possible exception of one or two of the smaller interactions. The situation with C_2Cl_4 is that one cannot decide finally between the solutions with large positive or small negative $\Delta r_{C=C} \times \Delta r_{C-Cl}$ interaction constant; this might be a case where direct quantum mechanical calculation might be of assistance even at its present stage. A study of the mutual dependence of the force constants and their relation to form of vibration, in the probable region of the real solutions, has been made for some C–H bending vibrations of substituted ethylenes,[7,8] the study of the planar vibrations[7] being an interesting example of an attempt on comparatively high-order equations. In the group of non-planar C–H bending vibrations[8] it is thought that there is definite evidence for variation of the bending constants with different substituents, by pure analysis alone.

The present paper completes the detailed study of simple systems. Partly with the object of correlating with quantum mechanical treatments, but mainly as a pure study, the general solution for the potential well representing the symmetrical triatomic system is obtained.

II. Dependence of the Forms of Vibration of a System of Given Configuration on the Potential Function

The following preliminary general treatment is conveniently included in the present paper. The normal coördinates η_i for the system are defined in general in terms of the coördinates Δ_j of the potential function by the matrix equation

$$\eta = c\Delta \tag{1}$$

The forms of vibration are obtained from the related equation

$$\Delta = c^{-1}\eta \tag{2}$$

Thus in the kth normal mode, with normal coordinate η_k, the displacements are defined by

$$\Delta_1:\Delta_2:\cdots:\Delta_n: \ :(c^{-1})_{1k}:(c^{-1})_{2k}:\cdots:(c^{-1})_{nk} \tag{3}$$

where $(c^{-1})_{ij}$ is the ijth element of the inverse of c. It can be shown that

$$c'c = A^{-1} \tag{4}$$

$$c'Wc = d \tag{5}$$

where c' is the transpose of c, A is the inverse kinetic energy matrix for the coördinates Δ_j and W the diagonal matrix of the roots of the characteristic equation of the product matrix dA; these roots must correspond to the observed vibration frequencies. This summarizes the dependence of the transformation matrix c, which determines the forms of vibration, on the force constant matrix.

The conditions for a normal vibration to be localized in a particular part of the molecule are readily obtained. If a vibration of frequency ν_k is localized in a single coördinate Δk_4, (an extreme case), then the elements of any column of minors of the determinant $|dA - \lambda_k I|$ must be all zero except for the kth element.

The general condition is seen to be

$$B_{ki} = \begin{cases} 0 \text{ for } i \neq k \\ \lambda k \text{ for } i = k \end{cases} \tag{6}$$

where B is the product dA. It leads to the following expression for the kth row of elements in the force constant matrix

$$d_{ki} = (A^{-1})_{ki}\lambda_k = (|A|_{ki}/|A|)\lambda_k \tag{7}$$

where $|A|_{ki}$ is the cofactor of the element A_{ki} in the determinant $|A|$ of the kinetic energy matrix.

If ν_k is localized in the two coördinates Δ_k and Δ_m, then the conditions are either

$$B_{ki} = \begin{cases} 0 \text{ for } i \neq k \text{ or } m \\ \text{non-zero for } i = m, \\ \lambda_k \text{ for } i = k \end{cases} \quad B_{mi} = \begin{cases} 0 \text{ for } i \neq m \\ \lambda_m \text{ for } i = m \end{cases} \tag{8}$$

where λ_m is the secular parameter corresponding to a second frequency ν_m, or

$$B_{ki} = \begin{cases} 0 \text{ for } i \neq k \\ \lambda_m \text{ for } i = k, \end{cases} \quad B_{mi} = \begin{cases} 0 \text{ for } i \neq k \text{ or } m \\ \text{non-zero for } i = k \\ \lambda_k \text{ for } i = m \end{cases} \tag{9}$$

It is convenient to take the first set of conditions as general; clearly the two coördinates are equivalent, and it is a necessary consequence of localization in two coördinates, where the potential energy is expressed in terms of more than two, that there shall be a second frequency localized in one or other of these two coördinates. Thus, from Eq. (8), B_{mm} must be a root of the secular equation since all

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[2] Pauling and Wilson, "Introduction to Quantum Mechanics," p. 349.

[3] P. Torkington, *J. Chem. Phys.*, **17**, 357 (1949).

[4] P. Torkington, *Proc. Phys. Soc.*, **64**, 32 (1951).

[5] P. Torkington, *ibid.*, **63**, 804 (1950).

[6] Heath and Linnett, *Trans. Faraday Soc.*, **44**, 556 (1948).

[7] P. Torkington, *J. Chem. Phys.*, **17**, 1279 (1949).

[8] P. Torkington, *Proc. Roy. Soc.*, **A206**, 17 (1951).

other elements B_{mi} are zero, and consequently there is a mode ν_m localized in Δ_m alone. The approximation to this theorem will presumably be a physical truth; the theorem itself underlies the well-known phenomenon of group frequencies, showing how if one frequency is localized then so must another be. If the form of ν_k is defined by $(\Delta_m/\Delta_k) = p$, then explicit expressions for the force constants d_{ki} follow from the identity

$$B_{km} + pB_{mm} = p\lambda_k \qquad (10)$$

which is a consequence of the definition of the displacement; the constants d_{mi} are given by the analog of Eq. (7). These expressions enable one to decide what interactions, in a given configuration, are most likely to lead to localisation of the normal modes.

III. Preliminary Analysis of the Triatomic Molecule Problem

It is first convenient to express the potential energy for the symmetrical vibrations in terms of a single displacement coördinate. This is possible if we choose the displacement vector of one of the terminal atoms as variable. Taking r_1, the vector for the terminal atom 1, (see Fig. 1), if this has magnitude r_1, direction β, then it can be shown that the potential energy of the system is given by

$$V = 2r_1^2(A \sin^2 \beta + B \sin \beta \cos \beta + C \cos^2 \beta) \qquad (11)$$

where

$$A = d_{11} \sin^2 \alpha + d_{22} \cos^2 \alpha + d_{12} \sin 2\alpha$$
$$B = (1 + 2\mu)[(d_{11} - d_{22}) \sin 2\alpha + 2d_{12} \cos 2\alpha]$$
$$C = (1 + 2\mu)^2 (d_{11} \cos^2 \alpha + d_{22} \sin^2\alpha - d_{12} \sin 2\alpha)$$

d_{11}, d_{22} and d_{12} are the elements of the force constant matrix for the valence coördinates $\Delta_1 = \Delta r_{12} + \Delta r_{23}$, $\Delta_2 = r_{12}\Delta\theta$; 2α is the angle of the system, and $\mu = m_1/m_2$. Equation (11) enables us to plot a polar diagram of the potential energy for any conceivable displacement of the system satisfying the symmetry requirements, and the condition for no translation. It will be perhaps of some interest to study the dependence of the type of diagram obtained on the force constants (these of course being always sets for the correct vibration frequencies). For any particular solution for the force constants there will be two particular directions β_1 and β_2 corresponding to the normal modes of vibration. We will examine the way these directions are related to the potential energy diagram, and how the picture changes as we pass through the whole set of allowed solutions for the force constants. Since the potential energy function is parabolic we need only obtain a single curve for each set of force constants. It is convenient to take that for unit r_1. The diagrams are symmetrical about the origin and about two axes corresponding to maximum and minimum potential energy. These latter are mutually perpendicular, and their directions satisfy the equations

$$\tan 2\beta_m = B/(C - A) \qquad (12)$$

The directions for the normal modes can be shown to be given by

$$\tan \beta_{1,2} = (1/B)[(1 + 2\mu) A - C \pm \tfrac{1}{2}\mu(1 + 2\mu)(\lambda_1 - \lambda_2)] \qquad (13)$$

where λ_1 and λ_2 are related to the fundamental vibration frequencies by

$$\lambda_{1,2} = 4\pi^2\nu_{1,2}^2c^2m_2 \qquad (14)$$

If $\nu_1 > \nu_2$, the positive sign in the $(\pm)$ in Eq. (13) goes with ν_1. Further, it can be shown that

$$\tan \beta_1 \times \tan \beta_2 = -(1 + 2\mu) \qquad (15)$$

For the limiting case $\mu = 0$, the directions of the displacements in the normal modes always coincide with the axes of the diagram. Otherwise this coincidence only occurs for the two solutions in which $\beta_{1,2} = 0, \pi/2; \pi/2, 0$.

Going back to Eq. (11), it can easily be shown that the lines of equipotential are ellipses. With V a constant, Eq. (11) is that of a conic section, with center at the origin and axes given by Eq. (12). The discriminant of the conic, $(ab - h^2)$, is

$$4AC - B^2 = 4(1 + 2\mu)^2(d_{11}d_{22} - d_{12}^2) \qquad (16)$$

This quantity is always positive, since $(d_{11}d_{22} - d_{12}^2) = \lambda_1\lambda_2/|A|$ where $|A|$ is the determinant of the kinetic energy matrix. The problem is thus conveniently reduced to a determination of (1) the magnitudes of the axes of the elliptical potential energy contour for a standard displacement r_1; (2) the directions of the axes, for all allowed solutions of the force constants. However, it is instructive to obtain the polar diagrams of the potential energy as well. The relation between a polar diagram and the corresponding potential energy contour plot is quite simple. Rewriting Eq. (11) as

$$V = Kr_1^2 \qquad (17)$$

then $1/\sqrt{K}$ is the value of r_1 corresponding to unit V. Thus the contour of unit potential energy is the ellipse whose axes coincide with those of the polar diagram and are equal in length to the reciprocals of the square roots of the corresponding axes for the diagram for unit r_1.

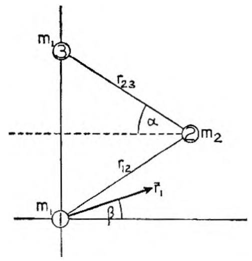

Fig. 1.—Coördinates for the class A_1 vibrations of the symmetrical triatomic molecule.

IV. Results for Three Typical Systems

Water, sulfur dioxide and chlorine monoxide have been chosen as three typical systems (as in a previous investigation[3]), representing a convenient range of m_1/m_2. The polar diagram for the potential energy, and its relation to the ellipsoidal equipotential contours, are shown in Fig. 2 for SO_2 at the solution with zero interaction constant and greater value of d_{11}; the directions of the two normal modes are indicated. The manner in which the shape and orientation of the potential well changes with the force constants is illustrated for the three molecules in Figs. 3, 4 and 5. In these,

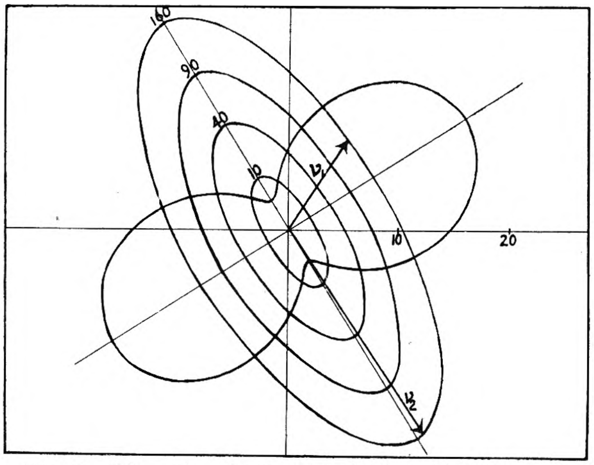

Fig. 2.—The polar diagram for the potential energy, and the equivalent potential well, for the symmetrical vibrations of SO_2, with zero interaction constant, in the range ν^+.

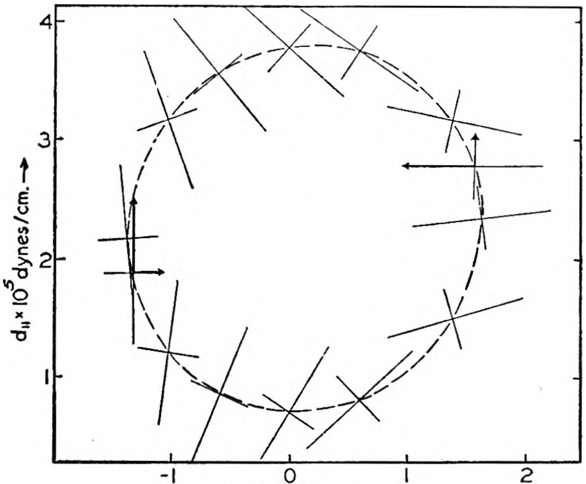

Fig. 3.—The variation of the potential well for the symmetrical vibrations of H_2O with the force constants.

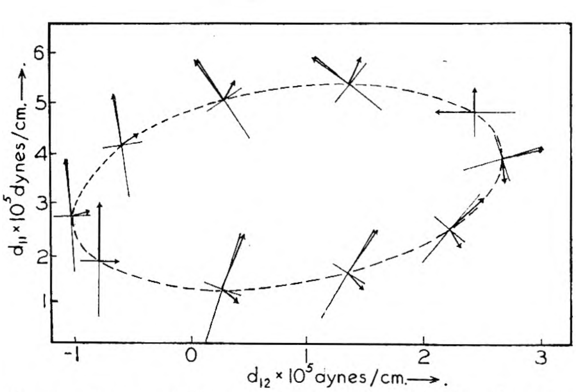

Fig. 4.—The variation of the potential well for the symmetrical vibrations of SO_2 with the force constants.

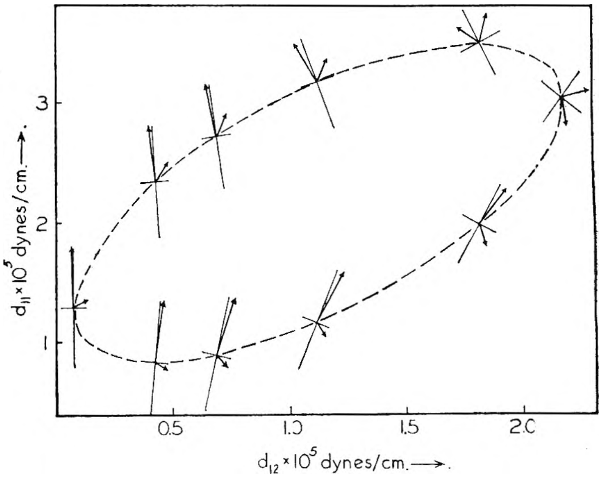

Fig. 5.—The variation of the potential well for the symmetrical vibrations of Cl_2O with the force constants.

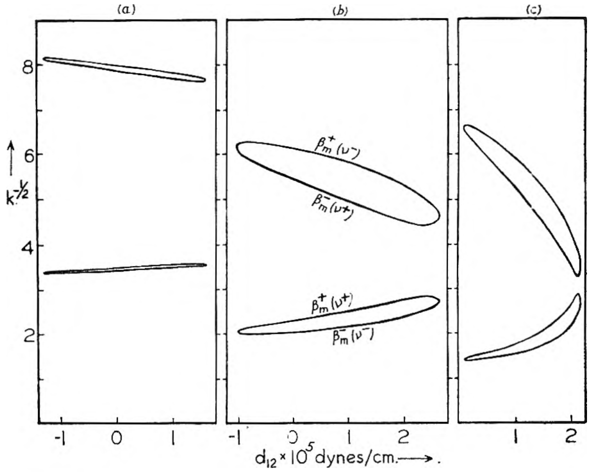

Fig. 6.—The variation of axis-lengths of the potential well, $(K^{-1/2})$, with the force constants, for (a) H_2O, (b) SO_2, (c) Cl_2O.

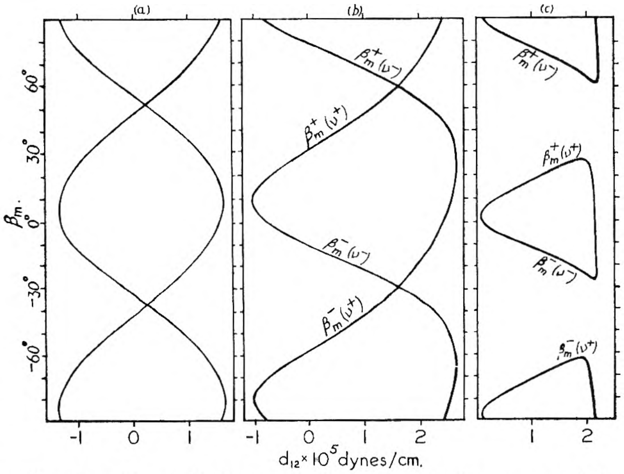

Fig. 7.—The variation of orientation of the axes of the potential well with the force constants for (a) H_2O, (b) SO_2, (c) Cl_2O.

the principal axes of a contour for a standard potential are drawn at various points along the $d_{11} - d_{12}$ curve, together with the displacement vectors of the normal modes. It will be seen that the contour rotates with change of value of d_{12}, and simultaneously its eccentricity alters. The magnitude of the latter change depends primarily on the mass-ratio m_1/m_2. For water it is hardly detectable, and it increases with increase in m_1/m_2. The absolute eccentricity at any solution is related to the magnitudes of the fundamental vibration frequencies. In general, the ratio of the axes is a function of the ratio of the vibration frequencies, the relationship being the more direct the smaller the value of m_1/m_2. At the two solutions corresponding to $\beta_{1,2} = 0, \pi/2$, where the directions of the normal modes coincide with the axes of the elliptical contours, the eccentricity is a maximum (for ν^-) or a minimum (for ν^+) (for nomenclature see ref. (3)). The defect of the direction of the normal mode vector from the principal axis is dependent on both vibration frequency and mass-ratio. For H_2O the directions nearly coincide for all solutions. The defect increases through SO_2 to Cl_2O, and is always greater for the mode of higher frequency (*i.e.*, nearer to the short axis). In Fig. 6, the variation of axis-length is shown as a continuous plot against d_{12}, and in Fig. 7 the directions of the axes are similarly plotted. The dependence of this plot on the mass-ratio is rather striking; in Cl_2O the type of curve is essentially different. However, this does not affect the continuity of the axis-length plots.

V. Conclusion

The above treatment of the symmetrical triatomic system gives a clear picture of the implications of any particular potential function; from the two directions allowed to the normal modes the potential gradient opposing motion along any other direction has been deduced. Such a treatment, or its inverse, would probably be found convenient in quantum mechanical calculations of potential functions, but the results have some intrinsic interest. The fact that all directions other than those corresponding to the normal modes are in general "unobservable" should be remembered; there is some evidence[9] that the value of a given force constant may be dependent on the directions of displacement. But this type of variation should be only of the order of an anharmonicity correction.

The above work has been carried out as part of the programme of fundamental research undertaken by the British Rayon Research Association. The author is grateful to Dr. Orville Thomas, of the Edward Davies Chemical Laboratories, University of Wales, Aberystwyth, for checking the calculation for Fig. 7 (c).

(9) P. Torkington, *Proc. Roy. Soc.*, in the press.

FORCE CONSTANTS IN HYDROGEN AND DEUTERIUM PEROXIDES

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Received December 26, 1951

The infrared spectrum of hydrogen peroxide was re-examined and that of deuterium peroxide was measured for the first time in the vapor state. For the isotopic molecule five bands were observed at 480, 947, 1944, 2680 and 5236 cm.$^{-1}$. The observed frequencies were combined with those of the Raman spectra to calculate the force constants of the various bonds.

Introduction

Hydrogen peroxide has a rather weak, non-revealing infrared spectrum.[1,2] Only two bands are prominent, corresponding to the asymmetric OH bending and stretching modes. The O–O vibration is hardly noticeable in the vapor and the overtones of O–H bands show multiple overlapping due to doublet splitting so that, even under high resolution, very little of the rotational structure is visible. Finally the torsional oscillation, to be expected from the model of Penney and Sutherland,[3] is very elusive; a broad absorption band at 16 μ in the spectrum of the liquid has been assigned to that mode[4] although it could arise merely from molecular perturbation in condensed phases. Therefore, a study of the isotopic molecule D_2O_2 was desirable to provide further information on the structure. The Raman[5] and infrared[4] spectra of this compound in the liquid phase have been investigated but no work has been reported yet on the vapor. It was hoped that such a study would throw further light on the controversial question of the O–O bond energy[6,7]; as it turned out, however, there still remains some uncertainty on the O–H bond length in hydrogen peroxide.

Discussion of Results

The vibrational spectrum of deuterium peroxide vapor was measured in the range 2–25 μ with a prism instrument. Experimental details, as well as related studies on the absorption of alkaline solutions of hydrogen peroxide, will be reported elsewhere. For the present purpose the observed frequencies are listed in Table I together with the Raman shifts[5] for both molecules. The coarse rotational structure of the band at 3.7 μ was partly resolved and from the 10 or 12 observed maxima the major rotational constants of D_2O_2 were calculated: $A' - B' = 4.8$ cm.$^{-1}$, $A'' - B'' = 5.1$ cm.$^{-1}$. Because of the limited resolution these figures are less accurate than those for the two overtone bands of hydrogen peroxide.

The assignment $\nu_2 + \nu_6$ (B) now seems the only possible one for the unexplained band at 2630 cm.$^{-1}$ in H_2O_2 and 1944 cm.$^{-1}$ in D_2O_2; anharmonicity requirements indicate that the frequency of ν_2 in the vapor must be slightly higher than had been thought previously. The broad band of medium intensity at about 660 cm.$^{-1}$ in the spectrum of crystalline H_2O_2 (at $-70°$) is shifted to 480 cm.$^{-1}$ in the isotopic compound. The ratio of these frequencies (1.37) is further evidence that they belong to the torsional oscillation.

(1) P. A. Giguère, *J. Chem. Phys.*, **18**, 88 (1950).

(2) L. R. Zumwalt and P. A. Giguère, *ibid.*, **9**, 458 (1941).

(3) W. G. Penney and G. B. B. M. Sutherland, *Trans. Faraday Soc.*, **30**, 898 (1934); *J. Chem. Phys.*, **2**, 492 (1934).

(4) R. C. Taylor, *ibid.*, **18**, 898 (1950).

(5) F. Fehér, *Ber.*, **72**, 1778 (1939).

(6) P. A. Giguère, *Can. J. Research*, **B28**, 17 (1950).

(7) A. D. Walsh, *J. Chem. Soc.*, 331, 398 (1918).

Isotope Effect.—Application of the Teller–Redlich product rule to hydrogen and deuterium peroxides leads to the following equations for the symmetric and the antisymmetric vibrations

$$\frac{\omega_1^D\omega_2^D\omega_3^D\omega_4^D}{\omega_1\omega_2\omega_3\omega_4} = \left(\frac{m}{m_D}\right)^{3/2} \times \left(\frac{M_{D_2O_2}}{M_{H_2O_2}}\right)^{1/2} \times \left(\frac{I_s^D}{I_s}\right)^{1/2} \quad (1)$$

$$\frac{\omega_5^D \cdot \omega_6^D}{\omega_5\omega_6} = \left(\frac{m}{m_D}\right)^{3/2} \times \left(\frac{M_{D_2O_2}}{M_{H_2O_2}}\right) \times \left(\frac{I_1^DI_2^D}{I_1I_2}\right)^{1/2} \quad (2)$$

TABLE I

VIBRATIONAL SPECTRUM OF HYDROGEN AND DEUTERIUM PEROXIDES

Assignment	H_2O_2 Infrared (vap.) (cm.$^{-1}$)	H_2O_2 Raman (liq.) $\Delta\nu$ (cm.$^{-1}$)	D_2O_2 Infrared (vap.) (cm.$^{-1}$)	D_2O_2 Raman (liq.) $\Delta\nu$ (cm.$^{-1}$).
ν_4 (a)	660^a (m.)		480^a (m.)	
ν_3 (a)	877 (v.w.)	877 (v.s.)		877 (v.s.)
ν_6 (b)	1266 (v.s.)		947 (v.s.)	
ν_2 (a)		1420 (w.)		1009 (w.)
$\nu_2 + \nu_6$ (B) ?	2630 (w.)		1944 (w.)	
ν_1 (a)		3414 (m.)		2510 (m.)
ν_5 (b)	3614 (s.)		2680 (s.)	
$\nu_1 + \nu_5$ (B)	7036.6 (v.w.) 7041.8 (v.w.)		5236 (v.w.)	
$3\nu_5$ (B) or $2\nu_1 + \nu_5$(B)	10283.7 (v.w.) 10291.1 (v.w.)			

^{a} In the solid at −70°.

where the symbols are those used by Herzberg (reference 8, p. 232). The superscript D refers to the isotopic molecule; I_s is the moment of inertia about the C_2 symmetry axis and I_1, I_2 are respectively the small and large moments about the other two axes. Since the symmetric vibrations have been observed only in the Raman spectrum their frequencies are not known accurately because of molecular association in condensed phases; consequently equation 1 cannot provide much significant information. The ratio $I_s^D/I_s = 1.12$ obtained from the Raman shifts in the two molecules is that to be expected within the limits of accuracy of experimental data.

If the observed frequencies are used in equation 2 the left-hand side will be greater than the right-hand side due to the anharmonicities of the O–H and O–D stretching vibrations. To correct for the use of first-order, instead of zero-order frequencies the left-hand side was multiplied by the factor

$$\left(\frac{k_{OH} + k'_{OH}}{k_{OD} + k'_{OD}}\right)^{1/2}$$

as suggested by Hedberg and Badger.[9] The force constants k and k' were calculated from the antisymmetric vibrations and appropriate structural parameters as described below. The choice of the latter has no great importance in the final result as the correction term amounts to less than 1.7% of the whole. The two sides of the modified equation

$$\frac{\nu_5^D\nu_6^D}{\nu_5\nu_6} \times \left(\frac{k_{OH} + k'_{OH}}{k_{OD} + k'_{OD}}\right)^{1/2} = \left(\frac{m}{m^D}\right)^{3/2} \times \frac{M_{D_2O_2}}{M_{H_2O_2}} \times \left(\frac{I_1^DI_2^D}{I_1I_2}\right)^{1/2} \quad (3)$$

now differ by less than 1% and the ratio $(I_1^DI_2^D)/(I_1I_2)$ is found to be $2.11_3 \pm 0.02$.

Moments of Inertia.—From the ratio of the moments of inertia obtained by means of equation 3 an attempt was made to determine the range of possible values for the azimuthal angle ϕ between the two H–O–O planes. These calculations were made using the equations derived by Wilson and Badger for H_2S_2[10] and verified following Hirschfelder's general method[11] of evaluating the moments of inertia of molecules for which the orientation of the three principal axes is not obvious. The O–O distance was taken as 1.49 Å. from X-ray[12] and electron diffraction data[13] and from application of Badger's rule to the 877 cm.$^{-1}$ frequency; the O–H distance and the O–O–H angle were varied from their value in H_2O, 0.957 Å. and 105.5°, respectively, to 1.01 Å. and 96°, the latter limits being set by the measured rotational constants of hydrogen peroxide.[1] The same parameters were used for deuterium peroxide in accordance with what has been found in other isotopic molecules.

The results of these numerous calculations are summarized in the curves of Fig. 1, from which it appears that the azimuthal angle is comprised within the range 82 ± 20°. Previously it had been concluded that this angle should not be between 85° and 95° because of irregular intensity dis-

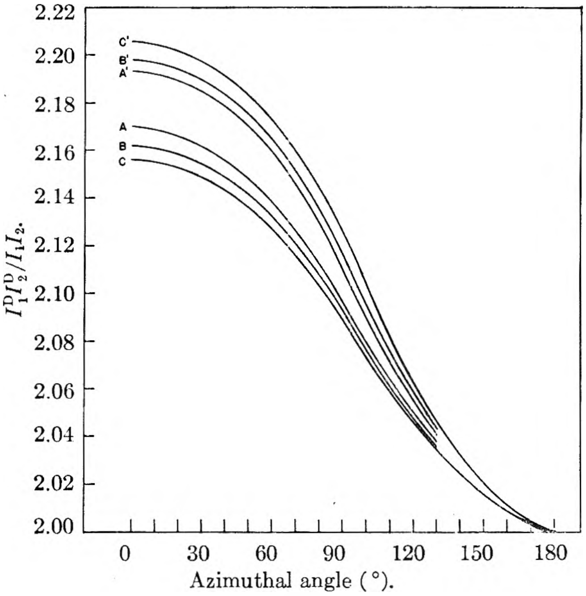

Fig. 1.—Variation of ratio $I_1^DI_2^D/I_1I_2$ with the azimuthal angle for the following values of the parameters:

Curve	$R_{O\text{-}H}$ (Å.)	$\pi-\alpha$ (°)	ϕ (°)
A	0.957	101.2	0
A′	.973	105.4	0
B	.957	97.8	90
B′	.987	105.4	90
C	.957	96.0	180
C′	1.01	105.4	180

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[8] G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1945.

[9] K. Hedberg and R. M. Badger, *J. Chem. Phys.*, **19**, 508 (1951).

[10] M. K. Wilson and R. M. Badger, *ibid.*, **17**, 1232 (1949)

[11] J. O. Hirschfelder, *ibid.*, **8**, 431 (1940).

[12] S. C. Abrahams, R. L. Collin and W. N. Lipscomb, *Acta Cryst.*, **4**, 15 (1951).

[13] P. A. Giguère and V. Schomaker, *J. Am. Chem. Soc.*, **65**, 2025 (1943).

tribution near the center of the combination band of H_2O_2 in the photographic infrared.[2] Angles of 94° and 106° have been found in the crystal of hydrogen peroxide[12] and its addition compound with urea[14] but these variations are easily understood in view of packing constraints. Figure 2 shows the locus of possible values for the three uncertain parameters.

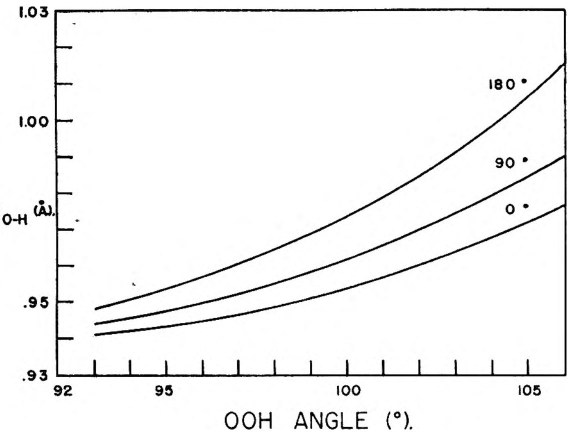

Fig. 2.—Locus of possible O–H distances and O–O–H angles for 0°, 90° and 180° azimuthal angles fitting the rotational constant X_{01} ° 9.23 cm.$^{-1}$ for H_2O_2.

Force Constants.—A quadratic potential function has been assumed by Morino and Mizushima[15] for the S_2Cl_2 molecule of C_2 symmetry, which in the case of H_2O_2 becomes

$$V = \frac{1}{2}k_{O-O}(\Delta R)^2 + \frac{1}{2}k_{O-H}[(\Delta r_1)^2 + (\Delta r_2)^2] - k'_{O-H}\,\Delta r_1\Delta r_2$$

$$+\frac{1}{2}\delta r_0^2[(\Delta\alpha_1)^2 + (\Delta\alpha_2)^2] - \delta' r_0^2\Delta\alpha_1\Delta\alpha_2 + \gamma r_0^2(\Delta\phi)^2 \quad (4)$$

The symbols have the following meaning: ΔR, Δr_1, Δr_2 are the changes in the O–O and the two O–H distances, r_0 being the equilibrium O–H distance, $\Delta\alpha_1$ and $\Delta\alpha_2$ are the changes in the angle between the O–H bonds and the extension of the O–O bond, and $\Delta\phi$, the change in azimuthal angle. k, δ and γ are the force constants for the squared terms, and k' and δ' are those for the crossed terms. This potential function has proved unsatisfactory in the case of D_2O_2 yielding imaginary values for k_{O-O} and ($k_{O-D} + k'_{O-D}$). It was therefore necessary to add to the potential function an interaction term of the form ($k''r_0\Delta R\Delta\alpha$) where k'' is a non-diagonal element which cannot be eliminated in the *d* matrix of Torkington.[16] The elements of the A matrix of Torkington associated with the appropriate internal coördinates have been given by Decius.[17]

The secular equation may be factored into two equations, one corresponding to the symmetric, and the other to the antisymmetric vibrations. As the antisymmetric vibrations have been measured directly in the vapor of hydrogen and deuterium peroxides the following quantities are obtained readily

$$k_{O-H} + k'_{O-H} = 7.29 \times 10^5 \text{ dynes/cm.}$$
$$k_{O-D} + k'_{O-D} = 7.56 \times 10^5 \text{ dynes/cm.}$$
$$\delta_{OOH} + \delta'_{OOH} = 0.848 \times 10^5 \text{ dynes/cm.}$$
$$\delta_{OOD} + \delta'_{OOD} = 0.858 \times 10^5 \text{ dynes/cm.}$$

The following data were used in calculating these force constants:

$$R_0 = 1.49 \text{ Å}. \qquad (\pi - \alpha_0) = 102°$$
$$r_0 = 0.97 \text{ Å}. \qquad \phi = 82°$$

The values of ($k_{O-H} + k'_{O-H}$) and (k_{O-D} and k'_{O-D}) are insensitive to the assumed azimuthal angle. Thus for $\phi = 90°$ there obtains

$$(k_{O-H} + k'_{O-H}) = 7.29 \times 10^5 \text{ dynes/cm.}$$
$$(k_{O-D} + k'_{O-D}) = 7.57 \times 10^5 \text{ dynes/cm.}$$
$$(\delta_{OOH} + \delta'_{OOH}) = 0.841 \times 10^5 \text{ dynes/cm.}$$
$$(\delta_{OOD} + \delta'_{OOD}) = 0.844 \times 10^5 \text{ dynes/cm.}$$

On the other hand the solution of the secular equation corresponding to the symmetric vibrations is much less accurate because of the uncertainty on the frequency of ν_1, ν_2 and ν_4. (ν_3 is certainly very close to 877 cm.$^{-1}$ in the vapor of both H_2O_2 and D_2O_2). The fundamental frequencies listed in Table II were selected as the most probable for calculating the force constants.

Table II

Fundamental Frequencies and Force Constants of Hydrogen and Deuterium Peroxides

ν (cm.$^{-1}$)	H_2O_2	D_2O_2	Force constants (dynes/cm.) × 10^{-5}	H_2O_2	D_2O_2
ν_1	3610	2670	k_{O-H}	7.28	7.53
ν_2	1315	1000	k'_{O-H}	<0.01	0.03
ν_3	877	877	k_{O-O}	3.84	4.04
ν_4	660	480	δ_{OOH}	0.89	0.95
ν_5	3614	2680	δ'_{OOH}	− .04	− .09
ν_6	1266	947	γ	.11	.11
			k''	.30	.58

The discrepancy of about 5% between the O–O stretching force constant in H_2O_2 and D_2O_2 is not considered significant in view of the uncertainty in some of the fundamental frequencies, specially ν_2. A further attempt is now being made to locate this vibration in the infrared spectrum of both molecules in the vapor state.

It is interesting to compare the present constant k_{O-H} in H_2O_2 with that in H_2O, 7.76 and in the O–H radical, 7.10[8]. From these the O–H bond length in H_2O_2 is estimated to be 0.97 ± 0.01 Å., a value slightly greater than in H_2O as already concluded from the measured rotational constants of the molecule.[1] The range of uncertainty on this datum could possibly be narrowed further by a study of the overtone bands of deuterium peroxide. Measurements of the microwave spectrum undertaken recently in another laboratory[18] may also be valuable in that connection.

This investigation is part of a research program supported by a grant from the National Research Council of Canada.

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(14) C. S. Lu, E. W. Hughes and P. A. Giguère, *J. Am. Chem. Soc.*, **63**, 1507 (1941).

(15) Y. Morino and S. Mizushima, *Sci. Papers Inst. Phys. Chem. Research*, **32**, 220 (1937).

(16) P. Torkington, *J. Chem. Phys.*, **17**, 1026 (1949).

(17) J. C. Decius, *ibid.*, **16**, 1025 (1948).

(18) J. T. Massey and D. R. Bianco, private communication.

REMARKS ON THE STRUCTURES OF THE VOLATILE FLUORIDES

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The molecular structures of a variety of volatile fluorides will be reviewed; electron diffraction data on several compounds not previously investigated will be presented. One of the objectives of this paper is to call attention to those compounds about which conflicting conclusions have been reached by diffraction and spectroscopic techniques. Another, is to discuss the "unexpected features" either in configuration or in interatomic distances which appeared in some of the fluorides. These molecules will be compared with their chloride and alkyl analogs. Finally, a number of compounds will be listed whose structures should be investigated in order to supply the crucial tests for the explanations offered to account for the differences between the fluorides and the alkyl derivatives.

The descriptions generally given of the bond-types which characterize the M–F linkages in the volatile fluorides involve the concepts "high electronegativity; ionic character" and "multiple bond resonance." When invoked simultaneously to account for the "unexpected features," the explanation must be considered as being no more than a formal restatement of the observed facts. Scrutiny of the latter suggests that insufficient consideration is generally given to the hybridization of atomic orbitals required to represent the molecular orbitals in these molecules.

Interest in fluorine and its compounds has been mounting steadily during the past two decades because in a number of respects the properties of that element are unique. In this review I wish to re-emphasize one of the particular characteristics of fluorine, the fact that it exhibits in its compounds a very wide range of bond types. Had we an adequate theory of valence which would present a unified interpretation of the structures of these compounds, their heats of formation, their dipole moments and spectra, it would indeed be a good *general* theory. We are not in this fortunate position, for there are many points which cannot be explained as yet, and the accounting which is offered consists mainly of a patchwork scheme of corrections to an oversimplified theory.

I have three objectives in presenting this review: (a) to call attention to the "unexpected" configurations, bond distances and bond angles which have been reported for a number of fluorides; (b) to indicate that inconsistencies among different experiments on the structures of some fluorine compounds are at present unresolved; and (c) to suggest some experiments which merit the expenditure of some thought and work. To facilitate this, I shall compare the structures of a number of fluorides with those of the corresponding chlorides and alkyl derivatives; also, I shall present unpublished preliminary results of structural studies of two fluorides.

This review will be limited to structural data, even though bond lengths and angles when determined to an accuracy of 1% may not be as sensitive measures of bond character as are other molecular constants.[1] Historically, interatomic separations have been recognized as direct criteria for chemical binding and are supposed to be simple to interpret. The review is further restricted to the volatile compounds containing fluorine even though much information may be uncovered from the study of the structures of the numerous fluoride complexes.[2] However, in spite of these limitations this summary may suggest a fresh approach to the general problem.

To define the field of discussion more carefully, I shall arbitrarily designate as "volatile" those compounds which are stable and which have sufficient vapor pressure at some temperature up to about 400° to give adequate electron diffraction photographs or micro-wave spectra for structure determinations. The range covered includes numerous compounds; a selection of typical ones for each element is presented in Table I.

Table I was prepared with the aid of the excellent summary of the chemical and physical properties of the volatile fluorides by Burg.[3]

In order that a unified analysis of the available data may be presented, I have formulated four questions, and I will attempt to answer these for groups rather than for individual compounds. (1) In MF_n, are all the M–F bonds equivalent? (2) For several states of oxidation of M, is there any evidence that the bond character[4] changes with increase in n? (3) In compounds of the type MX_pF_q, are the M–F and M–X bond distances dependent on p and q? (4) Aside from the obvious differences in physical properties, in the sequence MF_n, MCl_n, $M(CH_3)_n$, are there indications of changes in bond character—from "unexpected" values for the M–X distances?—from the magnitudes of bond angles?

The answer to the first question is "*generally*, but *not always*"; to the second, "all differences in interatomic distances which have been observed are no larger than the experimental error." To the third and fourth questions the answers are in the affirmative. Now for the details.

To date, the non-equivalence of M-F bonds has been established in five fluorides only, by diffraction techniques; in three of these cases this conclusion is contradicted by spectroscopic data. For a summary, refer to Fig. 1.

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(1) Perhaps the quantity which is the most direct gage of bond character is the heat of dissociation of the bond, leaving the fragments in their "valence states." Unfortunately, these molecular constants are very difficult to estimate, let alone measure. For a general discussion of heats of formation of various fluorine compounds, etc., see G. Glockler, Chapter X of "Fluorine Chemistry," J. H. Simons, Ed., Academic Press, Inc., New York, N. Y., Vol. I, 1950.

(2) For a brief summary of these complexes and for references to structural data, see H. J. Emeléus, Chapter I of "Fluorine Chemistry," ref. 1; A. F. Wells, "Structural Inorganic Chemistry," Oxford, 1945; J. L. Hoard and W. J. Martin, *J. Am. Chem. Soc.*, **63**, 11 (1941), and recent issues of *Acta Crystallographica*.

(3) A. B. Burg, reference 1, Chapter II.

(4) The term "bond character" implies the detailed electronic distribution in the region immediately adjacent to a selected pair of atoms. It includes factors which are generally called *polarity, hybridization, molecular resonance*, etc. One might consider the spectrum in "bond character" to extend from the extreme ionic, condensed type of binding present in crystalline NaF, through that which is present in NaF vapor, on to the intermediate cases BF_3 and OF_2; with F_2 at the other extreme (covalent).

TABLE I

TYPICAL VOLATILE FLUORIDES

Diatomic molecules which have been observed spectroscopically in electrical discharges, are not included. Compounds marked [ ] are currently under investigation in various laboratories. Compounds marked ( ) have been prepared and characterized, and found to be sufficiently volatile for study. Compounds marked (( )) have been prepared but may prove unstable or insufficiently volatile.

III	IV	V	VI	VII
BF_3	CF_4	NF_3	OF_2	F_2
$Me_3N:BF_3$	C_2F_4; C_2F_6	N_2F_4	NO_3F	
	C_6H_5F	ONF	(NO_2F)	
	$HC{\equiv}CCF_3$			
	$[F_2CO]$	PF_3	(SF_4)	ClF
	SiF_4	PF_5	SF_6	ClF_3
	$(SiCl_2F_2)$	POF_3	S_2F_{10}	
	(Si_2OF_6)	$(P_4N_4Cl_4F_4)$	(F_3CSF_5)	
	H_3CSiF_3		SO_2F_2	
			$[SOF_2]$ (SOF_4)	

IV_A & $_B$	V_B	V_A	VI_B	VI_A	VII_B	
		(VF_5)		(CrF_4)		
				(CrF_5)		
				(CrO_2F_2)		
(TiF_4)						
$(GeCl_2F_2)$			$(SeOF_2)$			
(GeF_4)	AsF_3		(SeF_4)		BrF	
$GeClF_3$	(AsF_5)		SeF_6		(BrF_3)	
		(CbF_5)		MoF_6	(BrF_5)	(RuF_5)
						$((RhF_5))$

IV_B	V_B	V_A	VI_B	VI_A	VII_B		
$((SnF_4))$	(SbF_3)		$((TeF_4))$		IF		
	(SbF_5)		TeF_6		IF_5		
					IF_7		
		(TaF_5)		WF_6		(ReF_6)	(OsF_6)
							(IrF_6)
						$[ReOF_4]$	OsF_8
	(BiF_5)						
				UF_6			

The electron diffraction data are presented in the form of the radial distribution curves because I wish to stress the fact that these data lead to the non-equivalence on direct analysis, without the necessity of introducing assumed models in the computation of intensity curves. The "expected" M–F separations were computed according to the equation of Schomaker and Stevenson[13] using reasonable magnitudes for the electronegativities, and estimates of the atomic radii from the M–M separations in the corresponding elements.[14] Clearly, further more extensive and careful electron diffraction studies will have to be undertaken for the iodine compounds, but the structures of the hexafluorides of molybdenum, tungsten and uranium have now been independently investigated in three laboratories, using samples of widely different origins; all lead to the same general conclusions.

The current difficulties with MoF_6, WF_6 and UF_6 may be summarized as follows: The electron diffraction data unequivocally require that two sets of distances (three each) be present in these molecules when in the vapor state. It is barely possible that the molecules have the symmetry V_h, with three sets of two, the difference between the last two pairs being so small that it is not resolved in the radial distribution curves. This unexpected type of bonding, however, must, it seems, be characteristic of both fluorine and these metals, since: (1) The hexafluorides of sulfur, selenium and tellurium were demonstrated to be regular octahedra by electron diffraction.[15] (2) The hexacarbonyls of molybdenum and tungsten, and the hexachloride of the latter were shown to be regular octahedra by electron diffraction.[15] On the other hand, the Raman spectra of MoF_6 and WF_6 are best interpreted on the assumption that the molecular symmetry is O_h.[16] Raman and infrared data on UF_6 are con-

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(5) R. C. Lord, *et al.*, *J. Am. Chem. Soc.*, **72**, 522 (1950)—spectroscopic study.

(6) R. Warthaftig and V. Schomaker, Atlantic City Meeting, A. C. S., April, 1947, Abst. 33 Phys. and Inorg. Division.

(7) R. L. Scott, *J. Chem. Phys.*, **18**, 1420 (1950).

(8) Unpublished (sector) data: S. H. Bauer.

(9) H. Browne and P. Pinnow, *Z. physik. Chem.*, **B35**, 239 (1937).

(10) Private communications from Dr. Otto Bastiansen, 1951. The visual technique was used in these investigations.

(11) S. H. Bauer, *J. Chem. Phys.*, **18**, 27, 994 (1950) (sector data).

(12) G. E. Kimball, *ibid.*, **8**, 188 (1940); F. G. Fumi and G. W. Castellan, *ibid.*, **18**, 762 (1950).

(13) V. Schomaker and D. P. Stevenson, *J. Am. Chem. Soc.*, **63**, 37 (1941).

(14) R. W. G. Wyckoff, "Crystal Structures," Interscience Publishers, Inc., New York, N. Y., 1948, Chapter II.

(15) For general summary of electron diffraction data refer to P. W. Allen and L. E. Sutton, *Acta Cryst.*, **3**, 46 (1950).

(16) K. N. Tanner and A. B. F. Duncan, *J. Am. Chem. Soc.*, **73**, 1164 (1951).

sistent with the same symmetry (O_h).[17] The measured entropy for UF_6 combined with the above spectral data require the assignment of a high symmetry number to the molecule ($\sigma \cong 24$).[18] Finally single crystal X-ray diffraction data on UF_6 are best accounted for by a structure of the symmetry D_{4h}, with four U–F distances in a plane (2.02 ± 0.05 Å.) and two extending perpendicular to that plane (2.13 ± 0.10 Å.).[19] Crystal powder data on UCl_6 are easily explained on the basis of a regular octahedral arrangement.[20] The dipole moment of UF_6 in the vapor phase is less than 0.3 *D*.[21]

At present, further repetition of the above experiments does not appear to be a fruitful pursuit, but the design of new crucial experiments is necessary. Electron diffraction studies of other volatile compounds of these three metals would indeed be worthwhile; a study of the infrared spectra of the three fluorides under very high dispersion may give a clue as to the basis of the difficulty; precision X-ray diffraction data on the gaseous fluorides may help. Furthermore, determination of the structures of the volatile fluorides of the elements adjacent to the VI_A group would indeed be interesting; for instance, if a sufficient vapor pressure of TeF_4 could be obtained it would prove to be an intriguing substance to investigate, since $TeCl_4$ was shown to have a distorted trigonal bipyramidal structure, rather than a tetrahedral configuration.[22] If the non-equivalence of the above M–F distances is substantiated, this unexpected feature will have to be specifically accounted for by any theory of valence which pretends to be adequate. In this connection, an unexpected result appeared in the structure of phosphorus pentafluoride, which is a trigonal bipyramid, with *equivalent* P–F distances (1.57 ± 0.02 Å.)[23]; electron diffraction data on pentachloride require two P–Cl distances.[24]

With regard to the second question, consider the following typical pairs of compounds, $MF_{n+2}:MF_n$

$OsF_8:OsF_6$
$IF_7:IF_5$
$SeF_6:SeF_4$
$AsF_5:AsF_3$
$GeF_4:GeF_2$
$TlF_3:TlF$
$UF_6:UF_4$
$VF_5:VF_3$

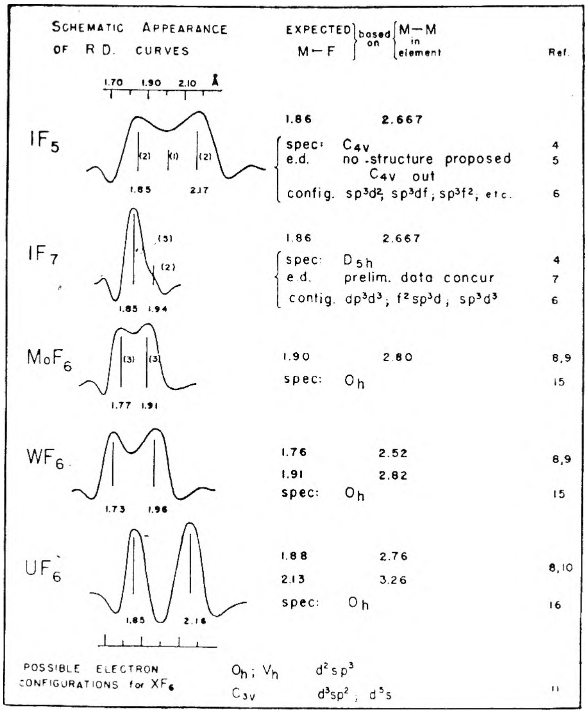

Fig. 1.[a]—Summary of structures of five volatile fluorides.

[a] NOTE ADDED IN PROOF. D. F. Smith [*Bull. Am. Phys. Soc.*, **27**, Abst. O11 (1952)] reported on the basis of microwave studies that ClF_3 is a planar molecule (sym. C_{2v}) with two Cl–F = 1.70 Å. and the other Cl–F = 1.56 Å. Hence chlorine trifluoride belongs with the above group of five molecules wherein the N–F distances are not all equivalent.

For pairs such as are included in the first and second columns, structural data for comparisons are available only for $IF_7:IF_5$, and $PF_5:PF_3$. Within the experimental error, the interatomic distances do not reflect differences in bond character for these pairs.

PF_3 (1.546 ± 0.010 Å.):PF_5 (1.57 ± 0.02 Å.)

IF_5 (1.85 and 2.17 Å.)[24a]:IF_6 (1.83 and 1.94 Å.)

However, that an effect due to differences in coördination is present appears from the marked differences in their physical and in their chemical properties. One might anticipate from the principle of "the tendency toward" electroneutrality[25] that the M–F bonds in MF_{n+2} have a somewhat lower polarity than those in MF_n, in order that too high a positive charge not accumulate on the central atom in the (n + 2) compounds. The higher volatility of the latter follows from their higher symmetry and more effective screening of the molecular quadrapoles, etc., by a slightly polarizable shell of fluorine atoms. Differences between pairs such as UF_6, UF_4 and VF_5, VF_3 are probably greater than can be accounted for from relatively small differences in the magnitudes of the dispersion forces. Since the cation–anion radius ratios favor the higher coördination, the much lower volatility of these (n) compounds is probably

---

(17) Bigeleisen, Mayer, Stevenson and Turkevich, *J. Chem. Phys.*, **16**, 442 (1948). See also, D. F. Heath and J. W. Linnett, *Trans. Faraday Soc.*, **45**, 264 (1949).

(18) (a) Brickwedde, Hodge and Scott, *J. Chem. Phys.*, **16**, 429 (1948), calorimetric heat capacities; (b) B. Weinstock and R. H. Crist, *ibid.*, **16**, 436 (1948), vapor pressures; (c) C. B. Amphlett, *et al.*, reference 21(b) also measured vapor pressures; (d) J. F. Masi, *J. Chem. Phys.*, **17**, 755 (1949), heats of vaporization; (e) H. J. Hoge and M. T. Wechsler, *ibid.*, **17**, 617 (1949), liquid densities; (f) J. R. White and A. E. Cameron, *Phys. Rev.*, **71**, 907 (1947), critical ionization potentials.

(19) J. L. Hoard and J. D. Stroupe, Columbia Report A-1242 (March 1944); declassified on October 7, 1946.

(20) W. H. Zachariasen, US—AEC publication, Tech. Inf. Division, Oak Ridge, No. AECD-2184 (Jan. 1948).

(21) (a) C. P. Smyth and N. B. Hannay, Princeton Report A-2130; (b) Amphlett, Mullinger and Thomas, *Trans. Faraday Soc.*, **44**, 927 (1948).

(22) D. P. Stevenson and V. Schomaker, *J. Am. Chem. Soc.*, **62**, 1267 (1940).

(23) L. O. Brockway and J. Y. Beach, *ibid.*, **60**, 1836 (1938).

(24) M. Rouault, *Ann. Phys. Leip.*, **14**, 78 (1940), reported 2.01 and 2.07 Å. Also, L. Pauling, "Nature of Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 103, quotes unpublished e. d. data by V. Schomaker which require that the two P–Cl bonds extending to the apices of the trigonal bipyramid are 2.11 Å., whereas the three in the plane are 2.04 Å.

(24a) Since the structure of iodine pentafluoride is still unsettled, and that of the heptafluoride has yet to be confirmed, the significance of the difference between the larger distances cannot be assessed.

(25) L. Pauling, "Contribution to the Study of Molecular Structure," Victor Henri Commemorative Volume, Desoer, Liege, 1948, p. 4.

TABLE II

EFFECT OF FLUORINE SUBSTITUTION ON M–F AND M–X BOND LENGTHS

( ) indicates assumed value

Compound	M–F	M–X	Ref.
H_3CF	1.384		30
HCF_3	1.323		30
F_3CCl	1.323	1.765	30
$HCCl_3$		1.761	31
H_3CCl		1.779	30
CCl_4		1.765	15
H_3CBr		1.936	30
F_3CBr	1.326	1.933	32
H_3CI		2.144	38
F_3CI	(1.326)	2.162	32
$H_3C—CN$		1.460	30
$F_3C—CN$	(1.326)	1.492	32
H_3SiF	1.593		30
$HSiF_3$	1.561		30
F_3SiCl	1.561	1.983	30
H_3SiCl		2.048	30
H_3SiBr		2.209	30
F_3SiBr	1.560	2.147	30
H_3GeCl		2.147	30
$ClGeF_3$	1.688	2.067	30

Compound	M–F	C=C C—C	M–X	Ref.
$H_2C═CH_2$		1.353		33
$H_2C═CF_2$	1.321	1.311		34
$F_2C═CF_2$	1.311	1.311		34
$Cl_2C═CCl_2$		1.30 (0.03)	1.72 (0.01)	35
$H_3C—C≡CH$		1.460	1.207	36
$H_3C—C≡N$		1.460	(1.160)	30
$F_3C—C≡CH$	1.335	1.464	(1.201)	37,37a
$H—C≡C—Cl$			1.211	38a
$H_3C—CH_3$		1.54–1.57		15
$F_3C—CH_3$	1.33	1.54		39
$F_3C—CF_3$	1.34	1.52		40

a consequence of coördination which extends throughout the crystals.[26]

Of special interest to the theory of valence is the affirmative answer to the third question, at least as it pertains to the M–F bonds. This might have been anticipated from the established effect of bond order of C–C bonds on the bond distance and bond force constant of adjacent C–H and C–Cl bonds.[27,28] The consequences of successive fluorine substitution for hydrogen in methyl fluoride on the C–F bond length were first pointed out by Brockway.[29] The redetermination of some of the structures from micro-wave absorption data leaves no doubt as to the reality of the effect; furthermore, it is definitely not limited to carbon as the central atom. Typical data are summarized in Table II.

Due to the fact that molecules of the type X_2CF_2, X_2SiF_2 are asymmetric rotors, and their micro-wave spectra cannot be readily analyzed in terms of interatomic distances, one cannot demonstrate directly the effect of successive substitution at each step, to the precision desired. However, the electron diffraction data suggest this, and it is evident from the micro-wave data that three fluorine atoms on a central M atom lead to smaller M-F distances than are present in the H_3MF compounds. This is reflected in the magnitudes of the force constant for stretching of the C–F bond; thus compare Cl_3CF [4.95×10^5 dynes/cm.] with CF_4, HCF_3 and $ClCF_3$ [6.25×10^5 dynes/cm.].[41] In an equally dramatic manner the effect appears in the heats of vapor phase chlorination[42] (Table III), and in the ultraviolet absorption spectra of perhaloethylenes and butadienes.[43,44]

TABLE III

HEATS OF VAPOR PHASE CHLORINATION

Compound	$-\Delta H$ (cal./mole)
$CF_2═CCl_2$	41,076
$CF_2═CF(CF_3)$	47,149
$CF_2═CFCl$	48,815
$CF_2═CF_2$	57,323

Whereas the consequence of successive substitution of fluorine for hydrogen on the M–F bonds in partially fluorinated compounds is clear cut, the effect on the adjacent M–X bonds appears to vary with the nature of the central atom and of X. The trend shown by Brockway's diffraction data on the fluorochloromethanes in the "shorten-

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(26) Recent crystal structure determination of the trifluorides of molybdenum, tantalum and vanadium were made by V. Gutmann and K. H Jack, *Acta Cryst.*, **4**, 244, 246 (1941). An interesting comparison is presented between these three fluorides and AlF_3, ScF_3.

(27) C. A. Coulson, "Contribution to the Study of Molecular Structure," ref. 25, p. 15, discusses the effect of varying *s–p* hybridization on the atomic radium of carbon.

(28) J. Duchesne, *ibid.*, p. 55, tabulates the force constants deduced for C–H and C–Cl bonds adjacent to C–C, C═C and C≡C bonds. See also M. Szwarc and J. W. Taylor, *Trans. Faraday Soc.*, **47**, 1293 (1951).

(29) L. O. Brockway, THIS JOURNAL, **41**, 185 (1937).

(30) Quoted from a summary paper by J. Sheridan and W. Gordy, *J. Chem. Phys.*, **19**, 965 (1951).

(31) R. R. Unterberger, *et al.*, *ibid.*, **18**, 565 (1950).

(32) J. Sheridan and W. Gordy, *Phys. Rev.*, **77**, 292 (1950).

(33) G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., Inc., New York, N. Y., 1945, pp. 439, 520.

(34) I. L. and J. Karle, *J. Chem. Phys.*, **18**, 971 (1950).

