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SYMPOSIUM ON VALENCY AND CHEMICAL BONDING, MADISON, WIS., June 20–22, 1956

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THE JOURNAL OF
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ACTIVATED COMPLEX ENERGIES[1]

BY RICHARD SNOW AND HENRY EYRING

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Received August 13, 1956

The reaction H + H_2 is being studied in terms of a more general trial wave function than has been used previously. Approximate calculations using a wave function with p-character for H_3^+ gives an improvement of some 10 kcal. in the energy over that found by varying the screening parameters, as reported by Barker and Giddings. Mulliken's approximation was used in both treatments to evaluate the three-center integrals. A comparative "p-character" and variable screening constant study of H_3 is in progress, and approximate calculations indicate a theoretical activation energy not too far from the experimental value of about 7 kcal. Using the usual valence bond approximations, an expression for the sum of the energies of the multiplets of an n-electron problem is obtained. $W_{n,r} = [(n-2)!/(n-r)!r!]\,[r(r-1) + (n-r)(n-r-1)]\Sigma$ where Σ is the sum of all possible exchange integrals between pairs of electrons, and $(n - 2r - 1)$ is the multiplicity An expression for the average energy of a term of a multiplet is also given in terms of n, r and Σ. $\overline{W}_{n,n-2r+1} = [(n-2)!/n!(n-2r+1)]\{(n-r+1)(n-r)(n-2r-1) + r(r-1)(n-2r+3)\}\Sigma$. The five and six electron problems reduce in an interesting way to the four electron case when one or two electrons, respectively, are removed to infinity. The five-rowed determinant, of course, reduces to the quadratic for the singlet states and to a cubic for the triplet states for four electrons. The London formula and possible generalizations are discussed. The structure of the activated complex is a balance between resonance energy gained at the expense of nuclear repulsion. Ionic catalysts frequently ionize the activated complex, much as any solvent of high dielectric constant does. Other catalysts lower the activation energy by accepting unwanted promoted electrons. The fact that the activated complex lives only about 10^{-13} second does not prevent it from posing much the same valence problems as stable molecules.

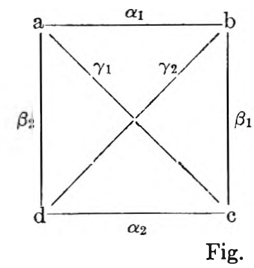
Introduction

Equilibria and reaction rates are most graphically portrayed in terms of potential surfaces in configuration space. Thus the chemistry of diatomic systems is readily inferred from the potential curve for the ground for the excited states using the Franck-Condon principle. With three atoms three positional coördinates are required to fix the molecular configuration and these with a coördinate for the energy would require a four-dimensional space for an energy surface. Lacking visual facility in four dimensions one operates readily from a table or with sections in fewer dimensions. The linear triatomic complex specified by two distances is customarily drawn on a plane with contour lines indicating the energy levels. Additional atoms simply increase the multidimensionality of the required space. In calculating these surfaces we usually have to be satisfied with the approximate calculations of the type first made by London for three and four atoms. Since such surfaces have formed the basis for the development of statistical rate theory it is of interest to review some aspects of the approximate theory before considering the more precise but much more laborious variational calculations.

Semi-empirical Theory.—In 1929[2] London published his formula for the energy of interaction of three or four electrons. The energy of interaction is given in terms of coulombic and exchange energies.

$$E = Q - \sqrt{\frac{1}{2}\{(\alpha-\beta)^2 + (\beta-\gamma)^2 + (\alpha-\gamma)^2\}} \quad (1)$$

In the four electron system represented schematically in Fig. 1 the symbols α, β, γ represent exchange energies. Q is the total coulombic interaction energy of the system. If one of the electrons, say a,



$\alpha = \alpha_1 + \alpha_2$

$\beta = \beta_1 + \beta_2$

$\gamma = \gamma_1 + \gamma_2$

Fig. 1.

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[1] Sponsored by the Office of Ordnance Research, U. S. Army.

[2] F. London, *Z. Elektrochem.*, **35**, 552 (1929).

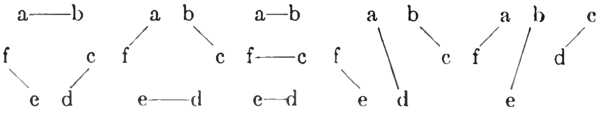
is removed to infinity the three electron case results. In this case α, β, γ denote only single exchange energies and not sums of exchange energies.

Polanyi, Eyring and co-workers[3] by using the Morse curve for atom pairs, constructed a great many approximate surfaces which formed the basis on which statistical reaction rate theory was built. Since the London formula allows the calculation of a potential energy surface it provides the necessary information for the configuration and the vibration frequencies of the activated complex as well as the activation energy. As John Polanyi[4] has recently emphasized these potential energy surfaces can be improved as we get more experimental data and better calculations. However, future developments will only make more quantitative but not replace our potential surfaces in configuration space.

There are several questionable assumptions in the derivation of equation 1. It is assumed that the total energy of interaction is divided into resonance and coulombic terms and that the coulomb term is a constant fraction of the total energy. Multiple exchange integrals are neglected in its derivation even though exact calculations have shown that they are not negligible. However "it now seems fairly well agreed that the method can serve as a semi-quantitative guide in cases where exact calculations are either too tedious or impossible and it can be fairly said that in the study of reaction velocities the method has been quite notably successful and suggestive."[5]

Extension of the London Formula.—Although the treatment of a system of three or four electrons by the London formula is simple, addition of two more electrons to the system makes the problem much more difficult. It is, however, interesting to attempt to formulate and solve this problem and inquire as to the possibility of obtaining a formula analogous to the London formula as well as a geometrical method which utilizes techniques similar to those previously used.[6]

Using for the six-electron system the usual linear combination of Slater determinants,[7] one finds[8] five independent functions with total spin zero and having three bonds. These functions represent the canonical or Rumer structures in Fig. 2 and some linear combinations of these structures describe the ground state of the system. Taking orthogonal linear combinations of the functions in Fig. 2 the matrix components of the secular equation are then calculated by the usual methods.[9]



(ab,cd,ef) (af,bc,de) (ab,cf,de) (ad,bc,ef) (af,be,cd)

Fig. 2.

The orthogonal functions and the matrix components of the secular determinant are then

$$\psi_1 = (\mathrm{ab,cd,ef})$$
$$\psi_2 = (\mathrm{ab,cf,ed}) - \tfrac{1}{2}(\mathrm{ab,cd,ef})$$
$$\psi_3 = (\mathrm{af,be,cd}) - \tfrac{1}{2}(\mathrm{ab,cd,ef})$$
$$\psi_4 = (\mathrm{ad,bc,ef}) - \tfrac{1}{2}(\mathrm{ab,cd,ef})$$
$$\psi_6 = (\mathrm{ab,cd,ef}) + 2(\mathrm{af,bc,de}) - (\mathrm{ab,cf,de}) - (\mathrm{af,be,cd}) - (\mathrm{ad,bc,ef})$$

In Table I we have entered the coefficients of the exchange integrals and $-S_{ij}$ for each matrix component $H_{ij} - S_{ij}W$. Thus from the table one sees that the first matrix component

$$H_{11} = S_{11}W = 8\mathrm{ab} - 4\mathrm{ac} - 4\mathrm{ad} - 4\mathrm{ae} - 4\mathrm{af} - 4\mathrm{bc} - 4\mathrm{bd} - 4\mathrm{be} - 4\mathrm{bf} + 8\mathrm{cd} - 4\mathrm{ce} - 4\mathrm{cf} - 4\mathrm{de} - 4\mathrm{df} + 8\mathrm{ef} - 8W$$

We use $W = E - Q$, where E and Q are the total energy and coulombic energy, respectively. The matrix components are combinations of 15 possible exchange integrals between the six electrons. It is interesting to note that only for the six electron case does the number of exchange integrals and the number of structures with three bonds happen to be the same, namely, 15. For four electrons there are six exchange integrals and three two-bond structures. Just as the three energies α, β and γ enter symmetrically into the London quadratic equation 1, so in the fifth degree equation for the five singlet energies the 15 possible energies for bonding states must enter symmetrically. Thus there must be a geometrical construction in five dimensional space yielding the five roots analogous to the usual procedure for four atoms where the appropriate sum of $\vec{\alpha}$, $\vec{\beta}$ and $\vec{\gamma}$ is taken. Each vector makes a 60° angle with respect to the preceding vector with γ further directed to most nearly close the figure. The resultant is the binding energy.

Due to the complexity of the fifth order secular determinant direct expansion is laborious. It is interesting however to examine some special cases to which the general fifth degree equation reduces. By inspection of the secular determinant one can write down a variety of special cases. When only the three bonds corresponding to one way of bonding, say ab, cd, and ef, are different from zero, the fifth degree equation factors to give

$$(\mathrm{ab} + \mathrm{cd} + \mathrm{ef} - W)(\mathrm{ab} - \mathrm{cd} - \mathrm{ef} - W)(-\mathrm{ab} + \mathrm{cd} - \mathrm{ef} - W)(-\mathrm{ab} - \mathrm{cd} + \mathrm{ef} - W)(-\mathrm{ab} - \mathrm{cd} + \mathrm{ef} - W) = 0$$

When all the bonds involving the orbitals e and f are zero the quintic reduces to the product of the cubic (2) and the quadratic (3).

$$W^3 + (\alpha + \beta + \gamma)W^2 + \{\alpha\beta + \alpha\gamma + \beta\gamma - [(\alpha_1 - \alpha_2)^2 + (\beta_1 - \beta_2)^2 + (\gamma_1 - \gamma_2)^2]\}W + \beta\gamma\alpha - [\alpha(\alpha_1 - \alpha_2)^2 + \beta(\beta_1 - \beta_2)^2 + \gamma(\gamma_1 - \gamma_2)^2] + 2(\alpha_1 - \alpha_2)(\beta_1 - \beta_2)(\gamma_1 - \gamma_2) = 0 \quad (2)$$

$$W^2 - (\alpha^2 + \beta^2 + \gamma^2 - \alpha\beta - \alpha\gamma - \beta\gamma) = 0 \quad (3)$$

(The notation is explained in Fig. 1.) The quadratic (3) gives the singlet energies for the four atom case and the cubic (2) gives the triplet energies in the four atom case. When the six electrons separate into two systems a, b, c, and d, e, f of three atoms each the quintic takes the form

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(3) S. Glasstone, K. Laidler and H. Eyring, "Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., 1941, Chap. 2, 3.

(4) J. Polanyi, *J. Chem. Phys.*, **23**, 1542 (1955).

(5) J. R. Partington, "An Advanced Treatise on Physical Chemistry," Vol. V, Longmans, London, 1954, pp. 241–259.

(6) See reference 5 pp. 89, 123.

(7) J. C. Slater, *Phys. Rev.*, **34**, 1293 (1929); **38**, 1109 (1931).

(8) H. Eyring and Walter Kimball, "Quantum Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1944, pp. 240–244.

(9) See reference 8, Chapter 13.

TABLE I

COEFFICIENT OF EXCHANGE INREGRALS IN H_{ij} AND COEFFICIENTS $-S_{ij}$ OF W

	ab	ac	ad	ae	af	bc	bd	be	bf	cd	ce	cf	de	df	ef	W
11	8	−4	−4	−4	−4	−4	−4	−4	−4	8	−4	−4	−4	−4	8	−8
12	0	0	0	0	0	0	0	0	0	0	−6	6	6	−6	0	0
13	0	0	0	−6	6	0	0	6	−6	0	0	0	0	0	0	0
14	0	−6	6	0	0	6	−6	0	0	0	0	0	0	0	0	0
15	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
22	6	−3	−3	−3	−3	−3	−3	−3	−3	−6	3	3	3	3	−6	−6
23	0	−3	3	0	0	3	−3	0	0	0	0	0	0	0	0	0
24	0	0	0	−3	3	0	0	3	−3	0	0	0	0	0	0	0
25	0	−6	−6	6	6	6	6	−6	−6	0	0	0	0	0	0	0
33	−6	−3	−3	3	3	−3	−3	3	3	6	−3	−3	−3	−3	−6	−6
34	0	0	0	0	0	0	0	0	0	0	−3	3	3	−3	0	0
35	0	6	−6	0	0	6	−6	0	0	0	−6	−6	6	6	0	0
44	−6	3	3	−3	−3	3	3	−3	−3	−6	−3	−3	−3	−3	6	−6
45	0	0	0	−6	6	0	0	−6	6	0	6	−6	6	−6	0	0
55	−12	0	0	0	0	0	0	0	0	−12	0	0	0	0	−12	−12

$$(W + R_1 + R_2)(W + R_1 - R_2)(W - R_1 + R_2)(W - R_1 - R_2)(W + \alpha + \beta + \gamma + \delta + \epsilon + \zeta) = 0 \quad (4)$$

Here $R_1{}^2 = \alpha^2 + \beta^2 + \gamma^2 - \alpha\beta - \alpha\gamma - \beta\gamma$ and $R_2{}^2 = \delta^2 + \epsilon^2 + \zeta^2 - \delta\epsilon - \delta\zeta - \epsilon\zeta$. The doublet energies for the two sets of three atom systems considered when separated are R_1, $-R_2$, and R_2, $-R_2$, respectively. Returning to the four atom system when atom d is moved to infinity the four atom system becomes a three atom plus a single atom system and the cubic (2) factors to give

$$(W^2 - \alpha_1{}^2 - \beta_1{}^2 - \gamma_1{}^2 + \alpha_1\beta_1 + \alpha_1\gamma_1 + \beta_1\gamma_1)(W + \alpha_1 + \beta_1 + \gamma_1) = 0 \quad (5)$$

Here the first two roots are the London quadratic for the doublet energy for three atoms and the last factor is the three atom quartet energy.

Other special cases which have properties which allow them to be treated more simply than the general quintic are (1) all exchange integrals equal, (2) a regular octahedral structure for the six atoms, and (3) a regular hexagonal structure (benzene) for the six atoms. Inspection gives for case (1)

$$(3\alpha + W)^5 = 0 \quad (6)$$

For cases (2) and (3) the symmetry of the systems also allows considerable simplification. In case (2) we take ef = bd = ac = β and all the other bonds equal to α. This yields the result

$$\{W^2 + (8\alpha - 2\beta)W + 12\alpha^2 - 3\beta^2\}(2\alpha + \beta + W)^2 (W + 3\beta) = 0 \quad (7)$$

where α represents an exchange integral between adjacent atoms and β is an exchange integral between non-adjacent atoms. For the benzene case we have the usual result

$$\{W^2 + (2\alpha - 2\gamma + 6\beta)W + 3\gamma(\gamma + 2\alpha - 2\beta) - 12\alpha(\alpha - 2\beta)\}(2\alpha + \gamma + W)^2(3\gamma + W) = 0 \quad (8)$$

where α, β and γ represent exchange integrals of types ab, ac and ad, respectively.

General Results for an n-Electron Problem.—Using the usual valence bond approximations a number of general results can be obtained for an n-electron problem. For a system of n-electrons the total number of Slater determinants is $2n$. As is well known this is also given by

$$\sum_{r=1}^{n} \frac{n!}{(n-r)!r!}$$

This last expression is the sum of the binomial coefficients for $(\alpha + \beta)^n$. The binomial coefficient $[n!/(n - r)!r!]$ is the number of different ways n positions can be filled with $(n - r)$ of one kind of things and r of the other. In forming Slater determinants for a particular problem there are two possible choices of the spin functions for each atomic orbital. Thus the appropriate coefficient in the binomial expansion

$$(\alpha + \beta)^n = \alpha^n + n\alpha^{n-1}\beta + \ldots + \frac{n!}{(n-r)!r!}\alpha^{n-r}\beta + \ldots \quad (9)$$

gives the number of possible Slater determinants in the n-electron problem having all orbitals different corresponding to a given number, $n - r$, assignments of α and r assignments of β. The eigenvalue for the z component of spin S_z is then $(n - 2r)\frac{h}{\pi}$. For example for four electrons we have

$$(\alpha + \beta)^4 = \alpha^4 + 4\alpha^3\beta + 6\alpha^2\beta^2 + 4\alpha\beta^3 + \beta^4 \quad (10)$$

S_z-eigenvalue	−2	−1	0	1	2
No. of determinations	1	4	6	4	1

Using the same binomial development we are also able to find the multiplet structure for an n-electron system. If S is the largest possible eigenvalue of S_z for a Slater determinant for n electrons the multiplicity (M) of the multiplet of highest order is given by the usual $M = 2S + 1$. This multiplet has functions corresponding to $M_s = S, S - 1, \ldots -S$. We have thus one function of each kind represented in the binomial in the highest order multiplet. If we subtract one from each binomial coefficient we are left with the total number of functions which make up the lower order multiplets. The largest eigenvalue of S_z for the functions remaining corresponds to the next order multiplet. In general there will be more than one multiplet of this multiplicity. Proceeding by subtracting successive binomial coefficients we are able to find the types of multiplets possible and number of each type. For example for the six electron case we find

$$(\alpha + \beta)^6 = \alpha^6 + 6\alpha^5\beta + 15\alpha^4\beta^2 + 20\alpha^3\beta^3 + 15\alpha^2\beta^4 + 6\alpha\beta^5 + \beta^6 \quad (11)$$

Thus we have one septet; $6 - 1 = 5$ quintets; $15 - 6 = 9$ triplets and $20 - 15 = 5$ singlets.

In general if r is the number of β's in a Slater determinant ($r \leq {}^1/_2 n$) the number of multiplets of multiplicity $n - 2r + 1$ is given by

$$\left(\frac{n}{r}\right) - \left(\frac{n}{r-1}\right) = \frac{n!}{(n-r)!n!} - \frac{n!}{(n-r+1)!(r-1)!} =$$
$$\frac{n!}{(n-r+1)!r!}[n - r + 1 - r] = \frac{n!(n-2r+1)}{(n-r+1)!\,r!} \quad (12)$$

Now proceeding with the London approximation, *i.e.*, assuming orthogonality of atomic orbitals centered on different nuclei and neglecting all multiple exchange integrals we can write a formula for the sum of the energies of the multiplets of an n-electron problem. Now if r ($r \leq {}^1/_2 n$) is the number of β's in the Slater determinants for the multiplets the sum of whose energies are desired we know that there are $[n!/(n-r)!r!]$ of these determinants. These determinants are orthogonal by assumption hence the sum of the diagonal matrix components in the secular equation will be the sum of the roots. Now since each of these Slater determinants has the same number of α's and β's the number of exchange integrals in each of the diagonal matrix components will be the same. The matrix components will differ however in the exchange integrals which they contain.

It is clear however as will be seen in an example below that the sum of all the diagonal matrix components will be a multiple of the sum of all possible exchange integrals for the system. In the case of four electrons take $r = 1$ then the Slater determinants are

$$\varphi_1 = \begin{pmatrix} \beta & \alpha & \alpha & \alpha \\ \mathrm{a} & \mathrm{b} & \mathrm{c} & \mathrm{d} \end{pmatrix} \qquad \varphi_3 = \begin{pmatrix} \alpha & \alpha & \beta & \alpha \\ \mathrm{a} & \mathrm{b} & \mathrm{c} & \mathrm{d} \end{pmatrix}$$
$$\varphi_2 = \begin{pmatrix} \alpha & \beta & \alpha & \alpha \\ \mathrm{a} & \mathrm{b} & \mathrm{c} & \mathrm{d} \end{pmatrix} \qquad \varphi_4 = \begin{pmatrix} \alpha & \alpha & \alpha & \beta \\ \mathrm{a} & \mathrm{b} & \mathrm{c} & \mathrm{d} \end{pmatrix}$$

and the diagonal matrix components are

$$\begin{aligned}
\int \varphi_1 H \varphi_1 \mathrm{d}\tau &= -\mathrm{bc} - \mathrm{bd} - \mathrm{cd} + Q \\
\int \varphi_2 H \varphi_2 \mathrm{d}\tau &= -\mathrm{ac} - \mathrm{ad} - \mathrm{cd} + Q \\
\int \varphi_3 H \varphi_3 \mathrm{d}\tau &= -\mathrm{ab} - \mathrm{bd} - \mathrm{ad} + Q \\
\int \varphi_4 H \varphi_4 \mathrm{d}\tau &= -\mathrm{ab} - \mathrm{ac} - \mathrm{bc} + Q
\end{aligned}$$

$$\sum_{i=1}^{4} \int \varphi_i H \varphi_1 \mathrm{d}\tau = -2(\mathrm{ab} + \mathrm{bc} + \mathrm{bd} + \mathrm{cd} + \mathrm{ac} + \mathrm{ad}) + 4Q = -2\Sigma + 4Q$$

where Σ is the sum of the exchange integrals. Now if we write as heretofore W for the total exchange energy, *i.e.*, the total energy minus the coulombic, the expression for the sum of the exchange energies of the multiplets for a given r is then

$$W_{n,r} = (\text{total no. of determinations of rth kind}) \times (\text{fraction of } \Sigma \text{ from each determinant}) \times \Sigma$$

$$W_{n,r} = \frac{n!}{(n-r)!r!} \frac{\left[\frac{r(r-1)}{2} + \frac{(n-r)(n-r-1)}{2}\right]}{\frac{n(n-1)}{2}} \sum$$

$$W_{n,r} = \frac{n!}{(n-r)!r!} \frac{r(r-1) + (n-r)(n-r-1)}{n(n-1)} \sum$$

$$W_{n,r} = \frac{(n-2)!}{(n-r)!r} [r(r-1) + (n-r)(n-r-1)] \sum$$

These formulas may be used to derive an expression for the average exchange energy of a term of a multiplet in terms of n, r and Σ. If r is the number of β's in the determinantal functions then the average exchange energy for a term of a multiplet of multiplicity $(n - 2r + 1)$ is

$$W_{n,n-2r+1} = \frac{\text{Sum of energies of terms}}{\text{no. of terms}}$$

$$\overline{W}_{n,n-2r+1} = \frac{(W_{n,r} - W_{n,r-1})}{\left(\frac{n}{r}\right) - \left(\frac{n}{r-1}\right)}$$

$$\overline{W}_{n,n-2r+1} = \frac{(n-2)!}{n!(n-2r+1)} \{(n-r+1)(n-r)(n-2r-1) + r(r-1)(n-2r+3)\}\Sigma$$

Activation Energy of H + H$_2$.—The reaction H + H$_2$ *M* H$_2$ + H has been studied by the semi-empirical method[10] and by more exact quantum mechanical methods.[11] Investigations of this reaction have attempted to calculate a theoretical activation energy and to determine the configuration of the H$_3$ intermediate.

By making "a reasonable assumption" as to the coulombic fraction (20%) of the total energy of the H$_2$ molecule semiempirical calculations yield an activation energy which agrees with the experimental value. However varying the per cent. coulombic energy changes the calculated activation energy. The configuration of the activated complex also depends upon the assumption regarding per cent. coulombic energy. Thus for 20% coulombic energy the activated complex is unsymmetrical while assuming 7% coulombic energy gives a symmetrical configuration.[12] The work of Hirschfelder and co-workers was the first extended study of H$_3$. This investigation was an attempt to calculate by means of the variation principal and quantum mechanics the binding energy of the H$_3$ system. The trial function used was a linear combination of Slater determinants chosen to have the appropriate multiplicity whose elements were products of 1s hydrogen orbitals and the appropriate spin function. Thus

$$\psi = c_1\varphi_1 + c_2\varphi_2 + c_3\varphi_3 + c_4\varphi_4$$

$$\varphi_1 = 2\begin{pmatrix} \mathrm{a} & \mathrm{b} & \mathrm{c} \\ \alpha & \beta & \alpha \end{pmatrix} - \begin{pmatrix} \mathrm{a} & \mathrm{b} & \mathrm{c} \\ \beta & \alpha & \alpha \end{pmatrix} - \begin{pmatrix} \mathrm{a} & \mathrm{b} & \mathrm{c} \\ \alpha & \alpha & \beta \end{pmatrix} \text{covalent structure (Heitler–London)}$$

$$\varphi_2 = \begin{pmatrix} \mathrm{a} & \mathrm{a} & \mathrm{c} \\ \alpha & \beta & \alpha \end{pmatrix} - \begin{pmatrix} \mathrm{c} & \mathrm{c} & \mathrm{a} \\ \alpha & \beta & \alpha \end{pmatrix} \qquad \text{ionic}$$

$$\varphi_3 = \begin{pmatrix} \mathrm{a} & \mathrm{b} & \mathrm{b} \\ \alpha & \beta & \alpha \end{pmatrix} + \begin{pmatrix} \mathrm{b} & \mathrm{b} & \mathrm{c} \\ \alpha & \beta & \alpha \end{pmatrix} \qquad \text{ionic}$$

$$\varphi_4 = \begin{pmatrix} \mathrm{b} & \mathrm{c} & \mathrm{c} \\ \alpha & \beta & \alpha \end{pmatrix} + \begin{pmatrix} \mathrm{a} & \mathrm{a} & \mathrm{b} \\ \alpha & \beta & \alpha \end{pmatrix} \qquad \text{ionic}$$

The result of this work is summarized in Table II.

TABLE II

Wave function	Parameter values		Binding energy, kcal./mole
Heitler–London	$R = 2.00$	$Z = 1.00$	53.11
Heitler–London Varying Z	$R = \frac{2.00}{Z}$	$Z = 1.059$	56.16
Heitler–London Plus ionic	$R = 2.00$	$Z = 1.00$	60.39
H.–L. plus ionic varying Z	$R = \frac{2.00}{Z}$	$Z = 1.086$	67.09

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[10] See reference 2, Chapters 2–4.

[11] J. O. Hirschfelder, *et al.*, *J. Chem. Phys.*, **1**, 121, 135 (1936); **5**, 695, 933 (1937); **6**, 795, 806 (1938).

[12] See reference 5.

These calculations prove that the activation energy for the reaction $H + H_2 \rightarrow H_2 + H$ must be less than 40 kcal. if we compare the best calculated H_3 energy with the experimental energy for H_2, or one estimates 25 kcal. for the activation energy from the calculated values for H_3 and for H_2 using Heitler–London-plus-ionic terms wave functions with variable Z for each system.

Subsequently calculations were made to determine the configuration of the activated complex. It was found that a triangular system is unstable relative to the linear system and that the activated complex is symmetrical for a linear system.

Improvement of Work on Hirschfelder.—The most direct methods of improving the results discussed above are (1) adding more independent parameters to the original trial function and/or (2) charging the original 1s atomic orbitals in the trail function by forming linear combinations of hydrogen-like orbitals to be used as the component functions of the Slater determinants. One such change would be inclusion of "p" character in the wave function similar to the work of Rosen[13] on H_2. As is well known this tends to concentrate more charge between the nuclei thus increasing the binding of the system.

Hirschfelder[14] first suggested that instead of varying the screening constants associated with the three nuclei simultaneously the screening constants associated with the outer nuclei be varied independently of the screening constant associated with the central nucleus. Exact calculations using unequal screening parameters in all integrals have not been completed. However calculations using approximations for the three center integrals have been carried out. These calculations are useful in (a) indicating possible energy improvement from use of new trial function, (b) finding best parameter values for exact calculations, (c) studying error in energy to be expected using approximations for the three center integrals.

Barker and Eyring[15] obtained an energy of 74.2 kcal./mole for the H_3 complex using a Heitler–London type trial function with different screening constants on central and outer nuclei for a symmetric system. This energy was calculated for $Z_m = 1.08$, $Z_0 = 1.00$ and $R = 1.80$. This energy seemed to be an improvement over the best previous value of 67.09 kcal./mole. However it appears that there was an arithmetical mistake since repetition of the calculation gave an energy of 61.3 kcal./mole. This result is still an improvement over the best covalent structure treatment (56.2 kcal./mole) but is 6 kcal. less than the best calculation by Hirschfelder. The distance normalized approximation was used for the three center integrals.

Calculations to determine the best parameter values for the covalent structure trial function have been carried out. Mulliken's approximation was used to evaluate the three center integrals. These calculations are summarized in Table III.

TABLE III

Z_m	Z_0	R	B. E.
1.12	1.00	1.80	53.1
1.08	1.00	1.85	51.0
1.08	1.00	1.80	52.2
1.14	1.00	1.75	51.1
1.18	1.00	1.70	48.0
1.12	0.95	1.80	48.0
1.12	1.05	1.80	55.0
1.08	1.05	1.80	53.8
1.12	1.10	1.80	52.6

	Z_0 1.00		R 1.80	Z_m 1.12
Z_m	R	B. E.	Z_0	B. E.
1.08	1.80	52.2	0.95	48.0
1.12	1.80	53.1	1.00	53.1
1.08	1.85	51.0	1.05	55.0
1.14	1.75	51.1	1.10	52.6
1.18	1.70	48.0		

These energy approximations indicate that the best values of the parameters for this type of treatment are $R = 1.80$, $Z_m = 1.12$ and $Z_0 = 1.05$. The work of Barker and Eyring[16] indicates that using the Mulliken approximation for the covalent structure gives a binding energy less than the true value by several kcal. Hence if exact calculations were carried out using the above parameter values a substantial improvement over the one structure best value would result.

The integrals not yet tabulated in the H_3 calculation area are of varying difficulty. Of them the three center exchange integrals $L_{ab,bc}$ and $L_{ab,ac}$ are the most difficult to evaluate. The other four integrals $L_{ab,ab}$, $K_{a,bc}$, and $L_{aa,bc}$ and $L_{bb,ac}$ are much simpler. Since this is the case it is interesting to investigate the dependence of the energy upon these integrals.

Taking $Z_0 = 1.00$, $Z_mR = 2.00$ and $R = 1.80$ for convenience of calculation we have calculated the four integrals $L_{ab,ab}$, $K_{a,bc}$, $L_{aa,bc}$, and $L_{bb,ac}$ exactly. Using approximations for $L_{ab,bc}$ and $L_{ab,ac}$ the binding energy was calculated. The Mulliken approximation gives B. E. = 43 kcal. and the distance normalized approximation of Barker gives B. E. = 44 kcal. The accuracy of the distance normalized approximation indicates that this result is within one kcal. of the actual value.

Another check on the dependence of the binding energy of the system on $L_{ab,bc}$ and $L_{ab,ac}$ was made by computing the energy for $R = 2.00$, $Z_0 = 1.00 = Z_m$ using the Mulliken approximation for $L_{ab\,bc}$ and $L_{ab,ac}$ and the complete covalent-plus-ionic-terms trial function. This result was 63.04 kcal. The actual value computed by Hirschfelder for these parameter values is 60.40 kcal. The error is thus 2.64 kcal. Since the distance normalized approximation is generally more accurate[16] the binding energy using it should be within 2 kcal. of the actual value and a great saving in labor is effected by its use in the preliminary calculations. As a check on the use of distance normalization we compare in Table IV actual, Mulliken, and distance normalized (D.N.) values for some integrals used in the above calculations.

There exist at present usable methods for the first four of these integrals listed above. An energy computation using the best parameter values can be carried out using exact values for all but two inte-

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[13] N. Rosen, *Phys. Rev.*, **38**, 2099 (1931).

[14] J. O. Hirschfelder, Ph.D. Thesis, Princeton University. 1935.

[15] R. Barker and H. Eyring, *J. Chem. Phys.*, **22**, 1182 (1954).

[16] R. Barker, *et al.*, *ibid.*, **22**, 699, 2072 (1954); **23**, 1381 (1955).

Table IV

Integral	Actual	Mulliken	D. N.
$L_{ab,ab}$	0.2142	0.2101	0.2133
$L_{aa,bc}$	.2197	.2249	.2161
$K_{ab,c}$	.2335	.2454	.2321
$L_{bb,ac}$	1293	.1126	.1279
$L_{ab,ac}$	....	.0530	.0564
$L_{ab,bc}$	....	.1771	.1705

$R = 1.80 \quad RZ_m = 2.00 \quad Z_0 = 1.00$

grals and an approximation for these. This would give the best return possible for the effort expended.

Calculations on $H_3{}^+$ using a "p" character refinement of the trial function have been carried out. Using one covalent structure and approximate integrals an improvement of 10 kcal. in energy was obtained. This result indicates that a similar calculation on H_3 would be worthwhile. The integral evaluations are now being carried out. In this one would like to include the "p" character in the orbital centered on the central nucleus, but such a function is noncombining with the ls orbitals in the basic trial function. The above calculations were made using p-orbitals on the outer nuclei. From the results here reported it appears that although a significant improvement will be made in the binding energy for the H_3 system by varying the parameters herein discussed still the activation energy thus obtained will be substantially larger than the experimental. A really satisfactory result will require the variation of additional parameters.

APPLICATION OF SELF-CONSISTENT MOLECULAR ORBITAL METHODS TO π-ELECTRONS

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The simplest molecular theory of the structure of π-electron systems is based on an incompletely defined Hamiltonian which does not include electron interaction. In this paper a self-consistent method is described in which systematic approximations are made for the electron repulsion integrals. The theory is applied to the following properties of hydrocarbons: 1, resonance energies; 2, ionization potentials and electron affinities of molecules and radicals; 3, bond orders and bond lengths; 4, relative stability of radicals and carbonium ions; 5, charge distribution in ions. It is found that, for a satisfactory theory of some of these properties, electron interaction terms must be included in the treatment.

1. Introduction.—Most of the early work on the application of molecular orbital theory to the mobile electrons of conjugated molecules was based on the semi-empirical method developed by Hückel,[1] Lennard-Jones,[2] Coulson and Longuet-Higgins[3] and others. In this method the mobile electrons are treated as occupying a set of delocalized molecular orbitals, which are linear combinations of atomic $2p\pi$ functions

$$\psi_r = \sum_{\mu} c_{r\mu}\,\phi_\mu \qquad (1)$$

and are chosen as approximate eigenfunctions of a one-electron Hamiltonian, whose form need not be specified in detail as its matrix elements are chosen empirically. This procedure effectively assumes that there is a definite energy associated with each orbital, independent of the number of electrons occupying other orbitals. This cannot be correct if the repulsion of the electrons is taken into account. Clearly, the energy required to ionize an electron from a given orbital will be smaller, the more electrons there are in other orbitals.

The basic difficulty in the Hückel theory is the neglect of these electron interaction terms. Strictly, the problem should be formulated in terms of the complete many-electron Hamiltonian where the interelectronic terms appear explicitly. More refined theories, of a non-empirical nature, have been developed along these lines, beginning with the work of Goeppert-Mayer and Sklar[4] on benzene. A completely non-empirical method, however, leads to a number of complicated electron repulsion integrals and the calculations become too heavy for any but the simplest systems. Recently, however, it has been shown that a set of simplifying approximations can be made which leave the main conclusions unaltered and which enable electron repulsion terms to be included in a semi-empirical method applicable to larger molecules. These approximations were originally suggested by Pariser and Parr[5] and have led to considerable advances in the theory of electronic spectra of aromatic compounds.

The present author and collaborators[6-9] have used approximations similar to those of Pariser and Parr to develop a self-consistent molecular orbital theory which can be compared directly with the original Hückel independent-electron model. In a self-consistent method, the molecular orbitals (1) are chosen to minimize the total energy calculated using the complete Hamiltonian, electron repulsion terms included. Energies calculated from these and related wave functions lead to theoretical expressions for the various energies that are measured in processes such as excitation

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(1) W. Hückel, *Z. Physik*, **70**, 204, 279 (1931).

(2) J. E. Lennard-Jones, *Proc. Roy. Soc. (London)*, **A158**, 280 (1937).

(3) C. A. Coulson and H. C. Longuet-Higgins, *ibid.*, **A191**, 39 (1947).

(4) M. Goeppert-Mayer and A. L. Sklar, *J. Chem. Phys.*, **6**, 645 (1938).

(5) R. Pariser and R. G. Parr, *ibid.*, **21**, 767 (1953).

(6) J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).

(7) A. Brickstock and J. A. Pople, *ibid.*, **50**, 901 (1954).

(8) N. S. Hush and J. A. Pople, *ibid.*, **51**, 600 (1955).

(9) J. A. Pople, *Proc. Phys. Soc.*, **68A**, 81 (1955).

and ionization. The aim of the present paper is to give an account of this work and bring out the role of electron interaction in determining various properties of hydrocarbons.

2. General Theory.—In the self-consistent theory, the basic problem is to determine the coefficients $c_{r\mu}$ in the molecular orbitals (1) so that the total energy is minimized. This general problem has been considered by Roothaan.[10] If the overlap integral between different atomic orbitals is neglected, the coefficients satisfy a set of equations

$$\sum_{\nu} F_{\mu\nu}\, c_{r\nu} = E_r\, c_{r\mu} \tag{2}$$

where E_r is an energy associated with orbital r and $F_{\mu\nu}$ is a matrix element of the Hartree–Fock Hamiltonian between atomic orbitals ϕ_μ and ϕ_ν. For those orbitals which are doubly occupied, E_r is an approximation to the corresponding ionization potential and for those which are empty, it is an approximation to the electron affinity.

This much is standard molecular orbital theory. The approximations that are made in simplifying these equations for conjugated hydrocarbons are as follows.

A. The σ-electrons are treated as a rigid core whose potential can be included in the Hamiltonian.

B. The overlap integrals are neglected and so are the electron repulsion integrals except those of the form

$$\gamma_{\mu\nu} = \int\int \phi_\mu^2(1)\,(1/r_{12})\phi_\nu^2(2)\,d\tau_1 d\tau_2 \tag{3}$$

representing the interaction of an electron on atom μ with one on atom ν. These are the most important electron repulsion terms and it is with the effect of these on theoretical expressions for various molecular properties that we shall be mainly concerned. Following the suggestion of Pariser,[5] the value of γ_{11}, that is, the interaction between two π-electrons on the same carbon atom, will be chosen as the difference

$$\gamma_{11} = (I - A)_c \tag{4}$$

between the ionization potential I and the electron affinity A of the appropriate valence state of carbon. The actual numerical values used for hydrocarbons are $\gamma_{\mu\nu} =$ 10.53, 7.30, 5.46 and 4.90 e.v. for internuclear distances 0, 1, $\sqrt{3}$ and 2 times the C—C distance in benzene. For larger separations $\gamma_{\mu\nu}$ is approximated by the interaction energy of unit point charges.

C. It is supposed that the attraction between an electron on one atom μ and the σ-core of another ν can also be approximated by $\gamma_{\mu\nu}$, penetration effects being neglected.

D. The remaining parameter is the "resonance integral"

$$\beta = \int \phi_\nu\ H^{\text{core}}\,\phi_\nu\ d\tau \tag{5}$$

for neighboring atoms μ and ν. This is essentially the same parameter as in the Hückel theory, representing the available bonding power between these atoms. Following Pariser and Parr,[5] it is chosen empirically as -2.39 e.v. to fit the energies of the excited states of benzene. Other $\beta_{\mu\nu}$ (μ and ν not neighboring) are taken to be zero.

With these approximations, the matrix elements reduce to[6,7]

$$F_{\mu\mu} = U_{\mu\mu} + \tfrac{1}{2}P_{\mu\mu}\,\gamma_{\mu\mu} + \sum_{\sigma(\neq\mu)} (P_{\sigma\sigma} - 1)\gamma_{\mu\sigma} \tag{6}$$

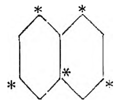
$$F_{\mu\nu} = \beta_{\mu\nu} - \tfrac{1}{2}P_{\mu\nu}\,\gamma_{\mu\nu} \tag{7}$$

$$P_{\mu\nu} = 2\sum_{r}^{\text{occ}} c_{r\mu}\,c_{r\nu} \tag{8}$$

Here $U_{\mu\mu}$ is the energy of an electron in ϕ_μ in the core field of its own atom. This may reasonably be supposed to depend on the nature of that atom only. In dealing with hydrocarbons there will only be one value U. The coefficients $P_{\mu\nu}$ also appear in the Hückel theory and are the charge densities (if $\mu = \nu$) and bond orders ($\mu \neq \nu$). The diagonal matrix element $F_{\mu\mu}$ represents the energy of an electron in ϕ_μ in its own core ($U_{\mu\mu}$), partly screened by other electrons on the same atom (second term) and also attracted by incompletely screened cores of other atoms (third term).

It should be noted that equations (2) for the coefficients are not linear as the matrix element $F_{\mu\nu}$ itself depends on the $c_{r\mu}$. However, they can be solved by iteration and lead fairly quickly to a set of self-consistent orbitals.

3. Even Alternant Hydrocarbons.—For the class of conjugated hydrocarbons known as alternants, it is possible to develop the theory rather further and to predict certain general properties. A hydrocarbon is said to be alternant if the carbon atoms can be divided into two classes, starred and unstarred, so that no two members of the same class are bonded together. If, further, there are an even number of conjugating carbon atoms, there will be an even number of mobile electrons and the system will generally be in a closed shell ground state. Naphthalene is an example of an even alternant molecule.



Charge Distribution.—Subject to the approximations described above, it is a possible to show[6] that the electron densities on all the atoms of an even alternant are equal, that is $P_{\mu\mu} = 1$ for all μ. The diagonal matrix elements then all reduce to

$$F_{\mu\mu} = U + \tfrac{1}{2}\gamma_{11} \tag{9}$$

This uniform charge distribution theorem had already been proved for the Hückel theory by Coulson and Rushbrooke.[11] This extension shows that their result is still true if electron interaction is included in this approximate manner.

Resonance Energies.—We can calculate a theoretical vertical resonance energy by subtracting the total self-consistent energy from the corresponding energy for one of the classical structures, the latter being obtained by using appropriate localized double bond orbitals instead of the final self-consistent set. It can be shown, to the same

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(10) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 61 (1951).

(11) C. A. Coulson and G. S. Rushbrooke, *Proc. Camb. Phil. Soc.*, **36**, 193 (1940).

approximation, that the energies of all the classical structures calculated in this way are the same, so the resonance energy is uniquely defined. The answer is[7]

$$\text{Resonance energy} = K\beta - \tfrac{1}{2}\sum_{\mu<\nu} P_{\mu\nu}(\gamma_{12} - \gamma_{\mu\nu}) \quad (10)$$

The first term is proportional to β (K being a combination of bond orders $P_{\mu\nu}$) and is close to the resonance energy expression in the Hückel theory. The second term gives the effect of electron interaction and (since $\gamma_{\mu\nu} \leqslant \gamma_{12}$) is such as to reduce the resonance energy. However, this sum is smaller than the $K\beta$ term, since there are no contributions from neighbors and the $P_{\mu\nu}$ fall off fairly rapidly with increasing separation. It appears then that for even alternants the simple theory is adequate for comparing resonance energies.

Ionization Potentials and Electron Affinities.[8]—Another result which can be extended from the Hückel to the self-consistent theory is the pairing of orbitals. Corresponding to each occupied orbital r, there is an unoccupied orbital r′ whose Hartree–Fock energy E_{r}' is such that

$$E_r + E_r' = 2U + \gamma_{11} \quad (11)$$

The constant on the right-hand side is the same for all even alternants. Now the Hartree–Fock energies represent ionization potentials and electron affinities for occupied and unoccupied orbitals, respectively. Further the highest occupied orbital will be paired with the lowest one unoccupied, so that the ionization potential I and the electron affinity A always satisfy

$$I + A = 2U + \gamma_{11} \quad (12)$$

The calculation of either of these quantities separately requires a detailed analysis of the energies E_r. Such calculations have been performed by Hush and Pople[8] and by Matsen.[12] Some of the results are shown in Table I and are compared with experimental data. It should be noted that, with the exception of U, the parameters used in these calculations are those which were originally chosen to fit spectroscopic data, so there is good correlation between these properties. The agreement with experiment is fairly satisfactory. The electron affinities are predicted to be uniformly low, but the relative values fit well. Both the ionization potentials and electron affinities extrapolate well to the work function of graphite in the limit of large molecules.

Table I

Ionization Potentials and Electron Affinities of Conjugated Hydrocarbons

	I, e.v.		A, e.v.	
	Calcd.	Obsd.	Calcd.	Obsd.
Benzene	9.87	9.43[13]	−1.40	−0.54[a]
trans-Butadiene	8.81	9.07[14]	−0.34	....
Styrene	8.76	8.86[15]	− .29	....
Naphthalene	8.61	8.68[16]	− .14	+0.65[18]
Phenanthrene	8.53	8.62[16]	− .06	+0.69[18]
Anthracene	7.83	8.20[16]	+ .64	+1.19[18]
Graphite	4.23	4.39[17]	+4.23	+4.39[17]

[a] Extrapolated.

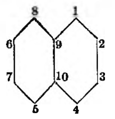
A clear result of this work is that the simultaneous calculation of ionization potentials and electron affinities with a single set of parameters is only possible if electron interaction is included explicitly. Otherwise the difference between them is underestimated. Thus, according to the Hückel theory, $I - A$ for benzene is only -2β or 4.8 e.v. In this theory it is $(-2\beta + {}^2/_3\,\gamma_{12} + {}^1/_3\gamma_{14})$ giving the values quoted above.

Bond Orders and Bond Lengths.—Another application of molecular orbital theory to conjugated hydrocarbons is the investigation of the correlation between bond orders $P_{\mu\nu}$ and the corresponding bond lengths. $P_{\mu\nu}$ is, in a sense, the number of π-electrons in the bond $\mu\nu$ (for neighboring atoms) and is therefore expected to increase as we go from the long weaker bonds to the shorter ones with more double bond character. It is of interest, therefore, to compare the self-consistent with the Hückel bond orders in this respect.

For naphthalene the self-consistent theory is significantly superior (Table II). The theory predicts the correct order of bond lengths and the central bond is no longer anomalous. This improvement does not extend to larger hydrocarbons, however. Pritchard and Sumner,[20] in an extensive investigation covering all hydrocarbons whose bond lengths have been determined sufficiently accurately, found that, on the average, self consistent bond orders were no better. The reasons for this are not clear at present.

Table II

Bond Orders and Lengths for Naphthalene



Bond	1–2	9–10	2–3	1–9
Bond order (Hückel)	1.72	1.52	1.60	1.55
Bond order (SCF)	1.78	1.60	1.54	1.50
Bond length[19] (A)	1.365	1.393	1.404	1.424

4. Odd Alternant Hydrocarbons.[7]—Hydrocarbons which possess an odd number of conjugating carbon atoms can also be classed as alternant or non-alternant. In neutral form, they will be radicals with an odd electron in the highest molecular orbital. As positive carbonium ions, they often play an important role as intermediates in reactions and their stability is a rate-determining factor.

The Hückel independent-electron model makes certain simple predictions about odd alternants.[21] All molecular orbitals but one are paired as with even molecules, and the remaining orbital has zero energy (relative to an atomic orbital). Further

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(12) F. A. Matsen. *J. Chem. Phys.*, **24**, 602 (1956).

(13) R. E. Honig, *ibid.*, **16**, 105 (1948).

(14) W. C. Price and A. D. Walsh, *Proc. Roy. Soc. (London)*, **A174**, 220 (1940).

(15) J. D. Morrison and A. J. C. Nicholson, *J. Chem. Phys.*, **20**, 1021 (1951).

(16) D. P. Stevenson, private communication.

(17) R. S. Mulliken, *Phys. Rev.*, **74**, 736 (1948).