(35) I. L. and J. Karle, private communication.

(36) R. Trambarulo and W. Gordy, *J. Chem. Phys.* **18**, 1613 (1950).

(37) W. E. Anderson, *et al.*, *Phys. Rev.*, **82**, 58 (1951).

(37a) J. N. Shoolery, *et al.*, *J. Chem. Phys.*, **19**, 1364 (1951).

(38) (a) J. W. Simmons, *Phys. Rev.*, **76,** 686 (1949); (b) A. A. Westenburg, *et al.*, *J. Chem. Phys.*, **17,** 1319 (1949).

(39) W. F. Edgell and A. Roberts, *ibid.*, **16**, 1002 (1948).

(40) S. H. Bauer, U. S. AEC, Document no. MDDC 1494 (1946).

(41) C. E. Decker, *et al.*, *J. Chem. Phys.*, **19**, 784 (1951).

(42) J. R. Lacher, *et al.*, *J. Am. Chem. Soc.*, **71**, 1330, 1334 (1949).

(43) E. Rutner and S. H. Bauer, unpublished data.

(44) J. R. Lacher, *et al.*, *J. Am. Chem. Soc.*, **72**, 5486 (1950).

TABLE IV

EFFECT OF FLUORINE SUBSTITUTION ON BARRIER HEIGHTS, ETC.

Compound	P—S P—O	P—F P—Cl	References
PF_3		1.546 (0.01)	46
PCl_3		2.043	47
PSF_3	1.87 (0.03)	1.53 (0.02)	48
$PSCl_3$	1.85 (0.02)	2.02 (0.01)	48
POF_3	1.47 (0.03)	1.52 (0.02)	48
$POCl_3$	1.45 (0.03)	1.99 (0.02)	48

Compound	Barrier, cal./mole	References
$H_3C—CH_3$	2700	33
$H_3C—CCl_3$	2840 ± 500	49
$H_3C—CF_3$	3450	33
	3000 ± 200	50
$F_3C—CF_3$	4350	51
$Cl_3C—CCl_3$	10 – 12 K	52
$H_3C—SiF_3$	1200	30
$Si\equiv(CH_3)_4$	1280	33
$C\equiv(CH_3)_4$	4200	33
$(CH_3)C—C(CH_3)_3$	4700[a]	52a
$H_3C—SiF_5$	625	52b

[a] Average value per group.

ing" of the C–Cl distance has been confirmed for the corresponding Si and Ge compounds. However, the C–Br distance in methyl bromide and in trifluorobromomethane are about equal. This is underlined by the near equality in the bond dissociation energies for C–Br in methyl bromide (67 kcal.) and trifluorobromomethane ($\simeq$ 64 kcal.).[45] The much lower dissociation energy for C–Br in trichlorobromomethane ($\simeq$ 48 kcal.) is somewhat surprising. The suggestion that in the methane derivatives, due to the shortness of the C-halogen bonds, steric factors undo the stabilizing effect of fluorine substitution is supported to some extent by the observed distances in the silane derivatives. The Si–Br bond distance in F_3SiBr is about 0.06 Å. less than in H_3SiBr.

The effect of fluorine substitution on the length of the C–C bond in ethane is probably negligible, but perhalogenation of ethylene leads to a short C=C distance, for either fluorine or chlorine. The C–C and C≡C bond distances in trifluormethylacetylene differ slightly from those in methylacetylene.

Lest we prematurely reach the conclusion that only fluorine substitution induces such effects on adjacent bonds, note that the C–Cl separation in chloroform and in carbon tetrachloride is reported to be equal to that in trifluorochloromethane, and that the P–S and P–O distances in PSX_3 and POX_3 do not depend on whether X is chlorine or fluorine (Table IV.) There are indications that the other halogens behave in a similar, though not in so striking a manner. This conclusion was reached by Skinner and Sutton[53] on the basis of electron diffraction studies of mixed halogen-alkyl compounds of tin, arsenic and nitrogen.

There is a marked effect of the height of the potential barrier hindering rotation about the C–C bond in ethane, when the hydrogen atoms on one carbon are replaced by fluorines; chlorine atoms show no such effect (Table IV). In perfluoroethane, the barrier appears to be even higher than CH_3CF_3. Spectroscopic data indicate that the C–C distance in methyl fluoroform is the same as in ethane.[39] A similar raising of the barrier height cannot be directly demonstrated for fluorine substitution on silicon, since specific heat and spectroscopic data are not yet available for methylsilane. One may infer that the effect is present from the near equality of the barrier for methyltrifluorosilane and tetramethylsilane; presumably, methylsilane would have a lower barrier than either of these, corresponding to the relative values for ethane and neopentane. The very large barrier hindering rotation in hexachloroethane is clearly a steric consequence of the bulky chlorine atoms.

It is probably correct to infer that the large barrier in hexafluoroethane is due to the large repulsions between the non-bonded fluorine atoms, rather than to the effect of perhalogenation on the C–C bond. Such large repulsive forces had to be postulated to account for the non-planarity of octafluorocyclobutane,[54] and for the apparent strain present in hexafluoropropane.[55] Although perfluorination induces at most a slight structural change in the adjacent C–C bonds, the chemical effects appear to be profound.[56] Indeed, the ease of formation of four-membered ring systems, as are present in C_4F_8, C_6F_{10}, C_8F_{12}, is anomalous from the point of view of hydrocarbon chemistry. The extent of fluorine substitution is crucial; thus no cyclobutane results from the heating of FClC=CClF but good yields are obtained from F_2C=CF_2 and F_2C=CCl_2.

The answer to the last question, as to whether the observed bond distances and angles in the volatile fluorides, chlorides and the alkyl analogs indicate trends in bond character, is also in the affirmative. The starting point of the following

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(45) M. Szwarc, *J. Chem. Phys.*, **18**, 1660, 1685 (1950).

(46) O. Gilliam, *et al.*, *Phys. Rev.*, **75**, 1014 (1949).

(47) P. Kisliuk and C. H. Townes, *J. Chem. Phys.*, **18**, 1109 (1950).

(48) W. Gordy, private communication.

(49) M. T. El-Sabban, *et al.*, *J. Chem. Phys.*, **19**, 855 (1951).

(50) H. S. Gutowsky and H. B. Levine, *ibid.*, **18**, 1297 (1950).

(51) E. L. Pace and J. G. Aston, *J. Am. Chem. Soc.*, **70**, 566 (1948). However, it is doubtful whether they used the correct moments of inertia for the molecule.

(52) S. Mizushima, *et al.*, 120th ACS Meeting (1951), Phys. and Inorg. Division; also, *J. Chem. Phys.*, **17**, 838 (1949).

(52a) D. W. Scott, *et al.*, XII International Congress (1951), Fuel, Gas and Petroleum Division.

(52b) P. Kisliuk and G. A. Silvey, private communication.

(53) H. A. Skinner and L. E. Sutton, *Trans. Faraday Soc.*, **40**, 164 (1944).

(54) H. P. Lemaire and R. L. Livingston, *J. Chem. Phys.*, **18**, 569 (1950); W. F. Edgell, *ibid.*, **18**, 57[illegible] (1950).

(55) F. A. M. Buck and R. L. Livingston, *ibid.*, **18**, 570 (1950).

(56) For a general review, refer to: Symposium, *Ind. Eng. Chem.*, **39**, 359 (1947); "Fluorine Chemistry," ref. 1, Chapters 11–15; J. H. Hildebrand and R. L. Scott, "Solubility of Non-Electrolytes," Reinhold Publishing Corp., New York, N. Y., 1950.

set of graphs is the postulate of the additivity of atomic radii. At this late date one need no longer attempt to justify its use (because its usefulness has been adequately demonstrated), but one should not grow weary stressing its empirical origin and its approximate validity. Whatever the scheme which appeals to a particular investigator, it starts with a table of assigned radii for ionic or covalent bonding, and a formula for combining these in order to make predictions of interatomic distances. In the following, the Schomaker–Stevenson[13] formula, and their table of radii (slightly adjusted and expanded for the heavier atoms) were used to compute the expected values. To facilitate the comparison with the observed distances, three quantities were defined:

$$
\begin{aligned}
d_{\mathrm{M-F}} &= r_{\mathrm{M}} + r_{\mathrm{F}} - 0.09\,|x_{\mathrm{F}} - x_{\mathrm{M}}| \\
\Delta &\equiv (d_{\mathrm{M-F}} - d_{\mathrm{obsd.}}) \\
\alpha &\equiv (d_{\mathrm{M-Cl}} - d_{\mathrm{M-F}}) = 0.36,\ \text{for } x_{\mathrm{Cl}} > x_{\mathrm{M}} \\
\beta &\equiv (d_{\mathrm{M-CH_3}} - d_{\mathrm{M-F}}) = 0.185,\ \text{for } x_{\mathrm{CH_3}} > x_{\mathrm{M}} \\
&= (0.635 - 0.18\,x_{\mathrm{M}}),\ \text{for } x_{\mathrm{CH_3}} < x_{\mathrm{M}}
\end{aligned}
$$

Thus Δ is a direct measure of the unreliability of this procedure for making predictions in the case of the fluorides; α and β measure the self consistency of the procedure, using the radii and electronegativities assigned to F, Cl and C. The magnitude of the deviations for α, β should be of second order, *unless* the bond character in the fluorides differs from that in the corresponding chlorides and alkyl compounds. The precision of the electron diffraction data is 1% in most instances, whereas the micro-wave values are good to 0.005-0.010 A. Reference to Fig. 2[57] shows that the deviations, Δ, are considerably outside the assigned limits of error. This should surprise no one; indeed, the expectation that simple additivity will hold in all cases would have been strikingly naive. The usual procedure is to correct the values computed by means of the formula, for "special effects." In doing so, the implicit assumption is introduced that the bond between any selected pair of atoms in a molecule depends primarily on the bond properties of the individual atoms, these properties being averaged over that empirically observed in many compounds where each atom appears to be in a "normal valence state." To make a good prediction for a bond in a particular case, corrections must then be made for the influence of the remainder of the molecule, either through the adjacent bonds or resonance involving the molecule as a whole.[58]

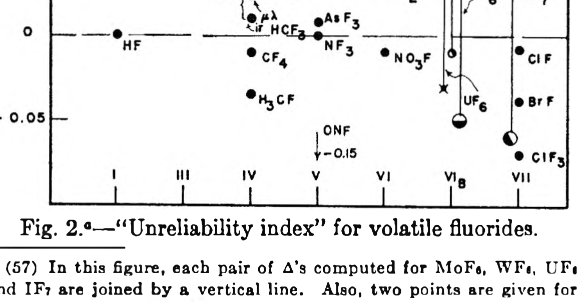

Fig. 2.[a]—"Unreliability index" for volatile fluorides.

Reference to Figs. 3[61] and 4[62] demonstrates in a direct manner that the bond character in the volatile fluorides must differ from that present in the corresponding chlorides and methyl derivatives, regardless of the interpretations proposed for the magnitudes of the Δ's in Fig. 2. Not only do the observed values of α and β differ from the predicted ones by much more than the assigned limits of error, but they vary in a way as to eliminate the possibility that a simple reassignment of the fluorine radius will set matters right.

This is not unexpected. Even though fluorine is considerably more electronegative than chlorine, its compact electronic structure necessitates that it approach closely to an atom in order that bonding take place. Possibly, this permits bond orders

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(57) In this figure, each pair of Δ's computed for MoF_6, WF_6, UF_6 and IF_7 are joined by a vertical line. Also, two points are given for HCF_3, marked $\mu\lambda$ and ir, to indicate the origin of the data. Were Gordy's radii used for carbon and oxygen (*J. Chem. Phys.*, **15**, 81 (1947)), the points for HCF_3, CF_4, H_3CF, OF_2 and NO_2F would be shifted *upward* by 0.01 Å.

(58) The "special effects" which have been proposed at various times as explanations for the deviations of the computed from the observed distances are numerous. Considerable data have accumulated in support of the following: (A) Molecular resonance results in over-all stabilization, and in giving most of the bonds an order higher than that used in the simple formula; $\Delta > 0$ (this is the most striking, and the first factor recognized).[59] (B) The extent of s–p–d Hybridization: Thus, if the tabulated radius is for sp^3 hybridization, then $\Delta < 0$ increasingly, as one goes to sp^2, sp; and conversely when the relative amount of *p* contribution is increased; this is less striking but important, and the factor most recently recognized.[27] (C) The appearance of formal charges[59]: The consequence of this may be the introduction of an excessive amount of ionic character, more than is automatically allowed for by the difference in electronegativity between adjacent atoms. Depending on the resulting charge distribution, this may lead either to a small increase or decrease in the computed distance. An early version of this argument states that depending on the sign of the formal charge, there occurs an increase or decrease in the "effective" atomic radius.[59a] An example of an increase in interatomic distance due to the accumulation of like charges on adjacent atoms was cited by Coulson. In N_2O_4, the nitrogen atoms assume a formal charge of +1; the computed repulsion leads to a separation of 1.58 ± 0.04Å., compared with the observed 1.64 ± 0.03 Å., and contrasted to the simple sum of radii, 1.48Å. (D) Additional pi bond resonance: brought in by partial neutralization of formal charges. This postulate was introduced by Pauling[60] in an attempt to account for the shorter than expected bond distances between second row elements and oxygen. (E) A number of other factors have been proposed, such as incompleteness of the valence shell,[59] etc. It is questionable whether sufficient data exist to substantiate them.

(59) L. Pauling, "Nature of Chemical Bond," Cornell University Press, Ithaca, N. Y., Chapter VII.

(59a) R. T. Sanderson, *J. Am. Chem. Soc.*, **74**, 272 (1952).

(60) L. Pauling, Symposium on Bond Strengths, 120th Meeting, A. C. S. (1951), Phys. and Inorg. Division.

(61) In Fig. 3, the M–Cl and M–F distances were compared for analogous compounds wherever possible. Where the data were insufficient, the compounds used are listed; thus, two points are given for the tellurium halides, ($TeCl_4$–TeF_6) and ($TeCl_2$–TeF_6). The pairs of points computed for the two sets of distances observed in the fluorides, IF_7, MoF_6, WF_6 and UF_6, are joined by vertical lines. For the oxygen and chlorine compounds, the expected values for α are 0.28 and 0.35, respectively.

(62) In Fig. 4, the M–C and M–F distances were again compared for analogous compounds, where the data were available. The point labeled Ge was obtained from [$GeMe_4$–$GeClF_3$]; the points for molybdenum and tungsten were computed using the metal–carbon distances observed in their hexacarbonyls.

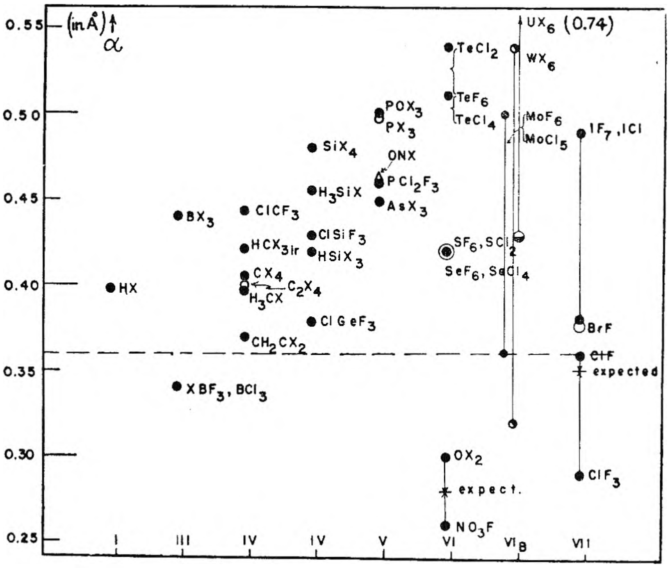


Fig. 3.ᵃ—Departures from "self consistency" between fluorides and chlorides.

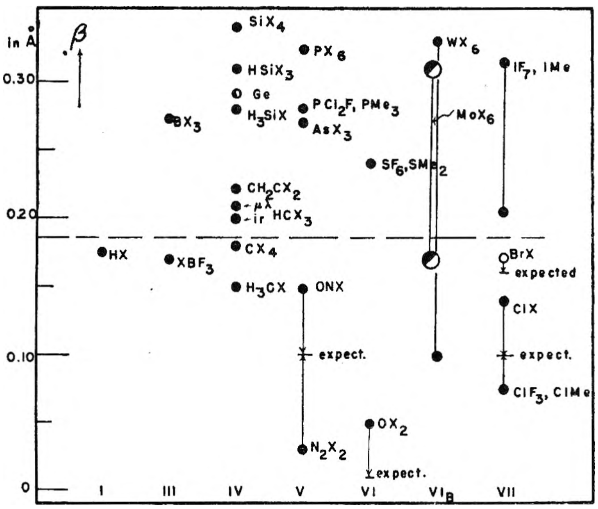


Fig. 4.ᵃ—Departure from "self consistency" between M–F and M–C bonds.

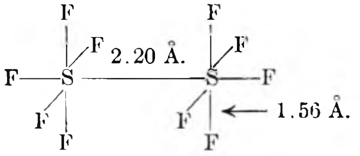
greater than unity, due to overlap of its *pi* orbitals with the hybridized orbitals of M.

Whereas a comparison of the interatomic distances in corresponding fluorides, chlorides and alkyl compounds unmistakably shows that the bond characters in these analogs differ, a parallel study of the valence bond angles on the central atom leads to no such definite conclusion. Coulson[27,63] showed that a relatively direct indication of the extent of s–p hybridization is furnished by the bond angles. I have therefore assembled the available data—regretfully meager—in Fig. 5.[64] It is interesting to note that the fluorides of silicon and phosphorus which appeared with the largest deviations in the three previous graphs seem to be rather close to the corresponding chlorides and methyl analogs in Fig. 5. The fluorides of nitrogen and oxygen for which the additivity relation was not particularly misleading, have bond angles which are quite different from their chlorides and alkyl derivatives.

The structures of two of the volatile fluorides included in the above graphs were recently determined in our laboratories. Since the results are quite interesting but have not yet been published, I shall describe them briefly. I have already mentioned iodine heptafluoride. The sample was furnished by Prof. Schumb (M.I.T.) and Dr. Lynch. Our preliminary analysis of the electron diffraction photographs leads to a structure in agreement with the infrared and Raman data—symmetry D_{5h}. The five I–F distances in the girdle are 1.83 Å.; the two extending toward the apices are 1.94 Å.

For the second compound, S_2F_{10}, one might write a structure with an S–S bond, with the remaining five bonds of each sulfur atom linked to fluorine atoms, as in SF_6. That is just what Dr. R. B. Harvey found.

S_2F_{10}	Expected distances	S–F	1.62 (ss)
			1.58 (SF_6)
		S–S	2.07 (S_8)



HINDERED ROTATION about S–S bond

Although no unified interpretation of the magnitudes of Δ, α and β has been presented, many of the compounds included in the figures have been discussed individually from a variety of points of view. Since the "special effects" proposed allow for both shortenings and extensions of the bond lengths,

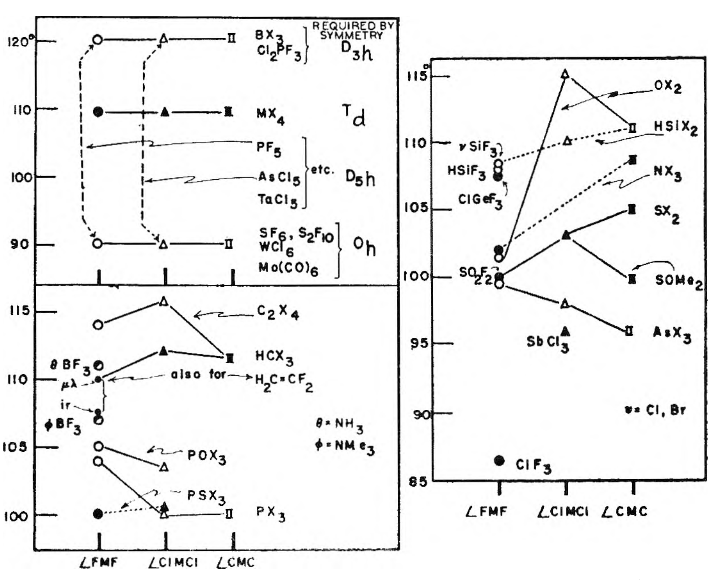


Fig. 5.ᵃ—Observed bond angles for corresponding compounds.

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(63) Also refer to P. Torkington, *J. Chem. Phys.*, **19**, 528 (1951).

(64) The trends suggested by the connecting lines in Fig. 5 should be interpreted with care, since the data are not of uniform quality. Except as indicated below, most of the angles quoted are precise at least to 1.5°.

PF_3 ± 3°; OCl_2 ± 4°; $S(CH_3)_2$ ± 5°; SO_2F_2 ± 8°; AsF_3 ± 5°

it is fairly clear that a judicious combination may be selected for each compound to account for the values observed. I shall merely refer readers to one theory for the effect on bond length of halogen substitution, as proposed by Pauling[59] for the methane series and extended by Gordy[30] to the silicon and germanium mixed halides; and call attention to a legitimate objection raised by Pitzer[65] against the postulate of resonance of multiple bond structures with the ground state, for second row elements attached to oxygen or fluorine. Further, we must consider the question whether such descriptions are useful, let alone whether the proper language is used. The underlying assumption is that the magnitudes of the deviations from additivity of atomic radii are monotonically related to deviations from normal covalent bonding, and thus serve as indices for bond character.

The valence bond orbital representation of bond formation suggests that additivity of atomic radii holds roughly, perhaps to an order of 3–10%. Due to its relatively low polarizability, the dimensions of an atomic kernel change little as an atom is bonded in turn to different atoms, particularly if the symmetry in coördination is approximately maintained. Also, the radial extensions of the orbitals of the valence electrons are not greatly altered by moderate changes in hybridization. Hence one may argue that in bond formation, the distance from the nucleus along a direction of a bond orbital at which the attractive and repulsive potentials balance is roughly a property of the particular atom.[65a] Actually, the shape and extension of atomic wave functions do change with hybridization, and the relative contributions of electron density to the bond wave function largely will be determined by the *relative* polarities of the participating atoms. Hence the detailed electron distribution in the vicinity of a bond will depend on the particular *pair of atoms* (even if one neglects non-bonded interactions). When one wishes to predict the distances between atoms to a precision of 1% or better, for comparison with refined data, he is barely justified in making the assumption that interatomic distances are *bond properties*, of course corrected for well defined resonance, such as is present in conjugated double bond systems, etc. Thus, for n atoms, the use of $n(n - 1)/2$ parameters in making interatomic distance predictions could be given a theoretical basis, parallel to the prediction of heats of formation from *bond energies*. General rules for additivity relations for *atomic vs. bond* quantities have been formulated by Zahn.[66]

In an unexcited molecule, the observed interatomic distances correspond to the minimum in the potential energy surface for the nuclei, *i.e.*, to those interatomic separations which will give the maximum heat of dissociation for the bonds, leaving the fragments in their valence states.[1] The concept of the additivity of bond energies follows immediately from the approximation that a molecular wave function may be represented properly by a linear combination of atomic orbitals in which the coefficients are obtained by minimizing the electronic energy associated with each bond (again excluding cases with obvious molecular resonance). This postulate is implicit in Mulliken's "magic formula".[67] Although he carried through no variational computation, he assumed[68] that the magnitude of the overlap integral (which includes both the radial and angular dependence of the wave functions) computed at the experimental bond distance for the two atomic orbitals which overlap when the bond is formed, is a good index for bond energy. But, in computing the energy he considered effects due to the overlapping of all the atomic orbitals (negative contributions to the energy from the overlap of bonding electron pairs, and positive contributions from non-bonding pairs). One can then imagine that given the essential information regarding the most suitable hybridization scheme for each atom of a selected pair which are approaching to form a bond, the energy so computed could satisfactorily represent a potential energy curve for the two molecular fragments of which these two atoms form spearheads. The nature of the fragments will determine the values for some of the parameters in the potential energy function. An energy-equilibrium distance relation can then be associated with the bonds formed by the particular atom pair; *i.e.*, r_e is monotonically related to D_e^b, which in turn depends on the values of overlap integrals for the wave functions of the electrons belonging to the two bonding atoms, the wave functions being somewhat modified by the nature of the groups attached to the spearhead atoms.

As an example, assume that one may lump all of the nuclear and electronic interactions for an atom pair into the potential function[69]

$$V(r) = -ar^{-n} + br^{-m}$$

Then the dissociation energy is related to the equilibrium distance by

$$D_e^b = b(m - n)r_e^{-m}/n = a(m - n)r_e^{-n}/m$$

Thus, the condition that for any selected atom pair, bond distance serve as a criterion of bond character, is that the interaction between the two atoms be *generally* expressible in terms of some potential function. This procedure has proved very satisfactory for the carbon compounds, where the relation between bond distance and "bond order" was set up.[70] One may thus account for the empirical relations between dissociation energy and carbon–halogen bond length, as reported by Sutton and Allen.[71] The fact that good predictions of bond distances can be made from a set of atom radii, provided they are corrected by a factor in-

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(65) K. S. Pitzer, *J. Am. Chem. Soc.*, **70**, 2140 (1940). The essence of the argument is that the observed heats of formation give no indication of the presence of resonance.

(65a) This argument will have a basis in theory, if it is proved that the "cellular" method leads to acceptable molecular wave functions, and to correct bond energies; V. A. Lewinson and G. E. Kimball, *J. Chem. Phys.*, **19**, 690 (1951).

(66) C. T. Zahn, *J. Chem. Phys.*, **2**, 671 (1934).

(67) R. S. Mulliken, *ibid.*, **19**, 911 (1951), and Symposium on Bond Strengths, 120th ACS Meeting (1951), Phys. and Inorganic Division.

(68) R. S. Mulliken, *J. Am. Chem. Soc.*, **72**, 4493 (1950).

(69) G. B. B. M. Sutherland, *J. Chem. Phys.*, **8**, 161 (1940).

(70) W. G. Penney, *Proc. Roy. Soc. (London)*, **A158**, 306 (1937); J. E. Lennard-Jones and C. A. Coulson, *Trans. Faraday Soc.*, **35**, 811 (1939).

(71) P. W. Allen and L. E. Sutton, *ibid.*, **47**, 236 (1951).

volving a *bond property* (energy)[72] supports the above contention that the interatomic distance is best considered as being a bond property.

The pleasingly surprising fact that in an appreciable number of cases the observed bond lengths for A–B empirically proved to be nearly equal to the mean of the separations A–A and B–B (corrected for differences in electronegativity), parallels the empirical observation that in many instances the bond energy for A–B is nearly equal to the mean of the bond energies of A–A and B–B (similarly corrected). It is obvious that these cannot be generally valid; and, as the precision of the measurements is increased, it is becoming clear that such simple relations do not hold exactly even in a restricted region. To use them in making predictions where data are not available is taking advantage of a confused situation without getting oneself involved; to base an elaborate theory on the deviation from the empirical relations which imply excessive oversimplification in nature, is to jump into the confusion with both feet and with one's thumbs tied together.

(72) M. L. Huggins, XIIth International Congress (1951), Phys. and Inorganic Division.

THE PHYSICAL PROPERTIES OF MOLECULES IN RELATION TO THEIR STRUCTURE. IV. BOND DISTANCE RELATIONS IN THE SUBSTITUTED METHANES AND ACYCLIC ALIPHATIC HYDROCARBONS

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The departure from strict additivity is expressed as a function of internuclear distance. Relations between bond lengths in the substituted methanes and acyclic aliphatic paraffins are then derived.

In the first paper[1] of this series the simple picture of additivity was extended to include the interactions between non-bonded atoms. Relations between the additive properties of molecules in several homologous series were derived then on the basis of strict additivity. The accurate evaluation of bond distances from rotational spectra obtained by means of the absorption of microwaves has shown that the C–Cl bond distance in methyl chloride[2,3] is about 0.02 Å. longer than the C–Cl bond distance in chloroform.[4] It has been established experimentally, therefore, that the C–Cl bonds have different lengths in methyl chloride and chloroform and that strict additivity does not prevail for the chloromethanes. The departure from strict additivity is small, however, and only of the order of a few per cent. It would seem reasonable, therefore, to express the contribution to the physical property as the sum of the strictly additive portion, which is by far the greater part, and a very small portion due to changes in bond distance and valence angle from the value of the distance and angle associated with the bond in the tetrahedral molecule.

The Substituted Methanes $CX_{4-n}Y_n$.—In the substituted methanes the contribution to the physical property from the CX bond in the n^{th} substituted methane may be expressed in terms of the contribution from the CX bond in the tetrahedral molecule, p_{CX_4}, and changes in bond distances and angles, *viz.*

$$p_{CX}^{(n)} = p_{CX_4} + \alpha f(R_{CX}^{(n)} - R_{CX_4}) + \beta f(\theta_{XCX}^{(n)} - t) + \gamma f(\theta_{XCY}^{(n)} - t) \quad (1)$$

and similarly the contribution from the CY bond may be written as

$$p_{CY}^{(n)} = p_{CY_4} + af(R_{CY}^{(n)} - R_{CY_4}) + bf(\theta_{YCY}^{(n)} - t) + cf(\theta_{XCY}^{(n)} - t) \quad (2)$$

where $R_{CX}^{(n)}$ and $R_{CY}^{(n)}$ are the CX and CY bond distances respectively in the n^{th} substituted methane, R_{CX_4} and R_{CY_4} are the CX and CY bond distances in CX_4 and CY_4 respectively, $\theta_{XCX}^{(n)}$, $\theta_{YCY}^{(n)}$ and $\theta_{XCY}^{(n)}$ are the XCX, YCY and XCY valence angles in the n^{th} substituted methane, t is the tetrahedral angle, α, β, γ, a, b and c are constants, and $f(R_{CX}^{(n)} - R_{CX_4})$ is a function of $(R_{CX}^{(n)} - R_{CX_4})$ etc.

In general, all contributions to physical properties which are considered to be additive are functions of bond distances and valence angles. The functional relationship, however, is in most cases unknown. Several methods[5] of relating the bond distance with the bond energy show that it is not unreasonable to expect a smooth relationship between bond energy and bond distance for bonds in molecules in the same homologous series even though it may be too much to expect a smooth relation between bond energy and bond distance in general.

From bond energy/bond distance curves derived from thermochemical data[5] and from theoretical considerations[6,7] it is readily seen over a small

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(1) H. J. Bernstein, *J. Chem. Phys.*, **20**, 263 (1952).

(2) (a) W. Gordy, *Phys. Rev.*, **20**, 668 (1948); (b) W. Gordy, private communication.

(3) G. Matlack, G. Glockler, D. R. Bianco and A. Roberts, *J. Chem. Phys.*, **18**, 332 (1950).

(4) R. R. Unterberger, R. Trambarulo and W. V. Smith, *ibid.*, **18**, 565 (1950).

(5) J. J. Fox and A. E. Martin, *J. Chem. Soc.*, 2106 (1938); H. A. Skinner, *Trans. Faraday Soc.*, **41**, 645 (1945); G. Glockler, *J. Chem. Phys.*, **16**, 842 (1948).

(6) M. A. Cook, THIS JOURNAL, **51**, 407 (1947).

(7) From the relations between bond order and bond distance and bond order and bond energy, the bond energy may be found in terms of bond distance. See, for example, H. J. Bernstein, *J. Chem. Phys.*, **15**, 284 (1947); **15**, 339 (1947), and others.

range of bond distances, that the bond energy is a linear function of the bond distance. Thus

$$f(R_{\mathrm{CX}}^{(n)} - R_{\mathrm{CX}_4}) = R_{\mathrm{CX}}^{(n)} - R_{\mathrm{CX}_4} = \delta R_{\mathrm{CX}}^{(n)} \quad \text{(say)} \qquad (3)$$

and

$$f(R_{\mathrm{CY}}^{(n)} - R_{\mathrm{CY}_4}) = R_{\mathrm{CY}}^{(n)} - R_{\mathrm{CY}_4} = \delta R_{\mathrm{CY}}^{(n)} \quad \text{(say)} \qquad (4)$$

Theoretical considerations of the variation in bond strength with change in valence angle show that the change in bond strength is proportional to the square of the change in valence angle.[8] Thus for small changes in R and θ the term in θ may be neglected in comparison with the term in R in considering changes in bond energy.

If we define the bond energy of the CX bond in the n^{th} substituted methane as $B_{\mathrm{CX}}^{(n)}$ and the bond energy of the CY bond as $B_{\mathrm{CY}}^{(n)}$ then (1) and (2) may be written

$$B_{\mathrm{CX}}^{(n)} = B_{\mathrm{CX}_4} + \alpha\delta R_{\mathrm{CX}}^{(n)} \qquad (5)$$

$$B_{\mathrm{CY}}^{(n)} = B_{\mathrm{CY}_4} + a\delta R_{\mathrm{CY}}^{(n)} \qquad (6)$$

where B_{CX_4} and B_{CY_4} are the CX and CY bond energies in the tetrahedral molecules CX_4 and CY_4, respectively. If $\delta R_{\mathrm{CX}}^{(n)}$ is positive then α is negative since longer bonds are weaker bonds.[5]

We now consider the heat of atomization of a molecule to be made up of the bond energies of the valence bonds plus the contributions from the interactions between the non-bonded atoms. Thus the heat of atomization of CX_4 is

$$Q_{\mathrm{CX}_4} = 4B_{\mathrm{CX}_4} + 6B_{\mathrm{XX}} \qquad (7)$$

where B_{XX} is the contribution to Q_{CX_4} from the interaction between two non-bonded X atoms. In most cases the sign of B_{XX} will be negative but the following treatment is valid irrespective of the sign of the non-bonded contributions. Similarly

$$Q_{\mathrm{CX}_3\mathrm{Y}} = 3B_{\mathrm{CX}}^{(1)} + B_{\mathrm{CY}}^{(1)} + 3B_{\mathrm{XX}} + 3B_{\mathrm{XY}} \qquad (8)$$

Here, we have assumed that the contributions from the interactions of non-bonded atoms are strictly additive. Thus the reasonable assumption that B_{XX}, B_{YY} and B_{XY} remain unchanged in the series has been made. The remaining expressions for heats of atomization are given then as

$$Q_{\mathrm{CX}_2\mathrm{Y}_2} = 2B_{\mathrm{CX}}^{(2)} + 2B_{\mathrm{CY}}^{(2)} + B_{\mathrm{XX}} + 4B_{\mathrm{XY}} + B_{\mathrm{YY}} \qquad (9)$$

$$Q_{\mathrm{CXY}_3} = B_{\mathrm{CX}}^{(3)} + 3B_{\mathrm{CY}}^{(3)} + 3B_{\mathrm{XY}} + 3B_{\mathrm{YY}} \qquad (10)$$

$$Q_{\mathrm{CY}_4} = 4B_{\mathrm{CY}_4} + 6B_{\mathrm{YY}} \qquad (11)$$

Substituting from (5) and (6) in (8), (9) and (10) we get

$$Q_{\mathrm{CX}_3\mathrm{Y}} = 3B_{\mathrm{CX}_4} + B_{\mathrm{CY}_4} + 3B_{\mathrm{XX}} + 3B_{\mathrm{XY}} + 3\alpha\delta R_{\mathrm{CX}}^{(1)} + a\delta R_{\mathrm{CY}}^{(1)} \qquad (12)$$

$$Q_{\mathrm{CX}_2\mathrm{Y}_2} = 2B_{\mathrm{CX}_4} + 2B_{\mathrm{CY}_4} + B_{\mathrm{XX}} + 4B_{\mathrm{XY}} + B_{\mathrm{YY}} + 2\alpha\delta R_{\mathrm{CX}}^{(2)} + 2a\delta R_{\mathrm{CY}}^{(2)} \qquad (13)$$

$$Q_{\mathrm{CXY}_3} = B_{\mathrm{CX}_4} + 3B_{\mathrm{CY}_4} + 3B_{\mathrm{XY}} + 3B_{\mathrm{YY}} + \alpha\delta R_{\mathrm{CX}}^{(3)} + 3a\delta R_{\mathrm{CY}}^{(3)} \qquad (14)$$

It is readily seen that

$$2Q_{\mathrm{CX}_3\mathrm{Y}} - (Q_{\mathrm{CX}_4} + Q_{\mathrm{CX}_2\mathrm{Y}_2}) - \Delta = 6\alpha\delta R_{\mathrm{CX}}^{(1)} + 2a\delta R_{\mathrm{CY}}^{(1)} - 2\alpha\delta R_{\mathrm{CX}}^{(2)} - 2a\delta R_{\mathrm{CY}}^{(2)} \qquad (13)$$

where

$$\Delta = -B_{\mathrm{XX}} - B_{\mathrm{YY}} + 2B_{\mathrm{XY}}$$

and

$$2Q_{\mathrm{CX}_2\mathrm{Y}_2} - (Q_{\mathrm{CX}_3\mathrm{Y}} + Q_{\mathrm{CXY}_3}) - \Delta = 4\alpha\delta R_{\mathrm{CX}}^{(2)} + 4a\delta R_{\mathrm{CY}}^{(2)} - 3\alpha\delta R_{\mathrm{CX}}^{(1)} - a\delta R_{\mathrm{CY}}^{(1)} - \alpha\delta R_{\mathrm{CX}}^{(3)} - 3a\delta R_{\mathrm{CY}}^{(3)} \qquad (14)$$

and

$$2Q_{\mathrm{CXY}_3} - (Q_{\mathrm{CX}_2\mathrm{Y}_2} + Q_{\mathrm{CY}_4}) - \Delta = 2\alpha\delta_{\mathrm{CX}}^{(3)} + 6a\delta R_{\mathrm{CY}}^{(3)} - 2\alpha\delta R_{\mathrm{CX}}^{(2)} - 2a\delta R_{\mathrm{CY}}^{(2)} \qquad (15)$$

Subtraction of (13) and (14), (14) and (15) gives

$$-Q_{\mathrm{CX}_4} - 3Q_{\mathrm{CX}_2\mathrm{Y}_2} + 3Q_{\mathrm{CX}_3\mathrm{Y}} + Q_{\mathrm{CXY}_3} = \alpha[9\delta R_{\mathrm{CX}}^{(1)} - 6\delta R_{\mathrm{CX}}^{(2)} + \delta R_{\mathrm{CX}}^{(3)}] + a[3\delta R_{\mathrm{CY}}^{(1)} - 6\delta R_{\mathrm{CY}}^{(2)} + 3\delta R_{\mathrm{CY}}^{(3)}] \qquad (16)$$

$$+Q_{\mathrm{CX}_3\mathrm{Y}} - 3Q_{\mathrm{CX}_2\mathrm{Y}_2} + 3Q_{\mathrm{CXY}_3} - Q_{\mathrm{CY}_4} = \alpha[3\delta R_{\mathrm{CX}}^{(1)} - 6\delta R_{\mathrm{CX}}^{(2)} + 3\delta R_{\mathrm{CX}}^{(3)}] + a[\delta R_{\mathrm{CY}}^{(1)} - 6\delta R_{\mathrm{CY}}^{(2)} + 9\delta R_{\mathrm{CY}}^{(3)}] \qquad (17)$$

Subtraction of (13) and (15) is merely the difference between (16) and (17). To the approximation, therefore, that the contributions due to interactions between non-bonded atoms are strictly additive, equations (16) and (17) provide two relations among the eight bond distances in the substituted methanes $\mathrm{CX}_{4-n}\mathrm{Y}_n$.

Approximations (**a**).—In practice the additive property is very nearly a parabolic function of the number of substituents; thus the L.H. sides of (16) and (17) are very nearly zero. It is readily seen, if there is a linear relation between $R_{\mathrm{CY}}^{(n)}$ and n which may be written

$$R_{\mathrm{CY}}^{(n)} = R_{\mathrm{CY}_4} + \frac{4-n}{3}(R_{\mathrm{CY}}^{(1)} - R_{\mathrm{CY}_4}) \qquad (18)$$

substitution of (18) in (16) and (17) with the L. H. sides equal to zero gives

$$R_{\mathrm{CX}}^{(n)} = n(R_{\mathrm{CX}}^{(1)} - R_{\mathrm{CX}_4}) \qquad (19)$$

which may be expressed also as

$$\delta R_{\mathrm{CX}}^{(3)} = 3\delta R_{\mathrm{CX}}^{(1)} \qquad (19a)$$

and

$$\delta R_{\mathrm{CX}}^{(2)} = 2\delta R_{\mathrm{CX}}^{(1)} \qquad (19b)$$

(**b**).—If the relation between the additive property and the number of substituents is linear, then for the heats of atomization

$$Q_{\mathrm{CX}_{4-n}\mathrm{Y}_n} = Q_{\mathrm{CX}_4} + \frac{n}{4}(Q_{\mathrm{CY}_4} - Q_{\mathrm{CX}_4}) \qquad (20)$$

Substitution for B_{CX} from (7) and B_{CY} from (11) in (12), (13) and (14) and using (20) gives

$$3\alpha\delta R_{\mathrm{CX}}^{(1)} + a\delta R_{\mathrm{CY}}^{(1)} = \frac{3}{2}\Delta \qquad (21)$$

$$2\alpha\delta R_{\mathrm{CX}}^{(2)} + 2a\delta R_{\mathrm{CY}}^{(2)} = 2\Delta \qquad (22)$$

$$\alpha\delta R_{\mathrm{CX}}^{(3)} + 3a\delta R_{\mathrm{CY}}^{(3)} = \frac{3}{2}\Delta \qquad (23)$$

Eliminating Δ gives

$$\frac{\alpha}{a} = \frac{3\delta R_{\mathrm{CY}}^{(2)} - 2\delta R_{\mathrm{CY}}^{(1)}}{6\delta R_{\mathrm{CX}}^{(1)} - 3\delta R_{\mathrm{CX}}^{(2)}} \qquad (24)$$

$$= \frac{6\delta R_{\mathrm{CY}}^{(3)} - 3\delta R_{\mathrm{CY}}^{(2)}}{3\delta R_{\mathrm{CX}}^{(2)} - 2\delta R_{\mathrm{CX}}^{(3)}} \qquad (25)$$

$$= \frac{3\delta R_{\mathrm{CY}}^{(3)} - \delta R_{\mathrm{CY}}^{(1)}}{3\delta R_{\mathrm{CX}}^{(1)} - \delta R_{\mathrm{CX}}^{(3)}} \qquad (26)$$

These are two relations independent of α and a between the eight distances. Again if there is a

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[8] H. A. Skinner, ref. 5, p. 646; J. E. Kilpatrick and R. Spitzer, *J. Chem. Phys.*, **14**, 463 (1946).

linear relation between R_{CY} and n there is also one between R_{CX} and n and equations (19), (19a) and (19b) are valid.

Applications.—The C–Cl bond distances obtained from rotational spectra in the microwave region are found to be 1.780 ± 0.002 Å. in methyl chloride,[3] 1.7724 ± 0.0005 Å. in methylene chloride,[9] and, 1.761 ± 0.004 Å. in chloroform.[4] The electron diffraction method yields the value of 1.755 ± 0.005 for carbon tetrachloride.[10] Within the experimental error, therefore, the C–Cl bond distance is a linear function of the number of substituted chlorine atoms in the chloro methanes. Since an equation similar to (18) can be written for the C–Cl distances there is also a linear relation like (19) for the C–H distances (assuming the L. H. sides of (16) and (17) are zero) so that

$$\delta R^{(2)}_{\mathrm{CH}} = 2\delta R^{(1)}_{\mathrm{CH}} \tag{27}$$

and

$$\delta R^{(3)}_{\mathrm{CH}} = 3\delta R^{(1)}_{\mathrm{CH}} \tag{28}$$

If the L. H. sides of (16) and (17) are calculated from the heats of formation[11] of the chloromethanes, and using the value[12] $\alpha = -260$ cal./mole/ångström, it is found that 0.004 Å. is to be added to the R. H. S. of (27) and 0.002 Å. is to be added to the R. H. S. of (28). The assumption that the L. H. sides of (16) and (17) are zero introduces, therefore, only a negligible correction.

Taking the value of 1.103 ± 0.006 Å. for the CH bond distance in methyl chloride[3] and the value of 1.093 Å. for the CH distance in methane[13] we have $\delta R^{(1)}_{\mathrm{CH}} = 1.103 \pm 0.006 - 1.093 = 0.010 \pm 0.006$ Å. From (27) and (28)

$$\delta R^{(2)}_{\mathrm{CH}} = 0.020 \pm 0.012 \text{ Å. so } R^{(2)}_{\mathrm{CH}} = 1.11 \pm 0.01 \text{ Å.}$$

and

$$\delta R^{(3)}_{\mathrm{CH}} = 0.030 \pm 0.018 \text{ Å. so } R^{(3)}_{\mathrm{CH}} = 1.12 \pm 0.02 \text{ Å.}$$

Recent measurements of the CH distances in methylene chloride[9] and chloroform,[2b] however, yield 1.069 ± 0.006 Å. and 1.073 ± 0.020 Å., respectively. Since these distances were determined from absorption of microwaves by isotopic molecules containing deuterium and hydrogen a large zero-point configurational error is to be expected. This may be large enough so that no trend in CH distance can be established from the microwave data.

Evidence supporting the linear increase in CH bond distance in the series $CH_4 \rightarrow CHCl_3$ is obtained from the relation between force constant and bond distance.[14] From this relation it is readily seen that, for CH bonds

$$\delta K \approx -20\delta R \tag{29}$$

where K is in units of 10^5 dynes per cm., R is in Å. and the force constant for the CH bond in methane is taken as 4.8 × 10^5 dynes/cm.[15] For $\delta R^{(1)}_{\mathrm{CH}} = 0.010 \pm 0.006$ Å.

$$\delta K^{(1)} = -20\delta R^{(1)}_{\mathrm{CH}} = -0.20 \pm 0.12$$

$$\delta K^{(2)} = -0.40 \pm 0.24 \text{ from (27) in (29)}$$

and

$$\delta K^{(3)} = -0.60 \pm 0.36 \text{ from (28) in (29)}$$

A corresponding calculation gives $\delta K_{\mathrm{CCl}} \approx -6\delta R_{\mathrm{CCl}}$ for $K_{\mathrm{CCl_4}} = 1.75 \times 10^5$ dynes cm.$^{-1}$ (ref. 15). Thus the force constants of the CH and CCl bonds in CH_4, CH_3Cl, CH_2Cl_2, $CHCl_3$ and CCl_4 are calculated as 4.8, 4.6 ± 0.1, 4.4 ± 0.2, and 4.2 ± 0.4 for CH bonds and 1.60 ± 0.03, 1.65 ± 0.02, 1.70 ± 0.01, and 1.75, respectively, for the CCl bonds. Good agreement between the frequencies observed for the chloromethanes and those calculated[15] using an Urey–Bradley type of potential function is obtained when the following values of the CH force constants in the chloromethanes are used· 4.8, 4.5, 4.2 and 3.9 × 10^5 dynes/cm., respectively. These values compare quite favorably with those calculated from the bond distances considering the fact that the CCl force constant was assumed constant and equal to 1.75 × 10^5 dynes/cm.

Let H be X and CH_3 be Y in the series $CX_{4-n}Y_n$, then the members of the series are CH_4, CH_3CH_3, $CH_3CH_2CH_3$, $(CH_3)_3CH$ and $(CH_3)_4C$. It has been shown previously[1] that the general physical property of this series is a parabolic function of the number of CH_3 groups so that the equations derived above for the substituted methanes may be applied directly. Thus, if there is a linear relation between the CC distance and n the number of methyl groups substituted into the molecule there is also a linear relation for the CH bond distances given by equation (19). Since the —CH_3, >CH_2 and ⩾C–H bonds are referred to as being attached to primary, secondary and tertiary carbon atoms we have from (19).

$$\delta R^{(\text{secondary})}_{\mathrm{CH}} = 2\delta R^{(\text{primary})}_{\mathrm{CH}} \tag{30}$$

and

$$\delta R^{(\text{tertiary})}_{\mathrm{CH}} = 3\delta R^{(\text{primary})}_{\mathrm{CH}} \tag{31}$$

The Aliphatic Acyclic Hydrocarbons of the Series C_nH_{2n+2}.—In what follows the notation for the hydrocarbons is the same as given in Table X of reference (1). We can form the second differences from Table X as

$$2P_2 - (P_1 + P_3) = -x \quad \text{(say)} \tag{32}$$

$$2P_3 - (P_2 + P_4) = -y \quad \text{(say)} \tag{33}$$

$$2P_4 - (P_3 + P_5) = 0 \tag{34}$$

$$2P_5 - (P_4 + P_6) = 0 \quad \text{etc.} \tag{35}$$

Also

$$P_{4a} - P_4 = x - y = P_{2\text{-methylpropane}} - P_{n\text{-butane}} \tag{36}$$

and

$$P_{5b} - P_5 = 3x - 2y = P_{\text{neopentane}} - P_{n\text{-pentane}} \tag{37}$$

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[9] W. D. Gwinn, private communication.

[10] L. O. Brockway, *Rev. Mod. Phys.*, **8**, 231 (1936).

[11] F. R. Bichowsky and F. D. Rossini, "Thermochemistry of the Chemical Substances," Reinhold Publ. Corp., New York, N. Y., 1936.

[12] This value is obtained by differentiating Cook's relation (reference 6) with respect to bond distance, using Badger's relation for K in terms of R (see reference 14). To get a "suitable" value for the bond in polyatomic molecules, it is then multiplied by the ratio

$$\frac{\text{bond energy of diatom in polyatomic molecules}}{\text{dissociation energy of the diatomic molecules}}$$

[13] G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1945.

[14] R. Badger, *J. Chem. Phys.*, **2**, 128 (1934), gives $K = A/(R - 0.34)^3$ for CH bonds. Thus $\delta K = -3K\delta R/(R - 0.34)$; for $K = 4.8 \times 10^5$ dynes per cm. for CH_4, and since $R = 1.10 \pm 0.03$, $\delta K = \approx 20\delta R$.

[15] T. Simanouti, *J. Chem. Phys.*, **17**, 848 (1949).

If the contributions from non-bonded interactions are additive, these relations become

$$P_{4a} - P_4 = x - y + a_H[3\delta R^{(p)}_{CH} + \delta R^{(t)}_{CH} - 4\delta R^{(s)}_{CH}] + 3a_C[\delta R^{(4a)}_{CC} - \delta R^{(4)}_{CC}] \quad (38)$$

and

$$P_{5b} - P_5 = 3x - 2y + a_H[6\delta^{(p)}_{CH} - 6\delta^{(s)}_{CH}] + 4a_C [\delta R^{(5b)}_{CC} - \delta R^{(5)}_{CC}] \quad (39)$$

provided all contributions from primary, secondary and tertiary CH's are strictly additive. In these equations the superscripts p, s and t stand for CH bonds attached to primary, secondary and tertiary carbons, respectively, and a_H and a_C, are the changes in CH and CC bond energy, respectively, per unit length; the reference CH distance is that in methane and the reference CC distance is that in diamond.

Similarly $2P_2 - (P_1 + P_3)$ is now

$$- x + 3a_H\ [2\delta R^{(p)}_{CH} - \delta R^{(s)}_{CH}] + 2aC\ [\delta R^{(2)}_{CC} - \delta R^{(3)}_{CC}] \quad (40)$$

and $2P_3 - (P_2 + P_4)$ is now

$$- y + a_C\ [4\delta R^{(3)}_{CC} - \delta R^{(2)}_{CC} - 3\delta R^{(4)}_{CC}] \quad (41)$$

The second differences (34), (35), etc., lead to the relation

$$\delta R^{(n)}_{CC} = \frac{(2n - 4)\delta R^{(3)}_{CC} - (n - 3)\ \delta R^{(2)}_{CC}}{n - 1} \quad (42)$$

for $n \geq 3$. Substituting for x and y from (40) and (41) into (38) we find

$$a_H[9\delta R^{(p)}_{CH} + \delta R^{(t)}_{CH} - 6\delta R^{(s)}_{CH}] = - a_C[3\delta R^{(4a)}_{CC} + 3\delta R^{(2)}_{CC} - 6\delta R^{(3)}_{CC}] + P_{4a} - P_4 + [2P_2 - (P_1 + P_3)] - [2P_3 - (P_2 + P_4)] \quad (43)$$

and substituting for x and y from (40) and (41) into (39)

$$a_H[24\delta R^{(p)}_{CH} - 12\delta R^{(s)}_{CH}] = - a_C[4\delta R^{(5b)}_{CC} - 4\delta R^{(5)}_{CC} - 14\delta R^{(3)}_{CC} + 8\delta R^{(2)}_{CC} + 6\delta R^{(4)}_{CC}] + P_{5b} - P_5 + 3[2P_2 - (P_1 + P_3)] - 2\ [2P_3 - (P_2 + P_4)] \quad (44)$$

If there is a linear relation between the CC distance in ethane, propane, isobutane and neopentane and the number of substituted methyl groups, we have

$$\delta R^{(3)}_{CC} = \frac{2}{3}\ (\delta R^{(2)}_{CC} - \delta R^{(5b)}_{CC}) \quad (45)$$

and

$$\delta R^{(4a)}_{CC} = \frac{1}{3}\ (\delta R^{(2)}_{CC} - \delta R^{(5b)}_{CC}) \quad (46)$$

Substituting from (45) into (42) we find for the normal paraffins that

$$\delta R^{(n)}_{CC} = \frac{(n + 1)}{3(n - 1)} \times \delta R^{(2)}_{CC} - \frac{2(2n - 4)}{3(n - 1)} \times \delta R^{(5b)}_{CC} \quad (47)$$

Substituting from (45), (46) and (47) into (43) and (44) makes the term in CC distances on the R. H. sides of (41) and (44) equal to zero, thus

$$\delta R^{(s)}_{CH} = 2\delta R^{(p)}_{CH} - \frac{1}{2a_H}\{(P_{5b} - P_5) + 3[2P_2 - (P_1 + P_3)] - 2[2P_3 - (P_2 + P_4)]\} \quad (48)$$

From (44), and from (43) and (48) we get

$$\delta R^{(t)}_{CH} = 3\delta R^{(p)}_{CH} + \frac{1}{a_H}\left\{P_{4a} - P_4 - \frac{(P_{5b} - P_5)}{2} - \frac{1}{2}\ [2P_2 - (P_1 + P_3)]\right\} \quad (49)$$

Usually the quantities in the large brackets on the R. H. sides of (48) and (49) when divided by a_H are very small[16] and may be neglected in comparison with the other terms, thus the relations given previously in (30) and (31) respectively may be obtained, *viz.*

$$\delta R^{(s)}_{CH} \backsimeq 2\delta R^{(p)}_{CH}$$

and

$$\delta R^{(t)}_{CH} \backsimeq 3\delta R^{(p)}_{CH}$$

Arguing by analogy with the other substituted methanes in which the CY distance is greatest in the monosubstituted compound[2] one would expect the CC bond distance to get smaller in the series ethane, propane, isobutane and neopentane. There is indeed some supporting experimental evidence for this since the CC bond in ethane appears to be greater than 1.55 Å. from spectroscopic data[17] and it is not unreasonable to expect that the CC distance in neopentane is not very different from the value in diamond[18] (1.545 Å.). These considerations would make $\delta R^{(2)}_{CC}$ positive and greater than $\delta R^{(5b)}_{CC}$ so that from equation (47) we see that the CC bond distance gets progressively smaller as the chain length of the normal hydrocarbon increases and in the limit is greater than the CC distance in diamond by the amount $\frac{\delta R^{(2)}_{CC}}{3} - \frac{4\delta R^{(5b)}_{CC}}{3}$. Whereas these results indicate that the CC distance becomes shorter as the number of C atoms increases, the results obtained from bond energy/bond distance considerations[19] in which some corrections due to the interaction between non-bonded atoms have been neglected and others estimated empirically from too few data, show that the CC distance becomes greater as the number of C atoms is increased.

Equations (48a) and (49a) show that there is a linear decrease[14] in the force constant in the CH bonds linked to primary, secondary and tertiary carbons. This is substantiated by the use of 4.5 × 10^5 dynes per cm. for the force constant in polyethylene[20] and the ensuing good agreement between calculated and observed frequencies. Relations (29) for CH bonds gives the change in CH bond length associated with a change of 0.3 × 10^5 dyne per cm. as 0.015 Å. This would appear to be a little high since the increase in the CH distance when a halogen atom is substituted into methane seems to decrease with decreasing electronegativity of the substituent,[2a] so the value for substituting a CH_3 group might be expected to be

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[16] If the observed values for the heats of atomization are used ["Selected Values of Properties of Hydrocarbons" (A.P.I. Research Project 44) Bureau of Standards, Washington, D. C., 1947], we have

$$2Q_2 - (Q_1 + Q_3) = -2.3 \text{ cal./mole}$$
$$2Q_3 - (Q_2 + Q_4) = -0.4 \text{ cal./mole}$$
$$Q_{4a} - Q_4 = 1.6 \text{ cal./mole}$$
$$Q_{5b} - Q_5 = 4.7 \text{ cal./mole}$$

Using a_H = − 260 cal./mole/angstrom (see reference 12) we find

$$\delta R^{(s)}_{CH} = 2\delta R^{(p)}_{CH} - 0.0005 \text{ Å.}$$
$$\delta R^{(t)}_{CH} = 3\delta R^{(p)}_{CH} - 0.0015 \text{ Å.}$$

[17] L. G. Smith, *J. Chem. Phys.*, **17**, 139 (1949).

[18] D. P. Riley, *Nature*, **153**, 587 (1944).

[19] G. Glockler, *J. Chem. Phys.*, **17**, 747, 748, 749 (1949).

[20] T. Simanouti, *ibid.*, **17**, 245 (1949).

approximately equal to the value observed[2a] for CH_3I (*i.e.* 0.007 Å.).

Assuming $\delta R^{(p)}_{CH} = 0.007$ Å. so that the CH distance in $-CH_3$ is 1.100 Å. then the CH distance in $> CH_2$ is 1.107 Å., and in $\geqslant CH$ it is 1.114 Å. From the observed moments of inertia for ethane[17] the corresponding CC distance is 1.553 Å., therefore

$\delta R^{(2)}_{CC}$ is 0.008 Å.

$\delta R^{(3)}_{CC}$ is $\sim$ 0.005 Å. for $\delta R^{(5b)}_{CC} \sim 0$

$\delta R^{(4a)}_{CC}$ is $\sim$ 0.003 Å. from (46)

and

$$\delta R^{(n)}_{CC} \text{ is } \sim \frac{(n + 1)}{3(n - 1)} \times 0.008 \text{ from } (47)$$

STUDY BY RAMAN EFFECT OF THE Ge–H BOND IN $GeHX_3$ MOLECULES AND OF THE MOBILITY OF THE HALOGEN BOND IN HALOGENATED DERIVATIVES OF THE CARBON FAMILY

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Raman spectra were used to follow the course of certain reactions of germanium and other fourth group elements to equilibrium and also for the identification of certain ion species.

I. The Ge–H Bond.—The existence of the Ge–H covalent bond has been hitherto denied. Brewer[1] in 1927 said "the chloroform series ceases to exist, at least as a non-polar series, with the element germanium." In 1934 Volkringer, Tchakirian and Mme. Freyman studied the Raman spectrum of $GeCl_2$ in an aqueous solution of hydrochloric acid.[2] In 1935 Tchakirian and Volkringer studied the Raman spectrum of $GeBr_2$ in an aqueous solution of hydrobromic acid.[3] They said "there is no covalent Ge–H bond."

With Professor Francois, who died in September, 1950, I studied the Raman spectra of anhydrous $GeHCl_3$ and $GeHBr_3$.[4,5] These spectra are similar to that of chloroform. Table I shows Raman spectra of $CHCl_3$ and $CHBr_3$, $SiHCl_3$ and $SiHBr_3$, and $GeHCl_3$ and $GeHBr_3$. Two frequencies, δ_{45} (bending vibration) and γ_4 (stretching vibration) characterize the bond A–H for C, Si and Ge. The Ge–H bond is characterized by the bond-stretching force constant $f = 2.7 \times 10^5$ dynes/cm. For Si–H, $f = 2.88 \times 10^5$ and for C–H, $f = 4.92 \times 10^5$.

Table I

ν: stretching vibration; δ: bending vibration; d = depolarized; p = polarized.

	$\delta_{1,2}$ d	δ_3 p	ν_1 p	$\nu_{2,3}$ d	$\delta_{4,5}$ d	ν_4 p
					C–H	
$CHCl_3$	261	366	667	761	1216	3018
$CHBr_3$	154	222	539	655	1144	3021
					Si–H	
$SiHCl_3$	179	250	489	587	799	2258
$SiHBr_3$	111	169	358	466–480	769	2232
					Ge–H	
$GeHCl_3$	149	181	409	438	699	2159
$GeHBr_3$	95	128	273	325	674	2116

Table II

	$\delta_{1,2}$	δ_3	ν_1	$\nu_{2,3}$	$\delta_{4,5}$	ν_4
$GeHCl_3$	149 d	181 p	409 p	438 d	699 d	2159 p
$GeCl_3^-$	139 d	162 p	253 d	320 p		
	$\delta_{1,2}$	δ_3	$\nu_{2,3}$	ν_1		
$AsCl_3$	158 d	195 p	370 d	405 p		
$SnCl_3^-$	120 (broad band)		220 d	278 p		

Stability of These Molecules.—$GeHCl_3$ and $GeHBr_3$ are unstable molecules.[6] They decompose in three ways: (1) $GeHCl_3 \rightleftarrows GeCl_2 + HCl$: by using anhydrous compounds and holding the temperature below 50°. Tabern prepared $GeHCl_3$ to high purity (direction 1). However, when $GeHCl_3$ is heated, decomposition takes place (direction 2). When $GeHCl_3$ is dissolved in aqueous hydrochloric acid, bubbles of hydrogen chloride gas are released immediately and later go into solution. The Raman spectrum obtained for the new solution does not correspond to that of $GeHCl_3$, but is similar to the spectra of $AsCl_3$ and $SnCl_3^-$ (Table II), and is identical to the spectrum obtained by Volkringer, Tchakirian and Mme. Freyman of $GeCl_2$ in aqueous hydrochloric acid. These authors reported only the frequencies of the various Raman lines. We made measurements of the depolarization of Raman lines and thus were able to establish the structure of the ion. There are two mechanisms which explain the decomposition

$$(A) \begin{cases} (1) & GeHCl_3 = GeCl_2 + HCl \\ (2) & GeCl_2 + Cl^- = GeCl_3^- \end{cases}$$

$$(B) \quad GeHCl_3 = GeCl_3^- + H^+$$

(2) $GeHCl_3 \rightleftarrows GeCl_3^- + H^+$: When $GeHCl_3$ is dissolved in the anhydrous alcohols $CH_3OH \ldots C_{10}H_{21}OH$ we observe the Raman spectra of both $GeHCl_3$ and $GeCl_3^-$. The amount of dissociation in these solvents decreases as the number of carbon

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(1) Brewer, *J. Phys. Chem.*, **31**, 1817 (1927).

(2) Volkringer, Tchakirian and Freyman, *Comp. rend.*, **199**, 292 (1934).

(3) Tchakirian and Volkringer, *ibid.*, **200**, 1758 (1935).

(4) M. L. Delwaulle and F. Francois, *ibid.*, **228**, 1007 (1949).

(5) M. L. Delwaulle and F. Francois, *ibid.*, **230**, 743 (1950).

(6) M. L. Delwaulle and F. Francois, *ibid.*, **228**, 1585 (1949).

TABLE IIIa

		$\delta_{1,2}$	$\delta_{3,4,5}$	ν_1	$\nu_{2,3,4}$
CCl_4		217	313	460	789
	ρ	6/7	6/7	0.05	6/7
	J = I + i	6.5	8	10	M
			δ_3 $\delta_{4,5}$		
CCl_3Br		192	248 295	422	716 778
	ρ	6/7	0.35 6/7	0.05	0.7 0.7
	J	5	6 3.5	10	M W
CCl_2Br_2		154 174	230 241 262	380	683 733 769
	ρ	0.65 0.65	6/7 0.24 6/7	0.05	D P D
	J	3 2	3 6 0.8	10	S W W
$CClBr_3$		141	214 270	328	680 742
	ρ	6/7	0.5 ?	0.05	0.7 0.7
	J	8.5	9 W	10	M W
CBr_4		128	182	268	673
	ρ	6/7	6/7	0.05	6/7
	J	4	6	10	M

TABLE IIIb

		$\delta_{1,2}$	$\delta_{3,4,5}$	ν_1	$\nu_{2,3,4}$
$SiCl_4$		150	221	424	610
	ρ	6/7	6/7	0.05	6/7
	J = I + i	3	2	4	1
			δ_3 $\delta_{4,5}$		ν_4 $\nu_{2,3}$
$SiCl_3Br$		135	191 205	368	545 610
	ρ	6/7	0.55 6/7	0.05	P D
	J	8	3.5 4	10	W W
$SiCl_2Br_2$		111 122	174 182 191?	326	508 563 605
	ρ	0.75 0.75	D 0.55 ?	0.05	D P D
	J	5 4	W 7.5 VW	10	W E W
$SiClBr_3$		101	159 173	288	498 579
	ρ	6/7	0.55 D	0.05	D P
	J	7.5	5.5 W	10	W W
$SiBr_4$		90	137	249	487
	ρ	6/7	6/7	0.05	6/7
	J	3	3	4	1

atoms increases. These solutions of $GeHCl_3$ in anhydrous alcohols are unstable. There is a third mode of decomposition which takes place.

(3) $2GeHCl_3 = GeCl_4 + GeCl_2 + H_2\uparrow$: At the beginning, 3 cc. of hydrogen was produced per day from 5 cc. of $GeHCl_3$ when dissolved in octyl alcohol.

II. Mobility of the Halogens: Cl, Br, I. (a) **Tetrahalogenated Molecules,** AX_4.—Chlorobromides and chloroiodides of carbon and silicon can be isolated.[7] The Raman spectra of the series CCl_4....CBr_4[8] and $SiCl_4$....$SiBr_4$[9] have been studied,[9] and more recently the Raman spectra of the series $SiCl_4$....SiI_4 by the writer. It can be seen in Table III, that the Raman lines which evolve are exactly of the same shape for the three

TABLE IIIc

		$\delta_{1,2}$	$\delta_{3,4,5}$	ν_1	$\nu_{2,3,4}$
$SiCl_4$		150	221	424	610
	ρ	6/7	6/7	0.05	6/7
	J	3	2	4	1
			δ_3 $\delta_{4,5}$		
$SiCl_3I$		123	169 197	333	519 600
	ρ	6/7	P 6/7	0.05	P D
	J	M	M W	S	W W
$SiCl_2I_2$		83 111	149 160 ?	276	418, 436 538 589
	ρ	P D	D P	0.05	D P D
	J	S M	M S	S	W W W
$SiClI_3$		73	114 134	220	411 557
	ρ	D	P D	0.05	D P
	J	S	S W	S	W W
SiI_4		63	94	168	405
	ρ	D	D	0.05	D
	J	M	S	S	W

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(7) L. Dennis, W. R. Orndorff and D. L. Tabern, THIS JOURNAL, **30**, 1050 (1926).

(8) M. L. Delwaulle and F. Francois, *Comp. rend.*, **214**, 226 (1942).

(9) M. L. Delwaulle and F. Francois, *ibid.*, **219**, 335 (1944).

TABLE IV

	$\delta_{1,2}$		δ_3	ν_1	$\nu_{2,3}$		$\delta_{4,5}$		ν_6
$GeHCl_3$	149 d		181 p	409 (ρ = 0.05)	438 d		699 d		2159 p
	δ_1	δ_2			ν_2 p	ν_3 d	δ_4 p	δ_5 d	
$GeHCl_2Br$	one is 123		167	309 (ρ = 0.05)	350	near 432	680>	<695	near 2144 p
$GeHClBr_2$	one is 123		147 p	290 (ρ = 0.05)	near 320	419	676>	<686	near 2135 p
					ν_2 d	ν_3 p	δ_4 d	δ_5 p	
$GeHBr_3$	95 d		128 p	273 (ρ = 0.05)	325 d		674 d		2116 p

series. For titanium, germanium and tin, the systems come to equilibrium when we mix AX_4 and AY_4. From the Raman spectra of the mixtures, we get proof that the systems are in equilibrium. If we examine the Raman spectra of many mixtures of $AX_4 + AY_4$, we can identify nearly all the frequencies of AX_3Y, AX_2Y_2 and AXY_3. This study was made for chlorobromides of titanium, germanium and tin.[10-12] When AX_4 and AY_4 are mixed, if three frequencies are found which are strong and nearly completely polarized lines, lying between the ν_1 frequencies of AX_4 and AY_4, they are surely the ν_1 frequencies of the new molecules AX_3Y, AX_2Y_2 and AXY_3; we can be sure that the system is in equilibrium. With M. Delhaye, a study was begun of mixtures $GeCl_4 + GeI_4$ and $SnCl_4 + SnI_4$. The frequencies 258, 222 and 190 between ν_1 of $GeCl_4$ (396 cm.$^{-1}$) and ν_1 of GeI_4 (161 cm.$^{-1}$) show the existence of the chloroiodides of germanium. The frequencies 218, 194, 172 between ν_1 of $SnCl_4$ at 367 cm.$^{-1}$ and ν_1 of SnI_4 at 154 cm.$^{-1}$ show the existence of the chloroiodides of tin.

It is interesting to note that the reaction is more rapid for tin than for germanium.[13] For $GeCl_4 + GeBr_4$, the course of the reaction with time was studied. The first Raman spectrum shows only the lines of $GeCl_4$ and $GeBr_4$; the second shows, besides $GeCl_4$ and $GeBr_4$, a small amount of $GeBr_3Cl$ and $GeBr_2Cl_2$. Finally, since an excess of $GeBr_4$ was used, the last Raman spectrum shows principally lines of $GeBr_4$ and $GeBr_3Cl$. Velocity changes with temperature and with catalysts such as a very small amount of HCl. The reaction is more easy for the Cl–Br exchange than for the Cl–I exchange. No reaction takes place between $GeCl_4$ and GeI_4 at room temperature; if heated for an hour at about 100°, a state of equilibrium is reached. All the chloroiodides are now present and it is possible to cool to room temperature without changing this equilibrium. GeI_4 crystallizes out when the mixture is cooled after being heated for 15 minutes. In $SiCl_4$ the first halogen is the most difficult to substitute. The reaction of HI gas with $SiCl_3I$ goes more readily than the reaction of HI gas with $SiCl_4$.

$SnBr_4$ can exchange one halogen with $GeCl_4$ or with $TiCl_4$ but there is no reaction between $SnCl_4$ and $GeBr_4$. When $SnBr_4$ and $GeCl_4$ are mixed, the Raman spectra of the mixture shows the strongest lines of $SnBr_3Cl$ and $GeBrCl_3$ in addition to the Raman lines of $SnBr_4$ and $GeCl_4$.

(b) **Trihalogenated Molecules,** AHX_3.—An equilibrium mixture giving $GeHCl_2Br$ and $GeHClBr_2$ by mixing $GeHCl_3$ and $GeHBr_3$ was studied.[14] Table IV gives the Raman lines of the new molecules. The reaction is very rapid.

$GeBr_4$ can exchange halogen with $GeHCl_3$ and $GeCl_4$ can exchange halogen with $GeHBr_3$. The mixtures show the Raman lines of $GeBr_4$, $GeBr_3Cl$, $GeBr_2Cl_2$, $GeBrCl_3$, $GeCl_4$ and $GeHCl_3$, $GeHBrCl_2$, $GeHBr_2Cl$, $GeHBr_3$. From a series of Raman spectra, we can follow the course of the reaction with time. With the aid of Raman spectra the following equilibria also can be proved

$$CHCl_3 + GeHBr_3 \rightleftharpoons CHCl_2Br + GeHClBr_2$$

$$CHBr_3 + GeHCl_3 \rightleftharpoons CHClBr_2 + GeHCl_2Br$$

In conclusion it can be said: Halogens are more mobile in AHX_3 molecules than in AX_4 ones. The mobility of halogens increases in following the series C, Si, Ti, Ge, Sn.

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[10] M. L. Delwaulle and F. Francois, *Comp. rend.*, **220**, 173 (1945).

[11] M. L. Delwaulle and F. Francois, *ibid.*, **219**, 64 (1944).

[12] M. L. Delwaulle and F. Francois, *ibid.*, **227**, 1229 (1948).

[13] M. L. Delwaulle, *ibid.*, **232**, 54 (1951).

[14] M. L. Delwaulle, *ibid.*, **230**, 1945 (1950).

THE DISSOCIATION ENERGY OF FLUORINE

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Chemical bonds of abnormal strength are formed by combination of fluorine with nearly all other elements. Most of these bonds are of an ionic character because of the extreme density of the electron distribution in fluorine. Ionic binding forces must be unimportant for bonds between the fluorine atoms. Thus a relatively small dissociation energy for the fluorine molecule might be expected. Whereas direct spectroscopic methods proved to be unsuccessful, combination of the spectroscopically determined dissociation energies for ClF and Cl_2 (60.3 kcal./mole and 57.2 kcal./mole, resp.) with the heat of formation of ClF obtained from calorimetric measurements, yields 33.4 kcal./mole and 40.2 kcal./mole for the dissociation energy of the fluorine molecule. The first value results by making use of a heat of formation of ClF of 15 kcal./mole, the second by inserting 11.6 kcal./mole.

The results of accurate thermal conductivity measurements on gaseous fluorine by means of the hot wire method using pure nickel tubes and filaments showed no dissociation influence on the heat transport and its pressure dependence up to 500°. Sensitivity and reproducibility were considered to be sufficient to rule out data smaller than 40 kcal./mole. Probably the energy of dissociation of fluorine has to be assumed to be somewhat higher than 40 kcal./mole but not to be beyond 45 kcal./mole.

1. Introduction

Among all halogen molecules fluorine is until now the only one to which the well known spectroscopic methods of determining the dissociation energy are not applicable. Discrete absorption from the ground level of the molecule hitherto could not be observed, probably the excited state referred to is merely a repulsive one without potential minimum.[1] Making use of the continuous absorption of fluorine and the other halogens, von Wartenberg some 20 years ago extrapolated the dissociation energy of fluorine to $D(F_2) = 63$ kcal./mole.[2] Meanwhile a series of indirect determinations as well as estimations has been carried out, which yield an appreciably lower value, even lower than the dissociation energy of chlorine.

The mentioned indirect methods are based on spectroscopic determinations of the dissociation energy of diatomic fluorides. If these are gaseous, for instance ClF and HF, then the relation holds

$$0.5D(F_2) = D(XF) - Q_f(XF) - 0.5D(X_2) \quad (1)$$

with Q_f = thermochemical heat of formation of the fluoride considered. As far as metal fluorides are concerned, such as RbF, CsF, TlF, the equation may be written

$$0.5D(F_2) = D(XF) + L(XF) - L(X) - Q_f(XF) \quad (2)$$

wherein $L(XF)$ and $L(X)$ are the heats of vaporization of the fluoride and the metal, respectively. The statement which can be made hitherto by evaluating these equations is summarized in Table I.

Disregarding ClF, among these values, the spectroscopic dissociation energies of the fluorides and their heats of vaporization are especially uncertain. According to equations (1) and (2) these insecurities enter with double amount into the values of the dissociation energy of fluorine. Nevertheless regarding the conformity of the figures in the last column of Table I the dissociation energy of this molecule should apparently lie between 40 and 50 kcal./mole.

Another possibility to estimate this value is offered by half-empirical relations between the dissociation energy and the vibrational frequency as well as the internuclear distance of diatomic molecules. One of the most simple of these relations

$$\nu = C(D/M_r)^{1/2} \quad (3)^{8}$$

(ν = vibrational frequency, D = dissociation energy, M_r = reduced mol. mass) yields for diatomic molecules grouped near fluorine in the periodic system the C-values listed in Table II.

Table I

Values of $D(F_2)$ from Eqns. (1) and (2)

Energies in kcal./mole at 18°; uncertain values bracketed

XF	D(XF)	Q_f(XF)	$D(X_2)$	L(XF)	L(X)	$D(F_2)$
ClF	60.5[3]	11.6[4]	58.0	....	....	40
HF	(140)[5]	64.5	104.2	....	....	(47)
RbF[6]	(125.5)	133.2	...	(52.2)	18.9	(51.2)
CsF[6]	(130)	131.7	...	(45.7)	18.8	(50.4)
TlF[7]	≤110	76.8	...	(29)	(39.7)	(≤45)

Table II

$C \times 10^{+12}$ According to Eq. (3)

ν in sec.$^{-1}$, D in kcal./mole

C_2	13.1	N_2	12.4	O_2	12.2	F_2	?
		PN	(10.3)	SO	11.4 10.1	ClF	10.6
		P_2	8.5 9.4	S_2	9.8	Cl_2	9.4
		As_2	8.2	Se_2	9.4	Br_2	9.1
				Te_2	8.3	I_2	8.6

In the horizontal lines the C-values remain nearly constant, while decreasing in the vertical columns. By extrapolation a C-value of fluorine comes out between 13 and $11.5 \times 10^{+12}$, corresponding to a dissociation energy of likewise 40 to 50 kcal./mole. Finally a series of splitting energies of 7-electron systems: $D(H_3C\ldots CH_3) = 90$; $D(H_2N\ldots NH_2) = 60$; $D(HO\ldots OH) = 52$ kcal./mole points to a dissociation energy of fluorine below 50 kcal./mole.

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(1) R. S. Mulliken, *Rev. Mod. Phys.*, **4**, 1 (1932).

(2) H. von Wartenberg, G. Sprenger and J. Taylor, *Z. physik. Chem.*, Bodenstein-Festband, 61 (1931).

(3) L. Wahrhaftig, *J. Chem. Phys.*, **10**, 248 (1942); H. Schmitz and H. J. Schumacher, *Naturforschg.*, **2a**, 359 (1947).

(4) E. Wicke, *Nachr. Akad. Wiss. Gottingen*, 89 (1946). Using Q_f(ClF) = 15 kcal./mole according to H. Schmitz and H. J. Schumacher, *Naturforschg.*, **2a**, 362 (1947), $D(F_2)$ comes out to 33 kcal./mole.

(5) Birge–Sponer extrapolation of the vibrational quanta of HF molecule.

(6) Values according to A. D. Caunt and R. F. Barrow, *Nature*, **164**, 753 (1949).

(7) Values according to A. D. Caunt and R. F. Barrow, *Trans. Faraday Soc.*, **46**, 154 (1950).

(8) A. Eucken, *Ann.*, **440**, 111 (1924); see also A. Eucken and E. Wicke, *Naturwiss.*, **37**, 233 (1950).

2. Dissociation and Thermal Conductivity[9]

From the range of $D(F_2)$ = 40 to 50 kcal./mole mentioned above, the fluorine molecule should be dissociated into atoms already at 600° and 1 atm. to an amount of about 0.1 to 1% and to correspondingly higher percentages at lower pressures. A very sensitive test of dissociation is the measurement of thermal conductivity of the gas in question. The dissociation on the hot side of the temperature drop, used for measurement, and the recombination on the cold side gives rise to an additional term to the normal molecular conductivity

$$\lambda_\alpha = \alpha \times \frac{1-\alpha}{1+\alpha} \times \frac{DpW_p{}^2}{R^2T^3} \qquad (4)^{10}$$

with α = ratio of dissociation at the (mean) temperature T, D = coefficient of diffusion of the atoms in the molecular gas, p = total pressure, W_p = heat of dissociation at temperature T. Ratios of dissociation in the order of about 1% are able to cause an increase in thermal conductivity of eventually 20 to 30%.

The thermal conductivity of fluorine was measured by use of the well known method of an electrically heated wire. This wire, 25 cm. long and consisting of pure nickel, was stretched in a nickel tube, 9 mm. diameter, by means of an appended Ni-weight, see Fig. 1 (diameter of wire usually 0.04 mm., at the highest temperature of conductivity measurement 0.08 mm.). The leads consisting of 0.4 mm. Ni-wires connect the apparatus with the Wheatstone bridge. The use of three lead-in wires as shown in Fig. 1 serves to eliminate their resistance. The nickel tube was held at constant temperatures during measurement by means of suitable cooling baths or an electric furnace. The nickel wire was electrically heated to an amount of 5 to 10° above the temperature of the tube wall and served at the same time as resistance thermometer to determine this temperature difference. To obtain the thermal conductivity from the measured heat current, argon was used for comparison and calibrating, because its thermal conductivity is known or can be calculated with sufficient accuracy at all interesting temperatures.

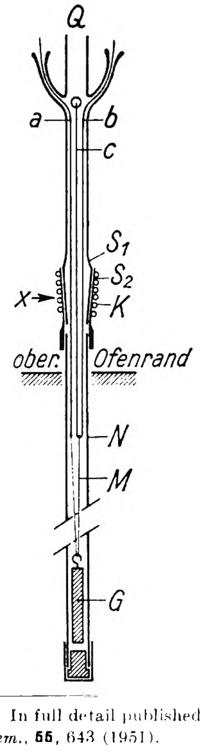

Fig. 1.—Hot-wire cell for measuring thermal conductivities: Q, 8 mm. tube of fused silica to evacuate and fill the measuring cell; a,b,c, lead-in wires (0.4 mm. Ni); X,S_1,S_2, ground joint between fused silica and steel; K, copper capillary soldered on the steel for water cooling; N, Ni-tube, 9 mm. diameter, 35 cm. long; M, Ni-measuring-wire, 0.04 mm. and 0.08 mm. diameter, respectively; G, Ni-weight to stretch the measuring wire, 25 cm. long.

The fluorine was prepared by thermal splitting of ClF_3 at about 700° and subsequent freezing out of the simultaneously formed ClF (as well as remaining ClF_3). It was led to the nickel tube by means of a vacuum assembly made from fused quartz. The measurements covered the temperature range from 90 to 800° K. Already 20 to 30° above this temperature the nickel wire was seriously corroded by the hot fluorine atmosphere and its resistance varied continuously to such an extent that further measurements proved to be unreliable.

The results achieved are shown in Fig. 2, together with measured curves of several other gases. The dashed lines demonstrate the temperature dependence of the total thermal conductivity ($\lambda_{\text{molecular}} + \lambda\alpha$) at p = 1 atm. calculated by means of Eq. (4), if the values of the heat of dissociation at temperature T noted in Fig. 2 are used (the dissociation energies at 0°K. are about 1.5 kcal./mole smaller). In these calculations the diffusivity of the atomic fluorine in the molecular gas was taken relatively small as

$$D_{F-F_2} = 0.20(T/273)^{1.75} \text{ cm.}^2\text{/sec. at 1 atm. total pressure}^{11}$$

The λ values measured at the highest temperature (515°) however, taking into account their range of uncertainty, noted in Fig. 2, fit into the curve to be expected for "normal" thermal conductivity. At this temperature all together 12 measurements with fluorine were carried out in the pressure range 50 to 340 mm., which yield the mean value

$$\lambda_{515°} = 1.46 \pm 0.06 \times 10^{-4} \text{ cal./cm. sec.°C.}$$

A pronounced dependence from total pressure, as can be expected by influence of dissociation, was not observed in this measurement (using W_p = 45 kcal./mole one calculates λ_α at p = 50 mm. about 0.2 × 10^{-4} kcal./cm. sec. °C. larger

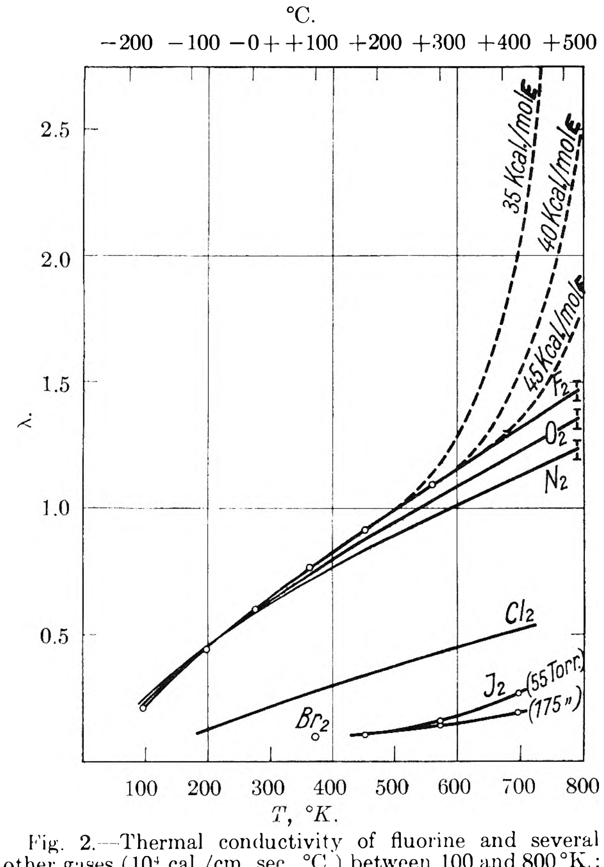

Fig. 2.—Thermal conductivity of fluorine and several other gases (10^4 cal./cm. sec. °C.) between 100 and 800°K.: (full lines, measured values; dashed lines, total conductivity of fluorine as calculated by equation (4) at p = 0.1 atm. using the values of the heat of dissociation noted on the curves).

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[9] In full detail published by E. U. Franck and E. Wicke, *Z. Elektrochem.*, **55**, 643 (1951).

[10] W. Nernst, *Ann. Phys.*, Boltzmann-Festschrift, 904 (1904).

[11] The coefficient of self-diffusion of molecular oxygen, according to Winter, *Trans. Faraday Soc.*, **47**, 342 (1951), amounts to 0.175 cm.²/sec. at 0° and 1 atm.

than at p = 340 mm.). Since no sign of dissociation could be detected in this work on the thermal conductivity of fluorine, this result argues against values smaller than 43 kcal./mole for the dissociation energy of this molecule.

By means of a similarly constructed glass apparatus containing a heated platinum wire, the dissociation of gaseous iodine however could be observed very distinctly, see Fig. 3. Although the vapor of iodine dissociation at the assigned pressures and above 400° is merely 0.1–0.2%, this dissociation causes an appreciable increase of the thermal conductivity above the "normal" molecular value (dashed straight line in Fig. 3). The normal value was calculated by making use of known data of viscosity. Even the pressure dependence of thermal conductivity, being expected as a result of dissociation, appears quite obvious in this case. The dotted curves show the calculated total conductivities at 55 and 175 mm. according to eqn. (4). They correspond to the measured values within 10% satisfactorily.

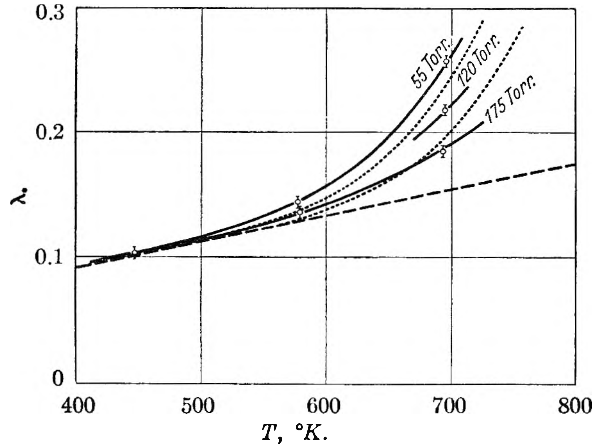

Fig. 3.—Thermal conductivity of iodine vapor (10^4 cal./cm. sec. °C.) between 450 and 700°K. at different pressures: (full lines, measured values; dashed straight line, calculated without dissociation; dotted lines, calculated considering dissociation at 55 and 175 mm.).

3. The Explosion Method

The data of thermal conductivities communicated in Fig. 2 are valuable results; especially those of the difficult fluorine. It must be pointed out, however, that the determination of the dissociation energy of fluorine by means of its thermal conductivity fails at present for want of a wire material of sufficient chemical resistance. Efforts are in progress to overcome this difficulty and to raise the temperature of measurement by 100° at least, where the dissociation effect in all probability will appear. Nevertheless the problem has been attacked from another side too, namely, by measuring the pressure impact brought about by explosion of an H_2–F_2 mixture in a suitable spherical steel vessel.[12] The heat of formation of HF and the specific heats of the partaking molecules being known, the adiabatic maximum temperature and the maximum pressure of such an explosion can be calculated. Applying an excess of fluorine in the original mixture the "effective" specific heat will appreciably increase with beginning dissociation and cause a corresponding decrease in the temperature and pressure produced by the explosion. From the difference between the measured peak of the explosion pressure and the one calculated from normal specific heats the value of the dissociation energy can be derived.

After filling known quantities of both gases into the steel sphere of 30 cm. diameter the mixture is ignited by means of an electric spark. A steel membrane placed in the wall of the sphere serves as plate of a condenser, which changes its capacity by the effect of the explosion pressure. These capacity alterations were observed by a recording apparatus after suitable amplification. Hitherto we have obtained pressure-time-curves such as shown in Fig. 4. One perceives the electrical effect of the ignition-spark and after an induction period of about $^1/_{500}$ second the steep increase of the explosion pressure. Because of the oscillations following this pressure increase, these curves are not yet suitable to be evaluated. We hope however it will be possible to reduce these oscillations by altering the explosion conditions, thus obtaining a further method of determining the dissociation energy of fluorine. If it turns out that this value is larger than 45 kcal./mole (but surely smaller than 50), the heat of formation of ClF would decrease to the improbably small amount of 6.5 to 9 kcal./mole (see Table I, first line). In this case a new determination of this value would be necessary too.

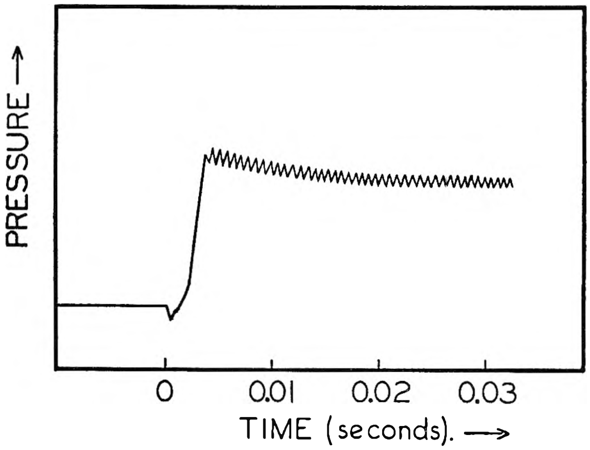

Fig. 4.—Pressure–time–curve of the explosion of an H_2–F_2 mixture in a steel sphere.

With these small values of the dissociation energy of the fluorine molecule, the electron affinity (E_a) of the fluorine atom will decrease as well. By means of the lattice energies of the alkali fluorides the two values are related by

$$E_a(F) = 62.5 + {}^1/_2 D(F_2) \text{ kcal./mole} \qquad (5)$$

With $D(F_2)$ = 45 kcal./mole, $E_a(F)$ = 85 kcal./mole, whereas $E_a(O)$ = 53.5; $E_a(Cl)$ = 87; $E_a(Br)$ = 81; $E_a(J)$ = 72 kcal./mole, respectively. Chlorine therefore will be more electronegative than fluorine, regarding the electron affinity of the free atoms. Nevertheless, fluorine continues to be the most electronegative element with respect to chemical bonds. There has to be made a sharp distinction between the electron affinity of free fluorine atoms on the one side and the electronegativity of bonded fluorine atoms on the other side (see the analogy in the case of oxygen). This distinction is of a similar type as that between excited states of free atoms and their promoted valence states in chemical bonds.

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(12) H. Friz, Dissertation, Göttingen, 1952.

INTERATOMIC DISTANCES AND BOND CHARACTER IN THE OXYGEN ACIDS AND RELATED SUBSTANCES

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In a complex such as the sulfate ion the sulfur–oxygen bond assumes multiple-bond character through resonance involving one sigma bond and two pi bonds. An empirical equation has been formulated connecting interatomic distances and bond number for resonance of this sort. On application of this equation it is found that in many complexes the amounts of multiple-bond character are such as to cause all atoms to conform rather closely to the principle of electroneutrality.

A number of years ago there was developed in our laboratories[1] an interpretation of observed interatomic distances in the oxygen acids and related substances in terms of the partial double-bond character of the bonds. For example, the Si–O distance 1.60 Å. observed in the silicate group in silica and many silicate crystals, which is 0.23 Å. less than the sum of the single-bond radii, was interpreted as indicating that the silicon atom forms with each of the four adjacent oxygen atoms a bond that is essentially a double bond, making use to some extent of the 3*d* orbitals of silicon, as well as the 3*s* and 3*p* orbitals. This interpretation is not completely satisfactory, in that bonds of this sort, even with a reasonable amount of ionic character for the σ bond (about 40%), would correspond to a negative charge on the silicon atom, which however would be expected to have a positive charge.

Schomaker and Stevenson[2] have introduced a revised set of single-bond covalent radii for the first-row elements, and an equation by means of which the effect of partial ionic character of a bond on the interatomic distance may be computed; the use of their system leads to a smaller difference between the observed interatomic distances and those calculated for single bonds with the normal amount of ionic character, as given by the difference in electronegativities of the bonded atoms. Pitzer[3] has recently stated that he does not believe that these bonds have any multiple-bond character whatever; he suggested that the observed short distances are due entirely to the Schomaker–Stevenson shortening plus a bond-lengthening effect that operates in bonds between second-row atoms (such as the Si–Si bond) because of a great repulsion of inner shells. The question of the nature of the bonds has been discussed also by Wells[4] and Moffitt.[5]

A few years ago[6,7] I proposed an electroneutrality principle—the postulate that the electron distribution in stable molecules and crystals is such that the electrical charge that is associated with each atom is close to zero, and in all cases less than ±1, in electronic units. In a molecule involving single bonds we expect a transfer of charge from atom to atom as a result of the partial ionic character of the bonds. For the Si–O bond, for example, the difference in electronegativity of the two atoms corresponds to a partial ionic character of the σ bond amounting to roughly 50%, as found by use of the empirical function based on dipole-moment data.[8] The partial ionic character of four Si–O single bonds would thus confer on the silicon atom a charge of approximately +2, which is incompatible with the electroneutrality principle. A reasonable way to neutralize this large positive charge is through the formation of π bonds between oxygen and silicon, with use of the extra outer electron pairs of the oxygen atom. If each Si–O bond were to have about 50% π-bond character enough negative charge would be transferred to the silicon atom to give it the resultant charge zero, and thus to cause silica and the silicates to satisfy the electroneutrality principle.

I have found that the assumption that in molecules and crystals in which there are atoms with extra electron pairs the bonds have somewhat less π-bond character than necessary to neutralize the charges on the atoms due to the σ bonds, as calculated from differences in electronegativity of the bonded atoms, leads to calculated interatomic distances, electric dipole moments, and bond angles in good general agreement with experiment. Use is made in this calculation of a new equation that is proposed for representing the shortening effect of π-bond character when two pairs of π electrons are involved, and also of a revised relation between the partial ionic character and the electronegativity difference.

Interatomic Distances for π-Bond Resonance

In calculating the interatomic distance with use of the amount of π-bond character we need an equation different from the original equation representing resonance between single bonds and double bonds. The original equation[9]

$$R = R_1 - (R_1 - R_2)\,3n'/(2n' + 1) \qquad (1)$$

in which n' is the amount of double-bond character, leads with $R_1 - R_2$ given the value 0.21 Å. to satisfactory agreement with the observed carbon–carbon interatomic distances for graphite and benzene in relation to those of ethane and ethylene. The curve corresponding to this equation is shown in Fig. 1. It falls below the curve $R = R_1 - 0.706 \log n$, in which n is the bond number, by about

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(1) See L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, Chap. 7.

(2) V. Schomaker and D. P. Stevenson, *J. Am. Chem. Soc.*, **63**, 37 (1941).

(3) K. S. Pitzer, *ibid.*, **70**, 2140 (1948).

(4) A. F. Wells, *J. Chem. Soc.*, **1949**, 55.

(5) W. E. Moffitt, *Proc. Roy. Soc.* (*London*), **A200**, 409 (1950)

(6) L. Pauling, Victor Henri Memorial Volume, Liège, Maison Desser, 1948.

(7) L. Pauling, *J. Chem. Soc.*, 1461 (1948).

(8) Reference 1, Sec. 12.

(9) Reference 1, Chap. 5.

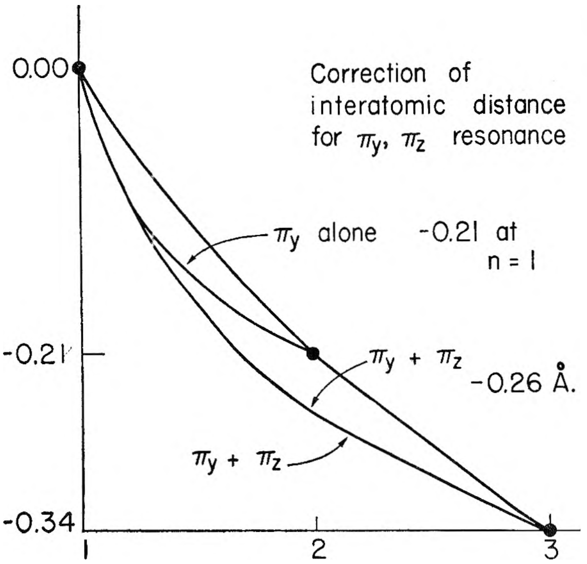

Fig. 1.—Curves representing the dependence of interatomic distance on amount of π-bond character for resonance with a single π electron pair, and with two π electron pairs. The uppermost curve represents the function $R = R_1 - 0.706 \log n$, in which n is the bond number; it corresponds to the dependence of interatomic distance on bond number without correction for resonance shortening. The numbers 1, 2, 3 as abscissas are bond numbers, which are 1 greater than n_π.

0.03 Å. in the neighborhood of 50% double-bond character, because of the stabilizing effect of resonance.[10] In case that two pairs of π electrons, corresponding to the wave functions p_y and p_z (with the x axis taken in the direction of the bond), are involved, a larger amount of resonance energy would be expected for the same amount of π character than in case that only one pair of π electrons is involved. It is found by solution of the appropriate secular equation that the resonance energy for 50% π-bond character when equally divided between π_y and π_z is about twice as great as the resonance energy for 50% π-bond character of a single type; we would accordingly predict that the interatomic distance would be about 0.03 Å. less for the former case than for the latter case.

In the following discussion use is made of an equation that has been formulated by the method given earlier in a discussion of the equation for resonance between a single bond and a double bond[11] and of the interatomic distances in the carbon monoxide molecule and carbon dioxide molecule.[12] The potential function for the bond is assumed to have the form

$$V(R) = \frac{1}{2}\alpha_1 k_1(R - R_1)^2 + \frac{1}{2}\alpha_2 k_2(R - R_2)^2 + \frac{1}{2}\alpha_3 k_3(R - R_3)^2 \quad (2)$$

in which α_1, α_2, α_3 represent the extents to which the single-bond structure, the double-bond structure, involving either the π_y or the π_z electron pair, and the triple-bond structure, involving both of these electron pairs, contribute to the state of the molecule, the k's are their force constants, and the R's their interatomic distances. For single, double, and triple bonds the k's may be taken in the ratio 1:3:6. The equilibrium value of R is found by equating the derivative dV/dR to zero and solving for R, which leads, with introduction of the empirical values 0.21 Å. for $R_1 - R_2$ and 0.34 Å. for $R_1 - R_3$, and by taking the values of α_1, α_2, and α_3 as $\left(1 - \frac{1}{2}n_\pi\right)^2$, $n_\pi\left(1 - \frac{1}{2}n_\pi\right)$, and $\frac{1}{4}n_\pi^2$, corresponding to independent resonance of the π_y and π_z electron pairs, to the result

$$R = R_1 - \frac{0.63n_\pi + 0.195n^2_\pi}{1 + 2n_\pi + \frac{1}{4}n^2_\pi} \quad (3)$$

Here n_π is the total amount of π-bond character.

The curve corresponding to this equation is also shown in Fig. 1. It is seen that it lies below the curve representing resonance between a single bond and a π_y (or π_z) double bond by the amount 0.026 Å. at $n_\pi = 0.5$, and by 0.045 Å. at the point for a pure double bond, $n_\pi = 1.0$, these differences representing the effect of the extra resonance stabilization when two π electron pairs are involved. Values corresponding to the curve are given in Table I.

TABLE I

BOND SHORTENING BY π-BOND RESONANCE

n_π[a]	$-\Delta R$	n_π	$-\Delta R$
0.0	0.000	0.8	0.227
.1	.054	0.9	.241
.2	.095	1.0	.255
.3	.127	1.2	.276
.4	.154	1.4	.294
.5	.176	1.6	.310
.6	.195	1.8	.325
.7	212	2.0	.340

[a] Here n_π is the amount of π character (the sum of π_y and π_z, which are equal), and $-\Delta R$ is the bond shortening, in Å.

For calculating the interatomic distance for a single bond, R_1, involving an atom of nitrogen, oxygen, or fluorine (or two such atoms), we use the equation of Schomaker and Stevenson; namely

$$R_1 = R_A + R_B - 0.09|x_A - x_B| \quad (4)$$

The radii 0.74 Å. for nitrogen, 0.74 Å. for oxygen, and 0.72 Å. for fluorine are to be used with this equation.

The question may be raised as to the extent to which the Schomaker–Stevenson correction includes recognition of the double-bond effect. Equation 4 applies to trimethylamine and dimethyl ether, in which there is no double-bond formation expected because the more electropositive atom in the C–N and C–O bonds, the carbon atom, is given a negative charge by the partial ionic character of its bonds to hydrogen that is larger in magnitude than the positive charge conferred on it by the C–N or C–O bond, and hence does not have a free π orbital to accept an electron from the nitrogen or oxygen atom. We conclude that separate consideration must be given to the effect of the formation of π bonds by atoms of second-row elements with use of 3d orbitals. The correction for this effect is made by application of Equation 1 or Equation 3.

The Partial Ionic Character of σ Bonds

A number of years ago an equation was proposed[13] for calculating the partial ionic character of a σ bond between two atoms A and B from their electronegativity difference $x_A - x_B$

$$\text{partial ionic character} = 1 - e^{-a(x_A - x_B)^2} \quad (5)$$

This equation, with $a = 0.25$, was based on the observed electric dipole moments of HCl, HBr, and HI. Since then the value of the dipole moment of HF has been determined; it is 1.98 D, which corresponds to 47% ionic character, whereas Equation 5 with $a = 0.25$ gives 59%. It seems justified to formulate an empirical function, based on the values 5, 11, 17, and 47% for the hydrogen halides HI, HBr, HCl, and HF, as calculated from their

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(10) L. Pauling, *J. Am. Chem. Soc.*, **69**, 542 (1947).

(11) Reference 1, Sect. 22.

(12) Reference 1, Sect. 25.

(13) Reference 1, Chap. 2.

electric dipole moments and internuclear distances. The values given in Table II were obtained by making uniform slight adjustments, by not over ±0.03, in the curve of Equation 5 with $a = 0.18$, so as to conform to the values for the hydrogen halides. Several authors have pointed out that other structural features (unshared electron pairs, asymmetry of electron distribution for pure covalent bond between unlike atoms) contribute to the dipole moment, but lack of knowledge of the magnitude of their contributions prevents us from making corrections to the values given in Table II.

TABLE II

PARTIAL IONIC CHARACTER OF BONDS IN RELATION TO ELECTRONEGATIVITY DIFFERENCE

Δx^a	I^a	Δx	I	Δx	I
0.0	0	0.9	17	1.8	44
.1	1	1.0	20	1.9	47
.2	2	1.1	23	2.0	51
.3	3	1.2	26	2.2	58
.4	5	1.3	29	2.4	64
.5	7	1.4	32	2.6	70
.6	9	1.5	35	2.8	75
.7	11	1.6	38	3.0	80
.8	14	1.7	41	3.2	83

[a] I is the per cent. partial ionic character, and Δx is the electronegativity difference $x_A - x_B$.

The Extent of π-Bond Formation

In a molecule such as SiF_4, in which the central atom forms several bonds with a large amount of ionic character (58%), it is to be expected that a compensatory mechanism, the formation of π bonds, would operate to reduce the charge on this atom; but it also seems likely that this mechanism would not reduce the charge to zero, but rather would leave it at an intermediate value. An experimental determination of the charge distribution for this molecule is not easily made. The consideration of values of electric dipole moments and interatomic distances for many substances has indicated that the extent to which π bonds are formed is dependent on the row-numbers of the atoms involved and on the number of bonds formed by the central atom. Let us consider a molecule MX_n, in which each atom X is attached to the central atom M by a σ bond and $n_\pi \pi$ bonds. Let the electronegativity difference of M and X be such as to transfer the charge ϵ from each X to M. The charge distribution is then $M^{n(\epsilon - n_\pi)}$ $X^{-(\epsilon - n_\pi)}$. We assume that the energy E of the molecule contains a quadratic term in the charge of each atom: $\frac{1}{2}k(\epsilon - n_\pi)^2$ for each atom X and $\frac{1}{2}kn^2(\epsilon - n_\pi)^2$ for M. This term represents the electroneutrality principle: it operates to minimize the charges on the atoms. The value of k depends, of course, on the nature of the atom; for simplicity, we shall neglect this dependence. We also assume that E contains a similar term $\frac{1}{2}k'n_\pi^2$ for each bond, representing the resistance of the π electron pairs of X to being drawn into π bonds. The expression for E is thus

$$E = \frac{1}{2}kn^2(\epsilon - n_\pi)^2 + \frac{1}{2}kn(\epsilon - n_\pi)^2 + \frac{1}{2}k'nn_\pi^2 \quad (6)$$

The energy has a minimum value relative to the structural parameters. Hence we place

$$\partial E/\partial n_\pi = -k(n^2 + n)(\epsilon - n\pi) + k'nn_\pi = 0 \quad (7)$$

which leads to

$$\frac{n_\pi}{\epsilon} = \frac{n + 1}{k'/k + n + 1} \quad (8)$$

This equation gives the calculated extent of neutralization of the charge due to the σ bonds through π-bond formation, as a function of the number of X atoms in the molecule, n, and the ratio k'/k of the two force constants, the electroneutrality constant k and the π-electron constant k'. With $k'/k = 1.5$, for example, the values 0.77 for $n = 4$ and 0.57 for $n = 1$ are obtained.

Dipole-moment and interatomic-distance data indicate that Equation 8 can be used generally for compounds MX_n by giving k'/k the values $0.0555 \times 3^{(a+b)}$, in which a and b are the row-numbers of atoms M and X, respectively: 1 for O and F, 2 for Si, P, S, Cl, and so on. Table III contains values of n/ϵ_π calculated in this way.

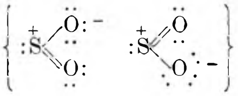
TABLE III

PERCENTAGE OF NEUTRALIZATION OF BOND MOMENT BY π-BOND FORMATION FOR MOLECULES MX_n

$a + b =$	3	4	5	6	7
$n = 1$	57	31	13	5	2
2	67	40	18	7	2
3	73	47	23	9	3
4	77	53	27	11	4

Sulfur Dioxide and Other Oxides

For sulfur dioxide, with resonating Lewis structure



a charge $-\frac{1}{2}$ is placed on each oxygen atom and +1 on the sulfur atom. In addition, the electronegativity difference 1.0 leads to 20% ionic character for each σ bond. The charge distribution without π-bond formation would be $S^{+1.40}O_2^{-0.70}$. From Table III ($a + b = 3$, $n = 2$) we obtain 67% as the amount of neutralization of charge through π-bond formation, which gives $n_\pi = 0.47$ and the charge distribution $S^{+0.46}O_2^{-0.23}$.

This charge distribution, with the known structural parameters[14] S–O = 1.433 Å. and ∠ O–S–O = 119.5°, leads to 1.61 D as the calculated value of the dipole moment. This value agrees exactly with the experimental value.

For S–O the single-bond distance is 1.69 Å., and the π-bond correction (for $n_\pi = 0.97$, the sum of the π-bond character given by the Lewis structure, 0.50, and that induced by the charge distribution, 0.47) is 0.25 Å. Hence the predicted S–O distance is 1.44 Å., in satisfactory agreement with the experimental value 1.433 Å.

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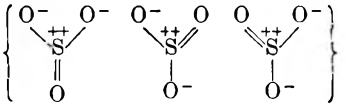
[14] B. P. Dailey, S. Golden, and E. B. Wilson, Jr., *Phys. Rev.*, **72**, 871 (1947).

For sulfur trioxide, with resonating Lewis structure



and 0.20 ionic character of the σ bonds, the charge distribution before π-bond neutralization is $S^{+2.60}$ $Q_3^{-0.87}$. Table III gives 73% neutralization, which leads to n_π = 0.97 (including 0.33 for the Lewis double bond). The predicted S–O distance is hence 1.44 Å., which agrees satisfactorily with the observed value, 1.43 ± 0.02 Å.

For dimethyl sulfone, $(CH_3)_2SO_2$, the predicted amount of π-bond character is 0.67 × 1.10 = 0.80, which leads to S–O = 1.46 Å., slightly larger than the experimental value, 1.43 ± 0.02 Å. In dimethyl sulfoxide, $(CH_3)_2SO$, the predicted value of n_π is 0.57 × 1.20 = 0.68, and the predicted value of S–O, 1.48Å., agrees with the observed value, 1.47 Å.

An interesting example is provided by the trimer of sulfur trioxide. In this molecule the three sulfur atoms are joined together into a six-membered ring by bridging oxygen atoms, and each sulfur atom also has attached to it two unshared oxygen atoms, in addition to the two bridging oxygen atoms, the four oxygen atoms being arranged tetrahedrally about it. The sulfur–oxygen distance is 1.60 Å. for the bridging oxygen atoms, and 1.40 Å. for the others. The Lewis structure, with 20% ionic character of σ bonds, gives the charge distribution $S^{+2.80}O_3^{-0.40}O_6^{-1.20}$. We make use of the value for n = 4 of Table III, 77%, which leads to 0.15 and 0.92 for n_π, and hence to 1.61 Å. and 1.44 A. for the two kinds of S–O bonds, in reasonably good agreement with experiment.

Molecules of the oxides of phosphorus P_4O_6 and P_4O_{10} also contain bridging oxygen atoms. The predicted amounts of π-bond character, 0.73 × 0.32 = 0.23 and 0.77 × 0.32 = 0.25, respectively, lead with use of the single-bond distance 1.71 Å. and Equation 1 to the predicted value 1.61 Å. for P–O in P_4O_6 and 1.60 Å. in P_4O_{10}. The observed values, 1.65 ± 0.02 Å. in P_4O_6 and 1.62 + 0.02 Å. in P_4O_{10}, are slightly larger.

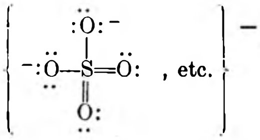
For the oxygen atoms in P_4O_{10} that are bonded to only one phosphorus atom the predicted amount of π-bond character, 1.02, leads to 1.45 Å. for the P=O distance. This is in only rough agreement with the observed distance, 1.39 ± 0.02 Å.

Salts of Oxygen Acids

The discussion of interatomic distances in salts of oxygen acids of the second-row elements is presented in Table IV. In the first row of this table, below the names of the salts, there are given values of the electronegativity difference $x_A - x_B$, in the second row the sum of the single-bond radii, in the third row the Schomaker–Stevenson correction, and in the fourth row the single-bond interatomic distance. The next row contains the fractional amount of ionic character of the σ bond, as given by the electronegativity difference with use of Table II. The next row contains the amount of positive charge placed on the central atom, per bond, by the single-bond formula; that is, it is equal to the oxidation number of the central atom diminished by 4 and divided by 4. The sum of these two quantities, given in the following row, is the amount of charge placed on the central atom by one bond of the single-bond structure. This number multiplied by 0.77, from Table III, in the next row, represents the amount of π-bond character. The following row gives the change in interatomic distance corresponding to this amount of π-bond character, as calculated with Equation 3, and the row below it the predicted interatomic distance, according to our assumptions. Finally, in the last row there are given values of the observed interatomic distances in crystals of salts of these acids. It is seen that the agreement with experiment is good.

The charges on the oxygen atoms due to partial ionic character of the bonds to the metal atoms in the silicates and other salts should be taken into consideration in making this calculation. These charges lead to further decreases in the Si–O, P–O, S–O, and Cl–O distances, of amount depending on the nature of the metal and the structure of the crystals. Because of uncertainties in the system of equations used in this paper, this refinement in the calculation has not been carried out.

It is interesting that the amount of π-bond character in these oxygen complexes varies from about 1/3 to about 2/3, and that for the sulfate ion it corresponds closely to the resonance formula



in which the central atom is shown with zero formal charge.

TABLE IV

INTERATOMIC DISTANCES IN SALTS OF OXYGEN ACIDS

Salt	Silicate	Phosphate	Sulfate	Perchlorate
Electronegativity difference	1.7	1.4	1.0	0.5
Sum of radii	1.91	1.84	1.78	1.73
$-0.09\,\lvert x_A - x_B \rvert$	−0.15	−0.13	−0.09	−0.05
Single-bond distance	1.76	1.71	1.69	1.68
Ionic character of σ bond	0.41	0.32	0.20	0.07
Formal charge per bond	.00	.25	.50	.75
Sum	.41	.57	.70	.82
Amount of π-bond character	.32	.44	.54	.63
Correction for π-bond	−0.13	−0.16	−0.18	−0.20
Predicted distance	1.63	1.55	1.51	1.48
Observed distance	1.62[a]	1.55[b]	1.50[c]	1.49[d]

[a] Average of reported values for zircon, andalusite, sillimanite, staurolite, topaz, titanite, thortveitite, muscovite, apophyllite, hardystonite, analcite, carnegieite, sodalite, danburite, scapolite, and cristobalite; mean deviation 0.02 Å. [b] Average for BPO_4 (1.54 Å.) and KH_2PO_4 (1.56 Å.). [c] For K_2SO_4 and other sulfates. [d] For $Mg(ClO_4)\cdot6H_2O$.

It may be emphasized that bonds corresponding to a completed sp^3 octet for the second-row atom are to be distinguished from those involving orbitals beyond the octet. It is the octet bonds—the Lewis structures—that are of primary importance in determining the bond angles and general configuration of the complex, with the additional π bonds, involving d orbitals, effective mainly in changing the interatomic distances and the charge distribution.

It might be possible to formulate an empirical system of quadratic energy terms, like those in Equation 6, that would reproduce many properties of molecules in a satisfactory way. Efforts to this end have not yet been successful; even the simple treatment of Equation 6 fails when it is applied to molecules in which atoms of two or more kinds are attached to a central atom, and a similar treatment of the charge distribution (electric dipole moment) in molecules in which polar bonds interact with one another through induction has been found to be only partially satisfactory. The practical difficulties attending the quantum-mechanical treatment of the electronic structure of molecules are so great that the main hope for future progress in the treatment of molecular structure may well lie in the development of a quantitative empirical theory of this sort.

BOND LENGTH CALCULATION IN CONJUGATED MOLECULES

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Hartmann has recently introduced the notion of bond type. The bond type in a purely conjugated hydrocarbon is determined by the number of the adjacent C–C bonds. Vroelant and Daudel, using the spin states method, have shown that to a rather good approximation Penney's bond order for such a bond depends only on the types of the adjacent C–C bonds. A given bond is designated by a notation based upon the types of adjacent bonds.

It is possible to show that there is for each notation a good relation between its exact Penney's bond order and the Pauling double bond character taking account of only the Kekule formulas. In this manner the evaluation of the Penney bond orders requires only the calculation of the Pauling double bond characters which are very easy to obtain.

Following an idea of Pauling and work by P. and R. Daudel, A. Laforgue has established an empirical self consistent method of evaluating the bond orders and the atomic charges in a conjugated molecule. This method uses the relations between interatomic distances, bond orders and the β integrals, and the relations between charges, electronegativities and the α integrals. This method has been applied to the evaluation of the interatomic distances in some molecules like N_2O_4. The large N–N bond length found experimentally in this molecule is accounted for.