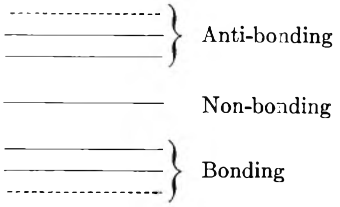
(18) R. Blackedge and N. S. Hush, in course of publication.

(19) R. Ahmed and D. J. Cruickshank, *Acta Cryst.*, **5**, 852 (1952).

(20) H. O. Pritchard and F. Sumner, *Proc. Roy. Soc. (London)*, **A226**, 128 (1954).

(21) H. C. Longuet-Higgins, *J. Chem. Phys.*, **17**, 265 (1950).

this single molecular orbital has non-zero coefficients on one class of atoms only. It is frequently called the non-bonding orbital. The energy level diagram has the structure



The non-bonding orbital is singly occupied in the radical but empty in the positive ion. The Hückel theory also predicts that, in the radical, the charge distribution is uniform. Since an electron is moved from the non-bonding orbital to form the lowest state of the positive ion, the positive charge is predicted to be on one class of atoms only. Electron repulsion terms will undoubtedly cause some rearrangement of charge in the ion, however. This would all be allowed for in a self-consistent treatment.

The problem of determining self-consistent orbitals in a radical, where one of the orbitals is only singly occupied, is rather different from the closed shell case considered by Roothaan. Various approaches to the radical problem have been considered,[22,23] and it recently has been shown[24] that the odd alternants will still have paired orbitals in this approximation.

Resonance Energies of Radicals and Carbonium Ions.—One of the predictions of the Huckel theory which is not substantiated by the refined method concerns the relative stability of radicals and carbonium ions. Since the non-bonding orbital has zero energy (in units of β), the Hückel theory predicts that the energy required to remove the electron from the non-bonding orbital in the radical is the same as that required to remove it from the odd atom in one of the classical structures. Thus for allyl as an example

$$E(\text{allyl}) - E(\text{allyl}^+) = E(\text{C=C—C}^\cdot) - E(\text{C=C—C}^+) \tag{13}$$

In other words, the simple theory predicts that the resonance energies of radical and ion are equal.

These energies can also be compared in the theory with electron interaction if we assume that the self-consistent orbitals for the ion are approximately the same as for the corresponding radical. Then, writing out the full expressions for the energy and subtracting, we find that the difference in resonance is given by[7]

$$E_{\mathrm{R}}(\text{ion}) - E_{\mathrm{R}}(\text{radical}) = \tfrac{1}{2}\left\{\gamma_{11} - \sum_{\mu\mu} c_{0\mu}\, c_{0\mu}\, \gamma_{\mu\mu}\right\} \tag{14}$$

where $c_{0\mu}$ are the coefficients of the non-bonding orbital. In other words the ion has an additional stability equal to half the difference between the interaction of two electrons on the same atom and the interaction between two in the non-bonding orbital.

There is some direct experimental evidence supporting this conclusion. Resonance energies of radicals can be estimated from dissociation energy differences such as

$$E_{\mathrm{R}}(\mathrm{R}^\cdot) = D(\mathrm{RX}) - \mathrm{D}(\mathrm{MeX}) \tag{15}$$

and those of carbonium ions from the appearance potential of R^+ in the process[25]

$$\mathrm{RX} \longrightarrow \mathrm{R}^+ + \mathrm{X}\cdot + e^- \tag{16}$$

Calculated resonance energies are compared with those estimated from experimental data in this way are shown in Table III.

Ionization Potentials and Electron Affinities of Radicals.[8]—The ionization potentials and electron affinities of radicals cannot be interpreted in terms of the Hückel theory according to which the non-bonding orbital always has the same energy. Making use of the self-consistent functions, it can be shown that the relation

$$I + A = \text{constant} = 2U + \gamma_{11} \tag{17}$$

still holds, the constant being the same as for even alternants. The difference between I and A is just equal to the interaction of a pair of electrons in the non-bonding orbital

$$I - A = \sum_{\mu\nu} c_{0\mu}\, c_{0\nu}\, \gamma_{\mu\nu} \tag{18}$$

as might be expected on qualitative grounds.

Since the non-bonding orbital coefficients can be approximated by their values in the Hückel theory which are easily calculated, equations 17 and 18 lead directly to estimates for I and A. These are compared with some experimental measurements in Table IV.

Charge Distribution in Carbonium Ions.[7]—As mentioned above, the self-consistent orbital method is a sounder procedure for determining the distribution of charge in a positive ion. We have already noted that the radical has uniform charge density and an odd electron in a non-bonding orbital. If the remaining orbitals were unaltered on ionization therefore, the positive charge would be distributed according to the squares of the coefficients of the non-bonding orbital, that is only on alternate atoms. But the effect of the electron repulsion terms will be to modify this distribution somewhat; the self-consistent orbitals should be determined afresh for the carbonium ion. Some self consistent charge distributions found in this way are compared in Fig. 1 with the predictions of the Hückel theory.

These results generally confirm those of the simpler method, although certain new features are apparent. There appears to be a tendency for electrons to concentrate in the central parts of a positive ion and to keep away from the perimeter. For all the phenyl groups considered, the charge density on the *meta*- and *para*-atoms is less than that predicted by the Hückel orbitals. The physical reason for this is that the potential energy in the field of a completely stripped σ-core is lower in the central regions, particularly at those atoms

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[22] J. A. Pople and R. K. Nesbet, *ibid.*, **22**, 571 (1954).

[23] H. C. Longuet-Higgins and J. A. Pople, *Proc. Phys. Soc.*, **68A**, 591 (1955).

[24] C. Moser and R. Levefre, private communicaton.

[25] J. Halpern, *J. Chem. Phys.*, **20**, 744 (1952).

[26] M. Szwarc, *Chem. Revs.*, **47**, 75 (1950).

[27] J. L. Franklin and H. E. Lumpkin, *J. Chem. Phys.*, **19**, 1073 (1951).

Table III

Resonance Energies of Hydrocarbons Ions and Radicals (Kcal./mole)

Energy	Theoretical estimate	Exptl. estimate	Source[26, 27]
E_R(allyl)	31.0	19.0	D(CH$_2$:CH.CH$_2$—Br) − D(CH$_3$—Br)
		24.0	D(CH$_2$:CH.CH$_2$—CH$_2$.CH:CH$_2$) − D(CH$_3$—CH$_3$)
		24.0	D(CH$_2$:CH.CH$_2$—Cl) − D(CH$_3$—Cl)
E_R(allyl$^+$)	60.2	58.0	Appearance potential of allyl$^+$ from allyl chloride
E_R(benzyl) − E_R(benzene)	21.9	23.5	D(PhCH$_2$—H) − D(CH$_3$—H)
		17.0	D(PhCH$_2$—Br) − D(CH$_3$—Br)
		19.5	D(PhCH$_2$—CH$_2$Ph) − D(CH$_3$—CH$_3$)
E_R(benzyl$^+$) − E_R(benzene)	61.5	50.0	Appearance potential of benzyl$^+$ from benzyl chloride

Table IV

Ionization Potentials and Electron Affinities of Radicals (E.v.)

	I		*A*	
	Calcd.	Obsd.	Calcd.	Obsd.
Methyl	9.50	9.95[28]	−1.03	1.1[29]
Allyl	8.23	8.16[28]	+0.24	2.1[29]
Benzyl	7.78	7.73[28]	+0.69	1.8[29]

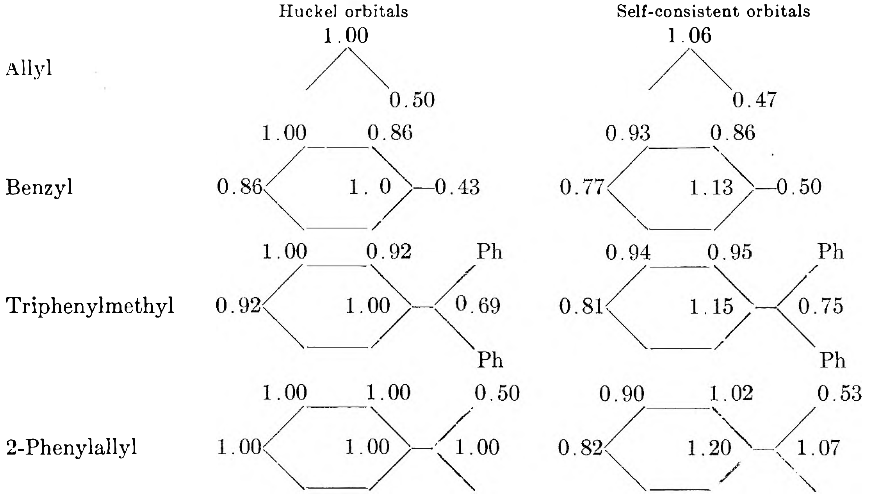
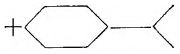


Fig. 1.—Charge densities for carbonium ions.

bonded to three other carbons. For neutral molecules, this is precisely balanced by the screening effect of other π-electrons, and uniform charge density is obtained. For positive ions, on the other hand, this screening is incomplete and there is a residual tendency for electrons to avoid the perimeter. 2-Phenylallyl illustrates this point well, for the Hückel theory predicts that there is no resultant positive charge on the *para*-carbon atom. Correspondingly, there is no simple valence structure of the type



Nevertheless, the self-consistent charge density on this atom is not much greater than for the corresponding position on the benzyl ion.

The positive charge distribution is important in determining the further stabilization of a substituted carbonium ion. The greater the positive charge on a given atom, the greater will be the energy lowering if an electron-donating group is attached to this position. The charge densities quoted in Fig. 1 suggest that it may not always be possible to interpret these in terms of appropriate simple valence structures.

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(28) F. P. Lossing, K. U. Ingold and I. H. S. Henderson, *J. Chem. Phys.*, **22**, 621 (1954).

(29) N. S. Hush and S. Oldham, in course of publication.

STABILITY AND REACTIVITY OF MOLECULES FROM THE STANDPOINT OF MOLECULAR ORBITALS[1]

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A formal procedure for discussing the qualitative aspects of chemical binding and chemical interaction between atoms and molecules within the framework of the molecular orbital theory has been proposed. This procedure is based on the comparison of the degeneracy of the molecular wave function with that of the reactants (atoms or molecules) and on the number and position of the nodes occurring in the molecular orbitals. This procedure has been illustrated for a few simple four atom systems. Four atom systems were chosen as the simplest systems which demonstrate the most general problems involved in as much as the energy can be expressed as a linear superposition of terms involving no more than four centers. Some quantitative calculations on simple systems have been reviewed. It has been emphasized that the occurrence and removal of degeneracy by changing the internuclear parameters is an important factor in all chemical problems. "Accidental degeneracies" occurring in heteronuclear problems seem to play a similar role to that of the orbital degeneracies occurring in symmetric systems and in determining chemical properties. The usefulness of the molecular orbital theory in a discussion of chemical reactions has been confirmed.

Recent calculations have demonstrated that the LCAO–SCF molecular orbital approximate solution of the Schroedinger equation for the many electron, many center system gives a good description of the ground states of polyatomic systems. It is for this reason that we have been using this method to study the ground state interactions of atomic and molecular systems. From the results of these studies and their correlation with the experimental data from atomic spectroscopy it has become apparent that the removal of degeneracies existing in the electronic ground states of the atoms is the basic reason for the existence of stable polyatomic molecules. We believe that this concept can also be extended to a discussion of crystals and metals as "big molecules." With the exception of a few molecules which are highly reactive, all stable molecules have a non-degenerate, totally symmetric ground state. Thus, stable molecule formation nearly always takes place so that the spatial arrangement of the nuclei results in the complete removal of the degeneracy (Jahn–Teller Theorem)[2] existing in the separated atoms. It is interesting to note that Kemble and Zener[3] as early as 1928 stated, "The rule that molecule formation is contingent on the removal of degeneracy from the wave functions of the interacting atoms seems to have a greater range of applicability thag London's rule. The latter is no doubt correct for a great variety of cases." The valence-bond method emphasizes the removal of spin degeneracy while the molecular orbital method allows one to consider the removal of both spin and orbital degeneracy. When this idea is extended in the light of recent developments it seems to us to be fundamental to most of chemistry. We will now summarize the qualitative conclusions we have reached from the consideration of the importance of the occurrence of removal of degeneracy when coupled with the molecular orbital method.

Not only does the tendency for the removal of degeneracy explain the existence of stable molecules, but it also explains the chemical reactivity of radicals and those few molecules having degenerate ground states. These species interact to form "dimers" or interact with other molecules to form other products with a zero or small energy of activation.

Furthermore, the "activated complex" of a chemical reaction is an intermediate state (degenerate or ambivalent complex[4]) between two different sets of products which result in removing the degeneracy of the wave function of the separated atoms.

In general, one set of products will be more stable than the other and a potential hill will lie between. In a chemical reaction, one usually starts with the reacting molecules or radicals and discusses the process of the formation of different products rather than starting with the separated atoms.

A catalyst may either supply one of its orbitals for the promoted electrons or lower the promotion energy by supplying an electron to the lowest unfilled orbital of the complex. That is, if one can mix in orbitals from the surface with less energy than is required to mix in the excited states of the reacting molecules one would expect a lowering of the activation energy. This certainly occurs with many catalysts.

We have previously[4] shown that a bi-molecular reaction between two saturated molecules can be treated from the molecular orbital point of view.

The molecular orbitals of the combined complex of the original molecules widely separated is degenerate. This degeneracy is split as the two molecules move together; for the occurrence of a bimolecular reaction leading to stable molecules the activated complex must have a degenerate electron configuration.

Since the energy necessary to allow such a degenerate configuration, when the reacting molecules are close to each other (~1–2.5 Å.), is usually higher than the bond energy for the weakest bond in a given molecule the predominance of free radical mechanisms in the thermal decomposition of most molecules is explained. Accidental orbital degeneracies in heteronuclear systems seem to be equally as important as orbital degeneracy due to spatial symmetry. The charges on the nuclei and the internuclear distances are both important and ap-

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[1] The work reported in this paper has been supported by the Office of Naval Research and the Air Force.

[2] O. Jahn and E. Teller, *Proc. Roy. Soc.* (*London*), **A161**, 220 (1937).

[3] E. C. Kemble and C. Zener, *Phys. Rev.*, **33**, 812 (1929).

[4] V. Griffing, *et al.*, *J. Chem. Phys.*, **23**, 1015 (1955).

pear in a similar way as the fundamental parameters in an n-electron system, even though the charges are fixed for a given system.

Even though it is the degeneracy of the total wave function that can be formally shown to be of importance in chemical processes, these same degeneracies arise in the molecular orbital approximation. Further degeneracies arise in the orbital approximation but these additional degeneracies can be removed by a configuration–interaction calculation. The way in which they must be removed gives an indication of the choice of the best configurations which should lead to improved results in the higher approximations and thus indicates mixed configurations for the exact solutions. Thus, the molecular orbital approximation is particularly suited for both a qualitative and, in many simple cases, a quantitative discussion of chemical problems. It is the purpose of this paper to illustrate the usefulness of the MO method for discussing the role of the occurrence and removal of degeneracies as outlined above and to illustrate the qualitative conclusions stated above.

I. Degeneracy in Atoms.—Attempts to solve the Schroedinger equation for the many-electron atoms led to the development of the "configurational theory" of atomic spectra which assigns each electron to one of a set of orthogonal wave functions called atomic orbitals. The atomic orbitals are designated by quantum numbers: the order of the ground and lower excited states of the lighter atoms (L–S coupling) can be determined according to the following rules applied in order, always satisfying the Pauli Principle: (a) the lowest n must be filled first—lowest energy; (b) the lowest l must be filled—lowest energy. Then each atom has an n-electron state designated with analogous quantum numbers. The n is that of the last electron, l is replaced by the vector sum $L = \sum_{i=1} \vec{l}_i$ and s is replaced by the vector sum $S = \sum_{i=1} \vec{s}_i$. The following rules due to Hund are then applied: (c) the highest S satisfying the Pauli Principle and a and b, the lowest energy; (d) the highest L, the lowest energy. Thus, after a and b have been satisfied, the atomic state having the *highest degeneracy* lies the lowest.[5]

The application of these rules to obtain the ground state configuration and resulting atomic states for the O atom is demonstrated in Fig. 1. The outer electrons (valence) on the atoms determine the configuration of the atom since filled shells (in this case 1s, 2s) make no contribution to the L or S value of the atom as a whole. The one-to-one correspondence between these configurations and the periodic table of Mendeleef leads to the obvious conclusion that the chemical properties are due to the valence electrons. All elements in the same group of the periodic table have the same configuration for the valence electrons, the same ground state configuration, and similar chemical properties.

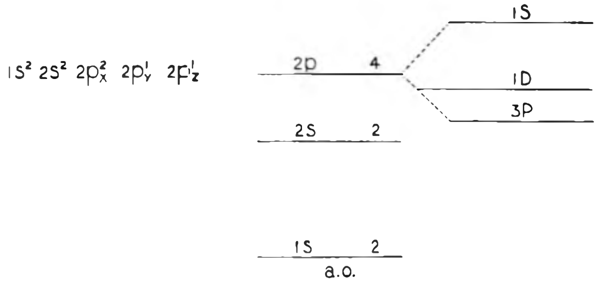

Fig. 1.—Schematic energy level diagram for an O atom. The usual notation is used. The numbers on the atomic orbital levels indicate the occupation numbers.

II. General Features of Molecular Orbital Theory.—In considering the formation of stable molecules the natural starting place is with the atoms. One would expect that the heat of formation of molecules and the properties of molecules might best be obtained by starting with the separated atoms and doing an ordinary perturbation calculation. For example the total energy of the water molecule is 2080.6 e.v. (*i.e.*, with reference to nuclei and electrons infinitely separated from each other, and, moreover, this is the quantity given by the exact solution of the Schroedinger equation) while the heat of formation[6a] from the atoms is only 10.1 e.v.[6b] However, the mathematical difficulties of applying the Pauli Exclusion Principle in allowing for exchange of all the electrons between the atoms, and the slow convergence of the perturbation theory due to the new form of the Hamiltonian in the many-electron case because of the exchange, has led to the development of the orbital theories.

In the M.O. theory the electrons are assigned to molecular orbitals in such a way that the Pauli exclusion principle is satisfied by allowing only two electrons of opposite spin to occupy each molecular orbital. Space does not permit a detailed review of the mathematical formalism which has already been discussed by Roothaan, Mulliken, Lennard-Jones, Löwdin and others.[7] However, we would like to emphasize the following pertinent features of this theory which will be used in this paper.

1. If the molecule or complex has any spatial symmetry "primitive molecular orbitals" or "symmetry adapted functions" can be determined with the help of group theory. The coefficients are not yet determined. All orbitals having different symmetry properties are orthogonal to each other. Orbitals of the same symmetry must be made orthogonal[8] and their energies cannot cross over for any value of the internuclear distances.

2. If real functions are used for the atomic orbitals and the coefficients, the molecular orbitals will have nodal properties determined by the spatial symmetry. Herzfeld has shown[9] that the nodal surfaces in one-electron functions are preserved, although deformed, as one brings the atoms from infinity to finite values of the internuclear parameters. In addition, for cases in which the atomic or-

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(5) The ground state of stable and normally unreactive molecules and rare gas atoms are always non-degenerate singlets.

(6) (a) Activation energies and bond dissociation energies are even smaller; (b) H. Shull and F. O. Ellison, *J. Chem. Phys.*, **23**, 12, 2348 (1955).

(7) See J. C. Slater, Atoms and Molecules "Technical Report," MIT, for a complete bibliography up to 1952.

(8) This is called "forced hybridization" by Mulliken.

(9) K. F. Herzfeld, *Z. Naturf.* (*Sommerfeld-Heft*), **3a**, 457 (1948); *Rev. Mod. Phys.*, **41**, 527 (1949).

bitals are alike, he shows that no two states of different energy can have the same number of nodal surfaces of the same kind, and this number increases by one if one goes to the state of next higher energy. Furthermore, if the nodal surfaces are changed adiabatically the amount of charge contained in the region between the nodes is conserved as long as the molecular orbital is non-degenerate. We will illustrate how these properties can be extended to linear combinations of different orbitals. We will use these two principles under the restrictions of the Pauli exclusion principle to determine the ground state electron configuration of a given molecule or complex.

Furthermore, Berlin[10] has shown that the presence in a wave function of a node between two atoms means that the electrons are anti-bonding for those two atoms. The absence of a node between two atoms means bonding. A node passing through a nucleus is usually non-bonding. The magnitude of the bonding or anti-bonding requires a knowledge of the SCF coefficients, and is a function of the internuclear distance, the charges on the nuclei and the spatial symmetry. At large distances the differences between bonding and anti-bonding is small.

3. If an orbital or spin degeneracy occurs in the polyatomic system, Hund's rules (c and d) are equally valid as long as there is L–S coupling.

4. It can be shown that the MO approximation leads to an exact solution of the Schroedinger equation for the many-electron complex if a complete set of atomic functions are used in the expansion. The molecular orbitals must be orthonormal. It is for this reason that all of the electrons must be included in the quantitative application of the MO theory. It has been conceptually difficult to accept the necessity for including the "inner shell" electrons in considering molecular formation, but it is now clear that this is a mathematical requirement due to the fact that approximate molecular orbitals of the same symmetry having different eigenvalues are not necessarily orthogonal. For a qualitative discussion only the valence electrons and valence shell wave functions need be considered: however, in the many center case, valence shell atomic functions are defined as all of the functions having the same total quantum number as the last valence electron on the atom. Thus, for a discussion of diatomic molecules Li_2 to F_2, the 2s and 2p functions on both atoms must be included.

5. In as much as the Hamiltonian is a sum of a one-electron and a two-electron operator, the energy is expressed as

$$E = \Sigma \text{ one-electron integrals} + \Sigma \text{ two-electron integrals}$$

This sum can be rearranged and collected with reference to the nuclear field as

$$E = \Sigma \text{ one center integral} + \Sigma \text{ two center integrals} + \Sigma \text{ three center integrals} + \Sigma \text{ four center integrals}$$

Thus the energy is a linear superposition of terms involving no more than four centers, even if an infinite set of atomic orbitals converging to the exact solution is used. Consequently, one would expect that all the general features of molecular structure and atomic and molecular interaction would emerge from a study of four-atom systems. It is for this reason that we have been studying four-atom systems. Of course, in order to determine the detailed electronic structure of any particular polyatomic molecule all of the nuclei must be used. The one center and the two center integrals between neighboring atoms make the largest contribution to the energy emphasizing the importance of the atoms and the bond picture. However, three and four center integrals are important in most polyatomic problems, and must always be included in any numerical molecular orbital study.

6. The Jahn–Teller theorem shows that a linear molecule can be stable even if the total wave function is orbitally degenerate. Thus a few linear molecules also have spin-degenerate stable states. However, according to the hypothesis that removal of degeneracy leads to a more stable system one would expect all of these molecules to be very reactive. According to this theorem a stable non-linear molecule cannot have any remaining orbital degeneracy but it does not say anything about spin degeneracy or "accidental degeneracies." In molecules, spin degeneracy occurs, *e.g.*, when the last occupied M.O. is degenerate and has two electrons occupying it. This degeneracy may be "accidental" or due to symmetry. The fact that no stable non-linear molecule has a spin degenerate ground state (doublet states must be excluded as only magnetic interactions can remove this degeneracy) the removal of both spin degeneracy and "accidental degeneracies" must be equally fundamental in chemistry. The Jahn–Teller[2] theorem probably can be extended to show that the removal of this additional degeneracy is fundamental to the formation of crystalline solids and metals. Melvin[11] has indicated that such an "accidental degeneracy" must be shown to be an intrinsic degeneracy if one uses the theory of arithmetic substitution groups in conjunction with the group theory of spatial symmetry used in the Jahn–Teller[2] paper.

III. The Qualitative Discussion of Homonuclear Four-center Systems.—In this part of the discussion, the symmetry adapted functions will not be stated in algebraic form but will be diagrammed according to the notation for the atomic orbitals on each nucleus as explained under Fig. 2.

The molecular orbitals are chosen and filled according to the rules outlined in II, always observing the restrictions imposed by the Pauli exclusion principle. In all cases, except for H-atoms, the 1s electrons are ignored, and sixteen symmetry orbitals are formed from the four 2s and twelve 2p atomic orbitals. In considering the linear C_4 complex, we assume the four carbon nuclei always lie on a line and the distances between nearest neighbors are always equal. The symmetry orbitals for the linear case are given in Fig. 2. In C_4 we have 16 valence electrons. Eight of these will go in the first four molecular orbitals, which are $2s\sigma$ orbitals. ϕ_1 will hold two electrons and is bonding for all three bonds. ϕ_2 is bonding for ab and cd, but is an-

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[10] J. Berlin, *J. Chem. Phys.*, **19**, 208 (1951).

[11] M. A. Melvin, *Rev. Mod. Phys.*, **28**, 38 (1956). The importance of the removal of degeneracy is related to the "Many-one symmetry principle" discussed in this paper.

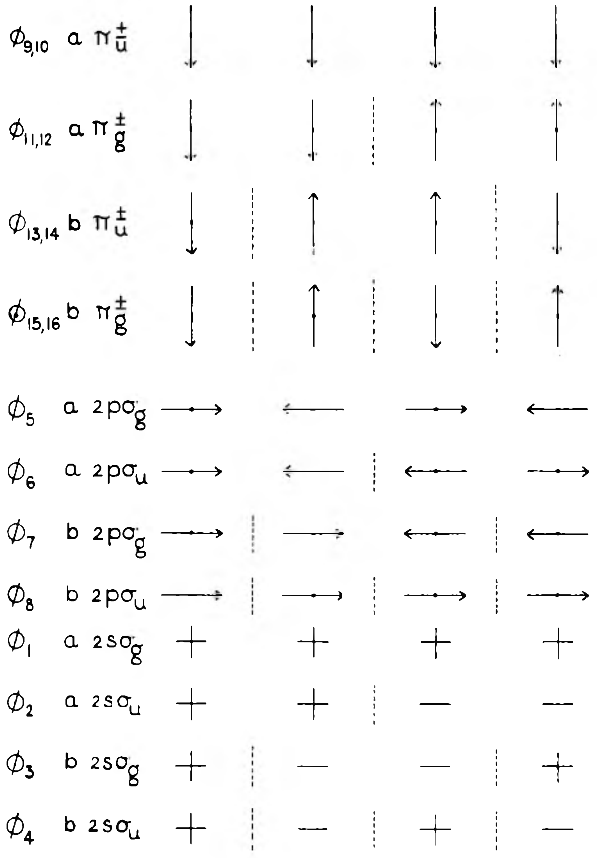

Fig. 2.—Symmetry orbitals for a linear four atom complex having 2s and 2p orbitals on the separated atoms. The σ-orbitals are non-degenerate and can accommodate two electrons each. The π-orbitals are twofold degenerate and can accommodate four electrons. Dotted lines indicate nodal planes.

+2s — "+"

−2s — "−" (Here the negative sign indicates a phase difference in going from one atom to another.)

$2p_x$ — "—•→", where the arrow represents the $2p_x$ function ±, and the + and − represent a phase difference on opposite sides of the nucleus.

All 2p functions or linear combinations of 2p functions on the same atom will be represented by an arrow. When two arrowheads or two arrowtails from different atoms point toward each other there is bonding. If an arrowhead connects with an arrowtail there is anti-bonding and a node lies between.

¦— The dotted line will indicate anti-bonding.

tibonding for bc. ϕ_3 is anti-bonding for ab and cd, but is bonding for cd. Thus ϕ_2 and ϕ_3 would just compensate for each other and form a non-bonding pair of molecular orbitals. The next two, when placed in ϕ_4, produce antibonding between all of the atoms. Thus the 2s electrons are approximately non-bonding. However, the next two electrons (total 10) are bonding electrons in ϕ_5. Since ϕ_5 and ϕ_1 have the same symmetry they will need to be replaced by linear combinations of the two orbitals. ϕ_1 will be pushed to lower energies and ϕ_5 to higher energies. In this respect some bonding may come from ϕ_1. The next four electrons are placed in the bonding degenerate aπ_u orbitals ϕ_9 and ϕ_{10}. The last two electrons (total 16 valence electrons) will probably go in the degenerate aπ_g orbital since the anti-bonding of the π orbital between c and d would be energetically more favorable than the bpσ_u anti-bonding orbital. Thus, since there are more bonding than anti-bonding electrons between each pair of atoms one would expect C_4 to be stable. However, the last orbital is only partially filled giving a spin degenerate ground state. Thus one would expect C_4 to be reactive with other C, C_2 or C_4, etc., species in a given reaction vessel. Consequently, this would predict that carbon atoms would have a stable form in long chains or other structures which would continue until the degeneracy of the functions is removed. This is indeed true except at very high temperatures where it is possible to spectroscopically observe C_2,[12] C_3 and C_4. One obtains similar results for several other geometrical arrangements of the nuclei.

This degeneracy also can be removed by adding hydrogen atoms to the structure and, indeed, stable polyenes do form. If we add two additional electrons to this structure filling π one would still expect some stability and the degeneracy removed. The reactivity would be reduced also because of the removal of the degeneracy. Thus $C_4^{=}$ might be stable as far as electronic structure is concerned but no stable negative ion exists in the gas phase. However, if one neglects for the moment the effect of different charges,[13] C_2N_2 would be neutral and isoelectronic with $C_4^{=}$. This is a stable molecule.

If we now consider N_4 and add two more electrons, these would go into the b-2pσ_u orbital which is bonding between ab and cd, but is anti-bonding between bc. The four anti-bonding electrons in ϕ_{11} and ϕ_{12} just compensate for the bonding in the middle bond due to ϕ_9 and ϕ_{10}. The two electrons in ϕ_6 just compensate for the bonding in the middle bond due to ϕ_5 so this discussion shows that the N_4 complex would decompose into two diatomic molecules which would be stable in agreement with experience. If we consider O_4, we must add four more electrons. These would fill ϕ_{13} and ϕ_{14} giving bonding in the center bond but anti-bonding in the two end bonds. Thus O_4 might be slightly stable in the linear form. However, the bonding is weak between the two strongly bonded molecules and it is likely that some other spatial arrangement which would distribute the bonding energy more evenly between the bonds might be more likely to occur. For F_4 we have four additional electrons which probably occupy the last π orbital, or two of these electrons would go into the π orbital and two into ϕ_7. π_4 is anti-bonding between all the atoms and would thus compensate for the combined bonding of π_1, π_2 and π_3 leaving the two F_2 molecules bonded by the a2pσ_g and b2pσ_u. However the b2pσ_u orbital is anti-bonding between the two molecules. The alternative degenerate configuration would also be anti-bonding between the two diatomic molecules, but would also weaken the end bonds. One of these electronic structures might represent the "activated complex" for a bimolecular exchange reaction between two fluorine molecules. It is unlikely that F_4 would be very stable for any spatial configuration as the number

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[12] C_2 is stable by 3.6 e.v. and is a good example of the necessity of distinguishing between stability and reactivity.

[13] The effect of changing the charge will be shown later.

of nodes is preserved and too many orbitals with two and three nodes are needed for so many electrons. If we add four more electrons, we have Ne_4; all of the molecular orbitals are filled and for every bonding electron moving between each pair of atoms there is a corresponding anti-bonding electron. Thus all the molecular orbitals are filled and ordinary chemical bonding is impossible. This result could have been obtained from an inspection of the atomic states of the neon atoms. The neon has a $^1S_0$ ground state; there is no degeneracy to be removed from the separated atoms and consequently no stable molecules are formed.

This method can be used just as well in considering other spatial configurations. In Fig. 3, the symmetry orbitals for the four atoms placed at the corners of a square are shown using the same notation as Fig. 2. Just consider the case of four B atoms, *i.e.*, B_4. We now have twelve valence electrons. If we place eight electrons in the a_{1g}, e_u and b_{2g} orbitals made up from the 2s functions, these together would be essentially non-bonding. This would leave two electrons for the non-degenerate a_{2u} bonding orbital due to the π electrons perpendicular to the plane and the last two electrons for the bonding a_{1g} orbital due to the $2p\sigma$ atomic functions in the plane. Thus, there would be four bonding electrons for binding the four atoms together. However, the bonding due to the a_{2u} orbital is π type bonding and would require the nuclei to be quite close together to be very effective, but in this case the nuclear repulsions would be quite high. In addition, the charge distribution in this orbital would indicate that the addition of an atom above and below the plane would increase the effective bonding of the electrons in this orbital. A further argument against its stability is the fact that the a_{1g} bonding is along the diagonal, with its larger distance, rather than along the direction of the bonds. Thus these orbitals indicate that some other geometrical configuration, non-planar, would be more stable.[14] In addition a_{1g} and b_{1g} are probably not too much separated in energy and the ground state in this form may be a triplet with one electron in each. In this case, square B_4 would be very reactive and interact with other atoms to give more stable electron configurations. A similar discussion can be made for other cases. The orientation of the p-functions so that only minimum bonding is possible in the plane gives a qualitative reason for the absence of square molecules.

These two examples illustrate the qualitative indications one can get from a consideration of molecular orbital theory. Of course, a good quantitative calculation or a good experiment is the only positive evidence in any case. However, certain selected model calculations, using only a few electrons and four nuclei, would place these qualitative considerations on a much firmer base.

IV. Quantitative Study of H_4 Complexes.—Quantitative calculations have been completed[15] for a few simple systems and the results will be briefly presented here. The bimolecular interaction of two hydrogen molecules will be discussed first. This system was chosen as a model to illustrate the application of MO theory in discussing chemical reactions between two molecules and on the basis of an assumption that the chemical interaction between many saturated molecules can be treated as a four electron problem. In addition, the understanding of simple systems is necessary before more complicated systems can be considered. In Fig. 4, a correlation diagram is given for the reaction path in which two hydrogen molecules approach each other along a rectangular path. For a bi-molecular exchange reaction to take place, *i.e.*

$$H_A\,H_B + H_C\,H_D \longrightarrow H_A\,H_C + H_B\,H_D \quad (1)$$

the "degenerate" complex must be at least a square in order for reaction 1 to be possible. When the two original hydrogen molecules are infinitely separated from each other (left side of the figure), the filled twofold degenerate symmetry orbitals of the complex are given by $\sigma_g(AB) \pm \sigma_g(CD)$. The Pauli exclusion principle must be applied to this system as a whole throughout the interaction. There is also an unfilled twofold degenerate excited symmetry orbital $\sigma_u(AB) \pm \sigma_u(CE)$.[16] As the inter-molecular distances $R_{AC} = R_{BD}$ are decreased and the internuclear distances $R_{AB} = R_{CD}$ are increased, always maintaining a rectangular form (*i.e.*, $R_{AC} > R_{AB}$), the degeneracy is split as shown in the figure. In order to reach the square complex, the orbital ϕ_2 and the orbital ϕ_3 must intersect as represented in the middle of the diagram. The lowest a_g orbital will be filled with two electrons leaving only two electrons for the degenerate e_u state. This represents the electronic configuration of the "activated complex." One can see qualitatively why the activation energy for this kind of reaction is so high.

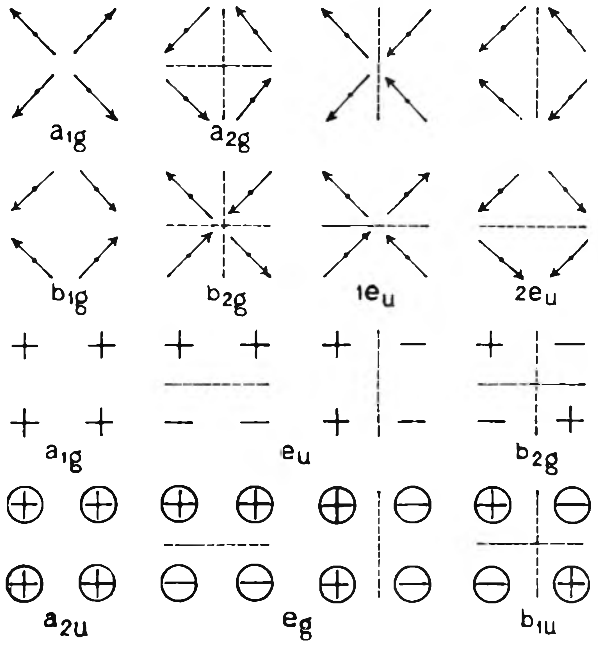

Fig. 3.—Symmetry orbitals for a square four atom system having 2s and 2p orbitals on the separated atoms. Dotted lines indicate nodal planes.

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[14] A non-planar configuration would mix the π and σ orbitals. The linear B_4 would have four electrons for the three bonds; however this would be degenerate similar to the C_4 complex. B_4^- should be quite stable.

[15] For the details, see ref. 4.

[16] The rules used here are the same as those given in II except that we start in this case with two molecules instead of two atoms.

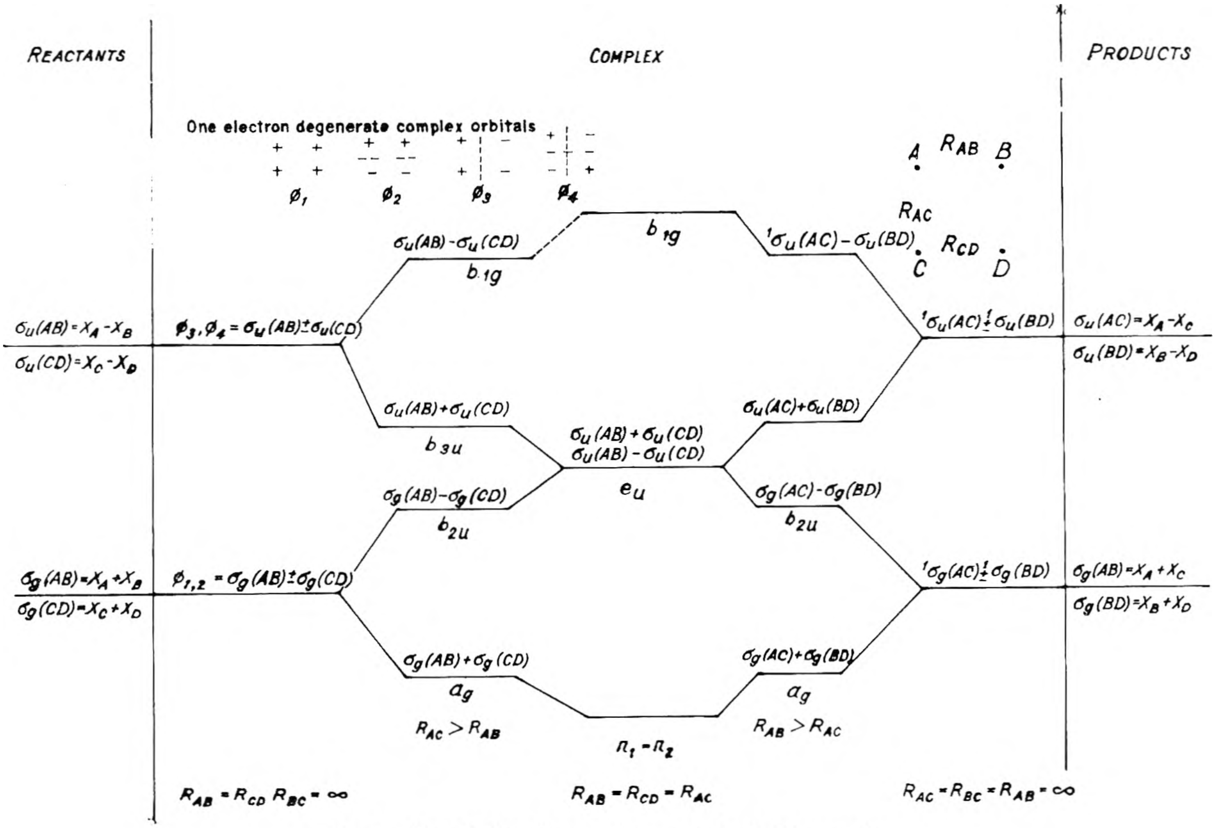

Fig. 4.—Correlation diagram for a quadratic H_4 complex.

It necessitates the mixing in of the high energy excited states of the separated hydrogen molecules. Spin–orbit interaction will split this degenerate configuration giving a $^3B_{2g}$ ground state (lying 1.6 e.v. below the degenerate configuration) and a $^1B_{2g}$, $^1B_{1g}$ and $^1A_{1g}$, with the $^1B_{2g}$ state lying lowest. The energies for these states all lie above the energy of the four hydrogen atoms; even though configuration interaction might lower the energy below this value, this path will require too much energy to permit any reaction along it. However, this illustrates the fact that activation energy in a bimolecular reaction is a promotion energy and also shows why radical mechanisms predominate in thermal decomposition of most molecules.

In general it takes much less energy to break a bond, *i.e.*, to form a vibrationally excited molecule which can decompose into two radicals, than to produce the "degenerate complex.[17] If the molecules are unsaturated or different, the energy of the complex would be much lower. *E.g.*, two C_2 molecules can probably react to form a square complex with a very small activation energy but this structure would be very reactive and an addition reaction would probably continue until graphite is formed. This diagram also illustrates the relative values of the activation energies between a radical and a molecule. This can be considered as a three electron problem; two electrons go into the first nodeless orbital which is binding and only one electron needs to be placed in the anti-bonding upper orbital. Thus the activation energy would be much less. In addition, if the upper orbital is degenerate, the total wave function of the complex would also be degenerate. Thus, according to the Jahn–Teller Theorem, the complex would be unstable and decompose along an asymmetrical vibration. If two radicals interact, this can be considered as a two electron problem and only the lowest bonding orbital need be filled. Thus one would expect either a zero or quite small energy of activation. Indeed the combination of two radicals to form a stable molecule usually removes degeneracy from the total wave function.

Calculations for the linear complex of four molecules have also been undertaken. This reaction can be represented as

$$H_A\,H_B + H_C\,H_D \longrightarrow H_A + H_B\,H_C + H_D \quad (2)$$

Reactions of this type occur much more frequently. The correlation diagram for this case is given in Fig. 5. One starts with the two hydrogen molecules in their ground state and brings them together along a line. At the left-hand side of the figure the degenerate symmetry orbitals for the two infinitely separated molecules are the same as in Fig. 4. However, as the two molecules begin to interact, the degeneracies are split differently and this time the complex is linear with neighboring atoms separated by the same internuclear distance. The symmetry orbitals are shown in the upper left-hand corner of the diagram and only ϕ_1 (a bonding orbital) and ϕ_2 (an anti-bonding orbital) are filled. However, the charge distribution in the upper orbital for the distance of the minimum is particularly interesting. The two electrons in this orbital

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[17] Here the degeneracy refers to the symmetry orbital but not to the total wave function.

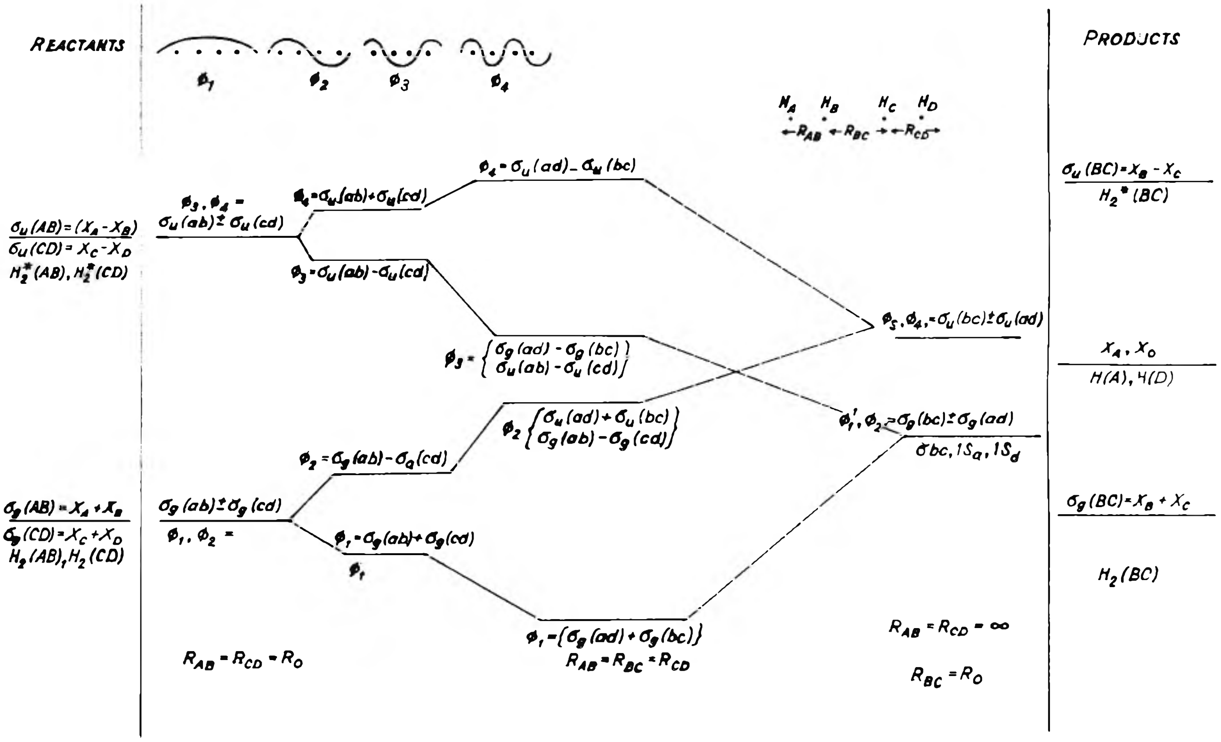
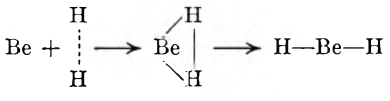


Fig. 5.—Correlation diagram for a linear H_4 complex.

have an equal probability of being around each atom. Consequently this orbital can be expressed as $\sigma_g(AB) - \sigma_g(CD)$ or as $\sigma_u(AD) + \sigma_u(BC)$; that is, as a linear combination of the molecular orbitals of the reactants or the products. We have called this an "ambivalent complex." If the reaction is to proceed according to (2), atoms A and D will have to move apart and atoms B and C will have to move together. However, at some point at large internuclear distances for the end atoms, ϕ_3 will have to cross over ϕ_2 (degenerate complex) in order to give H_BH_C in its ground state. ϕ_2 and ϕ_3 are of different symmetry and can consequently cross over, the complex decomposing along ϕ_3. However, the probability of such a transition would be low. If ϕ_3 was occupied by two electrons the two electron state would be of the same symmetry as the filled ϕ_2 state. From this point of view the two states would interact and repel each other. In other words, if we knew the exact wave functions these two levels would not intersect, but might come near to each other. From the molecular orbital point of view this means that configuration interaction is important in this problem and the two important configurations are $\phi_1(2)\phi_2(2)$ and $\phi_1(2)\phi_3(2)$. This configuration interaction lowers the activation energy below the value given by the single configuration calculation. The minimum energy for the linear ambivalent complex occurs at the value of the internuclear parameter $R_{AB} = R_{AC} = R_{CD} = 2.1$ a.u. The calculated value of this barrier is 18 kcal./mole above the calculated dissociation energy of a mole of H_2. Thus, if the configuration interaction is very important for the ambivalent complex this energy may be lowered to a value comparable to the energy required for the atomic mechanism. In any case, this would only occur at the beginning as the atomic mechanism would seem predominant. The lower energy in comparison with the square complex is due to the smaller nuclear repulsions (~20%) and the fact that the excited orbital need only be mixed in at large values of the internuclear parameters, where the excited state of the hydrogen molecule (H_{AD}) is much lower.