Introduction

This paper is devoted to the description of some methods useful in the calculation of interatomic distances in conjugated molecules.

In the first part we are concerned with a very simple method of estimating bond lengths in purely aromatic hydrocarbons.

In the second part we describe a possible way of evaluating with a rather good accuracy the bond lengths in some more complicated molecules.

A Very Rapid Method of Estimating Bond Lengths in Purely Aromatic Hydrocarbons

The simplest method of estimating the bond lengths in aromatic hydrocarbons is to determine the "double bond character" using only the Kekule formulas as Pauling suggests.[1]

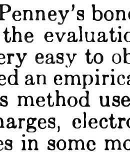
It is now well known,[2] that the calculation of the bond orders using the molecular orbital method, or the valence bond treatment lead to better results. Evidently such a process is very laborious for large and non-symmetrical molecules, such as benzanthracene, for example.

Here, we describe a method as simple as Pauling's process but giving about the same accuracy as the molecular orbital treatment. It is applicable to the estimation of bond lengths in such polyaromatic compounds as naphthalene, anthracene, pyrene, coronene, ovalene, and so on.

Hartmann[3] has recently introduced the notion of bond type. The bond type in a purely conjugated hydrocarbon is determined by the number of the adjacent C–C bonds. As an example the α–β bond in naphthalene is designated as bond type 2 and the central bond as type 4.

Vroelant and Daudel,[4] using the spin method, have shown that *with a rather good approximation the bond order of such a bond depends upon only the types of the adjacent C–C bonds.*

A particular bond is more fully described by means of a notation in terms of the bond types of adjacent C–C bonds. The following diagram shows the types of the bonds in naphthalene. As an example of the notation the α–β bond is designated,[2,3] the β–β bond (2,2), and the central bond (3,3,3,3).



Now it follows from the Vroelant and Daudel approximation that the bond order of a bond is related to the above notation.

As there is a relation between bond order and length we are able to construct Table I giving for

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(1) Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, N. Y.

(2) See for example Coulson, Daudel and Robertson, *Proc. Roy. Soc. (London)*, in the press.

(3) Hartmann, *Z. Naturforschung*, **A**, Feb., 1947.

(4) Vroelant and Daudel, *Bull. soc. chim. France*, **16**, 36, 217 (1949).

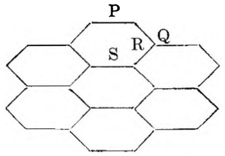
each bond (designated by the notation described above) the bond order and the bond length.[5]

Table I

Bond[a]	Penney's π-bond order	Length	Bond[a]	Penney's π-bond order	Length
(2)	0.827	1.362	(2,3,3)	0.493	1.423
(3)	0.873	1.353	(2,3,4)	0.508	1.420
(1,1)	0.437	1.438	(2,4,4)	0.537	1.414
(1,2)	0.524	1.416	(3,3,3)	0.537	1.414
(1,3)	0.566	1.408	(3,3,4)	0.556	1.410
(2,2)	0.612	1.398	(3,4,4)	0.578	1.405
(2,3)	0.652	1.388	(2,2,3,3)	0.324	1.465
(2,4)	0.676	1.385	(2,2,3,4)	0.346	1.460
(3,3)	0.692	1.380	(2,2,4,4)	0.367	1.455
(3,4)	0.714	1.377	(2,3,3,3)	0.367	1.455
(4,4)	0.735	1.373	(2,3,3,4)	0.387	1.450
(1,2,3)	0.367	1.455	(2,3,4,4)	0.407	1.445
(1,2,4)	0.387	1.450	(2,4,4,4)	0.428	1.440
(1,3,3)	0.407	1.455	(3,3,3,3)	0.407	1.445
(1,3,4)	0.428	1.440	(3,3,3,4)	0.428	1.440
(1,4,4)	0.440	1.436	(3,3,4,4)	0.440	1.436
(2,2,2)	0.412	1.443	(3,4,4,4)	0.469	1.430
(2,2,3)	0.452	1.433	(4,4,4,4)	0.489	1.425
(2,2,4)	0.472	1.428			

[a] The numbers in parentheses give the bond types of C–C bonds adjacent to the bond in question.

Table II



Bond	Notation	Length[6] Calcd.	Obsd.
P	(3,3)	1.380	1.385
Q	(2,3,4)	1.420	1.415
R	(3,3,4,4)	1.436	1.43
S	(4,4,4,4)	1.425	1.43

Using Table I, we can obtain immediately the length of a bond in a conjugated molecule when we know its formula.

Table II compares with experiments the results obtained in the coronene case. The agreement is extremely good: That is to say, a conjugated hydrocarbon without substituent or heteroatom.

It is nevertheless possible to increase the accuracy of the process. For a given notation, the bond orders are subject to small variations from one molecule to another. We can draw for each notation of bond, a curve giving the bond order (using the Coulson's definition or the Penney definition) as a function of its Pauling's double bond character.

Figure I[7] shows the results for the notations (2,2), (2,3) and (3,3) and gives an idea of the accuracy of this method.

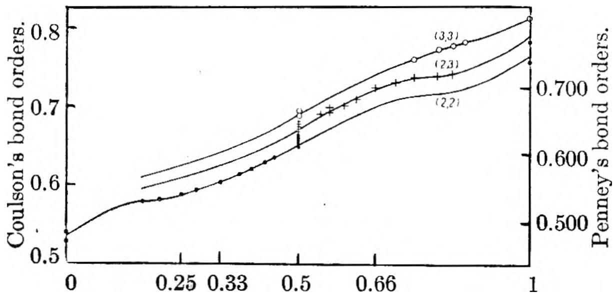


Fig. 1.—The plots correspond to some molecules for which the bond orders have been yet rigorously calculated.

Calculation of the Bond Lengths in the Case of More Complicated Molecules

In the case of more complicated molecules such as substituted hydrocarbons like toluene or heteroatomic conjugated molecule like quinoline, benzoic acid, N_2O_4 and so on, no simple methods are presently known.

Here we shall describe a rather complex method giving good determinations of the bond lengths in such molecules and taking into account a large number of factors.

This method which is based on the molecular orbital theory, is an iterative one, and it is rather similar to the process used by Wheland and Mann,[8] but is more systematical.

In a first approximation the α integrals are taken as proportional to the Pauling electronegativities of the neutral atoms,[9] and the β integrals are assumed to be unity.

With such parameters the usual L.C.A.O. secular equation is solved and the bond orders and the atomic charges are evaluated.

From these values we must calculate the new α and the new β.

The general method is as follow: Evaluation of the new α: In the first approximation the α integrals have been taken proportional to the electronegativities of the neutral atoms.

Since we know the approximative atomic charge, and since there is a relation between the charge and the electronegativity of an atom we are able to evaluate a more accurate electronegativity and consequently a more accurate α.[10]

The formulas used in such determinations are

$$E_0 = E + \delta Q \qquad (1)$$

where E is the electronegativity of a neutral atom and E_0 the electronegativity for this atom with an effective charge Q. δ is a parameter which depends on the atom[10] but is usually 0.3.

$$\alpha_0 = E_0/M \qquad (2)$$

where M is a parameter usually near 1[10]; Evaluation of the new β: The bond orders obtained at the end of the first approximation are used to estimate a first value of the bond lengths as there is usually a known relation between the bond orders and the interatomic distances.[11] In many cases (as in N_2O_4) it is necessary to correct the obtained lengths, taking into account the coulombic interaction due to the effective charges.

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(5) Vroelant and Daudel, *Compt. rend.*, **228**, 399 (1949).

(6) Robertson and White, *J. Chem. Soc.*, 607 (1945); 358 (1947).

(7) Chalvet, *Compt. rend.*, **232**, 165 (1951).

(8) Wheland and Mann, *J. Chem. Phys.*, **17**, 264 (1949).

(9) As proposed by Mulliken, *J. chim. phys.*, **46**, 497, 675 (1949).

(10) See about this question P. and R. Daudel, *J. Phys.*, **7**, 12 (1946); Laforgue, *J. chim. phys.*, **46**, 568 (1949).

(11) See Gordy, *J. Chem. Phys.*, **15**, 305 (1947); Bernstein, *ibid.*, **15**, 668 (1947).

This may be done using the formula

$$d_{Q,Q'} = d + (Q,Q'/kd^2) \qquad (3)$$

where $d_{Q,Q'}$ is the corrected distance, d the distance corresponding directly to the bond order obtained, Q and Q' the effective charges of the two atoms constituting the bond and k the force constant which is usually given as a function of the bond order.[12] Since β is expressible as a function of the length[13] we are able to evaluate the new β. From the new α, and the new β, a new L.C.A.O. secular equation is solved and the total process repeated until the desired accuracy is obtained. Usually the first interation is sufficiently good to lead to convenient lengths.

Such a process has been applied to the study of molecules like N_2O_4[14] and N_3^- or N_3CH_3.[15]

The results are now summarized and compared with the experimental determinations.

Interatomic Distances in N_2O_4.[14]—Figure 2 gives the assumed distribution of the electrons in this molecule and Fig. 3 shows the bond orders and the charges obtained. Gordy's relations[16] have been used to determine the force constants and the interatomic distances from the bond orders.

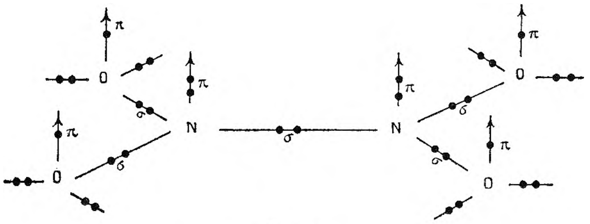


Fig. 2

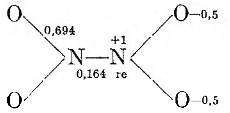
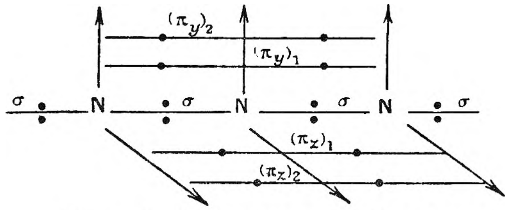


Fig. 3

Thus we obtain for the N–O bond the distance: 1.205 ± 0.020 Å. and the experimental value[17] is 1.17 ± 0.03 Å.

For the N–N bond we find 1.58 ± 0.04 Å. and thus explain the particularly large experimentally determined length (1.64 ± 0.03 Å.)

Interatomic Distances in N_3^- and N_3CH_3.[15]—Figures 4 and 5 show the results which are in good agreement with the experiments.

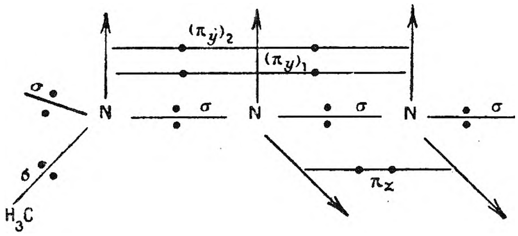


Electronic distribution assumed in N_3^-.

−0.83 +0.66 −0.83
N——————N——————N
2,374 2,374

Charges and Bond Orders. The corresponding length is 1.13 Å.

Fig. 4.



Electronic distribution assumed in N_3CH_3.

−0.37 +0.52 −0.15
N——————N——————N
H_3C 1,701 2,701

Charges and bond orders. The corresponding lengths are respectively: Λ, 25 and Λ, 12 Å.

Fig. 5.

Finally as some recent works have shown it would be possible to improve such calculations introducing the β integrals for non-adjacent bonds[18] and the configuration interaction.[19]

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(12) Gordy, *J. Chem. Phys.*, **14**, 305 (1946).

(13) See ref. 9.

(14) Chalvet and Daudel, *Compt. rend.*. **231**, 855 (1950).

(15) Bonnemay and Daudel, *ibid.*, **230**, 2300 (1950).

(16) See ref. 11 and 12.

(17) Broadley and Robertson, *Nature*, **164**, 915 (1949).

(18) See for example Fernandez. *Compt. rend.*, **233**, 56 (1951).

(19) See for example Craig, *Proc. Roy. Soc.* (*London*), **A200**, 272, 401, 474, 498 (1950); Coulson and Fischer, *Phil. Mag.*, *II*, 386 (1949); Sandorfy, *Compt. rend.*, **232**, 2449 (1951).

ENERGY PROBLEMS OF MOLECULE FORMATION PROCESSES

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The energetics of various types of dissociation processes of a molecule are considered. Terms such as heat of atomization, bond dissociation energy, average bond energy, etc., are defined. The factors affecting these are examined. Differences in bond dissociation energy are compared with differences in heats of substitution. Special attention is given to dissociation processes in which the same fragments are produced from different molecules. Tentative values of resonance energy of radicals are derived from variations in bond dissociation energies.

The formation of a molecule from separated gaseous atoms is an exothermic process, the liberation of energy being attributed to the formation of chemical bonds. Interpreting this process in quantum-mechanical language, we would say that the electrons which moved initially in atomic orbitals have been directed to molecular orbitals, and consequently the system has passed to a lower energy level—if a stable molecule has been formed. The reverse process, the dissociation of a molecule into the atoms composing it, would of course require an expenditure of energy, the latter being referred to as the heat of atomization of a molecule into its constituent atoms. The numerical value of the heat of atomization is given by the difference between the heat content of the relevant free gaseous atoms and the heat content of the gaseous molecule; hence it is obvious that this value must not depend on the way by which the respective molecule has been formed from the atoms. On the other hand, the numerical value of the heat of atomization does depend on the electronic states of the relevant atoms, and therefore the complete definition of the heat of atomization must involve a statement describing exactly the electronic states of the atoms.

It appears that no fundamental advantage is gained by choosing this or another electronic state as the reference state of a particular gaseous atom. The choice of the reference electronic states seems to be rather a matter of convenience. Usually, the lowest and therefore the most stable state of atoms is regarded as their reference state. In such a case we deal with the heat of atomization referring to the atoms in their ground state. One might prefer, however, the choice of another electronic state as the reference state, *e.g.*, some authors[1] suggested the use of the quintet ^5S state of carbon atom instead of the lowest triplet ^3P state, as its electronic reference state. Such a choice would mean that the "new" heat of atomization would be higher than those based on the ground reference state by $n(E_{5S} - E_{3P})$, n denoting the number of carbon atoms present in the respective molecule, while $E_{5S} - E_{3P}$ denotes the separation energy of the ^5S and ^3P states of a carbon atom.

The heat of atomization is an experimentally determinable entity. Its evaluation demands the determination of the heat of formation of the respective compound (in its gaseous state), and of the heats of formation of the relevant gaseous atoms. In addition, determinations of the electronic excitation energies are required if the electronically excited states are chosen as reference states. It is unfortunate, however, that at present some of the required data are lacking. Thus, we still do not know with certainty what are the correct values for the heats of atomization of graphite and of nitrogen. The difficulties arise in the estimation of the heat of sublimation of carbon and in the determination of dissociation energies of such molecules as CO, NO, N_2 and a few others.

Some workers suggested the use of the hypothetical valency state of an atom as its electronical reference state.[2] Such a suggestion has, however, one considerable disadvantage. The valency state of an atom is a hypothetical state, and therefore it is *in principle* unobservable. Hence, the heat of atomization referring to atoms in their valency states ceases to be an experimentally determinable entity.

The formation of a molecule from gaseous atoms involves the interactions between the various components from which the molecule is built up. Each of these interactions is responsible for the liberation of some amount of energy, and the heat of atomization measures the combined effect of all these interactions. We might inquire, of course, how much is contributed to the heat of atomization by every individual interaction. We have to realize, however, that any method of partitioning of the heat of atomization depends on the way in which the building-up process takes place. For example, say that we build up a molecule of methane by gradually adding hydrogen atoms, each of them being in its ground state, to a carbon atom which is also in its ground, *i.e.*, ^3P, electronic state. Moreover, let us carry out the addition process in such a way that in every step we produce a "stable" fragment, *i.e.*, a fragment which lies on the 0 level in the respective hollow of the potential energy surface. Such a process can be represented by four equations

$$\begin{aligned} C + H &\longrightarrow CH \\ CH + H &\longrightarrow CH_2 \\ CH_2 + H &\longrightarrow CH_3 \\ CH_3 + H &\longrightarrow CH_4 \end{aligned}$$

and the amount of energy liberated in each step would be equal to the respective bond dissociation energy, namely, D(C–H), D(CH–H), D(CH_2–H) and D(CH_3–H). Let us remark at this junction, that the four steps described above can be observed *in principle*, and the amounts of energy liberated in each of these steps can be measured *in principle*. Of course, their sum is equal to the heat of atomiza-

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(1) L. H. Long and G. W. R. Norish, *Proc. Roy. Soc.* (*London*), **A187**, 337 (1946)

(2) L. Pauling, *Z. Naturforsch.*, **3a**, 438 (1948); *Proc. Nat. Acad. Sci.*, **35**, 229 (1949).

tion of methane in respect of atoms in their ground states

$$D(\mathrm{C{-}H}) + D(\mathrm{CH{-}H}) + D(\mathrm{CH_2{-}H}) + D(\mathrm{CH_3{-}H}) = Q_a(\mathrm{CH_4})$$

The four processes discussed above are certainly quite complex. They involve a considerable rearrangement of the fragments, *e.g.*, the structure of the CH_3 radical is probably different from the structure of the CH_3 group in the molecule of methane; and therefore the theoretical calculation of the amount of energy liberated would be difficult, although *possible in principle.*(3) That seems to be an important point which needs stressing. Dissociation energies are essentially measurable entities, they can also be calculated by applying the first principles, and thus the theory can be verified by experiment. Let us add one more point. Dissociation energies are the entities which are of paramount importance to a chemist. Chemical reactions involve the breaking and forming of bonds, and therefore the knowledge of the amount of energy required for a rupture of a bond (*i.e.*, bond dissociation energy) is indeed essential.

The process of formation of methane, considered above, is not the only one which leads to the formation of a molecule from the atoms. We might visualize other processes, and some of them deserve a detailed discussion. Say that we start with a carbon atom in its valency state (sp^3), and add to it a hydrogen atom in its ground state. Let us carry out the addition in such a way that the C–H line coincides with the axis of symmetry of one of the sp^3 orbitals, the hydrogen atoms moving from infinity to the distance equal to the C–H bond length in the molecule of methane (see Fig. 1).

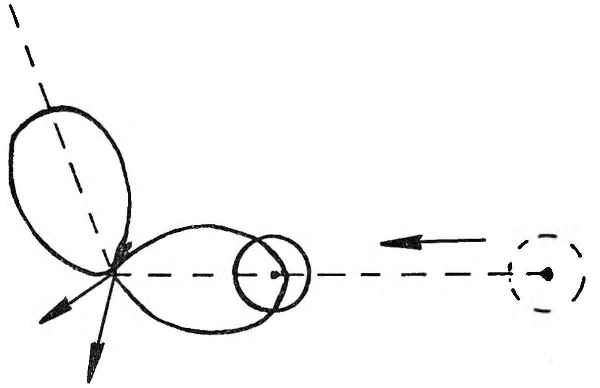

Fig. 1.—First CH bond in methane.

The amount of energy liberated in this process might be calculated; the result would be different from D(C–H) − excitation energy ($^3P \rightarrow sp^3$) since the C–H distance in the final state of the present process is different from the C–H distance in the C–H radical. Moreover, the energy calculated here need not be equal to one quarter of the heat of atomization of methane in respect of a carbon atom in its valency state (this point is to be explained later).

Now, let us add the second hydrogen atom in a manner described in Fig. 2. The CH_2 fragment thus obtained would have the shape of the CH_2 group in the molecule of methane. The amount of energy liberated in the second process would be different from that produced in the first step, since the potential energy of the system CH...H is different from that of C...H. Hence, if one continues the building up of a molecule of methane in the manner described here, one would be able to represent its heat of atomization as a sum of four *different* terms, each representing the amount of energy liberated by adding one more hydrogen in the process discussed. The four values derived from these calculations would be of little importance. They do not represent any observable entity, they cannot be used as measures for "basic" C–H bond energy since they are not mutually equal, they do not, either, represent the "average bond energy."

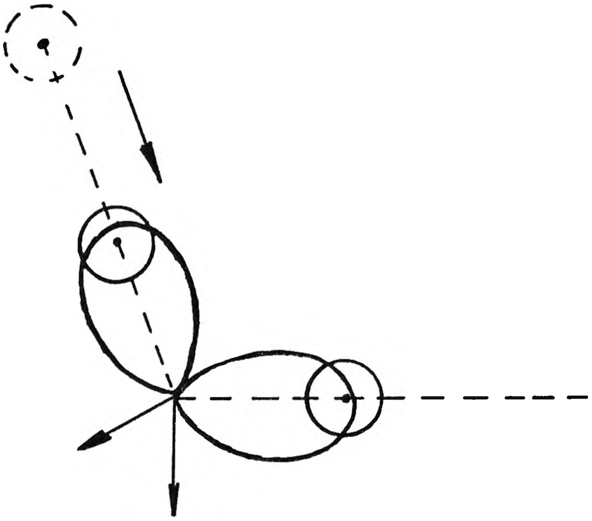

Fig. 2.—Second C–H bond in methane.

To derive the "average bond energy" we have to choose a process which would lead to four *identical* numbers. Such a process has been suggested by M. G. Evans and the present writer(4); it is the reverse of an adiabatic dissociation process in which the whole molecule swells in an unlimited way without losing its geometrical form. In this process the work required to break any particular bond would be equal to the "average bond energy," and mathematically it is defined by

$$\int_{r_i = r_{i_0}}^{\infty} \frac{\partial E}{\partial r_i} \times \mathrm{d}r_i$$

the integration being carried out along the dissociation path as defined above, E denoting the energy of the system corresponding to any configuration of the atoms composing it, r_i denoting the distance between atoms bounded by the i-th bond, the equilibrium distance being r_{i_0}.

The concept of "average bond energy" as defined in ref. 4 might be useful in characterizing the static

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(3) These calculations involve the theoretical determination of the heats of atomization of two fragments, *e.g.*, the determination of the heats of atomization of CH_4 and CH_2 for evaluating $D(CH_3–H)$. The writer is aware of the fact that these calculations are untractable from practical reasons. This does not change the fact that the theory provides us with a method for performing these computations.

(4) M. Szwarc and M. G. Evans, *J. Chem. Phys.*, **18**, 618 (1950).

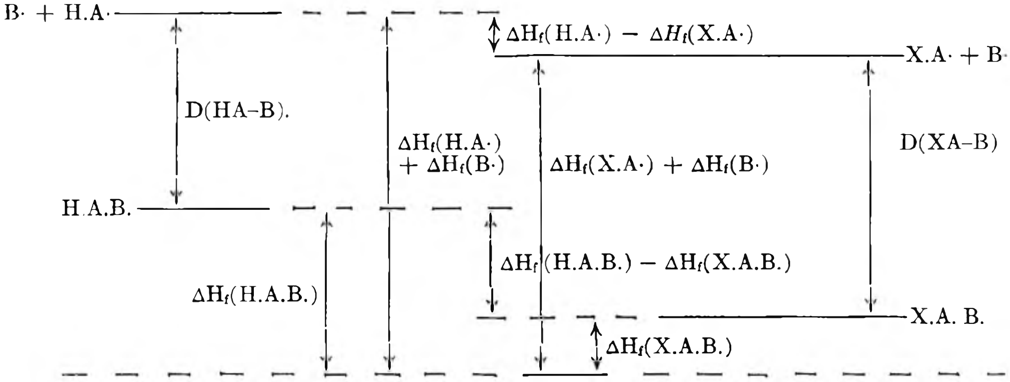

Fig. 3.—Energy relations of the molecules HAB and XAB.

properties of a molecule. For example, it is conceivable that some relation should exist between the "average bond energy" and the length of a bond. On the other hand, it has to be recognized that this "average bond energy" does not characterize the two bonded atoms only, but it is affected by the structure of the whole molecule. Hence, the "average C–H bond energy" in methane need not be equal to the "average C–H bond energy" in ethane, and so on.

It might be the feeling of some chemist that the concept of some basic "theoretical" bond energy should be introduced. Such a "theoretical" bond energy should be a constant characteristic for the two bonded atoms, and independent of molecular environment. The heat of atomization of any molecule would then be given by the sum of all the relevant "theoretical" bond energies plus all the required correction terms accounting for the interaction between the non-bonded atoms, for some deformations which might exist in the molecule, and generally for all the perturbations of the molecular system. Introduction of such a concept could be easy, if the heat of atomization would be an additive property of a molecule. The additive property of the heat of atomization was postulated in the 1920's, and on this basis the system of "bond energies" has been derived. However, we do know that the additivity rule is valid only in the first approximation, the condition being that the molecular force field should be a "simple valency force field" (see ref. 4).

Nevertheless, the concept of "bond energy," introduced into chemical literature by Fajans, and developed in a masterly way by Pauling, led to the clarification of many problems. Its utilization for various aspects of molecular structure, chiefly by Pauling and his school, has had a most inspiring influence on a whole generation of chemists. It is questionable, however, if this concept may be developed further in a fruitful way. Indeed, it appears that much work following on the pioneering papers by Pauling has confused the whole issue.

There is an inclination to introduce the system of basic "theoretical" bond energies as a set of constants which might be utilized for quantum-mechanical calculations. These calculations would then take care of "corrections" resulting from the existence of other interactions, and ultimately they would provide us with the theoretically calculated heats of atomization of various molecules. The "theoretical" bond energy would measure therefore, the energy contribution arising from some interactions which have been arbitrarily considered as the "basic" ones; and hence the concept would be to a greater extent characteristic of a particular method of mathematical approximation applied in a theoretical approach to the problem, than a characteristic feature of the nature of a molecule.

It is my feeling that the theoretical treatment of "bond energies" leads to the invention of too many concepts which correspond to non-observable entities. It appears that interest should be shifted to experimentally measurable quantities, such as bond dissociation energies, ionization potentials, electron affinities and so forth. It is very important to account theoretically for the observed variations of these entities—variations which result from the changes of molecular environment.[5] Some experimental data are now available, and indeed they indicate the very profound effect of molecular environment on bond dissociation energies (see *e.g.*, Table I) and on ionization potentials of radicals.

Table I

Compound	C–C bond dissociation energy (kcal./mole)
NC–CN	110?
Ph–Ph	103?
CH_3–CH_3	83
$C_6H_5\cdot CH_2$–$CO\cdot CH_3$	63
$CH_3\cdot CO$–$COC\cdot H_3$	60
$C_6H_5\cdot CH_2$–$CH_2\cdot C_6H_5$	47
$CH_2{:}CH\cdot CH_2$–$CH_2\cdot CH{:}CH_2$	42
$Ph_3\cdot C$–$C\cdot Ph_3$	11

On the whole, changes in molecular environment affect both the initial and the final state of a system. For example, let us consider the dissociation of the molecule HA–B and of its derivative, say XA–B. The respective bond dissociation energies are equal to

$$D(\text{HA–B}) = \Delta H_f(\text{HA}\cdot) + \Delta H_f(\text{B}\cdot) - \Delta H_f(\text{HA.B})$$

and

$$D(\text{XA–B}) = \Delta H_f(\text{XA}\cdot) + \Delta H_f(\text{B}\cdot) - \Delta H_f(\text{XA.B})$$

Hence, the difference $D(\text{HA–B}) - D(\text{XA–B})$

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[5] (a) M. Szwarc, *J. Chem. Phys.*, **18**, 1660 (1950); (b) M. Szwarc and J. W. Taylor, *Trans. Faraday Soc.*, **47**, 1293 (1951).

which reveals the effect of the substituent X on A–B bond dissociation energy results from two factors, one affecting the undissociated molecule which is equal to $\Delta H_f(\text{XA.B}) - \Delta H_f(\text{HA.B})$, and the second influencing the radical formed which is equal to $\Delta H_f(\text{HA}\cdot) - \Delta H_f(\text{XA}\cdot)$. This interrelation is clearly shown in Fig. 3 (see in this connection ref. 5).

The effect of aromatic substitution on the C–Br bond dissociation energy of substituted benzyl bromides has been investigated in some detail.[6] It seems that the substitution of a hydrogen atom in the benzene ring by chlorine or bromine atoms has no effect on the C–Br bond dissociation energy Phs·CH$_2$–Br.[7] This result recalls a similar observation of the effect of fluorination on the Phs·CH$_2$–H bond dissociation energy showing that $D(\text{C}_6\text{H}_5\cdot\text{CH}_2\text{–H})$ is equal to $D(\text{C}_6\text{H}_4\text{F}\cdot\text{CH}_2\text{–H})$, fluorine being in the *p*-, or *m*- or *o*-position.[8] On the whole, the substitution in nucleus seems to affect only slightly the Phs·CH$_2$–Br bond dissociation energy (see Table II).

TABLE II

Substituted benzyl bromides	ΔD, kcal./mole	Substituted benzyl bromides	ΔD, kcal./mole
o-Chloro	0.9	*m*-Methyl	0.0
m-Chloro	.1	*p*-Methyl	1.4
p-Chloro	.4	*m*-Nitro	2.1
m-Bromo	.3	*p*-Nitro	1.1
p-Bromo	.3	*m*-Nitrile	1.4
o-Methyl	2.0	*p*-Nitrile	0.7

It is interesting to compare the effect of methyl groups on the C–Br bond dissociation energy in PhsCH$_2$–Br and on the PhsCH$_2$–H bond dissociation energy in methylated toluenes.[9] In both cases the substitution in meta position seems to have no effect whatever on the respective bond dissociation energy. On the other hand, the substitution in *p*- or *o*-position seems to decrease the respective bond dissociation energy, probably by increasing the stabilities of the relevant radicals (see Table III).

TABLE III

Compound	D(C–H) kcal./mole	ΔD, kcal./mole	Compound	D(C–Br) kcal./mole	ΔD kcal./mole
$\text{C}_6\text{H}_5\text{CH}_2\text{–H}$	77.5	..	$\text{C}_6\text{H}_5\text{CH}_2\text{–Br}$	50.5	..
m-$\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{–H}$	77.5	0	*m*-$\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{–Br}$	50.5	0
p-$\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{–H}$	75	2.5	*p*-$\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{–Br}$	~49.0	1.4
o-$\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{–H}$	74	3.5	*o*-$\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{–Br}$	~48.5	2.1

The halogenation of methyl bromide seems to affect greatly the relevant C–Br bond dissociation energy[10] (see Table IV). The difference between $D(\text{CH}_3\text{–Br})$ and $D(\text{CCl}_3\text{–Br})$ or $D(\text{CBr}_3\text{–Br})$ appears to be of the order of 18 kcal./mole; on the other hand $D(\text{CH}_3\text{–Br}) - D(\text{CF}_3\text{–Br})$ seems to be 3 kcal./mole only. This result is very striking and it might indicate that the steric interaction between Br atom and X (X = H, F, Cl or Br) plays an important role in decreasing the C–Br dissociation energy in the series of halogenated methyl bromides. This is tentatively illustrated by Fig. 4.

TABLE IV

Compound	D(C–Br), kcal./mole	Compound	D(C–Br), kcal./mole	Compound	D(C–Br), kcal./mole
CH_3Br	(67.5)	CH_3Br	(67.5)	CH_3Br	(67.5)
....	....	CH_2ClBr	61.0	CH_2Br_2	62.5
....	....	CHCl_2Br	53.5	CHBr_3	55.5
CF_3Br	64.5	CCl_4Br	49.0	CBr_4	49.0

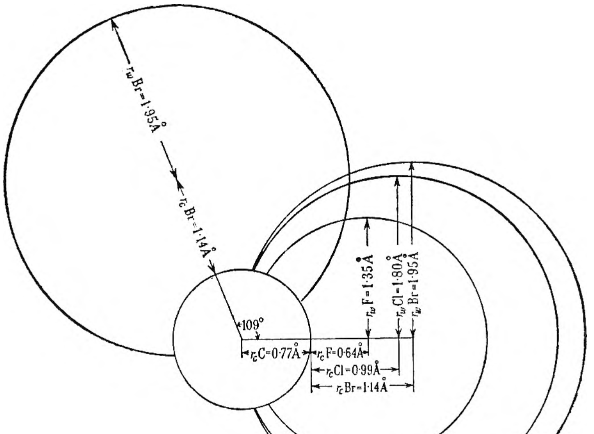

Fig. 4.—Interaction of the bromine atom and atom X (X = F, Cl, Br).

It is instructive to discuss briefly the series: methane, ethane, propane and isobutane. The C–H dissociation energies in this series of compounds and the ionization potentials of the respective radicals have been reviewed recently by Stevenson,[11] the relevant data being given in Table V. One can see clearly, that the decrease in the ionization energy is much greater than the decrease in the C–H bond dissociation energy. This result has been pointed out by A. G. Evans,[12] who discussed the relative effect of methyl groups on the stabilization of radicals and the respective carbonium ions.

TABLE V

Compound	D(C–H), kcal./mole	ΔD, kcal./mole	Radical	$I^z(R)$, kcal./mole	ΔI^z, kcal./mole
$\text{CH}_3\text{–H}$	101	..	CH_3	232	..
$\text{CH}_3\cdot\text{CH}_2\text{–H}$	97	4	$\text{CH}_3\cdot\text{CH}_2$	200	32
$(\text{CH}_3)_2\cdot\text{CH–H}$	94	7	$(\text{CH}_3)_2\cdot\text{CH}$	172	60
$(\text{CH}_3)_3\cdot\text{C–H}$	88	13	$(\text{CH}_3)_3\cdot\text{C}$	159	73

It is significant to compare the ionization potential of methyl radicals with the ionization potential of the alkyl radical. The latter has been computed recently at 9.05 e.v.[13] It appears that

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[6] C. H. Leigh, A. H. Sehon and M. Szwarc, *Proc. Roy. Soc.* (*London*), **A209**, 97 (1951); *J. Chem. Phys.*, **19**, 657 (1951).

[7] Phs denotes the substituted benzene ring.

[8] M. Szwarc and J. S. Roberts, *ibid.*, **16**, 609 (1948).

[9] M. Szwarc, *ibid.*, **16**, 128 (1948).

[10] A. H. Sehon and M. Szwarc, *Proc. Roy. Soc.* (*London*), **A209**, 110 (1951); *J. Chem. Phys.*, **19**, 656 (1951).

[11] D. P. Stevenson, *Faraday Soc. Disc.*, **10**, 35 (1951).

[12] M. G. Evans, *Nature*, **157**, 438 (1946).

[13] M. G. Evans and M. Szwarc, *J. Chem. Phys.*, **19**, 1322 (1951).

the allyl type resonance does not affect the relative stabilities of the allyl radical and allyl carbonium ion. This point has been discussed elsewhere.[13,14]

The examples discussed in this paper show the complexity of processes of bond formation. Their better understanding is of great importance to Chemistry and deserves further studies, both experimental and theoretical.

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[14] M. G. Evans, *Faraday Soc. Disc.*, **10**, 1 (1951).

THE RATE-DETERMINING STEPS IN RADIAL ADSORPTION ANALYSIS

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Equations have been derived based upon various kinetic, liquid and solid diffusion rate mechanisms for the saturation of an initially empty radial adsorption disc. Three experimental systems were employed in an endeavor to test the validity and usefulness of the equations under a variety of operating conditions. The results indicate that for certain of the solute concentrations studied a single rate mechanism can be chosen with a fair degree of certainty.

The kinetics of adsorption columns have received a considerable amount of attention by various authors in the past few years. However, a careful perusal of the literature reveals the fact that a vast majority of the publications have been primarily of a theoretical nature. Hiester and Vermeulen[2] have summarized very adequately the various theoretical postulates presented up to 1948 and the Faraday Society[3] has since published a symposium on chromatography which contains a number of pertinent papers. Application of the various kinetic and diffusion equations to actual experimental data in an endeavor to confirm or disprove the theoretical postulates has received little attention. Of the attacks made on this problem,[3-11] the theoretical equations have not been subjected to sufficient variation in the operating variables to allow the authors to make any definite statements as to the applicability of the equations.

The present authors, therefore, undertook the collection of data under a variety of operating conditions obtained on a radial adsorption disc. The choice of a radial disc rather than the usual vertical column was based on the number of commercial advantages that the former method presents.[12] These data were then applied to theoretical equations based on kinetic and diffusional mechanisms and the results analyzed for the applicability of the equations. It was hoped that by pursuing this course a more adequate basis would be established toward understanding the phenomenon of rate-dependent adsorption analysis.

Theoretical

In a previous publication[13] the authors have presented under very general conditions the solution of the mathematical problem which results when one considers the flow of solution containing a single solute through a radial adsorption disc. For the sake of continuity this paper will be summarized first, and the equations changed into forms more desirable for actual usage.

Let:

r = distance from origin to any point in the disc, cm
h = mass of adsorbent per unit area of disc, g./cm.^{2}
R = radius of circular hole into which solution is introduced, cm.
c = amount of solute in solution per unit volume of solution, mmol./ml.
n = amount of solute adsorbed per unit mass of adsorbent, mmol./g.
$\bar{v}$ = volume rate of flow of solution, ml./min.
m = porosity of adsorbent bed, ml./g.
c_0 = initial solute concentration.
n_0 = total solute capacity of adsorbent.
c^* = concentration of solute in equilibrium with adsorbed solute.
D_1 = diffusion constant for solute in solution.
D_s = diffusion constant for solute in solid.
b = distribution coefficient.
k_g = mass-transfer coefficient.
k_1, k_2 = kinetic velocity constants.
a_0 = particle radius, cm.
Δa = film thickness.
ρ = mass of adsorbent/unit volume, g./ml.
j k = constants.
γ = shape factor.

The system of equations which has been shown to define the physical problem is

$$\bar{v}\frac{\partial c}{\partial r} + 2\pi rh\frac{\partial n}{\partial t} + 2\pi rhm\frac{\partial c}{\partial t} = 0 \qquad (1)$$

$$\frac{\partial n}{\partial t} = k_1c(n_0 - n) - k_2n \qquad (2)$$

$$c(r,t) = c_0(t), \text{ when } r = R \qquad (3)$$

$$n(r,t) = n_0(r), \text{ when } \bar{v}t \leqslant \pi hm(r^2 - R^2) \qquad (4)$$

Equation 1 is the conservation equation for the process and equation 2 is the mathematical relation which is chosen to represent the local rate of solute removal or deposition. For the present, we shall assume that this rate process may be described by a kinetic second order-first order rate equation. Equations 3 and 4 describe the condition of the entering solution and the initial distribution of solute in the bed.

To facilitate the solution the following changes of variables can be made

$$y = r - R \qquad (5)$$

$$z = \bar{v}t - \pi hm(r^2 - R^2) \qquad (6)$$

where z represents the volume of solution which has passed the distance y in the disc.

But equation 1, in terms of the variables y and z implies a function F, such that

$$dF = cdz - 2\pi h(y + R)ndy \qquad (7)$$

and

$$c = \frac{\partial F}{\partial z}, n = -\frac{1}{2\pi h(y + R)}\frac{\partial F}{\partial y} \qquad (8)$$

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[1] Forrestal Research Center, Chemical Kinetics Division, Princeton University, Princeton, N. J.

[2] N. K. Hiester and T. Vermeulen, *J. Chem. Phys.*, **16**, 1087 (1948).

[3] "Chromatographic Analysis," Discussion Faraday Soc., No. 7 (1949).

[4] R. H. Beaton and C. C. Furnas, *Ind. Eng. Chem.*, **33**, 150 (1941).

[5] G. A. Bohart and E. O. Adams, *J. Am. Chem. Soc.*, **42**, 523 (1920).

[6] C. N. Hinshelwood, *et al.*, *J. Chem. Soc.*, 918 (1946); 401 (1947).

[7] E. R. Tompkins, J. X. Khym and W. E. Cohn, *J. Am. Chem. Soc.*, **69**, 2769 (1947).

[8] J. J. Kipling, *J. Chem. Soc.*, 1487 (1948).

[9] W. A. Selke, Ph.D. Thesis, Yale Univ., 1949.

[10] L. G. Sillen and E. Ekedahl, *Arkiv. Kemi Mineral Geol.*, **A22**, No. 16 (1946).

[11] F. C. Williams, N. K. Hiester and T. Vermeulen, in press.

[12] H. Weil, *Can. Chem. and Proc. Ind.*, 956 (1949).

[13] L. Lapidus and N. R. Amundson, THIS JOURNAL, **54**, 821 (1950).

Equation 8 in conjunction with the rate equation leads to a non-linear hyperbolic differential equation

$$\frac{\partial^2 F}{\partial z \partial y} + A(y + R)\frac{\partial F}{\partial z} + B\frac{\partial F}{\partial z}\frac{\partial F}{\partial y} + D\frac{\partial F}{\partial y} = 0 \quad (9)$$

where

$$A = \frac{k_1 n_0 2\pi h}{\bar{v}},\ B = \frac{k_1}{\bar{v}},\ D = \frac{k_2}{\bar{v}}$$

By letting

$$BF = \ln\left\{e^{-\left[Dz + A\left(\frac{y^2}{2} + yR\right)\right]}U(y,z)\right\} \quad (10)$$

equation 9 is transformed into

$$\frac{\partial^2 U}{\partial z \partial y} = AD(y + R)U \quad (11)$$

and the boundary conditions become

$$U(z,0) = \exp\left\{\int_0^z [Bc_1(s) + D]\mathrm{d}s\right\} = f_2(z) \quad (12)$$

$$U(0,y) = \exp\left\{\int^y [A - n_1(s)2\pi hB][s + R]\mathrm{d}s\right\} \quad (13)$$
$$= f_1(y)$$

s is the variable of integration and

$$c_1(z) = c_0\left(\frac{z}{\bar{v}t}\right)$$
$$n_1(y) = n_0(y + R)$$

Equation 8 is also transformed to

$$c = \frac{1}{B}\left[\frac{1}{U}\frac{\partial U}{\partial z} - D\right];\ n = \frac{A}{2\pi hB} - \frac{1}{2\pi h(y + R)BU}\frac{\partial U}{\partial y} \quad (14)$$

Using the LaPlace Transform method, the authors[13] have solved the system of equations 11, 12 and 13. The solution is

$$U(y,z) = \int^y f_1'(s)I_0\left(2\sqrt{ADz\left[\frac{y^2 - s^2}{2} + (y - s)R\right]}\right)\mathrm{d}s + \int_0^z f_2'(s)I_0\left(2\sqrt{AD\left(\frac{y^2}{2} + yR\right)(z - s)}\right)\mathrm{d}s + I_0\left(2\sqrt{ADz\left(\frac{y^2}{2} + yR\right)}\right) \quad (15)$$

From equation 14 the concentrations c and n as functions of the radial distance and the volume of solution through the bed may be obtained. However, the application of the resulting formulas to experimental data is a formidable problem from a computational point of view. If, instead, one considers the saturation of an initially empty bed by a solution entering at constant composition, considerable simplification occurs. Equations 3, 4, 12, 13 and 15 become

$$c = c_0 \quad , \quad r = R \quad (16)$$

$$n = 0 \quad , \quad \bar{v}t \leqslant \pi hm(r^2 - R^2) \quad (17)$$

$$f_2(z) = \exp\left\{\int_0^z (Bc_0 + D)\mathrm{d}s\right\} \quad (18)$$

$$f_1(y) = \exp\left\{\int_0^y A(s + R)\mathrm{d}s\right\} \quad (19)$$

$$U(y,z) = \int_0^y A(s + R)\exp\left[A\left(\frac{s^2}{2} + sR\right)\right]I_0\left(2\sqrt{ADz\left[\frac{y^2}{2} + yR - \frac{s^2}{2} - sR\right]}\right)\mathrm{d}s + \int_0^z (Bc_0 + D)\exp[(Bc_0 + D)s]I_0\left(2\sqrt{AD\left(\frac{y^2}{2} + yR\right)(z - s)}\right) + I_0\left(2\sqrt{ADz\left(\frac{y^2}{2} + yR\right)}\right) \quad (20)$$

Now make use of the definite integral (18)

$$\phi(u,v) = e^u\int_0^u e^{-p}I_0(2\sqrt{vp})\mathrm{d}p = \sum_{m>n\geq 0}^{\infty}\frac{u^m v^n}{m!n!} \quad (21)$$

This transforms equation 20 into

$$U(y,z) = \phi\left[A\left(\frac{y^2}{2} + yR\right), Dz\right] + \phi\left[Fz, G\left(\frac{y^2}{2} + yR\right)\right] + I_0\left(2\sqrt{ADz\left(\frac{y^2}{2} + yR\right)}\right) \quad (22)$$

where

$$F = \frac{k_1c_0 + k_2}{\bar{v}}\ ,\ G = \frac{2\pi h}{\bar{v}} \times \frac{k_1k_2n_0}{k_1c_0 + n_2}$$

one may now return to the variable F by means of equation 10, and then further to equation 8. Using the fact that $c = c_0$ at $y = 0$, there results

$$c/c_0 = \frac{\phi\left[Fz, G\left(\frac{y^2}{2} + yR\right)\right] + I_0\left(2\sqrt{ADz\left(\frac{y^2}{2} + yR\right)}\right)}{\phi\left[Fz, G\left(\frac{y^2}{2} + yR\right)\right] + \phi\left[A\left(\frac{y^2}{2} + yR\right), Dz\right] + I_0\left(2\sqrt{ADz\left(\frac{y^2}{2} + yR\right)}\right)} \quad (23)$$

This is the final equation which describes the concentration c as a function of y and z.

As indicated previously the rate equation 2 upon which equation 23 is based is derived from purely kinetic effects and implicitly assumes that the rate of liquid diffusion of the solute to the surface of the particle and of solid diffusion into the interior of the particle are very rapid in comparison to the kinetic velocity. From a theoretical point of view there is no reason why one should say that the kinetic velocity is the rate-determining step of the three or even why the kinetic mechanism chosen is a correct one to describe an adsorption process. A survey of the literature indicates that the rate mechanism, which is identical for the vertical column or the radial disc, has been written in various other kinetic and diffusional forms Let us now consider each of these and note what effect they will have upon the final equation 23.

A, Kinetic Mechanism: (1) Second order–second order. Designated as K22.[14]

$$\frac{\partial n}{\partial t} = k_1c(n_0 - n) - k_2n(c_0 - c) \quad (24)$$

(2) Second order–first order. Designated as K21.[15]

[14] H. C. Thomas, *J. Am. Chem. Soc.*, **66**, 1664 (1944).

[15] H. C. Thomas, *Ann. New York Acad. Sci.*, **49**, 161 (1948).

$$\frac{\partial n}{\partial t} = k_1c(n_0 - n) - k_2n \qquad (25)$$

(3) Second order–first order. Designated as K20.[5]

$$\frac{\partial n}{\partial t} = k_1c(n_0 - n) \qquad (26)$$

(4) First order–first order. Designated as K11.[15]

$$\frac{\partial n}{\partial t} = k_1cn_0 - k_2c_0n = k_1'c - k_2'n \qquad (27)$$

B, Liquid Diffusion Mechanism: (1) First order–first order. Designated as L11.[16]

$$\frac{\partial n}{\partial t} = k_g(c - c^*) \qquad (28)$$

where k_g is the mass transfer coefficient and c^* is the concentration of solute in equilibrium with the adsorbed solute. Equation 28 can be written in another form which allows greater usage.[16]

$$\frac{\partial n}{\partial t} = \frac{3D_l}{a_0\Delta ab\rho}(bc - n) \qquad (29)$$

It has been assumed that the isotherm which describes the adsorption is a linear one

$$n = bc^* \qquad (30)$$

Further, if we call $\Delta a = \Delta a_{\text{ave.}}$, where $\Delta a_{\text{ave.}}$ = average film thickness in the disc, we may write

$$\Delta a = j\bar{v}^k \qquad (31)$$

j and k being constants such that $-0.5 < k < -0.7$.

Thus equation 29 may be written as

$$\frac{\partial n}{\partial t} = \frac{3D_l}{a_0b\rho j\bar{v}^k}(bc - n) \qquad (32)$$

C. Solid Diffusion Mechanism.—(1) First order–first order. Designated as D11.[17]

$$\frac{\partial n}{\partial t} = \frac{D_s}{(\gamma a_0)^2\rho b}(bc - n) \qquad (33)$$

where a linear isotherm has again been assumed.

It can be shown that if any of the above rate equations are used instead of the K21, equation 9 would have still resulted differing only in the value of the constants A, B and D. Table I gives a complete tabulation of these constants.

From Table I it can be seen that in some cases $B = 0$ while in others $B \neq 0$. This would seem to cause a divergence in the method of solution, but by a proper substitution, equation 9 may be reduced to a single form, namely, equation 11. To accomplish this, let

$$F = e^{-\left[Dz + A\left(\frac{y^2}{2} + yR\right)\right]}U'(y,z) \text{ for } B = 0$$

$$BF = \ln\left\{e^{-\left[Dz + A\left(\frac{y^2}{2} + yR\right)\right]}U(y,z)\right\} \text{ for } B \neq 0$$

Thus the method of solution of the problem is analogous no matter which rate equation is employed. As a consequence the final equation will be of the same form in each case differing only in the value of the constants A, B and D. Table II lists the final c/c_0 equations for each of the rate mechanisms obtained in the same way as equation 23.

TABLE I

TABULATION OF THE CONSTANTS A, B AND D FOR EQUATION 9

Rate mechanism	A	B	D
K22	$2\pi hk_1n_0/\bar{v}$	$k_1 - k_2/\bar{v}$	$k_2c_0/\bar{v}$
K21	$2\pi hk_1n_0/\bar{v}$	$k_1/\bar{v}$	$k_2/\bar{v}$
K20	$2\pi hk_1n_0/\bar{v}$	$k_1/\bar{v}$	0
K11	$2\pi hk_1n_0/\bar{v}$	0	$k_2c_0/\bar{v}$
L11	$\frac{6\pi hD_l}{a_0\rho j\bar{v}^{1+k}}$	0	$\frac{3D_l}{a_0\rho bj\bar{v}^{1+k}}$
D11	$\frac{2\pi hD_s}{(\gamma a_0)^2\bar{v}}$	0	$\frac{D_s}{(\gamma a_0)^2\bar{v}b}$

Application of Equations to Numerical Computations

As so frequently arises in a theoretical development, the application of the derived equations to numerical computation is a problem in itself. Considering the K11 case

$$c/c_0 = e^{-\left[Dz + A\left(\frac{y^2}{2} + yR\right)\right]}\left\{I_0\left(2\sqrt{ADz\left(\frac{y^2}{2} + yR\right)}\right) + \phi\left[Dz, A\left(\frac{y^2}{2} + yR\right)\right]\right\}$$

it is seen that to obtain a numerical value of c/c_0, the functions $I_0(2\sqrt{uv})$, $e^{-(u+v)}$ and $\phi(u,v)$ must be evaluated. While tables of the first two functions are readily available the same cannot be said for $\phi(u,v)$. Thus, the problem reduces itself to tabulating values of $\phi(u,v)$ over the complete u and v range to be used or to find some other function which will, in effect, accomplish the same result. Two other functions have been considered by the authors.

(1) Brinkley[18] has defined and tabulated the function

$$g(\sqrt{u}, \sqrt{v}) = e^{-(u+v)}\phi(u, v) \qquad (34)$$

(2) Hiester[19] has defined and tabulated the function

$$J(u, v) = 1 - e^{-(u+v)}\phi(v, u) \qquad (35)$$

The main advantage to the usage of the $J(u,v)$ function is that for the K11, L11 or D11 cases the value of c/c_0 reduces to a very simple form, $c/c_0 = J(u,v)$.

After a large number of preliminary calculations, it was decided to make use of the tabulated $J(u,v)$ function of Hiester in the present work. Thus, the equations given in Table II have been transformed to give Table III. Figure 1 is a plot of c/c_0 *vs.* $J(u,v)$ as taken from Hiester.[19]

Prediction of the Rate-determining Step

It is the interpretation of the constants A, B and D which enables a single rate mechanism to be differentiated from the other mechanisms. By consulting Table I, in conjunction with a series of experimental runs, a considerable amount of qualitative information may be obtained.

Consider the situation which occurs when the operating variable which is of interest during a series of experimental runs is the adsorbent particle diameter. The constants of the kinetic equa-

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[16] G. E. Boyd, A. W. Adamson and L. S. Myers, Jr., *J. Am. Chem. Soc.*, **69**, 2836 (1947).

[17] E. Glueckauf and J. I. Coates, *J. Chem. Soc.*, 1315 (1947).

[18] S. R. Brinkley, Jr., and R. F. Brinkley, personal communication.

[19] N. K. Hiester, Ph.D. Thesis, University of California, 1949.

TABLE II

FINAL EQUATIONS FOR EACH OF THE RATE MECHANISMS IN TERMS OF $\phi(u,v)$

Rate mechanism	c/c_0
K22	$\dfrac{\phi\left[Fz, G\left(\frac{y^2}{2}+yR\right)\right]+I_0\left(2\sqrt{ADz\left(\frac{y^2}{2}+yR\right)}\right)}{\phi\left[Fz, G\left(\frac{y^2}{2}+yR\right)\right]+\phi\left[A\left(\frac{y^2}{2}+yR\right), Dz\right]+I_0\left(2\sqrt{ADz\left(\frac{y^2}{2}+yR\right)}\right)}$ where $F = \dfrac{k_1c_0}{v}$ and $G = \dfrac{2\pi hn_0k_0}{v}$
K21	Same as K22, where $F = \dfrac{k_1c_0+k_2}{v}$ and $G = \dfrac{2\pi h}{v}\dfrac{k_1k_2n_0}{k_1c_0+k_2}$
K20	$\dfrac{e^{Fz}}{e^{Fz}+e^{A\left(\frac{y^2}{2}+yR\right)}-1}$, where $F = \dfrac{k_1n_0}{v}$
K11, L11, D11	$e^{-\left[Dz+A\left(\frac{y^2}{2}+yR\right)\right]}\left\{I_0\left(2\sqrt{ADz\left(\frac{y^2}{2}+yR\right)}\right)+\phi\left[Dz, A\left(\frac{y^2}{2}+yR\right)\right]\right\}$

TABLE III

FINAL EQUATIONS FOR EACH OF THE RATE MECHANISMS IN TERMS OF $J(u,v)$

Rate mechanism	c/c_0
K22	$\dfrac{J\left[Fz, G\left(\frac{y^2}{2}+yR\right)\right]}{\exp\left((D-F)z+(A-G)\left(\frac{y^2}{2}+yR\right)\right)1-J\left(Dz, A\left(\frac{y^2}{2}+yR\right)\right)+J\left[Fz, G\left(\frac{y^2}{2}+yR\right)\right]}$
K21	Same as K22
K20	$\dfrac{e^{Fz}}{e^{Fz}+e^{A\left(\frac{y^2}{2}+yR\right)}-1}$
K11, L11, D11	$J\left[Dz, A\left(\frac{y^2}{2}+yR\right)\right.$

tions are independent of the particle size while in contrast, the diffusion constants take into account the effect and magnitude of changing the particle size. Further, particle size has a linear effect in liquid diffusion and a square effect in solid diffusion. Thus, the particle size can be used to differentiate between all three types of mechanisms.

Another operating variable of importance is the flow rate. From Table I it can be seen that the constants of the K and D equations are affected by the flow rate to the first power while the L equations vary between the 0.3 to 0.5 power. The flow rate can thus serve to differentiate between liquid diffusion or solid diffusion and chemical kinetics.

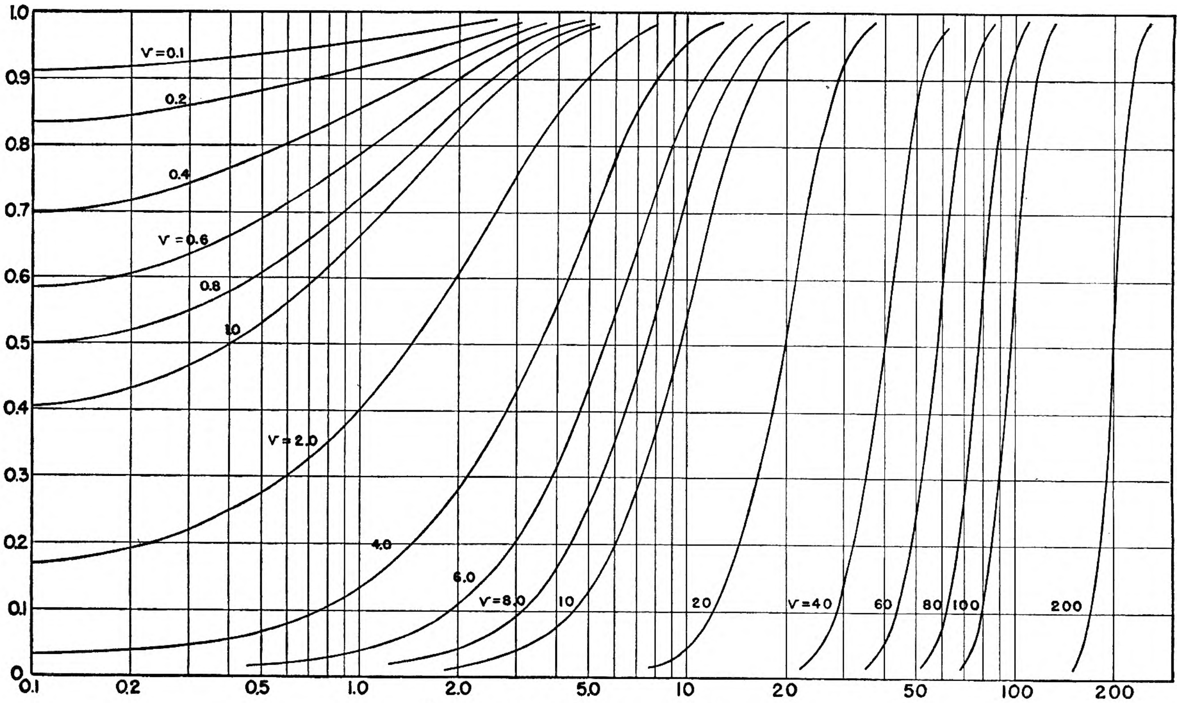

Fig. 1.—Plot of c/c_0 vs. $J(u,v)$.