V. Interaction between a Be Atom and a Hydrogen Molecule.—The molecular orbital method was applied to the interaction of a beryllium atom and a hydrogen molecule.[18] This system was chosen because the ground state of the beryllium atom is a non-degenerate closed shell configuration in the same sense as molecules have closed shells (not a rare gas atom). In addition, we wished to investigate the effect of the different charges in a heteronuclear system. The two 1s electrons were buried in the beryllium nucleus and the problem considered as a four electron problem. The reaction path considered is



$$\mathrm{Be} + \begin{matrix} \mathrm{H} \\ \vdots \\ \mathrm{H} \end{matrix} \longrightarrow \mathrm{Be}\begin{matrix} \diagup \mathrm{H} \\ \vert \\ \diagdown \mathrm{H} \end{matrix} \longrightarrow \mathrm{H{-}Be{-}H}$$

For this system we have three atomic orbitals, and

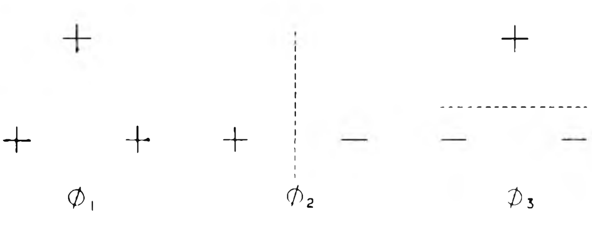


Fig. 6.—Symmetry orbitals for the BeH_2 triangular complex.

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(18) V. Griffing, J. P. Hoare and J. Vanderslice, *J. Chem. Phys.*, **24**, 71 (1956).

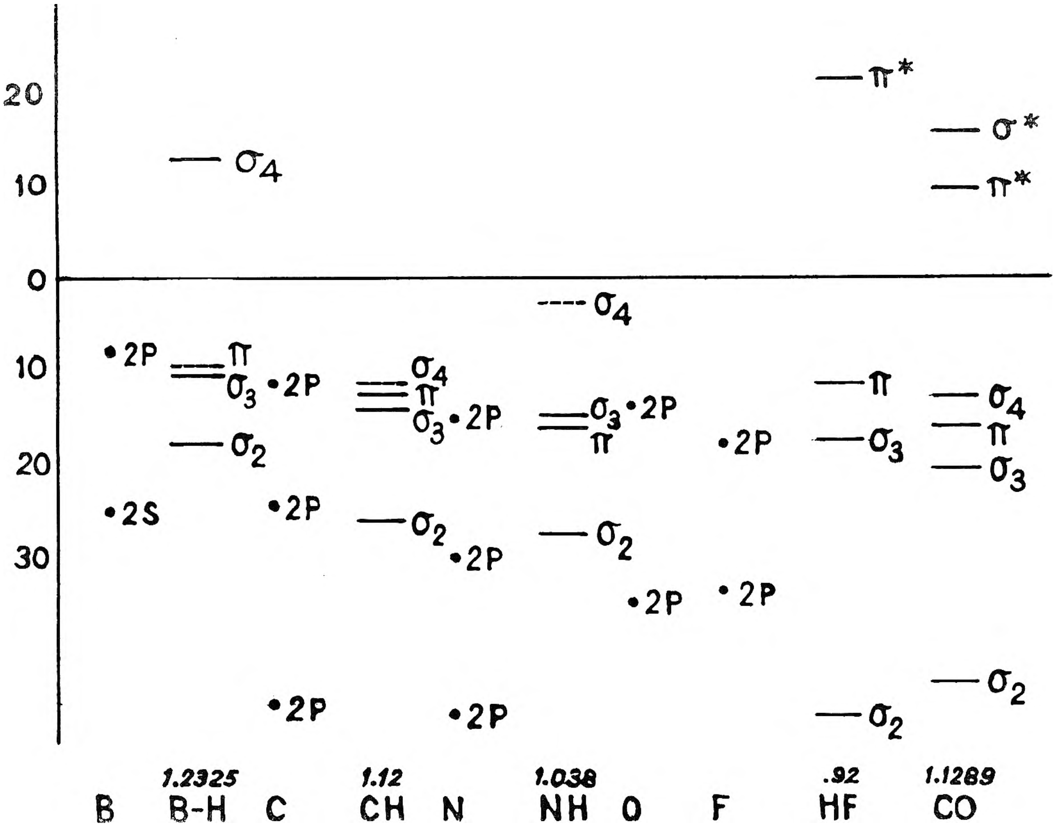

Fig. 7.—Vertical ionization energies (Hartree–Fock eigenvalues) for some diatomic molecules. These values were taken from the following published papers:

For: CO R. C. Sahni, *Trans. Faraday Soc.*, **49**, 1246 (1953).
BH Roop C. Sahni, Molecular Quantum Mechanics Conference Reports, University of Texas, 5, (1955).
CH J. Higuchi, *J. Chem. Phys.* **22**, 1339 (1954).
NH J. Higuchi, *ibid.*, **24**, 535 (1956).
HF A. B. F. Duncan, *J. Am. Chem. Soc.*, **77**, 2107 (1955).

consequently three molecular orbitals are available for the complex. The correlation diagrams have been constructed and are discussed in reference 18. The symmetry orbitals for this case are given in Fig. 6. It exhibits no new features except that a degenerate complex occurs in spite of the absence of spatial symmetry (a threefold axis is necessary to allow degenerate orbitals). The symmetry orbitals are shown schematically in Fig. 6. The calculations were made as functions of the Be–H distance.

The Be–H distance was varied from ~1.5 to 2.5 a.u. The H–H distance was held constant at 1.4 a.u. Since ϕ_1 and ϕ_2 each have one node it was difficult to predict which would lie lower. Thus two sets of calculations were carried out; in both calculations two electrons were kept in ϕ_1; the other two were placed in ϕ_2 for one calculation and in ϕ_3 for the second calculation. However, the SCF-coefficients in ϕ_1 differed depending upon which orbital was filled. The energies resulting from these two calculations intersect for a Be–H distance of 1.48 a.u. The Hartree–Fock eigenvalues for both ϕ_1 and ϕ_1', ϕ_2 and ϕ_3, and the total energy all showed an "accidental degeneracy" for this geometrical arrangement. Thus the orbitals ϕ_1 and ϕ_3 show all the characteristics of an orbital degeneracy. One knows that these two orbitals are degenerate for the equilateral H_3 complex.[19] Thus we conclude that the effect of the double charge of the Be atom does not prevent an "accidental degeneracy" in the heteronuclear complex. That is, an electron moving in such an orbital cannot distinguish, as far as degeneracies are concerned, between an H atom placed at 1.4 a.u. or a Be atom placed at 1.48 a.u. from the original H atoms in the H_2 molecule. The effect of different charges on the orbitals thus appears to be one of distorting the spatial symmetry, changing the length of the bonds and shifting the nodes so they cut the bond off the geometrical center. These "accidental degeneracies" should be just as important as the geometrical degeneracies of highly symmetrical molecules in chemistry. This indicates that considerable qualitative insight can be obtained for heteronuclear systems from diagrams such as those given in Fig. 2 and Fig. 3. The orbitals only need to be distorted somewhat in order to take into account the modified nuclear repulsions. The change in repulsive energy due to nuclear repulsions is compensated in part by the change in the number of electrons to maintain electrical neutrality.

VI. The Mono-hydrides of the First Row of the Periodic Table.—An analysis has been made of some M.O. calculations on the hydrides which have recently appeared in the literature.[20] In Fig. 7, the calculated vertical ionization energies are plotted for the filled orbital for these hydrides. The series

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[19] J. O. Hirschfelder, *J. Chem. Phys.*, **6**, 795 (1938).

[20] References are given under the figure.

goes from BH to HF with only OH missing. The molecular orbitals for these systems have the same symmetry properties and are thus designated by the same symbols. One can see that the internuclear distance steadily decreases as one goes from BH to HF. More important, the orbitals having the same symmetry properties are in the same order with the exception of the partially occupied π orbital of NH which drops slightly below the σ_3 orbital. This does not affect the extension of the general principles outlined in III (b) to heteronuclear systems as the π functions have angular nodes and thus are not comparable to the nodes in the σ functions. The occupied orbitals are indicated by solid lines; the unoccupied orbitals are indicated by dotted lines. The corresponding experimental ionization energies of the atom iso-electronic to the hydride are to the right and are indicated by the dots. In the last column on the right, the vertical ionization energies for the CO molecule are indicated. Here the 1s electrons have been buried in the nucleus and thus the symbols σ_2, σ_3, σ_4 and σ^* refer to linear combination of 2s and 2pσ orbitals. However if one neglects the nodes of the pσ orbitals passing through the nuclei, the orbitals have nodal properties corresponding to the orbitals bearing the same numbers in the hydrides.[21] These also lie in the same order, thus confirming the usefulness of the nodal properties in determining the order of the symmetry orbitals over a wide variety of cases. Another interesting feature shown in Fig. 7 is that all of the radicals have unfilled orbitals (dotted lines) which have negative Hartree–Fock eigenvalues while for the stable molecules, HF and CO, these unfilled orbitals lie quite high. It is difficult to assess the real significance of this effect in as much as the unfilled orbitals are usually not self-consistent solutions. However, it probably can be interpreted as meaning these radicals have a high electron affinity and are quite reactive.

A similar comparison has been made for the calculated results on the triatomic systems NH_2,[22] H_2O[23] and CO_2[24] and similar results are observed both in the order of the orbitals and the location of the unfilled orbitals.

VII. Conclusions.—It has been demonstrated that the molecular orbital theory is useful in understanding the stability and reactivity of atoms and molecules. The nature of the activated complex is discussed and the activation energy is identified with promotion energy as the internuclear parameters are adiabatically varied. Four center systems are sufficiently complicated to discuss the general aspects of chemical problems. The importance of the occurrence and removal of orbital and spin degeneracy has been demonstrated. Accidental degeneracies play a similar role in heteronuclear systems.

Acknowledgments.—The authors wish to thank Professor Karl F. Herzfeld and Professor F. O. Rice for many helpful discussions in connection with the material presented in this paper.

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[21] The 2s and 2pσ orbitals on the C atom replace the 1s orbital on the H-atom in the hydrides.

[22] J. Higuchi, *J. Chem. Phys.*, **24**, 535 (1956).

[23] F. O. Ellison and H. Shull, *ibid.*, **23**, 2348 (1955).

[24] J. F. Mulligan, *ibid.*, **19**, 347 (1951).

MOLECULES WITH ALMOST SPHERICAL SYMMETRY[1]

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Contribution from University College, London

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A comparison is made of the calculated properties of tetrahedral molecules derived (a) by the Thomas-Fermi method, (b) by orbital methods, using the approximation of spherical symmetry. The difficulties associated with a more precise treatment of such molecules are discussed with particular reference to CH_4, CCl_4 and CF_4. It is concluded that if satisfactory results for most molecular properties are to be obtained, both electron exchange effects and departures from spherical symmetry must be allowed for. A study of the PH_5 molecule with assumed bipyramidal structure is described, showing that the peripheral atoms effectively contract the 3d orbitals and thereby promote the formation of pentavalent bonds.

The treatment of molecules with more than about 20 electrons by molecular orbital methods has so far proved too difficult for detailed calculations to be attempted. Among the larger molecules to have been tried by the usual LCAO-MO technique is the 70 electron system, SF_6, with octahedral symmetry. However, the problem was here simplified to one involving 12 valence electrons, and the results were not very satisfactory.[2]

In this paper we shall first discuss two related methods which are especially applicable to molecules with tetrahedral and octahedral symmetry. Both depend on the close approximation which such molecules have to spherical symmetry, which enables the molecular orbital treatment to be simplified to an atomic orbital one. Thus, in a tetrahedral molecule, CX_4, the potential of the four exterior nuclei has type A_1 symmetry, and when expanded in terms of spherical harmonics centered on nucleus C, takes the form

$$V_{\mathrm{N}} = -\frac{4N}{r}\left[1 + \frac{1}{6\sqrt{3}}\left(\frac{R}{r}\right)^3 P_3{}^2(\cos\theta)\sin 2\phi + \frac{7}{9}\left(\frac{R}{r}\right)^4 \left\{P_4{}^{\circ}(\cos\theta) - \frac{1}{336}P_4{}^4(\cos\theta)\cos 4\phi\right\} + \ldots\right] \tag{1}$$

where N is the charge of each X nucleus, R the bond length and (r, θ, ϕ) suitable polar coördinates. This holds for $r > R$, and there is a complementary form when $r < R$. Ignoring the third and higher order harmonics in this expansion would appear to provide an excellent approximation to the nu-

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[1] Supported by Contract AT(11-1)-298 of the U. S. Atomic Energy Commission at the University of Wisconsin.

[2] A. B. F. Duncan, *J. Chem. Phys.*, **20**, 951 (1952).

clear potential, and is equivalent to spreading the nuclear charge evenly over a sphere of radius R. One then assumes for the total nuclear potential

$$\begin{aligned} V_n &= -\left(\frac{Z}{r} + \frac{4N}{R}\right), & r \leq R \\ &= -(Z + 4N)/r, & r > R \qquad (2) \end{aligned}$$

and this provides the basis for the applications now to be described.

The Thomas–Fermi Method.—N. H. March and his co-workers[3a,b] have solved the atomic Thomas–Fermi equation, neglecting exchange terms, and have derived an electron density $n_1(r)$ which depends only on the radial distance from the central nucleus. The molecules to which this has been applied include CH_4, CF_4, CCl_4, SiH_4, SiF_4, GeH_4 and SF_6. The calculation differs from the usual atomic one only in that the regions $r < R$ and $r > R$ must be considered separately and the solutions chosen to satisfy two additional boundary conditions when $r = R$.

For a given value of R, the energy of such a system may be written

$$E_1(R) = T_1(R) + U_1(R) + A_1(R) \qquad (3)$$

where

kinetic energy $T_1(R) = c_k \int n_1{}^{5/3}\, d\tau$

potential energy $U_1(R) = U_N - e \int n_1 (\tfrac{1}{2}V_e + V_n) d\tau$

exchange energy $A_1(R) = -c_e \int n_1{}^{4/3}\, d\tau$

U_N is the nuclear-nuclear potential energy, V_e the potential from the electron distribution, and V_n is given by (2); c_k and c_e are constants.

The energy $E_1(R)$ can be minimized with respect to variations in R to obtain a theoretical estimate of the bond length, and d^2E/dR^2 provides the force constant for the breathing mode of vibration. If this is done with omission of the exchange term $A_1(R)$—the density $n_1(r)$ having been derived from the TF and not the TFD equation—the results are very disappointing. Thus for the lighter molecules (CH_4, SiH_4) the bond length is considerably overestimated, and the force constant is much too small. For heavier molecules, such as the tetrachlorides and tetrabromides of C, Si, Ge, Sn and Pb, the opposite occurs (as shown by Bowers[4]) and the bonds are too short by a factor of 3 or 4, and too strong by factors up to 10^3.

This situation is improved somewhat by including the term $A_1(R)$. However, if this is done without modifying $n_1(r)$, an undesirable violation of the virial theorem occurs, but this is avoided by introducing a radial scaling factor λ, and a modified electron density

$$n_\lambda(r) = \lambda^3 n_1(\lambda r) \qquad (4)$$

for which

$$E_\lambda(R) = T_\lambda(R) + U_\lambda(R) + A_\lambda(R) = \lambda^2 T_1(\lambda R) + \lambda U_1(\lambda R) + \lambda A_1(\lambda R) \qquad (5)$$

Now if, for a given R, λ is chosen to minimize E_λ the virial theorem is satisfied in the form

$$2T_\lambda(R) + U_\lambda(R) + A_\lambda(R) = -R\frac{\partial E_\lambda}{\partial R}$$

The corrections involved in this scaling are not large, *e.g.*, in SiH_4, λ never departs from unity by more than 3%, and tends to contract the charge distribution slightly. The estimated bond lengths and force constants are substantially improved (see Table I, in which results modified for exchange are denoted by TFX).

TABLE I

BOND LENGTH R (IN UNITS OF a.u.)

	TF	TFX	AX	SCF	SCFX	Obsd.
CH_4	4.0	2.57	1.98	(2.32)[a]	(1.99)	2.06
NH_4	..	..	1.84	....	....	(1.95)[a]
SiH_4	4.7	3.06	3.49	(3.35)[a]	(3.10)[a]	2.76
GeH_4	..	3.6	..	....	....	2.80

[a] Values in brackets obtained by scaling procedures. Observed value for NH_4^+ derived from ND_4Cl.

The Use of Analytic and SCF Orbitals.—The replacement of multicenter molecular orbitals by single center atomic orbitals, suggested long ago by Mulliken,[5] was applied to the methane molecule by Buckingham, Massey and Tibbs.[6] The method of calculation was that of the Hartree self-consistent field, the molecular configuration $(1A_1)^2 (2A_1)^2 (2T_2)^6$ being replaced by the neon-like configuration, $(1s)^2 (2s)^2 (2p)^6$. The results will be discussed shortly. Other calculations along the same lines are

$$\text{Neon-like:}\left\{\begin{array}{ll} \mathrm{CH_4} & \text{Analytic functions (AX)} \\ \mathrm{NH_4^+} & \text{Analytic and S.C.F. functions} \end{array}\right\}\text{Bernal}^{7}$$

Argon-like: SiH_4 and $(PH_6)^{++}$ SCF functions Carter[8]

Calculations similar to these in the use of the spherical approximation, but in general less rigorous, have been carried out by Neugebauer[9] (CH_4), Horvath[10] (NH_4^+ and SiH_4) and Hartman[11] (CH_4 and NH_4^+).

In the AX calculations, it is possible to include exchange terms in the total energy, which is conveniently written in the form

$$E(R,\alpha) = \frac{T_0(\alpha)}{R^2} + \frac{U_0(\alpha) + A_0(\alpha)}{R}$$

where T_0, U_0, A_0 depend only on parameters in the orbital functions other than R (and denoted collectively by α). Minimization with respect to R is therefore easy; with respect to the other parameters it may be laborious.

The SCF calculations, however, have not included exchange terms, and have been carried out for a single value of R in each case (*e.g.*, 2.0 a.u. for CH_4, 1.84 a.u. for NH_4^+, 2.80 a.u. for SiH_4). Accordingly, the theoretical bond length can only be estimated indirectly, by assuming that the radial wave functions can be scaled in a simple way as R is varied. The effect of exchange also can be allowed for approximately by including an exchange contribution to $E(R)$, and using a scaling procedure somewhat similar to that in (4) and (5).[8]

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[3] (a) N. H. March, *Proc. Camb. Phil. Soc.*, **48**, 665 (1952); (b) R. A. Ballinger and N. H. March, *ibid.*, **51**, 504, 511 (1955).

[4] W. A. Bowers, *J. Chem. Phys.*, **21**, 1117 (1953).

[5] R. S. Mulliken, *ibid.*, **1**, 490 (1933).

[6] R. A. Buckingham, H. S. W. Massey and S. R. Tibbs, *Proc. Roy. Soc.* (*London*), **A178**, 119 (1941).

[7] M. J. M. Bernal, *Proc. Phys. Soc.*, **A66**, 514 (1953).

[8] C. Carter, *Proc. Roy. Soc.* (*London*), **A235**, 321 (1956). (PH_6 unpublished.)

[9] T. Neugebauer, *Z. Physik*, **98**, 638 (1936).

[10] J. I. Horvath, *J. Chem. Phys.*, **16**, 851, 857 (1948); **18**, 1115 (1950).

[11] H. Z. Hartmann, *Z. Naturf.*, **2** [a] 489 (1947).

A different scaling parameter can be used for each of the important orbitals, *e.g.*, (3s) and (3p) in SiH_4.

Discussion of Results

Among the molecular properties which can be used to compare theoretical results with observation, we may include (a) bond lengths and force constants, (b) energies, particularly molecular binding energy and ionization potential, (c) magnetic susceptibility, (d) polarizability.

Table I presents theoretical and observed bond lengths for the tetrahedral hydrides, and Table II some values of the force constant k_1 associated with the breathing mode.

TABLE II

FORCE CONSTANT k_1 (IN 10^5 DYNE/CM.)

	TFX	SCFX	Obsd.
CH_4	9	(25)	20.3
SiH_4	5	(9.6)	11.4
GeH_4	3	...	10

It will be seen that the approximate inclusion of exchange energy brings the calculated values of R appreciably closer to the observed. In the TFX treatment the result for SiH_4 is better than for CH_4, as one might expect for a system with more electrons, but that for GeH_4 is anomalous, the observed value being unexpectedly low. The SCFX method provides reasonably good estimates of k_1.

With respect to binding energies the theoretical position is far from satisfactory. The TF approach is not suitable here, mainly because of the singular behavior (as $r^{-3/2}$) of the electron density near the central nucleus, which introduces a rather large negative error; this of course occurs also in atomic systems. However, although somewhat better, no SCF calculation using the spherical approximation has so far provided a positive binding energy, as Table III shows. The energy ΔE for XH_4 here represents the difference $E(X + 4H) - E(XH_4)$, where $E(X)$ is calculated by a method similar to that for $E(XH)_4$, *i.e.*, AX, TF or SCF.

TABLE III

CALCULATED ENERGIES (IN $e.^2$/a.u.)

	TF		AX		SCF		SCFX
	$-E$	ΔE	$-E$	ΔE	$-E$	ΔE	$-E$
CH_4	51	−2	39.33	−0.35	39.48	−0.20	39.53
SiH_4	..	..	289.14	− .31	290.02	− .35	290.04

The total energy calculated by Bernal for NH_4^+ is −55.68 $e.^2$/a.u., but no estimate of ΔE is available.[12]

Estimates of the ionization energy required to remove an outer shell electron, as provided by the corresponding energy parameter ϵ in the solution of the SCF equations, are somewhat better. Some values are given in Table IV.

The value for atomic Si, obtained in the course of deriving ΔE for SiH_4, is given for comparison.

TABLE IV

IONIZATION ENERGIES (IN $e.^2$/a.u.)

	Calcd.	Obsd.
CH_4	ϵ_{2p} = 0.654	0.484
SiH_4	ϵ_{3p} = .5127	.451
Si	ϵ_{3p} = .3910	.380

The PH_5 Calculation.—A calculation similar to the SCF calculations just considered has also been carried out for the molecule PH_5. The object of this was to examine the fact that phosphorus in common with other elements of the second row, exhibits two valencies, and forms molecules such as PF_3 and PF_5, whereas nitrogen forms only NF_3. This is usually ascribed to d-orbital hybridization, the trivalent and pentavalent forms of P being associated with $(3s)^2$ $(3p)^3$ and (3s) $(3p)^3$ (3d) configurations, respectively. The observed bipyramidal form of PF_5 can be explained in this way. However, Craig, *et al.*,[13] in a semi-quantative study of PCl_5 and SF_6 using overlap integrals as a criterion of bond strength, concluded that a Slater 3d orbital is too diffuse to hybridize effectively with 3s and 3p atomic orbitals. It is possible that the presence of peripheral atoms in a molecule effectively contracts the d orbital and thereby promotes hybridization, and a study of the hypothetical PH_5 molecule was therefore undertaken to investigate this point.

An approximate SCF calculation of $(PH)_5^{++}$ was first carried out, using an argon configuration. The H atoms were assumed to be arranged in bipyramidal fashion, all at a distance 2.70 a.u. from the central P nucleus. The Hartree equation was then solved for a 4s and a 3d electron in the field of this core, assumed unperturbed. For the 3d electron it is practicable to include contributions from angular-dependent harmonics in the 5H potential. The following values of the energy parameter for the outer electron were obtained: ϵ(4s), 0.55; ϵ(3d) (omitting angular-dependent terms), 0.50; ϵ(3d) (including angular-dependent terms), 0.62. By Koopman's theorem, ϵ is a measure of the binding of the outer electron; hence we see that a 3d electron in PH^+_5 is more tightly bound than a 4s and that this is a consequence of the non-spherical potential in which it moves.

As a further step, a configuration of PH_5 was considered in which both occupied ($4A_1$) orbitals were taken to have the form $3d_{z^2}$, though a better result might be obtained by adding an s component. In Table V a comparison is made of the position and height of the principal peak in the normalized radial wave functions, $P_N(r)$, obtained in this way for the PH_5 molecule, with those of a P atom having the "pentavalent" configuration (3s) $(3p)^3$ (3d). The effect of the peripheral atoms in contracting the (3d) function, and raising the peak value, is remarkable.

One can conclude that any molecular orbital of the LCAO type formed from the atomic 3d orbital would not at all resemble the molecular 3d orbital exemplified in PH_5, and this may help to explain, for instance, Duncan's poor results for SF_6 using Slater 3d orbitals.

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(12) An interesting application of the NH_4^+ calculation may be mentioned here, concerning the interior of the planets Uranus and Neptune, in which ammonia and hydrogen are known to be abundant. It is to be expected that under sufficiently high pressure these molecules combine to form metallic ammonium (NH_4), and Massey and Bernal (*Mon. Not. Roy. Astr. Soc.*, **114**, 172 (1954)) showed that this transition should occur at a pressure below 250,000 atmospheres.

(13) D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel and L. E. Sutton, *J. Chem. Soc.*, 332 (1954).

TABLE V

	Atomic P (3s) $(3p)^3$ (3d) r_{max}, a.u.	 P_N (max)	PH_5 $(3s)^2$ $(3p)^0$ $(3d_{z^2})^2$ r(max), a.u.	 P_N(max)
3s	1.6	0.81	1.75	0.73
3p	1.85	.70	2.2	.66
3d	7.9	.32	3.0	.60

The conclusions of Craig, *et al.*, are thus confirmed, and the qualitative explanation seems to be that the H atoms are sufficiently electronegative both to expand the 3s and 3p functions and contract the 3d, bringing the maxima nearer to $r = R$. This may well be accentuated when H atoms are replaced by strongly electronegative F or Cl atoms, and so help to explain the known stability of PF_6 and PCl_5. Another factor which tends to enhance the 3d contraction in PH_5 is that each electron of the 3d pair screens the other only slightly, and this adds to the fall in screening due to the initial 3d contraction. In the P atom, however, screening of a single 3d electron by inner electrons remains strong.

Further Developments.—The failure of the spherically symmetric approximation to give satisfactory binding energies shows that the effect of angular-dependent terms in the nuclear potential must be examined. When other properties of the molecule are considered, the same conclusion is reached; thus, the addition of such terms is particularly important for the magnetic susceptibility, as shown by Carter,[8] and the same applies to the molecular polarizability. We shall therefore discuss the possibility of improving the theoretical treatment by considering in particular the molecules CH_4, CF_4 and CCl_4.

CH_4.—As the simplest tetrahedral molecule this is the one which more sophisticated methods are most likely to prove practicable. However, a thorough MO treatment using configurational interaction will involve a large number of configurations, and is unlikely to be carried out for some time. As an obvious step beyond the approximation of spherical symmetry, one can assume a molecular configuration $(1s)^2$ $(2A_1)^2$ $(2T_2)^6$, in which

$$\psi(2A_1) = a_0\phi(2s) + a_1\phi(4f_{xyz})$$
$$\psi(2T_{2x}) = t_0\phi(2p_x) + t_1\phi(3d_{yz}) \quad \text{etc.}$$

the additional terms being those indicated by the potential (1) as most important. The corresponding SCF equations include a pair of coupled equations for the radial components of the (2p) and (3d) functions. However, it is not essential to solve these in detail in order to estimate the effect which ϕ (3d), for instance, has on the energy of the molecule. Thus, if $R_{3d}(r)$ represents the radial part of ϕ(3d), one can assume a form

$$R_{3d}(r) = \left(\frac{8\beta^7}{45}\right)^{1/2} r^2 e^{-\beta r}$$

and minimize the energy with respect to variations in both t_1/t_0 and β. The result of doing so is to lower the energy by about 0.21 e.^{2}/a.u. The corresponding value of β is 1.36, which again gives a 3d function much more compact than the Slater atomic function.

Although this energy change is substantial, it suggests that the convergence toward the correct binding energy by including more angular dependent terms in the orbital functions will not be rapid.[14] However, for properties such as magnetic susceptibility, the inclusion of one or two such terms may be more rewarding.

CCl_4.—This molecule exhibits very clearly the difficulties which occur when the outer atoms are relatively large. It was noted by March[3a] that the elementary TF treatment of CCl_4, in which all 74 electrons were assumed to move freely in the spherically symmetrical field, involved a marked shift of electrons away from the chlorine nuclei. Thus the electronic charge within a spherical shell of thickness 0.64 a.u. about the radius R = 3.32 a.u. (the assumed bond length) was 25, compared with 40 for 4 undisturbed Cl atoms. In a more recent calculation[15,16] the electron system has been broken down into 3 groups: (i) 4 Cl inner groups, $(1s)^2$ $(2s)^2$ $(2p)^6$, 40; (ii) carbon K shell, $(1s)^2$, 2; (iii) "valence" electrons, 32. If the spherically-averaged potentials of these groups are denoted by V_i, V_c and V_e, respectively, the total spherical potential field acting on the electrons is

$$V = V_n + V_i + V_c + V_e$$

where V_n is given by (2). Neglecting mutual disturbance of the corresponding electron distributions, V_i and V_c can be predetermined from atomic calculations, and the problem reduced to the calculation of V_e.

However, at this stage it is essential to give effect to the exclusion principle, otherwise a distribution of "valence" electrons is obtained which is too concentrated about the spherical radius R. In the procedure actually followed it is assumed that the 42 inner shell electrons occupy states with energy $E \leq E_l$ (*i.e.*, the lowest available levels in the spherical potential field), and that for the remaining 32 electrons, $E_l < E \leq E_0$. Since the value of E_l is not initially known, its determination together with the electron density $n_e(r)$ has to follow a process of successive approximations.

One result which emerges is that the distribution of valence electrons is still surprisingly diffuse, so that of the 28 electrons originating from the Cl atoms, 20 appear to be outside the radius R. However, this complex calculation has been completed for the observed bond length only (3.32 a.u.), and it is not clear how far the rather peculiar electron distribution is related to this choice of bond length (unlikely to be the equilibrium value), to the assumption of spherical symmetry, to the method of inserting the exclusion principle, or to the neglect of detailed exchange effects.

CF_4.—The investigation of CCl_4 outlined above suggests that a molecule of intermediate complexity, such as CF_4, treated along similar lines but by an orbital method, would provide very useful information. In this case the electrons can be grouped as follows: (i) 4 F systems, $(1s)^2$ $(2s)^2$

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(14) This conclusion is supported by the calculations (unpublished) of R. K. Nesbet, using an SCF-MO method, which shows that a theoretical binding energy of 40–45% of the observed, even with a moderate amount of configurational interaction, is the best that one can expect.

(15) C. A. Coulson and N. H. March, *Proc. Camb. Phil. Soc.*, **52**, 114 (1956).

(16) K. E. Banyard and N. H. March, *ibid.*, **52**, 280 (1956).

$(2\pi)^4$, 32; (ii) carbon K shell, $(1s)^2$, 2; (iii) valence electrons, 8. The electron clouds in (i) and (ii) do not overlap to any serious extent, and a satisfactory solution is achieved if the orbital functions for the 8 valence electrons can be made orthogonal to those of both (i) and (ii).

It is feasible here to consider some interactions between all three groups. Thus if $Z_F(r_F)$ is the effective nuclear charge for potential within an F system, expressed as a function of radial distance r_F from the F nucleus, the potential field of all four F systems can be expanded in spherical harmonics about the C nucleus; the dominant term is the zero-order one, which can be written

$$V_F(r) = \frac{2}{rR}\int_{|r-R|}^{r+R} Z_F(r_F)\,dr_F$$

This acts on systems (ii) and (iii). Likewise the potential of (ii) and (iii) can be expanded about each F nucleus in turn, and as a result of shielding the field of the other 3 F systems on the chosen one is approximately that of a single proton at each of the three F nuclei. The zero order terms in the various expansions provide a basis for an SCF calculation covering all electrons in the molecule. Calculations along these lines are proceeding. Subsequently it may be possible to examine the effect on the valence electrons of angular-dependent terms in the effective potential.

Conclusions

From this study of the approximation of spherical symmetry applied to tetrahedral molecules we would conclude that the approximation has rather limited value. Provided adequate allowance is made for electron exchange it may yield reasonable values for bond lengths and force constants, but this has yet to be demonstrated for heavier molecules such as CCl_4. For other properties such as polarizability and magnetic susceptibility, the inclusion of angular-dependent harmonics is important, and these may also have a decisive effect on the valence properties of the central atom. Good results for binding energies cannot be expected even with the inclusion of higher harmonics. Some further progress with the heavier molecules seems possible if the electrons are suitably grouped and the inner shells of the peripheral atoms protected from excessive perturbation, the exclusion principle being properly maintained.

Acknowledgment.—One of the authors (R.A.B.) is particularly indebted to Professor J. O. Hirschfelder for the opportunity to work for six months at the Naval Research Laboratory, University of Wisconsin.

VALENCE IN THE BORON HYDRIDES

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The nature of the bonding and charge distribution in the known boron hydrides is discussed from the point of view of a simplified localized three-center orbital, and briefly from the more general molecular orbital point of view.

In a remarkable series of papers from 1912–1936, Stock[1] and his co-workers characterized the known boron hydrides, B_2H_6, B_4H_{10}, B_5H_9, B_5H_{11}, B_6H_{10} and $B_{10}H_{14}$. Undoubtedly other members of this series exist, perhaps B_6H_{12}(?) referred to by Stock, a B_8 or B_9 hydride, and reaction intermediates such as BH_3 and B_3H_9. Closely related to these are polymeric higher hydrides, borides such as CaB_6, LaB_6, $B_{12}C_3$, and elementary boron itself.

The theory of valence of these structures is of interest for several reasons. The hydrides themselves have an unusual set of formulas, and one might hope that a theory would correlate these and predict other members of the series. But more important, because these hydrides are "electron deficient" in the sense that there are more orbitals than electrons one might hope that their electronic and geometrical structures will aid in the understanding of the large number of intermetallic compounds, and of the border-line between metals and non-metals. This interpretative problem is comparatively simpler for boron, which uses only the 2s and the three 2p orbitals, and hydrogen, which uses only the 1s orbital, in the approximation discussed here. Such an approximation will be best in the smaller hydrides, but may need to be modified in more exact discussions of large hydrides and infinite solids.

In saturated hydrocarbons, for example C_2H_6, each carbon supplies four orbitals and each hydrogen supplies one. Bonds are formed by overlapping of one of the four tetrahedral sp^3 orbitals of carbon with either the 1s orbital of hydrogen to form a C–H bond, or another sp^3 orbital of carbon to form a C–C bond. When the total number of electrons exceeds the number of available atomic orbitals, such as in NH_3 or N_2H_4, excess pairs occur in hybrid orbitals. In these compounds the chemist writes chemical bonds, and unshared pairs if necessary, and regards the orbitals as filled if each element of the first row has an octet of electrons, and if hydrogen has two electrons.

Now in B_2H_6 there are only 12 electrons for 14 orbitals, and hence in this sense the compound is called electron deficient. But the chemist's intuition tells him that a molecule with unfilled orbitals should not exist, and that if such a molecule really exists, it should adopt an orbital geometry capable of description in terms of closed shells. Such a description is indeed possible for B_2H_6, and some extension of the ideas to the higher boron hydrides is also possible. The essential idea

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[1] A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933.

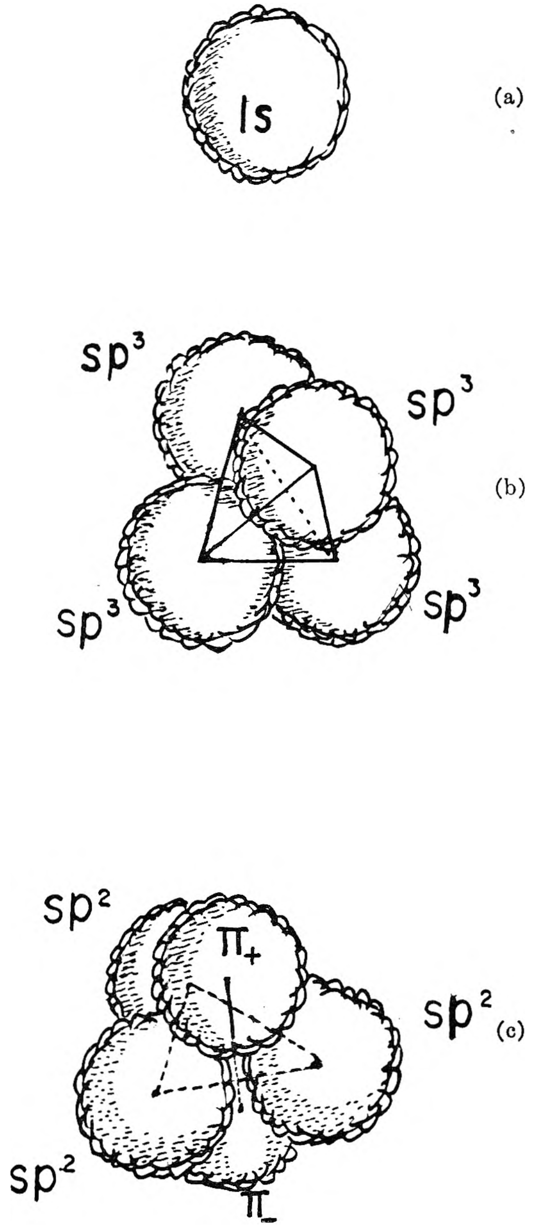
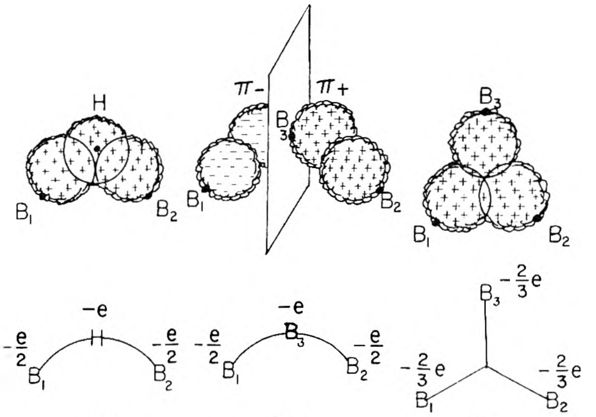


Fig. 1.—(a) The spherically symmetrical 1s orbital for H; (b) tetrahedral hybrid orbitals for B; (c) trigonal hybrid orbitals for B, showing the π-orbital extending above and below the plane of the sp^3 hybrids.

is that of an electron-pair three center bond, which can be regarded as a localized molecular orbital extending over three atomic nuclei with no change of sign in its wave function. This description is a simple extension of an ordinary electron pair bond, which can be regarded as a localized two-center orbital extending over two atomic nuclei with no change in the sign of its wave function.

I. The Three Center Bond.—The usual hybrid orbitals for boron in its better-known chemistry are tetrahedral (*e.g.*, BH_4^-) or trigonal (*e.g.*, BF_3). We shall start our description with these hybrids, and with the 1s orbital of hydrogen (Fig. 1). Then we may form the types of three-center bonds shown in Fig. 2. Intermediate types also may occur.

The results of a simple LCAO discussion,[2] in which the molecular orbital is formulated as a linear combination, $a_1\,\Psi_A + a_2\,\Psi_B + a_3\,\Psi_C$, from the atomic orbitals Ψ_A, Ψ_B and Ψ_C of atoms A, B and C, respectively, yield only one lowest energy state for reasonable assumptions of the geometries and interaction parameters. Thus for the ground state only a single electron pair is required. The details of this discussion[2] will not be repeated here, but the results are summarized in Fig. 3.



(a) (b) (c)

Fig. 2.—Examples of three-center bonds. Boron orbitals from B_1 and B_2, and from B_3 of (c) may be sp^2 or sp^3. The simplest LCAO calculations distribute the bonding electron pair equally among the three atoms of the central three-center bond in (c), and place $-e$ on H or on B_3 of the open three-center bonds, (a) or (b).

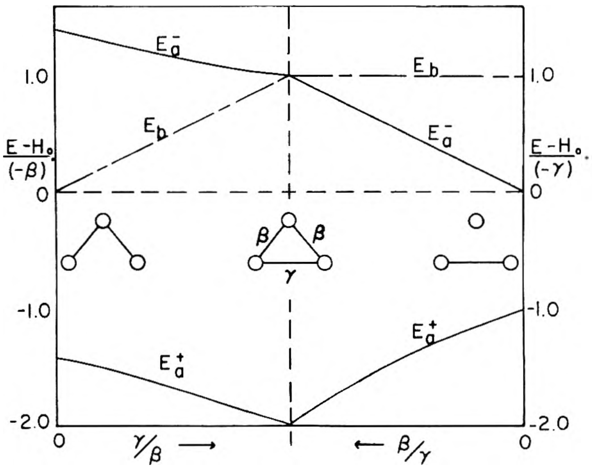


Fig. 3.—Results of simplified LCAO discussion of the three-center orbital. Orthogonality of the AO's and constancy of the coulomb integrals have been assumed. The ratio of resonance integrals $\gamma/\beta = 0$ corresponds to an open three-center bond, that for $\gamma/\beta = 1$ to a central three-center bond, and that for $\beta/\gamma = 0$ to an ordinary electron pair bond. The lowest energy state is E^+_a.

We now outline two approaches to a description of valence in the boron hydrides. The first employs three-center bonds. This particular kind of localized molecular orbital seems most suitable for the smaller, more open hydrides. Its use in the more complex hydrides will require delocalization of the bonding electrons either *via* a molecular orbital modification or a resonance description. The second approach is simply that of molecular orbitals, which is particularly effective in the more condensed and symmetrical hydrides. These ap-

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[2] W. H. Eberhardt, B. L. Crawford, Jr., and W. N. Lipscomb, *J. Chem. Phys.*, **22**, 989 (1954).

proaches merge as the discussion becomes more complete. It is an important result that filled orbital descriptions are obtainable for the known boron hydrides. Also some remarks about charge distribution in the boron hydrides are possible. But the incompleteness of both theory and experiment is indicated by the large number of unknown hydrides consistent with these assumptions.

B_2H_6.—The molecular geometry and three-center bonding scheme[3] for B_2H_6 are shown in Fig. 4. If we assume that two of the sp^3 hybrid orbitals of boron have maxima directed toward the singly bonded hydrogen atoms with $\angle HBH = 121.5°$, then the equivalent[4] hybrid orbitals in the three-center bond should make an angle $\angle H_bBH_b = 101°$. The observed value of this angle is 97°, in excellent agreement considering the experimental uncertainties.

Although the atoms are neutral in this simplified valence theory, there is experimental evidence from a study of the proton magnetic resonance spectrum[5] that the two bridge protons are more negative than are the four terminal protons. Such differences in the diamagnetic shielding have not yet been put on a satisfactory quantitative basis. However, a thorough theoretical study of the molecular orbitals, in a complete LCAOSCF discussion of the 4-electron problem involving the bridge hydrogen atoms and the boron orbitals directed toward them, indicates[6] that the bridge protons have about -0.2 e. excess charge. In our discussion of the more complex boron hydrides we shall make some use of these indications of charge distribution about bridge and terminal hydrogen atoms in discussions of their dipole moments.

Comparison of the bonding in diborane and ethylene is illuminating. In the usual description each C atom of ethylene has planar sp^2 orbitals, two directed toward H and the third directed toward the other C atom. Overlap of this sp^2 orbital directed toward the other C atom, and of the remaining π orbital normal to the plane of sp^2 hybridization with the corresponding orbitals of the other C atom gives the two molecular orbitals of the double bond. If we call these molecular orbitals ψ_σ and ψ_π we may then form equivalent orbitals $\chi_1 = \psi_\sigma + \psi_\pi$, and $\chi_2 = \psi_\sigma - \psi_\pi$, without altering the description of the ground state or of the molecular wave function. But if we remember that ψ_σ has the same sign above and below the plane of the molecule, while ψ_π changes sign in this molecular plane, we then observe that χ_1 is almost completely above the molecular plane, and χ_2 is almost completely below this plane (Fig. 5). The equivalent molecular orbital, χ_1 for example, can be thought of as being formed from two atomic approximately sp^3 hybrids, one from each C atom. This two-center orbital can be thought of as an electron pair bond. In order to obtain the 3-center electron pair bond in B_2H_6 one has only to superimpose the 1s orbital of hydrogen, and replace C by B. Thus the general appearance of the orbitals is not greatly changed, and in particular the symmetry properties and number of nodes remains exactly the same.

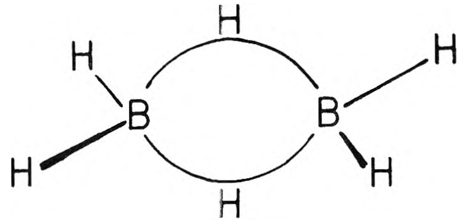

Fig. 4.—Bonding in B_2H_6.

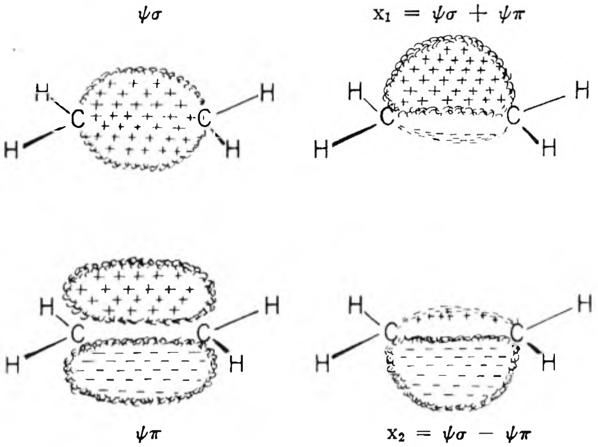

Fig. 5.—Equivalent orbitals in the ground state of ethylene.

Higher Hydrides.—The use of three-center bonds in describing bonding in the higher hydrides has been discussed in some detail,[2] and hence only a brief summary is given here with a few modifications.

As a first illustration of the procedure consider B_4H_{10} (Fig. 6). Electron pair bonds to six H atoms, and three-center bonds to the four bridge hydrogens employ ten electron pairs out of the total of eleven. These ten pairs also use up all of the hydrogen orbitals and all but two of the boron orbitals, one on each B_I. Thus we have one electron pair for two boron orbitals, which are directed toward each other, and hence form a single electron-pair bond between atoms B_I.

As a second illustration consider B_5H_{11}. Bonds to the eight terminal hydrogen atoms and to the three bridge hydrogen atoms require all but two electron pairs, and use up all but six boron orbitals. Hence, we must then form two three-center bonds to utilize the remaining two electron pairs in these six orbitals, and the two methods of doing so consistent with the molecular plane of symmetry are shown in Fig. 5 as a resonance hybrid.

That predictions can be made with this valence bond approach is illustrated in Fig. 5 for B_6H_{10}. The boron arrangement has been established by X-ray diffraction methods,[7] which also require that the molecule shall have a plane of symmetry. Then on the assumption that the bonding is similar to that in B_5H_{11}, the structure shown in Fig. 5 was arrived at. The result is not unique, but other structures appear to involve new principles or not so much similarity to B_5H_{11}. The hydrogen ar-

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[3] H. C. Longuet-Higgins, *J. Chem. Phys.*, **46**, 275 (1949); discussion. See also ref. 2.