The initial concentration, c_0, may be used for choosing between a chemical reaction and a diffusion mechanism as indicated by Table I.

One final criterion remains which may be used to differentiate between liquid or solid diffusion. This may be accomplished by means of the interrupted run. This procedure involves allowing an experimental run to proceed until the concentration history corresponds to the steepest portion of the c/c_0 *vs.* z curve. The flow of liquid is then stopped and the bed allowed to stand for a long period of time. The liquid flow is resumed and the remainder of the c/c_0 curve obtained. If solid diffusion controls the process, the diffusion will continue during the time interruption and a discontinuity will be observed in the c/c_0 *vs.* z plot. If liquid diffusion is controlling no discontinuity will be apparent.

Evaluation of the Equation Parameters

The procedure decided upon to calculate the constants A, B and D and to choose a rate mechanism, is as follows:

(1) Given an experimental set of c/c_0 *vs.* z curves they are surveyed and the effect of the particle size variation noted. If a large change in the shape of the curves is observed, the kinetic mechanisms are immediately discarded. If no effect is seen, the diffusional mechanisms are discarded. This first step is an essential one if the calculation time is to be held down to a reasonable value.

(2) The value of y will in all cases be known, it being merely a constant determined by the weight of adsorbent used. The weight of adsorbent added to the disc is

$$\pi h(r^2 - R^2) = 2\pi h\left(\frac{y^2}{2} + yR\right)$$

(3) Having decided on either a kinetic or diffusion mechanism, a trial and error method is used on each experimental curve to obtain values of A, B and D. This consists in choosing five c/c_0 *vs.* z points on a curve, assuming values of A (actually $A\left(\frac{y^2}{2} + yR\right)$) until the quantities B and D obtained are the same for each point.

(4) The constants $A\left(\frac{y^2}{2} + yR\right)$, B and D are then surveyed for variation in their absolute values and a rate mechanism decided upon.

(5) Various external means may be employed in an attempt to check the indicated mechanism. For the case where a kinetic mechanism is decided upon, the external method consists of determining a complete adsorption isotherm from which the constants k_1 and k_2 may be evaluated. These values are then compared with those obtained from the constants A, B and D. If a liquid diffusion mechanism is decided upon, k_g values can be calculated and the numerical consistency of these quantities checked with the constants A and D. If solid diffusion is indicated, the behavior of the interrupted runs can be used as a check.

Apparatus and Experimental Procedure

After considerable preliminary work three experimental systems were chosen: (1) KCl solution adsorbed on H^+-form Dowex 50. (2) $CuSO_4$ solution adsorbed on Al_2O_3. (3) HAc solution adsorbed on Al_2O_3.

The two adsorbents, Al_2O_3, granular adsorbent consisting essentially of aluminum trihydrate, and Dowex 50, a spherical ion-exchange resin possessing aromatic sulfonic acid exchange groups, were chosen after consideration of a variety of different adsorbents. Both were available in extensive size ranges.

In all experimental runs saturation of a column initially free of solute was employed.

The air-dried adsorbents were first screened two or three times through a set of U.S. Standard Screens to ensure an adequate grading of the samples. The large size Dowex particles were also rolled on an inclined plane to effectively separate the completely spherical particles from the broken ones.

The Dowex was converted to the H^+-form by contacting 50 g. of the resin with 3 l. of 5% H_2SO_4 solution in an agitated vessel for one hour. This was repeated twice more and the resin then filtered on a buchner funnel, washed with distilled water until the wash waters were neutral to methyl orange and no test for sulfate ions was obtained. This was followed by air-drying for 24 hours and storage in closely stoppered bottles. The Al_2O_3 was activated by heating for four hours at 200° and then stored in ground-glass stoppered bottles over P_2O_5.

The physical property of the Dowex particles which causes them to swell appreciably when first placed in water required that measurements be made of the effective sphere diameter of the swollen particles. A large number of particles, approximately 100, were allowed to swell in water and the diameters measured with a moving cathetometer. These values were averaged to give an effective diameter. The size of the Al_2O_3 particles was taken directly from the mesh size.

To obtain a constant flow rate, a constant head was maintained by means of a breaking-siphon arrangement in conjunction with calibrated capillaries placed at the point of outlet of effluent solution.

The main portion of the experimental equipment was the radial disc proper and all the other apparatus was built around it. The disc was machined from block lucite. Figures 2 and 3 illustrate the over-all setup.

The main body of the disc was used as the adsorbent holder and completely encircling the periphery of the adsorbent space was a series of holes through which the effluent solution flowed. The solution then passed through a very narrow passage, out of the disc by means of the center hole and finally passed through the capillary tubing. Resting in the center of the main body, in prepared grooves, was a very thin circular insert. This insert had a large number of holes drilled in its sides to allow passage of solution. The disc cover, containing the saturating solution inlet, rested on a shoulder of the main body and also had a circular groove in its face to allow the top part of the insert to fit snugly. The path of the saturating solution may be described as follows: from the constant head device through the disc cover and into the hollow insert, then out of the side holes of the insert, through the adsorbent, through the periphery holes and out of the disc body.

Very thin strips of filter paper were placed around the outside of the hollow insert and also inside of and against the periphery holes. This kept the adsorbent from passing through the holes. To ensure a uniform bed packing, 20 or 25 ml. of water was poured into the disc and then followed by the adsorbent. As the adsorbent was added a glass rod was used to stir and move the bed about in order to remove air bubbles and to level the bed.

Effluent samples were collected at certain designated intervals, analyzed for solute concentration and the concentration plotted *vs.* the volume of solution through the disc.

For both the K^+-H^+ exchange and the HAc–Al_2O_3 system, a pipetted volume of each effluent sample was titrated with standardized NaOH to yield the H^+ concentration. The K^+ content for the first system was evaluated by difference using the initial concentration c_0 as determined by a Mohr titration for Cl^-. In the case of $CuSO_4$ on Al_2O_3 the effluent samples were analyzed by using the intense blue color of the $Cu(NH_3)_4^{++}$ complex in conjunction with a Coleman Spectrophotometer set at 600 mμ.

The weight of adsorbent added was determined by using varied amounts of adsorbent until two runs using the same

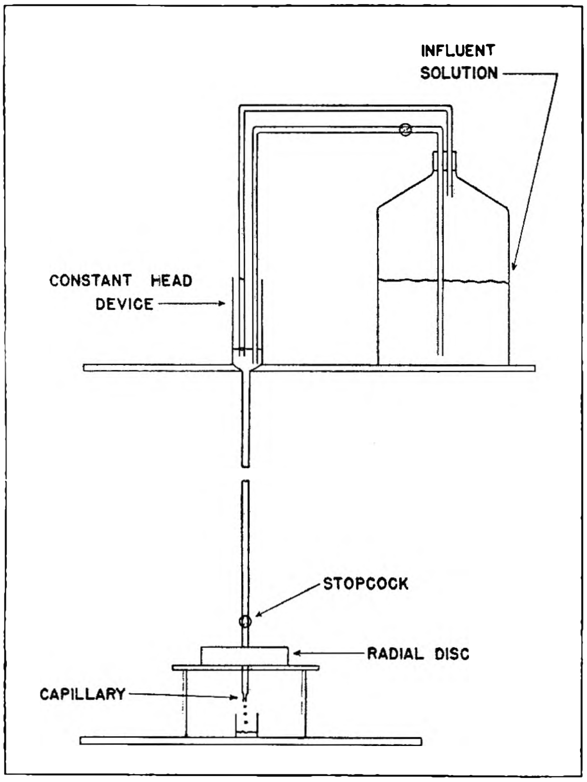

Fig. 2.—Schematic drawing of over-all apparatus.

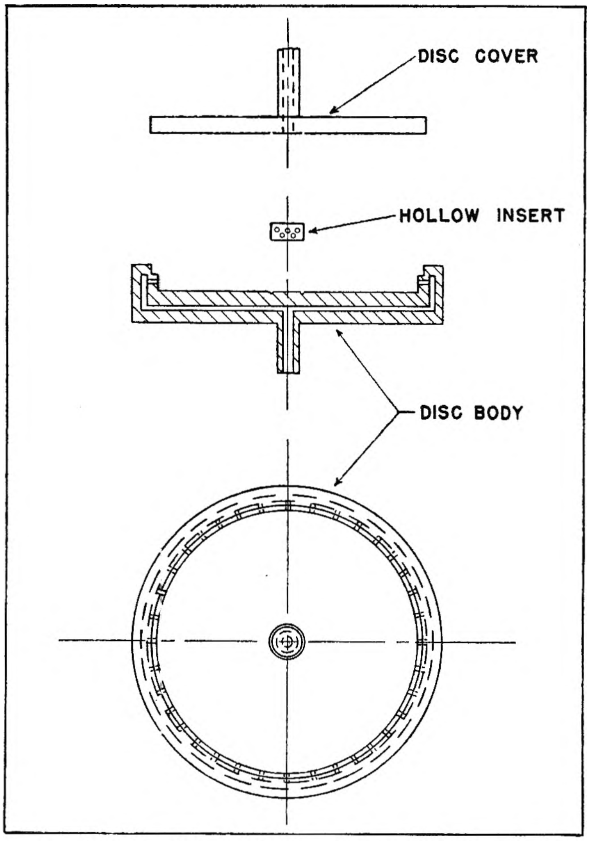

Fig. 3.—Schematic drawing of radial disc.

weight gave break-through volumes which checked within ±5% of each other.

In all cases the experimental runs were made at such times that the temperature did not vary over ±3%.

Once an actual experimental run was started there were two criteria which were used to determine if the results were to be regarded as of value. It was required that the flow rate remain constant throughout the complete run within ±2%, and also that the effluent solution must have completely wet the periphery of the disc. If either of these factors were not attained, the curves were not considered reliable for calculation.

The adsorption isotherms were obtained by standard methods. These consisted of mixing known amounts of solute and adsorbent, allowing the mixture to stand with occasional shaking and analyzing the supernatant liquid.

Results and Discussion

In order to place a severe test upon the equations, the experimental runs were carried out with a fourfold variation in flow rate, and a fivefold variation in particle size for each system; in addition a tenfold change in the initial concentration, c_0, for the Dowex 50 was employed. In all three systems, a decrease in flow rate or in particle size had the effect of causing the concentration history curves to become steeper. Changing the initial solute concentration, c_0, however, had very little effect.

Let us now consider in detail the results of first the K^+–H^+ exchange and then the HAc and $CuSO_4$ adsorption on Al_2O_3.

A. Exchange of K^+ on H^+ - form Dowex 50.—Consulting Figs. 4 and 5, which represent a part of the data obtained, it is evident that the particle size had a definite effect on the shape of the saturation curves. In addition the changes in the shape of the curves are quite small when compared to the variation in c_0 employed. These factors seem to rule out the chemical process as a major rate-determining step.

From the data obtained in calculating the isotherm of K^+ on Dowex 50 (not shown), calculations have been made for the equilibrium constant, K

$$K = \frac{c_{HS}c_{KR}}{c_{HR}c_{KS}}$$

where c_{HS} represents the H^+ concentration in the solution, c_{HR} in the resin, etc. The values obtained indicate that the exchange is a reversible one.

These considerations leave only the D11 and L11 mechanisms to be considered. To help differentiate between these two, an interrupted run was made at each concentration using the largest particle size, 20/30 mesh, and the highest flow rate, 21.5 ml./min. The choice of these operating variables was dictated by the desire to make the experimental conditions such that particle diffusion has the highest probability of occurrence. This would be at large particle diameters and high flow rates. The results are shown in Fig. 6, and no discontinuity is observed. This causes doubt that the D11 mechanism is the desired one.

However, this does not mean that we can say that the L11 case is the rate-determining one. Instead we must see if the data actually fit the theoretical equations derived for liquid diffusion. To do this the constants $A\left(\frac{y^2}{2} + yR\right)$ and D were calculated in the manner outlined previously for each experimental curve in the range $0.15 < c/c_0 <$

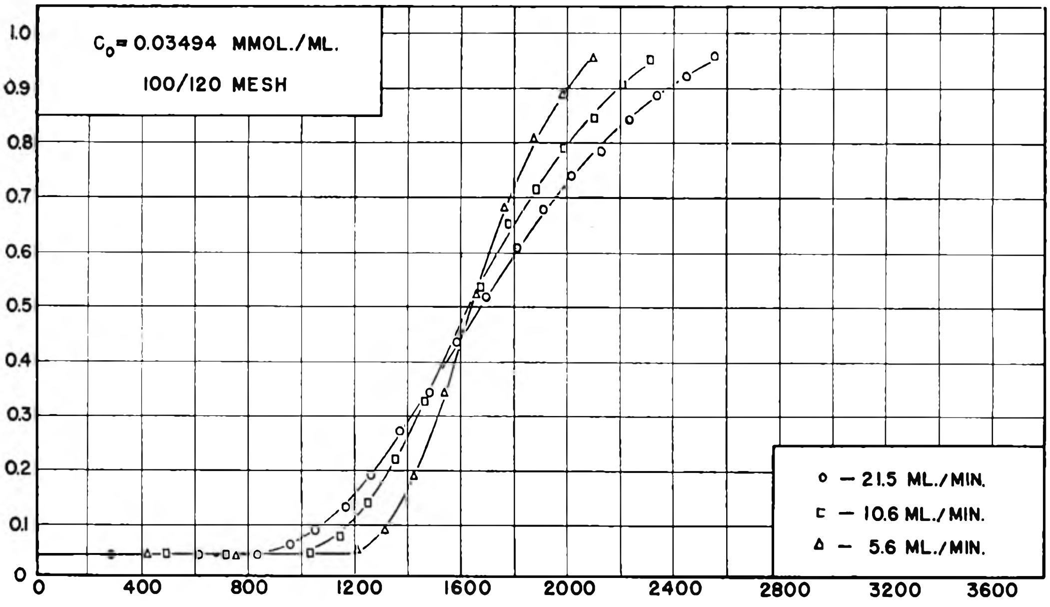

Fig. 4.—Saturation of H$^+$-form Dowex 50 with KCl solution.

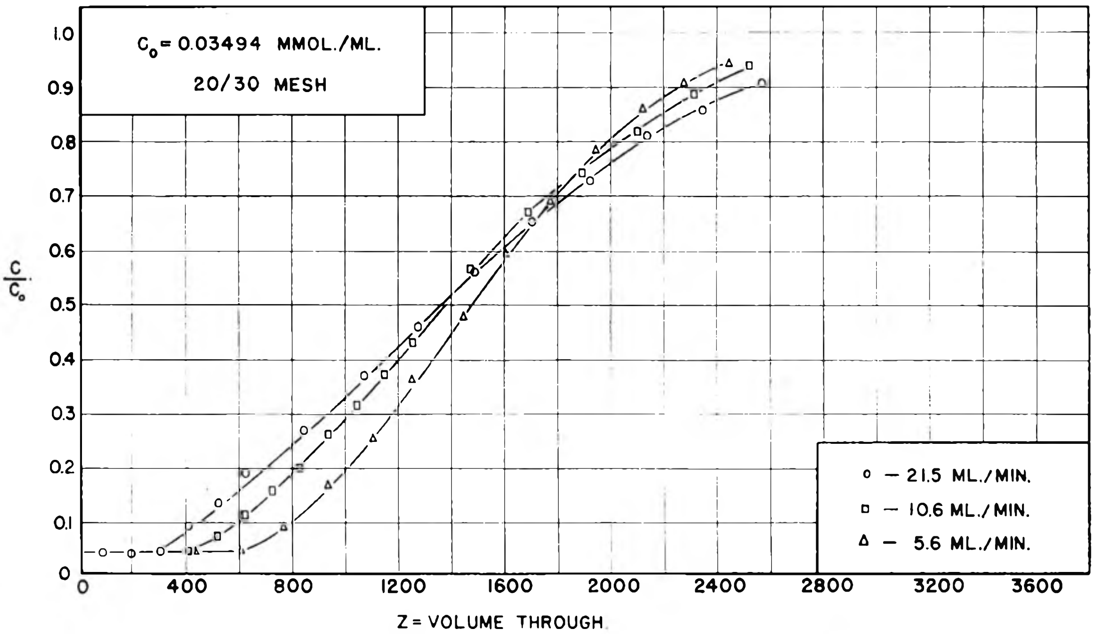

Fig. 5.—Saturation of H$^+$-form Dowex 50 with KCl solution.

0.90 and with the aid of the data given below, Table IV has been constructed.

a_0 (100/120 mesh) = 0.0081 cm.
a_0 (60/70 mesh) = 0.0137 cm.
a_0 (20/30 mesh) = 0.0421 cm.

$$\text{weight of resin used}\begin{cases}100/120 \text{ mesh} = 16.2 \text{ g.}\\ 60/70 \text{ mesh} = 16.0 \text{ g.}\\ 20/30 \text{ mesh} = 15.7 \text{ g.}\end{cases}$$

The constant k has been set equal to -0.60 because it yields the best correlation.

For $c_0 = 0.03494$ mmol./ml., the numerical constants $\frac{3D_l}{\rho j}$ and $\frac{3D_l}{\rho jb}$ in Table IX show average deviations of ±16%. The experimental and calculation deviation have been estimated as ±10%. Visual evidence has been observed to indicate to the authors that the 20/30 values are a little high. With this fact in mind, the results seem to be close to the desired range. As c_0 increases to 0.3738 mmol./ml. the per cent. deviation increases to very high values. This deviation could be caused by the non-linearity of the adsorption isotherm in this concentration range or perhaps by a changing of the rate determining mechanism.

Calculations were also made for the D11 mechanism but no correlation was found.

A liquid diffusion mechanism is thus indicated as the rate-determining step for $c_0 = 0.03494$ mmol./ml. An attempt to confirm this mechanism by means external to the disc operations themselves was also made. It can be shown that

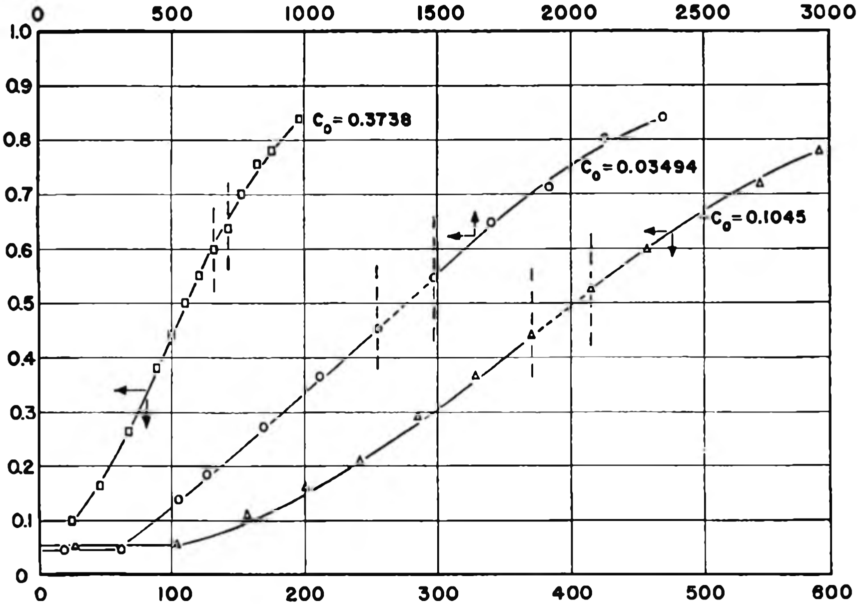

Fig. 6.—Interrupted runs for saturation of H$^+$-form Dowex 50 with KCl solution.

TABLE IV

NUMERICAL CORRELATIONS FOR SATURATION OF H$^+$-FORM DOWEX 50 WITH KCl SOLUTION

Mesh size	Flow rate, ml./min.	$v = A\left(\frac{y^2}{2} + yR\right)$	$\frac{3D_l}{\rho j} = \frac{v a_0 \bar{v}^{0.40}}{\pi h(r^2 - R^2)}$	D	$\frac{3D_l}{\rho j b} = \frac{D a_0 \bar{v}^{0.40}}{\pi h(r^2 - R}$
100/120[a]	21.5	25	0.0423	0.174	0.00483
100/120	10.6	34	.0427	.272	.00550
100/120	5.6	48	.0478	.372	.00600
60/70	21.5	14	.0422	.108	.00502
60/70	10.6	20	.0431	.159	.00545
60/70	5.6	28	.0467	.210	.00575
20/30	21.5	5	.0453	.0426	.00615
20/30	10.6	8	.0535	.0736	.00720
20/30	5.6	11	.0570	.0979	.00690
100/120[b]	21.5	24	.0406	.0532	.00148
100/120	10.6	38	.0477	.0784	.00158
100/120	5.6	52	.0518	.106	.00172
60/70	21.5	16	.0482	.035	.00175
60/70	10.6	24	.0520	.0522	.00180
60/70	5.6	35	.0582	.0724	.00198
20/30	21.5	7	.0640	.0164	.00236
20/30	10.6	12	.0800	.0250	.00251
20/30	5.6	16	.0720	.0340	.00270
100/120[c]	21.5	17	.0338	.00162	.000450
100/120	10.6	30	.0377	.00184	.000373
100/120	5.6	55	.0545	.00335	.000540
60/70	21.5	8	.0241	.00522	.000253
60/70	10.6	15	.0323	.000953	.000330
60/70	5.6	28	.0450	.00180	.000492
20/30	21.5	5	.0458	.00335	.000483
20/30	10.6	10	.0670	.000818	.000362
20/30	5.6	16	.0720	.00118	.00091

[a] c_0 = 0.03494 mmol./ml. [b] c_0 = 0.1045 mmol./ml. [c] c_0 = 0.3738 mmol./ml.

$$k_{g(\text{ave.})} = \frac{\int_R^{r_0} k_g(r)\mathrm{d}r}{r_0 - R} = \frac{v\bar{v}}{\pi h(r^2 - R^2)} \tag{36}$$

where $k_{g(\text{ave.})}$ represents an average k_g across the disc. Its value can be approximated for an experimental run by using the data of McCune and Wilhelm[20] to obtain pointwise k_g's and then taking a five point Gaussian distribution to obtain the average value. Looking at equation 36 it can be seen that the right-hand side is evaluated from experimental data obtained in this work wholly, while the left-hand side involves external data.

For the initial concentration under consideration,

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[20] L. K. McCune and R. H. Wilhelm, *Ind. Eng. Chem.*, **41**, 1124 (1949).

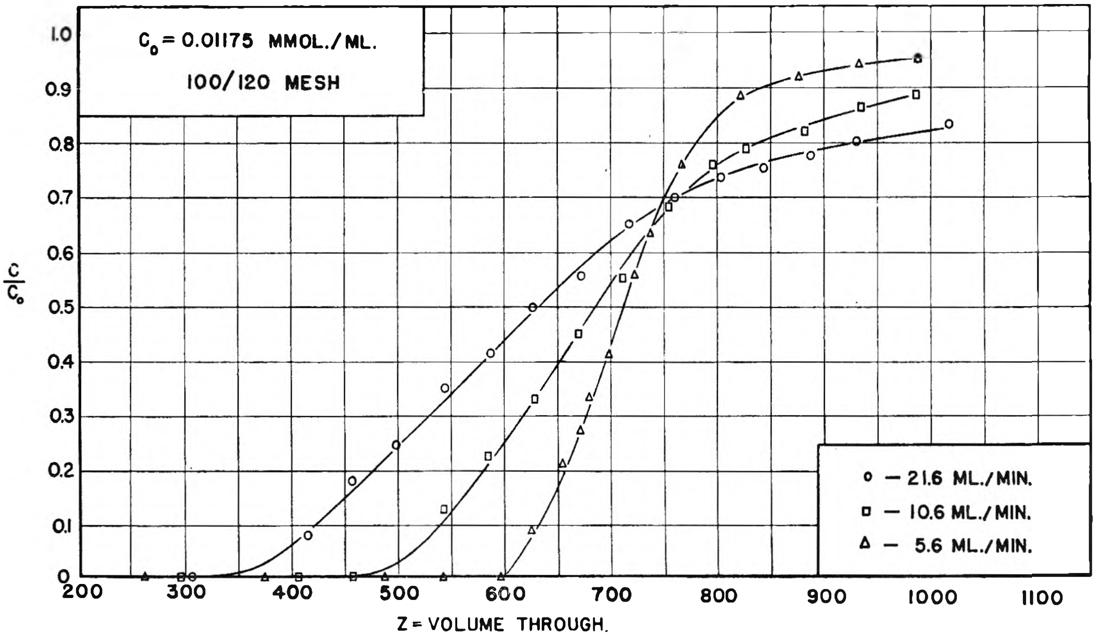

Fig. 7.—Saturation of Al_2O_3 with $CuSO_4$ solution.

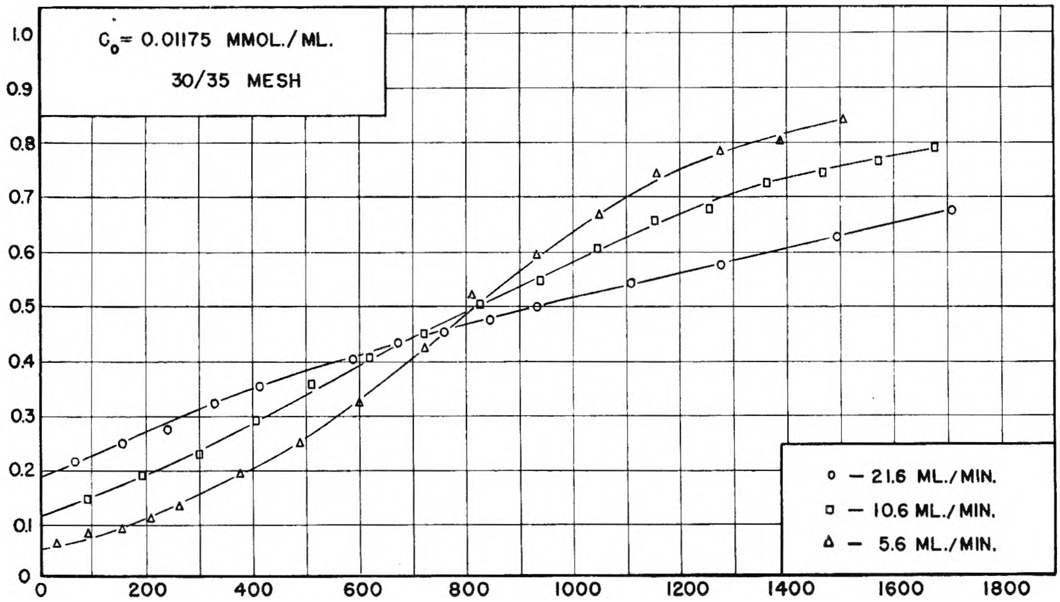

Fig. 8.—Saturation of Al_2O_3 with $CuSO_4$ solution.

both sides of equation 36 have been calculated. Some of the results are given below:

Particle size	Flow rate, ml./min.	$\frac{v\bar{v}}{\pi h(r^2 - R^2)}$	$k_{g(\text{ave.})}$
100/120 mesh	10.6	21.7	6.15
60/70 mesh	10.6	13.3	4.06
20/30 mesh	10.6	5.4	2.46

In each case the numerical values of $\frac{vv}{\pi h(r^2 - R^2)}$ and $k_{g(\text{ave.})}$ are approximately of the same magnitude. Considering the number of assumptions and external quantities used in calculating the values of $k_{g(\text{ave.})}$ this numerical similarity lends confirmation to the choice of liquid diffusion as rate-determining step for c_0 = 0.03494 mmol./ml.

B. Adsorption of $CuSO_4$ on Al_2O_3 and of HAc on Al_2O_3.—Using the same reasoning as before in conjunction with Figs. 7 and 8 and 9–10 the kinetic mechanism may be discarded. Figure 11 shows the results of an interrupted run in each system and a definite and distinct discontinuity is found. These discontinuities are of sufficient magnitude as to leave no doubt of their validity and thus indicate that a solid diffusion mechanism is controlling; at least in the range of c/c_0 where the interruptions were made.

The adsorption isotherms indicate that for the $CuSO_4$ concentration employed and for c_0 = 0.01976 mmol./ml. in the HAC system, the processes may be considered reversible ones following a linear isotherm. For c_0 = 0.04626 mol./ml. in the HAc

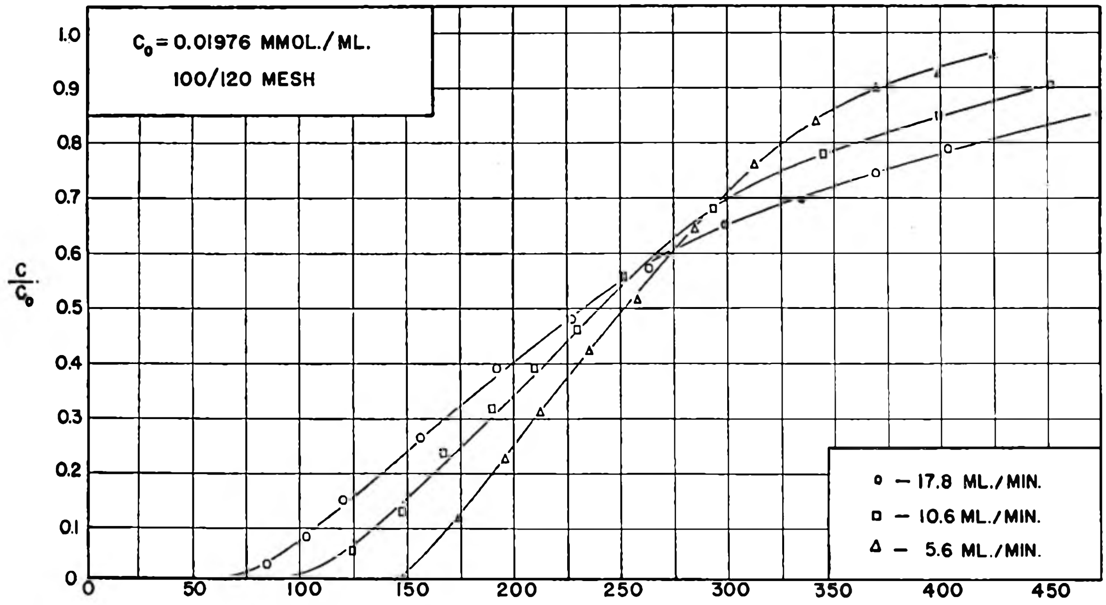

Fig. 9.—Saturation of Al_2O_3 with HAc solution.

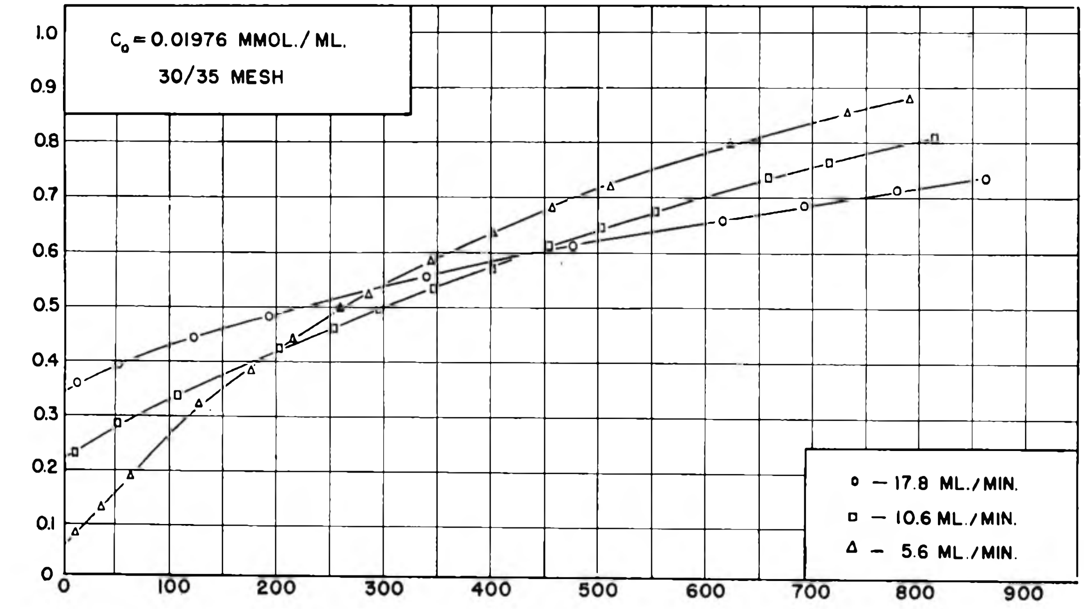

Fig. 10.—Saturation of Al_2O_3 with HAc solution.

system, the isotherm may no longer be considered linear. From these facts the most plausible mechanism is D11.

Using the equations for D11, and the data given below Tables V and VI have been constructed for the range, $0.05 < c/c_0 < 0.75$.

a_0 (100/120 mesh) = 0.00675 cm.
a_0 (50/60 mesh) = 0.0136 cm.
a_0 (30/35 mesh) = 0.0271 cm.

$$\text{weight of adsorbent used}\begin{cases}100/120 \text{ mesh} = 24.0 \text{ g.}\\ 50/60 \text{ mesh} = 23.4 \text{ g.}\\ 30/35 \text{ mesh} = 21.8 \text{ g.}\end{cases}$$

The deviation of values of the constant $\frac{D_s}{\gamma^2\rho}$ in Tables V and VI average approximately ±18% as compared to the ±10% experimental and calculation deviations. Liquid diffusion calculations are worthless. Thus the data can best be explained

TABLE V

NUMERICAL CORRELATIONS FOR SATURATION OF Al_2O_3 WITH $CuSO_4$ SOLUTION

Mesh size	Flow rate, ml./min.	$v = A\left(\frac{y^2}{2} + yR\right)$	$\frac{D_s}{\gamma^2\eta} = \frac{vv_0a^2}{\pi h(r^2 - R^2)}$
100/120	21.6	35	0.00141
100/120	10.6	70	.00139
100/120	5.6	130	.00136
50/60	21.6	8	.00136
50/60	10.6	20	.00167
50/60	5.6	35	.00159
30/35	21.6	2.7	.00191
30/35	10.6	4	.00140
30/35	5.6	8	00146

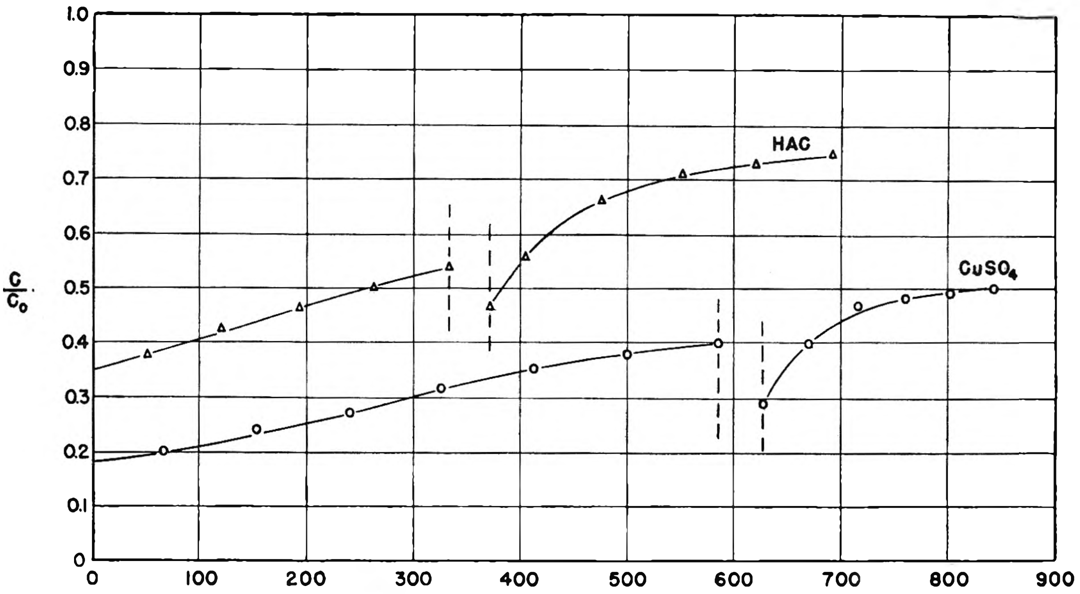

Fig. 11.—Interrupted runs for saturation of Al_2O_3 with $CuSO_4$ and HAc.

by the assumption that solid diffusion is the rate-determining step.

A further point to be considered in both $CuSO_4$ and HAc adsorption on Al_2O_3 is that the shape of the particles employed did not conform to the theoretical postulates. Instead of being spherical in shape as the Dowex 50 was, the Al_2O_3 particles were slabular. This causes two difficulties. First, the particle diameters used in the calculations were taken directly from the mesh size which does not represent the actual spherical diameter. However, it was felt that the mesh size would represent an average physical dimension (or equivalent diameter) of the particles and with the use of the shape factor could be applied in the calculations. Second, in the original derivation of the equations it was implicitly assumed that the fluid advanced uniformly through all the interstices of the bed. This will not be completely valid for non-spherical particles because of the irregular interstitial spacing. Neither of these difficulties are readily amenable to experimental testing so that they must tactfully be assumed not to cause any appreciable error.

TABLE VI

NUMERICAL CORRELATIONS FOR SATURATION OF Al_2O_3 WITH HAc SOLUTION

Mesh size	Flow rate, ml./min.	$v = A\left(\frac{y^2}{2} + yR\right)$	$\frac{D_s}{\gamma^2\rho} = \frac{\bar{v}c_0a^2}{\pi h(r^2 - R^2)}$
100/120[a]	17.8	8	0.000269
100/120	10.6	12	.000240
100/120	5.6	23	.000243
50/60	17.8	2	.000280
50/60	10.6	3.5	.000293
50/60	5.6	6	.000268
30/35	17.8	0.6	.000358
30/35	10.6	1.0	.000355
30/35	5.6	1.8	.000340
100/120[b]	17.8	6	.000202
100/120	10.6	10	.000211
100/120	5.6	21	.000222
50/60	17.8	2	.000280
50/60	10.6	3	.000250
50/60	5.6	6	.000268
30/35	17.8	0.7	.000417
30/35	10.6	1.2	.000440
30/35	5.6	1.8	.000340

[a] c_0 = 0.01976 mmol./ml. [b] c_0 = 0.04626 mmol./ml.

APPROXIMATE ADSORPTION ISOTHERMS FOR A MIXTURE OF TWO ISOTOPES[1]

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The Brunauer–Emmett–Teller (B.E.T.) theory[2] of multimolecular adsorption is generalized to include the case of a mixture of two isotopes, where the consideration of anomalous adsorption is necessary. An expression is obtained for the adsorption isotherm which is useful in the case of adsorption of helium isotopes. An expression for the concentration of isotopes in the film is deduced and the results are illustrated graphically for various values of the parameters.

I. Introduction

Terrell L. Hill[3] has given the general extension of the B.E.T. theory of multi-layer adsorption to mixtures of gases. In recent experiments on the adsorption of helium by Earl A. Long and Lothar Meyer,[4] it was observed that the first layer of the adsorbed atoms appears to pack in with anomalously high density. This led to a generalization[5] of the B.E.T. theory in which the packing parameter occurs as an arbitrary constant. In Hills' theory of adsorption of mixtures of two components, even without the first layer packing parameter, eight different energy parameters are needed to work out the model rigorously. In order to compare experimental data, it is desirable to reduce this number. This paper presents an approximate theory that succeeds in doing this. The resulting equations are applicable only to mixtures in which one component is present in very small proportions. This is, however, no problem in the case of helium isotopes where the concentration, He_3 in He_4, is usually extremely low.

As in the B.E.T. theory the energies of adsorption are assumed independent of the number of atoms in the first layer, thus neglecting horizontal interactions. The energies of adsorption of the second and higher layers are taken as equal to the heats of evaporation of the respective atoms from the bulk liquid of the same composition as the film at the saturation pressure. It is assumed that the energy of adsorption of one atom on any layer is independent of the type of atoms forming the site of adsorption; this is not too serious here because of the low concentration. Also it will be assumed that the total number of adsorbed atoms in the first layer (including both isotopes), when the gas mixture is at the saturated vapor pressure, is independent of the concentration of the mixture. Although the potential energy of adsorption can compress the second layer to a certain extent as well as the first layer, such a possibility is excluded in order to avoid mathematical difficulties. It is assumed that the packing parameter is nearly independent of the isotopic composition of the first layer. This assumption is again questionable except at weak mixtures of one isotope in the other. It is, however, very necessary to the mathematical argument, because the isotopic composition of the first layer varies slightly with the pressure, or with the thickness of the film, therefore unless the packing parameter were independent of this composition it would not be constant for any one isotherm. It is for this reason that the isotherm may be applied only to weak mixtures.

II. Theoretical

The classical number of complexions is made up of a number of terms: the first term is the number of possible arrangements of the atoms of the first layer within that layer times the number of arrangements of the atoms of the second layer on the sites formed by the first layer and so on

$$\left[\frac{B!}{(B-A_1)!}\,\frac{(\gamma A_1)!}{(\gamma A_1-A_2)!}\,\frac{A_2!}{(A_2-A_3)!}\cdots\frac{(A_{n-1})!}{(A_{n-1}-A_n)!}\right] \tag{1}$$

where

B = number of adsorbed atoms of both isotopes in the first layer when the gas mixture is at the saturated vapor pressure
$A_r = X_r + Y_r$ = total number of sites for $r + 1$st layer
X_r = atoms of the x-isotope adsorbed in the rth layer at a given pressure
Y_r = corresponding number of atoms of the y-isotope

We have stipulated that A_1 equals the number of atoms adsorbed in the first layer; due to the packing effect we have less than A_1 sites available to the atoms forming the second layer and consequently introduce a factor γ, such that γA_1 is the actual number of sites available to the second layer atoms.

The second term in the count involves the number of ways in which X_1 atoms may be originally assigned to the first layer, X_2 to the second layer and so on, an analogous expression existing for y-atoms. Let X = total x-atoms adsorbed; Y = total y-atoms adsorbed, then the second term is

$$\left[\frac{X!}{X_1!X_2!\cdots X_n!}\right]\cdot\left[\frac{Y!}{Y_1!Y_2!\cdots Y_n!}\right] \tag{2}$$

The third term in the count involves the number of ways of choosing X, total x-atoms adsorbed, and N_{xg}, number of x-atoms in the gas, from the total number of x-atoms, N_x. A similar choice is involved in the case of the y-atoms.

$$\left[\frac{N_x!}{N_{xg}!X!}\right]\left[\frac{N_y!}{N_{yg}!Y!}\right] \tag{3}$$

The last term in the count involves the number of ways in which the x-atoms may be placed in the energy states for the gas, with an analogous expression involving the y-atoms

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(1) This work was supported by funds from the Office of Naval Research.

(2) S. Brunauer, "The Adsorption of Gases and Vapors," Princeton University Press, Princeton, N. J., 1945.

(3) Terrell L. Hill, *J. Chem. Phys.*, **14**, 268 (1946).

(4) E. A. Long and L. Meyer, *Phys. Rev.*, **76**, 440 (1949).

(5) W. Band, *ibid.*, **76**, 441 (1949)

$$\left[N_{xg}!\,\frac{W_{xgj}{}^{n_{xgj}}}{n_{xgj}!}\right]\left[N_{yg}!\,\frac{W_{ygj}{}^{n_{ygj}}}{n_{ygj}!}\right] \qquad (4)$$

n_{xgj} = number of x-atoms in the j th quantum state in the gas; n_{ygj}, number of y-atoms

W_{xgj} = statistical weight of the jth state of the x-atoms in the gas; W_{ygj}, for the y-atoms

It is assumed that any adsorbed atom has only one quantum state. Taking the product of the terms (1) through (4), multiplying by $1/N_x!N_y!$ to correct the count for indistinguishability of the x- and y-type atoms when considered separately, and simplifying, the count assumes the form

$$\Omega = \left[\frac{B!}{(B-A_1)!}\,\frac{\gamma A_1!}{(\gamma A_1 - A_2)!}\,\frac{A_2!}{(A_2-A_3)!}\cdots\frac{A_{n-1}!}{(A_{n-1}-A_n)!}\right]$$
$$\left[\frac{1}{X_1!\cdots X_n!}\right]\left[\frac{1}{Y_1!\cdots Y_n!}\right]\left[\mathop{\pi}_{j}\frac{W_{xgj}{}^{n_{xgj}}}{n_{xgj}!}\,\mathop{\pi}_{j}\frac{W_{ygj}{}^{n_{ygj}}}{n_{ygj}!}\right]. \qquad (5)$$

The following restrictions must be imposed: Total numbers of x- and y-atoms are to remain constant separately

$$N_x = \sum_j n_{xgj} + \sum_r X_r;\quad N_y = \sum_j n_{ygj} + \sum_r Y_r \qquad (6), (7)$$

Total energy of the mixture is to remain constant

$$E = \sum_j \epsilon_{xgj}\, n_{xgj} + \sum_j \epsilon_{ygj}\, n_{ygj} - X_1\zeta_1 - Y_1\eta_1 - \sum_{r>1} X_r\zeta_L - \sum_{r>1} Y_r\eta_L \qquad (8)$$

where

ϵ_{xgj} and ϵ_{ygj} = energy of the x- and y-atom, respectively, in the gas in the j th quantum state

ζ_1 and η_1 = energy of adsorption of the x- and y-atoms, respectively, in the first layer

ζ_L and η_L = energy of adsorption of the x- and y-atoms, respectively, in the second and higher layers

Since the most probable distribution in energy is the one which has the maximum count, we maximize the count or number of complexions and introduce the undetermined Lagrangian multipliers, α_x and β, to take care of the conditions (6), (7), (8). Taking partial derivatives with respect to X and Y in the first, second and rth layers, these equations assume the general form

$$\frac{\partial}{\partial X_r}\left[\ln\Omega - \alpha_x N_x - \beta E\right] = 0 \qquad (9)$$

Analogous expressions exist involving Y, these will be omitted throughout, until needed later.

Using the Sterling approximation, $\ln N! = N \ln N - N$, and performing the differentiation we obtain

$$\frac{\gamma A_1{}^{\gamma}(B-A_1)}{(\gamma A_1 - A_2)^{\gamma} X_1} = e^{\alpha_x}e^{-\beta\zeta_1} \qquad (10)$$

$$\frac{A_2(\gamma A_1 - A_2)}{(A_2 - A_3)X_2} = e^{\alpha_x}e^{-\beta\zeta_L} \qquad (11)$$

$$\frac{A_r(A_{r-1} - A_r)}{(A_r - A_{r+1})X_r} = e^{\alpha_x}e^{-\beta\zeta_L} \qquad (12)$$

We may now obtain expressions for A_1, total atoms adsorbed in the first layer, by adding X_1 from (10) and Y_1 from the analogous equation involving Y_1; similarly for A_2 and A_r

$$A_1 = \frac{\gamma A_1{}^{\gamma}(B-A_1)}{(\gamma A_1 - A_2)^{\gamma}}\, e^{-\alpha_x + \beta\zeta_1} + e^{-\alpha_y + \beta\eta_1} \qquad (13)$$

$$A_2 = \frac{A_2(\gamma A_1 - A_2)}{(A_2 - A_3)}\, e^{-\alpha_x + \beta\zeta_L} + e^{-\alpha_y + \beta\eta_L} \qquad (14)$$

$$A_r = \frac{A_r(A_{r-1} - A_r)}{(A_r - A_{r+1})}\, e^{-\alpha_x + \beta\zeta_L} + e^{-\alpha_y + \beta\eta_L} \qquad (15)$$

Defining

$$x = e^{-\alpha_x + \beta\zeta_L};\quad y = e^{-\alpha_y + \beta\eta_L} \qquad (16)$$

$$c_1 = e^{\beta(\zeta_1 - \zeta_L)};\quad c_2 = e^{\beta(\eta_1 - \eta_L)} \qquad (17)$$

$$z_1 = c_1x + c_2y \qquad (18)$$

(13) becomes

$$(\gamma A_1 - A_2)^{\gamma} = z_1\gamma^{\gamma}A_1{}^{\gamma-1}(B - A_1) \qquad (19)$$

(14) and (15) become through the use of these definitions

$$(A_2 - A_3) = z(\gamma A_1 - A_2) \qquad (20)$$

$$z = \frac{(A_r - A_{r+1})}{(A_{r-1} - A_r)};\qquad r = 3, 4\ldots \qquad (21)$$

The final expression for the adsorption isotherm is obtained by mathematical manipulation of the equations (19), (20) and (21). Multiply all equations of the form (21) together from $r = 3$ to $r = m - 1$

$$z^{m-3} = \frac{(A_{m-1} - A_m)}{(A_2 - A_3)} \qquad (22)$$

Combine equations (22) and (20)

$$(A_{m-1} - A_m) = z(\gamma A_1 - A_2)z^{m-3} \qquad m \geqslant 3 \qquad (23)$$

Add all equations like (23) from $m = 3$ to $m = n$

$$(A_2 - A_n) = (\gamma A_1 - A_2)z\sum_{k=0}^{n-3} z^k \qquad (24)$$

Add all equations of the form (23) cumulatively in the following manner

$(A_2 - A_3) + 2(A_3 - A_4) + \cdots + (n-2)\,(A_{n-1} - A_n)$:

$$A - A_1 - (n-1)A_n = (\gamma A_1 - A_2)z\sum_{k=1}^{n-2} kz^{k-1} \qquad (25)$$

Solve (20) for A_2

$$-A_2 = z_1{}^{1/\gamma}\,\gamma A_1{}^{(1-1/\gamma)}(B - A_1)^{1/\gamma} - \gamma A_1 \qquad (26)$$

Put this into (24)

$$(\gamma A_1 - A_n) = \gamma(B - A_1)^{1/\gamma}z_1{}^{1/\gamma}A_1{}^{(1-1/\gamma)}\left[1 + z\sum_{k=0}^{n-3} z^k\right] \qquad (27)$$

Put (26) into (24)

$$A - A_1 - (n-1)A_n = \gamma(B - A_1)^{1/\gamma}z_1{}^{1/\gamma}A_1{}^{(1-1/\gamma)}\, z\sum_{k=0}^{n-3} kz^{k-1} \qquad (28)$$

Take the ratio of (27) and (28)

$$\frac{\gamma A_1}{(A - A_1)} = \frac{1 + z\sum\limits_{k=0}^{n-2} z^k}{z\sum\limits_{k=1}^{n-1} kz^{k-1}} = \frac{1 + z\left\{\dfrac{1}{1-z}\right\}}{z\left\{\dfrac{1}{(1-z)^2}\right\}} \qquad (29)$$

Simplify and solve for A_1

$$A_1 = \frac{A(1-z)}{\gamma z + (1-z)} \qquad (30)$$

Add equations (24) and (25) and neglect terms involving A_n (at some finite value of n, A_n will go to zero since there are a given finite number of atoms in the film)

$$A = (B - A_1)^{1/\gamma}z_1{}^{1/\gamma}A_1{}^{(1-1/\gamma)}\left[1 + \frac{z}{(1-z)} + \frac{z}{(1-z)^2}\right] \qquad (31)$$

Raise (31) to the power γ, separate the $(B - A_1)$

term and divide through by the term in square brackets to the γ power

$$\frac{A^{\gamma}}{\left\{\frac{\gamma z + (1 - z)}{(1 - z)^2}\right\}^{\gamma}} + A_1{}^{\gamma} z_1 = Bz_1 A_1{}^{\gamma - 1} \tag{32}$$

Substitute the value of A_1 from (30) into (32):

$$A\left[\frac{1}{\left\{\frac{\gamma z + (1 - z)}{(1 - z)^2}\right\}^{\gamma}} + \left\{\frac{(1 - z)}{\gamma z + (1 - z)}\right\}^{\gamma} z_1\right] = Bz_1\left[\frac{(1 - z)}{\gamma z + (1 - z)}\right]^{\gamma - 1} \tag{33}$$

Multiply through by $\left[\frac{\gamma z + (1 - z)}{(1 - z)}\right]^{\gamma}$ we obtain the final adsorption isotherm

$$\frac{Bz_1}{A\,(1 - z)} = \frac{z_1 + (1 - z)^{\gamma}}{1 - z(1 - \gamma)} \tag{34}$$

II. Physical Significance of x, y and z

In order to attach physical significance to the terms x and y and therefore to z and z_1, terms which appear in the adsorption isotherm, we turn to the use of that portion of equation (5) depending on the gas. Use is made of the following equation analogous to (9)

$$\frac{\partial}{\partial n_{xgj}}\,[\ln\Omega - \alpha N_{xg} - \beta E_{xg}] = 0 \tag{35}$$

The solution is

$$N_{xg} = \sum_{j} n_{xgj} = e^{-\alpha x} Q_{xg} \tag{36}$$

where

$$Q_{xg} = \sum_{j} W_{xgj} e^{-\epsilon_{xgj}/kT}$$

Substitute in (36) for Q_{xg}, the partition function for the perfect gas, one obtains

$$N_{xg} = e^{-\gamma_x} V_x(2\pi m_x kT/h^2)^{3/2} \tag{37}$$

where V_x and m_x are, respectively, the volume and mass of the x-atoms. Substitute (37) into the ideal gas law: $P_x V_x = N_{xg}kT$ to derive

$$e^{-\alpha x} = P_x(kT)^{-5/2}(2\pi m_x/h^2)^{-3/2} \tag{38}$$

Substitute this in (16)

$$x = P_x(kT)^{-5/2}(2\pi m_x/h^2)^{-3/2} e^{\zeta L/kT} \tag{39}$$

where $\beta = 1/kT$. If y were equal to zero and one had only the x-atoms to consider, it is easily seen from (34) that as x approached unity, the ratio A/B would approach infinity. This would correspond to the saturation pressure, therefore we may write (39) as

$$x = 1 = P_{x\,\text{sat}}(kT)^{-5/2}(2\pi m_x/h^2)^{-3/2} e^{\zeta L/kT} \tag{40}$$

Taking the ratio of equations (39) and (40)

$$x = \frac{P_x}{P_{x\,\text{sat}}};\ \text{and similarly } y = \frac{P_y}{P_{y\,\text{sat}}} \tag{41}$$

where the saturation pressure of either isotope is to be measured in the absence of the other isotope.

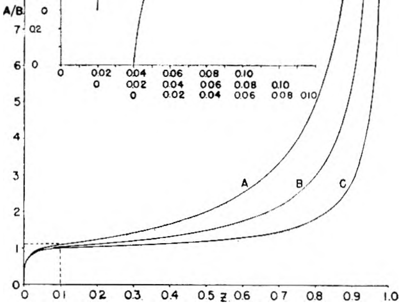

Fig. 1.—Total adsorption in the first layer *vs.* sum of the partial pressure ratios: curve A, $y/x = 0.01$, $c_2/c_1 = 2.5$, $c_1 = 300$, $\gamma = 1.0$; curve B, $\gamma = 0.5$; curve C, $\gamma = 0.2$; curves 1, $c_1 = 300$; curves 2, $c_1 = 200$; curves 3, $c_1 = 100$; curves a, $\gamma = 1.0$; curves b, $\gamma = 0.5$; curves c, $\gamma = 0.2$.

III. Results

The adsorption isotherm is illustrated in Fig. 1. The expression for A/B is obtained from the adsorption isotherm (34) by simple mathematical manipulation and is valid for all values of z

$$A/B = \frac{\{1 - z(1 - \gamma)\}\,\{c_1 z/(1 + y/x)\}\,(1 + c_2 y/c_1 x)}{(1 - z)[\{c_1 z/(1 + y/x)\}\,(1 + c_2 y/c_1 x) + (1 - z)^{\gamma}]} \tag{42}$$

z is the sum of the ratios of the partial pressures of the x- and y-isotopes to their respective saturated vapor pressures, while A/B expresses the ratio of the total number of adsorbed atoms, x- and y-isotopes, to the number of sites in the first layer. The curves within the inset represent enlargements of portions of the isotherms lying below $z = 0.1$. The parameters have been defined above, see equation (16), and are given various possible values as noted in Fig. 1. The curves A, B and C are effectively dependent only upon γ, the packing parameter, while the inset curves 1, 2 and 3 are dependent also upon c_1. From equation (17), the greater the difference between heats of adsorption of the x-isotope in the first and subsequent layers, the greater the adsorption at low pressures. Also within each group of curves of constant c_1 the ratio A/B is seen to increase with an increase in the packing parameter from curve c, $\gamma = 0.2$ to curve a, $\gamma = 1.0$, since B is five times as great in the former as in the latter case.

Long and Meyer[4] find that in the neighborhood of the lambda-temperature the saturation number of atoms in the first layer is about four times that expected from the liquid density. We would therefore expect the curve C, corresponding to a packing parameter of 0.2 to approximately predict the adsorption of helium isotopes, at least in the lower pressure region where the B.E.T. approximation is in good agreement with experiment for the adsorption of single components. Apparently no data have been published as yet on the adsorption of helium isotopes. Even though the theoretical isotherms are restricted to low concentrations, as in the case of mixtures of He_3 and He_4, an interesting comparison can be made between curve A, where anomalous packing is absent ($\gamma = 1$), and the adsorption of mixtures of oxygen and nitrogen as reported by J. R. Arnold,[6] at several concentrations. Comparison is made on the assumption that we may ascertain from the experimental isotherm the approximate point on the curve corresponding to the completion of the first layer.[2] Arnold compares the adsorption of a mixture of 50.2% oxygen and 49.8% nitrogen with the extended B.E.T. theory developed by Hill[3] and finds that between $z = 0.05$ and $z = 0.30$ the observed and calculated isotherms run parallel, above $z = 0.30$ the predicted isotherm diverges increasingly toward increased adsorption. Comparison here is made between curve A and the experimental isotherm (Fig. 2). The agreement here seems to run as high as 0.40 for z. Comparison is also made with a mixture of 85.1% nitrogen and 14.9% oxygen where excellent agreement is observed to a pressure corresponding to $z = 0.55$. There apparently are no experimental data for concentrations lower than this, but the trend would indicate an increase in agreement with the theory with decreased concentration. Again for pressures above 0.40 for the higher concentration and above 0.55 for the lower concentration the theory predicts greater adsorption than is actually observed.

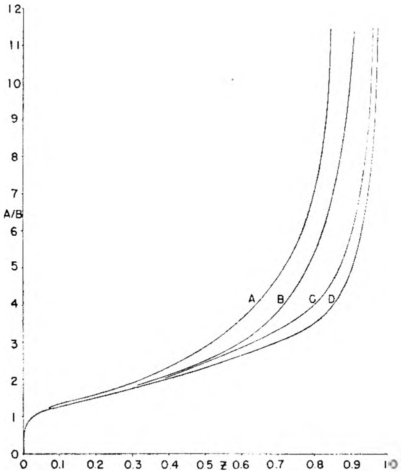

Fig. 2.—Curve A, old B.E.T. isotherm; curve B, new B.E.T. isotherm, corresponds to curve A of Fig. 1; curve C, experimental isotherm, 85.1% nitrogen, 14.9% oxygen; curve D, experimental isotherm, 49.8% nitrogen, 50.2% oxygen.

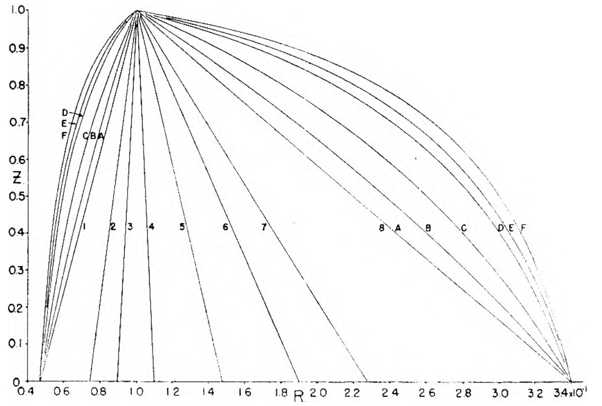

Fig. 3.—Relative isotope adsorption R vs. sum of the partial pressure ratios z; $y/x = 0.1$.

Curves	c_2/c_1	γ	Curves	c_2/c_1	γ
1 A	0.50	1.0	5	1.5	1.0
B	.50	0.75	6	2.0	1.0
C	.50	.50	7	2.5	1.0
D	.50	.30	8 A	5.0	1.0
E	.50	.25	B	5.0	0.75
F	.50	.20	C	5.0	.50
2	.75	1.0	D	5.0	.30
3	.90	1.0	E	5.0	.25
4	1.10	1.0	F	5.0	.20

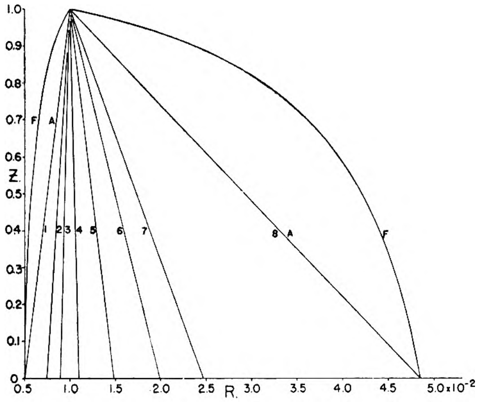

Fig. 4.—$y/x = 0.01$.

The theory also yields an expression giving the concentration of the isotopes in the film. Remembering that the total number of adsorbed atoms A, is equal to $X + Y$, sum of the x- and y-isotopes adsorbed, again by mathematical manipulation of (34) we may obtain an expression for the ratio Y/X, the concentration in the film

$$Y/X = R = (y/x)\left\{1 + (c_2/c_1 - 1)\frac{(1 - z)(1 + y/x - c_2y/c_1x)}{1 - (1 - \gamma)z}\right\} \quad (43)$$

This is plotted against z in Figs. 3 through 6. All parameters in these four figures are identical except for the variations in the concentrations of the isotopes in the gas, y/x, values of which are small since the isotherm is only valid in the case of weak mixtures. Curves 1 through 8 give the concentration in the film as a function of the pressure for the various values of the ratio c_2/c_1, which is related to the heats of adsorption as previously seen. For each value of c_2/c_1 the concentration in the film varies with the packing parameter as illustrated in curves A through F, associated for convenience only with curves 1 and 8. It is seen that all the curves converge at the saturation pressure to the value of the concentration in the gas. The curves of varying packing parameter with constant c_2/c_1 converge at zero pressure to the value of the concentration shown by the straight lines, where $\gamma = 1$. The curves 1, 2 and 3 have negative slopes since the values of c_2/c_1 are less than unity and from equation (43) the concentration in the film is less than the concentration in the gas. It is obvious that for c_2/c_1 less than unity, the concentration in the film decreases from A to F, that is from larger to smaller values of the packing parameter. For c_2/c_1 greater than unity a decrease in the packing parameter from $\gamma = 1.0$ to $\gamma = 0.2$ yields an increase in the concentration in the film as illustrated in curves 8A through 8F at any constant pressure excluding the two points

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(6) J. R. Arnold, *J. Am. Chem. Soc.*, **71**, 104 (1949).

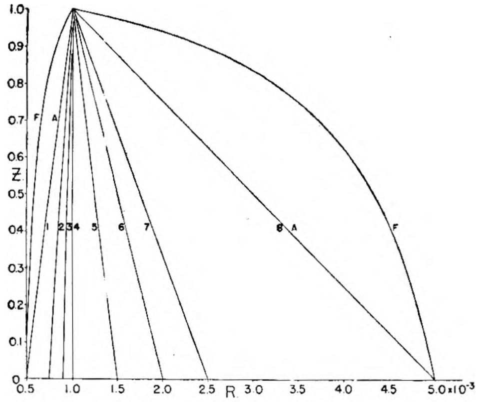

Fig. 5.—$y/x = 0.001$.

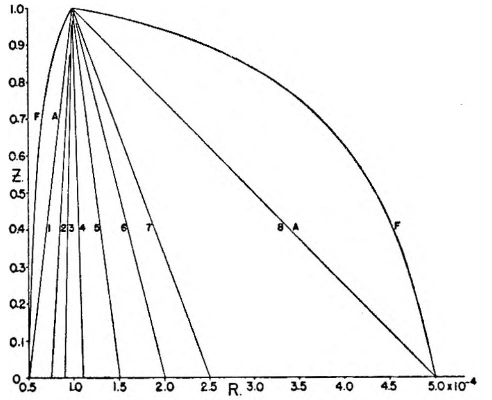

Fig. 6.—$y/x = 0.0001$.

of convergence at zero and saturation pressures. Here again there seems to be no experimental data for comparison with the theory. Such data would, through equation (43), yield an additional check on the values of the parameters c_2/c_1 and γ derived from the observed isotherms.

THE EFFECT OF HEAT TREATMENT ON THE SURFACE PROPERTIES OF GIBBSITE. PART III. THE CHEMICAL NATURE OF THE PRODUCTS FORMED

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Samples of gibbsite have been heated for five hours at a succession of fixed temperatures, and the product examined by X-rays and by measurements of volatile matter, specific gravity and bulk density. Results show that from *ca.* 300 to *ca.* 500° the product is a mixture of boehmite and γ-alumina, from *ca.* 500 to 1000° is γ-alumina of crystallite size progressively diminishing as temperature rises, and at 1200° is corundum.

The present paper reports another part of a systematic examination of the active material obtained by heating gibbsite under controlled conditions. Parts I and II deal[1,2] with the effects of the temperature of pretreatment on the adsorption isotherms of nitrogen and of oxygen at −182.7°, and of carbon tetrachloride at 25°. The present part is concerned mainly with the chemical nature of the active products. For this purpose, measurements have been made of the volatile matter, specific gravity in carbon tetrachloride and bulk density, and also a few X-ray photographs have been taken.

It is already known with some certainty that the substances formed during the thermal decomposition of gibbsite are boehmite, γ-alumina and corundum (α-Al_2O_3) according to the temperature. This is confirmed by new evidence, mainly from density determinations, in the present study.

Experimental

The different experimental methods will be dealt with in turn along with the results they have yielded. The synthetic gibbsite, constituting starting material, was taken from the two batches of pure Bayer Hydrate already described.

(1) The Thermal Balance and Preparation of Samples.—This simple device, already described by several workers[2,3,4] consists in directly weighing a substance in a vertical electric furnace by means of an analytical balance mounted overhead. In this way the changes in weight occurring when a solid disengages a gaseous product on heating may be followed very easily. In the present study a preliminary experiment was carried out (on 4.500 g. of Bayer Hydrate) with a steadily rising temperature. Comparison of the curve of weight against time with that of furnace temperature against time showed that the rate of loss of weight was almost negligible until 290° was reached, and then became very rapid. A further set of preliminary experiments at constant temperature was now carried out: the furnace had been raised to a definite temperature before inserting the sample and it was kept there (±5° or better) during the whole experiment. It was thus found that at 425° and higher temperatures the rate of loss became very small (though not zero) after 4–5 hours; a standard time of 5 hours was accordingly adopted in the preparation of samples used for the present work and also for the adsorption experiments described in Parts I and II. It is recognized that equilibrium was not reached in this time—for this may take periods of several weeks or more (15)—but the object of the present study was to prepare not equilibrium samples (which would almost certainly be badly sintered) but an active product, obtained by a standard and reproducible heat treatment.

Samples to be used in the following experiments were prepared at temperatures over the range 200 to 1300° at intervals of approximately 100° and sometimes less. Immediately on removal from the furnace each sample was divided into several portions, which were sealed up in small glass bulbs until ready for examination. (Most experiments were carried out within a day of preparation.) Portions of these same samples were used for the adsorption experiments of Parts I and II.[1,2]

(2) Volatile Matter.—The small bulb containing the sample was broken at the neck and the contents quickly transferred to a weighed alundum crucible, the whole

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(1) Gregg and Sing, Part I, THIS JOURNAL, **55**, 592 (1951).

(2) Gregg and Sing, Part II, *ibid.*, **55**, 597 (1951).

(3) Dubois, *Bull. soc. chim.*, [v] **3**, 1178 (1936).

(4) Gregg and Winsor, *Analyst*, **70**, 336 (1945).

weighed and then ignited at 1250° in a horizontal electric furnace; it was finally weighed after cooling in a desiccator.

Since all samples prepared below 1100° are hygroscopic, it is very difficult to avoid some adsorption of water vapor whilst transferring and weighing the sample. Again, samples prepared below 400° on ignition at 1250° are liable to evolve water so rapidly that some spurting and loss of solid material is likely to occur. From these two causes therefore, values for volatile matter are liable to be too high. It seems reasonable to suppose that the volatile matter is almost entirely water, since unheated samples gave 34·80% loss on ignition (theoretical for $Al_2O_3 \cdot 3H_2O$ is 34·65%).

The results obtained with both batches of gibbsite are represented in Fig. 1 as the plot of percentage volatile matter against temperature of preparation. The two batches give independent curves, although both curves have the same general form: one sudden fall in the volatile matter at *ca.* 300° and another at *ca.* 500°. There is clearly no arrest corresponding to either $Al_2O_3 \cdot H_2O$ or $Al_2O_3 \cdot 2H_2O$.

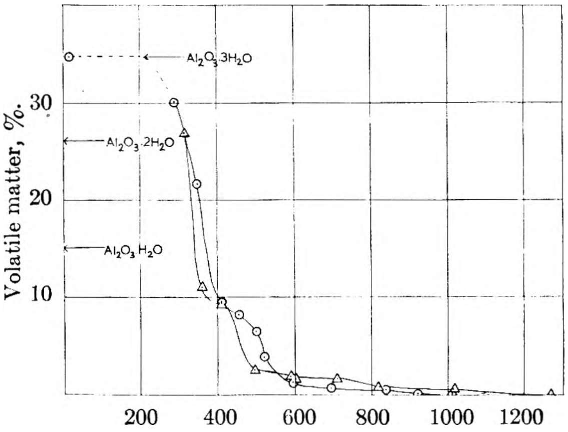

Fig. 1.—Volatile matter content (water content) of the product of heating Bayer Hydrate to different temperatures for 5 hours: ⊙, batch I of Bayer Hydrate; △, batch II of Bayer Hydrate.

(3) Specific Gravity in Carbon Tetrachloride.—For these determinations a technique similar to that described by Culbertson and Dunbar[5] was used. A small soda glass bulb containing 1–2 g. of the sample was evacuated for about one hour whilst heating to 200°. The stem of the bulb was sealed off under vacuum leaving about 3–4 cm. length, and the bulb was weighed in air (M_1 g.). After a small file mark had been made on the stem, the tip was broken off cleanly under pure carbon tetrachloride (previously boiled to expel air) using a special breaking device. The bulb was then left in carbon tetrachloride until the weight became constant (M_2 g.); 18 hours were found to be sufficient. It was then emptied, rinsed with dilute acid and water, dried and reweighed together with the tip in air (M_3 g.), and finally weighed without the tip in carbon tetrachloride (M_4 g.). All weighings were made with the bulb held in a platinum sling, suspended from the arm of an analytical balance.

The specific gravity, ρ, of the solid is then given by[6]

$$\rho = \frac{(M_1 - M_3)\,\rho_{CCl_4}}{(M_1 + M_4) - (M_2 + M_3)}$$

(ρ_{CCl_4} is the specific gravity of carbon tetrachloride[7] at the experimental temperature).

It was sometimes noted that a small bubble was present on breaking the bulb under carbon tetrachloride, no matter how long or how well the evacuation had been carried out. (It is suspected that gases came from the glass on heating.) This had little effect on the result, however, and 1% agreement was easily obtained. The accuracy of the method was later[8] checked by using NaCl as an inert reference substance. This gave values of 2.163 and 2.166, compared with the accepted value of 2.17.

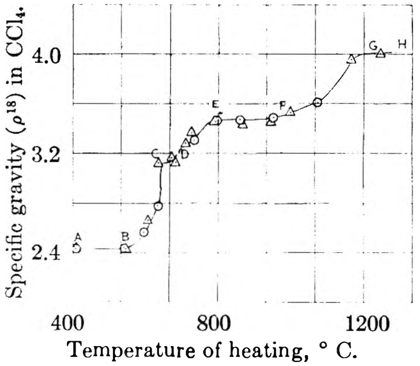

Fig. 2.—Specific gravity of the product of heating Bayer Hydrate to different temperatures for 5 hours.

Figure 2 shows the plot of specific gravity in carbon tetrachloride *versus* the temperature of preparation for samples taken from both batches of Bayer Hydrate. There are several definite breaks in this curve and it seems probable that the flat portions, AB, EF and GH, correspond to the presence of definite chemical individuals. In Table I these values of ρ are compared with the average values taken from the literature for the most likely hydrates and forms of alumina. Up to 220° (AB) gibbsite is still stable; from 550 to 820° the nearly constant value of 3.47 (EF) is consistent with either diaspore or γ-alumina, the latter being much the more probable on general grounds; and finally, at 900° or so the formation of corundum begins and is complete at 1200°. The break at CD, where ρ is 3.12 to 3.16, would seem at first to show that the solid is all boehmite between 360 and 430°, for it corresponds to the value 3.12 given by some workers as the specific gravity of boehmite; as against this, however, the water content is considerably below the requirement for boehmite throughout this range. Moreover, the X-ray data (*vide infra*) for the 420° sample show it to be a mixture of boehmite and γ-alumina. If one accepts Fricke and Severin's value, ρ = 3.02, for pure boehmite, our specific gravity results fall into line with the water content and X-ray data, and point to the presence of a mixture of boehmite and γ-alumina over the range 360 to 430°. The deviation between the curves for the two batches of material between B and E (as compared with their coincidence elsewhere) would thus correspond with a difference in the *proportions* of boehmite and of γ-alumina, due presumably to small but unavoidable differences in the preparation of the two batches.

TABLE I

THE DENSITY IN CERTAIN RANGES OF FIG. 3, COMPARED WITH VALUES FROM THE LITERATURE

	Range, °C.	Experimental density, ρ^{18}_4	Density from the literature	Reference, ρ^{18}_4
AB	15–220	2.43–2 45	Gibbsite, 2.43[a,b,c]	
CD	360–430	3.12–3 16	Boehmite, 3.02 Boehmite, 3.12[b]	4
EF	550–820	3.46	Diaspore, 3.41[a,b] γ-Alumina, 3.32[d] γ-Alumina, 3.65[b]	
G	Above 1200	4.01	Corundum, 3.99[a,b,e]	

[a] "International Critical Tables," Vol. 1, 1926, p. 136. [b] Montoro, *Gazz. chim. ital.*, 73, 43 (1943). [c] de Schulten, *Compt. rend.*, 122, 1427 (1896). [d] Rooksby, *Trans. Ceram. Soc.*, 28, 399 (1929). [e] Mellor, "Treatise on Inorganic and Theoretical Chemistry," Vol. 5, Longmans, Green and Co., New York, N.Y., 1924.

(4) Bulk Density.—It is well known that there is a loose correlation between bulk density and "activity," in the sense that "light" powders are usually more reactive than "heavy" ones; but quantitative data on the subject are few. It was therefore considered of interest to determine the bulk densities of the samples of the present study.

A portion of the freshly prepared sample was introduced

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(5) Culbertson and Dunbar, *J. Amer. Chem. Soc.*, **59**, 306 (1937).

(6) Lowry, *ibid.*, **46**, 824 (1924).

(7) "International Critical Tables," Vol. 3, 1928, p. 22.

(8) Gregg and Hill, unpublished work.

into a 10-cc. graduated cylinder and reweighed after well corking the top. The cylinder was mechanically tapped until there was no detectable change in the volume of the solid; the tapping was done by fixing the cylinder at the end of a rocker arm which was actuated by a cam turned by an electrical gramophone motor suitably geared down; the shape of the cam was such that the cylinder dropped rather suddenly on to a bakelite button once per revolution, from the height of approximately one inch.

Preliminary experiments indicated that the results were nearly independent of the weight of the sample, and that a suitable rate was three drops per second; agreement to within ±1 to 2% could be obtained by using a standardized procedure.

Figure 3 shows the curve of bulk volume *V* (the reciprocal of the bulk density) plotted against the temperature of preparation; its general similarity to the curve of surface area against temperature (Fig. 6, Part II) is obvious, and clearly shows the correlation between the "lightness" of the powder and its activity. The marked increase in *V* between 200 and 400° corresponds to the decomposition of the gibbsite to boehmite and γ-alumina.

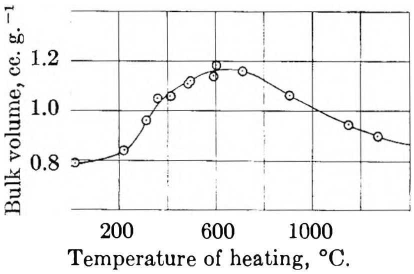

Fig. 3.—Bulk volume of the product of heating Bayer Hydrate to different temperatures for 5 hours.

The bulk density is a composite quantity, of course, and a *simple* relationship with surface properties is scarcely to be expected: the volume of a given weight of porous powder packed in a standard container is made up of the separate volumes of (a) the solid material itself, (b) the visible and the microscopic pores, (c) the ultramicropores (of molecular dimensions), (d) the space between the granules. The last, (d), will depend on the exact manner of packing of the granules, and this is a function not only of the shape of the latter but also of their adhesion to one another—an adhesion which is considerably influenced by the adsorption of gases on the surface of the solid.[9] For higher accuracy, therefore—as subsequent work in these laboratories has proved—bulk density should be determined with the powder either in vacuum or in an atmosphere of a standard humidity. However, the variation of *V* with the temperature of preparation exceeds this variation due to adsorption and there is little doubt that the curve of *V* against temperature of preparation would still retain the general shape of Fig. 3 if carried out under the more rigorous conditions.

(5) X-Ray Analysis.—A few of the decomposed gibbsite samples from Bayer Hydrate (Batch II) were kindly examined, by means of the Debye–Scherrer technique for X-ray powder photography, by J. Chatt and Miss Aldridge. Specimens for photographing were prepared by making the powder into rods (by grinding with about 10% gum tragacanth and a few drops of water to form a paste which was rolled into thin rods of diameter 0.3 mm.). The photographs, obtained with a 9 cm. camera and CuK radiation, were compared with those of known aluminas taken with the same camera.

The results obtained are summarized as follows: Bayer Hydrate (Batch II) heated for 5-hour periods; 420°, fairly well crystalline boehmite and some γ-alumina; 500°, γ-alumina; 595°, γ-alumina; 705°, γ-alumina; 819°, γ-alumina; 905°, γ-alumina.

With increase in temperature of preparation there was slight increase in the cuptallite size of the γ-alumina.

Discussion

The nature of the chemical changes that occur on heating gibbsite seem reasonably clear. X-Ray studies by many workers[10-15] have shown that the following stages occur as the temperature rises progressively:

$$\begin{array}{ccccccc} \text{Gibbsite} & \longrightarrow & \text{Boehmite} & \longrightarrow & \gamma\text{-Alumina} & \longrightarrow & \text{Corundum} \\ \gamma\text{-}Al_2O_3\cdot 3H_2O & & \gamma\text{-}Al_2O_3\cdot H_2O & & \gamma\text{-}Al_2O_3 & & \alpha\text{-}Al_2O_3 \end{array}$$

These stages have been confirmed in the present study on the basis of the results of specific gravity and the X-ray photographs. Heating below 200° caused practically no chemical change. Between 220 and 370° (mainly after 300°) loss of chemically combined water occurred, leaving mainly boehmite. From about 400 to 550° most of the remaining water was lost and the solid phase became largely γ-alumina. X-Ray examination showed that the product remained γ-alumina up to 900° (possibly a little higher); the specific gravity indicated that a sample prepared above 1200° contained only corundum (α-Al_2O_3). Thus the general picture is quite clear, but the results of the water-content determination call for discussion.

If any intermediate hydrates are formed the thermal dehydration curve should be stepwise provided the conditions are isobaric, since according to the Phase Rule when the number of phases becomes three (two solids and one vapor) there is one degree of freedom; thus since in the present work the pressure is fixed by the atmospheric humidity there is only one temperature at which two solids are in equilibrium with the vapor. But the experimental points of Fig. 1 do not represent equilibrium conditions, of course, so that the absence of steps corresponding to definite hydrates is not surprising; nevertheless neither Fricke and Severin[16] nor Weiser and Milligan,[15] found that any evidence whatever for the formation of a monohydrate, even though in their isobaric dehydrations particular care was taken to heat each sample to constant weight (several weeks being required for a single point in some cases). Hüttig and Wittgenstein,[17] on the other hand, did obtain a small break in their dehydration isobar of natural gibbsite, corresponding to the formation of $Al_2O_3\cdot H_2O$; but it is doubtful, in the light of the other work, whether much significance should be attached to this break. It is of interest that the curves of Fig. 1 are very similar in form to the curve obtained by La Lande, McCarter and Sanborn[11] for samples of natural gibbsite heated for half-hour periods.

In conclusion we draw attention to the following points: (a) The first and second stages in the thermal decomposition of gibbsite must overlap, so that boehmite and γ-alumina co-exist over a considerable range of temperature. This is clear from the X-ray photographs and from the results for water content, and is substantiated by the values for specific gravity if we accept the value for boehmite given by Fricke and Severin.[16]

(b) Many workers have found a residual per-

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[9] Obriemov, *Proc. Roy. Soc.* (*London*), **A127**, 290 (1930).

[10] Feachem and Swallow, *J. Chem. Soc.*, 267 (1948).

[11] Lalande, McCarter and Sanborn, *Ind. Eng. Chem.*, **36**, 99 (1944).

[12] Milligan, THIS JOURNAL, **26**, 247 (1922).

[13] Schwiersch, *Chem. Erde*, **8**, 252 (1933).

[14] Taylor, *J. Soc. Chem. Ind.*, **68**, 23 (1949).

[15] Weiser and Milligan, THIS JOURNAL, **38**, 1175 (1934).

[16] Fricke and Severin, *Z. anorg. Chem.*, **205**, 287 (1932).

[17] Hüttig and Wittgenstein, *Z. anorg. Chem.*, **171**, 323 (1928).

centage of water in γ-alumina, which is very difficult to remove (observed in the present work for samples prepared between 600 and 1000°). This small amount of water is often regarded as adsorbed,[15] but it would appear to be too firmly held for ordinary van der Waals adsorption: it is difficult to believe that physically adsorbed water would require a temperature of 1000° to disengage it.

(c) Different samples of gibbsite, even though of high purity, do not decompose at exactly the same temperature. It is likely that a mere trace of impurity would exert a great effect of the rate of decomposition; moreover the precise experimental conditions during the initial preparation of the gibbsite would probably be very critical. This point has been stressed previously, and it was the reason why a whole series of experiments was done with the same batch of starting material.

(d) Increase in the crystallite size of γ-alumina occurred between 500 and 905°, and corundum could not be detected in the X-ray photograph of the 905° sample. The specific gravity, however, whilst remaining constant at about 3.47 between 550 and 820, showed a rise to 3.53 at 905°, probably owing to the elimination of some of the finer pores, into which the carbon tetrachloride molecule could not penetrate. It seems likely that the considerable variation in the values of ρ reported for γ-alumina is caused in the same way; if this explanation is correct then the true value should be close to 3.53.

(e) The adsorption studies (Parts I and II) show that samples heated below *ca.* 200 and above 1100° give no measurable adsorption of nitrogen at $-182.7°$ or of carbon tetrachloride vapor at 25°. Thus no "activation" of gibbsite occurs before chemical decomposition takes place, and activity is lost when corundum is formed. Samples prepared between 300 and 1000°, however, are all "active," giving well defined adsorption isotherms. The curves of surface area S against temperature of preparation (Part II, Fig. 6) show a maximum at about 410°; the most active product therefore contains both boehmite and γ-alumina. By 500° the boehmite has almost entirely disappeared; as the temperature rises from 500 to 1000° the crystallite size of the γ-alumina increases and the surface area decreases steadily.

Acknowledgment.—We wish to thank Dr. J. Chatt and Miss Aldridge for taking the X-ray photographs and Messrs. Peter Spence & Co. for supplying the Bayer Hydrate and certain apparatus, and also for providing one of us (K.S.W.S.) with a Research Scholarship.

The work was carried out at University College, Exeter.

THE INTERPRETATION OF PUBLISHED X-RAY MEASUREMENTS ON DETERGENT SOLUTIONS ON THE BASIS OF AN INTERMICELLAR EQUILIBRIUM

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Received February 12, 1951

Published X-ray measurements on solutions of colloidal electrolytes and ethylene oxide derivatives are shown to be qualitatively in accord with an intermicellar equilibrium such as that indicated in Fig. 1. The conception of an equilibrium between three main types of micellar configuration, which has been used earlier to interpret the phase relationships and electrical conductivity behavior of certain solubilized systems, has been shown to give a coherent qualitative interpretation of published X-ray measurements on detergent solutions.

Introduction

It is agreed by all investigators of aqueous solutions of detergents and of such solutions containing dissolved (*i.e.*, "solubilized") organic liquids that the hydrophilic groups of the detergent and of the organic molecules present tend to associate with one another and with the water molecules. The lipophilic groups of the detergent on the other hand tend to segregate themselves from the water molecules, and, in the case of solubilized systems, to associate with the non-polar portions of the molecules of the organic liquids present.

Different views are held by different workers on the detailed mechanism by which these tendencies are fulfilled. The view taken in this account is that there is an equilibrium between three possible types of micellar configuration (Fig. 1) the position of the equilibrium within a single phase depending on its composition and temperature.

The idea of a micellar equilibrium, first advanced by McBain, has also frequently been used by other workers.[1–4]

According to McBain[5] "If there is any way in which ions or ion pairs can come together or associate with any reduction in free energy as by reducing interfacial energy or by more uninterrupted hydrogen bonding of the water, then that complex must exist to some extent, however slight, in soap solutions. Each size, shape, and arrangement will form in proportion to the reduction in free energy

(1) W. D. Harkins, R. W. Mattoon and R. S. Stearns, *J. Chem. Phys.*, **16**, 646 (1948).

(2) W. D. Harkins, R. W. Mattoon and R. S. Stearns, *ibid.*, **16**, 652 (1948).

(3) J. W. McBain, "Alexanders Colloid Chemistry," Vol. V, Reinhold Publishing Corp., New York, N. Y., 1944, p. 114.

(4) J. W. McBain and S. S. Marsden, *Acta Cryst.*, **1**, 270 (1948) (in relation to X-ray diffraction).

(5) J. W. McBain, "Frontiers in Colloid Chemistry," Interscience Publishers, Inc., New York, N. Y., 1949, p. 144.

that it offers under each condition of concentration, temperature and presence of other salts and materials."

The conception of the intermicellar equilibrium indicated in Fig. 1, which is in agreement with the above principle, was originally based on a study of the phase changes occurring in solubilized systems on change of composition and temperature.[6]

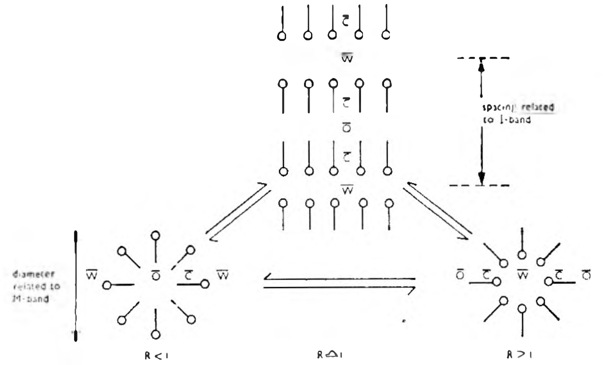

Fig. 1.—Intermicellar equilibrium and associated phase changes shown by certain series of solubilized systems. Suggested correlation with S-, M-, and I- X-ray diffraction bands. $\bar{W}$ = hydrophilic section of micelle; $\bar{C}$, amphiphilic section of micelle; $\bar{O}$, lipophilic section of micelle; R, ratio of dispersing tendencies on lipophilic and hydrophilic faces of $\bar{C}$, respectively. (The S-band arises from as far as possible random arrangement of the hydrocarbon chains in the $\bar{C}$ and $\bar{O}$ sections of all types of micelle.)

Good corroboration of this idea and further insight into the details of the equilibrium were furnished by a study of the changes in electrical conductivity of a series of solubilized systems with changes in composition and temperature.[7]

In the present paper an attempt is made to correlate the published X-ray measurements on detergent solutions and solubilized systems, also recently reviewed by W. Philippoff,[8] with the operation of the intermicellar equilibrium suggested in Fig. 1. Before this is done, however, a brief recapitulation will be given of the considerations underlying this suggested equilibrium and of the related phase changes indicated in Fig. 1.

Nature of Intermicellar Equilibrium

Consider a small region within a detergent solution or solubilized system in which a plane layer of amphiphilic molecules ($\bar{C}$), not necessarily all of one species, is temporarily in equilibrium with its lipophilic surroundings ($\bar{O}$, *i.e.*, solubilized organic liquid or the lipophilic groups of other amphiphilic molecules) on one face and its hydrophilic surroundings ($\bar{W}$, water, water soluble organic liquid, dissolved ions) on the other (Fig. 2). This local equilibrium is considered to be only temporary and subject to displacement one way or the other, by local thermal fluctuations of concentration within the system.[9]

During the time that the monolayer is in equilibrium it does not tend to bend. Hence the tendency ($A_{\bar{C}\bar{O}}$) to disperse on its lipophilic face must be equal to that ($A_{\bar{C}\bar{W}}$) on its hydrophilic face. Let

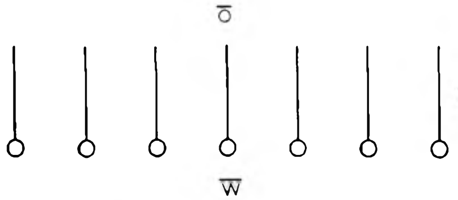

Fig. 2.

$$R = A_{\bar{C}\bar{O}}/A_{\bar{C}\bar{W}}$$

For the planar layer in equilibrium

$$R = 1$$

If a bulk change in composition of the system or a fluctuation within a system of constant bulk composition causes an alteration in the ratio $A_{\bar{C}\bar{O}}/A_{\bar{C}\bar{W}}$ so that R becomes > 1, the monolayer will tend to become convex toward its lipophilic face. If R becomes < 1, the monolayer will tend to become convex toward its hydrophilic face.

Within a given single phase detergent solution or solubilized system it is envisaged that the local fluctuations of concentration due to thermal motion are accompanied by corresponding local variations in micellar form. The equilibrium between three main types of micellar configuration, shown in Fig. 1, thus arises. The predominant micellar form in a given phase will depend on its composition and temperature. The general manner of this dependence has already been discussed.[6] It is important to emphasize that a micelle is not part of a separate phase, as is the case with an emulsion droplet, but merely represents a favored configuration of molecules (cybotactic complex) within a single phase.

S_1, G- and S_2-Phases.—Of the numerous phases which can occur in solutions of colloidal electrolytes under various conditions of concentration and temperature[10] three particular phases, S, G and S_2, were encountered frequently in our earlier work.[6] It was suggested that the respective properties and conditions for formation of these phases could be connected with differences in the balance of the intermicellar equilibria within them as indicated in Fig. 1. Examples of these phases may briefly be given as follows.

S_1-Solutions.—Typical isotropic aqueous solutions of detergents above the critical concentration. These may contain solubilized hydrocarbon or small amounts of *n*-alkanol, etc. The predominant micellar form is supposed to be the S_1-micelle ($R < 1$). This is in equilibrium with S_2- and lamellar micelles in greater or less concentration.

G-Gels (Liquid Crystalline Solutions).—On increase of the detergent concentration or on addition of *n*-alkanols to S_1-solutions a birefringent gel phase G frequently separates. It is supposed that within this phase the temperature and composition correspond to that of a stable lamellar micelle or liquid crystal structure. Under this condition there is minimum limitation to the size and lifetime of the lamellar micelles and these are supposed to

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(6) P. A. Winsor, *Trans. Faraday Soc.*, **44**, 376, 451 (1948).

(7) P. A. Winsor, *ibid.*, **46**, 762 (1950).

(8) W. Philippoff, *J. Colloid Sci.*, **5**, 183 (1950), (Table I).

(9) P. Debye and E. W. Anacker, This Journal, **53**, 1 (1949).

(10) (Annual Review) *J. Amer. Oil Chem. Soc.*, 181 (1948).

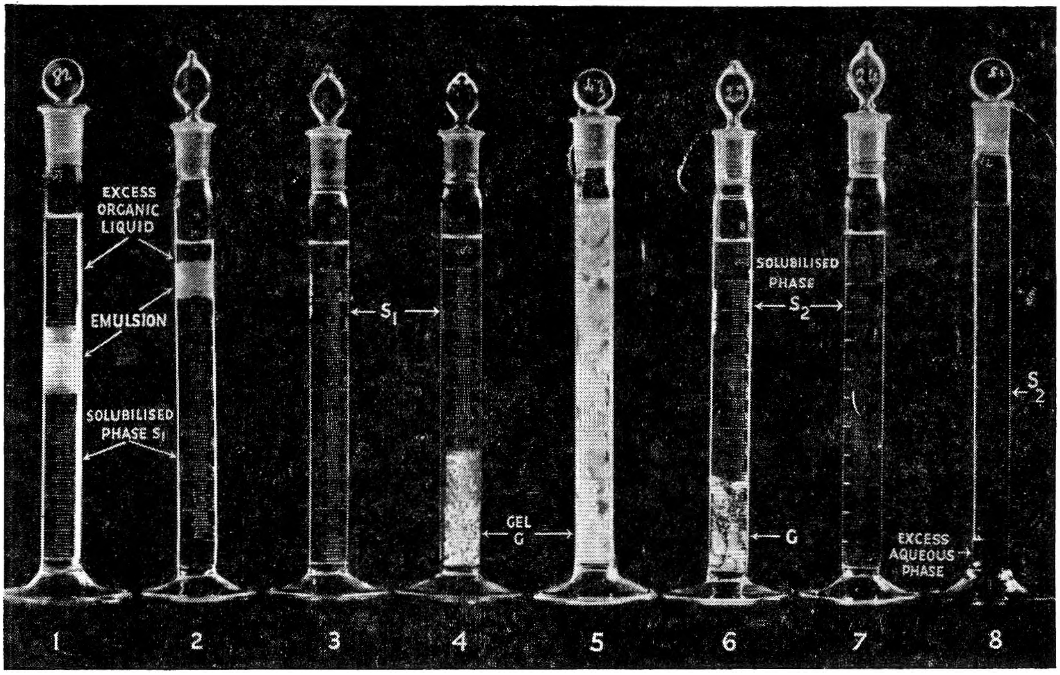

Fig. 3.—Accompanying phase changes at 20° on adding *n*-octanol to a mixture of undecane-3 sodium sulfate solution (5 ml., 20%w.) with hydrocarbon B (5 ml.); systems photographed between crossed polaroid sheets.

(1) No octanol added (Type I system)
(2) 0.85 ml. octanol added (Type I system)
(3) 0.91 ml. octanol added S_1 (isotropic)
(4) 1.00 ml. octanol added S_1 + G
(5) 1.20 ml. octanol added G (birefringent)
(6) 1.38 ml. octanol added G + S_2
(7) 1.70 ml. octanol added S_2 (isotropic)
(8) 2.13 ml. octanol added Type II system.

extend throughout the system and to be of the same average composition as the systems as a whole. This extensive lamellar micelle organization confers its special properties on the G systems. Thus (i) this phase is liquid crystalline, (ii) shows an enhanced density,[7] (iii) shows high viscosity and gel character, (iv) gives highly oriented X-ray diagrams, (v) the X-ray diagrams interpreted on the basis of the lamellar model are often consistent with the composition of the lamellar micelle being the same as the composition of the system as a whole,[11] a relation which does not hold for S_1 or S_2 solutions.

S_2-Solutions.—Isotropic S_2-solutions may be produced from the gels on further continuation of the processes, *e.g.*, addition of *n*-alkanol, which produce G from S_1. The S_2-micelle ($R > 1$) is supposed to be predominant in S_2-solutions and to be in equilibrium with lesser or greater amounts of lamellar and S_1-micelle. An example of the interconversion of the various phases discussed above is shown in Fig. 3.

In some cases it is possible by change of temperature or composition to effect a continuous transition of solutions from the S_1- into the S_2-conditions and *vice versa*[7] (Figs. 4 and 6 of Ref. 7). The change is marked, however, by a considerable though gradual change in electrical conductivity. It appears therefore that it is necessary to envisage the possibility either of a direct equilibrium between S_1- and S_2-micellar forms or of an equilibrium which involves a concentration, size and stability of lamellar (or leaflet) micelles too small to cause the formation of a gel phase. The existence within a single solubilized phase of regions where both hydrocarbon—and (water + salt)—uptake are simultaneously limited is clearly indicated by the coexistence of such solubilized phases in equilibrium with an excess of both aqueous and organic liquid phases (Type III systems).[12] Such a system for example is produced at 22.5° from undecane-3 sodium sulfate (20% soln. (by wt.) 10 ml.), aromatic free hydrocarbon (b.p. 188–213°; $d^{20}{}_4$ 0.777; n^{20} 1.4320; 65 ml.) octanol-1 (1.6 ml.) and sodium sulfate (1.5 g.). In this case a slight fall of temperature causes solution of the excess organic liquid phase and a slight rise of temperature solution of the excess aqueous phase. Presumably in such three phase systems the limited miscibility arises through the production by thermal fluctuations within the solubilized phase of regions of limiting stability of the S_1- and S_2-micellar forms, respectively.

Correlation between X-Ray Measurements and the Micellar Equilibrium Proposed in Fig. 1

(A) Nature of the S-, M- and I-bands.—Figure 4 taken from Harkins[1] illustrates the relations between certain of the bands which have been identified in X-ray measurements on aqueous detergent solutions and solubilized systems. Of the bands shown the S-, M- and I-bands only will be considered in this account.

S-Band.—This band is interpreted by all workers as related to the spacing of the hydrocarbon chains within the hydrocarbon portion of the

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[11] J. W McBain and W. Philipoff, *Nature*, **164**, 885 (1949).

[12] P. A. Winsor, *Trans. Faraday Soc.*, **44**, 377, 384 (1948).

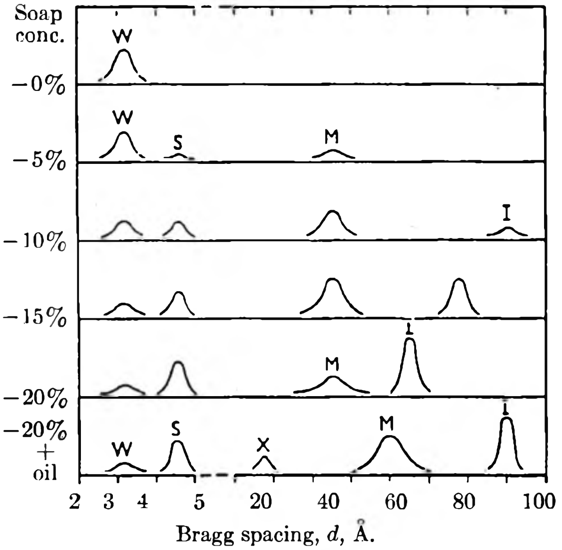

Fig. 4.—General illustration of the X-ray bands diffracted from clear liquid aqueous solutions of straight long-chain colloidal electrolytes at room temperature, showing the effects of concentration and solubilized hydrocarbons. The spacings represent only the order of magnitude (after Harkins[1]).

micelles. The band is broad indicating a liquid type of arrangement of the hydrocarbon chains and it has the value of the similar spacing in a liquid hydrocarbon[13] or liquid palmitic acid.[14]

Beyond the indication of this liquid arrangement, the evidence afforded by the S-band concerning the geometrical structure of micelles seems to be slight. It was originally taken as indicating the side spacing in lamellar micelles but if it is merely characteristic of liquid hydrocarbon it is consistent with any form of micelle in which the paraffin chains maintain random liquid arrangement.[15] This qualification is, however, important since it contra-indicates any periodic parallel alignment of the hydrocarbon chains as in Harkins' cylindrical model.[16,17] Even in G systems, where lamellar micelles are strongly indicated by the X-ray measurements (*v.i.*) although the long spacings are very highly oriented the short spacings (S-band) are not oriented.[18] This seems to indicate a less regular lateral disposition of the hydrocarbon chains in the lamellar micelles, even in the liquid crystalline systems, than is frequently represented,[19] *i.e.*, than that in crystalline fatty acid. In ref. 20, increasing the so-called "angle of tilt" may actually only represent a reduction in closeness of packing of the polar heads in the layers with a consequent contraction in the effective thickness of the random liquid hydrocarbon layer.

M-Band.—The M-band, discovered by Harkins in X-ray measurements with soap solutions, appears to indicate a spacing which is independent of concentration and which is closely equivalent to twice the length of the soap molecule.[21] The M-band, which appears at the same concentration of soap as that at which the S-band appears and at considerably lower concentrations than those required for the appearance of the I-band, was initially interpreted by Harkins as related to the thickness of a cylindrical micelle consisting of one double layer of soap molecules, the polar groups being in the plane faces.[17] As already pointed out this model represents a liquid crystalline micelle whereas at the concentrations of the measurements the X-ray evidence indicates a liquid micelle. In a more recent paper[16] Harkins therefore revises his earlier view as follows: "The interfacial tension between the micelle and the water with ionic atmosphere is very small but the small size of the micelle gives a relatively high internal pressure so that the micelle takes on as nearly a spherical shape as possible when the other constraints are involved.... At the present time no phenomenon or quantitative relationship is known which indicates the spherical model to be inapplicable." A point which may be of relevance is that within an isotropic soap solution or solubilized system all the polar groups of a given molecular species would be expected to exert a statistically similar function. This is represented only by an inter-micellar equilibrium or by models of spherical or indefinitely extended lamellar type. For cylindrical models of finite size and stability the functions of the polar groups are different according as they are found toward the center or toward the periphery of the faces of the cylinder.

I-Band.—The X-ray long spacings used exclusively by all investigators[20,22,23] other than the Harkins school and also, initially, by Harkins himself[22] are somewhat longer than the M-band spacing and only become evident at rather higher concentrations. These spacings increase with dilution of the soap solution and with solubilization of hydrocarbon. They were interpreted by the original German investigators, by McBain and, at first, by Harkins on the basis of a lamellar micelle. More recently Harkins considers these spacings as related to the intermicellar distance[24] an idea also advanced by Hartley.[25] McBain maintains the original view.[26] Hughes, Vinograd and Sawyer[27] prefer a lamellar micelle model but one in which the ordered regions in the case of S_1-solutions are much less extended and regular than in the models used by the other authors.

A marked difference in character exists between the S- and I-bands. Thus while in isotropic solutions at rest neither show orientation, marked orientation of the I-band may appear under flow (Hess)[23] or in liquid crystal systems. The S-band remains unoriented.

(13) W. D. Harkins and R. Mittleman, *J. Colloid Sci.*, **4**, 370 (1949).

(14) J. Stauff, *Koll. Z.*, **89**, 224 (1939).

(15) G. S. Hartley, *Ann. Reps.*, **55**, 49 (1948).

(16) W. D. Harkins and R. Mittleman, *J. Colloid Sci.*, **4**, 369 (1949); W. D. Harkins and R. Mittleman, *ibid.*, **4**, 371 (1949).

(17) W. D. Harkins, *J. Chem. Phys.*, **16**, 156 (1948).

(18) J. W. McBain and S. S. Marsden, This Journal, **52**, 122 (1948).

(19) J. W. McBain and S. S. Marsden, *ibid.*, **52**, 114 (1948).

(20) J. W. McBain and S. S. Marsden, *ibid.*, **52**, 110 (1948).

(21) W. D. Harkins, R. W. Mattoon and R. S. Stearns, *J. Chem. Phys.*, **15**, 209 (1947).

(22) W. D. Harkins, R. W. Mattoon and M. L. Corrin, *J. Amer Chem. Soc.*, **68**, 220 (1946); *J. Colloid Sci.*, **1**, 105 (1946).

(23) K. Hess, *Fette und Seifen*, **49**, 81 (1942).

(24) W. D. Harkins and R. Mittleman, *J. Colloid Sci.*, **4**, 367 (1949).

(25) G. S. Hartley, *Nature*, **163**, 767 (1949).

(26) J. W. McBain and O. A. Hoffman, This Journal, **53**, 39 (1949).

(27) E. W. Hughes, W. M. Sawyer and J. R. Vinograd, *J. Chem. Phys.*, **13**, 131 (1945).

(B) Preliminary Assumptions Used as the Basis for the Correlation between X-Ray Results and Intermicellar Equilibria Suggested in Fig. 1

The correlation of a number of reported X-ray results with the intermicellar equilibria suggested in Fig. 1 will now be considered on the basis of the following assumptions: (1) The S-band corresponds to a liquid arrangement of hydrocarbon chains within all forms of micelle. (2) The M-spacing as calculated by Harkins corresponds to the mean S_1-micelle diameter. (3) The I-band corresponds to the layer spacing within lamellar micelles.

(C) Changes in Character and Relations of S-, M- and I-Bands with Changes in Composition

(a) Effect of Concentration.—The relations between the intensities of the S-, M- and I-bands for aqueous detergent solutions of various concentrations are shown in Fig. 4 (after Harkins[1]).

The character of the S-band has already been discussed above.

The concentration at which the I-band appears is considerably above that at which the M-band appears. Harkins states[28] "The intensities of the two bands might have been interpreted as a measure of the relative abundances of two kinds of micelle. However, a single kind of micelle may give the M-band and at higher concentrations when these micelles are necessarily closer together the I-band may result from a network of micelles giving an intermicelle spacing" (since the M- and I-bands overlap, *cf.* Harkins, ref. 1, Fig. 4). "At high concentrations the total diffracted intensity would then be partitioned between that for the single micelles (M) and that for the intermicelle arrangement (I). Under this supposition, with increasing concentration the M-spacing should remain constant whereas the I-spacing should decrease. This is what is observed."

Although the suppositions of the last two paragraphs accord with the intensity variations of the two bands, the earlier supposition, namely, that the intensities of the two bands might be interpreted as a measure of the relative abundance of two types of micelle seems equally acceptable and retains the interpretation, preferable on other grounds (*v.i.*), that the I-band arises from lamellar micelles (G-micelle Fig. 1) of greater or less extension. The origin of the M-band, which as already discussed is consistent with a spherical micelle, is then assigned to the S_1-micelle.

For a given constitution of its $\overline{C}$ (and $\overline{O}$) layers a lamellar micelle will tend more to pass into an S_1-micelle the more the dispersion of its polar groups is facilitated, *i.e.*, the less the surrounding concentration of ions in the vicinity of its polar face and the greater the concentration of water. In the case of S_1-solutions (mean value of $R<1$) this would lead one to expect lamellar micelles to arise, if at all, in regions of the solution where thermal fluctuations have caused a temporarily high concentration of detergent. That is, the lamellar micelles if present in equilibrium in S_1-solutions should be poorer in water than either the S_1-micelles or the bulk solution. This conforms with the results calculated from the I-spacings using the lamellar model (*cf.* Harkins[22]).

The thickness of the water layer of the lamellar micelles in equilibrium with S_1-micelles can be envisaged as arising from a compromise between the tendency for the lamellar micelles to be of lower water content than the bulk solution, as mentioned above, and the tendency for equalization of concentration throughout the solution. The ratio [(water/soap) in lamellar micelle/(water/soap) over-all] should be less than 1 and increase with increasing concentration becoming unity when the stability of the lamellar micelle is maximum, *i.e.*, on formation of the gel phase. These relationships conform to those calculated from the observed I-spacings using the lamellar model. Unit value of the ratio [(water/soap) in lamellar micelle/(water/soap) over-all] appears to occur in the gels derived from Aerosol OT, hexanolamine oleate, glyceryl monolaurate and diglycol laurate.[11]

(b) Effect of Inorganic Salts.—Addition of inorganic salt to an aqueous solution (S_1) containing lamellar micelles in equilibrium with S_1-micelles should, by opposing the dispersion of the polar heads, increase the stability of lamellar micelles of higher water content and thus displace the I band toward the longer spacings. This latter result is observed[29] except at very low salt concentration.[30] However if the range of composition consistent with the stability of the birefringent gel phase gives an indication of the stability of lamellar micelles, the effect of inorganic salt on this stability is complex (ref. 7, Fig. 5). Also in a system consisting of sodium octane-1 sulfate, water, nonanoic acid and sodium chloride we have found that for systems containing S_1 and G or G and S_2 in equilibrium the NaCl/water ratio and the NaCl/sodium octane-1 sulfate ratio are considerably less in the gels than in the equilibrium sols. This would seem to indicate a comparative intolerance of the gel (lamellar) structure for inorganic ions. Examples are given in Table I.

(c) Effect of *n*-Alkanols-1. (i) Effect on M-Band.—There is strong evidence[24] that *n*-primary alcohols solubilize in micelles by penetration between the long chain soap ions. In Fig. 1 they thus become part of the $\overline{C}$ layer and have their polar groups in contact with $\overline{W}$. In the case of the S_1-micelles in these solutions the diameter, on account of the liquid character of the micelle interior, will be derived from the average chain length of the various molecular types present.

When alcohols of chain length below C_{12} are solubilized in sodium dodecyl sulfate solution they diminish the M-spacing and the derived micelle diameter (Harkins, ref. 1). This was accounted for along the foregoing lines by Harkins.

It is remarked in Harkins paper that "addition of 4.08 g. of hexanol to 100 g. of 24.8% sodium dodecyl sulfate gave a clear but stiff gel at room temperature." We have frequently observed this

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[28] W. D. Harkins, R. W. Mattoon and R. S. Stearns, This Journal, 16, 650 (1948).

[29] W. D. Harkins, R. W. Mattoon and M. L. Corrin, *J. Amer. Chem. Soc.*, **68**, 226 (1946).

[30] A. P. Brady, This Journal, **53**, 947 (1949).

Table I

Analysis of Equilibrium Phases Formed on Addition of Nonanoic Acid to a Mixture of Octane-1 Sodium Sulfate Solution (5 ml., 40%w.) and Sodium Chloride (0.2 g.)

Vol. nonanoic acid added (ml.)	0.7		1.0		3.5		4.0	
Nature of phases	S_1	G	S_1	G	G	S_2	G	S_2
Composition of phases (% by wt.)								
Nonanoic acid	6.5	17.7	2.3	21.4	32.9	37.6	34.2	41.4
Octane-1 sodium sulfate	28.3	42.8	10.7	43.4	26.9	19.2	26.6	19.7
Sodium chloride	4.1	1.04	7.1	0.72	1.57	2.9	1.34	2.5
Water	61.1	38.5	79.9	34.5	38.6	40.3	37.9	36.4
$NaCl/C_8H_{17}SO_4Na$	0.15	0.024	0.66	0.017	0.058	0.15	0.050	0.13
$NaCl/H_2O$	0.067	0.027	0.089	0.021	0.041	0.072	0.035	0.069
Volumes of phases (ml.)	4.1	1.6	2.3	3.7	4.5	4.0	2.6	6.4

formation of gel on addition of a *n*-alkanol to a *n*-soap solution and interpret it as due to the production of an extensive and stable lamellar micelle structure. The inclusion of water-insoluble alkanol within the $\bar{C}$ layer of a micelle will reduce the tendency of its hydrophilic face to spread in water, since the tendency to disperse of a face composed of mixed hydroxyl and ionic groups will be less than that of one composed wholly of ionic groups. The lamellar micelle thus becomes stabilized with respect to the S_1-micelle by the addition of *n*-alkanol and at a certain concentration of alkanol it becomes sufficiently stable and extended to lead to the separation of the birefringent gel phase.

Harkins further states "It is interesting to note in this case" (*i.e.*, that of the gel) "that instead of the usual broad and diffuse appearance of the M-band—especially at higher detergent concentrations—now it becomes a broad but distinct band with about the same spacings as when gel is not formed."

It seems likely that this effect may be due to the M-band being differently derived in the S_1- and G-systems.

In the S_1-solutions the "broad and diffuse appearance of the band especially at higher concentrations" may be due to the process of the equilibration of comparable concentrations of S_1- and G-micelles at these concentrations whereas at lower concentrations the S_1-micelle is overwhelmingly preponderant and in the gel the lamellar micelle alone is significant.

(ii) Effect on I-Band.—As explained above, solution of water insoluble alcohols in soap solutions should facilitate the formation of lamellar micelles and thus enable these to form in regions of the solution of water content which would otherwise be too high for their existence.

On this view water insoluble alcohols should: (1) intensify the I-band and allow it to appear at lower concentrations of soap; (2) increase the I-spacing by increasing the thickness of the $\bar{W}$ layer at which the lamellar micelles show a given stability. In cases where the chain length of the alcohol is less than that of the soap this would tend to be off-set by a reduction in the thickness of the $\bar{C}$-layer as discussed above for the case of the diameter of the S_1-micelle.

Both these effects were recorded by Harkins (ref. 1, Fig. 4) but were not satisfactorily accounted for by him. According to Harkins "the I-spacings deserve consideration as giving a qualitative idea of the distance between micelles." Harkins further assumes that these are the same micelles whose diameters are indicated by the M-spacing. Now these M-spacings are reduced by addition of water insoluble alcohols of chain length less than the soap. The number of the micelles should therefore be increased both by the reduction of their diameter and by the incorporation of further micellar material. Hence on this view the intermicellar spacing should be diminished. Actually however the I-spacing is increased.

The likely effect of water soluble alcohols on the micellar equilibrium is more difficult to foresee than the effect of the water insoluble alcohols. In our phase studies addition of water soluble alcohol has been considered to increase the tendency $A_{\bar{C}W}$ of the $\bar{C}$ layer to disperse in water. The general physical evidence strongly supports this view. Water soluble alcohols should therefore have an effect opposite to that of water insoluble alcohols and of inorganic salts. They should therefore diminish the stability of lamellar micelles in equilibrium with S_1-micelles and diminish the thickness of the water layer at which the lamellar micelle shows a given stability. The I-spacing should therefore be reduced.

This result was actually observed by Harkins for methanol, ethanol and propanol. For butanol, which is incompletely miscible with water, only a small effect on the spacing was observed.

With regard to the effect of these alcohols on the intensity of the I-band Harkins reports that addition of methanol or ethanol to sodium dodecyl sulfate solutions makes the X-ray pattern more diffuse. Butanol, in common with the higher alcohols intensifies the I-band.

(d) Effect of Hydrocarbons (i) Effect on M-Band.—Table II (reproduced from Harkins (2)), shows the effect of various solubilized hydrocarbons on the M-spacing.

Under comparable conditions a given quantity of benzene produces a much smaller increase in spacing than the same amount of heptane. Thus 5.08 g. benzene in 100 g. of 12% potassium myristate solution produces an increase of 9.1 A. while only 1.59 g. of heptane produces a similar increase. This result cannot be accounted for by the inclusion of the two hydrocarbons in a similar manner in similar micelles. If spherical micelles alone are concerned it would appear possible that the

Table II

M-Spacings for Aqueous Solutions of Potassium Laurate (KC_{12}) and Potassium Myristate (KC_{14}) Saturated with Hydrocarbons at 25°

With no solubilized hydrocarbon, d_M = 35.3 for KC_{12} and d_M = 40.3 Å. for KC_{14} independent of soap concentration. At the higher soap concentrations, the values of Δd_M are less accurate because of the influence of the I-band. At 25° the density of n-heptane is 0.679, ethylbenzene is 0.862 and benzene is 0.873 g./cc. At 25° the solubility in 100 g. of water for n-heptane is 0.005, ethylbenzene is 0.015 and benzene is 0.185 g. Aqueous solutions of sodium lauryl sulfate saturated with hydrocarbons give similar relations.