[4] C. A. Coulson, V. Henri Memorial Volume, "Contribution a l'Etude de la Structure Moleculaire," Desoer, Liege, 1948, 25.

[5] R. A. Ogg, Jr., *J. Chem. Phys.*, **22**, 1933 (1954).

[6] W. C. Hamilton, *Proc. Roy. Soc. (London)*, **A235**, 395 (1956).

[7] K. Eriks, W. N. Lipscomb and R. Schaeffer, *J. Chem. Phys.*, **22**, 754 (1954).

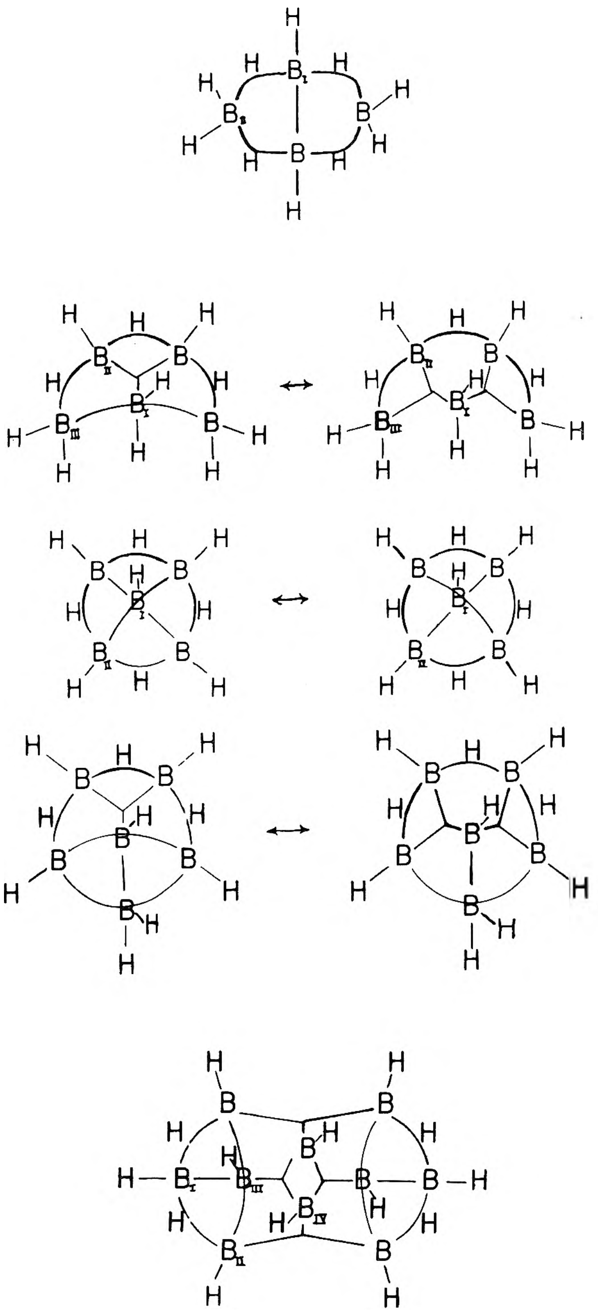

Fig. 6.—A topological valence bond description of the known higher hydrides of boron. Resonance hybrids are indicated by the symbol, ←→. If the bonding geometry at each boron atom is recognized as tetrahedral or trigonal, the correct three-dimensional structures can be realized. The hydrogen arrangement in B_6H_{10} has not been established experimentally, but all other boron and hydrogen geometries have been established with reasonable certainty chiefly by X-ray diffraction methods.

rangement shown leaves four electron pairs and 11 boron orbitals for framework bonds, and hence requires one electron pair bond and three three-center bonds.

As an additional prediction consider B_3H_9, a reaction intermediate. This molecule has 9 electron pairs, all of which would be required for bonds to terminal hydrogen or to bridge hydrogen atoms. The most satisfactory model has three BH_2 groups linked with bridge hydrogen atoms.

II. Molecular Orbitals.—Useful as the three-center bond concept is in forming a common basis for describing the known boron hydrides in terms of filled orbitals, and in making some predictions, it seems clear that the electrons in the more complex and symmetrical boron hydrides must be much more delocalized. Consider the three center bond approximation in B_5H_9, in which three electron pairs are left to fill molecular orbitals from seven boron orbitals after all bonds to H have been formed. We would then expect one three-center bond and two two-center bonds. The resulting bonds (Fig. 6) indicate that the apex boron atom B_I forms three electron pair bonds (one to H and two to B_{II}) and one open three-center bond to two other boron atoms. Now, if we divide the electron pairs equally, and use the simplest LCAO approach (Fig. 2) for the charge distribution in the open three center bond, we then find that the apex boron atom has a net charge of -1, and hence the four other boron atoms have a charge of $+{}^1/_4$. This result, which comes from the assumption[2] of constant single-electron Coulomb integrals, will evidently be modified if variation of the magnitudes of these integrals is allowed. An attempt to introduce this variation into the ordinary secular equation method with the use of Moffitt's linear relation[8] between the coulomb integral and the number of electrons on the atom in question has been made by Eberhardt, Crawford and Lipscomb.[2] The net result has been to reduce the total formal charges on these atoms by about a factor of two, and hence to result in dipole moments in rough agreement with experiment, assuming that the excess charge is centered on the atoms in question.

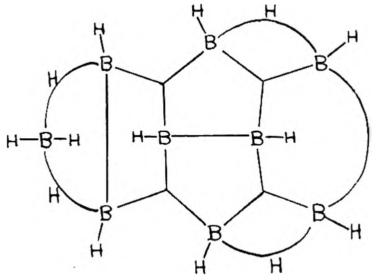

Fig. 7.—A recent study (R. E. Dickerson, P. J. Wheatley, P. A. Howell, W. N. Lipscomb and R. Schaeffer, *J. Chem. Phys.*, **25**, 606 (1956)) has established the boron arrangement with certainty and the hydrogen arrangement with reasonable certainty in B_9H_{15}. The X-ray diffraction data have indicated the structure shown above, and clearly eliminated the second plausible hydrogen arrangement mentioned by these authors. In addition, this second arrangement seems less reasonable on chemical grounds because of the larger number of BH_2 groups.

A more detailed consideration[9] of the charge distribution in the hybrid orbitals about boron atoms in B_5H_9 and B_5H_{11} indicates that this assumption, that the excess charge is centered on the atoms in question, is incorrect within a limit of a factor of about two in the dipole moment calculation from the charge distribution. Even when reasonable charges of about -0.2 e. are placed on the bridge hydrogens, as suggested by the B_2H_6 discussion,[6] the resulting charge distribution in hybrid orbitals

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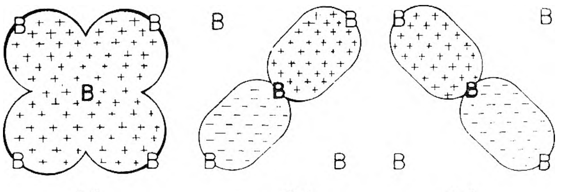
(8) W. Moffitt, *Proc. Roy. Soc. (London)*, **A196**, 510 (1949).

(9) W. N. Lipscomb, *J. Chem. Phys.*, **25**, 38 (1956).

seems to require much less formal total charge on the boron atoms than that given by either the simplified LCAO discussion or its modification[2] with the use of Moffitt's equation. In other words, in order to avoid unreasonably high calculated values of the dipole moments the formal charges have been reduced to 0 to ±0.3 e. on the B atoms. Hence, the previous discussion of these dipole moments is at least incomplete. But it would be difficult to believe that the formal charges are zero or reversed from the previous discussion, and so the apex boron atom in B_5H_9 is still to be regarded as slightly more negative than the basal boron atoms.

In slightly more detail the qualitative picture for B_5H_9 is as follows. Assume as the geometry around B_{II} (Fig. 6) suggests, that the hybridization is tetrahedral. The two boron orbitals of each B_{II} atom directed toward the bridge protons are deficient in electrons, compared with the other two B_{II} orbitals which are directed toward, respectively, the terminal hydrogen and B_I. This situation can be thought of as arising from the relative deficiency of electrons in the boron orbitals of the three-center bonds involving bridge hydrogens, as compared with the electron pair in the bond toward the terminal hydrogen on the framework electrons in the bond toward B_{II}. This result has been shown[9] to be almost independent of hybridization about the apex boron atom, B_I, and can be attributed to the unbalance of the relatively large atomic moments in hybrid orbitals about B_{II}. Assuming at first neutral hydrogen atoms and neutral B atoms, the resulting dipole moment of B_5H_9 is about 6 debyes, where the negative end of the molecule is toward the apex. As in B_2H_6 one would anticipate that the bridge hydrogens carry a slight excess of negative charge,[10] and hence this calculated value will then be reduced to a value in reasonably good agreement with the experimental value[11] of 2.13 debyes. In any event, it appears that reasonable assumptions of the charge, about −0.2 e., on the bridge hydrogens will not reverse the sign of the dipole moment.

The symmetry characteristics of the molecular orbitals for B_5H_9 have already been discussed.[2] The orbital of lowest energy does not change sign throughout the molecule, and can be thought of as a five-center orbital. The orbitals of next lowest energy change sign at the apex boron atom and each has one node, which corresponds to the node in the "π" orbitals perpendicular to the symmetry axis of the molecule. These three orbitals take up the six bonding electrons (Fig. 8), in agreement with the Pauli exclusion principle.



(a) (b) (c)

Fig. 8.—Topological representation of the lowest framework orbital (a) in B_5H_9, and the doubly degenerate pair, (b) and (c). Six bonding electrons go into these three orbitals.

This molecular orbital description is certainly the most natural one, and the relation between this description and the three-center bond description has been discussed in detail.[2]

Discussion of the orbitals in the more complex hydrides, *e.g.*, B_5H_{11}, B_6H_{10} and $B_{10}H_{14}$ follows similar lines, but their symmetries are lower and hence there are more parameters in the molecular orbitals. The results are similar to those for B_5H_9, however, and the resulting charge distributions appear to place the negative end of the molecule as a whole at or near the apex, away from the bridge hydrogen atoms. As in B_5H_9 the dipole moments arise chiefly as a result of the atomic moments about boron atoms, if one chooses to discuss atoms in terms of hybridization. Consider, for example, one of the four tetrahedrally hybridized boron atoms at the base of the tetragonal pyramid of B_5H_9. The two boron orbitals directed toward bridge hydrogen are considerably more deficient in electrons than either the orbital directed toward terminal hydrogen or the orbital directed toward the boron framework. As a result a large atomic moment is created, which is partially stabilized by a shift of charge toward the orbitals to bridge hydrogen. Hence the bridge hydrogen atoms are more negative than the terminal hydrogen atoms. Nevertheless, a large atomic moment remains, and the negative end of the molecular dipole remains directed toward the apex of B_5H_9 in spite of the slight extra negative charge on the bridge hydrogen atoms.

One may hope as we understand more about the charge distribution that its relation to the chemistry of the hydrides will become apparent. For example, if indeed the atoms B_{III} of $B_{10}H_{14}$ are the most negatively charged, as is suggested by the three-center bond description, one might predict that the hydrogen atoms most susceptible toward substitution to form[12] $B_{10}H_{12}Br_2$ and $B_{10}H_{12}I_2$ are those attached to boron atoms of type III.

Acknowledgment.—It is a pleasure to acknowledge support of the experimental program by the United States Office of Naval Research.

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(10) J. N. Shoolery, *Disc. Faraday Soc.*, 3616 (1955).

(11) A. J. Hrostowski, R. J. Myers and G. C. Pimentel, *J. Chem. Phys.*, **20**, 518 (1952).

(12) Reference 1, pp. 120–121.

ELECTRON SPIN RESONANCE AND THE STRUCTURE OF FREE RADICALS[1]

BY S. I. WEISSMAN, T. R. TUTTLE, JR., AND E. DE BOER

Contribution from Washington University, Saint Louis, Missouri

Received August 13, 1956

The hyperfine structure of the electron spin resonance of a polyatomic free radical yields information concerning the electronic structure of the radical. The hyperfine interaction is conveniently separated into an isotropic and a non-isotropic part. Only the former is observed in fluid solutions. From it the value of the electron spin density at the position of each magnetic nucleus in the molecule may be deduced. The spin density at $\vec{r_0}$ is the expectation value of $\sum_k \sigma_{zk}\delta(\vec{r_k} - \vec{r_0})$ where σ_{zk} is the Pauli operator for z component of spin of the k the electron and $\vec{r_k}$ its position. The non-isotropic part is observable in detail in dilute single crystals and in certain average properties in rigid glassy solutions. It yields expectation values of $\sum_k \frac{\sigma_{zk}(3\cos^2\theta_k - 1)}{|\vec{r_k} - \vec{r_0}|^3}$ θ_k is the angle between $\vec{r_k} - \vec{r_0}$ and the external magnetic field. If the electronic wave function of a free radical is represented by a single configuration consisting of filled orbitals and one singly occupied orbital, the spin density at each point is proportional to the square of the amplitude of the singly occupied orbital at that point. In planar aromatic free radicals the unpaired electron is usually placed in a π orbital which yields zero spin density in the plane of the molecule. Nevertheless, experiments reveal non-vanishing spin densities in the molecular plane for many aromatic free radicals. These are interpreted through admixture of configurations containing unfilled σ orbitals. The contribution of such an admixture to spin density is linear in the amplitude of the admixture. The above considerations apply to the proton and C^{13} hyperfine splittings in negative ion hydrocarbons, triarylmethyls and other free radicals. Several examples are discussed.

Introduction

A large number of polyatomic free radicals exhibit complex electron spin resonance spectra. The spectra are generally symmetrical about a center which lies close to the position for the spin resonance of a free electron. It is now well established that the origin of the structure in the spectra is the hyperfine coupling between the electrons of the free radical and some or all of the magnetic nuclei within the molecule. The hyperfine coupling may be described in terms of several distinct interactions. These include interactions between spin magnetic moments of electrons and nuclei, between orbital electronic motion and spin magnetic moments of nuclei and between electric fields of the electrons and electric quadrupole moments of nuclei. We will be concerned with the former of these interactions. The latter two are unimportant for our purposes. Both of them produce, to a sufficiently good approximation, equal shifts in all pairs of levels between which transitions occur. Further, the nuclei which are currently of most interest—H^1, H^2, C^{13}, N^{14}—have either zero or very small quadrupole moments.

The Hamiltonian representing the spin–spin interaction has been discussed by many authors.[2] The spin–spin part of the Hamiltonian is conveniently represented as the sum of two parts $H^{(1)}$ and $H^{(2)}$. In the presence of a strong magnetic field along the z-axis these are

$$H^{(1)} = \mu_0 \sum_{k,n} \frac{H_n\, \sigma_{zk}\, \sigma_{zn}\,(1-3\cos^2\theta_{kn})}{|\vec{r_k} - \vec{r_n}|^3}$$

$$H^{(2)} = -\frac{8\pi}{3}\mu_0 \sum_{k,n} \mu_n\, \sigma_{zk}\, \sigma_{zn}\, \delta\left(\vec{r_k} - \vec{r_n}\right)$$

where μ_0 is the Bohr magneton, μ_n is the magnetic moment of the nth nucleus, σ_{zk} and σ_{zn} are the Pauli operators for the z component of spin of the kth electron and nth nucleus, respectively, $\vec{r_k}$ and $\vec{r_n}$ are the position vectors of kth electron and nth nucleus, and θ_{kn} is the angle between $\vec{r_k} - \vec{r_n}$ and the z-axis. The index k runs over all the electrons, n over all the nuclei. It will be noted that the contribution to $H^{(2)}$ of a particular nucleus α is proportional to $\sum_k \sigma_{zk}\delta(\vec{r_k} - \vec{r_\alpha})$. The expectation value of $\sum_k \sigma_{zk}\delta(\vec{r_k} - \vec{r_\alpha})$ is called the spin density at $\vec{r_\alpha}$.[3] It is a useful quantity for the discussion which follows. A convenient unit for it is the spin density at the proton in a hydrogen atom in its 1s state. We shall give spin densities in terms of this unit.

The hyperfine splittings arising from $H^{(1)}$ are of great interest since parameters associated with the distances between unpaired electrons and nuclei may be deduced from them. They are, unfortunately, not readily observed. In liquid solutions the expectation value of $H^{(1)}$ is zero because of rapid molecular tumbling. Solid solutions in diamagnetic crystals are required for observation of the details of the splitting produced by $H^{(1)}$. Preparation of such crystalline solutions of large polyatomic free radicals is, in most cases, not easy.

$H^{(2)}$, being rotationally invariant, may be observed in liquid solution. Since the space dependent part of $H^{(2)}$ is a delta function, only orbits whose amplitudes do not vanish at a particular nucleus contribute through $H^{(2)}$ to hyperfine splittings by that nucleus. The simplest example of a hyperfine structure arising solely from $H^{(2)}$ is afforded by the hydrogen atom in its normal state. Here $H^{(1)}$ vanishes because of the spherical symmetry of the orbital part of the wave function. $H^{(2)}$, however, produces a large splitting because the 1s function has its maximum amplitude at the nucleus.

Orbital Approximation.—We now proceed to a discussion of the interpretation of hyperfine splittings when the electronic states of free radicals are described by molecular orbitals. An odd free radical containing $2k + 1$ electrons in a doublet

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(1) This work has been supported by the United States Air Force through the Office of Scientific Research of the Air Research and Development Command.

(2) See for instance A. Abragam and M. H. L. Pryce, *Proc. Roy. Soc. (London)*, **205**, 135 (1951).

(3) A. A. Abragam, J. Horowitz and M. H. L. Pryce, *ibid.*, **230**, 169 (1955).

state may be described by configurations $(\gamma_1)^2$-$(\gamma_2)^2 \ldots (\gamma_k)^2\ \gamma_{k+1}$. The γ's are one electron orbitals appropriate for the molecule in question. In case a free radical may be described by a single configuration, the filled orbitals contribute neither to $H^{(1)}$ nor $H^{(2)}$. Only the singly occupied orbital contributes and it is legitimate to speak of the properties of "the unpaired electron."

We may cite as an example in which the one electron description appears to be adequate the free radical ion $ON(SO_3)_2^-$ (peroxylamine disulfonate).[4-6] In liquid solution this substance yields a spectrum of three equally spaced lines of equal intensities. The separation between adjacent lines is 13 oersteds. The only abundant magnetic isotope in this molecule is N^{14}, and it is certain that the splitting arises from a hyperfine interaction with this nucleus. The spin density at the nitrogen nucleus, in terms of the unit defined earlier, is 0.36. If the singly occupied orbital is given as a linear combination of atomic function, the spin density at the nitrogen will arise for the most part from nitrogen 2s function. In order to determine the square of the amplitude of the nitrogen 2s function in the orbital of the unpaired electron, we require the value of the spin density at the nucleus for this function. For a hydrogenic function with $Z = 3.9$, $n = 2$, the spin density at the nucleus is 7.4. The square of the amplitude of such a function in the orbital under discussion is then $0.36/7.4 = 0.049$. The latter number should not be taken very seriously since it is given in terms of a rather arbitrarily chosen atomic function. The value of the spin density on the other hand is reliable.

In dilute solutions of $(SO_3)_2NO^=$ in single crystals of the diamagnetic $K_2(SO_3)_2NOH$ the splittings from both $H^{(1)}$ and $H^{(2)}$ may be observed. The spectrum depends on the orientation of the crystal in the field. It is found that the maximum separation between adjacent lines is 27 oersteds, the minimum separation 6 oersteds. Since we have an isotropic splitting of 13 oersteds, the maximum splitting corresponds to a contribution to the splitting by $H^{(1)}$ of 13 oersteds, the minimum to a contribution of 7 oersteds in the opposite direction. If we assume that the $H^{(1)}$ splitting arises from a nitrogen p function we may evaluate $\langle 1/r^3\rangle$. It may be shown that for a p function with $m = 0$ relative to some axis that $\langle 1 - 3\cos^2\theta\rangle = 2/5(1 - 3\cos^2\gamma)$ where γ is the angle between the axis and the external field. We then find

$$\frac{2}{5}\mu_N\left\langle\frac{1}{r^3}\right\rangle(1-3\cos^2\gamma) = -14 \text{ at } \gamma = 0$$

and

$$\frac{2}{5}\mu_N\left\langle\frac{1}{r^3}\right\rangle(1-3\cos^2\gamma) = 7 \text{ at } \gamma = \frac{\pi}{2}$$

(It will be noted that both equations give the same value for $\langle 1/r^3\rangle$). We find $\langle 1/r_3\rangle = 8.6 \times 10^{24}$ cm.$^{-3}$. As in the case involving the nitrogen 2s contribution, an estimate of the amplitude of nitrogen 2p functions depends on the kind of function which is used. Dousmanis[7] has estimated $\langle 1/r^3\rangle = 22.5 \times 10^{24}$ cm.$^{-3}$ for a self consistent field nitrogen 2p function. Our result corresponds to admixture of the function used by Dousmanis with the square of its amplitude equal to $(8.6 \times 10^{24})/(22.5 \times 10^{24}) = 0.38$.

Another instance of splitting by a single nucleus is that of C^{13} in the methyl position in triphenylmethyl. The splitting in liquid solution is 26 oersteds. The corresponding spin density at the carbon nucleus is 0.22. A difficulty arises with the interpretation of this quantity in terms of a single occupied orbital. This orbital is a π-orbital and cannot contain the carbon s components needed to explain the observed spin density if the three central bonds are coplanar. We shall see later that while π-σ interactions may account for some similar splittings, the splitting under consideration is too large to be so explained. The simplest explanation is that the three central bonds are not coplanar and that the single occupied orbital contains carbon 2s component. Again the amplitude of this component depends on the nature of the carbon 2s function which is used. The square of the amplitude of a hydrogenic function with $Z = 3.25$, $n = 2$ is 0.051.

No reliable measurements of the anisotropic splitting have as yet been made. In all the crystalline and glassy solutions which we have thus far investigated the signals have been extremely weak owing to unusually long thermal relaxation times. The maximum anisotropic splittings seem to lie between 5 and 20 oersteds, correspondingly $\langle 1/r^3\rangle$ lies between 0.9×10^{24} cm.$^{-3}$ and 3.6×10^{24} cm.$^{-3}$. Barnes and Smith[8] have calculated 8.4×10^{24} cm.$^{-3}$ for $\langle 1/r^3\rangle$ of a carbon 2p function in the configuration $(2s)^2(2p)^2$. The square of the amplitude of the function used by Barnes and Smith lies between 0.1 and 0.4.

Configurational Mixing.—Both cases discussed in the preceding paragraphs are relatively simple. They involve splitting by only one nucleus and can be treated in a reasonable manner in terms of one singly occupied orbital. Neither statement can be made about most of the splittings which have been observed in aromatic free radicals. Thus normal triphenylmethyl exhibits an extensive pattern of closely spaced proton hyperfine components.[9] Triphenylmethyl with C^{13} in the methyl position shows both the large C^{13} splitting described previously and the proton splitting. A reproduction of the spectrum of a liquid solution of triphenylmethyl containing 53 atom per cent. in the methyl position is given in Fig. 1. Under higher resolution each of the lines displayed in the figure is further split into several components. These splittings are typical of those observed in many aromatic free radicals.

The discussion of the proton splittings in triphenylmethyl is complicated by the large number of lines in the spectrum and by structural properties of triphenylmethyl. Both the lack of coplanarity of the three central bonds and the propeller twisting of each of the benzene rings introduce difficulties.

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[4] G. E. Pake, J. Townsend and S. I. Weissman, *Phys. Rev.*, **86**, 683 (1952).

[5] J. Townsend, S. I. Weissman and G. E. Pake, *ibid.*, **89**, 606 (1953).

[6] S. I. Weissman and D. Banfill, *J. Am. Chem. Soc.*, **75**, 2534 (1953).

[7] G. J. Dousmanis, *Phys. Rev.*, **97**, 967 (1955).

[8] R. G. Barnes and W. V. Smith, *ibid.*, **93**, 95 (1954).

[9] H. S. Jarrett and G. J. Sloan, *J. Chem. Phys.*, **22**, 1783 (1954).

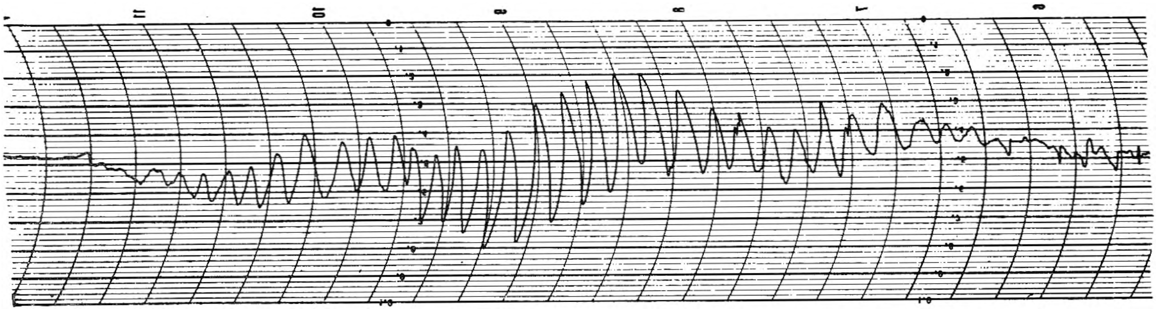

Fig. 1.—Derivative of absorption *vs.* field for triphenylmethyl containing 53% methyl position. The solvent is toluene.

We shall take up a more simple case—that of naphthalene negative ion. Under moderate resolution this free radical exhibits a spectrum of 17 lines. Under higher resolution 23 lines are observed. The interval between centers of peaks at the extremes of the pattern is 27.2 oersteds.

Description of naphthalene negative ion by a single configuration with a π-orbital singly occupied leads to zero spin density at each of the protons. Nevertheless the observed spectrum requires the assignment of non-vanishing spin densities at the positions of the protons. Various suggestions have been made concerning the origin of these spin densities. An early proposal[10] that zero point deformations lead to the observed splittings has been proved erroneous by the observations that the spin densities are unaffected by substitution of deuterium for hydrogen.[11-13]

Several authors[11, 14-16] have suggested that π-σ interactions may produce the observed splittings. The various treatments are similar in content although somewhat different in language. A very brief version, in terms of molecular orbitals, is the following. Only single occupancy of orbitals which have non-vanishing amplitude at a particular proton can lead to splitting by that proton. In the usual description these are σ-orbitals. If σ_f is one of the filled orbitals in the principal configuration of the ground state and σ_e one of the empty ones, admixture of a configuration of proper symmetry in which σ_f and σ_e are each singly occupied leads to a splitting. If the amplitude of the admixture is λ with $|\lambda| < < 1$, the predominant part of the splitting will be linear in λ. The splitting produced by a proton at $\vec{r}_0$ will be proportional to $\lambda\sigma_f(\vec{r}_0)\sigma_e(\vec{r}_0)$. This term arises from slight unpairing of a pair of electrons which are predominantly paired in a single σ-bond. They unpair through promotion of one of them to an unoccupied σ-orbital. The total spin of the molecule is preserved through proper coupling of the unpaired σ-electrons with the single π-electron. Numerical estimates by McConnell and Bersohn indicate that this mechanism yields splittings of the correct order of magnitude.

Having indicated the existence of a plausible mechanism for production of the spin densities at the positions of the protons in aromatic free radicals, we return to a discussion of naphthalene negative ion and other negative ion hydrocarbons. Since naphthalene has only two kinds of protons we seek two values of spin density which will fit the spectrum. If the lines were very narrow there would be, in general, 25 of them. Each set of four protons splits the resonance into 5 lines with intensity ratios 1:4:6:4:1. We find that the naphthalene negative ion spectrum is matched in all details by assignment of spin density 0.010 to the positions of one set of protons, and 0.0036 to the other. Experiments with the negative ions of α-deuteronaphthalene and β-deuteronaphthalene[12] confirm the values of spin density given above and in addition unambiguously assign the higher value to the α position. In Fig. 2 are shown the spectra of normal naphthalene negative ion and of β-deuteronaphthalene negative ion.

Only in the case of naphthalene negative ion among the hydrocarbon free radicals has the assignment of spin density been confirmed by deuterium substitution. In other cases plausible assignments have been made to fit the spectra of the undeuterated molecules. This procedure has been carried out for the negative ions of biphenyl, anthracene and phenanthrene. The spectra of many other negative ions, including those of p-terphenyl, triphenylene, α-methylnaphthalene and pyrene, have been observed, but analyses of them have not yet been completed.

The results with naphthalene, biphenyl and anthracene negative ions suggests an approximate connection with simple molecular orbital theory. The spin densities at the various protons are approximately proportional to the squares of the coefficients of carbon 2p function on the adjacent carbon in the singly occupied π-orbital. Thus for naphthalene the observed ratio of spin densities at the α- and β-protons is 2.8; the ratio of the squares of the coefficients in the Hückel approximation is 2.62. The spectra of anthracene and biphenyl negative ions are also in approximate agreement with those predicted on the basis of proportionality between square of Hückel coefficient on a carbon atom and spin density on the adjacent proton.[17] In py-

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[10] S. I. Weissman, J. Townsend, D. E. Paul and G. E. Pake, *J. Chem. Phys.*, **21**, 2227 (1953).

[11] B. Venkataraman and G. K. Fraenkel, *ibid.*, **24**, 737 (1956).

[12] T. R. Tuttle, Jr., R. L. Ward and S. I. Weissman, *ibid.*, **25**, 189 (1956).

[13] Venkataraman and Fraenkel (reference 11) have cited the fact that distinct spectra from molecules in excited vibrational states are not observed as proof that the vibrational contribution is negligible. In our opinion this is an unwarranted conclusion. Since lifetimes of vibrational states in condensed media are usually considerably shorter than the precession periods associated with the hyperfine interactions, the observed spectra are sharp averages over all populated vibrational states, not superpositions.

[14] H. McConnell, *ibid.*, **24**, 764 (1956).

[15] R. Bersohn, *ibid.*, **24**, 1066 (1956).

[16] S. I. Weissman, *ibid.*, in press.

[17] E. deBoer, *ibid.*, **25**, 190 (1956).

rene negative ion, however, while the spectrum has not been analyzed in detail, it is clearly not in agreement with the predictions based on the Hückel approximation.

Our recent observation of the spectrum of benzene negative ion indicates further that the data cannot be represented by a single constant of proportionality between square of the coefficients in the molecular orbital and the corresponding spin densities. If there were such a proportionality, we would expect the total splittings for naphthalene and benzene negative ions to be the same. In the former symmetry requires that there be a node in the singly occupied molecular orbital at the two carbons not attached to protons, while in the latter, all carbons are attached to protons. The observed total splittings are 22.5 oersteds for benzene negative ion and 27.2 for naphthalene negative ion. The discrepancies appear to be even larger in other cases.

We conclude with one further point concerning splittings by C^{13}. In the discussion of triphenylmethyl we ascribed the 26 oersted splitting by C^{13} to a first order admixture of carbon 2s function into the singly occupied orbital. One might argue that this splitting arises from a second order effect similar to the one which has been invoked in connection with the proton splittings. If the σ-orbitals involved in the proton splittings are non-vanishing at the carbon nuclei, we would expect second order C^{13} as well as proton splittings. Recent measurements reveal that the splitting by C^{13} in the α-position in naphthalene negative ion is 7.1 oersteds.[12] (The spectrum of naphthalene ion containing 53 atom per cent. C^{13} in the α-position is shown in Fig. 3.) Since we would expect approximately the same second-order splittings in both cases, it is likely that at least the major part of the C^{13} splitting in triphenylmethyl is first order.

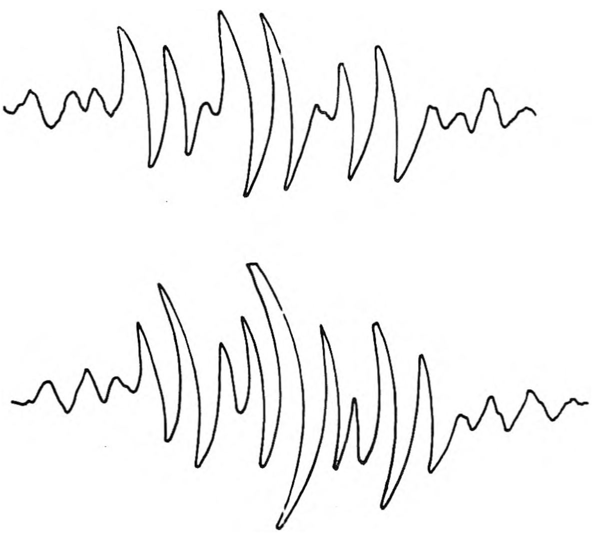

Fig. 2.—Below, spectrum of normal naphthalene negative ion in dimethoxyethane; above, spectrum of β-deuteronaphthalene negative ion in dimethoxyethane.

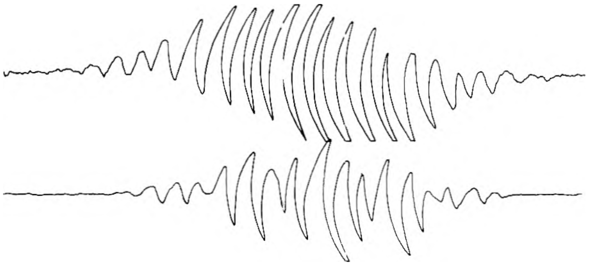

Fig. 3.—Below, spectrum of normal naphthalene negative ion in dimethoxyethane; above, spectrum of naphthalene negative ion containing 53 atom % of C^{13} in the α-position.

RELATION BETWEEN BOND ENERGIES AND BOND DISTANCES

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In an earlier study it was found that a parabola would represent the empirical relation between carbon–carbon bond energies (B(CC)) and the corresponding carbon–carbon distances (R(CC)) in hydrocarbons. Similarly the carbon–hydrogen bond energies (B(CH)) and the related bond distances were shown to be linearly connected. In order to study the cycloparaffins it was necessary to assume a fourth power relation for B(CC) and $R(\mathrm{CC})^{-1}$ and a linear relation for B(CH) and $R(\mathrm{CH})^{-1}$. These empirical relations are in terms of $r = R(\mathrm{CC})^{-1}$ and $\rho = R(\mathrm{CH})^{-1}$. $B(\mathrm{CC}) = br + cr^2 + dr^3 + er^4 = 68.2477r - 423.5984r^2 + 1050.6534r^3 - 380.5358r^4$ and $B(\mathrm{CH}) = A + B\rho = -53.7136 + 163.0571\,\rho$. Benzene, butadiene, methane and its radicals, the cycloparaffins, allene and the methylacetylenes were studied in reference to resonance and strain energies.

Introduction

In earlier papers[1] the relation that chemical bonds with large bond energies have small internuclear distances and *vice versa* was expressed for hydrocarbons by a parabolic curve between carbon–carbon bond energies (B(CC)) and carbon–carbon bond distances (R(CC)). A linear relation was assumed to hold between carbon–hydrogen bond energies (B(CH)) and their corresponding carbon–hydrogen bond distances (R(CH)). This procedure yields only estimates of bond energies and bond distances. When these considerations were extended to the cycloparaffins, it was found that the parabola could not be extrapolated satisfactorily near the ethane point $B(\mathrm{CC}) = 85.18$ kcal. and $R(\mathrm{CC}) = 1.543$ Å. (Fig. 1). Hence a new set of equations was constructed which permitted this extrapolation. In the case of both relations, (B(CC):R(CC)) and (B(CH):R(CH)), it is necessary to have these bond energies approach zero for large distances and become large for small ones. A similar behavior is shown by force constants and inter-

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[1] G. Glockler, *J. Chem. Phys.*, **19**, 124 (1951) (I); **21**, 1242, 1249 (1953) (II).

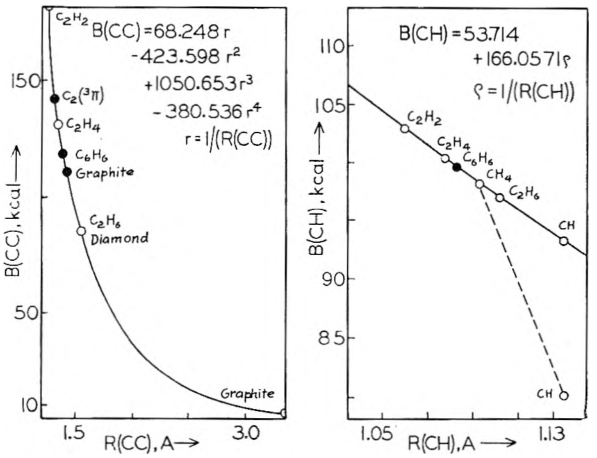

Fig. 1.—Relation between carbon–carbon and carbon–hydrogen bond energies and distances (eq. 4 and 5).

nuclear distances (*I*). A fourth power relation for $B(\mathrm{CC})\!:\!R(\mathrm{CC})$ was found necessary, and a linear relation for $B(\mathrm{CH})\!:\!R(\mathrm{CH})$ is sufficient because only a small interval of about 0.07 Å. is involved for the molecules studied. The summation of the bond energies in a given molecule gives the heat from atom formation or the heat of atomization ($\Sigma B = Q$). The material presented here could also be described by the use of the ordinary heat of formation (Qf_0^0). However the heat quantity (Q) is found to be more convenient. All values are taken at 0°K. and distances are in ångströms.

NOTATION

$B(\mathrm{CC,C}_x\mathrm{H}_y)$ = CC-bond energy in $\mathrm{C}_x\mathrm{H}_y$
$B(\mathrm{CC},1.42)$ = CC-bond energy at 1.42 Å.
$B(\mathrm{CC,th})$ = CC-bond energy of $Q(\mathrm{th})$
$B(\mathrm{CC,m})$ = CC-bond energy of $Q(\mathrm{m})$
$B(\mathrm{CC,ee})$ = CC-bond energy of $Q(\mathrm{ee})$
$B(\mathrm{CH,C}_x\mathrm{H}_y)$ = CH-bond energy in $\mathrm{C}_x\mathrm{H}_y$
$B(\mathrm{CH},1.093)$ = CH-bond energy at 1.093 Å.
$B(\mathrm{CH,th})$ = CH-bond energy of $Q(\mathrm{th})$
$B(\mathrm{CH,m})$ = CH-bond energy of $Q(\mathrm{m})$
$B(\mathrm{CH,ee})$ = CH-bond energy of $Q(\mathrm{ee})$
C_k = compression energy
$D(\mathrm{CH}_x\text{-H})$ = bond dissociation energy
$D(\mathrm{H}_2)$ = heat of dissociation of H_2
(ee) = ethane, ethylene, acetylene base
$L(\mathrm{C}_n)$ = heat of sublimation of graphite into n-atomic carbon gas molecules
(m) = moment of inertia
P.I. = paraffin increment ($-\mathrm{CH}_2-$)
Q = Qa_0^0 = heat of atomization
Qf_0^0 = heat of formation from elements in their standard states
Q_i = $Q(\mathrm{th})$ for the ith molecule
Q_{0i} = $Q(\mathrm{th})$ for ith reference state
$Q(\mathrm{th})$ = Q from Qf_0^0, $L(\mathrm{C}_1)$ and $D(\mathrm{H}_2)$
$Q(\mathrm{m})$ = Q of reference structure; base m
$Q(\mathrm{ee})$ = Q based on $\mathrm{C_2H_6}$, $\mathrm{C_2H_4}$ and $\mathrm{C_2H_2}$
r = $1/(R(\mathrm{CC}))$
ρ = $1/(R(\mathrm{CH}))$
$R(\mathrm{CC,C}_x\mathrm{H}_y)$ = CC-bond length in $\mathrm{C}_x\mathrm{H}_y$
$R(\mathrm{CH,C}_x\mathrm{H}_y)$ = CH-bond length in $\mathrm{C}_x\mathrm{H}_y$
$R(\mathrm{th})$ = bond length for $Q(\mathrm{th})$
$R(\mathrm{m})$ = bond length for $Q(\mathrm{m})$
$R(\mathrm{ee})$ = bond length for $Q(\mathrm{ee})$
R.O.E. = reorganization energy
R.E.(th,ee) = Th.R.E. = thermal resonance = $Q(\mathrm{th}) - Q(\mathrm{ee})$
R.E.(th,m) = $Q(\mathrm{th}) - Q(\mathrm{m})$
S.E.(th,ee) = $Q(\mathrm{th}) - Q(\mathrm{ee})$
S.E.(th,m) = $Q(\mathrm{th}) - Q(\mathrm{m})$
(th) = thermochemical
V.R.E. = vertical resonance energy

The Empirical Equations.—The values of $B(\mathrm{CC})$, $R(\mathrm{CC})$, $B(\mathrm{CH})$, $R(\mathrm{CH})$ and $Q(\mathrm{C}_x\mathrm{H}_y)$ used in determining the constants of the empirical equations are (kcal. and Å.): $L(\mathrm{C}$, graphite$)$ = 170.39[2]; $B(\mathrm{CC}$, graphite$)$ = 111.1; $L(\mathrm{C}$, diamond$)$ = 169.81[2]; $B(\mathrm{CC}$, diamond$)$ = 84.90[2]; $D(\mathrm{H}_2)$ = 103.24[2]; $R(\mathrm{CC}$, diamond$)$ = 1.5445 Å.[3]; $R(\mathrm{CC,C_2H_6})$ = 1.543 Å.[4]; $R(\mathrm{CC,C_2H_4})$ = 1.344 Å.[5]; $R(\mathrm{CC,C_2H_2})$ = 1.207 Å.[6]; $R(\mathrm{CC}$, graphite$)$ = 1.421 Å.[7]; $R(\mathrm{CC}$, graphite$)$ = 3.354 Å.[7]; $B(\mathrm{CH,CH_4})$ = 98.22[2]; $Q(\mathrm{C_2H_6})$ = 667.02[2]; $Q(\mathrm{C_2H_4})$ = 532.74[2]; $Q(\mathrm{C_2H_2})$ = 389.69[2]; $R(\mathrm{CH,CH_4})$ = 1.093;[6] $R(\mathrm{CH,C_2H_6})$ = 1.102[4]; $R(\mathrm{CH,C_2H_4})$ = 1.0771;[6] $R(\mathrm{CH,C_2H_2})$ = 1.0597. Six equations of the type

$$B(\mathrm{CC}) = rb + r^2c + r^3d + r^4e \qquad (1)$$

were set up for the carbon–carbon bonds, where $r = R(\mathrm{CC})^{-1}$ and b, c, d and e are constants. Four equations of the type

$$B(\mathrm{CH}) = A + B\rho \qquad (2)$$

concern the carbon–hydrogen bonds. The quantity $\rho = R(\mathrm{CH})^{-1}$ and A and B determine these linear equations. Another relation between $B(\mathrm{CC}$, graphite, 1.42), $B(\mathrm{CC}$, graphite, 3.35) and the heat of sublimation of graphite is

$$1.5B(\mathrm{CC},1.42) + 0.5B(\mathrm{CC},3.35) = L(\mathrm{C}_1) \qquad (3)$$

The heats from atom formation are related to the carbon–carbon and carbon–hydrogen bond energies, as for example in the case of ethane

$$B(\mathrm{CC,C_2H_6}) + 6B(\mathrm{CH,C_2H_6}) = Q(\mathrm{C_2H_6})$$

There are altogether 14 equations, but only eleven are independent. Their solution gives the values of eleven unknowns: $B(\mathrm{CC,C_2H_6})$, $B(\mathrm{CC,C_2H_4})$, $B(\mathrm{CC,C_2H_2})$, $B(\mathrm{CC}$, graphite, 1.42), $B(\mathrm{CH,C_2H_6})$, $B(\mathrm{CH,C_2H_4})$, $B(\mathrm{CH,C_2H_2})$, and c, d, e, B. Other quantities such as $B(\mathrm{CC}$, graphite, 3.35), b and A are obtained from the 14 equations in terms of the other unknowns. If there are several like bonds in the molecule, then only the average bond energy ($\bar{B}$) is obtained. The final result is

$$B(\mathrm{CC}) = 68.2477r - 423.5984r^2 + 1050.6534r^3 - 380.5358r^4 \qquad (4)$$

and

$$B(\mathrm{CH}) = -53.7136 + 166.0571\rho \qquad (5)$$

They can now be used to calculate carbon–carbon and carbon–hydrogen bond energies if the corresponding distances and the heat of atomization are known. The latter quantity is derived from the ordinary heat of formation (Qf_0^0), the heat of sublimation of graphite ($L(\mathrm{C}_1)$) and the heat of dissociation of hydrogen $D(\mathrm{H}_2)$. The carbon atoms are considered to be in their ground state (^{3}P) and the hydrogen atoms in their lowest level (^{2}S). The

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(2) Selected Values of Properties of Hydrocarbons, Circ. C461, Nat. Bur. Standards (U. S. Government Printing Office, Washington, 1947).

(3) D. Riley, *Nature*, **153**, 587 (1944).

(4) G. E. Hansen and D. M. Dennison, *J. Chem. Phys.*, **20**, 313 (1952).

(5) B. P. Stoicheff, *Canad. J. Phys.*, **33**, 811 (1955).

(6) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1945.

(7) R. W. G. Wyckoff, "The Structure of Crystals," Chemical Catalog Co., Inc., New York, N. Y., 1931.

heat of sublimation of graphite into atoms has been taken to be 170.39[2] kcal. because the work of Brewer, Gilles and Jenkins,[8] Chupka and Inghram[9] and Honig[10] makes this value now quite certain.

Table I and Fig. 1 show the calculated bond energies. The procedure of using equations 4 and 5 is as follows. If the carbon–carbon and carbon–hydrogen distances are known then the corresponding bond energies are calculated. Their sum can then be compared with the Q-value for the compound. If the latter quantity is known, a few trials with assumed distances will lead to a set of bond energies and distances that will match the known heat from atom formation. Carbon–hydrogen bond distances can be calculated from equation 6 if the carbon–carbon bond distance is known or assumed and *vice versa*. Resonance and strain energies can be evaluated by calculating Q of the reference structure, as for example the Kekule structures of benzene or butadiene. The strain energies of the cyclopropanes can be obtained by a comparison of their Q's with their ethane-like reference structures.

TABLE I

CARBON–CARBON AND CARBON–HYDROGEN BOND ENERGIES AND BOND DISTANCES

	R(CC,m), Å.	B(CC,th), kcal.	R(CH,m), Å.	B(CH,th), kcal.	Q(th), kcal.
C_2H_2	1.207	183.80	1.060	102.94	389.69
$C_2(^3\Pi)$	1.314	142.05	...	....	142.05
C_2H_4	1.348	131.20	1.078	100.39	532.74
C_6H_6	1.393	118.41	1.083	99.61	1308.08
Graphite	1.421	111.08	...	....	166.64
C_2H_6	1.543	85.18	1.102	96.97	667.02
Diamond	1.545	84.91	...	....	169.80
Graphite	3.354	7.48	...	....	3.74
CH_4	...	....	1.093	98.21	392.86
CH_3	...	....	(1.101)	97.1	291.4
CH_2	...	....	(1.116)	95.1	190.3
$CH(^2\Pi)$	...	....	1.13	93.2	93.2

R(CC):R(CH) Relation.—From the known bond distances of ethane and acetylene (Table I) a straight line relation between carbon–carbon and carbon–hydrogen distances can be derived

$$R(\mathrm{CH}) = 0.908 + 0.126R(\mathrm{CC}) \qquad (6)$$

Since the interval in carbon–hydrogen distance is small a straight line relation is satisfactory. For example Stoicheff[5] gives $R(\mathrm{CC}, C_6H_6) = 1.3973$ Å. and $R(\mathrm{CH}, C_6H_6) = 1.084$ Å. Using this R(CC) value, equation 6 yields $R(\mathrm{CH}) = 1.084$ Å.