Hydrocarbon solubilized	Per cent. by weight of soap	Bragg M-spacing $d_M + 1A$	Bragg M-spacing increment due to hydrocarbon $\Delta d_{M\,sat} \pm 2A$	Solubility, grams hydrocarbon per 100 g. soap solution, G_{sat}
Ethylbenzene	7.00 KC_{12}	40.7	5.4	1.07
	8.84	41.1	5.8	1.48
	10.09	41.5	6.2	1.77
	12.05	41.8	6.5	2.23
	13.60	42.0	6.7	2.63
n-Heptane	4.47 KC_{14}	50.0	9.7	0.46
	7.16	51.0	10.7	0.84
	9.82	51.2	10.9	1.24
	12.00	49.2	8.9	1.59
	13.74	48.2	7.9	1.89
Ethylbenzene	4.47 KC_{14}	50.4	10.1	1.13
	7.16	52.2	11.9	2.02
	9.82	51.4	11.1	2.99
	12.00	48.4	8.1	4.03
	13.74	47.8	7.5	4.56
Benzene	4.47 KC_{14}	51.2	10.9	1.57
	7.16	52.0	11.7	2.66
	9.82	49.6	9.3	3.82
	12.00	49.4	9.1	5.08
	13.74	49.0	8.7	5.96

more polar benzene penetrates further between the hydrocarbon chains toward the polar groups, thus approaching the oil-soluble alcohols (which do not increase the M-spacing) in behavior. On the other hand at different concentrations of soap the same hydrocarbon does not produce an increase in d_m which is even approximately directly related to the (wt. hydrocarbon solubilized/wt. of soap). This seems strongly indicative that the M-band is derived from one of two or more types of micelle in equilibrium.

(ii) Effect on I-Band.—The influence of solubilized hydrocarbons on the I-band has been described by Harkins[31] and the implications of the experimental results examined on the basis of the lamellar model.[22] These implications were later held by Harkins to make the lamellar model unlikely.[17]

Calculations were made[13,16] of the thickness τ of the oil layer within the micelle by dividing the volume of the oil solubilized by the area of the double soap layers assuming that all the soap was in the form of lamellar micelles and taking 28 sq. Å. as the cross sectional area of the soap molecules. In calculations for n-heptane, triptane and ethylbenzene the calculated thickness (τ) was found to be only about 0.4 times the increase in thickness of the lamellae indicated by the I-spacing (Δd_I). For example for 3.5% heptane in 25% potassium laurate τ = 5.5 Å. but Δd_I = 13.6 Å. or 2.5 times higher than it should be. Harkins therefore concluded "Δd_I is not the distance between layers in a lamellar micelle, but the change in the intermicellar distance (d_I)."

In making the above calculations, however, Harkins assumed that all the soap was in the form of lamellar micelles and that all the oil was included in these. If however the lamellar micelles exist, in the S_1-systems under investigation, in equilibrium with S_1-micelles and if further the solubilized oil is distributed between the two forms of micelle no difficulty arises in the qualitative understanding of the results. The ratio of oil/soap would be expected to be greater in the more lipophilic lamellar micelle regions of the solution than in the more hydrophilic spherical micelle regions. It would thus be greater than in the solution as a whole depending on the ratio of lamellar/spherical micelle. With increasing proportion of lamellar micelle, *i.e.*, with increasing concentration of soap one would expect $\tau/\Delta d_I$ to approach unity (see Part C (a) Effect of Concentration). This expectation is apparently substantiated by the collected results recently published by W. Philippoff.[8]

(D) Further Considerations Concerning the Significance of the I-Band

Harkins's rejection[1] of the interpretation of the I-band on the basis of the lamellar model was also because he was unable to conceive a mechanism for the control of the water spacings in conformity with those calculated with this model. A qualitative mechanism, on the basis of the intermicellar equilibrium (Fig. 1), has already been suggested.

Brady[30] has shown how in a system of lamellar micelles in equilibrium with other forms the water spacing may be calculated from the experimentally observed osmotic coefficient g. On the basis of certain simplifying assumptions the positive ion distribution between two infinite parallel negative plates is calculated. The osmotic pressure in the center of the region is then equated to the osmotic pressure of this system as a whole and an expression is derived for the water thickness which accords satisfactorily with experiment. Greater difficulties arise, however, when the theory is extended to solutions containing inorganic salt (*cf.* also above).

Objections to the interpretation of the I-band on the basis of intermicelle distance have been given by McBain and Hoffman.[26] Attention is drawn in particular to the following points: (1) Changes in the intensity of the long spacing diffraction with the concentration and electron density of the solubilized oil appear to give definite evidence of the presence of lamellar micelles in isotropic solutions of potassium laurate[27] and of cetyl pyridinium bromide (ref. 26).

(2) With the lamellar model only molecules capable of agglomerating to form discs, *i.e.*, linear molecules can yield a long spacing diffraction, whereas according to the interparticle spacing

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(31) W. D. Harkins, R. W. Mattoon and R. S. Stearns, This Journal, **16**, 654 (1948); W. D. Harkins, R. W. Mattoon and M. L. Corrin, *J. Colloid Sci.*, **1**, 105 (1946).

hypothesis all colloidal electrolytes should yield this line. Studies of X-ray diffraction with a number of compounds whose molecular geometry seemed to preclude the existence of lamellar micelles showed that with these no I-band was produced.

(3) On the basis of the lamellar model the relative diameters of the first, second and third order diffractions will be 1:2:3. On the other hand with independent bimolecular leaflets a hexagonal lattice would result giving different relative diameters. All recorded observations on isotropic colloidal electrolytes show the relative positions of the rings to be those expected from the lamellar structure.

(E) X-Ray Diffraction by Aqueous Systems of Non-ionic Detergents

McBain and Marsden[20] have presented some X-ray measurements on solutions of non-ionic emulsifiers which afford strong evidence for the existence in these solutions of an intermicellar equilibrium such as shown in Fig. 1.

The following results are especially significant from this standpoint.

(a) *α-n*-Decyl Glyceryl Ether (m.p. 38°), Water Systems.—This gives single phase liquid crystalline systems between 62 and 100% concentration in water. Below 62% two phases in equilibrium separate. One (probably S_1) is isotropic, gives no long spacing and probably consists mainly of water. The other phase (G) is birefringent and gives a highly oriented X-ray spacing which varies over the whole range of composition 62–100% in a manner which is consistent with the view that the composition of the diffractive lamellar micelle is the same as that of the system in bulk.

(b) Triton X-100, Water, Benzene Systems.—Triton X-100 is the condensation product of diisobutyl phenol and ethylene oxide estimated to contain an average of 9–10 ethylene oxide units per molecule.

The tentative phase diagram (Fig. 5, ref. 20, Fig. 9) gives the phase relationships found by McBain with the phase nomenclature used in Fig. 1 inserted.

In the G-region the X-ray long spacings are highly oriented, the short spacings not oriented. It is concluded from the variation in the I-spacings with composition that, within this phase, the compositions of the lamellar micelles corresponding to the long spacings are identical with those of the phase as a whole.

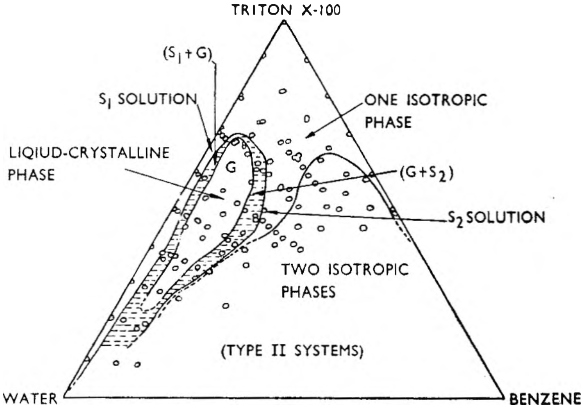

Fig. 5.—Phase diagram for the Triton X-100–water–benzene system (after McBain[20]).

In the heterogeneous regions (shaded) which contain both liquid crystalline and isotropic phases, the two phases have different long spacings. In every case the long spacing of the isotropic phase is either equal to or greater than that of the co-existing liquid crystalline phase. The long spacings of the isotropic phases are not oriented and are less sharply defined than those in the liquid crystalline region.

Triton X is miscible with water and probably with benzene in all proportions. Neither solutions (S_1) of Triton X in water or in benzene (S_2) give long spacings. The addition of 1% of benzene to the S_1-solutions or of 10% of water to the S_2 solutions is necessary to produce the minimum amount of lamellar structure required to give a long spacing.

The solubilization of benzene in the S_1 solutions increases the long spacing very rapidly, much more rapidly than can be accounted for on a model in which all the Triton is in the form of lamellar micelles in which the benzene is solubilized in the hydrocarbon portion. (This model as mentioned above adequately represents the behavior in the G-region.) The behavior is analogous to that noted by Harkins for the solubilization of hydrocarbons in (S_1) soap solutions which has been discussed above (see part (c) (d) ii, Effect on I-band).

A similar type of behavior appears to occur on solubilization of water in the S_2-solutions. This would be expected if these solutions contain lamellar and S_2-micelles in equilibrium, the argument being the reverse of that already given for S_1-solutions containing lamellar and S_1-micelles in equilibrium.

(F) X-Ray Measurements Involving S_2 Phases

Most of the systems on which the X-ray results have been considered in the foregoing pages have been either in the S_1- or G-condition. They would therefore be expected to contain little of the S_2-micelle. Exceptions occur in the Triton X system as indicated in Fig. 5. In the case of Triton X (Fig. 5) the passage from S_1 into S_2 may be either continuous or through the gel phase. The formal distinction used between S_1- and S_2-solutions is thus whether they are of more ($R < 1$) or less ($R > 1$) hydrophilic character, respectively, than the gel ($R = 1$) or than the composition corresponding to the maximum stability of the lamellar micelle.

S_2-Solutions were also present at higher concentrations (>92%) in the hexanolamine oleate–water systems investigated by Ross and McBain.[32] In this system the whole sequence of phase changes

$$\begin{array}{ccccccccc} S_1 & \longrightarrow & S_1 + G & \longrightarrow & G & \longrightarrow & G + S_2 & \longrightarrow & S_2 \\ <30\% & & 30\text{–}40\% & & 40\text{–}85\% & & 85\text{–}92\% & & >92\% \end{array}$$

occurs with gradually increasing concentration. It is interesting that for the gel system the ratio [(water/soap) in lamellar micelle/(water/soap) in total system] as deduced from the I spacings is

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[32] J. W. McBain and S. Ross, *J. Am. Chem. Soc.*, **68**, 296 (1946).

unity.[34] It may readily be calculated that in the S_1-region this ratio is less than unity and in the S_2-region more than unity. This is exactly the relation to be expected on the basis of an intermicellar equilibrium as in Fig. 1, the argument being along the lines already given.

Small angle X-ray scattering measurements on solutions of Aerosol OT in *n*-dodecane[33] were held to indicate the presence of S_2-micelles about equal in radius to the OT molecule. Water expands them up to at least twice their diameter.

X-Ray and light scattering investigations on a series of mobile isotropic solutions (mostly S_2-solutions) containing potassium oleate, water, hydrocarbon and alkanol have been made by Schulman and collaborators.[34,35] Very wide (up to 550 Å.) spacings were calculated.

In several of the non-conducting S_2-solutions (intermicellar equilibrium well in favor of S_2-micelle) the spacings could be reasonably interpreted as being derived from the intermicellar distance of a system consisting of "oleophilic hydromicelles" (S_2-micelles) in which the oleate and alkanol formed a mixed monolayer.

In the conducting systems the X-ray diffraction effects were markedly weaker than with the non-conducting systems. In two cases (both notably containing a relatively high proportion of water and low proportion of alkanol) the results indicated systems composed mainly of spherical "hydrophilic oleo micelles" (S_1).

In the "oil continuous" systems of intermediate conductivity the X-ray diffraction in two cases was particularly weak. It seems likely that these solutions were in the S_2-region but in its more hydrophilic section close to the gel region. We have also observed that such S_2-solutions show marked conductivity, particularly when they contain lower and cyclic alkanols.[7] In these cases it is probable that considerable concentrations of G- and S_1-micelle are in equilibrium with the S_2-micelle. If this were so the diffuseness of the X-ray diffraction would be readily understandable. Further, since the structure of those systems is extremely sensitive to temperature (Winsor[7]), even a small variation in temperature during irradiation would also produce additional diffuseness.

From the foregoing examples the general conclusion to be reached from Schulman's work seems to be that, while in some cases his results are in agreement with the micellar material existing very largely as "oleophilic hydromicelles" (S_2) or "hydrophilic oleomicelles" (S_1), in most cases other forms of micelle are also present. This conclusion is in agreement with the type of intermicellar equilibrium suggested in Fig. 1.

Acknowledgment.—The author wishes to thank Messrs. Shell Refining & Marketing Co., Ltd., for permission to publish this paper.

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(33) R. W. Mattoon and M. B. Mathews, THIS JOURNAL, **17**, 496 (1949).

(34) J. H. Schulman and D. P. Riley, *J. Colloid Sci.*, **3**, 383 (1948).

(35) J. H. Schulman and J. A. Friend, *ibid.*, **4**, 497 (1949).

COMPETITIVE ADSORPTION FROM SOLUTION BETWEEN HYDROPHOBIC AND HYDROPHILIC MOLECULES AND IONS

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By considering the variation in concentration with *p*H of water-soluble amines and their ions in aqueous solution, it has been shown that hydrophobic films on platinum are primarily due to the adsorption of free amine in the more alkaline regions of the *p*H scale. In the less alkaline regions hydrophobicity is due to the adsorption of amine ion. The adsorption of amine ion results in hydrophobic films exhibiting lower contact angles than do the films resulting from adsorption of free amine. A similar situation exists in the case of water-soluble carboxylic acids, except that hydrophobic films in the more acid regions are due to undissociated acid molecules, whereas in the more alkaline regions hydrophobicity is due to the adsorption of carboxylate ions. In the quantitative treatment of the data both hydrophobic and hydrophilic species have been taken into consideration. The maximum degree of hydrophobicity occurs at the same *p*H as does the maximum mole fraction of the hydrophobic species present. Other marked changes in the degree of hydrophobicity also occur in the same *p*H regions where corresponding variations in the mole fraction of hydrophobic species are evident. The effect of varying the concentration and dissociation constant on the *p*H at which maximum hydrophobicity occurs have been computed and the results have been generalized to any weak acid or base.

Introduction

Recent reports from this Laboratory have been concerned with the aqueous adsorption of hydrophobic films of primary *n*-alkyl amines[2] and with a variety of carboxylic acids[3] on platinum foil. Only a qualitative treatment has been given of the effect of the nature of the polar group and concentration of solute on the remarkable contact angle *vs.* *p*H curves reported there. This report is concerned with the dissociation equilibria of the hydrophobic molecules and ions present in such experiments and the effect on the competitive adsorption of the ions and polar molecules caused by varying *p*H, dissociation constant, and concentration. The adsorption equilibria will be considered to involve only the dissolved aqueous ions and amphipathic molecules. This is because solutions more dilute than 10^{-2} to 10^{-3} moles/liter of the compounds discussed here do not contain colloidal

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[1] The opinions or assertions contained in this article are the authors' and are not to be construed as official or reflecting the views of the Navy Department.

[2] E. G. Shafrin and W. A. Zisman, *J. Colloid Sci.*, **4**, 571 (1949).

[3] H. R. Baker, E. G. Shafrin and W. A. Zisman, THIS JOURNAL, **56**, 405 (1952).

micelles according to past published work on critical micellar concentrations and their relation to molecular weight and salt concentration.[4-6]

Adsorption of Amines.—The work of Shafrin and Zisman[2] on the adsorption of primary *n*-alkyl amines on platinum from aqueous solution has shown how the hydrophobicity of the resulting films, as measured by contact angles, is dependent on the *p*H of the solution. The results obtained for *n*-octylamine, which was typical of the amines studied, are shown in Fig. 1. Variation in *p*H was obtained by the addition of potassium hydroxide or hydrochloric acid. It will be observed that for the higher concentrations the contact angle ϑ has a peak value at a *p*H of about 10. With increasing *p*H (10–12) the value of ϑ decreases sharply until complete wetting occurs. With decreasing *p*H (10-8) the value of ϑ decreases rather sharply to an inflection point designated as ϑ plateau. In the *p*H range of 8 through 5 the contact angle decreases only slightly with decreasing *p*H. However, after a *p*H of 5 is reached, ϑ decreased sharply with decreasing *p*H. With decreasing concentration it is seen that the width of the plateau or shoulder of the curve becomes smaller. Also with decreasing concentration the peak value of ϑ becomes smaller and in general appears to occur at decreasing *p*H values.

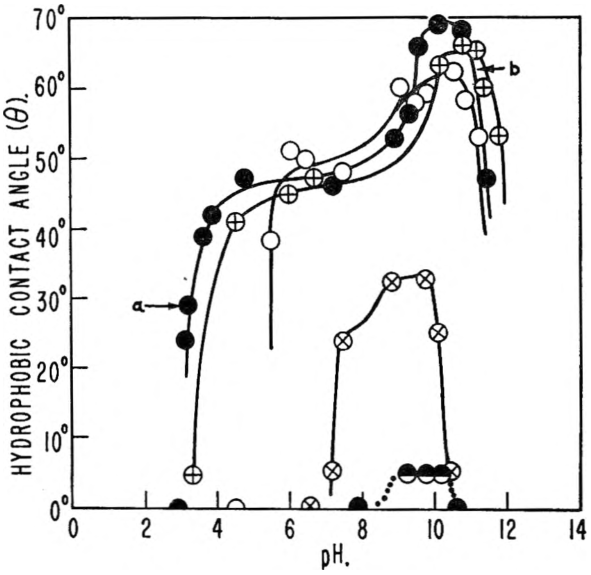

Fig. 1.—Adsorption of *n*-octylamine on platinum from aqueous solution, concentration (C_0) in moles/liter: ●, 5.18×10^{-4}; ⊕, 2.07×10^{-4}; ○, 5.18×10^{-5}; ⊗, 1.04×10^{-5}; ◓, 7.80×10^{-6}; wet, 2.34×10^{-6}.

Other investigators have also found that organic amines adsorb from aqueous solution most effectively in the more alkaline region of the *p*H scale on such materials as activated charcoal[7] and sphalerite, chalcocite and galena ores.[8-10]

Consideration is needed of the concentrations of the ions and molecular species present in the aqueous solutions from which adsorption occurred. These are H^+, OH^-, K^+, Cl^- and B and BH^+, where the last two symbols refer to the amine molecule and the amine ion derived from it. A calculation of the equilibrium concentrations of these ions and molecules can be based on the mass action law and the assumed dissociation equilibrium using concentrations rather than activities since the solutions are so dilute. The reaction assumed is

$$B + H_2O = BH^+ + OH^- \qquad (1)$$

Letting the dissociation constant of the amine be K_b, and the molar concentrations be C_{OH^-}, C_{BH^+} and C_B, and the concentration of the amine originally added to the water be C_0, then

$$\frac{(C_{BH^+})(C_{OH^-})}{C_B} = K_b \qquad (2)$$

where

$$C_{BH^+} + C_B = C_0 \qquad (3)$$

and

$$(C_{H^+})(C_{OH^-}) = 10^{-14} \qquad (4)$$

In these experiments K_b and C_0 were of the order of magnitude of 10^{-4}, hence we will assume $K_b = 10^{-4}$ and $C_0 = 10^{-4}$ mole/liter to simplify the calculations. Since K_b varies from 10^{-3} to 10^{-4} for nearly all aliphatic primary amines, this is a reasonable assumption. Now since by using equation (4) the concentration of hydroxyl ion is known for any particular *p*H, it is possible to calculate the corresponding concentrations of BH^+ and B utilizing expressions (2) and (3). The concentrations of K^+ and Cl^- are easily calculable from the respective amounts of potassium hydroxide or hydrochloric acid necessary to produce a given *p*H in the presence of the particular concentration of amine added (C_0).

If the hydrophobic behavior is assumed to be solely dependent on the solution concentration of free amine (C_B) and independent of the other species present, and since to a first approximation the amount adsorbed and hence the contact angle is directly proportional to some function of the concentration, a plot of C_B, or for convenience log C_B *versus* *p*H should be comparable with respect to the location of points of inflection with the experimental plot of ϑ *vs.* *p*H. Such a plot is shown in Fig. 2 where log C_B is the ordinate and the negative logarithm of the hydrogen ion concentration (*p*H) is the abscissa. It is seen that the concentration of free amine is essentially constant over the *p*H range of 10 to 12, and consequently the contact angle ϑ could be expected to be fairly constant. However, as seen in Fig. 1, ϑ decreases sharply in this *p*H range. Since in this *p*H region C_{BH^+}, C_{Cl^-} and C_{H^+} are negligible in comparison with C_B, C_{K^+} and C_{OH^-} and since C_B remains constant while C_{K^+} and C_{OH^-} are increasing, it can be concluded that either the K^+ or OH^- ion or both of these ions are adsorbed in preference to the free amine (B). Thus since adsorption of K^+ or OH^- ions would lead to hydrophilic behavior, the contact angle would decrease in this region of the *p*H scale. The absence of a plateau region in the plot of log C_B *versus* *p*H

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(4) M. L. Corrin and W. D. Harkins, *J. Am. Chem. Soc.*, **69**, 683 (1947).

(5) H. B. Klevens, *Chem. Revs.*, **47**, 1 (1950).

(6) J. W. McBain, "Colloid Science," D. C. Heath Co., Boston, 1950, Chap. 17.

(7) A. H. Andersen, *Acta Pharmacol. Toxicol.*, **3**, 199 (1947).

(8) A. M. Gaudin, *Mining and Metallurgy*, **10**, 19 (1929).

(9) H. H. Kellogg and H. Vásquez-Rosas, *Mining Technol.*, **9**, 1 (1945).

(10) I. W. Wark, "Principles of Flotation," Australasian Inst. Mining & Met., 1938.

is also significant, for the data in Fig. 1 lead one to conclude that the adsorbable species maintains a more or less constant concentration over the plateau segment of the curve. Since as shown in Fig. 2 the concentration of free amine is decreasing rapidly over this portion of the curve, it is apparent that one of the ion species in the system is adsorbing to yield hydrophobic films. Further evidence for such a belief is furnished through a consideration from Figs. 1 and 2 of the actual concentration of free amine at *p*H 8 (*ca.* 1 × 10^{-6}) and comparing this with the concentration of free amine at which complete wetting occurred (2.34 × 10^{-6}). Thus if the free amine (B) were the only species leading to hydrophobic behavior, complete wetting should have occurred around *p*H 8. Actually, as seen in Fig. 1 a contact angle of approximately 46° was evidenced at *p*H 8. Therefore, it is concluded that the hydrophobic behavior in the *p*H range of 8 to 3 is due to the adsorption of some species other than free amine.

Of the inorganic ions present (H^+, K^+, OH^- and Cl^-) none would yield hydrophobic films when adsorbed on platinum. Thus the only ion present which could lead to hydrophobic film formation is the amine (BH^+) ion. Others also have reported the adsorption of amine ions on films adsorbed at the oil–water interface,[11] on negatively charged monomolecular films,[12] on colloidal silver iodide,[13] various minerals,[8,10] and on steel in numerous pickling inhibitors.[14]

A plot of log C_{BH^+} *versus* *p*H is also shown in Fig. 2. By comparison of this curve with those of Fig. 1 and using arguments analogous to those presented concerning the free amine, it can be shown that the BH^+ ion is not the only adsorbable species leading to hydrophobic film formation nor is the adsorption of BH^+ ions independent of the concentrations of the other species present. Thus it has been shown that the hydrophobic films obtained from aqueous solutions of amines at varying *p*H are due to the adsorption of free amine (B) and amine ion (BH^+) and that the adsorption of these species decreases as the concentration of hydrophilic species increases.

The variation with *p*H of log X_B, the logarithm of the mole fraction of the amine (B), and of log X_{BH^+}, the logarithm of the mole fraction of the amine ion (BH^+), are also shown in Fig. 2. Considering X_B, it is significant that the maximum occurs at a *p*H of approximately 10, about the same *p*H at which the maximum contact angle occurs as seen in Fig. 1. With increasing *p*H, the mole fraction of B decreases rapidly. Contact angles also decreased rapidly in this region. Thus, insofar as the position of the maximum and the decrease from the maximum with an increase in *p*H, the plot of log X_B *versus* *p*H agrees very well with the experimental results of Fig. 1. With decreasing *p*H, *i.e.*, below 10, log X_B decreases rapidly without evidence of a plateau region in the *p*H range of 8 through 5. This is contrary to the experimental results of Fig. 1, but since in this *p*H range it has already shown that the other hydrophobic species, the BH^+ ion, must be the significant species leading to hydrophobic behavior, and since the concentration of free amine (B) is negligible compared to that of amine ion (BH^+), we will now consider the plot of log X_{BH^+} *versus* *p*H. This curve (Fig. 2) agrees well with Fig. 1 in that it possesses a plateau over the *p*H range of 8 through 5 while in the *p*H range of 5 to 2, it decreases rapidly with decreasing *p*H.

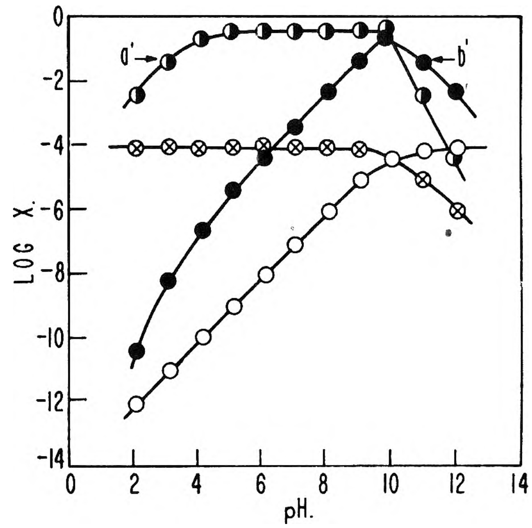

Fig. 2.—The effect of *p*H on the concentration of free amine (B) and amine ion (BH^+),

$$\text{assuming}\begin{cases} C_B + C_{BH^+} = C_0 = 10^{-4}\ \text{moles/liter} \\ K_b = 10^{-4} \end{cases}$$

○, $X = C_B$; ⊗, $X = C_{BH^+}$;

$$●,\ X = \frac{C_B}{C_B + C_{BH^+} + C_{H^+} + C_{OH^-} + C_{K^+} + C_{Cl^-}} = X_B;$$

$$◑,\ X = \frac{C_{BH^+}}{C_B + C_{BH^+} + C_{H^+} + C_{OH^-} + C_{K^+} + C_{Cl^-}} = X_{BH^+}.$$

At this point it is worth mentioning that since the relationships derived have been purely qualitative in nature, the inference is not justifiable that equal mole fractions of the hydrophobic ion (BH^+), where C_B is negligible, and of the hydrophobic amine molecule (B), where C_{BH^+} is negligible, would yield equal contact angles. To illustrate this factor, observed contact angles were taken from the data of Fig. 1 at *p*H values where X_{BH^+} is equal to X_B in Fig. 2. As seen in Fig. 2, X_{BH^+} at a *p*H of 3 is equal to X_B at a *p*H of 11. These points are shown as a′ and b′ in Fig. 2. Observed contact angles at *p*H 3 and *p*H 11 are shown as points a and b in Fig. 1. These values are 28 and 63°, respectively. Thus it is seen that under the conditions of the experiment, the adsorption of free amine (B) to the platinum surface results in a much greater degree of hydrophobicity than the adsorption of amine ion (BH^+). Since the ion (BH^+) differs from the molecule (B) only in that it possesses one more hydrogen atom and a positive charge, one is tempted to conclude that a more closely packed film results upon adsorption of free amine than from the adsorption of the amine ion. This appears reasonable since the repulsive forces between

(11) W. A. Zisman, *J. Chem. Phys.*, **9**, 534 (1941).

(12) D. J. Crisp, *Research (London) Suppl. Surface Chemistry*, 65 (1949).

(13) S. Bodforss, *Kgl. Fysiograf. Sällskrap. Lund. Handl.*, No. 12, 52 (1943).

(14) C. A. Mann, B. E. Lauer and C. T. Hultin, *Ind. Eng. Chem.*, **28**, 159 (1936).

positively charged (BH^+) ions would be expected to lead to a more loosely packed film structure.

Since the free amine (B) and the amine ion (BH^+) are both capable of hydrophobic film formation, the total mole fraction X_{B+BH^+} of hydrophobic species is the subject of interest, and evidently

$$X_{B+BH^+} = X_B + X_{BH^+} = \frac{C_B + C_{BH^+}}{C_B + C_{BH^+} + C_{H^+} + C_{OH^-} + C_{K^+} + C_{Cl^-}} \quad (5)$$

The plot of log X_{B+BH^+} *versus* pH is shown in Fig. 3 for an amine ($K_b = 10^{-4}$ and $C_0 = 10^{-4}$ moles/liter). It will be noted that this quantity reaches a maximum value at a pH of about 10, the same pH at which X_B reaches a maximum in Fig. 2, and approximately the same pH where ϑ has a peak value in Fig. 1. Since it has already been shown that adsorption of free amine results in films exhibiting higher contact angles than films arising from BH^+ ion, it is significant that the maximum mole fraction of free amine (B) occurs at about pH 10. Figure 3 is also qualitatively comparable with Fig. 1 for the two curves plotted for higher concentrations of amine than $C_0 = 10^{-4}$, *i.e.*, the location of maximum, the plateau region and the regions of numerically large slope. Clearly the mole fraction of hydrophobic species X_{B+BH^+} is one of the most significant quantities we can calculate for interpreting such adsorption experiments.

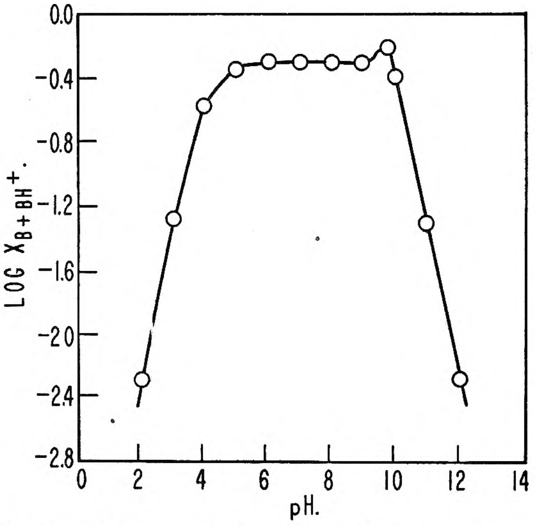

Fig. 3.—The effect of pH on the mole fraction of hydrophobic species for an amine. Calculated for

$$\begin{cases} C_B + C_{BH^+} = C_0 = 10^{-4} \text{ moles/liter} \\ K_b = 10^{-4} \end{cases}$$

Here $X_B + X_{BH^+} = \dfrac{C_B + C_{BH^+}}{C_B + C_{BH^+} + C_{H^+} + C_{OH^-} + C_{K^+} + C_{Cl^-}} = X_{B+BH^+}$

Effect of Varying Concentration and Dissociation Constant of Amine.—It is interesting to determine the effect of variation in concentration (C_0) on the position of maximum, width of the plateau segment, etc. The calculations were carried out utilizing expressions (2), (3) and (4) for an amine ($K_b = 10^{-5}$) at values of C_0 of 10^{-1}, 10^{-2}, 10^{-3}, 10^{-5} and 10^{-7} mole/liter. A plot of log X_{B+BH^+} *versus* pH for each concentration is shown in Fig. 4. With decreasing concentration, the maximum mole fraction of hydrophobic species becomes smaller and also the maximum occurs at decreasing pH values. It is also evident that the breadth of the plateau segment of the curve becomes smaller with decreasing concentration. Thus, the effect of concentration on the mole fraction of hydrophobic species is in agreement with the effect of concentration on the contact angle data shown in Fig. 1.

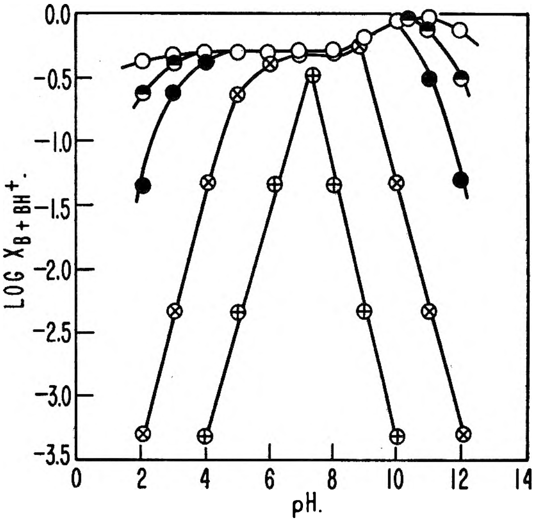

Fig. 4.—The effect of concentration on the relation of X_{B+BH^+} to pH for an amine ($K_b = 10^{-5}$), concentration (C_0) in moles/liter: ○, 10^{-1}; ◓, 10^{-2}; ●, 10^{-3}; ⊗, 10^{-5}; ⊕, 10^{-7}.

The effect on the log X_{B+BH^+} *vs.* pH curves of varying the dissociation constant (K_b) of the amine is shown in Fig. 5 for a concentration (C_0) of 10^{-3} mole/liter. With increasing values of the dissociation constant (increasing basicity of the amine), it is apparent that the maximum mole fraction of hydrophobic species decreases and occurs at increasing pH values. It is also seen that the width of the plateau segment of the curve increases with increasing values of K_b. Hence a very basic amine

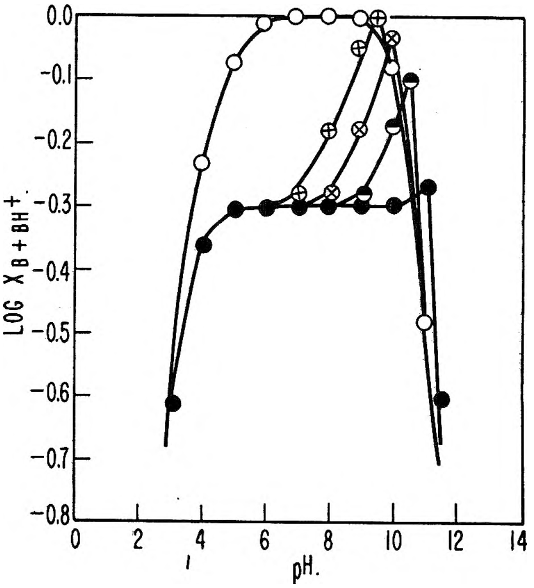

Fig. 5.—The effect of varying the dissociation constant (K_b) on the X_{B+BH^+} *vs.* pH curves for an amine (C_0 = 10^{-3} moles/liter): ○, $K_b = 10^{-10}$; ⊕, $K_b = 10^{-6}$; ⊗, $K_b = 10^{-5}$; ◓, $K_b = 10^{-4}$; ●, $K_b = 10^{-2}$.

($K_b \geqq 10^{-2}$) will exhibit a nearly flat-topped curve of ϑ *vs.* pH over nearly the entire range of pH. For a very weak base such as aniline ($K_b = 4.6 \times 10^{-10}$), it is evident that the mole fraction of hydrophobic species existing over the plateau region of the curve is essentially the same as the maximum mole fraction of hydrophobic species. It will subsequently be shown that this type of behavior could be predicted for a very slightly dissociated or undissociated hydrophobic compound.

Adsorption of Carboxylic Acids.—Recent research by Baker, Shafrin and Zisman[3] on the adsorption of water-soluble carboxylic acids on platinum has yielded analogous results to those just discussed for the *n*-alkyl amines. The results obtained for cyclohexylcarboxylic acid are shown in Fig. 6. The location of the points of inflection on this curve can be derived by the same method of calculation just used for the amines. The dissociation equilibrium involved is

$$\mathrm{HA} = \mathrm{H}^+ + \mathrm{A}^- \qquad (6)$$

where

$$\frac{(C_{\mathrm{H}^+})(C_{\mathrm{A}^-})}{C_{\mathrm{HA}}} = K_a \qquad (7)$$

and

$$C_{\mathrm{H}^+} + C_{\mathrm{A}^-} = C_0 \qquad (8)$$

Using exactly the same procedure as that previously described for an amine, it can be shown that both free acid (HA) and acid ion (A$^-$) are capable of adsorbing to a platinum surface to yield films exhibiting hydrophobic behavior. A plot of the logarithm of $X_{\mathrm{HA+A^-}}$, the total mole fraction of hydrophobic species, shows the essential features of Fig. 6 including a maximum at pH 4. Here

$$X_{\mathrm{HA+A^-}} = X_{\mathrm{HA}} + X_{\mathrm{A^-}} = \frac{C_{\mathrm{HA}} + C_{\mathrm{A^-}}}{C_{\mathrm{HA}} + C_{\mathrm{A^-}} + C_{\mathrm{H^+}} + C_{\mathrm{OH^-}} + C_{\mathrm{K^+}} + C_{\mathrm{Cl^-}}} \qquad (9)$$

However our initial assumption that the degree of hydrophobicity is proportional to $X_{\mathrm{HA+A^-}}$ leads to the implication that all ions and molecules are competing on an equal basis. As with the amines this is not true, and it is evident that our initial assumption could only lead to an approximate prediction of points of inflection and pH regions where the slope is large in magnitude. Nevertheless, the mole fraction of hydrophobic species is a valuable quantity in interpreting the adsorption experiments. It is interesting that the results of other investigators on the adsorption of carboxylic acids from aqueous solution have reported a maximum adsorption in the acid pH region for activated charcoal.[15,16]

Calculations of log $X_{\mathrm{HA+A^-}}$ were made and plotted against pH for an acid having a dissociation constant $K_a = 10^{-5}$ assuming a concentration C_0 of 10^{-1}, 10^{-2}, 10^{-3}, 10^{-5} and 10^{-7} mole/liter. With decreasing concentration, the maximum mole fraction of hydrophobic species becomes smaller and occurs at increasing pH values. The plateau segment as in the case of the amines contracts with decreasing concentration. These results on the effects of decreasing the concentration agree well with the contact angle *vs.* pH curves of Fig. 6.

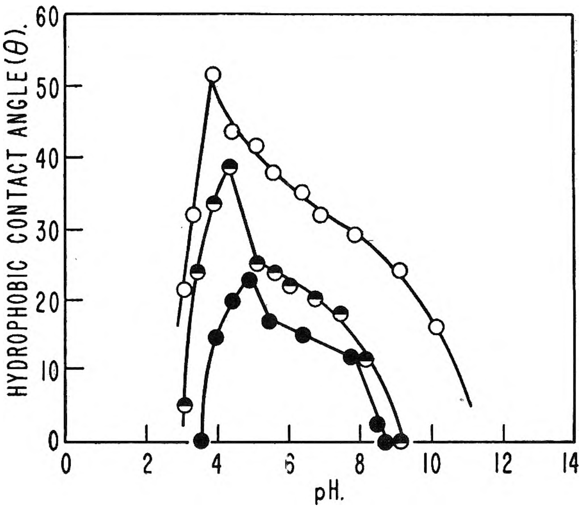

Fig. 6.—Adsorption of cyclohexyl carboxylic acid on platinum from aqueous solution, concentration (C_0) moles/liter: ○, 1.5×10^{-2}; ◒, 1.5×10^{-3}; ●, 1.5×10^{-4}; wets, 1.5×10^{-5}.

In Fig. 7 is shown the effect of varying the dissociation constant (K_a) of the carboxylic acid while maintaining a concentration (C_0) of 10^{-3} mole/liter. With increasing K_a, the maximum value of $X_{\mathrm{HA+A^-}}$ decreases and the pH at which the maximum occurs decreases. The breadth of the plateau segment of the curve increases with increasing values of K_a. Hence for the stronger acids ($K_a \geqq 10^{-2}$), the maximum practically has disappeared.

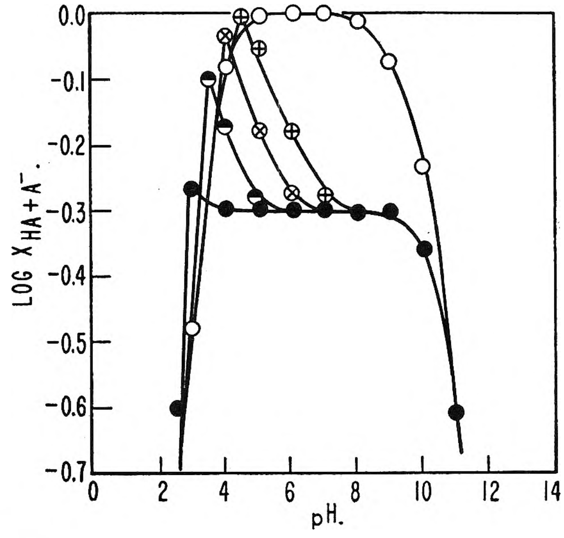

Fig. 7.—The effect of varying the dissociation constant K_a on the $X_{\mathrm{HA+A^-}}$ *vs.* pH curves for a carboxylic acid ($C_0 = 10^{-3}$ moles/liter): ○, $K_a = 10^{-10}$; ⊕, $K_a = 10^{-6}$; ⊗, $K_a = 10^{-5}$; ◒, $K_a = 10^{-4}$; ●, $K_a = 10^{-2}$.

Extension to Organic Bases, Acids and Non-ionized Compounds.—Although the arguments presented have been concerned with amines and carboxylic acids, they apply equally well to any organic base or acid for which the law of mass action holds over the concentration range of 10^{-6} to 10^{-2} mole/liter. It also can be extended to non-ionized molecules by either of two ways: (a) by considering the limiting case where either

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[15] G. Hesse and O. Sauter, *Naturwissenschaften*, **34**, 251 (1947).

[16] J. J. Kipling, *J. Chem. Soc.*, 1483 (1948).

$K_a = 0$ or $K_b = 0$, or (b) by calculating the mole fraction of the hydrophobic species for a system consisting of undissociated molecules and the H^+ ions, Cl^- ions K^+ ions and OH^- ions which are necessary to adjust the *p*H to each value of interest. Case (a) has already been covered in Fig. 5 by noting the envelope of maxima of the curves shown as K_b progressively decreased from 10^{-2} to 10^{-10}. A similar treatment with acids produces the same envelope in Fig. 7 as K_a is varied from 10^{-2} to 10^{-10}. It is interesting to work out case (b), and the calculations lead to the same conclusions as by method (a). Hence, it is concluded that for the highest concentration of hydrophobic material, the mole fraction of non-ionizable hydrophobic species X_U is essentially constant over a wide range of the *p*H scale and only commences to decrease significantly from this constant value in the very acid and very alkaline regions. With decreasing concentration of hydrophobic compound, X_U remains constant over a shortening range of *p*H values. A dilute aqueous solution of a non-ionized hydrophobic compound, therefore, would be expected to manifest the greatest hydrophobicity at *p*H 7.

A simpler method for visualizing both the effect of dissociation constant and concentration on the contact angle *vs.* *p*H curves is shown in Fig. 8. There the logarithm of the dissociation constant (*pK*) is plotted as ordinate and the abscissa is the *p*H of the peak of the curve of the mole fraction of the hydrophobic species *vs.* *p*H. Curves for concentrations (C_0) of either acid or base of 10^{-2}, 10^{-3}, 10^{-4}, 10^{-5} and 10^{-6} mole/liter are plotted. This is a useful summary of the effect of both concentration and dissociation constant on the contact angle *vs.* *p*H curves. It is evident from Fig. 8 that water-soluble organic acids and organic bases are always distinguished by the fact that the peak of the ϑ *vs.* *p*H curve occurs below *p*H 7 for acids and above *p*H 7 for bases.

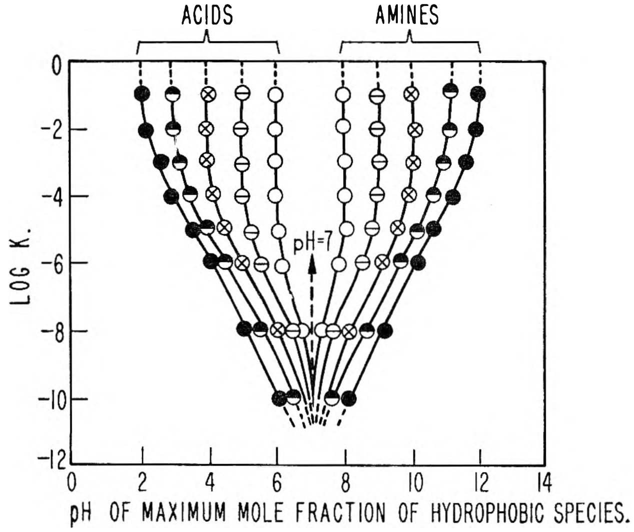

Fig. 8.—The effect of dissociation constant (*K*) and concentration on the *p*H for peak hydrophobic adsorption on platinum of an amine or an acid, concentration (C_0) moles/liter: ○, 10^{-6}; ⊖, 10^{-5}; ⊗, 10^{-4}; ◓, 10^{-3}; ●, 10^{-2}.

Discussion

Throughout these calculations it has been assumed that the physical condition and chemical nature of the adsorbing solid surface was not affected by the changes of *p*H and of concentrations of molecules or ions present. This was entirely reasonable as far as platinum foil was concerned. As the results are entirely concerned with physical adsorption, they should apply equally well to other unreactive metals like gold, silver, nickel, molybdenum, chromium and stainless steel, and even to many non-metallic and unreactive solids.

One of the striking features of all the graphs of contact angle *vs.* *pH* or of mole fraction of hydrophobic species (*X*) *vs.* *p*H, is the rapid drop of ϑ (or log *X*) with rising *p*H around *p*H 11 to *p*H 12 due to the increasing competitive adsorption of hydrophilic hydroxyl ions. It is worthy of note that the same effect occurs widely in the mining technology of froth flotation where it is commonly described as the "flotation depressant action" of alkalies.[10] The equally striking rapid decrease in ϑ as the *p*H decreases below 3 is due to the preferential adsorption on platinum of the hydrophilic hydrogen ion. Where more ionizable metals than platinum (those above hydrogen in the electrochemical series of elements) are studied, it is evident that affairs cannot be so simply described because they become complicated by the evolution of hydrogen gas or by other chemical changes.

The conclusions reached here should be of interest in connection with research on (a) the inhibition of corrosion by organic type compounds, (b) electrode phenomena in the field of electrochemistry and (c) wear prevention in aqueous lubricants, for they make more understandable the role played by physical adsorption and the effect of the competition between the hydrophobic and hydrophilic ions and molecules. Where the surface chemical reaction occurs slowly or after a series of preliminary steps, the entire process cannot be understood without proper recognition being given to the initiating physical adsorption mechanism and the variables influencing it.

Acknowledgments.—The authors wish to express their appreciation of the interest and cooperation of Elaine G. Shafrin and H. R. Baker.

THE ADSORPTION OF HYDROPHOBIC MONOLAYERS OF CARBOXYLIC ACIDS[1,2]

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The adsorption technique reported previously has been successfully extended to the study of monolayers physically adsorbed onto platinum from aqueous solutions of a variety of types of mono- and dicarboxylic acids. The effects have been investigated of varying the molal concentration of organic acid over a 10,000-fold range. The condition for maximum adsorption, as evidenced by peak hydrophobic behavior (θ_p), has been found to lie between *p*H 4 and 6. Both the shape of the θ *vs.* *p*H curve and the positions of the points of inflection were in good agreement with the results predicted by the theoretical treatment of Merker and Zisman[2]; it was therefore concluded that the *p*H effects observed were due primarily to the competitive adsorption between the molecular and ionic species in solution rather than to micelle formation or association. Progressive increases in solute concentration for a given acid have been found to result in the asymptotic approach of θ_p to a characteristic, limiting value, θ_{lim}.

A new and convenient "thermal-gradient method" using the pure, molten compound has been found by which adsorbed, close-packed monolayers can be prepared and isolated on metal in the absence of solvent. It is more general than the oleophobic methods described in previous reports, since it has been found applicable to all amphipathic compounds tried, whether straight-chain, branched or cyclic. The equivalence of the contact angle (θ_{melt}) obtained from films made from the molten polar compounds with that (θ_{lim}) of the films adsorbed from aqueous and non-aqueous solutions has been demonstrated.

The way in which the contact angle characteristic of each polar compound (θ_{lim} or θ_{melt}) varies with the nature of the acid and with homology has been studied and a correlation of the results with molecular orientation, structure and packing has been attempted.

A previous study of hydrophobic monomolecular films of primary *n*-alkyl amines adsorbed on platinum and isolated from aqueous solution[3] had established an effective technique for investigating physically adsorbed monolayers of compounds which are not capable of forming oleophobic films.[4,5] In that study, the critical concentrations for hydrophobic film formation and the degree of wettability of hydrophobic films of the alkylamines were reported as functions of the alkyl chain length, the amine concentration, and the *p*H of the aqueous solution. This report is concerned with the extension of the same methods to the adsorption from aqueous solution of various carboxylic acids, including representative monocarboxylic acids of the *n*-alkyl, cyclo-alkyl, and aryl-alkyl types, some homologous α,ω-dicarboxylic acids, and a group of alkyl-substituted succinic acids.

Experimental

The experimental procedure employed was essentially that described previously.[3] The films were always adsorbed, isolated and measured at 20.0 ± 0.1°. The films were adsorbed upon freshly flamed dippers of carefully selected, scratch-free, commercial platinum foil, as in earlier studies. Contact of the adsorbing surfaces with the aqueous solutions of organic acids was limited to an immersion period of 30 seconds.

The solutions used in the adsorption measurements were made as in our earlier paper.[3] The organic acids employed represented, with the exception of those mentioned in the Acknowledgments, compounds of the highest purity available commercially; the majority of these materials were subjected to further purification by repeated recrystallization from appropriate solvents. The melting points of the compounds as used have been listed in the second column of Table I. The *n*-alkylamines were the same compounds used in previous work.[4,5]

Table I

Hydrophobic Contact Angles[a] For Monolayers of Carboxylic Acids Adsorbed on Platinum

Acid	N[b]	M.p., °C.	Films prepared from aqueous solution, θ_{lim}	Films prepared from molten compound by thermal gradient method θ_{melt} Receding drop	θ_{melt} Advancing drop
		n-Alkyl monoacids			
Caproic	6	....	52°	49°	53°
Caprylic	8	16	62	59	64
Capric	10	31.5	70	66	70
Lauric	12	42-43	76	71	75
Myristic	14	52-53	..	75	78
Palmitic	16	61-62	..	79	83
Stearic	18	68-69.5	..	81	88
Behenic	22	80.0-80.3	..	89	96
		Cycloalkyl monoacids			
Cyclohexylcarboxylic	7	29.5-30.5	53	44	52
Cyclohexylacetic	8	28.5	..	65	76
Cyclohexylpropionic	9	15.0	64	66	76
Cyclohexylbutyric	10	29	..	64	74
Cyclohexylcaproic	12	>32	66	64	75
		Aromatic monoacids			
Benzoic	7	123-125	53	46	48
Phenylbutyric	10	49-50	..	45	49
		α,ω-Alkane dicarboxylic acids			
Succinic	4	185-186	29	24	26
Adipic	6	151	40	35	40
Sebacic	10	129	54	52	56
Dodecanedioic	12	125-126	..	62	65
Tetradecanedioic	14	124.5-125.5	..	72	76
		n-Alkyl succinic acids			
Octylsuccinic	12	88-89	71	69	73
Decylsuccinic	14	92.5-95	72	71	76
Octadecylsuccinic	22	104-106	77	72	79

[a] Contact angle measurements made at 20.0 ± 0.1°. [b] N = Total number of carbon atoms per molecule.

Measurements of the hydrophobic contact angle (θ) on films isolated from aqueous solutions were made, as before, with drops of the generating solutions at the same concentration and *p*H at which the individual films were formed. Since conditions of solution equilibrium obtained, dissolution of the film into the superjacent drop was avoided. Changes in *p*H were effected by the dropwise addition of

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(1) Presented at the Symposium on Surface Chemistry in Corrosion which was held under the auspices of the Division of Colloid Chemistry of the American Chemical Society at the 119th National Meeting (Divided) at Cleveland, Ohio, April 9, 1951. The opinions or assertions contained in this paper are the authors' and are not to be construed as official or reflecting the views of the Navy Department.

(2) R. L. Merker and W. A. Zisman, This Journal, **56**, 399 (1952).

(3) E. G. Shafrin and W. A. Zisman, *J. Colloid Sci.*, **4**, 571 (1949).

(4) W. C. Bigelow, E. Glass and W. A. Zisman, *ibid.*, **2**, 563 (1947).

(5) W. C. Bigelow, D. L. Pickett and W. A. Zisman, *ibid.*, **1**, 513 (1946).

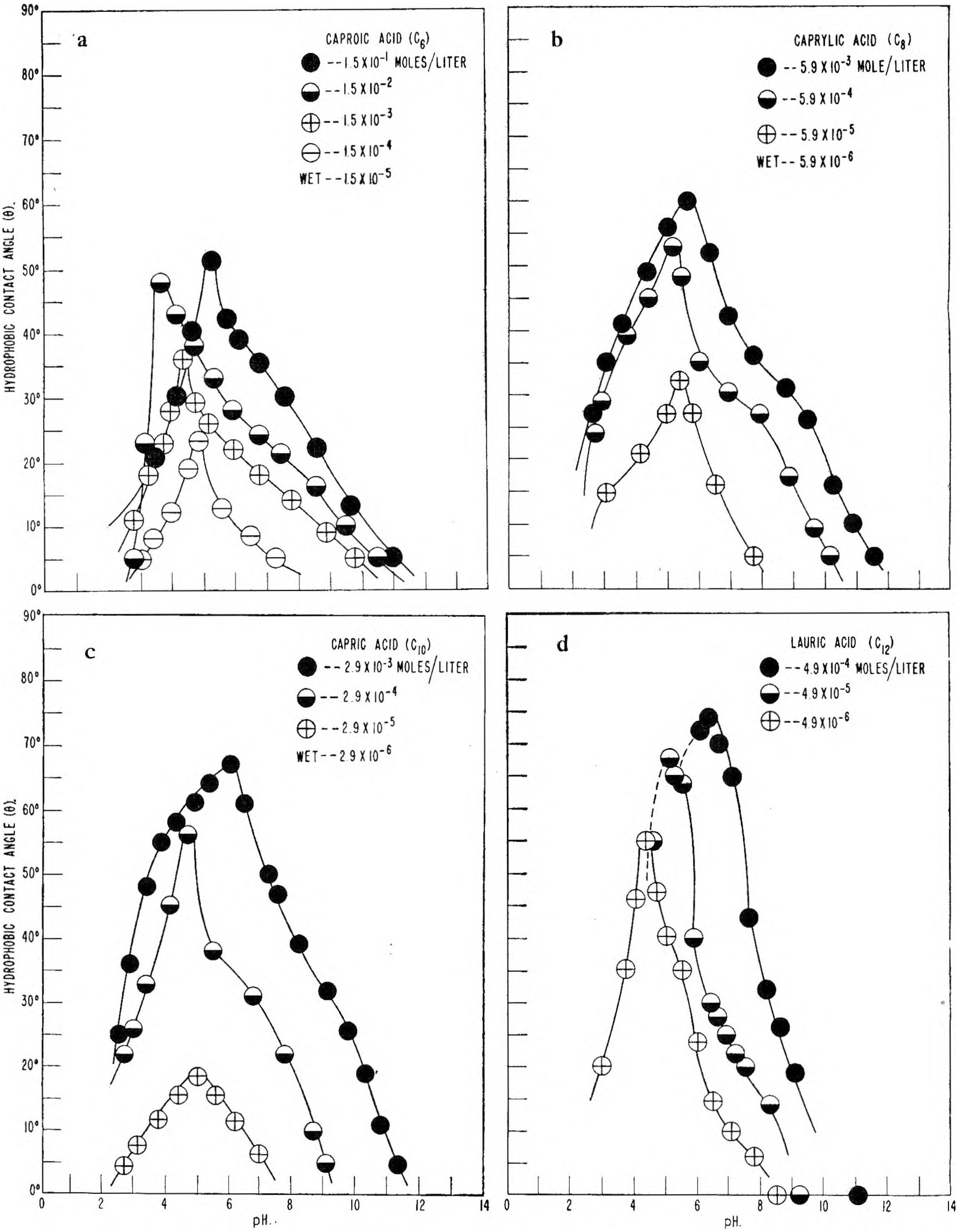

Fig. 1.—Effect of pH on hydrophobicity of n-alkyl monocarboxylic acids: a, n-caproic acid (C_6); b, n-caprylic acid (C_8); c, n-capric acid (C_{10}); d, n-lauric acid (C_{12}).

aqueous HCl or KOH to the acid solution with continuous stirring. The presence of electrolytes is known to influence markedly the adsorption of hydrophobic films on minerals,[6] the critical concentration for micelle formation in aqueous soap solutions,[7] and the surface tension of solutions.[8] Precautions were therefore observed to keep the concentration of added electrolytes as low as possible, consistent with the adjustment of the pH. For the more soluble compounds and for low concentrations, the pH response was investigated for two separate portions of the solution, to one of which was added HCl only and to the other KOH only. For the more insoluble acids the initial addition of KOH was sometimes required to facilitate the dissolving at higher concentrations; in such cases it was impossible to avoid the presence of neutral salts. Periodic checks to determine the effect of excess electrolytes on the reproducibility of the θ $vs.$ pH curves, with one exception, revealed no significant differences. Attempts to retrace the acidic portion of a

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[6] I. W. Wark, "Principles of Flotation," Australasian Institute of Mining and Metallurgy, Melbourne, Australia, 1938.

[7] F. A. Long, G. C. Nutting and W. D. Harkins, *J. Am. Chem. Soc.*, **59**, 2197 (1937).

[8] J. Powney, *Trans. Faraday Soc.*, **31** 1510 (1935).

curve for benzoic acid solution from pH 2 to its peak, in the presence of an unavoidably high concentration of HCl, were only partially successful. Although the general shape of the curve was repeatable, subsequent values of the peak angle (θ_p) were never as high as the original value. The curve was more nearly reproducible when approached from the alkaline direction despite the presence of excess KOH.

Measurements of hydrophobic contact angles on films isolated directly from melts of pure compounds necessitated the use of distilled water, thus unavoidably increasing the probability that films of the more soluble organic compounds dissolved into the test drops. Because of the experimental difficulties involved in transferring a drop of water onto a highly hydrophobic surface, it was frequently difficult to ensure the initial existence of an advancing contact angle. The introduction of additional liquid into a drop already in contact with the monolayer was found to increase the contact angle from a somewhat low initial value to a reproducible, limiting, maximum value equivalent to the advancing contact angle.

Monocarboxylic Acids.—The change in contact angle (θ) with pH for each of several concentrations (W) of four n-alkyl monocarboxylic acids in aqueous solution is shown (Figs. 1a,b,c,d) for caproic (C_6), caprylic (C_8), capric (C_{10}) and lauric acids (C_{12}). At least four different concentrations, representing a 10,000-fold increase in solute, were investigated over a pH range of 2 to 13 at intervals of 0.5- to 1.0 pH unit. Each curve is the locus of points obtained from solutions having the same concentration.

The families of curves for the four acids followed the same general pattern: The individual curves rose sharply from some low value between pH 2 and 3 to a peak value (θ_p) in the region pH 3–6, then slowly declined (revealing an occasional secondary, plateau-like feature) until they intersected the $\theta = 0°$ axis between pH 8 and 12. The extreme insolubility of lauric acid precluded the completion of the low pH portion of the high-concentration curves; the presence of precipitate or solution cloudiness has been indicated by dashed lines over the appropriate pH range. The curves for successively less concentrated solutions of a given acid covered a smaller span of pH values, extended less into the alkaline pH range, and exhibited lower peak contact angles. Eventually a concentration was reached so dilute that no signs of hydrophobic film formation were obtained at any pH within the allotted, 30-second immersion period. The existence of a critical minimum concentration (W_0) necessary for formation of a solution repellent film had been established in previous studies,[3,5] where W_0 had been shown to be a measure of the total number of molecules available to an adsorbing surface within a given period of time, and thus to be a function of such experimental conditions as concentration, volume and rate of stirring of the solution.

A plot of θ_p as a function of W for each of these acids (Fig. 2) shows an initial, sharp rise for concentrations just above W_0, followed by an asymptotic approach (indicated by dashed lines) to some limiting angle (θ_{lim}). The regularity of the change in θ_{lim} in the homologous series of acids is evident in the third column of Table I. Proof that θ_{lim} is characteristic of the composition of the monolayer and independent of the method of film formation (providing maximum adsorption occurs) is afforded by a comparison of θ_{lim} with the values listed for the angles exhibited by drops of distilled water in contact with the corresponding monolayers adsorbed from the molten, pure compound by the thermal-gradient method described later. Values of θ_{melt} (advancing) have been indicated by bars at the extreme right of Fig. 2. There is good agreement between the several values despite the limitations imposed by the diverse experimental techniques. Since the molecular interstices of a film isolated from aqueous solution must be saturated with water,[9] θ_{lim} is the same as a receding contact angle. In determining θ_{melt}, however, both receding and advancing contact angle measurements are possible. The duplication of θ_{melt} for the more soluble homologs under conditions corresponding to receding contact angles is complicated by the lack of solution equilibrium between the films and the test drops. This tendency toward dissolution is eliminated in determining θ_{lim} since test drops of the generating solution are available.

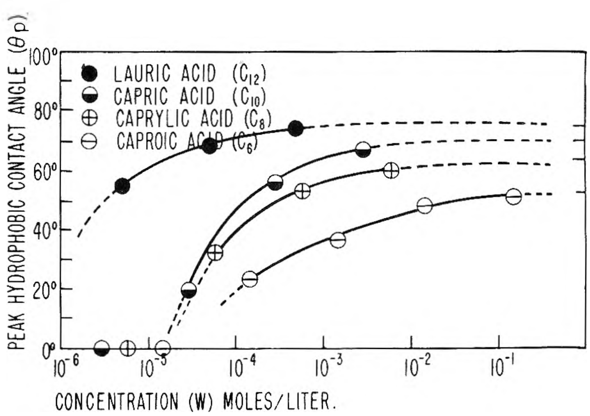

Fig. 2.—Correlation of peak contact angle (θ_p) with concentration for n-alkyl monocarboxylic acids.

The θ *vs.* pH curves for cyclohexylcarboxylic (C_7), cyclohexylpropionic (C_9) and cyclohexylcaproic (C_{12}) acids adsorbed from aqueous solution are essentially identical with those shown in Fig. 1; differences occur only in the concentrations investigated and in the relative hydrophobicity (*i.e.*, the magnitude of θ) of the acid films. The limited solubility of cyclohexylcaproic acid in water prevented completion of the curves for the higher concentrations since extensive precipitation occurred before θ_p could be determined. An indication that the highest value of θ_p obtainable experimentally (63°) approximated θ_{lim} lay in the value of 64° observed for θ_{melt} under conditions leading to a receding contact angle. The results obtained with benzoic acid, including the behavior to changes in pH and concentration as well as the value of θ_{lim}, were nearly the same as those obtained for the corresponding saturated cyclic acid.

In the plot of θ_p *vs.* W for the four cyclic acids (Fig. 3), the asymptotic approach to θ_{lim} is indicated by a dashed line and the appropriate value of θ_{melt} by a bar at the right of the figure.

Dicarboxylic Acids.—The general behavior of the graph of θ *vs.* pH for three homologous α,ω-dicarboxylic acids (succinic (C_4), adipic (C_6) and sebacic (C_{10}) acids) is similar to that previously observed

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[9] H. R. Baker and W. A. Zisman, *Ind. Eng. Chem.*, **40**, 2338 (1948).

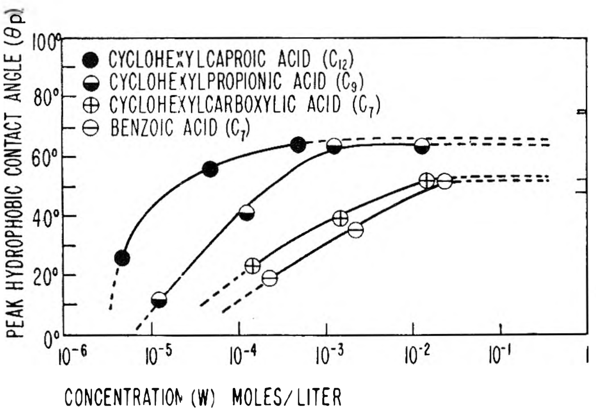

Fig. 3.—Correlation of peak contact angle (θ_p) with concentration for cyclic monocarboxylic acids.

for the monocarboxylic acids. A summary of the θ_p *vs.* W data for these compounds is to be found in Fig. 4.

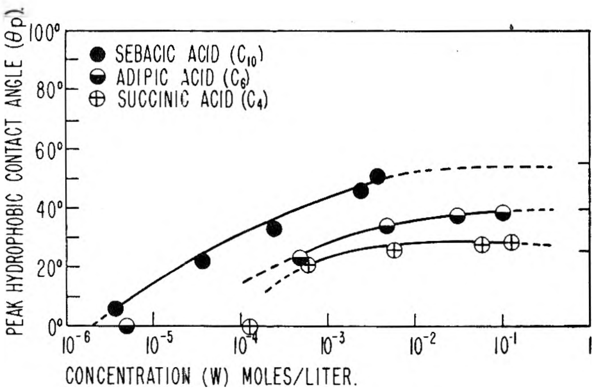

Fig. 4.—Correlation of peak contact angle (θ_p) with concentration for α,ω-alkyl dicarboxylic acids.

The θ *vs.* pH curves for decylsuccinic (C_{14}) and octadecylsuccinic (C_{22}) acids were similar to those shown in Fig. 1 over the alkaline region in which they were determinable; the acidic side of the curves could not be obtained owing to the extreme insolubility of these compounds. Indeed, the addition of ethyl alcohol was required for all pH values below 7.8 in order to determine θ_p for the most concentrated solutions of octadecylsuccinic acid. In the complete curves obtainable for the more soluble octylsuccinic acid (C_{12}) a reproducible, well-developed "shoulder" occurred on the acidic side of the peak.

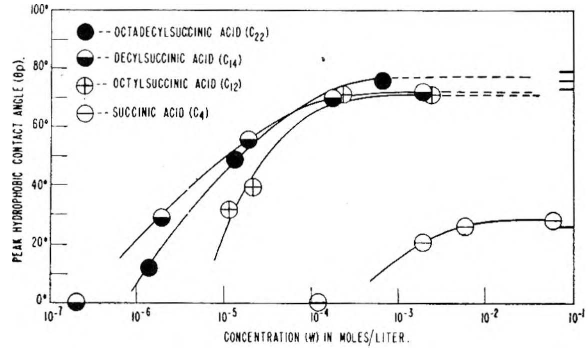

Fig. 5.—Correlation of peak contact angle (θ_p) with concentration for alkylsuccinic acids.

Thermal-Gradient Method.—Previous success in isolating adsorbed monolayers by withdrawing the platinum dipper from a pool of the molten polar compound[4] had been limited to those essentially paraffinic or unbranched types of compounds meeting the requirements of structure and orientation developed earlier[5] for formation of oleophobic films. It became possible, by this "isothermal method," to prepare monolayers of those lower series members which were not sufficiently oleophobic to permit their isolation from oil solution. This method was not effective, however, in isolating monolayers of highly-branched or cyclic compounds; even for straight-chain compounds, its effectiveness in preparing monolayers completely free of residual bulk compound was limited by the working range of temperature between the melting point of the compound and the temperature, τ, at which the monolayer became wetted by the melt.

The need for a method of preparing monolayers of any type compound in the absence of solvent led to much experimenting with ways other than the isothermal method of separating films from the melt. The result was the "thermal-gradient method." A small amount of pure compound was placed on a piece of platinum foil held with its plane slightly inclined from the horizontal. After the uppermost edge of the platinum was gently heated, the organic material melted and wet the metal surface. As the heating continued, the molten liquid suddenly receded to the lower, cooler edge of the platinum, exposing a dry area in a band immediately adjacent to the liquid. This occurred at a temperature slightly below that required for visible vaporization of the organic compound from the hot, upper edge of the foil. If the foil was cooled to room temperature (20°) while still tilted, the organic material remained at the lower edge where it either solidified or, if liquid, drained off upon contact with filter paper. Hydrophobic contact angle measurements taken at various positions over the surface of the foil were large and reproducible only over the "dry band" immediately adjacent to the bulk material. Lower and erratic contact angles were observed near the uppermost edge of the foil where the higher temperature may well have led to the vaporization of some of the organic film.

Proof that this thermal-gradient method gives rise to monolayers in the "dry band" identical with those prepared by earlier methods is afforded by a comparison (Table II) of the hydrophobic contact angles observed on monolayers of several n-alkyl pri-amines isolated from the melt by the isothermal and thermal-gradient methods with those obtained on monolayers adsorbed from dilute solution in cetane or water. The agreement between the several values is good, considering the experimental limitations. These include the impossibility of obtaining true advancing angles on films isolated from aqueous solution and the inability to duplicate conditions of solution equilibrium for films obtained from the melt. For those longer chain compounds for which solubility effects become negligible, the direct comparison of the values listed for the receding contact angles is warranted.

TABLE II

COMPARISON OF HYDROPHOBIC FILMS OF AMINES

		Films prepared from						
		Molten compound				Cetane soln. by oleophobic method[b]		Water soln. by hydrophobic method
		By thermal-gradient method[b]		By isothermal method[b]				
n-Alkyl amine	N[a]	Advancing	Receding	Advancing	Receding	Advancing	Receding	$\theta_{\lim}$
Butylamine	4	55°	48°	55°	51°	..	..	52°[c]
Octylamine	8	81	67	74	69	73°	68°	69[c]
Dodecylamine	12	90	83	89	83	89	83	85[c]
Tetradecylamine	14	91	84	92	87	90	86	86[c]
Hexadecylamine	16	96	87	96	89	96	89	89[c]
Octadecylamine	18	102	89	102	91	101	90	90[b]

[a] N = total number of carbon atoms per molecule. [b] Measurements were made at temperature 20.0 ±0.1°. [c] Measurements were made at temperature 25 ±1°. These data were reproduced from Table II in reference 3.

Because of the difficulty encountered in contacting drops of water to highly hydrophobic surfaces, the method of increasing the size of the drop was employed to ensure development of advancing angles. Since this precaution was not taken in the previous study of amine monolayers,[3] the contact angles reported earlier for water on amine films need not correspond to advancing angles, as do the values listed in Table II; the divergence is greater for the longer chain, more hydrophobic homologs. A similar qualification is believed applicable to the other contact angle values reported for water on highly hydrophobic monolayers.[4,5]

Possible mechanisms for the thermal-gradient method may involve one or more of the following factors: (a) the preferential evaporation of all the organic molecules except those strongly adherent ones adsorbed in direct contact with the metal surface; (b) a gravitational diffusion of all molecules except those anchored in the monolayer, involving, perhaps, the ease of slippage of the molecules in the liquid with respect to the external plane presented by the oriented array of adsorbed molecules; and (c) the existence of a relatively narrow range of temperatures over which the oleophobic property of the liquid and the adsorbed film can become operative. Definitive experiments are in progress to determine the actual mechanism.

By the use of the thermal-gradient method, monolayers have been obtained from the melt for every acid of interest in the present study. Data for the hydrophobic contact angles (θ_{melt}) have been listed in Table I for comparison with the values of $\theta_{\lim}$ obtained for films from aqueous solution. The maximum hydrophobicity obtainable from an adsorbed close-packed monolayer can evidently be measured quickly by the thermal-gradient method, eliminating the more laborious evaluation of $\theta_{\lim}$ based on θ_p *vs.* W data. Moreover, this method of film preparation makes possible the measurement of advancing angles, whereas receding angles only are obtainable for films adsorbed from aqueous solution. In addition, a fuller correlation of hydrophobicity with chain length and acid type becomes possible since there is no longer any restriction to the lower, more water-soluble members of the series. Thus, for the n-alkyl monocarboxylic acids, for which $\theta_{\lim}$ data are available only for the homologs up to $N = 12$, it has been possible, by this new method, to obtain monolayers and to measure the effect of chain length on hydrophobicity for the series through $N = 22$ (curve A, Fig. 6a).

TABLE III

COMPARISON OF EXPERIMENTAL CURVES OF θ_{melt} *vs.* N FOR SEVERAL HOMOLOGOUS SERIES

Homologous series	Slope (degrees/carbon increment)	θ for N = 10
n-Alkyl pri-amines	2.0°	80°
n-Alkyl monoacids	2.2	70
Cycloalkyl monoacids	0	75
Aryl–alkyl monoacids	0	49
α,ω-Alkane dicarboxylic acids	4.9	56
n-Alkyl succinic acids	0.5	73

In Figs. 6a and 6b are presented data showing the effect on θ_{melt} of the length of the alkyl chain. Within each series the data for all but an occasional lowest homolog are well represented by a straight line. Changes in the hydrocarbon portion of the molecule or in the number and type of functional groups in going from one homologous series to another are reflected in the slopes and positions of the lines. These slopes are listed in Table III; the relative positions of the lines have been indicated by listing the arbitrarily chosen intercepts of the lines with the ordinate $N = 10$. The implications of these data will be more fully developed in the next section.

Discussion

Numerous investigators have described the effects of pH variation on the surface–chemical properties of aqueous solutions of the carboxylic acids and their salts. These include effects on surface and interfacial tension,[7,8,10,11,12] detergency,[13] flotation of minerals,[6,14] and stability of foams.[15,16] In most cases the variations observed were attributed to the relative proportions, solubilities and surface activities of the carboxylic acid anions, the hydrolytic free acid, the undissociated soap molecules, the acid–soaps, and the colloidal micelles or other aggregates. In general, maximum surface activity was obtained at those pH values which corresponded to partial or complete hydrolysis of the soap, indicating the molecular form of the acid to be

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(10) L. Chromy, *Roczniki Chem.*, **18**, 434 (1938).

(11) H. L. Cupples, *Ind. Eng. Chem.*, **29**, 924 (1937).

(12) J. K. Davis and F. E. Bartell, THIS JOURNAL, **47**, 40 (1943).

(13) W. W. Niven, Jr., "Fundamentals of Detergency," Reinhold Publishing Corp., New York, N. Y., 1950.

(14) H. H. Kellogg and H. Vasquez-Rosas, *Mining Technology*, **9**, 1 (1945).

(15) C. L. Baker, *Ind. Eng. Chem.*, **23**, 1025 (1931).

(16) G. D. Miles and J. Ross, THIS JOURNAL, **48**, 280 (1944).

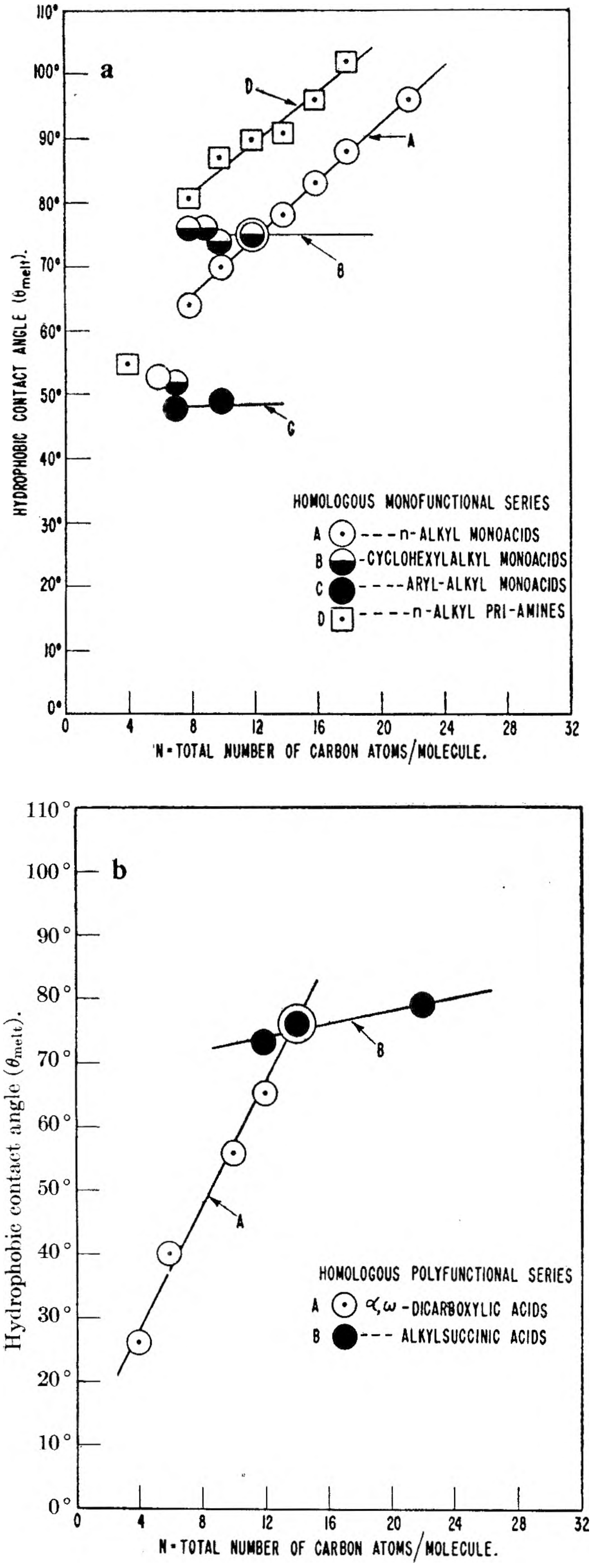

Fig. 6.—Effect of chain length on hydrophobic contact angle: *a*, homologous monofunctional series; *b*, homologous polyfunctional series.

the more surface active species, at least in dilute solution. The results of research have recently been summarized on the critical micelle concentration (CMC) of various soaps and the effects of salts in decreasing the CMC.[17,18] From these it is concluded that the concentrations of acids and soaps used in this investigation in the more dilute solutions were too low to permit micelle formation.

The relative importance of the various ions and molecules of organic acid present in aqueous solution and their influence on the adsorption of hydrophobic monolayers are being reported separately in a related paper by Merker and Zisman.[2] As a result of a preliminary report of the experimental observations related here, they were led to attempt the correlation of hydrophobic behavior with composition of the adsorbed films. Curves representing the concentration in solution of the various adsorbable entities present at different *p*H values were derived by them from the application of the law of mass action. By postulating an adsorption equilibrium in which, as a first approximation, the same relative proportions of the various species were maintained in the adsorbed film as in the generating solution, they were able to conclude that the sharp decrease in hydrophobicity noted for films prepared at both extremes of the *p*H scale is due to the competitive adsorption of the appropriate hydrophilic aqueous ions (H^+ or OH^-) whereas the hydrophobic character of films adsorbed in the intermediate *p*H range is due to the adsorption of the hydrophobic carboxylate ions and neutral acid molecules. The peak angle was shown to occur at the *p*H favoring the adsorption of a film composed primarily of the undissociated acid. This *p*H value was shown by them to be predictable, given the dissociation constant for a weak acid. Good agreement was obtained between the theoretically derived curves and subsequent experimental observations.

From its definition, it is evident that θ_{lim} is characteristic of monolayers in the closest packed arrangement obtainable by adsorption from aqueous solution. Provided the solubility of the organic compound is sufficient, θ_{lim} will also correspond to the maximum packing obtainable from solution in any solvent; the only exceptions to be expected occurring under conditions of adsorption of mixed films of solvent and solute. Hence it is not surprising that essentially the same values of θ have been reported for saturated films prepared by adsorption from water, ethanol–water, benzene, dicyclohexyl or hexadecane. Since in the limit a solution of increasing concentration will approach in behavior that of the pure molten acid, θ_{lim} should equal θ_{melt}, the exceptions occurring where there are marked effects on the orientation or packing of the adsorbed film due (a) to the higher temperature often needed to produce monolayers from the melt, or (b) to any differences in the films because of mixed film formation. This agreement of θ_{lim} and θ_{melt} is well exhibited in Tables I and II.

The thermal-gradient method is valuable in making available data on the relative hydrophobicity of closest packed monolayers not otherwise obtainable. Since this method requires less experimental manipulation than other adsorption techniques, its use facilititates the rapid survey of the

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(17) H. B. Klevens, *Chem. Revs.*, **47**, 1 (1950).

(18) J. W. McBain, "Colloid Science," D. C. Heath Co., Boston, Mass., 1950, chapter 17.

film-forming possibilities for a wide variety of structural types of polar compounds. It should also prove useful in future studies of the adsorption of polar compounds on metals more reactive than platinum.

In curves A and D of Fig. 6a, data for the two most comparable homologous series, the *n*-alkyl monocarboxylic acids and pri-amines, are seen to be represented by two parallel straight lines (Table III). Since this type of molecule adsorbs with the dipole at the metal surface and the hydrocarbon chain extended and oriented approximately normal to the adsorbing plane,[19] lengthening the alkyl chain increases the van der Waals cohesive forces between adjacent chains and thus leads to a closer packing of the chains; this, in turn, is reflected in an increased water repellency for the films. For compounds of longer chain length than those reported here, a saturation effect can be expected for θ at or below 108°, the value frequently seen in the literature for water on paraffin. The identity of the slopes for the acid and amine series is indicative of the equivalent effectiveness of increasing chain length on the hydrophobicity of monolayers characterized by this molecular orientation. The displacement of the acid curve some 10° below that for the amines is consistent with the following, previously reported, relative adsorptive properties of amines and acids for a given chain length: (a) amines adsorbed from solution in hexadecane or dicyclohexyl have the longer lifetimes of adsorption,[4,5] and (b) amine monolayers are more resistant than acid monolayers to thermal desorption effects, since the former require approximately an 80° increase in τ, the temperature characteristic for the wetting of the film by the pure molten compound.[4]

A horizontal straight line represents the data for all of the cyclohexylalkyl monoacids with one exception (Curve B in Fig. 6a). In the case of cyclohexylcarboxylic acid, the absence of a methylene link between the polar group and the cyclic group is reflected by a sharp drop in the hydrophobicity of the monolayer. The existence of a limiting, maximum water repellency, independent of chain length above $N = 8$, may be explained if it is assumed that: (a) the plane of the cyclic group is approximately normal to the adsorbing surface, and (b) the maximum hydrophobicity observed corresponds to the closest packing possible for the cyclohexyl groups. If the effective cross-sectional area of the terminal cyclohexyl group is greater, for saturation packing, than that of the underlying alkyl chain, increases in the length of the chain should have no effect on the hydrophobic contact angle; this would account for the horizontal line obtained experimentally for θ for values of N from 8 to 12. The lower hydrophobicity of cyclohexylcarboxylic acid films may reflect some basic difference in the orientation of the adsorbed molecules possibly resulting from the decreased flexibility of the molecule. This problem merits further investigation by some more direct method such as electron diffraction.

Although only two members of the corresponding series of aromatic monoacids were available for study, the limited data again led to a horizontal line (curve C, Fig. 6a). By analogy with the cycloalkyl acids, the existence of the maximum water repellency may be attributed to the saturation packing of the phenyl groups. The lower repellency characteristics (a 25° decrease in θ) for the aromatic compounds as compared with the corresponding aliphatic analogs may reflect the differences in polarity of these two types of hydrocarbons.

Comparison of the curve representing the homologous α,ω-alkyl dicarboxylic acids (A in Fig. 6b) with that for the alkyl monoacids reveals that the replacement of a methyl end-group by a second carboxylic group serves both to depress θ for the lower homologs (below $N = 12$) and to increase by a factor of 2.5 the effect of lengthening the methylene chain on θ (*i.e.*, the slope of the line). This divergence might prove instrumental in differentiating between the several orientations conceivable for these adsorbed diacids.

For configuration (a), in which only one acid group adsorbs while the remainder of the molecule lies extended normal to the adsorbing plane, an external surface of close-packed carboxylic groups results. Since such a surface would be expected to exhibit consistently lower contact angles than a surface of close-packed methyl groups, the consequent θ *vs.* N line should either coincide with the $\theta = 0°$ axis or remain displaced below that for the straight-chain monoacids for all values of N. Further, the slope of the line could not conceivably exceed that obtained for the monoacid curve.

In configuration (b) the simultaneous adsorption of both acid groups at the metal surface with the intervening aliphatic chain of methylene groups looped away from the adsorbing surface would result in a hydrophobic film. The longer chain compounds would form the taller, more closely packed loops which would more effectively shield the carboxylic groups from contact with the water drop. The effectiveness of each methylene increment in increasing θ would be expected to be somewhat less, however, than that obtained for a corresponding addition to a normally oriented straight chain.

In configuration (c) both acid groups adsorb and the intervening aliphatic chain is postulated as extending parallel to the adsorbing surface. For the lowest homologs the presence of a high proportion of exposed polar groups would be expected to depress θ considerably below that characteristic of the analogous *n*-alkyl monoacid. Increasing the chain length would shift the ratio of exposed polar to nonpolar groups in favor of greater hydrophobicity. For the highest homologs the effect of the presence of the exposed carboxylic group might be largely suppressed.

Although the curve corresponding to configuration (c) appears somewhat consistent with the experimentally obtained curve, it remains for an independent experimental approach to decide among the several possibilities. Some indication as to probable configuration may be afforded by the comparison of the asymptotic maximum value of θ_{melt}, to be expected for high values of N, with the angle characteristic of films of known composition and orientation. A more direct approach, by electron diffraction, is now in progress.

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[19] L. O. Brockway and J. Karle, *J. Colloid Sci.*, **2**, 277 (1947).

In contrast, curve B (Fig. 6b), representing the homologous alkylsuccinic acids, shows very little increase in θ_{melt} with increasing chain length in going from octylsuccinic to octadecylsuccinic acid. This approximate constancy in angle, despite a ten carbon increase in the length of the aliphatic side-chain, indicates that the lateral forces between adjacent alkyl chains do not predominate in the packing of the molecules. The presence of the more bulky succinic acid portion of the molecule apparently limits the closeness of packing of the alkyl side-chains. This suggests an orientation in which the side-chains are oriented normal to the adsorbing surface so that their effective projected areas are less than those of the succinic acid groups.

Acknowledgments.—The authors gratefully acknowledge the assistance of Mr. J. G. O'Rear and Mr. N. L. Smith of this Laboratory in the preparation and purification of a number of the compounds studied. The recent observations of Mr. E. M. Solomon, also of this Laboratory, that the advancing hydrophobic contact angle on films of stearic acid or octadecylamine adsorbed on platinum from cetane solution is 102° and the adoption of the resulting technique of increasing the size of the test drop of water to guarantee obtaining an advancing contact angle proved particularly valuable in this investigation. The decylsuccinic and octadecylsuccinic anhydrides were generously donated by Dr. George H. von Fuchs, Consulting Chemical Engineer. The phenylbutyric acid was kindly supplied by Dr. Abraham Schneider, Chemistry Department, Harvard University.

SURFACE HYDROLYSIS IN SODIUM LAURYL SULFATE SOLUTIONS AND ITS EFFECT ON SURFACE TENSION AND ON ADSORPTION AT THE SOLID-AQUEOUS SOLUTION INTERFACE[1a]

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Hydrolytic adsorption at the free surface of aqueous sodium lauryl sulfate solutions is shown (1) by *p*H measurements correlated with (foam) extraction of the soap, and (2) by means of surface tension *vs.* *p*H curves at constant concentration and ionic strength. Values of the (apparent) surface hydrolysis constant of 10^{-7} to 10^{-8} were obtained from the γ *vs.* *p*H curves. However, the hydrolytic adsorption may perhaps be due merely to a fatty acid impurity in sodium lauryl sulfate. A series of surface tension–concentration curves were obtained at various ionic strengths and a thermodynamic analysis and interpretation given.

Arguments presented in the flotation theory developed in this Laboratory[2,3] suggested that collectors always adsorb as whole molecules rather than as ions, usually, but not invariably, by hydrolytic adsorption, *i.e.*, as free acids or bases. The adsorption potential for hydrolytic adsorption is usually large enough in (chemisorbed) specific collectors that substantial surface coverage will occur on the mineral at effective collector concentrations of 10^{-10} to 10^{-15} N (*e.g.*, alkyl xanthic acids on metal sulfides). This collector theory is well supported by various independent experimental observations for the specific metal sulfide collectors.[4–9] Moreover, it has been shown that the inorganic depressants generally employed in these systems, namely cyanide and sulfide, adsorb as the free acids, HCN and H_2S, respectively. There appeared very early in this development, however, a serious problem in regard to the non-selective strongly surface active long chain paraffin collectors. Even the paraffin chain salts of strong acids and bases showed good collector properties over wide ranges of *p*H, *i.e.*, under conditions where acid soap concentrations in the bulk solution were quite negligible. Furthermore, the long chain paraffin salts in general behave very much alike as collector agents, irrespective of their hydrolysis constants, except when chemisorption is involved.[5] These long chain collectors are generally non-selective and non-specific, *i.e.*, they cause flotation of the metallic and/or non-metallic minerals and gangue alike.

Plante[10] and Rogers, *et al.*,[11] studied the collector properties of many synthetic and natural soaps, and mapped the *p*H and concentration ranges where these substances are applicable as hydrophobic film forming reagents. The non-specific collector properties of these compounds apparently preclude them as adsorbing ionically.[3,4] Also, the low potential associated with non-selective adsorption requires

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(1a) This work was sponsored by the Atomic Energy Commission, and was presented in the Symposium on Surface Tension of Solutions at the Boston Meeting of the American Chemical Society, April 1-5, 1951.

(1b) Now at Minnesota Mining and Manufacturing Co., St. Paul.

(2) M. A. Cook, *Eng. Min. J.*, **150**, No. 2, 110 (1949); "Mechanism of Collector-Mineral Attachment in Flotation," presented at El Paso meeting of A.I.M.M.E., Oct. (1948), San Francisco, Feb. (1949).

(3) M. A. Cook and J. C. Nixon, THIS JOURNAL, **54**, 445 (1950).

(4) C. M. Judson, A. G. Argyle, J. K. Dixon and D. J. Sally, *J. Chem. Phys.*, **19**, 378 (1951).

(5) M. A. Cook and A. W. Last, University of Utah Experiment Station Bulletin No. 57, 40 (May 1950).

(6) M. A. Cook and W. E. Wadsworth, "Free Acid and Base Adsorption on Solids From Aqueous Solutions of Strong Electrolytes." University of Utah Expt. Sta. Bull. No. 51, Vol. 41, No. 9 (April 1951).

(7) H. Mitsubishi Hagihari, Mining and Metallurgical Laboratory Research Report No. 1202 (1950).

(8) G. A. Last and M. A. Cook, "Theory of Collector-Depressant Equilibria," Accepted for publication, THIS JOURNAL.

(9) M. E. Wadsworth, R. G. Conrady and M. A. Cook, THIS JOURNAL, **56**, 1219 (1952).

(10) E. Plante, *Am. Inst. Mining Met. Eng.*, *Tech. Pubs.*, 2163, July (1947).

(11) J. Rogers, K. L. Sutherland, E. E. Wark and I. W. Wark, *Trans. Am. Inst. Mining Met. Eng.*, **169**, 287 (1946).

that the bulk solution concentrations of the effective collector should be much larger to obtain a given surface coverage than when the specific (high potential) adsorbates are used. In spite of this, one frequently obtains high contact angles on solids even when treated in very dilute solutions of the paraffin chain salts of strong acids. For example, sodium lauryl sulfate will cause flotation of minerals like fluorite or calcite at a total soap concentration as low as 10^{-5} N even in basic solutions of pH 8 to 10. What then is the source of the effective collector in such synthetic soap solutions?

The present study is the result of one attempt to answer this question. However, the work of Brady[12] and the earlier work of Miles and Shedlovsky[13] which came to our attention during the course of this study, showed clearly that a relatively small amount of a non-ionic impurity (evidently an alkyl alcohol) in sodium lauryl sulfate influenced the surface properties of the soap solution tremendously. They demonstrated, moreover, that the anomalous (type III) surface tension (γ)–concentration (C) curve of sodium lauryl sulfate was due (almost) entirely to this impurity. The word "almost" is added here because the results of the present study show another "trace impurity" effect, namely the influence of hydrolytic adsorption even in this strong acid salt! There now appears to be little or no doubt that one or anothers, or both of these factors are responsible for the collector properties of many of these synthetic soaps.

Our flotation studies also led us to suppose that some of the features of the anomalous (type III) γ *vs.* C curves as well as the normal (type I) ones could be explained by taking into account hydrolytic adsorption even in such strong acid salts as sodium lauryl sulfate and, in addition, the conditions associated with surface saturation and the effects of high surface pressures in the adsorbed films. Included in this paper, therefore, are the results of measurements of several γ–C curves at different ionic strengths and pH's and an interpretation of these curves.

Materials and Equipment.—The sodium lauryl sulfate used in this study was a high quality (inorganic free) sample obtained from the du Pont Company. Fresh solutions were used in each series of tests and were made with twice distilled and reboiled (carbonate free) water. Surface tension measurements were made with a "Cenco" du Nouy Precision Tensiometer. The γ–pH curves were obtained by measurements of γ and pH in the same solutions (under a nitrogen atmosphere) by inserting the electrodes from a Beckman Model G meter (glass–calomel electrodes) into a specially constructed test cell in which γ could also be measured directly. All solutions were stored in a thermostat at 29° until used, and the nitrogen atmosphere was maintained at 29°, all measurements being made at this temperature. The nitrogen both for the surface tension and the foaming experiments was purified by passing it successively through soda lime, pyrogallic acid in potassium hydroxide, sulfuric acid and silica gel. It was then saturated with distilled water at 29° before introducing it into the test system. The use of this conditioning atmosphere aided materially in obtaining reproducible results and in reducing the time for equilibrium in the surface tension measurements.

The foaming apparatus was a 30-mm. Pyrex column, one meter long equipped at the bottom with a sintered disk for dispersing the nitrogen stream, and with a stopcock for sampling. At the top was a side delivery tube for removing foam, and a glass stoppered neck for adding solution.

Foam Extraction Tests.—A solution of known concentration and pH was placed in the foaming column, and foam extracted with purified and water resaturated nitrogen gas forced through the sintered disk at a controlled rate such as to allow time for most of the entrained bulk solution to drain back as the foam ascended in the column. Measurements of pH were made by withdrawing and testing samples of the extracted solution at the end of the foaming test or, in some cases, at intervals during extraction. Foaming was usually continued until most of the soap was extracted to allow a maximum pH change. The soap concentration in the extracted solution was estimated only roughly from the approximate volume of foam extracted and subsequently from the surface tension of the solution which, at the end of the tests, was usually above 70 ergs./cm.^{2}.

Table I contains the initial and final results of the pH measurements of the foam extracted solutions.

TABLE I

EFFECT OF FOAMING ON THE pH OF SODIUM LAURYL SULFATE SOLUTIONS

Initial concentration (molal)	pH Initial	pH Final	$(OH)^-$ Generated (mols./l.) $\times 10^{-6}$
1×10^{-4} (no added salt)	6.55	7.65	0.67
1×10^{-4} (no added salt)	5.80	7.12	1.6
2×10^{-4} (no added salt)	6.50	7.94	1.2
2×10^{-4} (no added salt)	6.30	7.75	1.0
1×10^{-4} (0.1 N NaCl)	6.65	6.50	1.9
1×10^{-4} (0.1 N NaCl)	5.60	6.65	2.3
5×10^{-5} (0.1 N NaCl)	5.50	6.65	3.0
5×10^{-5} (0.1 N NaCl)	6.24	7.63	1.0
5×10^{-5} (0.1 N NaCl)	5.80	6.50	1.6

While no appreciable hydrolysis of sodium lauryl sulfate will occur in the bulk solution, it is not *a priori* certain that hydrolysis will not occur in the free surface or at a solid–aqueous solution interface. Actually the soap exists in the surface at concentrations as much as 10^5 times greater than in the bulk solution; also it may be shown that $K_s >> K_h$ for long chain soaps, where K_s is the (apparent) surface hydrolysis constant and K_h is the bulk hydrolysis constant. If the ratio HX/X^- (HX—free acid, X^-—soap anion) were the same in the surface as in the solution, foam extraction would not affect the pH of the solution.[14] One requires, therefore, that $(HX/X^-)_s >> (HX/X^-)$ to account for the appreciable increase in pH observed in these tests. This results from a shift toward the right (due to extraction of $(HX)_x$) of the equilibrium

$$(X_s^-) + H_2O \rightleftarrows (HX)_s + (OH^-)_s$$

Here the subscript s refers to the surface, and no subscript is used when solution concentrations are designated. Experimentally HX/X^- is quite negligible; we could detect no pH increase upon solution of dry sodium lauryl sulfate in pure water. Since the foaming resulted in a substantial increase in pH, this can mean only that the ratio $(HX/X^-)_s$ was appreciable as a result of which the continuous removal and reforming of the surface phase caused an accumulation of OH^- in the bulk solution as shown in the last column of Table I. From the (integral) values of $(OH)^-$ generated one obtains average (integral) values of $(HX/X^-)_s$ in the range 0.01 to 0.04. This gives for K_s (as defined in ref. 14) the value 10^{-8} to 10^{-9}, if it is assumed that the free acid soap results from surface hydrolysis of the sodium lauryl sulfate. However, one has no assurance that this "apparent" 1–4% hydrolysis may not be due to a fatty acid soap impurity present to about this extent in the sodium lauryl sulfate. A long chain fatty acid salt would be ionized completely but hydrolyzed to only a very small extent in the bulk solution at pH 7. However, it would be nearly completely hydrolyzed in the surface, at this pH as shown, for example, by the data of Long, Nutting, and Harkins,[15,16] and by the theoretical analysis of the β (degree of hydrolysis) *versus* C

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[12] A. P. Brady, THIS JOURNAL, **53**, 56 (1949).

[13] G. D. Miles and L. Shedlovsky, *ibid.*, **48**, 57 (1944).

[14] M. A. Cook, *ibid.*, **55**, 383 (1951).

[15] F. A. Long and G. C. Nutting, *J. Am. Chem. Soc.*, **63**, 84 (1941).

[16] F. A. Long, G. C. Nutting and W. D. Harkins, *ibid.*, **59**, 2197 (1937).

curve of Pawney and Jordan given in reference 14. (On the other hand perhaps 15–50% hydrolysis of the fatty acid salt would have occurred in the solutions of minimum initial *p*H shown in Table I, but this would still allow for considerable increase in *p*H during foaming as the free acid soap is gradually extracted.)

Surface Tension *vs.* ***p*H Curves.**—One should also be able to demonstrate surface hydrolysis by means of surface tension *vs.* *p*H curves at constant soap concentration and total ionic strength. For this purpose a special flask was constructed so that either *p*H or γ could be measured in the same solution, as described previously. The *p*H was adjusted by additions of constant boiling HCl on the acid side and concentrated (CO_2-free) sodium hydroxide on the basic side. Measurements were made in 0.01 and 0.1 *N* NaCl solutions, thus the *p*H adjustments did not affect the total ionic strength appreciably. Figure 1 shows the results of two separate series of measurements. In both instances an increase in *p*H resulted in an increase in γ occurring primarily over a range of about two *p*H units, which theoretically would include about 90% of the change if one were dealing with surface hydrolysis. The point of maximum change of γ with *p*H should correspond to the condition $pH = pK_{sa}$ from which one obtains $K_{sa} \cong 10^{-6}$ in one case and 10^{-7} in the other. Here K_{sa} is the (apparent) acid dissociation constant in the surface phase. This gives for K_s the values 10^{-8} and 10^{-7}, corresponding to the different values obtained from the separate curves. The fact that this is around 10 to 100 times larger than the value estimated from the foam extraction test gives credence to the free acid impurity possibility. In any event it is clear from these experiments that there is adequate surface hydrolysis to account for the observed collector properties of sodium lauryl sulfate solutions by hydrolytic adsorption. In other words there are at least two sources of whole molecule adsorption in these solutions when the Brady impurity is also considered. Since sodium lauryl sulfate has no apparent special properties as a collector which cannot be obtained with a fatty acid soap, it did not seem worthwhile to go further into the source of the acid soap. Instead, attention was directed to the γ *vs.* *C* curves on the assumption that *p*H and ionic strength control might eliminate the anomalous minima in the Type III curves.

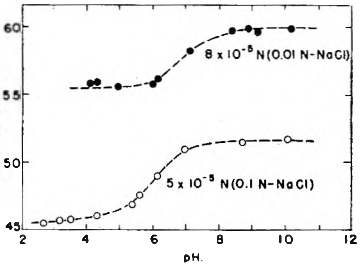

Fig. 1.—Surface tension *vs.* *p*H in sodium lauryl sulfate.

Surface Tension *vs.* **Concentration Curves of Sodium Lauryl Sulfate.**—Surface tension–concentration measurements were made with a platinum ring of *R*/*r* value 40.1, and in a platinum dish. Both ring and dish were flamed before each use, and measurements were carried out under a bell-jar. A small hole was bored in the top of the bell-jar to allow a quartz fiber, connecting the ring and tensiometer, to pass through. The solution and bell-jar could be raised and lowered by means of a threaded screw adjustment to keep the balance arm level. Pure (water saturated) nitrogen under a slight positive pressure and at 29° was maintained above the solutions during measurements. A weighed quantity of soap was dissolved in a known amount of water to make a stock solution from which other solutions were made up by dilution to volume after additions of a weighed amount of NaCl. Concentrated HCl or NaOH was added at the tip of a flamed platinum wire for *p*H adjustment. The samples were then stored at 29° until used. Measurements on each sample were continued every few minutes until the surface tension remained substantially constant over a period of 15 minutes. Harkins and Jordan[17] corrections were applied in all measurements.

Figure 2 shows the results obtained in solutions of 0.1 and 0.01 *N* NaCl at two *p*H values (5.5 and 10). One will observe that while the *p*H and ionic strength control did not completely eliminate the minima in the γ–C curves, it reduced the sharpness of them materially. The experimental points in Fig. 3 are the results obtained at different NaCl concentrations. Since previous tests showed that there was no hydrolysis in the bulk solutions, and only a very small *p*H effect anyway, no attempt was made to maintain *p*H control in obtaining the results shown in Fig. 3. While again the minima were observed, they were not nearly as pronounced as in the work of Brady (Fig. 4).

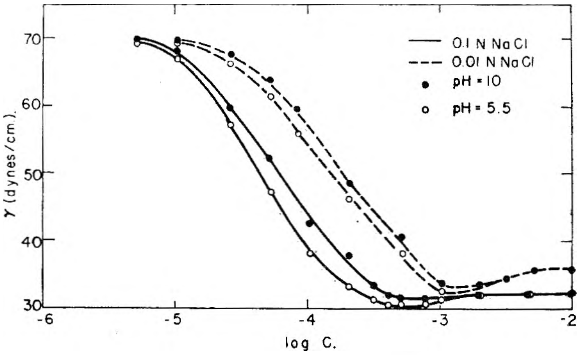

Fig. 2.—Surface tension *vs.* soap concentration at constant μ and *p*H.

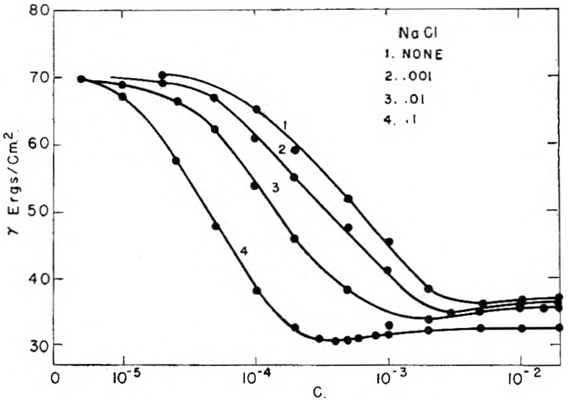

Fig. 3.—Effect of ionic strength on surface tension.

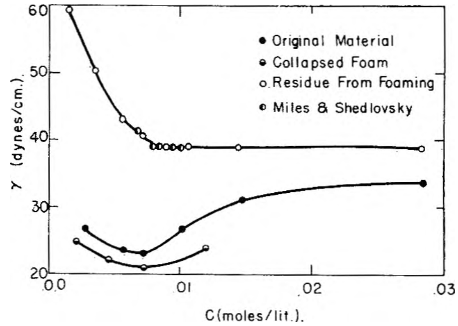

Fig. 4.—Surface tension of foam fractionated sodium lauryl sulfate (Brady[12]).

Discussion

It is of interest to evaluate the experimental surface tension–concentration curves thermodynamically in order to obtain approximate contributions of various factors to the total adsorption potential. For this purpose we shall assume that since the film is gaseous, the surface phase of aqueous sodium

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[17] W. D. Harkins and H. F. Jordan, *J. Am. Chem. Soc.*, **52**, 1751 (1930).

lauryl sulfate solutions obeys the two-dimensional van der Waals equation of state

$$\left(\pi + \frac{a}{\sigma^2}\right)(\sigma - b) = kT \qquad (1)$$

where π is the surface pressure, σ the area/molecule, and a and b are constants. Also we shall assume that at constant *p*H we may treat the soap solution as a single component system so that

$$\Gamma_2^{(1)} = \frac{\mathrm{d}\pi}{RT\,\mathrm{d}\ln(y_{\pm}C)} \qquad (2)$$

where $y_{\pm s}$ is the mean activity coefficient of the soap. The thermodynamic equilibrium constant of the reaction

$$\text{soap (solution)} \rightleftarrows \text{soap (surface)}$$

is

$$K = \frac{y_{\pm}C}{y_{\pm s}C_s} = e^{-\lambda(\sigma,T)/RT} \qquad (3)$$

where $y_{\pm s}$ is the activity coefficient in the adsorbed phase, λ is the adsorption potential [*i.e.*, $-\Delta F$ (adsorption)] which is a function of the density of solute in the surface phase (or σ), and the temperature. It is assumed that λ may be broken down as

$$\lambda = \lambda_0 + 625\,n + \phi(\sigma, T) \qquad (4)$$

where λ_0 is the contribution to λ of the head group–counter ion–solvent interaction. This component of λ might be considered to be dependent on the ionic strength (μ); however, we shall include this dependence in $y_{\pm s}$ and $y_{\pm}$. The second term is the Traube potential with n the number of carbon atoms in the chain. The ϕ term accounts for intractions between adsorbed molecules and will be taken as zero at some particular (large) σ_1, or (low) π_1. From the equations (2), (3) and (4) one obtains

$$\int_0^{\pi} e^{-\phi/RT}\,\mathrm{d}\pi = 10^{-3}\,RTe^{\frac{\lambda_0+625n}{RT}} \int_0^{C} \tau y_{\pm s}^{-1}\,\mathrm{d}(y_{\pm}C) \qquad (5)$$

where $\Gamma^{(1)}$ has been set equal to $10^{-3}\,C_s\tau$ with τ the average thickness of the adsorbed film which we shall assume is 6A and does not vary with C_s. It will also be assumed that $y_{\pm s} = y_{\pm s}(\mu)$ and we shall attempt to determine $y_{\pm s}(\mu)$ from the experimental data. At constant μ one obtains the relation

$$\int_0^{\pi} e^{\int_{\sigma}^{\sigma_1}\pi\,\mathrm{d}\sigma/RT}\,\mathrm{d}\pi = 10^{-3}\,RTe^{\frac{\lambda_0+625n}{RT}}\,\tau y_{\pm s}^{-1}y_{\pm}C \qquad (6)$$

The left side of Equation (6) may be set equal to

$$\frac{(\sigma_1 - b)}{RT}\,e^{\frac{a}{\sigma_1 RT}} \int_0^{\pi} e^{\frac{-a}{\sigma RT}}\left(\frac{RT}{\sigma - b}\right)\mathrm{d}\pi$$

and integrated graphically. It is assumed that equation (6) will apply to the γ–C curve for all soap concentrations below the effective solution saturation concentration C_2, *i.e.*, below the normal micelle region of the γ–C curves. At concentrations above C_2, γ should become constant (at constant *p*H and ionic strength) in a pure soap.

The minimum prevailing in the γ *vs.* C curve after *p*H and ionic strength control may possibly be simply a type of nucleation limitation of the impurity. In other words, at C_2 the impurity would not have reached solution saturation and γ would thus continue to drop above C_2 as the concentration of this impurity increases. However, when micelles become sufficiently abundant adsorption of the impurity on the micelles may be initiated and the potential for it increases with the average size of the micelle at sufficiently high concentrations as a result of which γ returns toward the C_2 value at sufficiently high concentrations. This implies simply that the impurity saturation concentration is greater in a solution containing only this impurity than in a solution containing a sufficiently large concentration and average size of sodium-lauryl sulfate micelles. Such an assumption can easily be justified theoretically.

Since C_s varies only slowly over the greater part of the γ–C between surface pressures above about 5 dynes/cm. and the micelle region, one might expect $\gamma_{\pm s}$ to be relatively constant over this region. Since $\gamma_{\pm}$ should vary exponentially with $\mu^{1/2}$, one would obtain $\log \gamma_{\pm s}^{-1}\gamma_{\pm} = k'\mu^{1/2}$ where k' is a constant. Experimentally this is not the case. Instead, the relation

$$y_{\pm s}^{-1}y_{\pm} = g\mu^{1/2} \qquad (7)$$

seems to fit the condition quite well, where g is a constant. We have no theoretical explanation for this situation as yet.

Assuming that Equation (7) is valid, one may write Equation (6) as

$$\int_0^{\pi} e^{-\phi/RT}\,\mathrm{d}\pi = 4 \times 10^6 e^{\lambda_0'/RT}\mu^{1/2}C \qquad (8)$$

where

$$\lambda_0' = \lambda_0 - RT\ln g \qquad (9)$$

TABLE II

RESULTS OF GRAPHICAL INTEGRATION OF EQUATION (6)

π	$\int_0^{\pi_1} e^{-\phi/RT}\,\mathrm{d}\pi$	$e^{-\lambda_0/RT}\gamma_{\pm s}^{-1}\gamma_{\pm}C$
0	0	0
1.0	1.2	3×10^{-6}
2.5	7.5	1.9×10^{-5}
5.0	70	1.75×10^{-4}
7.5	158	4.0×10^{-4}
10	295	7.3×10^{-4}
12.5	455	1.1×10^{-3}
15	700	1.75×10^{-3}
17.5	950	2.4×10^{-3}
20	1285	3.2×10^{-3}
22.5	1615	4.1×10^{-3}
25	2040	5.1×10^{-3}
27.5	2470	6.2×10^{-3}
30	2900	7.3×10^{-3}
32.5	2400	8.5×10^{-3}
35.0	4250	1.06×10^{-2}

Table II presents the results of the graphical integration of the left side of equation (6), using the values $a = 4 \times 10^4$ ergs. Å.^{4}/cm.$^2\cdot$molecules^2, $b = 50$ Å.^{2}. Figure 5 presents a comparison of experimental and computed γ–C data for the values $\lambda_0' = 3.25$ kcal./mole. The use of the empirical equation (7) seems to be well justified from the results shown in Fig. 5. Moreover the empirical values of λ_0', a and b seem entirely reasonable ones, although the shape of the π *vs.* log C curve is not very sensitive to small changes in either a or b. A variation of $y_{\pm s}$ with ionic strength in bulk solu-

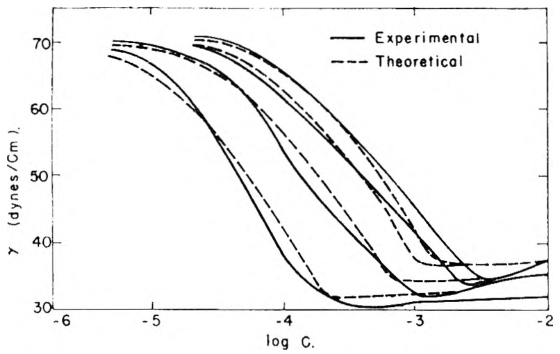

Fig. 5.—Comparison of experimental and theoretical surface tension–concentration curves at constant *p*H and ionic strength.

tion may possibly be explained qualitatively by considering the average ionic atmosphere radius in the various solutions. At $C = 10^4$ and no NaCl this radius is about 300 Å. Adsorption is then hindered by simple anion repulsion and the potential required to absorb counter-ions to overcome it. At the same soap concentration and 0.1 NaCl, the average atmosphere radius is about 10 Å. Hence the anion repulsion is largely eliminated at this high ionic strength because the counter-ions (Na^+) are then more easily brought into the surface film with the anions to produce charge stabilization.

Actually the absolute values of λ depend to some extent on the choice of a in equation (1). Since this choice cannot be made very accurately in the present study, because a influences the γ *vs.* C curve appreciably only at low surface pressures, *i.e.*, at high γ, the absolute values of λ_0 may be in error by perhaps as much as 0.5 kcal. Furthermore the inclusion of g in the λ_0 term obscures the significance of the numerical values of λ_0.

It is interesting to note that the minima were shifted to lower concentrations by increasing μ to almost the same extent as the displacement of C_π (*i.e.*, the concentration at constant surface pressure). The latter displacement in turn was almost independent of the surface pressure. The displacement of the minimum shows that the potential for micelle formation varies with ionic strength in about the same manner as the product $y_{\pm}^{-1/6}y_{\pm}$ which is consistent with the theory discussed in reference 14.

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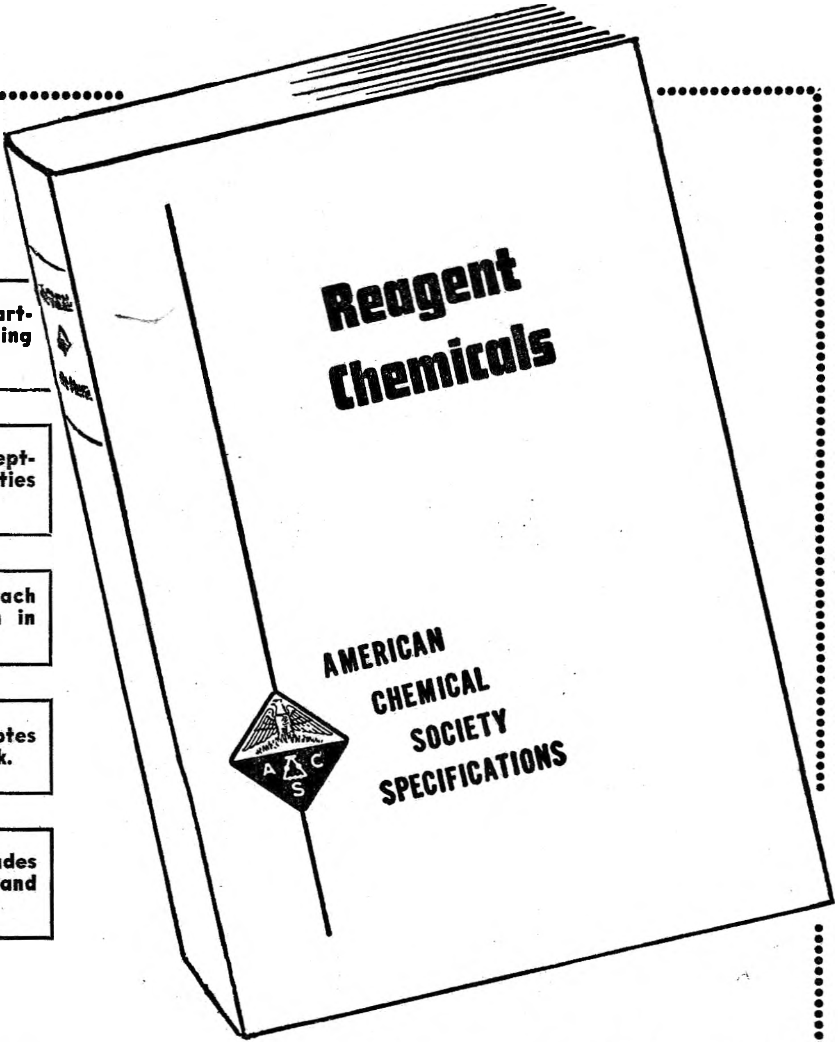
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