Graphite.—The bond energy of diamond is one-half its heat of sublimation into single atoms. In the case of graphite, equation 3 shows that there are two bond energies to be considered: one within the layers and another energy quantity related to the separation of the layers from one another. The latter is called a bond energy for convenience even though van der Waals forces only are holding the layers together. Equation 3 can be derived by counting the number of bonds that must be broken as one mole of graphite is cut into sheets, rows and finally atoms. If it is assumed that all bonds in the carbon crystal are alike, then equation 3 yields $B(\mathrm{CC, carbon}) = {}^1/_2L(C_1)$ as is the case with diamond. The same method of cutting a solid into sheets, strips and finally atoms shows that the evaporation of graphite into doublets (C_2) is

$$2B(\mathrm{CC},1.42) + B(\mathrm{CC},3.35) = L(C_2,1.42)$$

From Table I: $2 \times 111.1 + 7.5 = 229.7$ kcal. $= L(C_2)$ per mole C_2. The heat of sublimation of graphite into n-atomic molecules is given by the equation

$$((n + 2)/2)B(\mathrm{CC},1.42) + (n/2)B(\mathrm{CC},3.35) = L(C_n,1.42)$$

It should be noted that the diatomic C_2 molecules resulting from this process have the distance 1.42 Å. The reaction so far considered is a hypothetical one and amounts to a kind of vertical sublimation. If it is assumed that the final species in the carbon gas is $C_2(^3\Pi)$ with an interatomic distance of 1.31 Å., then the following set of reactions must be added

$$\begin{array}{ll}
2C(1.42) \longrightarrow C_2(1.42) & L(C_2,1.42) = -229.64 \text{ kcal.} \\
C_2(1.42) \longrightarrow 2C_1(^3P) & D(C_2,1.42) = -111.08 \text{ kcal.} \\
2C_1(^3P) \longrightarrow C_2(^3\Pi,1.31) & D(C_2,1.31) = +142.05 \text{ kcal.} \\
\hline
2C(1.42) \longrightarrow C_2(^3\Pi,1.31) & L(C_2,{}^3\Pi,1.31) = -198.67 \text{ kcal.}
\end{array}$$

The reorganization energy (R.O.E.) which refers to the change in the gas phase

$$C_2(1.42) \longrightarrow C_2(1.31);\ \text{R.O.E.} = -111.08 + 142.05 = 30.97 \text{ kcal.}$$

Similar calculations for C_3 gas molecules yield

$$\begin{array}{ll}
3C(1.42) \longrightarrow C_3(1.42) & L(C_3,1.42) = -289.1 \text{ kcal.} \\
C_3(1.42) \longrightarrow 3C_1(^3P) & 2B(\mathrm{CC},1.42) = -222.2 \text{ kcal.} \\
3C_1(^3P) \longrightarrow C_3(1.29) & Q(C{=}C{=}C,1.29) = +294.3 \text{ kcal.} \\
\hline
3C(1.42) \longrightarrow C_3(1.29) & L(C_3,{}^5\Sigma,1.29) = -217.0 \text{ kcal.}
\end{array}$$

C_3 molecules were assumed to be straight chains as in allene.[11] The reorganization energy (R.O.E.) is 72.1 kcal.

These estimates of carbon–carbon bond energies and the heats of sublimation into C_1, C_2 and C_3 molecular species in the case of graphite can be compared with the mass spectrographic studies of Chupka and Inghram[9] and of Honig[10] as shown in Table II.

TABLE II

COMPARISON OF EXPERIMENTAL VALUES AND THE PRESENT ESTIMATES OF C_2 AND C_3 BOND ENERGIES (KCAL.)

Reaction	Q	Ref. 10	G.G.
$2C(s) \rightarrow 2C_1(g)$	$2L(C_1)$	340	340
$C_2(g) \rightarrow 2C(s)$	$L(C_2)$	-210 ± 20	-199
$C_2(g) \rightarrow 2C_1(g)$	$D(C_2)$	130 ± 20	142
	D(C–C)	130	142
$3C(s) \rightarrow 3C_1(g)$	$3L(C_1)$	510	511
$C_3(g) \rightarrow 3C(s)$	$L(C_3)$	-190 ± 10	-217
$C_3(g) \rightarrow 3C_1(g)$	$2D(C_3)$	320 ± 10	294
	D(C–C)	160 ± 5	147

The Paraffin Increment.—The ordinary heats of formation of the saturated paraffins (Qf°_0) show a constant increase after hexane (the paraffin increment). It is on an average 3.673 kcal.[2] The next higher paraffin is obtained by adding one carbon–carbon bond and two carbon–hydrogen bonds. In order to find the heat from atom formation, the

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[8] L. Brewer, P. W. Gilles and F. A. Jenkins, *J. Chem. Phys.*, **16**, 797 (1948).

[9] W. A. Chupka and M. C. Inghram, *ibid.*, **21**, 1313 (1953).

[10] R. E. Honig, *ibid.*, **22**, 126 (1954).

[11] G. Glockler, *ibid.*, **22**, 159 (1954).

heat of sublimation of graphite and the heat of dissociation of hydrogen must be added

$$Q(\text{Par.Inc.}) = 3.573 + 170.39 + 103.24 = 270.30 \text{ kcal.}$$

The corresponding bond energies and bond distances are: B(CC, P.I.) = 83.64 and B(CH,P.I.) = 96.83 kcal. and R(CC) = 1.550 Å. and R(CH) = 1.103 Å. The paraffin increment is useful in the study of the saturated hydrocarbons.

Benzene.—Stoicheff[5] has determined R(CC,C_6H_6) = 1.3973 and R(CH, C_6H_6) = 1.084 Å. The CC distance used in equation 6 yields 1.084 Å. These two bond distances give bond energies which add up to Q = 1300.2 kcal., whereas Q(th) = 1308.1 kcal. A few trials produce a better match for Q(th):B(CC,C_6H_6) = 118.4 kcal., R(CC,C_6H_6) = 1.393 Å.; B(CH,C_6H_6) = 99.6 kcal. at R(CH, C_6H_6) = 1.083 Å. and Q(th) = 1308.1 kcal. The Kekule reference structure (ethane and ethylene-like bonds from Table I) has Q(ee) = 1241.2 kcal. The resonance energy is then 66.86 kcal. This estimate is smaller than the earlier one obtained (I) because of the change in the empirical equations. The benzene molecule can also be compared with butadiene as a reference structure. The needed bond energies are given in the next section and yield Q(C_6H_6, butadiene) = 1284.8 kcal., leading to a resonance energy of benzene of 23.28 kcal. which may be ascribed to the π electrons only.

The resonance energy of benzene can also be derived from the heats of hydrogenation of benzene to cyclohexane and the heat of hydrogenation of cyclohexene (at 0°K.)

$$\begin{array}{llr}
C_6H_6 + H_2 \longrightarrow C_6H_8 - 4.95 \text{ kcal.} & & (1) \\
C_6H_8 + H_2 \longrightarrow C_6H_{10} + 23.68 \text{ kcal.} & & (2) \\
C_6H_{10} + H_2 \longrightarrow C_6H_{12} + 25.28 \text{ kcal.} & & (3) \\
\hline
C_6H_6 + 3H_2 \longrightarrow C_6H_{12} + 44.01 \text{ kcal.} & & (4)
\end{array}$$

The needed data are taken from the work of Kistiakowsky and collaborators.[12] Pauling[13] assumed that "three times the heat of hydrogenation of cyclohexene to cyclohexane minus the heat of hydrogenation of benzene to cyclohexane equals the resonance energy of benzene" or

$$\text{R.E.}(C_6H_6) = 3 \times 25.28 - 44.01 = 31.83 \text{ kcal.}$$

It is seen that the rule does not hold. The reason is that the molecules cyclohexene and cyclohexane themselves have not exactly the bond energies of ethane and ethylene, but show individual differences due to near-bond effects, van der Waals interactions of the London type, etc. The rule can be revised so that the value of the resonance energy of benzene (66.84 kcal.) is obtained. The heats from atom formation of the Kekule structures are labeled Q_{oi}, and the molecules C_6H_6 to C_6H_{12} are numbered 1 to 4. The hydrogenations of these Kekule molecules with atomic hydrogen are then

$$Q_{02} - Q_{01} = Q_{03} - Q_{02} = Q_{04} - Q_{03}$$

or

$$3(Q_{04} - Q_{03}) - (Q_{04} - Q_{01}) = 0$$

since in these Kekule molecules all bonds of one kind are equal. By inserting into these equations the Q values of the Kekule structures (1 to 4) it is evident that these equalities hold. However, the real molecules (1 to 4) have heats of atom formation (Q_i; i = 1, 2, 3, 4) which differ from the Q_{oi} values by the corresponding resonance energy, etc. Then

$$Q_i = Q_{oi} + \text{R.E.}_i;\ i = 1,2,3,4$$

and substituting these Q_i values in the set of three equalities yields

$$3(Q_4 - Q_3) - (Q_4 - Q_1) = 3(\text{R.E.}_4 - \text{R.E.}_3) - (\text{R.E.}_4 - \text{R.E.}_1)$$

or

$$\text{R.E.}_1 = 2Q_{04} - 3Q_{03} + Q_1 = 66.84 \text{ kcal.}$$

if the Q-values of Table III are used. Hence $3(Q_4 - Q_3) - (Q_4 - Q_1)$ equals R.E.$_1$ only if R.E.$_3$ and R.E.$_4$ are zero. In this manner the direct determination of the resonance energy of benzene from Q and from the heats of hydrogenation yields the same value which differs from the usual one given by Pauling.[13] It should be noted that resonance energies are independent of $L(C_1)$.

Mulliken and Parr[14] define a vertical resonance energy of benzene (V.R.E.) distinct from the usual thermochemical one (Th.R.E.). The latter refers to the reaction

TABLE III

BENZENE RESONANCE ENERGIES FROM Q(TH) VALUES AND KEKULE BASE (Q(ee)), KCAL.

	Q(th)	Q(ee)	Resonance energy, etc.
$6C + 6H \rightarrow C_6H_6$	1308.06	1241.22	66.84
$6C + 8H \rightarrow C_6H_8$	1406.35	1385.72	20.63
$6C + 10H \rightarrow C_6H_{10}$	1533.27	1530.22	3.05
$6C + 12H \rightarrow C_6H_{12}$	1661.79	1674.72	−12.93

$$C_6H_6(\text{Kekule},1.54,\ 1.35) \longrightarrow C_6H_6(\text{Actual},\ 1.39);\quad \Delta E - \text{Th.R.E.} = 66.84 \text{ kcal.}$$

and the former to the process

$$C_6H_6(\text{Kekule},1.39) \longrightarrow C_6H_6(\text{actual},1.39);\quad \Delta E = -\text{V.R.E} = 103.4 \text{ kcal.}$$

These changes are combined with the transition of compressing the Kekule molecule (1.54, 1.35 A.) to the actual structure (1.39 Å.) and still maintaining the character of single and double bonds, or

$$C_6H_6(\text{Kekule},\ 1.54,\ 1.35) \longrightarrow C_6H_6\ (\text{Kekule},\ 1.39);\quad \Delta E = C_k = 36.6 \text{ kcal.}$$

C_k is the compression energy needed to effect this change. Their values are: V.R.E. = 73.1 kcal. (103.4), C_k = 36.6 (36.6) and Th.R.E. = 36.5 (66.8) kcal., with the corresponding present figures given in parentheses.

Butadiene.—The ordinary heat of formation Qf_0^0 of butadiene is −30.2 kcal.[15] which yields Q(th,C_4H_6) = 961.1 kcal. The central CC-bond distance is 1.475 Å. It is considerably shorter than the CC-bond in ethane (R(CC,C_2H_6) = 1.543 Å.). Schomaker and Pauling[16] find R(C–C,C_4H_6) = 1.46 ± 0.04 Å. by electron diffraction.

As in the case of benzene, the heats of hydrogenation have been determined by Kistiakowsky and

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[12] G. Kistiakowsky, *et al.*, *J. Am. Chem. Soc.*, **58**, 137, 146 (1936).

[13] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940.

[14] R. S. Mulliken and P. G. Parr, *J. Chem. Phys.*, **19**, 1271 (1951).

[15] J. G. Aston, *et al.*, *ibid.*, **14**, 67 (1946).

[16] V. Schomaker and L. Pauling, *J. Am. Chem. Soc.*, **61**, 1709 (1939).

co-workers.[12] These experiments yield the following thermochemical reactions (at 0°K.)

$$\begin{array}{l} C_4H_6 + H_2 \longrightarrow C_4H_8 + 25.04 \text{ kcal.} \\ C_4H_8 + H_2 \longrightarrow C_4H_{10} + 28.49 \text{ kcal.} \\ \hline C_4H_8 + 2H_2 \longrightarrow C_4H_{10} + 53.53 \text{ kcal.} \end{array}$$

According to Pauling[13] the following rule should yield the resonance energy of butadiene: "Twice the heat of hydrogenation of 1-butene to butane minus the heat of hydrogenation of butadiene to butane equals the resonance energy of butadiene" or

$$\text{RE(butadiene)} \neq 2 \times 28.49 - 53.53 \neq 3.45 \text{ kcal.}^{17}$$

The heats from atom formation of butadiene, 1-butene and butane, obtained from their ordinary heats of formation[2] are collected in Table IV.

If Q_{oi} = atomic heat of formation for Kekule structures with $C_4H_6(1)$, $C_4H_8(2)$, $C_4H_{10}(3)$, then

$$(Q_{03} - Q_{02}) = (Q_{02} - Q_{01})$$

or

$$2(Q_{03} - Q_{02}) - (Q_{03} - Q_{01}) = 0$$

As in the case of benzene the real molecules have $Q_i = Q_{oi} + \text{R.E}_i$ and

$$2(Q_3 - Q_2) - (Q_3 - Q_1) = 2(\text{R.E.}_3 - \text{R.E.}_2) - (\text{R.E.}_3 - \text{R.E.}_1)$$

or

$$\text{R.E.}_1 = Q_{03} - 2Q_{02} + Q_1 = 14.61 \text{ kcal.}$$

as expected and not 3.45 kcal.

Cycloparaffins.—The Q-values of the cycloparaffins were determined as usual from their ordinary heats of formation. The similar values for the ethane-like reference structures were obtained from equations 4, 5 and 6. After several trials good fits were obtained. For cyclopropane B(CC,th) = 75.88, B(CH,th) = 96.07 kcal.; R(CC,th) = 1.597 and R(CH,th) = 1.109 Å., fit $Q(C_3H_8,\text{th})$ = 804.1 kcal. $Q(C_3H_6,\text{m})$ = 861.7 kcal. yields B(CC,m) = 92.17 and B(CH,m) = 97.52 kcal. with R(CC,m) = 1.506 and R(CH,m) = 1.098 Å. The basic bonds (C_2H_6,C_2H_4 and C_2H_2) give Q(ee) = 837.6 kcal. Cyclobutane has the following structure: B(CC, th) = 78.20 and B(CH,-th) = 96.21 kcal. with R(CC,th) = 1.584 and R(CH,th) = 1.108 Å. with $Q(C_4H_8,\text{th})$ = 1082.4 kcal. B(CC,m) = 80.82 and B(CH,m) = 96.48 kcal. at R(CC,m) = 1.568 and R(CH,m) = 1.106 Å. which brings $Q(C_4H_8,\text{m})$ = 1094.2 kcal. The basic bonds (C_2H_2, C_2H_4,C_2H_6) give for cyclobutane Q(ee) = 1116.5 kcal.

TABLE IV

BUTADIENE RESONANCE ENERGY FROM Q(th) VALUES KEKULE BASE (Q(ee)) KCAL.

	Q(th)	Q(ee)	Resonance energy, etc.
(1) $4C + 6H \rightarrow C_4H_6$	961.08	946.47	14.61
(2) $4C + 8H \rightarrow C_4H_8$	1089.36	1085.87	3.49
(3) $4C + 10H \rightarrow C_4H_{10}$	1221.09	1225.27	−4.18

From these various Q-values so called strain energies (S.E.) can be derived. The reference state is usually taken to be Q(ee). Hence

$$\text{S.E.}(C_3H_6) = Q(\text{th}) - Q(\text{ee}) = -33.5 \text{ kcal.}$$

and S.E.(C_4H_8) = −34.1 kcal. If a similar relation be written with Q(m) as basis of reference the corresponding S.E. values would be −57.6 and −11.7 kcal. Since the reference state (Q(m) or Q(ee)) is arbitrary, a similar relation can be written with the bond energies of the paraffin increment as a reference point. The S.E. values for the cycloparaffins based on Q(ee) and Q(P.I.) are shown in Fig. 2. A five- or six-membered carbon–carbon ring is the most stable configuration as has been known for a long time. These strain energies are independent of the heat of sublimation of carbon. The CH_2-radical has been added because the double bond has been considered[18] to have the tetrahedral angle (109° 28′) between its two bonds.

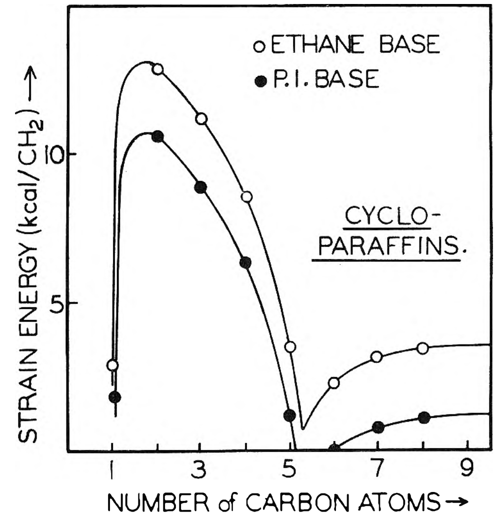

Fig. 2.—Strain energies of the cycloparaffins.

Allene.—The heat of hydrogenation of allene to propane is 71.28 kcal. at 355°K. according to Kistiakowsky.[12] Combining this value with the heat from atom formation of propane and the heat of dissociation of hydrogen yields Q(th) = 678.7 kcal. at 355°K. Using specific heat data given by Linnett[19] Q(th) = 670.0 kcal. at 0°K. The bond energies commensurate with this quantity are: B(C=C,th) = 133.97 and B(CH,th) = 100.54 kcal. and R(C=C,th) = 1.339 and R(CH,th) = 1.077 Å. The carbon–carbon bond distance does not agree with 1.309 A., obtained from the rotational Raman spectrum by Stoicheff.[5] This last mentioned value can be used to determine the corresponding carbon–hydrogen distance and ultimately Q(m) = 691.9 kcal. The ethylene-like reference structure has Q(ee) = 664.0 kcal. Q(m) = 691.9 kcal., yields B(C=C,m) = 143.8 kcal. at R(C=C,m) = 1.309 Å. and B(CH,m) = 101.1 kcal. at R(CH,m) = 1.073 Å.

Methane and its Radicals.—The values of $B(CH,CH_3)$ and $B(CH,CH_2)$ can roughly be estimated from $B(CH, CH_4)$ = 392.9 and B(CH, radical) = 93.2 kcal. if a number of assumptions are made: (1) $B(CH_4) > B(CH_3) > B(CH_2) > B$(CH, radical); (2) the bond dissociation energies $D(CH_x\text{–}H)$ are a smooth function of R(CH), not necessarily linear; (3) $\Sigma D(CH_x\text{–}H) = Q(CH_4) =$

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[17] G. Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944.

[18] G. N. Copley, *Chemistry and Industry*, **60**, 663 (1941).

[19] J. W. Linnett and W. H. Avery, *J. Chem. Phys.*, **6**, 686 (1938)

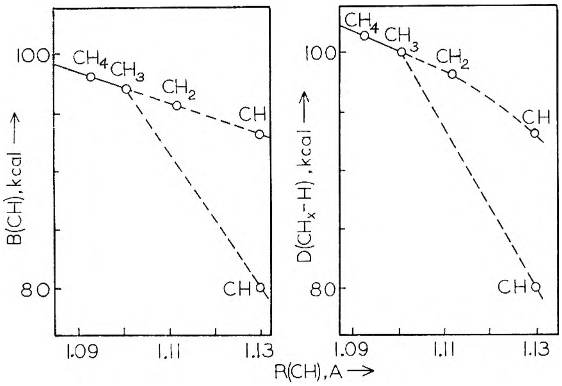

Fig. 3.—Methane and its radicals.

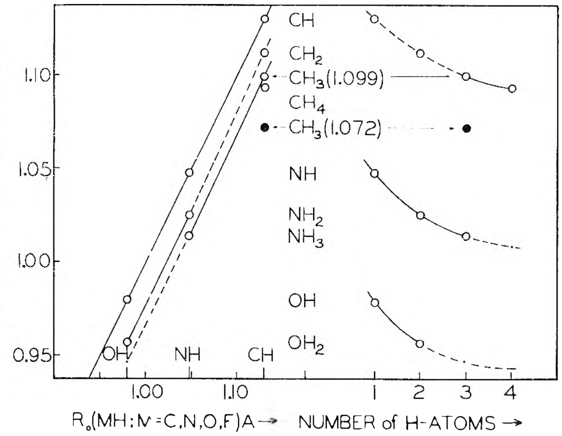

Fig. 4.—Bond distances for molecules and radicals MH_x (M = C, N, O, F and x = 1, 2, 3, 4): CH (1.130), NH (1.048), OH (0.980), HF (0.926), CH_2 (1.112), NH_2 (1.025), H_2O (0.957), CH_3 (1.099), NH_3 (1.016) and CH_2 (1.093).

392.9 kcal. From Table V, $D(CH_3-H) + D(CH_2-H) = 198.9$ kcal. By trial it was found that a smooth curve (Fig. 3) can be obtained if $D(CH_2-H) = 100.9$ and $D(CH-H) = 98.0$ kcal. $R(CH,CH_3) = 1.099$ A. is probably a good estimate. However $D(CH_2-H)$ and $D(CH-H)$ may vary because resonance may make these radicals more stable. Possibly $B(CH,CH_3) > B(CH,CH_4)$.

If similar considerations are made using $D(C-H) = B(CH$, radical) = 80 kcal.,[20] and $R(CH,CH_3) = 1.072$ Å. (Table V), then either $D(CH_2-H)$ or $D(CH-H)$ or both would be greater than $D(CH_3-H)$. The sum of $D(CH_2-H) + D(CH-H) = 392.9 - (89.3 + 80.0) = 223.6$ kcal. and the average value is 111.8 kcal. $R(CH, CH_3) = 1.099$ Å. fits better than 1.072 Å. into the scheme $R(MH)$ for the elements M = C, N, O, F (Fig. 4). If $R(CH,CH_3) = 1.072$ Å. is substantiated, it would mean that $B(CC):R(CC)$ and $B(CH):R(CH)$ are not like the similar relations for force constants $k(CC):R(CC)$ and $k(CH):R(CH)$.

Dissociation into Radicals.—The values of the bond energies of the radicals of methane just mentioned allow the calculation of dissociation energies as follows (Tables I and V)

$$\begin{array}{l} 2C + 4H \longrightarrow C_2H_4 + 532.7 \text{ kcal.} \\ \underline{2CH_2 \longrightarrow 2C + 4H - 382.4 \text{ kcal.}} \\ 2CH_2 \longrightarrow C_2H_4 + 150.3 \text{ kcal.} \end{array}$$

Price[21] and Hilgendorff[22] give respectively <162 and <159 kcal. from predissociation in the ultraviolet. The dissociation of ethane into two methyl radicals is calculated to be 82.8 kcal. Szwarc[23] mentions two values: 80 ± 6 kcal. obtained by Rice and Dooley[24] by the mirror technique and 82–87 kcal. calculated from $D(CH_3-H)$. The dissociation of acetylene into two CH-radicals is calculated to be 203.2 kcal. Price[22] obtained <187 kcal. from a study of predissociation in the Schuman ultraviolet. Many other cases can be calculated.

Methylacetylene.—The ordinary heat of formation is −46.02 kcal.,[2] giving $Q(th) = 671.6$ kcal. Gordy[25] determined all the distances of this molecule: $R(C{\equiv}C) = 1.207$, $R(C-C) = 1.46$; $R(H-C{\equiv}) = 1.056$ and $R(H-(CH_2)-) = 1.097$ Å. These distances lead to $Q(m) = 683.7$ kcal. The reference structure has a $Q(ee)$ value of 657.0 kcal. It is noted that $Q(m) > Q(th) > Q(ee)$.

Dimethylacetylene.—The ordinary heat of formation is −38.49 kcal.,[2] giving $Q(th) = 952.9$ kcal. Transferring the distances from methylacetylene appropriately yields $Q(m) = 977.6$ kcal., while $Q(ee) = 936.2$ kcal. Again $Q(m) > Q(th) > Q(ee)$.

TABLE V

METHANE AND ITS RADICALS

	$R(CH)$, Å.	$B(CH)$, kcal.	Q, kcal.	$D(CH_x-H)$, kcal.
CH_4	1.093	98.2	392.9	100.8[a]
CH_3	1.099	97.4	292.1	100.9
CH_2	(1.112)	95.7	191.2	98.0
CH	1.130	93.2	93.2	93.2
				392.9
CH_4	1.093	98.2	392.9	89.3
CH_3	1.072[b]	101.2	303.6	111.8
CH_2				111.8
CH	1.130	80.0	80.0	80.0
				392.9

[a] H. C. Andersen and G. B. Kistiakowsky, *J. Chem. Phys.*, 11, 6 (1943), and 12, 469 (1944). [b] G. Herzberg, "Mol. Spectroscopy Symposium," Ohio State University, June 1956.

Discussion

In the construction of the primary curves (Fig. 1) it has been assumed that two continuous curves would be sufficient to represent the relations $B(CC):R(CC)$ and $B(CH):R(CH)$. It is possible that either of these sets will need one or more segments of curves for their full representation, as more information becomes available. The equations (4, 5 and 6) have been obtained from thermochemical quantities (Q(th)) and the internuclear distances (R(m)), derived from the moments of inertia (m) of ethane, ethylene, acetylene and methane, etc. If these equations are now in turn used to derive distances for another compound, by fitting the thermochemical quantity (Q(th)) into the scheme, then the lengths so determined will of

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(20) G. Herzberg, "Molecular Spectra and Molecular Structure," D. Van Nostrand Co., Inc., New York, N. Y., 1950.

(21) W. C. Price, *Phys. Rev.*, **45**, 843 (1934); **47**, 444 (1935).

(22) H. J. Hilgendorff, *Z. Physik*, **95**, 781 (1935).

(23) M. Szwarc, *Chem. Revs.*, **47**, 75 (1950).

(24) F. O. Rice and M. D. Dooley, *J. Am. Chem. Soc.*, **55**, 4245 (1933).

(25) W. Gordy, W. V. Smith and R. F. Trambarulo, "Microwave Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1953.

course be internuclear distances (R(m)). However they also are considered to be the lengths of the corresponding bonds (R(th)). The assumption of the identity of R(m) and R(th) may not be correct in some cases, although usually these two lengths coincide in magnitude and direction. It is true for benzene, where the distances estimated to fit the general curves (Fig. 1) starting with Q(C_6H_6,-th) are actually equal to the internuclear distances R(CC,m) = 1.393 and R(CH,m) = 1.084 Å., as determined from the Raman rotation spectrum by Stoicheff.[26] Hence it can be said that with benzene, the relation Q(th) = Q(m) holds. This equality is also true for butadiene. It means that the bond distance and the corresponding internuclear distance are alike in length and direction.

In the case of cyclopropane R(th) $\neq$ R(m). R(th) from Q(th) = 804.1 kcal. is 1.597 Å. while R(m) = 1.506 Å. as determined by Neill[27] from the moment of inertia and leads to Q(m) = 861.7 kcal. A similar situation is found with other molecules (Table VI). Hence there exists the inequality Q(th) < Q(m) which means R(th) > R(m). Since both distances are presumed to start from the carbon nuclei, R(th) or the maximum values of the carbon orbitals must make an angle (one-half the strain angle) with the internuclear distance. The problem has been studied by Copley,[18] Coulson and Moffitt,[28] Kilpatrick and Spitzer,[29] and Weltner.[30]

The strain angle is here defined by the ratio R(m):R(th) and indicates the angular deviation of the maximum value of the bond orbital from the internuclear distance. For cyclopropane R(m)/R(th) is 1.506/1.597. This ratio is the cosine of one-half of the strain angle. The latter is therefore 20°. For cyclobutane R(m) = 1.568 Å. from electron diffraction[31] and R(th) = 1.584 Å. from Q(th), so that one-half of the strain angle is 9°. Instead of referring the strain to the internuclear axis it may be better to refer it to the tetrahedral angle directions. These calculations are compared in Table VII with earlier studies.

It is of interest to consider Q(m) as a reference point for the calculations of strain energies (S.E.-(th, m)). They are defined as

$$\text{S.E.(th,m)} = Q(\text{th}) - Q(\text{m});\ Q(\text{th}) < Q(\text{m})$$

and resonance energies on the same basis are

$$\text{R.E.(th,m)} = Q(\text{th}) - Q(\text{m});\ Q(\text{th}) > Q(\text{m})$$

The reference point (Q(m)) is not the one chosen ordinarily. Rather an arbitrary model such as the Kekule structures of benzene is used for reference. This procedure is equivalent to the choice of single, double and triple bond as in ethane, ethylene and acetylene.[32] The corresponding quantities are labeled Q(ee), B(CC, ee), R(CC, ee), etc. Both bases (Q(m) and Q(ee)) will be used for calculating strain and resonance energies (Table VI). For example there are now to be considered three sets of quantities for cyclopropane

$$Q(\text{m}) = 861.7 \text{ kcal.};\ R(\text{CC,m}) = 1.506 \text{ Å.}$$
$$Q(\text{ee}) = 837.6 \text{ kcal.};\ R(\text{CC,ee}) = 1.543 \text{ Å.}$$
$$Q(\text{th}) = 804.1 \text{ kcal.};\ R(\text{CC,th}) = 1.597 \text{ Å.}$$

The resonance and strain energies are calculated by subtracting from Q(th) the bases of either Q(m) or Q(ee)

$$\text{S.E.(th,m)} = -56.7 \text{ and S.E.(th,ee)} = -33.5 \text{ kcal.}$$

Hence the molecule shows strain energy on either base. From Fig. 5 it is seen that all the molecules there mentioned have strain energies in reference to the m-base except benzene and butadiene. These molecules therefore show no extra stability in this case and no special reference structures would have been proposed. The organic chemist would be denied to discuss the behavior of organic molecules on the resonance concept. On the presently accepted ee-base some molecules such as benzene, butadiene, methylacetylene, dimethylacetylene and allene show resonance. The m-base has the advantage that its Q(m) rests on experimentally determined internuclear distances. However, reso-

TABLE VI

STRAIN AND RESONANCE ENERGIES

	R(th) − R(m), Å.	Q(th) − Q(m), kcal.	R(th) − R(ce), Å.	Q(th) − Q(ee), kcal.
Cyclopropane	0.091	−57.6	0.054	−33.5
Cyclobutane	.02	−11.7	.045	−34.1
Butadiene	.0	0.0	− .068	15.3
Benzene	.0	0.0	− .150	66.9
Me-acetylene	.045	−12.1	− .038	14.6
DiMe-acetylene	.045	−24.7	− .038	16.7
Allene	.03	−22.0	− .009	6.0

TABLE VII

STRAIN ANGLES OF CYCLOPROPANE AND CYCLOBUTANE

Gas	CC-bond angle, degree	½ strain-angle, degree Internuclear base	Tetrahedral base	Ref.
C_3H_6	104	22	6	28
	101	20	9	29
	106	23	4	30
	100	20	9	G.G.
C_4H_{10}	108	9	1	28
	105	8	4	29
	108	9	1	30
	108	9	1	G.G.

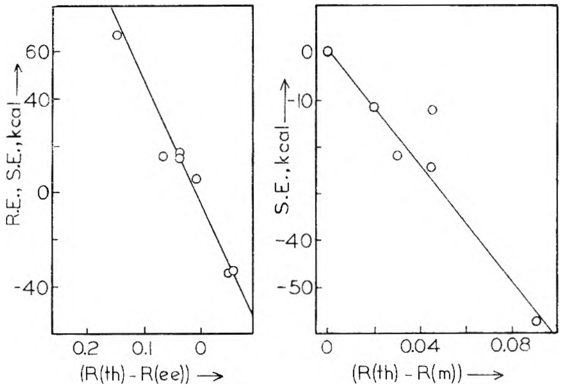

Fig. 5.—Resonance and strain energies of hydrocarbons (Table VI).

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[26] B. Stoicheff, *J. Chem. Phys.*, **21**, 1410 (1953).

[27] H. W. Neill, Thesis, University of Michigan, 1953.

[28] A. C. Coulson and W. E. Moffitt, *J. Chem. Phys.*, **15**, 151 (1947); *Phil. Mag.*, **40**, 1 (1949).

[29] J. Kilpatrick and R. Spitzer, *J. Chem. Phys.*, **14**, 463 (1946).

[30] W. Weltner, *J. Am. Chem. Soc.*, **75**, 4224 (1953).

[31] J. W. Dunitz and V. Schomaker, *J. Chem. Phys.*, **20**, 1703 (1952).

[32] G. Glockler, THIS JOURNAL, **56**, 289 (1952).

nance might not be possible on this basis because it would mean $Q(\text{th}) > Q(\text{m})$ and hence $R(\text{th}) < R(\text{m})$.

The ee-base has of course the advantage that the usual resonance structures are maintained. However the positive and negative differences ($Q(\text{th}) - Q(\text{ee})$) have quite a different interpretation. Resonance implies strengthened bonds and strain energy means dislocated bonds.

Perhaps it will be possible to define an *ideal carbon–carbon* bond which will serve as basis for all real bonds. The latter may then be described in terms of the basic bond, having added all influences real bonds are subject to, such as near bond effects, van der Waals interactions and hyperconjugation. Pitzer[33] showed that the anomalous value of the heat of dissociation of fluorine can be understood if London forces are considered. Similarly the idea of constant bond energies and London interaction permits the calculation of heats of formation (Qf_0^0) of the saturated hydrocarbons (methane to pentane).[34]

The present method of calculation of resonance and strain energies also indicates that some differences ($Q(\text{th}) - Q(\text{ee})$) must be ascribed to other effects but resonance and strain. In the case of cyclohexane $Q(\text{th}) = 1661.8$ and $Q(\text{ee}) = 1674.7$ kcal., whence a strain energy of -12.9 kcal. is indicated. On the paraffin increment base, $Q(\text{P.I.})$ is 1663.8 kcal. and a much smaller strain energy (-2.0 kcal.) is found. However, cyclohexane (chair form) should show no strain energy.[35] Hence the calculated quantities (-12.9 and -2.0 kcal.) must be due to other influences such as van der Waals interactions.

Finally it is necessary to recall the origin of the resonance concept. Certain integrals, called resonance or exchange integrals, appear in the calculations of atomic and molecular systems on the basis of wave mechanics. Their presence causes the total energy of the system to be lower, indicating greater stability. It is only because the wave equation cannot be solved exactly that perturbation methods are used to approximate the energy values. These methods cause the introduction of the exchange integrals. Were it possible to solve the wave equation exactly, the concept of resonance would not have been applied to molecular systems. The exact mathematical treatment would result in expressions for the eigenwerte in terms of constants and quantum numbers.

[33] K. S. Pitzer, *J. Chem. Phys.*, **23**, 1735 (1955).

[34] K. S. Pitzer, Mol. Quant. Mech. Conference, U. of Texas, Dec. 7–9, 1955.

[35] K. S. Pitzer, *Science*, **101**, 672 (1945).

A MASS SPECTROMETRIC APPEARANCE POTENTIAL STUDY OF DIBORANE[1]

BY JOHN L. MARGRAVE

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The appearance potentials of all the important singly charged positive ion fragments formed on bombarding diborane with electrons have been measured. Also, the appearance potentials of some doubly-charged species have been approximately determined. The ionization potential of B_2H_6 is 12.1 ± 0.2 e.v.

Over the past 20 years there has been a considerable interest in the structures and in the bond energies of the various boron hydrides, especially diborane. One of the few experimental tools which has not previously been applied to this problem is the mass spectrometer appearance potential. Hipple[2] observed the mass spectrum of diborane and later work was published by Dibeler and Mohler[3] and Norton.[4] The first two studies were on a sample with the normal B^{10}/B^{11} isotope ratio of approximately $^1/_4$, while the study of Norton was made on B^{10}-enriched diborane containing 96% B^{10}.

The fragmentation pattern of diborane with high energy electrons is indicated in Table I for the normal isotopic mixture as found in this work and by other investigators. One of the problems in interpreting the various peak heights is obviously that there are contributions from different isotopically constituted ions at each mass number. Since an appearance potential study requires one to make a determination of the voltage at which a given ion just begins to appear at the mass spectrograph detector plate, it is necessary to resolve the signal at each mass number given by the mass spectrograph into components which represent the intensity for each different ion fragment. Such a resolution is possible for B_2H_6 in the normal isotopic mixture as demonstrated by Dibeler and Mohler.[3]

Table II lists the fragmentation pattern for B^{10}-enriched diborane as observed in this work and by Norton. Resolution of a given mass signal into a contribution uniquely attributable to a given ion also requires a small correction for the isotope impurity present.

Experimental Methods and Results

Samples of diborane were prepared in the Callery Laboratory and kept frozen until ready for use. The diborane was admitted to the expansion bulb of a modified Consolidated 21-103B mass spectrograph and argon was added as a calibrating gas until the signal for A^+ was of the same height for 70 volt electrons as the signal for the ion of interest. A broad scan of the mass numbers was made covering either the range 10–14 or 20–28 in order to include a peak for

[1] Presented at the Symposium on Valency and Chemical Bonding of the Division of Physical and Inorganic Chemistry, American Chemical Society, in Madison, Wisconsin, on June 21, 1956.

[2] J. A. Hipple, *Phys. Rev.*, **57**, 350 (1940).

[3] V. H. Dibeler and F. L. Mohler, *J. Am. Chem. Soc.*, **70**, 987 (1948).

[4] F. J. Norton, *ibid.*, **71**, 3488 (1949).

every possible boron-containing fragment from B_2H_6 regardless of the isotopic composition. From the heights of the end peaks in these traces (which contain only B^{10} or B^{11} isotopes), one can calculate the contribution to each intermediate peak by the different ion fragments if he knows the isotope ratio. For the normal isotopic mixture in this work the ratio was taken as $B^{10}/B^{11} = {}^1/_4$ as found by observation of a number of boron compounds; for the enriched diborane, the ratio was taken as $B^{10}/B^{11} = 24$.

TABLE I

FRAGMENTATION PATTERN FOR A NORMAL ISOTOPIC MIXTURE SAMPLE OF B_2H_6

	Relative abundance		
m/e	Norton[a]	Dibeler and Mohler[b]	This work[c]
28	(2.4)	0.65	1.35
27	100.0	97.28	96.91
26	96.2	100.00	100.00
25	52.5	58.04	57.59
24	78.7	92.41	89.84
23	38.3	47.32	46.55
22	8.5	11.52	11.46
21	1.3	2.02	2.13
20	0.1	0.18	0.21
14	0.5	0.68	1.71
13	12.6	24.34	26.68
12	8.0	18.50	20.62
11.5	....	....	0.38
11	16.0	28.86	26.85
10	3.6	6.48	5.91
2	71.6	....	1.62
1	2.4	....	....

[a] 70 volt electrons. [b] 50 volt electrons. [c] 70 volt electrons.

TABLE II

FRAGMENTATION PATTERN FOR 96% B^{10}-ENRICHED DIBORANE

m/e	Norton[a]	This work[b]
28	...	0.96
27	0.5	0.80
26	9.4	11.08
25	100.0	100.00
24	46.9	53.19
23	28.6	33.32
22	61.0	72.62
21	5.1	7.91
20	1.9	3.11
14	...	0.40
13	0.9	3.26
12	9.7	23.88
11.5	...	0.08
11	4.6	14.63
10	11.5	19.45
2	45.7	2.29
1	1.6	....

[a] 70 volt electrons. [b] 70 volt electrons.

Corrected peak heights obtained by the procedure indicated above were then used for semi-log plots of current *vs.* voltage and the appearance potentials were evaluated by comparison with the well-known spectroscopic value for argon.[5]

The appearance potentials obtained by this procedure are presented in Table III. In column 2 are listed the appearance potentials as evaluated from a study of the normal isotopic mixture diborane while column 3 lists the results obtained with the B^{10}-enriched sample. The last column indicates the best value and the probable error limit. In several of the mass spectrographic traces peaks were observed at mass numbers 11.5 and 12.5. The appearance potential for mass 12.5 can be stated roughly as 60 ± 5 e.v. (probably for $B_2H_5^{++}$) and that for mass 11.5 is 35 ± 5 e.v. (either $B_2{}^{10}H_3{}^{++}$ or $B^{10}B^{11}H_2{}^{++}$; probably the latter).

Discussion

One of the most useful results of this work is the value for the ionization potential of B_2H_6 which has not been measured previously. The only available data are those of Price[6] who has studied the vacuum ultraviolet absorption spectrum of diborane and places the ionization potential between 11 and 12 electron volts on the basis of an extrapolation from strong absorptions at 1350 and 1200 Å. A quantum mechanical calculation of this quantity should be possible and would offer an interesting test for the molecular model of Crawford, Lipscomb and Eberhardt.[7]

TABLE III

APPEARANCE POTENTIALS FOR POSITIVE ION FRAGMENTS FROM DIBORANE

	Appearance potential in volts		
Ion	Normal isotopic mixture	B^{10}-enriched sample	Best value
$B_2H_6^+$	[a]	12.1 ± 0.2	12.1 ± 0.2
$B_2H_5^+$	11.3 ± 0.5	12.0 ± .2	12.0 ± .3
$B_2H_4^+$	12.6 ± 0.5	12.3 ± .5	12.4 ± .3
$B_2H_3^+$	12.0 ± 1.5	14.8 ± .5	14.8 ± .5
$B_2H_2^+$	13.9 ± 0.5	13.8 ± .2	13.8 ± .2
B_2H^+	....	21.4 ± .5	21.4 ± .5
B_2^+	....	26.3 ± .5	26.3 ± .5
BH_3^+	[a]	12.1 ± .2	12.1 ± .2
BH_2^+	12.0 ± 1.0	13.5 ± .2	13.5 ± .5
BH^+	....	16.6 ± .2	16.6 ± .2
B^+	20.1 ± 0.5	19.2 ± .2	19.5 ± .2

[a] From the observations on the normal isotopic mixture it is determined that the appearance potentials of $B_2H_6^+$ and BH_3^+ are identical within the experimental error.

In addition, one may deduce information as to the magnitude of the "bridge" bond strengths in diborane by considering the fragmentation to form BH_3^+

$$e^- + B_2H_6 = BH_3^+ + BH_3 + 2e^-$$

$$\text{A. P. of } BH_3^+ \geq \Delta H_{\text{reaction}}$$

$$\geq D(BH_3\text{-}BH_3) + I(BH_3)$$

Since there are no data for the ionization potential of BH_3, one can only approximate by comparison with CH_3(9.85 e.v.); CF_3(10.1 e.v.); CCl_3(8.8 e.v.); BF_3 (15.5 e.v.); BCl_3(12.0 e.v.); and $B(CH_3)_3$ (8.8 e.v.). One must choose a value of 10.9 e.v. for the ionization potential in order to get agreement for the dissociation energy of B_2H_6 into 2 BH_3 with the 28.4 ± 2 kcal. value which McCoy and Bauer[8] have derived recently from calorimetric studies of association reactions of diborane.

Further calculations of bond strengths may be made when it is possible to write definite reactions and to know whether or not fragments have been formed in excited states or with kinetic energy. At present, the same doubts that prevail for calculations of the heat of sublimation of graphite from

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(5) C. E. Moore, National Bureau of Standards Circular 467, Vol. II.

(6) W. C. Price, *J. Chem. Phys.*, **16**, 894 (1948).

(7) B. Crawford, W. Lipscomb and W. Eberhardt, *ibid.*, **22**, 989 (1954).

(8) R. E. McCoy and S. H. Bauer, *J. Am. Chem. Soc.*, **78**, 2061 (1956).

appearance potentials of C$^+$ from methane and substituted methanes must be considered as predominant here [9]

In the course of these investigations satellite peaks, believed to correspond to formation of ion fragments with excess kinetic energy, were observed on masses 12, 13 and 20, especially at 50–70 volts electron bombarding energy.

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[9] See, for example, A. Langer, J. A. Hipple and D. P. Stevenson, *J. Chem. Phys.*, **22**, 1836 (1954). The calculated heat of sublimation from appearance potentials is 133 kcal./mole while the accepted value is 170 kcal./mole.

THE CHARACTER OF BONDING OF RADICALS TO AROMATIC AND OLEFINIC COMPOUNDS[1]

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The addition of radicals to aromatic or olefinic molecules is discussed in terms of the repulsion curve and attraction curve. The repulsion curve is due mainly to the coulombic forces acting between the negative cloud of π-electrons of the aromatic or olefinic compound and the negative cloud representing the p electron of the radical. The attraction curve results from the interactions taking place between the excited aromatic or olefinic molecule and the radical. It is shown that starting from these premises one can deduce the experimentally observed relations between methyl affinities and Coulson's localization energy, or triplet–singlet excitation energy. Furthermore, one can understand the effects of electron donating and electron withdrawing groups on the reactivity. Finally, one gets a better understanding of the concept of the intrinsic reactivity of a radical and its relation to the shape of the repulsion curve.

A simple technique, developed recently in our laboratories,[2] permits measuring the relative rates of addition of radicals, like methyl or ethyl, to aromatic or olefinic compounds. It was reported[2–5] that the rate constants of these additions vary enormously with the nature of the substrate, *e.g.*, assuming the relative rate constant of addition of methyl radicals to benzene as unity,[6] one finds the relative rate constants of addition to naphthalene, anthracene and naphthacene to be 22, 800 and more than 9,000, respectively. It is desirable to inquire, what are the factors which affect so greatly the rates of these additions.

Let us consider a series of unsubstituted aromatic hydrocarbons. Coulson[7] has pointed out that the addition of a radical to an aromatic hydrocarbon ties up one of its π-electrons and leads to a change of the original n-electron π-system into an $n - 1$ electron π-system built around $n - 1$ carbon centers. Hence, he considers the difference in the resonance energies between the original and the final π-electron systems to be a measure of the reactivity of an aromatic molecule, and denotes this difference as the localization energy. It seems that his approach is justified, since a monotonic relation has been found between calculated localizations energies and observed methyl affinities, namely, as shown in Fig. 1, logarithms of methyl affinities are linearly related to localization energies.

The localization energy of an aromatic hydrocarbon is calculated by solving the two pertinent secular equations, and the result appears in the form $c\beta$. Here, c is a coefficient, the value of which depends only on the form of the secular equations, while β, the exchange integral, is a constant for the whole series of aromatic hydrocarbons. The relationship illustrated by Fig. 1 essentially demonstrates a functional dependence of methyl affinities on the coefficients c. The question arises, therefore, whether changes in β also lead to corresponding changes in the methyl affinities.

The exchange integral β depends on the extent of overlap of the two adjacent p orbitals. Since this overlap is affected by various deformations of the molecules, one may answer the question by investigating the reactivities of deformed molecules. Bending of an aromatic hydrocarbon out of its natural planar configuration, or twisting or stretching of a double bond, exemplifies the types of deformation which should decrease the extent of the overlap (see for illustration Fig. 2). Hence, one expects that molecules deformed in such a manner would exhibit an increase in their methyl affinities. This expectation is borne out by the data listed in Tables I and II. Table I shows how methyl affinities of benzo(c)phenanthrene derivatives increase as the molecules are bent more and more out of their planar configuration. The bending is achieved by inserting substituents into the 1, or 1- and 12-positions of the parent hydrocarbon, thus creating more and more steric hindrance. At

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[1] This research was supported by a grant from the National Science Foundation.

[2] M. Levy and M. Szwarc, *J. Am. Chem. Soc.*, **77**, 1949 (1955); see also M. Szwarc, *J. Polymer Sci.*, **16**, 367 (1955).

[3] A. Rembaum and M. Szwarc, *J. Am. Chem. Soc.*, **77**, 4468 (1955).

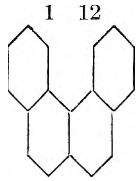
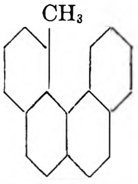
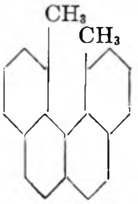
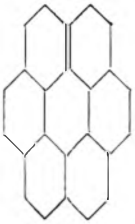
[4] M. Levy, M. Newman and M. Szwarc, *ibid.*, **77**, 4225 (1955); see also M. Szwarc and F. Leavitt, *ibid.*, **78**, 3590 (1956).

[5] F. Leavitt, M. Levy, M. Szwarc and V. Stannett, *ibid.*, **77**, 5493 (1955).

[6] In this paper, the relative rate constants of addition of methyl radicals to aromatic or olefinic compounds are referred to as methyl affinities.

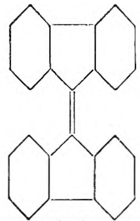
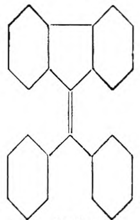
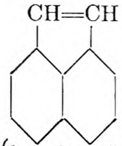
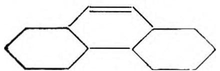
[7] C. A. Coulson, *J. Chem. Soc.*, 1435 (1955); see also Burkitt, Longuet-Higgins and C. A. Coulson, *Trans. Faraday Soc.*, **47**, 553 (1951).

TABLE I[a]

	Methyl affinity at 85°
 (Benzo[c]phenanthrene) and all the mono-methyl derivatives containing a methyl group in positions other than 1 or 12	55–75
	108
	183
 (Hexahelicene)	285

[a] These data are taken from the paper by M. Szwarc and F. Leavitt, *J. Am Chem. Soc.*, **78**, 3590 (1956).

TABLE II

	Methyl affinities
 (A)	1370
 (B)	~15
 (long bond)	1030
 (normal bond)	27

the same time it should be emphasized that the same substituent inserted in positions not leading to such steric hindrance, has a negligible effect on the reactivity.

Table II lists the data concerned with the reactivities of di-bisphenylene ethylene (A) and diphenyl-bisphenylene ethylene (B). The former compound contains a twisted double bond, since the close proximity of the two planar fluorene groups interferes with their coplanarity. On the other hand, the free rotation along the C–Ph bonds in compound (B) makes it possible to avoid the steric strain without twisting the double bond. The great difference in the methyl affinities of these two compounds, which otherwise closely resemble each other, demonstrates clearly the effect of twisting of a double bond on its reactivity. The other two examples listed in Table II represent closely related compounds with similar π-electron systems, one of which contains a stretched double bond, while the other is normal. The great difference in their methyl affinities seems to manifest the effect of stretching of a double bond on its reactivity.[8]

It would be interesting to find a compound containing a short double bond. We would expect the reactivity of such a compound to be lower than of the "normal" one. It is our belief that the acetylenic bond could be treated, at least formally, as a compressed double bond. Whether this approach is correct or not, it is encouraging to find that the acetylenic compounds are uniformly less reactive than the corresponding olefinic compounds, *e.g.*, methyl affinities of phenylacetylene, diphenylacetylene and methylacetylene are 390, 25 and 25, respectively, while the corresponding values for styrene, stilbene and propylene are 1630, 205 and 65.

The relation between methyl affinity and localization energy has an important consequence. There is no reason why methyl radicals should be unique in their behavior. Hence, if logarithms of methyl affinities are linearly correlated to localization energies so should be the logarithms of the relative rate constants of addition of any other radical. This implies, however, a linear relation between the logarithms of the relative rate constants of addition of any radical R to a series of aromatic hydrocarbons and the logarithms of methyl affinities. This conclusion is confirmed by experimental data,[9] and illustrated in Figs. 3, 4 and 5.

The slopes of the straight lines obtained in this way characterize the radicals, and not the aro-

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(8) It is impossible to deform a molecule in such a way that only the overlap of p orbitals would be changed. Unfortunately, any of the discussed deformations introduces many other changes which affect somehow the reactivity. Nevertheless, it is probable, in view of all the examples quoted, that the effects observed are at least partially due to the changes in β,

(9) In the relation between methyl affinities and localization energies the former variable is divided by the statistical factor representing the number of the most reactive points in the respective hydrocarbon, *e.g.*, 6 for benzene, 2 for anthracene, etc. Hence, the same factors should be introduced in the log-log relation correlating methyl affinities with the other rate constants. Such factors were not introduced in the paper by Levy and Szwarc (ref. 2) and this omission is corrected in the present communication, *i.e.*, in Fig. 3. These corrections are irrelevant if the slope of the line is unity.

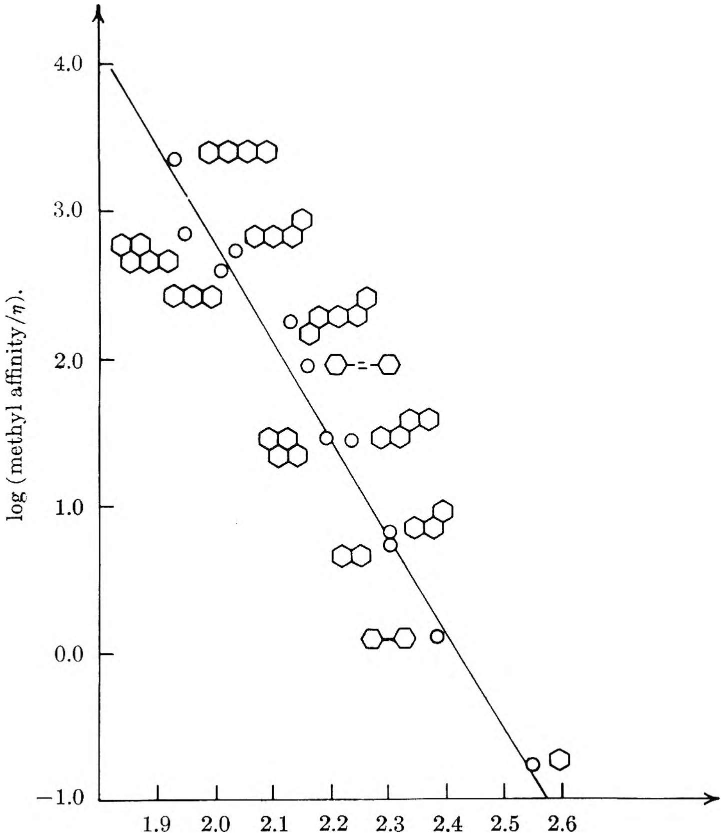

Fig. 1.—Relationship between logarithms of methyl affinities and localization energies.

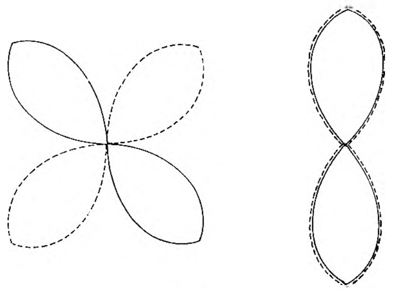

Fig. 2.

matic hydrocarbons. As the radical is more reactive it should show less discrimination in adding to a more or a less reactive hydrocarbon, while less reactive radicals should exhibit greater differences in their respective rate constants. This difference in behavior is measured by the slopes of the log-log lines, and hence the slope could be considered as a measure of the choosiness of a radical or, as suggested previously,[2,3] as a measure of its intrinsic reactivity. By this criterion we find the intrinsic reactivity of methyl and ethyl radicals to be approximately the same, while methyl radicals appear to be 1.8 times as reactive as trichloromethyl radicals. Further studies of intrinsic reactivities of radicals are in progress in our laboratories.

It is worth mentioning that the intrinsic reactivities of radicals resembles the ρ-factors in Hammett's σ-ρ scheme. If one wishes, one can consider methyl affinities as equivalent to σ-factors, and intrinsic reactivities as the corresponding ρ-factors.

To understand better the relations discussed above, it is desirable to consider the details of the addition reaction. The existence of an activation energy in a reaction implies that some repulsive forces participate in the interaction involving the reacting partners. In the case of a radical, say a methyl radical, approaching an aromatic hydrocarbon the repulsive forces result essentially from the coulombic forces operating between the negative π-electron cloud of the aromatic hydrocarbon and the negative cloud of a p electron of the approaching radical. On the other hand, the "prepared for the reaction" molecule of the hydrocarbon, *e.g.*, the one with a localized electron, attracts the approaching radical, forming with it a new C–C bond. We may represent, therefore, the progress of the addition reaction by the energy–distance diagram originally proposed by Evans and Polanyi[10] to account for the behavior of the sodium flame reaction. Such a diagram is represented on Fig. 6. The repulsion curve (R) represents the initial stages of the reaction, the Morse like attraction curve (A) represents the final stages of the addition, and the point of the interaction denotes the transition state of the process. The reaction path is represented, therefore, by the thick line in Fig. 6. The difference in the levels of the repulsion curve and the attraction curve when the separation distance of the reacting partners is infinitely great, represents the excitation energy, *e.g.*, in our present approach the energy required to localize one electron.[11] The height of the crossing point above the level of the repulsion curve represents the activation energy of the addition.

If we assume, now, that the slopes of the attraction and the repulsion curves remain constant for a series of reactions involving the same radical but different aromatic hydrocarbons, and if we suppose, furthermore, that all that is changed in Fig. 6, as a reaction involving one aromatic hydrocarbon is compared with a reaction involving another hydrocarbon, is the distance between the plateaus of the repulsion and attraction curves, then we can apply the treatment described by Evans and Polanyi.[11] This treatment, based entirely on the geometry of the curves, correlates the differences in the heights of the attraction curve above the repulsion curve, with the differences in the activation energies of the process. Since the heights of the attraction curves represent the excitation energies, denoted by E_{ex}, the Evans–Polanyi approach leads to the equation

$$\Delta E_{\text{act}} = \alpha \Delta E_{\text{ex}}$$

Now, if we assume that log k's are a linear function

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[10] M. G. Evans and M. Polanyi, *Trans. Far. Soc.*, **34**, 11 (1938).

[11] The attraction curve in Fig. 6 represents a molecule excited to its triplet state. However, this does not change our argument.

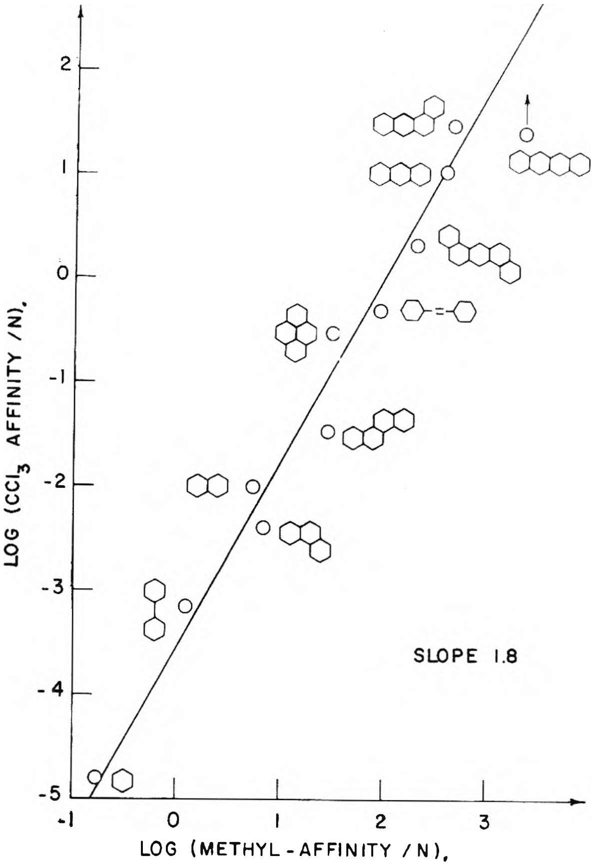

Fig. 3.

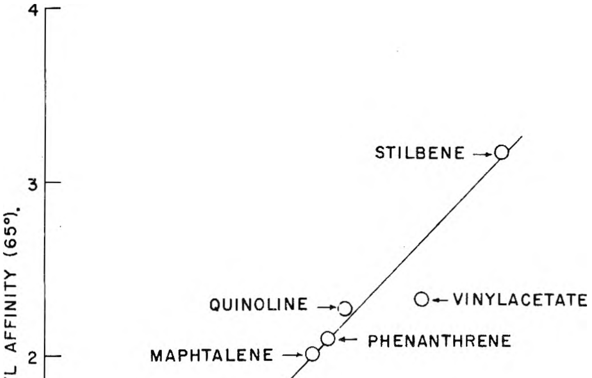

Fig. 4.

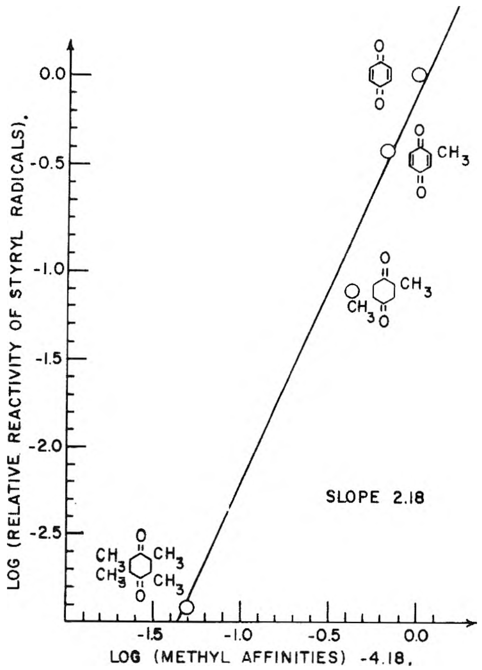

Fig. 5.

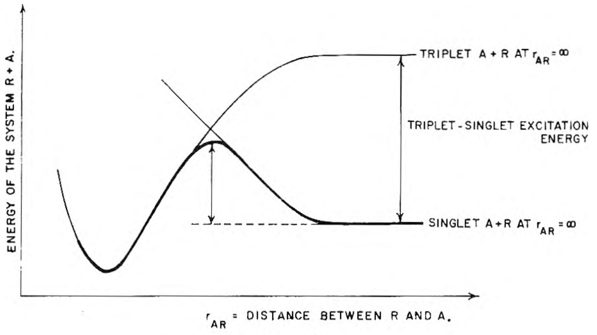

Fig. 6.

of E_{act}, *i.e.*, if we assume a constant entropy of activation for a whole series of reactions involving diferent aromatic hydrocarbons but the same radical, then we may conclude that logarithms of the rate constants of addition are linearly correlated to the excitation energy, *i.e.*, in the present approach to the localization energy. This is exactly the relation discussed in the first part of this paper, and verified by experiment.

The treatment discussed above can be generalized. One may assume different excitation processes leading to species which attract the radical. For example, the non-excited molecule of an aromatic hydrocarbon is diamagnetic, all its electrons being coupled and none are available for the formation of a new bond. On the other hand, the molecule excited to its triplet state contains two uncoupled electrons, and therefore it is able to attract a radical. Figure 6 can be reinterpreted therefore, by assuming that the attraction curve represents the interaction between the radical and the molecule of an aromatic hydrocarbon in its triplet state, while the repulsion curve represents the interaction between the same radical and the molecule in its ground singlet state. Hence, one expects a linear relation between logarithms of methyl affinities and singlet-triplet excitation energy, and Fig. 7 shows that such a relation does indeed exist.

In the approach, represented by Fig. 6, the transition state is determined by the initial state, and

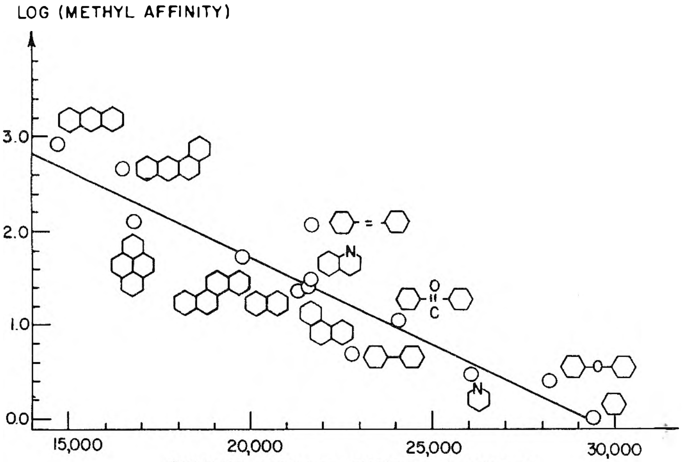

Fig. 7.—Observed triplet-singlet excitation energy in cm.$^{-1}$.

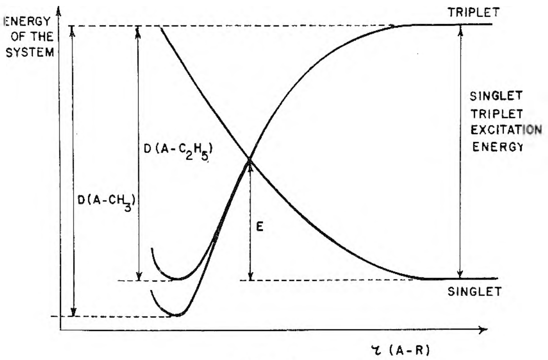

Fig. 8.

the depth of the attraction curve representing the final state is of no importance if the assumptions mentioned before are correct. There may be some justification in believing that the strength of a bond formed affects only a little the activation energy of the addition process. Undoubtedly, the new C–C bonds formed have different strengths if the radical is attracted, say, to benzene or to anthracene. Nevertheless, the linear relations discussed above do hold, confirming the belief that the strength of the newly formed C–C bond is relatively unimportant. An interesting corroborative evidence, supporting this view, has been obtained in studies of ethyl affinities[12] (see Fig. 8). Judging from the log-log relation (see Fig. 4), the intrinsic reactivities of methyl and ethyl radicals are the same. Hence, if we denote by k_2 the rate constant of addition of methyl radical to an aromatic hydrocarbon and by k_4 the corresponding rate constant of addition of ethyl radical, we expect $k_2 \simeq k_4$. What is determined in experiments is the ratio k_2/k_1 or k_4/k_3, where k_1 is the rate constant of hydrogen abstraction from a solvent by methyl radicals, and k_3 is the corresponding rate constant of the reaction involving ethyl radicals. Now, Table III lists the experimental data obtained for k_2/k_1 and k_4/k_3, and on inspection shows that k_4/k_3 is approximately eleven times greater than the respective k_2/k_1. It appears, therefore, that it is k_1 which is approximately eleven times greater than k_3. In reactions 1 and 3 a C–H bond is ruptured on account of a new C–H bond which is formed, and it is a CH_3–H bond which is formed in reaction 1 and a C_2H_5–H bond which is formed in reaction 3. Since $D(CH_3\text{–}H)$ = 101 kcal./mole, while $D(C_2H_5\text{–}H)$ = 98 kcal./mole, reaction 1 is about 3 kcal./mole more exothermic than reaction 3. In view of the symmetrical character of these reactions, in both a C–H bond is ruptured and a C–H bond is formed, one expects only one-half of the difference in the exothermicity to appear as the difference of activation energies.[13] Hence

$$k_1/k_3 \approx \exp(1.5/RT) \approx 12$$

which value fits well the experimental findings.

Let us now summarize these results. In the hydrogen abstraction reaction the driving force of the process comes from the energy of the C–H bond which is formed in the reaction. Hence, the strength of this bond affects directly the activation energy of the abstraction. On the other hand, in the case of addition the activation energy is determined by the energy of excitation and, therefore, the strength of the newly formed bond is of a minor importance. However, if the strength of the newly formed bond changes considerably, this will affect the rate of the addition reaction. For example, the addition of radicals to ethylene, styrene and 1,1-diphenylethylene is mainly affected by the difference in the strength of the formed bonds, or using alternative expression, by the stability of the new radicals formed in the process.

TABLE III

Compound	k_4/k_3	Ethyl affinity	k_2/k_1	Methyl affinity
Benzene	2.9	1	0.29	1
Biphenyl	11.0 ± 0.4	3.8	1.5	5.2
Naphthalene	100 ± 3	34.5	8.7	30
Phenanthrene	124 ± 3	43	10.7	37
Quinoline	182 ± 2	63	13.4	46
trans-Stilbene	1440 ± 40	496	109	376
Benzophenone	50 ± 1	17	4.2	14.5
Vinyl acetate	214 ± 3	74	37	130

Let us consider now, the factors affecting the repulsion curve. As was said earlier, the repulsion results from the coulombic forces acting between the two negative clouds, *i.e.*, the π-electron cloud of the aromatic or olefinic molecule and the p electron cloud of the radical. A decrease in the charge density of these clouds would mean, therefore, a flatter repulsion curve (see Fig. 9) and this in turn means a lower activation energy of the addition process, *i.e.*, a higher reactivity of the aromatic or olefinic compound.

The experiments seem to confirm these predictions. The electron withdrawing groups seem to increase the reactivity of the olefinic or aromatic compound. For example, while the methyl affinity of ethylene is about 80, the methyl affinity of tetrafluoroethylene is about 800.[14] The same results are

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[12] J. Smid and M. Szwarc, *J. Am. Chem. Soc.*, **78**, 3322 (1956).

[13] A. F. Trotman-Dickenson, *Disc. Faraday Soc.*, **10**, 111 (1951).

[14] R. P. Buckley and M. Szwarc, *J. Am. Chem. Soc.*, **78**, 5696 (1956).

observed when one compares the methyl affinities of quinone and chloroquinone,[3] naphthoquinone and 2-chloronaphthoquinone,[3] maleic anhydride and chloromaleic anhydride[15] and so forth. On the other hand, the electron donating groups seem to decrease the reactivity, compare, *e.g.*, methyl affinities of toluquinone and methoxyquinone.[3]

At this stage it is necessary to remark that steric hindrance is also a factor determining the reactivity. Blocking of "reactive points" decreases the reactivity. This effect is seen when one compares the reactivities of styrene, the diphenyl ethylenes, triphenyl ethylene, and tetraphenyl ethylene.[5] The steric effect is even more dramatically manifested in the series of chlorinated derivatives. Whereas one chlorine activates the double bond of a quinone, and the activation is even greater when each of the double bonds contains chlorine (*e.g.*, 2,5- or 2,6-dichloroquinones), the tetrachloroquinone is unreactive.[3] The same observations hold in other series. For example, vinyl chloride is more reactive than ethylene, vinylidene chloride is even more reactive, but tetrachloroethylene is unreactive. That this phenomenon is due to steric hindrance is shown well when one compares the very high methyl affinity of tetrafluoroethylene (a small substituent) with the low reactivity of tetrachloroethylene (a large substituent).

Finally, let us consider how the changes in the slope of the repulsion curve affect the intrinsic reactivity of the radical. Inspection of Fig. 9 shows that for a flatter repulsion curve the coefficient α in the relation $\Delta E_{act} = \alpha \Delta E_{ex}$ is lower. Since the reciprocal of α measures the intrinsic reactivity of a radical, this means that a flatter repulsion curve corresponds to a higher intrinsic reactivity.

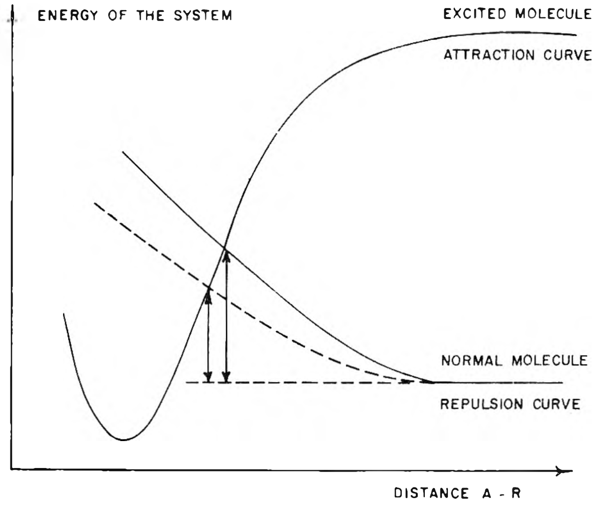

Fig. 9.

In conclusion, it is hoped that the studies of methyl affinities and of similar reactions will be helpful in understanding of factors influencing the rates of radical addition processes.

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[15] Unpublished data of Leavitt from our laboratories.

ELECTRON DEFICIENT COMPOUNDS[1,2]

BY R. E. RUNDLE

Contribution No. 478 from the Department of Chemistry and Institute for Atomic Research, Iowa State College, Ames, Iowa

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There are a number of compounds for which the number of chemical bonds exceeds the number of valence electron pairs, presenting a serious problem for classical valence theory. Historically, the boron hydrides provided the first example, but the problem is general to chemistry. Indeed, the first "electron deficient compound" to be given adequate structural study was the tetramethylplatinum tetramer, in which a quarter of the methyl groups are bonded equally to three platinums. The "cause" of electron deficient bonding is easily stated. When atoms, inevitably metallic, with fewer valence electrons than low energy bonding orbitals, form compounds with atoms or groups containing no unshared electron pairs, bonding is delocalized to make use of all of the low energy metallic orbitals. This arises from the same quantum mechanical principles that lead to chemical bonding, and has perhaps been best treated for the H_3^+ ion, which serves as a prototype for electron deficient compounds. It has been possible to predict where new electron deficient compounds are to be sought, but understanding of structure and compositions, both in the boron hydrides and generally, has come from structural work. The geometry of methyl bridges is singled out for special discussion. Delocalization of bonding arising from "excess" orbitals, always from metal atoms, provides an interesting correlation running from organic compounds, through organometallic compounds and interstitial compounds, to metals themselves, delocalization increasing with fraction of "excess" orbitals. Certain special features of the generalization giving rise to weak metal–metal bonds in dsp^2-square transition metal complexes will be noted. One might term this latter bonding "configuration interaction bonding."

Introduction

The formulation of the electron pair bond[3] and the discovery of the boron hydrides[4] occurred almost simultaneously, so that some of the first attempts to write bond structures for B_2H_6 were uninhibited by ideas of what a bond was. The correct geometry was, thereby, included in the many early proposals.[5] But it soon became evident that the boron hydrides presented a difficult problem for the electron pair theory of valence, since in these compounds the number of bonds is required to exceed the number of valence electron pairs, hence the term "electron deficient compounds."

Though there are some who still write as though boron hydrides were unique in this excess of bonds to electron pairs, the electron deficient bonding problem was extended to the rest of the third group elements by the discovery that trimethylalu-

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[1] Work was performed in the Ames Laboratory of the Atomic Energy Commission.

[2] Presented at the Symposium on Valence and Chemical Bonding, Madison, Wisconsin, June 22, 1956.

[3] G. N. Lewis, *J. Am. Chem. Soc.*, **38**, 762 (1916).

[4] A. Stock and K. Friederici, *Ber.*, **46**, 1959 (1913).

[5] W. Dilthey, *Z. angew. Chem.*, **34**, 596 (1921).

minum was a dimer.[6] The problem was further extended to chemistry generally when tetramethylplatinum was found to be a tetramer.[7]

It would be unfair to review the work of early theorists in the field of the boron hydrides. They were misled by wrong structures "determined" by over optimistic experimenters. Nor would it be fair to review the work of early experimenters who were misled by theorists into believing they could determine n parameters from $n - m$ pieces of data if they applied a little theory to reduce the number of parameters. Experiment and theory thereby confirmed each other and, with all problems apparently solved, progress in the field ceased until a reevaluation was initiated many years later.[8]

One historical footnote might be added, however. The field of electron deficient compounds is one to make the chemical theorists blush. For the most part they followed the experimentalist, reconciling whatever the experimentalist found or thought he found with theory. Nevertheless, theory was sufficiently developed that it could have led instead of following. It was suggested that B_2H_6 should be similar to isoelectronic ethylene.[9] Group theoretical arguments strongly reinforce this suggestion, since a B_2H_6 molecule with ethane-symmetry (D_{3h} or D_{3d}) should almost surely have a triplet ground state, while with ethylene-symmetry (D_{2h}) it should have a singlet ground state as observed. This argument was, indeed, made early enough to have changed the history of the boron hydrides,[10] but was so well qualified as to be considered less significant than doubtful experimental data. Some theorists were overly cautious and some experimentalists undercautious during a critical period for this subject.

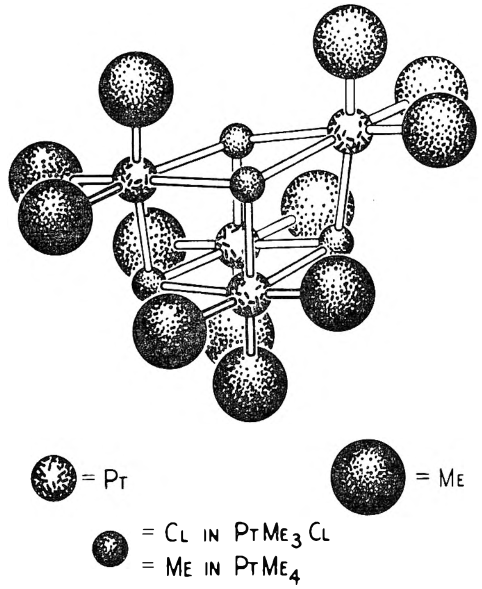

Fig. 1.—Structure of tetramers of tetramethylplatinum and trimethylplatinum chloride.

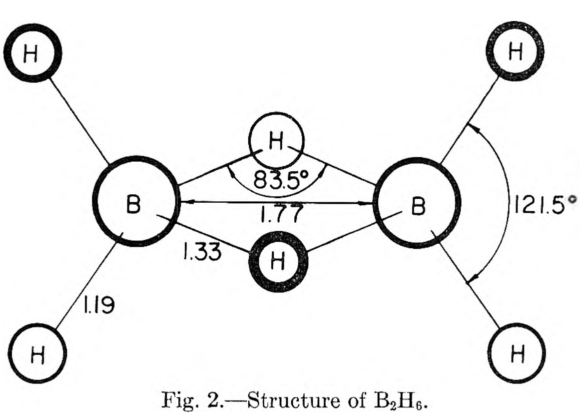

Fig. 2.—Structure of B_2H_6.

The first electron deficient compound whose structure was surely known was the tetramethylplatinum tetramer (Fig. 1),[7] though some shrewd examinations of spectral and other data made the bridge structure for B_2H_6 (Fig. 2) seem probable.[11] This model for B_2H_6 was finally established in 1948 by W. C. Price by an infrared study,[12] but bond angles and distances were not obtained by the much maligned electron diffraction method until 1951.[13]

Bond Delocalization

Cause and Consequences.—The structure of tetramethylplatinum, in which a single methyl group is bonded equally to three platinum atoms, does violence to the time-honored tetravalence of carbon. Another look at the structure reveals, however, the familiar octahedral configuration about platinum(IV), and this feature suggests the principle (below) which leads to electron deficient, or better, delocalized bonding.

For example, the common feature of B_2H_6, the trimethylaluminum dimer and the tetramethylplatinum tetramer is *an atom* (usually metallic) *with more low energy orbitals than valence electrons combined with atoms or groups containing no unshared electron pairs*, *i.e.*, four sp^3-orbital *vs.* three valence electrons for boron and aluminum, six d^2sp^3-orbitals *vs.* four valence electrons for platinum (IV). It appears that under these circumstances *delocalization of bonding occurs so as to use all of the low energy bonding orbitals of the metallic atom.*[14]

Such a generalization is easily justified by quantum arguments.[14b]

The valence bond approach had already been given by Hirschfelder, Rosen and Eyring in considering H_3^+,[15] where one electron pair serves to bond three atoms together very strongly. H_3^+ serves as a prototype for electron deficient bonding, just as H_2 furnishes a model of the electron pair bond, both valence bond and molecular orbital approaches

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[6] A. W. Laubengayer and W. F. Gilliam, *J. Am. Chem. Soc.*, **63**, 477 (1941). Earlier work, indicative of dimers, is referred to in the above article.

[7] R. E. Rundle and J. H. Sturdivant, *ibid.*, **69**, 1561 (1947).

[8] B. V. Nekrasov, *J. Gen. Chem.* (*U.R.S.S.*), **10**, 1021, 1156 (1940).

[9] E. Wiberg, *Ber.*, **69**, 2821 (1936). Also reviews all other suggestions very completely.

[10] R. S. Mulliken, *Phys. Rev.*, **43**, 765 (1933).

[11] Ref. 8. See also (a) Y. K. Syrkin and M. E. Dyatkina, *Acta Physicochim.* (*U.R.S.S.*), **14**, 547 (1941); *Compt. rend. acad. sci.* (*U.R.S.S.*), **35**, 180 (1942); (b) H. C. Longuet-Higgins and R. P. Bell, *J. Chem. Soc.*, 250 (1943); (c) K. S. Pitzer, *J. Am. Chem. Soc.*, **67**, 1126 (1945).

[12] W. C. Price, *J. Chem. Phys.*, **16**, 894 (1948).

[13] K. Hedberg and V. Schomaker, *J. Am. Chem. Soc.*, **73**, 1482 (1951).

[14] (a) R. E. Rundle, *ibid.*, **69**, 1327 (1947); (b) *J. Chem. Phys.*, **17**, 671 (1949).

[15] J. O. Hirschfelder, *ibid.*, **6**, 795 (1938), and earlier papers.

leading to qualitatively similar delocalized bonds for reasons that are quite like the reasons which lead to the electron pair bond, *i.e.*, the main energy terms are coulombic, but the electron pair has a lower kinetic energy the larger the volume it "occupies," finding a more stable orbital the more it is delocalized, provided, of course, that suitably low energy orbitals are available to it.

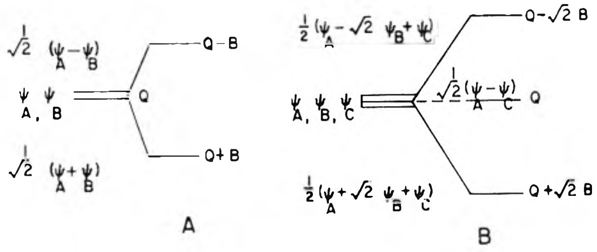
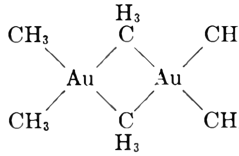


Fig. 3.—Simple M.O. correlation diagram for two-center and three-center bonds. Here A, B and C are similar atom arranged linearly, overlap neglected.

The results of a very simple molecular orbital treatment are illustrated in Fig. 3. Two like atoms, each with an orbital, can form by linear combination two molecular orbitals, one of lower (bonding) and one of higher (antibonding) energy than either of the originals. If there is *only one electron pair* it will occupy the lowest orbital possible, which is a bonding orbital. Similarly, if there are three atoms each with an orbital they may combine to form bonding, non-bonding and antibonding orbitals as shown in Fig. 3b, and again if there is *only one electron pair*, it will occupy the lowest orbital possible, which is a bonding orbital. In the illustration above there is a three-center bond. Clearly a four-center bond is necessary in tetramethylplatinum, where one electron pair serves to bind a methyl group to three platinums, and even higher delocalizations are possible.

The prediction of the occurrence of other electron deficient compounds arises simply from the principle above. These will be mainly among metallic hydrides and organometallic compounds, the stabilities of which leave much to be desired as far as the experimental determination of structures is concerned. It was, none-the-less, predicted and found that dimethylberyllium is a polymer in which beryllium, with four low energy orbitals but only two valence electrons, is tetrahedrally bonded to methyls (Fig. 4),[16] and many hydrides have properties consistent with the above principle. Likewise, in trimethylgold, gold should form four bonds in a plane to methyl. The structure should probably be



$$(CH_3)_2Au(\mu\text{-}CH_3)_2Au(CH_3)_2$$

The principle also permits one to note a hitherto unrecognized unity in chemistry. Delocalization of bonding increases with the ratio of low energy bond orbitals to valence electron pairs in a continuous way. Since "excess" orbitals are introduced by metals, delocalization increases in going from organic compounds, through organometallic compounds, through interstitial compounds, to metals themselves, where bond delocalization has proceeded so far that the concept of the localized bond is of little use. Indeed, the principle has made it possible to note the very interesting point that interstitial compounds of carbon and nitrogen occur only with metals having unfilled d-subshells, and the resulting structures seem to be dictated by the efficient use of the d-shell in bonding to carbon and nitrogen, and not by the original structure of the metal.[17] Thus these compounds are not strictly "interstitial."

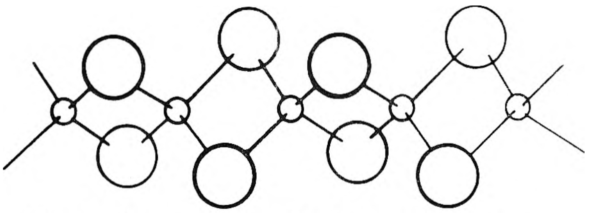


Fig. 4.—Structure of the dimethylberyllium polymer.

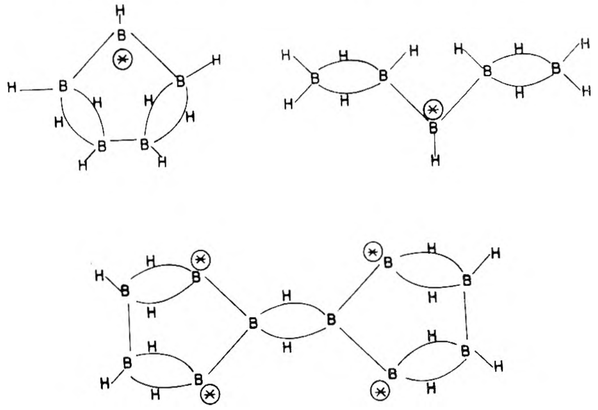


Fig. 5.—Proposed protonated double bond structures for boron hydrides. Note, starred borons do not use all low energy orbitals.

Recently, some of those who were important in causing the re-examination of the B_2H_6 structure have written as though the recognition of the bridge bond in B_2H_6 established the above principle.[18] That this is not so is clearly illustrated in the structures written for the higher boron hydrides by these authors (see, for example, Fig. 5) which did not exploit the principle, but left boron orbitals unused, as has been pointed out.[14b] Nor were any predictions made which would show appreciation of the principle.

Recognition of the cause of delocalization of bonds has made it possible to describe known structures in quantum mechanical language,[19] but pre-

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[16] A. I. Snow and R. E. Rundle, *Acta Cryst.*, **4**, 348 (1951).

[17] R. E. Rundle, *ibid.*, **1**, 180 (1948). See also W. Hume-Rothery, *Phil. Mag.*, [7] **44**, 1154 (1953), for some pertinent additions. However, I contend that the original discussion adequately pointed out the necessity of metallic d-orbitals. Indeed this was the major point. That the non-metal could *also* use octahedral holes efficiently seemed less conventional and perhaps undue space was given to it. Also an "interstitial" theory which allows M–M changes of even 0.2 Å. still does not appeal to me. I admit it has appealed to others.

[18] See for example, K. S. Pitzer, "Quantum Chemistry," Prentice-Hall, Inc., New York, N. Y., 1953, pp. 191–194. Compare with 14(b) and also with 11(c).

[19] For illuminating descriptions of the boron hydrides, see W. H. Eberhardt, B. Crawford and W. N. Lipscomb, *J. Chem. Phys.*, **22**, 989 (1954).

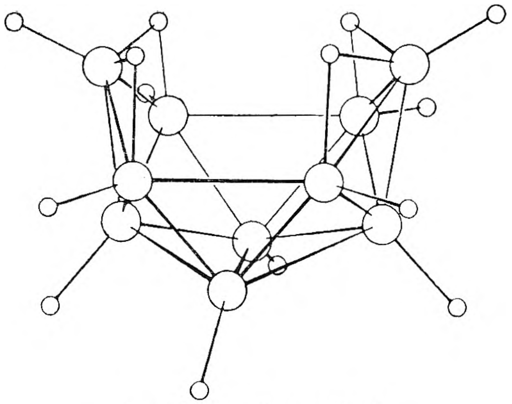

Fig. 6.—Structure of $B_{10}H_{14}$.

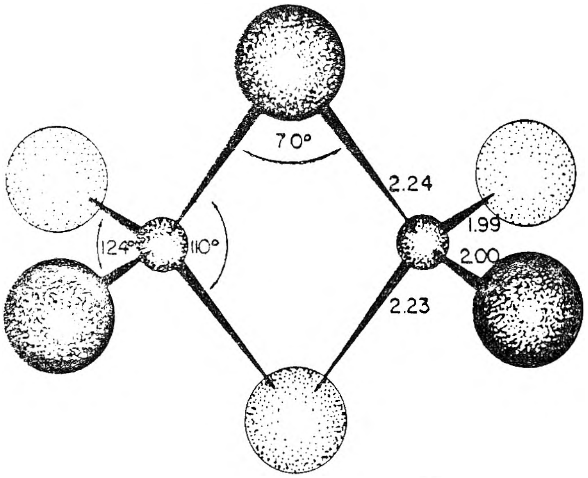

Fig. 7.—Structure of the trimethylaluminum dimer.

diction of structure would require a more quantitative treatment of the problem to find the structure of lowest energy, a nearly impossible undertaking. Consequently, structure prediction has been based on analogy, and has been successful only when the analog was close. The structures of electron deficient compounds have often been most unusual, as the structure of the boron hydrides,[20] particularly $B_{10}H_{14}$ (Fig. 6),[21] well illustrates. Since in this symposium the boron hydrides are dealt with elsewhere, I shall illustrate some of the peculiarities of methyl bridge bonds.

Methyl Bridges.—As shown in Fig. 7, $\angle$Be-C-Be in dimethylberyllium is only 66°, while $\angle$C-Be-C is, then, greater than tetrahedral. The corresponding angles in the trimethylaluminum dimer are 70° and 110° (Fig. 7).[22] Before there was any real understanding of the nature of the bonding, such sharp-angled models were eliminated from consideration in an electron diffraction study as completely unreasonable.[23] Now it seems reasonable to assume the sharp angle is due to the attempt of two metal orbitals to overlap efficiently with the one tetrahedral orbital of the bridge methyl (Fig. 8a). It is then seen that this causes too close a crowding together of the metal atoms if the metal atoms are large, as in trimethylaluminum, suggesting why it is that trimethyl compounds of the higher third group metals dimerize less readily than trimethylaluminum. It appears that though trimethylgallium forms an unstable dimer,[24] trimethylindium cannot form a dimer at all. There is still a tendency for indium to use all four sp^3-orbitals in bonding, since we have found that it is a tetramer in the crystal with the structure shown in Fig. 9.[25] Clearly, delocalization still oc-

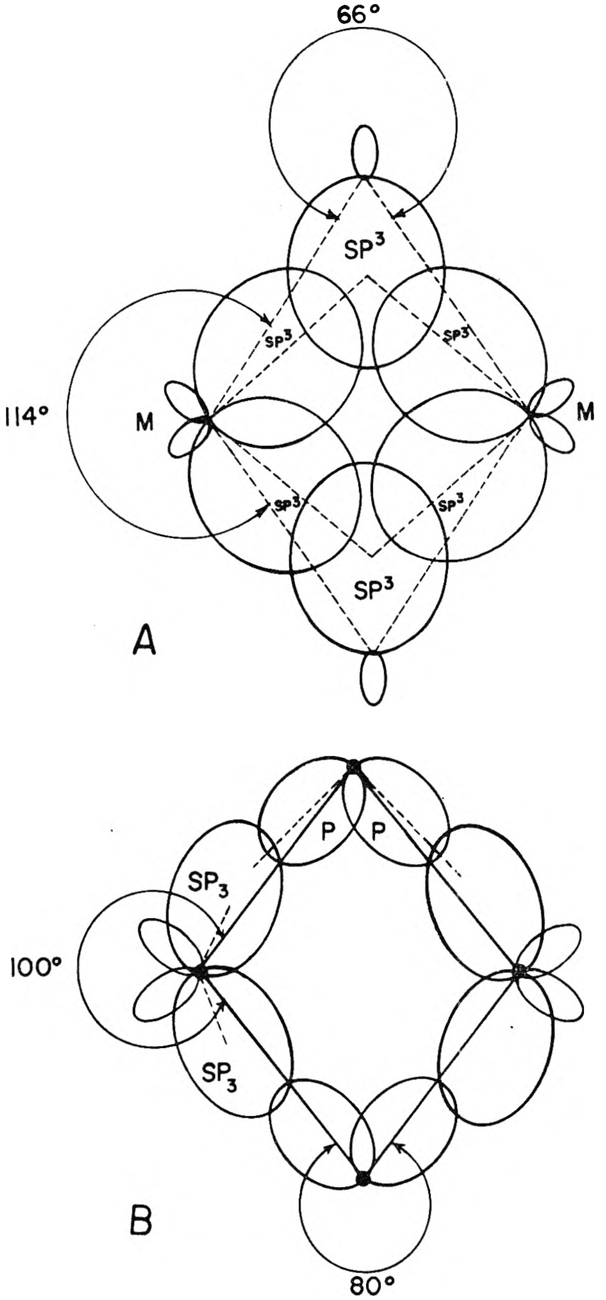

Fig. 8.—Schematic representations of interactions of atomic orbitals in methyl and halogen bridges. Note that in (a), metals crowd together to use single tetrahedral orbital of methyl, while in (b), metal angle tends to be less than tetrahedral to overlap two p orbitals of halogen.

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[20] See the review by W. N. Lipscomb, *J. Chem. Phys.*, **22**, 985 (1954).

[21] J. S. Kasper, C. M. Lucht and D. Harker, *Acta Cryst.*, **3**, 436 (1950).

[22] P. H. Lewis and R. E. Rundle, *J. Chem. Phys.*, **21**, 986 (1953).

[23] L. O. Brockway and N. Davidson, *J. Am. Chem. Soc.*, **63**, 3287 (1941).

[24] L. M. Dennis and W. Patnode, *ibid.*, **54**, 182 (1932); Dennis, Work, Rochow and Chamot, *ibid.*, **56**, 1047 (1934).

[25] R. E. Rundle and E. Amma, to be published.

curs but a new geometry for delocalization is necessary so as to avoid strong metal–metal repulsions.

No one correctly predicted the geometry of methyl bridges, though some attempts were made.[14,26a] Now that the geometry is known, however, the lower stability of the dimer for the higher and branched trialkylaluminum compounds can be understood as a purely steric effect arising from the new sharp bridge angle.[22] More complex explanations have been given by Coates[26b] and others[26a] but do not take explicit account of the geometry of the molecules.

Halogen Bridges.—Halogen bridges usually occur where methyl bridges do, *e.g.*, trimethylplatinum chloride is a tetramer with chlorine in the bridge position,[7] the trihalides of aluminum are dimers[27] and beryllium chloride is a chain polymer.[28] They are not, however, electronically similar, and should not be considered to be electron deficient bridges, as the bond angles and distances show (Fig. 10). Thus ∠C–Be–C is 114°, greater than tetrahedral, but ∠Cl–Be–Cl is only 100°, less than tetrahedral, and the C–Be distance is greater than the sum of the covalent radii, while the Be–Cl distance is equal to it. The halide angles seem explicable if the halogen uses two p-orbitals (at 90°) and one of its usually unshared pairs in the bonding, so that all bonds in the bridge are electron-pair bonds. There would then need to be a compromise between the tendency for a tetrahedral angle of the metal and the right angle tendency of the bridge halogen, leading to the lower than tetrahedral angle for the metal *vs.* the larger than tetrahedral angle for the metal in the methyl compound (Fig. 8).

It is to be noted that because of the larger bridge angles in the halides, metal–metal repulsions would not keep the trihalides of gallium, indium, etc., from dimerizing. It is, then, noteworthy that the trihalides of indium are dimers in the vapor.[29]

Metal Bonds in Planar Complexes.—A different application of the principle, that surplus low energy orbitals give rise to bond delocalization, has been found in the case of square planar complexes. According to the directed theory of valence dsp^2 hybrid orbitals are used by the metal in such cases, and except for planar copper complexes there is a vacant p-orbital in the valence shell.[30] It has been found that the square planar complexes of Ni(II), Pd(II), Pt(II),[31] and Au(III)[32] have a tendency to use this surplus p-orbital in forming bonds. Weak metal bonding causes Ni(II) and Cu(II) complexes to pack differently, *e.g.*, in their complexes with dimethylglyoxime, the nickel compound packs so as to form a metal chain, while the copper compound does not. The metal bonding causes the nickel compound, whose molecular geometry is nearly identical with the copper compound, to be about a millionth as soluble.

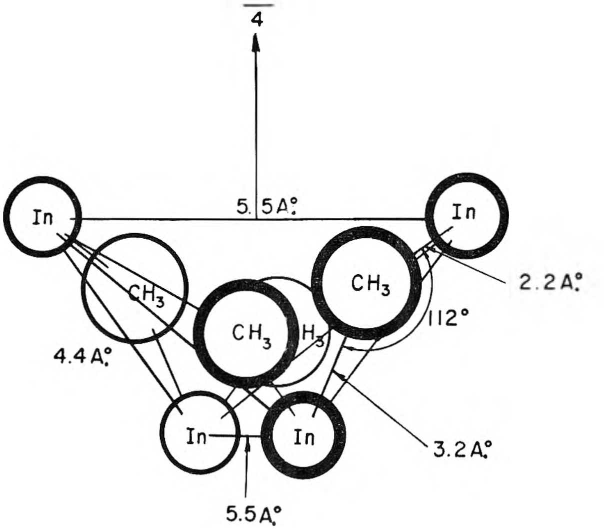

Fig. 9.—Structure of trimethylindium tetramer. Indium and bridging methyl groups are shown. External methyl positions are not yet certain.

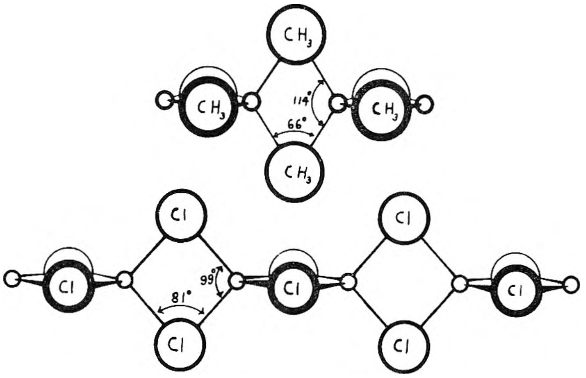

Fig. 10.—Bridge-bond angles and distances in $BeCl_2$ and dimethylberyllium.

Originally it was proposed that metal–metal bonding arose from a partial promotion of an inner 3d-electron to the vacant 4p-orbital, allowing a small contribution of d^2sp^3 octahedral bonding to the ground electronic state.[31a] This still seems to be an appropriate description. It was proposed further, that copper(II) was unable to form such bonds because of the extra electron, which was presumed to occupy the 4p-orbital. Recently, however, it has been shown that the odd-electron in Cu(II) complexes does not occupy a 4p-orbital, but, instead, occupies an antibonding orbital which should not interfere with metal-metal bond formation.[33] Consequently the weak metal–metal bonds in these complexes are here redescribed in molecular orbital terms, which appear to be more appropriate in this case.

In Fig. 11 is shown a molecular orbital correlation diagram for square planar complexes. The energy levels are probably correctly ordered relative to

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[26] (a) K. Pitzer and H. S. Gutowsky, *J. Am. Chem. Soc.*, **68**, 2209 (1946); (b) G. E. Coates and F. Glockling, *J. Chem. Soc.*, 22 (1954).

[27] K. Palmer and N. Elliot, *J. Am. Chem. Soc.*, **60**, 1852 (1938).

[28] R. E. Rundle and P. H. Lewis, *J. Chem. Phys.*, 20, 132 (1952).

[29] D. P. Stevenson and V. Schomaker, *J. Am. Chem. Soc.*, **64**, 2514 (1942).

[30] L. Pauling, "Nature of the Chemical Bond," 2nd Ed., Cornell Univ. Press, Ithaca, N. Y., 1945, p. 98.

[31] (a) L. E. Godycki and R. E. Rundle, *Acta Cryst.*, **6**, 487 (1953); (b) S. Yamada, *Bull. Chem. Soc. Japan*, **24**, 125 (1951).

[32] R. E. Rundle, *J. Am. Chem. Soc.*, **76**, 3101 (1954).

[33] (a) B. R. McGarvey, THIS JOURNAL, **60**, 71 (1956); (b) R. E. Rundle, "Proton Positions and Antiferromagnetic Ordering in $CuCl_2 \cdot 2H_2O$," 129th National A.C.S. Meeting, Dallas, April, 1956; (c) R. E. Rundle and J. W. Richardson, "The Electronic Structure of Square Copper Complexes," 129th National A.C.S. Meeting, Dallas, April, 1956.

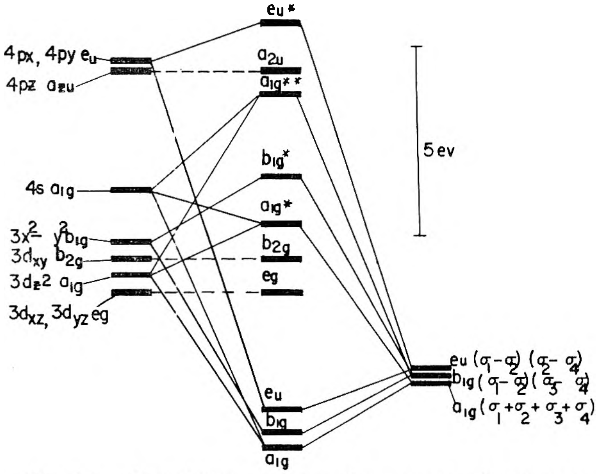

Fig. 11.—Correlation diagram for square planar complexes. In the above, e orbitals are doubly degenerate. In Ni(II), Pd(II), Pt(II) and Au(III) complexes, sixteen electrons fill all orbitals up through a_{1g}^*, while in Cu(III) complexes one electron occupies b_{1g}^*.

each other, but otherwise the scheme is meant to be only qualitative.[33c] In Ni(II), Pd(II), Pt(II) and Au(III), 16 electrons are placed in the lowest eight molecular orbitals. The lowest four are bonding orbitals, mixtures of ligand and metal orbitals, and closely parallel the directed theory of valence in that the metal orbital uses principally one d-, an s- and two p-orbitals in bonding. The next four orbitals are nearly pure metal d-orbitals.[34]

The chief difference from the directed theory of valence scheme comes in the higher energy orbitals. Thus, the odd electron in Cu(II) complexes occupies b_{1g}^*, an anti-bonding linear combination of $d_{x^2-y^2}$ of the metal with the b_{1g}, $(\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4)$, combination of the ligand σ-orbitals. The a_{1g}^* orbital is mainly d_{z^2} of the metal, and a_{2u} is a pure p-orbital of the metal. When two neighboring metal atoms approach along z, these latter two orbitals will interact with the corresponding orbitals of the neighboring metals so as to give somewhat bonding and antibonding a_{1g}^* and a_{2u} combinations, while in a linear array, as in nickel dimethylglyoxime,[29a] bands will be formed. The situation is now favorable for configuration interaction, effectively partially promoting electrons from the antibonding a_{1g}^* level to the bonding a_{2u} level. That is, the diagram in Fig. 11 with 16 electrons in the lowest levels shown there does not accurately represent the system, but it will be found that what are shown as higher states make some contribution to the ground level of the molecule. This "configuration interaction" can arise as long as the over-all state for the molecule keeps the same symmetry, in this case, A_{1g}, and generally it occurs to lower electron repulsion which is not adequately taken care of in simple treatments. Here it is enhanced by contributing some bonding as well.

Thus, in essence, d-electrons are promoted to outer p-orbitals as in the directed valence description of this interaction. The difference is that an odd-electron is not in 4p (a_{2u}) but in b_{1g}^*, of the Cu(II)-complexes, and will no longer interfere with metallic bonding. It seems not unreasonable to suppose, however, that in Cu(II) complexes, with a higher nuclear charge on the metal, the 4p- and 3d-orbitals are pulled in enough to lower overlap and enhanced configuration interaction as compared with Ni(II).

At any rate, even in this weaker type of "configuration interaction bonding" the extra metal p-orbital is responsible for the interaction whether it is viewed from the hybrid orbital theory of directed valence or by the molecular orbital viewpoint.

It has been noted by Mr. Lawrence Dahl at Ames that when the outer p-orbital of the metal forms part of a π-system of bonds, as in the metal–acetylacetone complexes, the metal no longer forms weak metal–metal bonds by this process. In this case palladium and copper acetylacetonates are isomorphous. Presumably the π-bonding utilizes the outer p-orbital sufficiently that metal–metal bonding is no longer profitable, much as hyper conjugation (partial double-bonding) uses the extra p-orbital in trimethylboron, so that, unlike trimethylaluminum, trimethylboron remains a monomer.[35]

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[34] π-bonding has been ignored here. For its influence see ref. 33c.

[35] R. S. Mulliken, *Chem. Revs.*, **41**, 207 (1947).

BONDING INFERENCES FROM NUCLEAR SPIN RESONANCE[1]

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Nuclei of non-zero spin take up discrete orientations in a magnetic field, and transitions between the spin energy levels occur as a resonant process with radiation in the radiofrequency region. The frequency of resonant absorption to a first approximation depends solely upon the nuclear species. More accurately, it may be modified by a number of effects. Besides resonant frequency, the absorption line amplitude and width may yield important information about the interactions of a nucleus with its atomic environment. Local magnetic fields due to other nuclei in a rigid solid may broaden or split a line. Paramagnetic ions may cause both a broadening and a shift. Shielding of the nucleus by outer electrons displaces a line and may give rise to a multiple-line spectrum if identical but chemically non-equivalent nuclei exist in the same molecule. The transmission of nuclear polarization effects through an electron-pair bond may lead to observable multiplicity. Rapid chemical exchange of non-equivalent nuclei leads to a single line intermediate between the positions of the separated lines. Solvent interactions—especially hydrogen bonding—may cause major shifts. Hydration of an ion may alter its resonance absorption line characteristics to a marked degree. When a nucleus possesses a quadrupole moment, the absorption line amplitude and width are very sensitive to electric field gradients arising from anisotropic interactions such as ion-pair or complex formation. Even sodium ion shows a marked sensitivity to its environment. Examples of such interactions are given for both inorganic and organic systems.

Ten years ago he would have been a bold man who predicted that in this interval radiofrequency spectroscopy would have become a strong fascination for an appreciable number of chemists, or that its results would be considered significant in a symposium on chemical bonding. This technique allows a fairly direct observation of molecular interactions orders of magnitude different in intensity, and has led to better understanding of old problems in addition to uncovering new phenomena. It is hardly conceivable that there is now a practicing chemist or physicist who has not heard of the term "nuclear resonance." Since there are other processes which are properly described by this title, the term "Nuclear Spin Resonance" or NSR will here be used to designate the study of the resonant exchange of radiofrequency radiant energy when nuclei of non-zero spin are located in a magnetic field of the appropriate intensity. The designation is thus naturally similar to that of its companion field in microwave spectroscopy for which many physicists have adopted the term "Electron Spin Resonance."

Those nuclei which have net angular momentum $\sqrt{I(I+1)}h/2\pi$ are characterized by their "spin" I, which for elements of odd atomic number will be half-integral, while for those of even number it will be integral. The number of isotopes with $I \neq 0$ exceeds 135, including a number which are radioactive. The property of uncompensated nuclear spin angular momentum is invariably accompanied by weak magnetism, characterized by the magnetic moment μ. The constant of proportionality γ which multiplies the maximum possible component of angular momentum in a fixed direction, $Ih/2\pi$, to give the magnetic moment μ, will be referred to as the magnetogyric ratio. Although it has not been possible to calculate values of γ theoretically, these have been determined for many nuclei with high precision. In the absence of a magnetic field the $2I + 1$ nuclear spin energy levels are coincident. Upon application of a field of magnitude H, these levels are separated uniformly by an amount $(\mu/I)H$. The lowest state will correspond most closely to the condition of alignment "with" the field, while the uppermost one will be most nearly "opposed" to the field. To conduct a resonance absorption experiment, one applies a radiofrequency field component which rotates in the appropriate sense about the axis of the stationary field. The nuclei may absorb energy from the rf. field if the frequency ν is such as to satisfy the condition

$$h\nu = \frac{\mu}{I}H^*$$

This may be rewritten in the form

$$\omega = 2\pi\nu = \gamma H^* \tag{1}$$

The symbol H^* is here used to emphasize the particular value of magnetic field for which eq. 1 is satisfied.

While absorption or stimulated emission may occur with equal probability, the Boltzmann distribution of nuclei among the various spin levels allows a net excess absorption to occur. Assuming that an appropriate detection system is available, one would keep the magnetic field constant and vary frequency if he were to follow ordinary spectroscopic practice. However, for the nuclear spin system, one may arbitrarily (within wide limits) adjust the spacing of the energy levels by varying the magnetic field. Thus one may make absorption observations at constant frequency and, since the field is the variable, may speak of the line half-width in gauss. While both variable-frequency and variable-field spectrometers are in common use, the latter type is often more convenient. As in other regions, one may record the spectrum continuously or under favorable circumstances, display it as a recurrent trace upon an oscilloscope.

It has been possible to make observations upon nuclei in atoms, ions or molecules in all physical states. To a good approximation the value H^* of the resonant field for a nucleus is independent of its environment or state of combination. However, certain factors to be detailed shortly may alter the characteristic behavior of an absorption line or severely limit the possibility of its detection. Besides the ratio of frequency to resonant field, one may obtain important information about the nuclear environment from amplitude, width and behavior under large radiofrequency fields (saturation effects).

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(1) Some of the research reported here was supported by the Air Force Office of Scientific Research.

It is apparent that no information is directly obtainable from nuclei of zero spin, which includes all the isotopes having both an even atomic number and an even atomic mass. The nuclei of non-zero spin can conveniently be subdivided into those of spin $^1/_2$ and those of greater spin. The former group can have no nuclear quadrupole moment, while the latter may have moments ranging from about 5×10^{-4} to about 10 units of $e \times 10^{-24}$ cm.[2]. Some of the important nuclei of spin $^1/_2$ are H^1, C^{13}, N^{15}, F^{19} and P^{31}. The possession of a nuclear quadrupole moment of appreciable magnitude seriously affects the possibility of obtaining information on a nuclear species which is involved in a covalently-bonded group. Such bonds produce very large electric field gradients at the nuclei, and lead to such broadening of the nuclear spin energy levels that one may not be able to detect the corresponding resonance absorption line. In ionic solids, electric field gradients arise from the neighboring ions. The quadrupole interaction shifts the (three or more) energy levels and the separate lines corresponding to the allowed transitions may overlap. The lines are broadened by relaxation effects to be mentioned later. However, if the charge distribution about the nucleus is effectively spherically symmetrical (or has cubic symmetry), the spin energy levels are well-defined and equally spaced. One would hope to observe resonant absorption not only for monatomic ions, but also for those which possess a sufficiently high symmetry. For example, one observes narrow resonance lines for both Cl^- and ClO_4^-, but not for ClO_3^- or other ions of lower symmetry.[1a] The tetrahedral symmetry of oxygen about the chlorine nucleus in the ClO_4^- ion gives a sufficiently isotropic charge distribution. Indeed, the line width for most perchlorate systems is narrower than for chlorides. This point will be discussed later. On the other hand, no absorption has been observed in any compounds in which the binding of chlorine is predominantly covalent.[1a] In ionic solids, minute deviations from perfect spacing greatly broaden absorption lines of ions with nuclear quadrupole moments. The random reorientation of molecules in solution tends to average out intermolecular gradients, but intramolecular gradients remain. One might expect that in solution the line width might be a sensitive measure of slight departures from isotropic charge distribution about an ion. Such broadening has indeed been observed for the aqueous Na^{23} and Cl^{35} ions.

While the width of an absorption line in other branches of spectroscopy is of concern principally because it may limit the resolution of closely-spaced groups, it assumes a central position in NSR work. Where the magnetic field is not uniform over the sample volume the various regions have different resonant field values. We assume here that no such instrumental broadening occurs. To date, gaseous samples have not often been used, and by far the most observations of interest to chemists have been made with liquids, though many solids have been investigated. In solids, the local magnetic fields contributed by neighbors broaden a nuclear spin absorption line. A further interaction arises because two adjacent dipoles of different orientation, both precessing about the applied field with the Larmor frequency, may simultaneously exchange orientations. Obviously, the spin exchange does not alter the energy of the system. Since this process limits the lifetime of the nuclear spin states, uncertainty-principle broadening of the transitions between them may occur. The much larger magnetic moments of paramagnetic ions may be involved in spin exchanges with nuclei, but in this case there is a mechanism whereby the energy of the nuclear spin system can be transferred to the environment. Spin-orbit coupling of the electrons makes this possible. In a non-rigid system, the Brownian motion of particles will lead to fluctuating magnetic fields, which will have a component at the precession frequency of the nuclei and induce transitions. The interaction of the nuclear quadrupole moment with fluctuating electric field gradients provides another means of communicating nuclear spin energy to the environment. This process is indeed a powerful relaxation mechanism where an appreciable quadrupole moment exists.[2-4] The process of nuclear spin energy transfer to the environment is described by a characteristic thermal relaxation time t_1. When t_1 is sufficiently short, the line will have the uncertainty-principle width of about $1/\Delta\omega$, where $\Delta\omega$ is the frequency deviation at half-height of the absorption line.

Converting to field units, we write $t_1 = 1/\gamma \ \Delta H$. The ΔH values range from less than 10^{-4} gauss in the case of protons up to the order of 1 gauss, all for liquid samples. In the proton case, the width in liquids is below the presently-observable limit of resolution, due to magnetic field inhomogeneities. Thus the relaxation time of protons in liquids can be of the order of seconds. The absorption lines become so broad for t_1 values of the order of 10^{-6} second that they escape detection. Values of this magnitude would be expected for the nuclei of paramagnetic ions. Hence NSR absorption for the transition elements has been observed only in covalently-bonded groups (usually of high symmetry), which are diamagnetic.

The chloride ion represents a case in which the line width is uncertainty-principle determined, for minute added amounts of cupric or manganous ions added to NaCl solutions increase the line width.[5] On the other hand, such ions as Cr(III) or Co(II) are so ineffective in shortening the relaxation time of Cl^- that one may easily observe resonant absorption in $CrCl_3$ or $CoCl_2$ solutions. This is interpreted as reflecting the different rates of exchange of bound hydrate water with the solution. For Cr(III) the rate of exchange is so low that it is rare that a chloride ion may form a part of the first coördination shell.[6] Hence the interaction distance is greater on the average than for an ion which ex-

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[1a] NOTE ADDED IN PROOF.—Failure to observe a line refers to the use of a narrow-line spectrometer. W. D. Phillips (private communication) has observed lines up to 15 gauss wide in covalently-bonded chlorine compounds.

[2] N. Bloembergen, "Nuclear Magnetic Relaxation," Martinus Nijhoff, the Hague, 1948, Chap. V.

[3] Y. Ayant, *Compt. rend.*, **238**, 1876 (1954).

[4] R. V. Pound, *Phys. Rev.*, **79**, 685 (1950).

[5] J. E. Wertz, *J. Chem. Phys.*, **24**, 484 (1956).

[6] J. P. Hunt and H. Taube, *ibid.*, **19**, 602 (1951).

changes hydrate water rapidly. Upon addition of a paramagnetic chloride to a NaCl solution, one should expect that at low concentrations the signal amplitude would be increased, owing to the chloride ions added. This is indeed found for such ions as Ti(III), Fe(III), Co(II), Cr(III), Nd(III) and Sm(III). For Cu(II) and Mn(II) this increase would occur at extremely low concentrations, perhaps below those ordinarily found in reagent-grade NaCl. For all of the paramagnetic ions, the Cl^- line width begins to increase at very low concentrations, as expected.

Returning to the ClO_4^- ion, one would expect that if its line width is uncertainty-principle determined, one might expect it to be less than that of Cl^-, if accidental contamination of such ions as Cu (II) or Mn(II) are present. The oxygen shell would limit the minimum distance of approach of a paramagnetic ion.

HCl solutions give a line width which increases with concentration, and this effect was interpreted as indicating the existence of ion pairs at high concentration. Masuda and Kanda have estimated that for their most concentrated solution the line width of 0.3 gauss is 1/20th as wide as would be expected from the known quadrupole coupling constant of HCl.[7] Perhaps one might consider the species at high concentration as a hydrated chloride ion with a water molecule replaced by a hydronium ion. On the basis of concentration-dependence of the proton resonant field value, it appears that concentrated solutions are fully dissociated, but the line width is probably a more sensitive measure.[8] The Raman data also indicate ionic association,[9] though one should probably not speak of "undissociated molecules." A similar concentration dependence of line width is observed for $HClO_4$, where the "undissociated" units are presumably the ion pairs $H_3O^+ClO_4^-$. The symmetrical oxygen shell should assure a small quadrupole coupling constant for the chlorine.

As the interaction between a chloride ion and its environment becomes stronger, the line may be so broad that it is not detected.[1a] This effect is marked in the case of $CdCl_2$, where no Cl^- resonance absorption has been detected.[10] In fact, when a 3 *M* solution of NaCl is made 0.02 *M* in $CdCl_2$, the line amplitude is reduced to about 15% of what it was in the original solution, while the line width is increased by about 70%. One must conclude first that covalently-bonded or strongly interacting chlorine will not be detected by this method since loss of intensity results. Line broadening might occur in two ways. First, neglecting chemical exchange between free and bound chlorine one may assume the interaction of those Cl^- ions detected is fairly weak and the line is slightly broadened. However, if one detects only purely ionic chlorine, one would expect only an amplitude decrease and no change of width if the exchange of free and "complexed" chlorine were negligibly slow. That the width increases linearly with increasing amounts of $CdCl_2$ added to the 3 *M* NaCl solution might then be taken to indicate that a rapid exchange occurs. The number of chlorine nuclei affected is far more than the number instantaneously complexed. The observed width would then be intermediate between the widths for purely ionic and "complexed" chlorine.

For other salts such as $LaCl_3$ one may observe resonant absorption in concentrated solutions of the pure salt, but the amplitude is less than that to be expected, so that formation of complex anion and cation types is indicated. The amplitude goes through a maximum, and the line width which is originally the same as for NaCl, begins to increase rapidly as higher concentrations are approached.

The resonant absorption of the sodium ion is of some interest, and its study was undertaken partially because of its biological interest. Like chlorine, only the sodium which has an essentially isotropic charge distribution is observed.[11] The quadrupole moments of Na^{23} and Cl^{35} are nearly the same. However, having a positive charge, one would expect ordinary contaminations of paramagnetic ions to have very little effect upon sodium ion resonance. The Na^+ line width for NaCl solutions is of the order of 30 milligauss, independent of concentration up to 3 *M*. In solutions of salts which are highly soluble, one may find marked line broadening and intensity decrease at high concentrations. Where the solutions have a high viscosity (such as concentrated NaOH) one would expect a shortened relaxation time and an uncertainty-principle broadening. The total intensity, however, should not be altered. In the concentrated solutions, there is insufficient water for complete hydration of the ions, and one would expect marked ion-pair formation. The asymmetrical charge distribution accompanying incomplete hydration might give rise to so strong an interaction that resonant absorption for these ions might escape detection. At concentrations of about 2 *M*, some of the sodium phosphates show a distinct maximum in line amplitude.

Simple organic anions have little or no effect on sodium NSR absorption. However, anions of acids which have a hydroxy or keto group in the α- or β-positions show marked line broadening and reduction of amplitude. Many of these substances have been found by other methods to show chelation with sodium ion. The method is therefore apparently a sensitive one for the detection of departures from non-ionic bonding in liquid systems.

With few exceptions, the resonant field H^* for a given isotope is a constant, independent of its state of binding, to a few parts in 10^4 or even less for nuclear species. However, with appropriate experimental arrangements, one may detect individual differences in resonant field which serve to communicate information on the environment of the nucleus. Often these "chemical shifts" are in such a direction as to indicate a diamagnetic shielding of the nucleus by the extranuclear electrons. Accompanying this there may be an opposite effect due to a temperature-independent paramagnetic contribution. Then upon comparing H^* for various compounds each of which has the nucleus of

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(7) Y. Masuda and T. Kanda, *J. Phys. Soc. Japan*, **9**, 82 (1954).

(8) H. S. Gutowsky and A. Saika, *J. Chem. Phys.*, **21**, 1688 (1953).

(9) L. Ochs, J. Gueron and M. Magat, *J. Phys. Radium*, **1**, 85 (1940).

(10) J. E. Wertz and J. Buckley, to be published.

(11) J. E. Wertz and O. Jardetzky, *J. Chem. Phys.*, **25**, 357 (1956).

interest in a different environment, one may tabulate the displacements from a reference point. If a single molecule has the nucleus in N chemically non-equivalent positions, one may hope to observe N lines under favorable circumstances. Fluorine compounds show especially large line separations for various groups, and their resolution is an easy matter. However, for hydrogen, the separations are of the order of 10^{-5} to 10^{-8} of the resonant field or less, and high resolution equipment is necessary. Not only may protons in groups such as CH_3 be distinguished from these in CH_2 or other groups, but one may observe multiple CH_3 lines in the same molecule. This may occur when they are attached in such different positions as on a benzene ring, as ester groups, etc. Dimethylformamide represents an interesting case in which the two methyl groups would be chemically equivalent if free rotation occurred about the N–C bond. That one resolves two lines indicates there is a considerable barrier to the rotation.[12,13]

Returning again to chlorine as an example, one may detect shifts in H^* from a number of causes. By far the largest are those which betray the presence in the solution of paramagnetic ions. These may contribute a local field—not averaged to zero—producing a fractional displacement of H^* by 5×10^{-3} in the case of Co(II). Perhaps of more direct interest are shifts arising from other causes. For example, in NH_4Cl solutions the Cl^- line intensity is a linear function of concentration and has the same width as in NaCl, but H^* is displaced to lower fields by about 5×10^{-6}. The displacement increases with atomic weight for the alkaline earth chlorides, though again no line broadening is noted. The subtle interaction which shifts H^* does not detectably distort the spherical charge symmetry. This may imply a well-ordered array of M^{++} ions about the chloride ions, leading to a different effective ionic radius for each cation type.

The chloride ions in dilute $CdCl_2$ solutions of 3 M NaCl show a displacement of H^* together with the line broadening mentioned before. Even though one does not observe the bound chlorine, if it is exchanged rapidly with the free chloride ions, the average value of the field which it "sees" during an observation will not be the same as if it were free. Moreover, it would depend upon the concentration of the various complex types present.

Another shift of interest is the displacement of H^* to higher fields for Cl^- in D_2O as compared to H_2O. One might again speak of a different "effective ionic radius," dependent upon the solvating species. Such effects should be smaller for the ClO_4^- ion.

The NSR spectrum may provide useful information on intra- or intermolecular interactions. For example, the existence of hydrogen bonding will often affect the resonant field value for an OH proton. This is especially true for phenols, in which H^* shows a far larger range of variation than for any other group thus far observed. In some of the *ortho*-substituted phenols (which show chelation), the resonant field is relatively lower than for the proton in many carboxyl groups, indicating very low diamagnetic shielding and hence a rather positive atom.[14] Such compounds as *o*-hydroxyacetophenone or methyl salicylate show little tendency to form hydrogen bonds with other molecules. This is indicated by the small variation in resonant field which is observed when such phenols are diluted with hydrogen bonding solvents. Phenols not showing marked chelation exhibit wide variations in H^* under such conditions. Those which have bulky substitutents in the 2,6-positions may show H^* values higher than for water (usually taken as a reference) or aliphatic alcohols. Marked concentration dependence of H^* is also found for compounds such as $CHCl_3$.[15]

When bond energies are so low that chemical exchange of the nucleus with another in a non-equivalent position may occur, the NSR spectrum will depend on the relative rate of such exchange.[8] When the rate of exchange is slow (compared with the reciprocal of the separation of the two lines, expressed in cycles per second), one may hope to observe the separate lines. For protons and a few other nuclei with sharp lines, this hope may be realized. For rapid exchange, one usually observes a single sharp line at a position which is the number average of the positions for the separate nuclei. At rates which are comparable to the inverse of the line separation, one observes a single broad line. One may thus be able to set a minimum or maximum value for the rate of exchange. When separate lines occur and one assumes an exponential variation of rate and a frequency factor, one may estimate an activation energy for exchange.

An interesting case of a missing line is represented by a group of hydroxy acids, both aliphatic and phenolic. These were observed in the liquid state or in solution.[14] For aliphatic alcohols, the OH proton is relatively far displaced from the proton line of a COOH group. One might reasonably therefore have expected to see both, but in no case examined have two lines appeared. A single line of about twice the expected intensity appears at an intermediate position. Several possible explanations present themselves. One of them would represent the hydroxy acid as a dipolar ion similar to the amino acids. The other would be based upon hydrogen bonding between molecules. Both OH and COOH protons could find themselves between two oxygen atoms and would be essentially equivalent.

In simple cases of chemical shielding, one observes multiple resonance lines of non-equivalent nuclei in the same molecule are displaced from one another by an amount proportional to the applied field. Another type of multiplicity is often observed in the liquid state in compounds containing such nuclei as hydrogen, boron, nitrogen, fluorine, aluminum, phosphorus and antimony. Perhaps the simplest example is HD, for which the proton spectrum is a triplet and the deuterium spectrum a doublet. The multiplicity of the spectrum of nucleus i is just $2I_j + 1$, where j refers to the other nucleus. Here the multiplet separation is independ-

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(12) H. S. Gutowsky, *Disc. Faraday Soc.*, **19**, 247 (1955).

(13) W. D. Phillips, *J. Chem. Phys.*, **23**, 1363 (1955).

(14) J. E. Wertz and R. L. Batdorf, to be published.

(15) C. M. Huggins, G. C. Pimentel and J. N. Shoolery, *J. Chem. Phys.*, **23**, 1244 (1955).

ent of field. Perhaps more striking is an example such as methylaminium ion at low pH.[16] Here the methyl proton group is a quartet from interaction with the three protons, of the NH_3^+ ion. The total quantum number for the NH_3^+ group protons can be $^3/_2$, $^1/_2$, $-^1/_2$ or $-^3/_2$, and the multiplicity would be $2\ \Sigma I + 1$. The NH_3^+ spectrum is a triplet arising from N^{14} with spin 1.

In the latter example especially, one observes that while the several portions of the molecule are undergoing relative reorientations there is nevertheless a mechanism whereby the effects of nuclear polarizations are communicated. This immediately excludes direct magnetic interaction. It is to be noted that whenever this type of multiplicity occurs, the bonds between the atoms affected are all covalent. On a naive picture, the spin orientation of the first nucleus shows some correlation with that of one of the bonding electrons. The orientation of the second electron of the bond is necessarily anti-parallel, and this electron may produce a correlation of the spin of the second nucleus. Transmission of polarization of protons may occur through at least three bonds *via* the s-electrons of the system. Thus nuclei which are remote from one another are indirectly coupled. When both s and p electrons are involved in a covalent bond, there will be an additional orbital interaction with the nuclei. For protons, McConnell has attempted to calculate proton bond orders.[17]

With very high resolution, one may detect more lines than the simple considerations outlined here would predict.[18] Anderson and Arnold found that such further multiplicity arises when second and third orders of perturbation of the chemically-shifted system are considered. In the simplest cases, these higher order effects serve to remove some of the energy level degeneracies which previously existed. McConnell[19] has observed a very large number of lines in fluorinated ethylenes and has shown how their multiplicity and intensity may be calculated by application of group theory.

In summary, nuclear spin resonance spectra may by their line position, shape or multiplicity reflect the subtle or gross interactions of atoms which chemists designate as bonds.

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(16) E. Grunwald, A. Loewenstein and S. Meiboom, *J. Chem. Phys.*, **25**, 382 (1956).

(17) H. M. McConnell, *J. Chem. Phys.*, **24**, 460 (1956).

(18) W. A. Anderson and J. T. Arnold, *Disc. Faraday Soc.*, **19**, 226 (1955).

(19) H. M. McConnell, A. D. McLean and C. A. Reilly, *J. Chem. Phys.*, **23**, 1152 (1955).

PRESENT SITUATION OF QUANTUM CHEMISTRY

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It is pointed out that the nature of the covalent bond may be understood only by means of modern quantum mechanics. The introduction of Planck's quantum of action h leads to Heisenberg's uncertainty relation for a single particle which indicates that the idea of the existence of the classical orbits has to be abandoned. In a many-electron system there is then no longer any possibility for identifying the individual particles, and all chemically and physically measurable results must hence be independent of the labeling of the particles. It is shown that this symmetry law leads to a new form of energy, the "exchange energy," which among other things also explains the chemical bond according to Heitler and London. A brief survey is given of the development of quantum chemistry, and the main problems of actual interest in the valence bond method and in the molecular orbital theory are discussed. The simplification in the interpretations recently obtained by introducing density matrices and natural spin-orbitals is finally described.

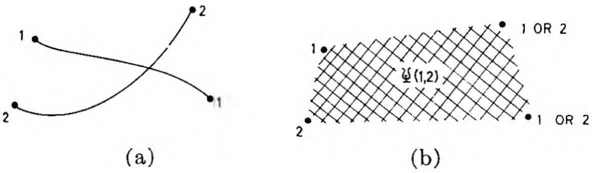
In investigating the highly different phenomena in nature, scientists have always tried to find some principles which explain the variety out from a basic unity. They have found not only that all the various kinds of matter are built up from a rather limited number of atoms, but also that these atoms are constituted of a few elementary particles. From the point of view of ordinary chemistry, an atom may be considered as consisting of a positive point charge, the nucleus, surrounded by an electronic cloud which determines its chemical properties and, in principle, all chemical problems may therefore be reduced to problems concerning the interaction between the electronic clouds and the nuclei. The laws which regulate the behavior of the electrons are therefore of basic nature, and the discovery of modern quantum mechanics has thus been of greatest importance for our understanding of the properties of molecules and crystals, the latter being nothing but molecules of a tremendous size.

Uncertainty Principle.—Planck's discovery that in nature there exists the smallest quantum of action, $h = 6.626 \times 10^{-27}$ erg sec., has been of revolutionary importance for the development of modern science. In physics and chemistry, only those quantities in nature which are physically and chemically measurable are studied. However, every measurement implies an interaction between the object to be measured and the apparatus, and the smallest interaction possible is regulated by the above-mentioned quantum of action. This means that every measurement will disturb the object concerned and that this disturbance cannot be brought under a certain limit. It was found by Heisenberg that, if one tries to measure the position x and the momentum p of a particle simultaneously, the uncertainties in the measurements, Δx and Δp, respectively, must fulfil the famous relation $\Delta x \cdot \Delta p \geq h/4\pi$, which is now known as Heisenberg's uncertainty relation. The implication of this result is that, from the point of view of the measurements, an elementary particle cannot simultaneously have a fixed position and a fixed momentum, and consequently the idea of the existence of a classical orbit for such a particle has to be abandoned.

In the discovery of modern quantum mechanics in 1925, it was found that, as a consequence of the existence of Planck's constant h, physical observables could no longer be considered as ordinary numbers, and that they instead should be described by mathematical quantities which do not fulfil the commutative law of multiplication. They may be represented by either matrices (Heisenberg), or by operators (Schrödinger), or simply by so called q-numbers (Dirac). The existence of the quantum of action led in this way to a quantization of the physical observables in the form of eigenvalue problems. However, from the chemical point of view, we are interested also in another consequence of a more indirect nature.

Identity Principle—Exchange Energies.—It was pointed out above that, because of the existence of the smallest quantum of action, an elementary particle cannot have a classical orbit. This implies that, if we consider a system of similar particles having the same charge and the same mass, it is impossible to distinguish the different particles individually, since one cannot follow them in any orbits. We have to observe that the individuality of a particle in the classical sense is intimately associated with the existence of its orbit. In a quantum-mechanical system, two particles may therefore exchange their places without any possibility to discover this phenomenon experimentally. This exchange phenomenon leads to a new form of energy, the "exchange energy" which is characteristic for modern quantum mechanics and which is of basic importance for the understanding of the nature of the electronic clouds within the atoms, the homopolar chemical bond, the ferromagnetism, the saturation of the nuclear forces, and many other phenomena.

In order to obtain a mathematical formulation of this "identity principle," let us consider any two particles 1 and 2 having the same mass and charge; see Fig. 1. If $F(1,2)$ denotes any physically or chemically measurable result, the outcome of the measurement must be independent of our attempt to label the two particles and thus we get the relation



(a) Classical physics; identification of the particles possible in principle by following their respective orbits.

(b) Quantum mechanics; no classical orbits exist and no identification of the two particles is possible, which leads to the fundamental symmetry law $F(2,1) = F(1,2)$ for any measurable quantity F.

Fig. 1.—Difference in behavior of two particles in classical physics and in quantum mechanics.

$$F(2,1) = F(1,2) \tag{1}$$

which is the basic symmetry law characteristic for modern quantum mechanics.

The quantum-mechanical situation of a system of N particles is described in full detail by a wave function $\Psi = \Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots \mathbf{x}_N)$, where $\mathbf{x}_i$ is a combination of the space and spin coördinates of the particle i. The physical meaning of this wave function is that $|\Psi|^2$ gives the probability density for finding the particles in the point $(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \ldots \mathbf{x}_N)$ in configuration space. However, since all physical results must be independent of the individuality of the particles, this quantity $|\Psi|^2$ must remain invariant when the coördinates of the particles change their places. If P is an arbitrary permutation of the coördinates, hence we have

$$P|\Psi(\mathbf{x}_1,\mathbf{x}_2, \ldots \mathbf{x}_N)|^2 = |\Psi(\mathbf{x}_1,\mathbf{x}_2, \ldots \mathbf{x}_N)|^2 \tag{2}$$

This implies also that, under a permutation, the wave function itself may be changed only by a phase factor of the absolute value one, and, if we assume that this phase factor for a single exchange of the coördinates of two particles is a constant characteristic for the particles under consideration, the only possible values are $+1$ and -1, corresponding to symmetric and antisymmetric wave functions, respectively. By using relativistic arguments, it may be shown that particles having half-integer spins are "antisymmetric," whereas those having integer spins are "symmetric." The electrons have therefore antisymmetric wave functions fulfilling the relation

$$P\Psi(\mathbf{x}_1,\mathbf{x}_2,\ldots \mathbf{x}_N) = (-1)^p\,\Psi(\mathbf{x}_1,\mathbf{x}_2,\ldots \mathbf{x}_N) \tag{3}$$

where p is the parity of the permutation P.

In $\Psi(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \ldots \mathbf{x}_N)$ each coördinate place corresponds to a particle state, and, if two such states are identical, the wave function should not change its value under a simple exchange of the coördinates in these places. This implies that an antisymmetric wave function having two particle states identical must vanish. An antisymmetric wave function is hence characteristic for a system of particles, where never more than one particle may be placed in every fully specified state. The electrons fulfil therefore automatically Pauli's famous exclusion principle, which leads to a certain saturation phenomenon in their symmetry property. It is this new property which is of such importance for the understanding of the behavior of the electronic structure of matter, and we emphasize again that this symmetry is only indirectly a consequence of the existence of Planck's quantum of action.

Stationary States.—The stationary states of a molecular system are characterized by the wave functions Ψ which are solutions to the Schrödinger equation

$$H_{\text{op}}\Psi = E\Psi \tag{4}$$

This equation has solutions, which are normalizable so that

$$\int|\Psi|^2(dx) = 1 \tag{5}$$

only for selected values of E, which are called the eigenvalues of the equation; the corresponding solutions are called the eigenfunctions. The eigenvalues form together the energy spectrum of the molecule under consideration, and they give the energies of the possible stationary states of the electronic structure. In addition to the discrete eigenvalues, there may also be a continuous spectrum corresponding to free particles within the molecular system; the corresponding wave functions have a somewhat generalized normalizability condition. The operator H_{op} in the left-hand member is the quantum-mechanical Hamiltonian, which is obtained from the classical Hamiltonian for the molecular system

$$H_{\mathrm{op}} = \frac{e^2}{2} \sum_{gh}{}' \frac{Z_g Z_h}{r_{gh}} + \sum_i \frac{\mathbf{p}_i^2}{2m} - e^2 \sum_g \frac{Z_g}{r_{ig}} + \frac{1}{2} \sum_{ij}{}' \frac{e^2}{r_{ij}} \qquad (6)$$

by replacing the classical momentum $\mathbf{p}_i$ by the operator

$$\mathbf{p}_i = \frac{h}{2\pi i}\left(\frac{\partial}{\partial x_i}, \frac{\partial}{\partial y_i}, \frac{\partial}{\partial z_i}\right) \qquad (7)$$

In the Hamiltonian the first term represents the electrostatic nuclear repulsion energy, the second term the kinetic energy of the electrons, the third term the attraction potential between the nuclei and the electrons, and the fourth term the electronic repulsion energy. In constructing this Hamiltonian, one has assumed that the nuclei have fixed positions and that relativistic effects may be neglected, which causes some approximations.

The Hamiltonian H_{op} is defined in a "configuration space" ($\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \ldots \mathbf{x}_N$), where each particle i has its own space-spin coordinate $\mathbf{x}_i$. Mathematically Heisenberg's uncertainty relation

$$\Delta x \cdot \Delta p \geq h/4\pi$$

follows now from the operator equation 7. We note further that the exchange phenomenon[1] and the basic symmetry law may be derived from (4) and the fact that the Hamiltonian is symmetric in the coördinates $\mathbf{x}_i$; the eigenfunctions are either automatically symmetry functions or may (in degenerate cases) be chosen as symmetry functions, *i.e.*, as eigenfunctions also to the permutation operators P. The Schrödinger equation 4 forms therefore the basis for the entire molecular theory with an auxiliary condition entering in the form of the mathematical formulation (3) of the Pauli principle.

Homopolar Chemical Bond.—In chemistry, the electrostatic nature of the heteropolar bond was rather well explained by a series of authors from Berzelius to Kossel, but the inner nature of the homopolar bond was a real mystery. According to Lewis, each covalent bond was supposed to be connected with an electron pair, but it was first the establishment of modern quantum mechanics which could explain its real nature. In 1927, Heitler and London[2] discovered that the covalent bond in the hydrogen molecule was associated with a pair of electrons and that the binding essentially arose from the above-mentioned "exchange effect," which is associated with the impossibility of individually distinguishing the two particles. They found that, if a and b are the space wave functions for the two separated hydrogen atoms, a combined wave function of the type $a(1)$-$b(2)$ would not correspond to a chemical bond, whereas a symmetrized combination

$$\Psi(1,2) = a(1)b(2) + a(2)b(1) \qquad (8)$$

would give a binding energy of the correct order of magnitude. The existence of the covalent chemical bond depends therefore on a typical quantum-mechanical phenomenon—the identity principle and the symmetry requirement—and, since there is no classical counterpart to this effect, it is certainly very difficult to give an elementary description of the nature of the covalent chemical bond. The saturation of the covalent bond is further explained by the Pauli principle.

Usually classical mechanics provides a first approximation to a quantum-mechanical system, but, as regards the symmetry properties, no such correspondence seems to exist. Heitler and London's discovery opened therefore an entirely new field, "Quantum Chemistry," which provides a natural link between the physics of the elementary particles and chemistry. Soon after the appearance of Heitler and London's work, Heisenberg recognized that the exchange phenomenon may be of fundamental importance also for the understanding of ferromagnetism. With the development of modern nuclear theory, it seems now as if the identity principle and the symmetry laws would be one of the most important consequences of the whole quantum theory.

Development of Quantum Chemistry.—Heitler and London's investigation of the hydrogen molecule gave a qualitative understanding of the homopolar chemical bond in general, and it started the development of modern quantum chemistry. There are several ways of constructing this link between chemistry and particle physics, and one of the most fruitful methods was explored by the chemists themselves by starting from the ordinary chemical terminology and translating and adapting it to the quantum-mechanical ideas. Of course, it is very hard to decide whether the electronic interpretations given in this way have a real background in nature or not, and the whole approach may hence be compared with building a tunnel in a certain direction under a mountain from one side without having yet reached the other side.

By unifying chemical and quantum-mechanical ideas, *semi-empirical theories* have been developed which are devices for correlating one set of experimental chemical data with another set. This approach has been particularly successful in organic chemistry in treating the conjugated systems. We will here only mention the explanation of the properties of the aromatic bond, the calculation of dipole moments, the directing power of substituents in aromatic systems, the color of organic molecules, the problem of addition to conjugated systems, the stability of free radicals, and so on. Important contributions have here been given by Hückel, Pauling, Wheland, Mulliken, Sklar, Coulson, Longuet-Higgins, Platt and others.

These semi-empirical theories have the advantage of being comparatively simple, and if their applications are not extended too far, the quantitative results are usually very good. They seem to be excellent devices for interpolation and extrapolation of chemical results. However, it has usually been found impossible to use the semi-empirical parameters determined for the ground state to describe also

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(1) W. Heisenberg, *Z. Physik*, **38**, 411 (1926); **39**, 499 (1926); **41**, 239 (1927).

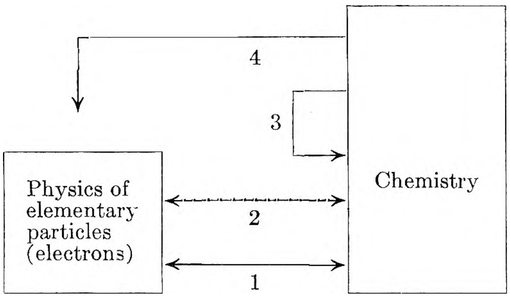
(2) W. Heitler and F. London, *ibid.*, **44**, 455 (1927).

the lower exited states, and the whole approach appears therefore to be oversimplified in many ways. Some of the parameters have also been determined purely theoretically, but the agreement with the semi-empirical values has usually not been as good as one would desire.

The other way of obtaining a connection between the theory of electrons and the ordinary chemistry is to start from the quantum-mechanical electron theory itself and try to derive solutions of the Schrödinger equation. The explanation of the homopolar covalent bond was found this way and, among other fundamental problems which have been at least approximately solved by this method, the derivation of the repulsive Born–Mayer forces within the ionic crystals, and the explanation of the Hume-Rothery-rules for alloys by Jones should be mentioned. The difficulty is here that the many-electron Schrödinger equation is very hard to solve even in an approximate form.

In distinguishing between "semi-empirical" and "pure" theories, one should always remember that all theories in physics and chemistry are basically semi-empirical in the sense that they correlate some experimental data with other experimental data—really pure theories belong to metaphysics and not to modern science. However, a theory is here called "pure" in a restrictive sense, if it derives for instance chemical data from the knowledge of only the physical values of the electronic mass and charge, Planck's constant, the atomic numbers, and the form of the Schrödinger equation, which itself represents the quintessence of a great deal of physical experience. A schematic survey of the various branches of quantum chemistry as a link between physics and chemistry is given in Fig. 2.

In this connection, it can also be discussed whether the Schrödinger equation itself forms a sufficient basis for our understanding of chemistry or not.



1. Theory of covalent bond (H_2).
2. Theory of van der Waals forces, repulsive forces in ionic crystals, Hume-Rothery rules for alloys, etc.
3. Semi-empirical theories of dipole moments, spectra of molecules, conjugation and aromatic bond, directing power of substituents, stability of free radicals, etc.
4. Chemistry in quantum-mechanical language, theory of resonance, etc.

Fig. 2.—Quantum chemistry as a link between chemistry and the physics of the elementary particles.

The Drastic Extrapolation.—When Bohr in 1913 established his theory of the hydrogen atom, it was soon found out that it was impossible to generalize the theory from one electron to the case of two or more electrons. Bohr's theory gave therefore a description of the simplest atom but failed in giving a quantitative explanation of the remaining part of the periodic system. One of the most important points after the discovery of modern quantum mechanics in 1925 was therefore the question whether it would give a satisfactory treatment of the helium atom and the higher atoms in the periodic system. The helium atom represents a three-body problem, and, from the very beginning, it is obvious that it is impossible to solve it in a closed form. In an important series of papers, Hylleraas investigated carefully this problem and could show that it was possible to obtain the different energy levels of the atom with any accuracy desired by the spectroscopists. Even the problems concerning the relativistic effects and the Lamb-shift seem now to be rather satisfactorily solved.

Another two-electron problem of great interest was the hydrogen molecule. Heitler and London had here given only an approximate solution and, by using the same technique as was developed by Hylleraas for helium, James and Coolidge could derive the eigenfunction for the ground state of H_2 and show that the quantum mechanical energy was in full agreement with the experimental value. The treatments of He and H_2 both were based on Schrödinger's equation in configuration space for two-electrons, and from these successful results one has then drawn the conclusion that the same type of Schrödinger equation should be valid for a system containing an arbitrary number N of particles, *i.e.*, one has drastically extrapolated from $N = 2$ to arbitrary values of N. The solutions of the Schrödinger equation for many-particle systems have not yet been determined with such an accuracy that one can decide whether this extrapolation is strictly valid or not, but so far there have been no objections in principle against this procedure. Dirac's general prediction in 1929 is famous in this connection:

"The general theory of quantum mechanics is now almost complete, the imperfections that still remain being in connection with the exact fitting in of the theory with relativity ideas. These give rise to difficulties only when high-speed particles are involved, and are therefore of no importance in the consideration of atomic and molecular structure and ordinary chemical reactions. . . . The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. . . ."

Solution of the Many-electron Schrödinger Equation.—It is evident that it is mathematically impossible to solve the many-electron Schrödinger equation in a closed form, but this does not mean that one cannot obtain solutions with any accuracy desired, and the existence of the eigenfunctions has been discussed by, among others, Kato. In order to find approximate solutions, a number of schemes are now in use and a diagrammatic survey of them is given in Fig. 3.

The simplest approach is based on the one-electron model in which the total wave function is built

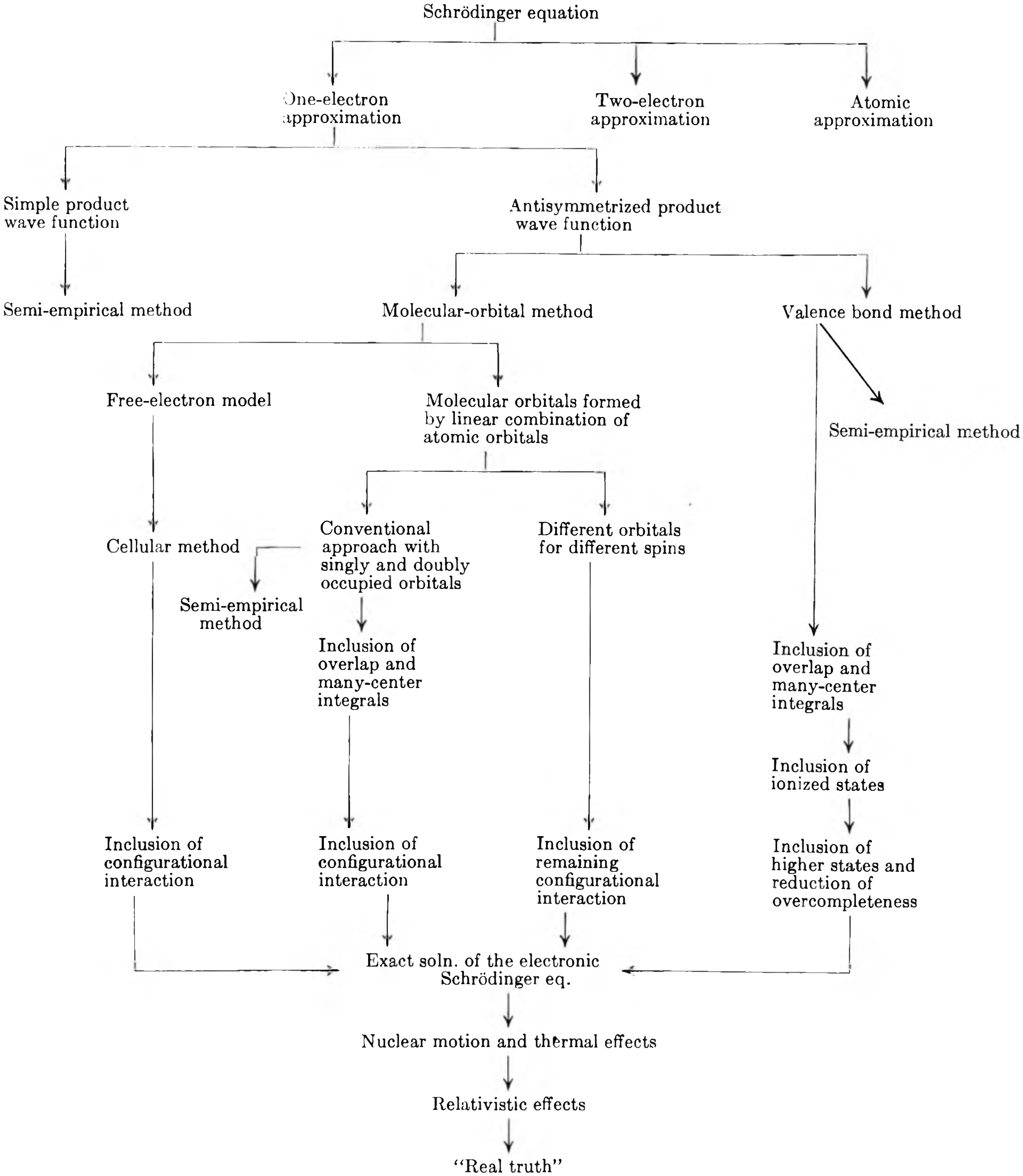


Fig. 3.—Quantum chemistry. Schematic survey of the various methods now used in molecular and solid-state theory for the solution of the Schrödinger equation.

up from one-electron functions or spin-orbitals. In a first crude approximation the total wave function for N electrons may be approximated by a product of N spin-orbitals containing each one electronic coördinate; since the total wave function is not antisymmetric, Pauli's exclusion principle has to be added as a supplementary condition. Many of the papers written on the theory of conjugated systems have been based on this approach, but it should be remembered that the accuracy in such a case cannot be too high, and usually the integrals involved have been estimated from empirical data.

If a product wave function is antisymmetrized, it is transformed to a determinant (Slater). The conventional methods have here been of two types, depending on the basic assumptions about the one-electron functions. If these one-electron functions have been taken from the atoms constituting the molecule, they have been called atomic spin-orbitals and the whole approach the valence bond method (Heitler–London, Slater, Pauling). On the other hand, if the electrons have been considered as belonging to the molecule as an entirety, the one-electron functions have been chosen as molecular orbitals which are extended over the molecule as a whole (Lennard-Jones, Hund, Mulliken). Some details of the calculations according to the different schemes will be discussed below.

Originally Heitler and London developed also another variant of the valence bond method, in which the total molecular wave function was built up from the atomic wave functions of the constituents. A semi-empirical form of this atomic approximation recently has been presented(3) under the name of "atoms in molecules." Even a two-electron scheme has now been proposed.(4)

A few words should be said about the mathematics. The strongest tool up till now for deriving approximate solutions of an eigenvalue problem of the type of the many-electron Schrödinger equation is the variation principle which says that the best approximation makes the expectation value of the Hamiltonian operator, given by the mathematical expression

$$<H_{\mathrm{op}}>_{\mathrm{av}} = \int \Psi^* H_{\mathrm{op}} \Psi (\mathrm{d}x) \qquad (9)$$

an extreme value, *i.e.*

$$\delta <H_{\mathrm{op}}>_{\mathrm{av}} = 0 \qquad (10)$$

If this is true for all variations, then the wave function is an exact solution to the eigenvalue problem. Usually one assumes that the total wave function Ψ has a specific form containing a series of parameters, the best values of which are then determined by the condition (10). Since the original equation is an eigenvalue problem in configuration space, the variation principle is often applied in the following way

eigenvalue problem in N-electron space

↓

simplifying assumptions about the eigenfunctions

↓

variation principle (11)

↓

new, simplified eigenvalue problem in one-electron space

The simplified eigenvalue problem is often expressed in the form

$$H_{\mathrm{eff}}\psi(\mathbf{x}) = \epsilon\psi(\mathbf{x}) \qquad (12)$$

where the "effective Hamiltonian" H_{eff} is a one-particle operator which corresponds to the classical energy of a single particle (moving in the average field of all the other particles) modified to take also the quantum-mechanical symmetry effects and the Pauli principle into account. The eigenvalues ϵ are called the orbital energies.

A standard method for solving an eigenvalue problem of this type is Ritz's method, in which the eigenfunction Ψ is expressed as a linear combination of a complete set Ψ_{K}

$$\Psi = \sum_{\mathrm{K}} \Psi_{\mathrm{K}} C_{\mathrm{K}} \qquad (13)$$

The undetermined coefficients C_{K} are here obtained by the variation principle, which leads to a series of linear equations containing the eigenvalue E as an unknown parameter

$$\sum_{\mathrm{L}} (H_{\mathrm{KL}} - E\delta_{\mathrm{KL}})C_{\mathrm{L}} = 0 \qquad (14)$$

$$H_{\mathrm{KL}} = \int \Psi^*_{\mathrm{K}} H_{\mathrm{op}} \Psi_{\mathrm{L}} (\mathrm{d}x)$$

The eigenvalue is then determined by the condition that the determinant of the coefficients of this homogeneous system should vanish

$$\det \{H_{\mathrm{KL}} - E\delta_{\mathrm{KL}}\} = 0 \qquad (15)$$

The secular equation obtained in this way may be solved either by numerical computations or by expansions which correspond to the conventional perturbation method. Since Ritz's method may be applied either to the original eigenvalue problem (4) in N-electron space or to the simplified eigenvalue problem (12) in one-electron space, there are two types of secular equations of the same mathematical form but of essentially different physical meaning. The mathematics used is nowadays of a standard form, and a schematic survey of the various steps needed in solving the Schrödinger equation is given in Fig. 4.

However, if the general scheme is almost the same for all the methods, the details are rather different, and we will now give some comments on the various approaches.

(a) **Valence Bond Method. The Theory of Chemical Resonance.**—The valence bond method developed by Heitler–London, Rumer, Slater, and Pauling is a direct generalization of the formers' pioneer work on the hydrogen molecule. It was found in this simple case that, if the electrons are assigned to atomic orbitals belonging to the two hydrogen atoms involved, the bond itself corresponded formally to a total function which could be written as the difference between two determinants having the spin functions α and β interchanged. The wave function for a molecule containing only a number r of single bonds is then built up analogously by forming the algebraic sum of the 2^r determinants which are obtained from a given determinant by carrying out an α-β reversal including change of sign for every single bond occurring in the chemical structure formula and taking all possible combinations.(5) This method for constructing a singlet state of the total spin has its great advantage in the close parallelism between the quantum-mechanical wave function and the corresponding chemical formula for the compound. However, the method is connected with mathematical difficulties which are not yet solved and which depend on the fact that the atomic orbitals involved overlap mutually with the effect that the various determinants are not orthogonal.(6) The matrix elements of two non-orthogonal determinants are easily constructed, but, so far, it has not been possible to give a simple expression for the matrix elements of two general valence bond structures taking the non-orthogonality into full ac-

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(3) W. Moffitt, *Proc. Roy. Soc.* (*London*), **A210**, 224, 245 (1951).

(4) Hurley, Lennard-Jones and Pople, *ibid.*, **A220**, 446 (1953); L. A. Schmid, *Phys. Rev.*, **92**, 1373 (1953).

(5) See, *e.g.*, G. Rumer, "Göttinger Nachr.," 1932; L. Pauling, *J. Chem. Phys.*, **1**, 280 (1933).

(6) The non-orthogonality problem was first emphasized by J. C. Slater, *Phys. Rev.*, **35**, 210 (1930).

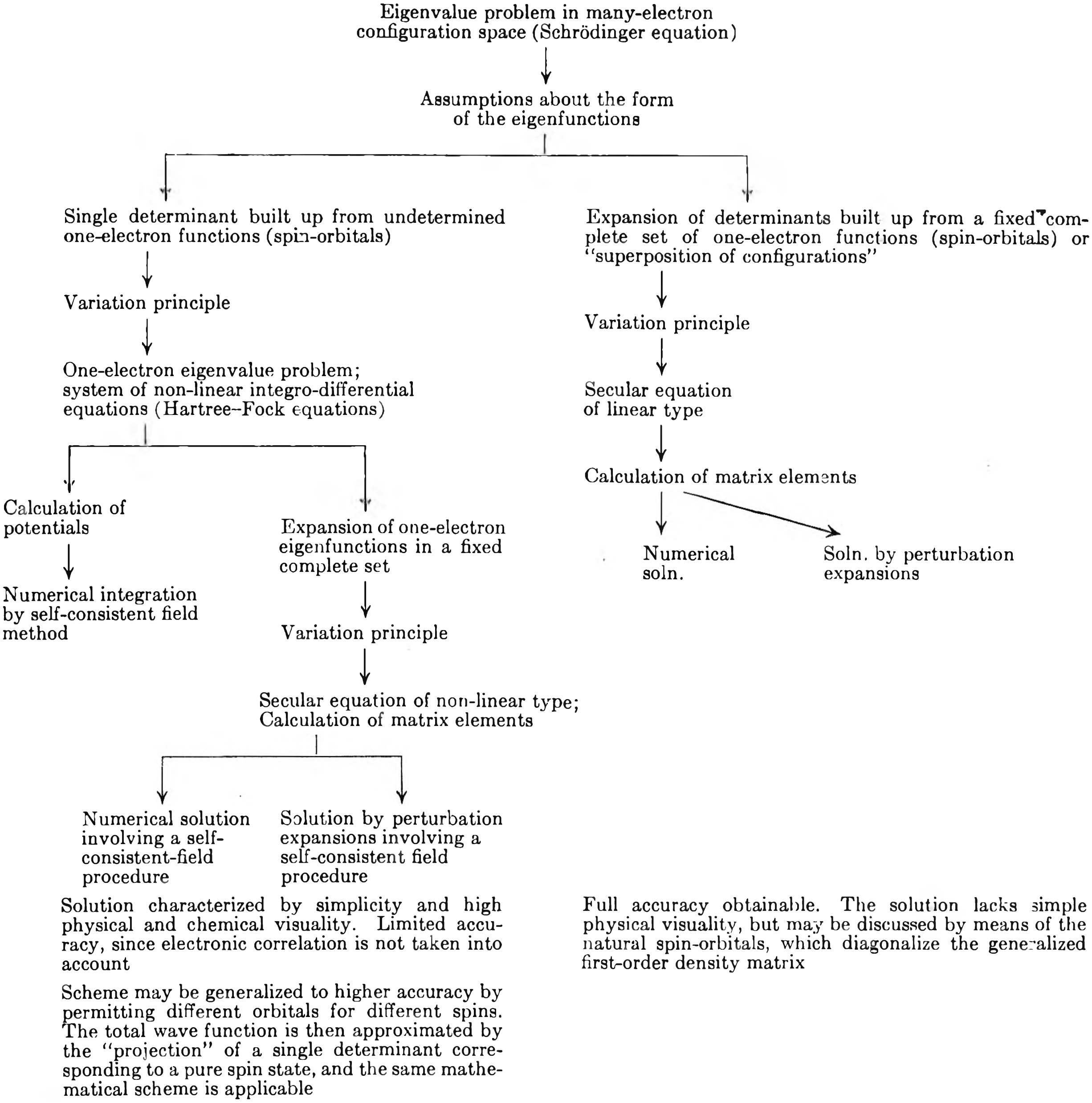

Fig. 4.—Quantum chemistry. Schematic survey of the various mathematical steps needed in solving the many-electron Schrödinger equation for a molecular or solid-state system. Combinations of the two approaches outlined above have also proved to be useful.

count.[7] It seems as if some new mathematical device in the form of a "superdeterminant" would be needed and, only in special cases, has it been possible to obtain a closed expression for the final result. If the overlap is neglected, the matrix elements are easily obtained, but it should be strictly emphasized from the very beginning that the overlapping of the electronic clouds of different atoms is fundamental for the understanding of the chemical forces and that the whole picture will break down, if this overlap is neglected. In the earlier literature within this field, the overlap usually has been universally neglected, and this is very unfortunate. In the theory of ionic crystals, it has been shown that, if the overlap integrals are omitted, there will be no repulsive forces at all, and the whole quantum mechanical description will then lose its validity.[8] The importance of the overlap integrals has successively been recognized, and usually they are now properly included. However, there is still no treatment of the original valence bond method which has really solved this problem.[9]

The valence bond method in its crudest form is based on the conventional chemical formula. However, in the case of the hydrogen molecule, it was already found that, if higher accuracy is desired, one has to include also the ionic structures, *i.e.*, the total wave function should be a linear combination of valence bond functions corresponding to the three structures

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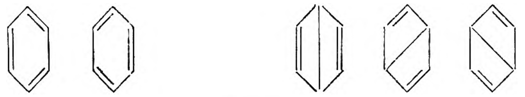
[7] See *e.g.*, J. C. Slater, Quarterly Progress Report of Solid-State and Molecular Theory Group, M.I.T., p. 3, October 15, 1953 (unpublished).

[8] P. O. Löwdin, *J. Chem. Phys.*, **18**, 365 (1950).

[9] P. O. Löwdin, *Adv. Phys.*, **5**, 1 (1956), particularly Sec. 10.1, p. 153.

$$\mathrm{H{-}H},\ \mathrm{H^+H^-},\ \mathrm{H^-H^+}$$

which are in "chemical resonance" with each other.[10] In the case of the conjugated systems in organic chemistry, the positions of the double bonds are not entirely fixed in the conventional chemical formulas and, for instance in the benzene molecule, one has the following five "canonical" structures



consisting of two Kekulé structures and three Dewar structures. The total wave function is then a linear superposition of the valence bond functions corresponding to these structures. This "theory of resonance" seems first to have been suggested by Slater,[11] and it has then in the hands of Pauling[12] and others been successfully developed and applied to many fundamental chemical problems.

The resonance theory has a simplicity and chemical visuality which is striking, and it is therefore unfortunate that the basic overlap and non-orthogonality problem still appears to remain unsolved. We have previously pointed out that the non-orthogonality problem has not yet been solved for the case of a single general valence bond structure, and the problem is still worse for molecules containing resonating bonds. It is often emphasized that it is mainly the coefficients for the resonating structures in the total wave function which have the basic chemical importance, but, in this connection, it should be remembered that the structures themselves are not strictly orthogonal to each other, which means that the coefficients are not even uniquely determined. In many of the leading textbooks in quantum chemistry, the theory of resonance is usually developed in a form where all overlap integrals are neglected. This does not prevent the theory from being useful for certain purposes, for instance interpolation or extrapolation of chemical data, but one should always remember that an essential refinement of this theory is needed to bring it in full connection with quantum mechanics.

In addition to the non-orthogonality problem, there is another fundamental question in the valence bond method which has not yet been solved, namely the problem of the degree of linear dependence of a system of atomic orbitals associated with two or more nuclei. Usually one introduces just the atomic orbitals which are occupied in the conventional chemical formula for the compound, but, even if all ionized states involving these orbitals are included, the accuracy of the total wave functions cannot be brought beyond a certain limit. In order to obtain a complete accuracy, it is necessary to introduce also the excited atomic orbitals. However, if a complete system of atomic orbitals is introduced on every nucleus, the total system of basic one-electron functions will certainly be overcomplete, and essential difficulties will then occur in the theory, since the secular equation for solving the variation problem will be identically vanishing, because of the existence of linear dependencies within the basic set. Even if only a limited number of atomic orbitals are introduced on every nucleus, there may exist approximate linear dependencies which are just as disastrous for the numerical solution of the secular equation as the overcompleteness.[13]

The problems of non-orthogonality and overcompleteness may both be solved by constructing an orthonormal set by linear combinations of the given atomic orbitals, for instance by a combination of the symmetric and successive orthonormalization procedures,[14] but this implies that one is losing the direct correspondence between the new valence bond method[15] and the simple chemical formulas and that the theory of resonance will then mainly be a mathematical scheme without direct chemical interpretation. For the moment, the whole valence bond method is therefore in a rather difficult dilemma.

(b) **The Molecular-Orbital Method.**—The valence bond method is partly based on the idea of the existence of individual atoms within the molecule. However, when the atoms are put together in a molecular system, the valence electrons may be considered as belonging to the molecule as a whole, and this point of view forms the basis for the molecular-orbital method (Lennard-Jones, Hund, Mulliken). This aspect has been particularly important for the understanding of the aromatic bond[16] and the general properties of the conjugated compounds. In this approach, the total wave function is approximated by a single determinant built up from the occupied spin-orbitals. In order to obtain the best approximation to a real eigenfunction, one may apply the variation principle, and this leads to certain equations for the orbitals involved which are usually called the Hartree–Fock equations and which have the form (12). These equations have been solved numerically for a whole series of atoms in the periodic system, but, only for a few molecules have they been investigated on a more exact basis. The Hartree–Fock equations are non-linear integro-differential equations of a rather complicated type, and they are usually solved by means of a self-consistent-field procedure.

For a system containing a large number of mobile electrons like the metals or the conjugated compounds, one may start from an approximate free-electron model, where the extension of the system gives the dimensions of the box within which the electrons are enclosed. For metals this model has been essentially refined in the cellular method, which is an attempt to solve the Hartree–Fock equations more accurately for a solid-state system having high symmetry.

For molecules, there is little hope that one will be able to apply the self-consistent-field method in the same way as in atoms and metals, and instead one may try to solve the basic equations by expanding

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(10) J. C. Slater, *Phys. Rev.*, **35**, 210 (1930).

(11) J. C. Slater, *ibid.*, **37**, 481 (1931), particularly p. 489.

(12) L. Pauling, *J. Chem. Phys.*, **1**, 280 (1933), and a series of papers in *J. Chem. Phys.* and *J. Am. Chem. Soc.*

(13) R. H. Parmenter, *Phys. Rev.*, **86**, 552 (1952).

(14) P. O. Löwdin, *J. Chem. Phys.*, **18**, 365 (1950); *Adv. Phys.*, **5**, 1 (1956), Sec. 3.2.

(15) R. McWeeny, *Proc. Roy. Soc.* (*London*), **A223**, 63, 306 (1954).

(16) E. Hückel, *Z. Physik*, **60**, 423 (1930); **70**, 204 (1931); **72**, 310 (1931).

the solutions in a fixed complete set.[17] This set may be chosen as consisting of the atomic orbitals of the molecule under consideration, and this leads to an approach usually denoted by the symbol MO-LCAO, which means that the molecular orbitals are formed by "linear combinations of atomic orbitals." When these orbitals are substituted in the total wave function, the matrix elements of the energy will contain integrals of the same type as in the valence bond method. In the molecular orbital method, there is no basic non-orthogonality problem of the same type as occurred in the valence bond method, but one must certainly take the overlap integrals into full account even in this approach. The calculation of the molecular integrals in general will be discussed below.

The molecular orbitals are of particular importance in the physical description of a molecule, since it may be shown that they may be used in constructing the wave functions for the ionized and excited states of the compound. The real and virtual solutions of the Hartree–Fock equations form further a complete system together, and this system may be used for describing the exact eigenfunctions to the total Hamiltonian. Each determinant built up from N spin-orbitals selected from a complete orthonormal system is called a "configuration"—a name which is borrowed from the theory of atomic spectra—and, since it may be shown that the exact wave function may be expanded in a sum of such determinants, the method is called "superposition of configurations" or sometimes "configurational interaction."

A determinant is invariant against unitary transformations of the orbitals under consideration. By carrying out a suitable transformation of this type, it has been shown that the molecule may be described by means of equivalent orbitals[18] which have the property that the corresponding exchange integrals are particularly small so that the chemical forces may be described as closely as possible by means of electrostatic forces of the "classical" type. The equivalent orbitals give hence a rather visual description of the electronic structure of the chemical bonds.

(c) **Calculation of Molecular Integrals.**—In both the valence bond method and the molecular orbital method, one has usually based the whole description of the system on a set of atomic orbitals, and the expectation values of physical and chemical quantities are then expressed as integrals containing these orbitals. In the energy calculations, the main problem is represented by the calculation of the electronic repulsion integrals, which may contain as many as four atomic orbitals, since each electron density is a product of two atomic orbitals. Such an electronic repulsion integral may therefore be associated with maximum four nuclei, but if two or more nuclei coincide, the integral will degenerate into a three-, two- or one-center integral. Some of the molecular integrals of atomic orbitals, which occurred in Heitler and London's theory for the hydrogen molecule, were only estimated, and the first "exchange integral" was actually evaluated by Sugiura. Different types of molecular integrals were later calculated by various authors, but it was soon discovered that, if it should be possible to work out the detailed structure of all molecules of interest, it would be necessary to standardize the integrals, since it would be too laborious and tedious to evaluate the integrals for every special case. The first extensive tables were worked out by Kotani and his school in Japan immediately before the war.

After 1945, the problems of the calculation of the molecular integrals have been taken up at several places. In the United States Mulliken in Chicago, Slater at M.I.T., Eyring in Utah and others have been interested in various aspects of the problem, in England Coulson and Barnett have prepared auxiliary tables, and in Germany Kopineck has investigated two-center integrals—many other important projects not mentioned. In Uppsala we have specialized on evaluating molecular integrals for the atomic self-consistent field functions. Numerical tables are now partly available[19] or under publication, but it will probably take several years until the problem of the standard integrals has been concluded. The two-center integrals may be tabulated in a rather condensed form, but it is evident that, for the tabulation of the three- and four-center integrals, a rather large number of books would be needed, and instead one has tried to work out accurate formulas for converting these integrals into two-center integrals, particularly overlap and coulomb integrals. The standard integrals are now evaluated for mostly Slater exponentials, but the question remains whether one should use hydrogen-like functions including the continuum or an entirely discrete set.

(d) **Configurational Interaction.**—If one looks at the diagram in Fig. 3 over the conventional methods now used for solving the many-electron Schrödinger equation, one will find that the whole development of quantum chemistry is hindered by the large amount of numerical work involved. In the valence bond method as well as in the MO-LCAO method, the evaluation of the molecular two-center integrals has represented a major problem, and it is evident that the question of the inclusion of the many-center integrals will be much harder to solve. The question of the non-orthogonality and the inclusion of the overlap integrals represents a theoretical and numerical problem which has now been solved successfully, at least for the molecular-orbital method.

The calculation of the molecular integrals is not the only obstacle, however. Even if all these numerical difficulties have been overcome, one cannot expect a too high accuracy of the two standard methods applied in their simplest or naive forms, since the basic sets are far from being complete.

In order to improve the accuracy, it is necessary to extend the basic set from N to M functions,

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[17] C. A. Coulson, *Proc. Camb.*, **33**, 104 (1937); C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951); P. O. Löwdin, *Phys. Rev.*, **97**, 1490 (1955).

[18] J. Lennard-Jones, *Proc. Roy. Soc. (London)*, **A198**, 1, 14 (1949), and a series of papers by him and his school in the same journal.

[19] A list of references may be found in A. Dalgarno, *Math. Tab. Aids. Comp.*, **8**, 203 (1954); see also Kotani, Amemiya, Ishiguro and Kimura, "Table of Molecular Integrals," Maruzen Co., Ltd., Tokyo, 1955, and H. Preuss, "Integraltafeln zur Quantenchemie," Springer, Berlin, 1956.

where M goes to infinity when the set tends to be complete. The total wave function may then be expanded in determinants over the configurations obtained by selecting N functions from the basic set, and, since the number of configurations is given by the binomial coefficient $\binom{M}{N} = M!/N!(M - N)!$, the secular equation will be of this order. Since the number $\binom{M}{N}$ is quickly increasing with M, the order of the secular equation goes up so rapidly that it may be possible to solve this equaion numerically, only if an electronic computer of sufficiently high capacity is available. The total wave function obtained in this way is complicated and difficult to interpret physically and chemically, but, by introducing the natural spin-orbitals[20] which diagonalize the generalized first-order density matrix, one obtains the configuration expansion of most rapid convergency, and the whole problem is then usually essentially simplified.

In this way it is possible to approach the exact solution with any accuracy desired, and it is evident that the final result will be independent of the starting point. The molecular orbital method including configurational interaction will therefore give the same result as the valence bond method including ionized and excited states—provided that, in the latter, one has taken the non-orthogonality into proper account and reduced away the linear dependencies caused by the overcompleteness. However, the numerical work involved in carrying out even a modest "configurational interaction" is of such an order of magnitude that one is eagerly looking for any possibilities of simplifying the procedure. In the molecular-orbital method, the main effect of the higher configurations is that they take the "electronic correlation" into account, and the question is whether this effect could be included in a simpler way.

(e) **Electronic Correlation.**—The molecular orbital method is based on the "independent-particle model" which assumes that, in a first approximation, one can neglect the mutual interaction between all the electrons or take it into account only by means of an "average" field. However, a repulsive potential, like the Coulomb potential e^2/r_{ij}, tries naturally to keep the particles i and j apart, and, since this "correlation" between the movements of the particles is entirely neglected in constructing a total wave function in the form of a simple product of the occupied spin-orbitals, the corresponding wave function and energy are affected by errors which are usually called "correlation errors." The situation is somewhat changed by the antisymmetrization procedure, which has the direct consequence that the probability density for two particles with the same spin to be in the same place will be zero of at least the second order (the "Fermi hole"). The main problem in treating antisymmetrized functions is therefore to take the correlation between electrons having anti-parallel spins into proper account. This problem is of fundamental importance for the understanding of the homopolar chemical bond, since this bond is associated with an electron pair having opposite spins. Extensive calculations have shown that each doubly filled orbital is associated with a correlation error which amounts to about 1 electron volt. The correlation energy is therefore a very important quantity in the theory of the chemical bond.

In the first successful treatments of the simplest two-electron systems, the He atom (Hylleraas) and the H_2 molecule (James and Coolidge), the interelectronic distance r_{12} was explicitly introduced into the total wave function, which is then called a "correlated" wave function. However, there are essential difficultics in generalizing this procedure to many-electron systems and recently one has therefore tried another approach, which is based on the idea of the existence of a more "static" correlation. One has abandoned the idea of the doubly filled orbitals which occur in the original formulation of Pauli's exclusion principle, and instead assumed that electrons having different spins may occupy different orbitals in space.[21] This means that the molecular orbitals have got a new degree of freedom and that the number of orbitals is twice as high as before. It is possible to extend the ordinary Hartree–Fock scheme to have different orbitals for different spins, and the main point is that even the generalized scheme preserves a great deal of the mathematical simplicity and physical visuality which is characteristic for the "independent-particle-model." In applications to simple atoms and molecules, it has been shown that the main part of the correlation energy may be taken into account in this simple way without any further configurational interaction.

In a scheme where there are different orbitals for different spins, a single determinant D is a mixture between spin states of various multiplicities so that, for an even number of electrons, we have

$$D = \text{singlet} + \text{triplet} + \text{quintet} + \dots \quad (16)$$

However, one can always select any pure spin component desired by means of a "projection operator" O having the simple property $O^2 = O$. Measuring the spin in units of h, we find for instance that the operator ^1O for selecting the singlet component has the form

$$^1O = \left(1 - \frac{S^2}{1.2}\right)\left(1 - \frac{S^2}{2.3}\right)\left(1 - \frac{S^2}{3.4}\right)\dots \quad (17)$$

In this operator the first factor will annihilate the triplet term in (16), the second factor the quintet term, etc., whereas the singlet term will survive the operation in an unchanged form. In the extended independent-particle model, the total wave function Ψ is therefore a projection of a single determinant, $\Psi = OD$, and this has the important mathematical consequence that the expectation value of any physical or chemical quantity is easily formally evaluated.

$$\int \Psi^* H_{op} \Psi (dx) = \int (O^* D^*) H_{op} (OD)(dx) = \\ = \int D^* O^+ H_{op} O D (dx) = \int D^* H_{op} (OD)(dx) \quad (18)$$

This is an essential difference against the valence bond method, where the problem of calculating

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(20) P. O. Löwdin, *Phys. Rev.*, **97**, 1474 (1955); P. O. Löwdin and H. Shull, *ibid.*, **101**, 1730 (1956).

(21) P. O. Löwdin, *Rep. Nikko Symp. Mol. Phys.*, 113 (1954); *Phys. Rev.*, **97**, 1509 (1955).

the matrix elements has not yet been fully solved. There is consequently good hope that the correlation problem may be solved with a comparatively high accuracy (≈ 0.15 e.v. per electron pair) without a more or less complete configurational interaction.

(f) The United Atom-Model. A Simple Solution of the Many-Electron Problem in Principle.—In the survey given above, it has been pointed out that large difficulties are involved in calculating for instance the two- and many-center integrals occurring in the standard treatments of the molecular problems. In this connection, it could be pointed out that the mathematical problem of the solution of the many-electron Schrödinger equation may be solved, at least in principle, in a very simple way. In order to describe the total wave function, one can select a basic set which is associated with a single center in space and forms a complete set. One set of this type is of the form

$$r^{\mathrm{l}}\, L_{\mathrm{n}+\mathrm{l}+1}^{2\mathrm{l}+2}\,(2\eta r)e^{-\eta r}Y_{\mathrm{lm}}\,(\vartheta,\varphi)$$

where the radial functions are Laguerre polynomials (without principal quantum number in the variable), η is an adjustable effective charge, and the functions Y_{lm} are the ordinary spherical harmonics. The matrix elements of the Hamiltonian of an arbitrary molecular system with respect to this set are easily constructed and evaluated, and, since the total wave function may always be expanded in Slater determinants built up from configurations of the basic set, one may solve the Schrödinger equation by means of "superpositions of configurations." The main problem is apparently to solve the secular equation corresponding to this problem, and this is possible if an electronic computer having sufficiently large capacity is available. With the development of the mathematical machines, one can expect to get higher and higher accuracy in this process, and there are no limitations in principle as to the accuracy obtainable. The essential difference with respect to the conventional methods is that here no many-center integrals are involved and that the matrix elements are easily calculated. Since only a single center is used, the mathematical scheme corresponds to some extent to the "united atom model," which was frequently discussed in the early days of molecular theory. No problem of including the continuum occurs, since the basic set is entirely discrete. It is clear that this model may be successful for molecules having a small extension in space, but that it also may be rather cumbersome and require an enormous number of configurations for describing a large molecule. It may be anticipated that the model should be particularly good for describing the excited states of the Rydberg type.

The choice between the conventional methods using atomic orbitals associated with different nuclei and the one-center model is therefore essentially a choice between the solution of a secular equation of lower order with complicated matrix elements and a secular equation of very high order having simple matrix elements. It is true that, in the one-center model, the basic set has no natural association with the problem itself, but, after having obtained the total wave function, one may transform the result to another basic set—the natural spin-orbitals—which is directly associated with the problem under consideration.

(g) Recent Development of Valence Theory. Density Matrices.—Some simplifications of the valence theory have recently been suggested. In quantum mechanics all physical and chemical quantities are represented by hermitean operators F_{op}, but we note that only the expectation values of these operators

$$<F_{\mathrm{op}}>_{\mathrm{av}} = \int \Psi^* F_{\mathrm{op}}\, \Psi\, (\mathrm{d}x) \qquad (19)$$

are really measurable. For a many-particle system, the operator F_{op} may be expressed in the form

$$F_{\mathrm{op}} = F_{(0)} + \sum_{\mathrm{i}} F_{\mathrm{i}} + \frac{1}{2!}\sum_{\mathrm{ij}}{}' F_{\mathrm{ij}} + \frac{1}{3!}\sum_{\mathrm{ijk}}{}' F_{\mathrm{ijk}} + . \qquad (20)$$

where $F_{(0)}$ is a constant, F_{i} a one-particle operator, F_{ij} a two-particle interaction, F_{ijk} a three-particle interaction, etc. The operator F_{op} is said to be of the order p, if the highest interaction occurring is of this order. It has recently been emphasized[22] that, in order to find the value of (19), it is not necessary to know the wave function in detail but only a certain density matrix of order p of the form

$$\Gamma(\mathbf{x}'_1\mathbf{x}'_2\ldots\mathbf{x}'_{\mathrm{p}}|\mathbf{x}_1\mathbf{x}_2\ldots\mathbf{x}_{\mathrm{p}}) = \binom{N}{p}\int \Psi^*(\mathbf{x}'_1\mathbf{x}'_2..\mathbf{x}'_{\mathrm{p}}\mathbf{x}_{\mathrm{p}+1}..\mathbf{x}_N)\,\Psi(\mathbf{x}_1\mathbf{x}_2..\mathbf{x}_{\mathrm{p}}\mathbf{x}_{\mathrm{p}+1}..\mathbf{x}_N)\,\mathrm{d}x_{\mathrm{p}+1}..\mathrm{d}x_N \qquad (21)$$

This matrix is hermitean and antisymmetric in each set of its indices, and it satisfies further the normalization condition

$$\int \Gamma(\mathbf{x}_1\mathbf{x}_2..\mathbf{x}_{\mathrm{p}}|\mathbf{x}_1\mathbf{x}_2.\ \mathbf{x}_{\mathrm{p}})\mathrm{d}x_1\mathrm{d}x_2..\mathrm{d}x_{\mathrm{p}} = \binom{N}{p} \qquad (22)$$

The expectation value of F_{op} is then given by the formula

$$<F_{\mathrm{op}}>_{\mathrm{av}} = F_{(0)} + \int F_1\,\Gamma(\mathbf{x}'_1|\mathbf{x}_1)\mathrm{d}x_1 + \int F_{12}\Gamma(\mathbf{x}'_1\mathbf{x}'_2|\mathbf{x}_1\mathbf{x}_2)\mathrm{d}x_1\mathrm{d}x_2 + \int F_{123}\Gamma(\mathbf{x}'_1\mathbf{x}'_2\mathbf{x}'_3|\mathbf{x}_1\mathbf{x}_2\mathbf{x}_3)\,\mathrm{d}x_1\mathrm{d}x_2\mathrm{d}x_3 + \ldots, \qquad (23)$$

where, in the integrals, we have introduced the additional convention that the operators F_1, F_{12}, F_{123}, . . . should work only on the unprimed coördinates and that, after the operations have been carried out, we put all $\mathbf{x}'_{\mathrm{i}} = \mathbf{x}_{\mathrm{i}}$. According to (9) and (22), the total energy of a molecular system is for instance given by the expression

$$<H_{\mathrm{op}}>_{\mathrm{av}} = \frac{c^2}{2}\sum_{gh}\frac{Z_{\mathrm{g}}Z_{\mathrm{h}}}{r_{\mathrm{gh}}} + \frac{1}{2m}\int \mathbf{p}_1{}^2\Gamma(\mathbf{x}'_1|\mathbf{x}_1)\mathrm{d}x_1 - e^2\sum_{g} Z_{\mathrm{g}}\int \frac{\Gamma(\mathbf{x}_1|\mathbf{x}_1)}{r_{1\mathrm{g}}}\,\mathrm{d}x_1 + e^2\int \frac{\Gamma(\mathbf{x}_1\mathbf{x}_2|\mathbf{x}_1\mathbf{x}_2)}{r_{12}}\,\mathrm{d}x_1\mathrm{d}x_2 \qquad (24)$$

which implies that the energy and the valence properties are determined already by the density matrix $\Gamma(\mathbf{x}'_1\mathbf{x}'_2 \mid \mathbf{x}_1\mathbf{x}_2)$ of the second order and that it is not necessary to know the total wave function $\Psi(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \ldots \mathbf{x}_N)$ of all N coördinates. The first term in (23) is the internuclear repulsion energy, the second is the kinetic energy of the electrons, the third

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(22) P. O. Löwdin, *Phys. Rev.*, **97**, 1474 (1955); R. McWeeny, *Proc. Roy. Soc. (London)*, **A232**, 114 (1955).

represents the interaction energy between the electrons and the nuclei, whereas the last one is the interelectronic repulsion energy.

The density matrix of order $p = N$ is defined by the relation

$$\Gamma(\mathbf{x}'_1\mathbf{x}'_2\ldots\mathbf{x}'_N|\mathbf{x}_1\mathbf{x}_2\ldots\mathbf{x}_N) = \\ = \Psi^*(\mathbf{x}'_1\mathbf{x}'_2\ldots\mathbf{x}'_N)\Psi(\mathbf{x}_1\mathbf{x}_2\ldots\mathbf{x}_N) \quad (25)$$

and the lower order density matrices may then be found successively by integration

$$\Gamma(\mathbf{x}'_1\mathbf{x}'_2\ldots\mathbf{x}'_{p-1}|\mathbf{x}_1\mathbf{x}_2\ldots\mathbf{x}_{p-1}) = \\ = \frac{p}{N-p+1}\int\Gamma(\mathbf{x}'_1\mathbf{x}'_2\ldots\mathbf{x}'_{p-1}\mathbf{x}_p|\mathbf{x}_1\mathbf{x}_2\ldots\mathbf{x}_{p-1}\mathbf{x}_p)\,dx_p \quad (26)$$

It would also be of interest to investigate the *reverse* problem and to see how much the knowledge of a lower-order density matrix ($p < N$) would determine the higher-order density matrices and the wave function. This problem is far from being solved and only a few special cases have been treated up till now.

It has been shown[21] that, in the Hartree–Fock scheme where the total wave function is approximated by a single Slater determinant, the first-order density matrix $\Gamma(\mathbf{x}'_1 | \mathbf{x}_1)$ fulfills the two basic relations

$$\Gamma^2 = \Gamma, \text{ trace }\{\Gamma\} = N \quad (27)$$

and that it further determines also all the higher-order density matrices according to the formula

$$\Gamma(\mathbf{x}'_1\mathbf{x}'_2\ldots\mathbf{x}'_p|\mathbf{x}_1\mathbf{x}_2\ldots\mathbf{x}_p) = \frac{1}{p!}\det\{\Gamma(\mathbf{x}'_i|\mathbf{x}_j)\} \quad (28)$$

where the determinant is of order p. This result implies that, in the molecular orbital treatment of for instance the ground state of a molecule, it would be possible to determine all chemical properties without the explicit knowledge of the individual molecular orbitals, since $\Gamma(\mathbf{x}'_1 | \mathbf{x}_1)$ describes entirely the quantum-mechanical situation. A practical method for the direct calculation of the first-order density matrix has also been constructed.[23] It should be observed, however, that the simple relation (28) is not valid in higher approximations than the Hartree–Fock scheme.

It would certainly be worthwhile to investigate under which conditions the variation principle (10) may be formulated in terms of the second-order density matrix $\Gamma(\mathbf{x}'_1\mathbf{x}'_2 | \mathbf{x}_1\mathbf{x}_2)$ instead of the wave function.[24] In this connection we note that not all hermitean matrices $f(\mathbf{x}'_1\mathbf{x}'_2\ldots\mathbf{x}'_p | \mathbf{x}_1\mathbf{x}_2\ldots\mathbf{x}_p)$ with the correct antisymmetry and normalization properties are necessarily density matrices and that, for instance for $p = N$, a necessary and sufficient condition for the existence of the product form (25) is expressed by the relation

$$\frac{\Gamma(\mathbf{x}'_1\mathbf{x}'_2\ldots\mathbf{x}'_N|\boldsymbol{\alpha}_1\boldsymbol{\alpha}_2\ldots\boldsymbol{\alpha}_N)\Gamma(\boldsymbol{\alpha}_1\boldsymbol{\alpha}_2\ldots\boldsymbol{\alpha}_N|\mathbf{x}_1\mathbf{x}_2\ldots\mathbf{x}_N)}{\Gamma(\alpha_1\alpha_2\ldots\alpha_N|\alpha_1\alpha_2\ldots\alpha_N)} = \\ = \Gamma(\mathbf{x}'_1\mathbf{x}'_2\ldots\mathbf{x}'_N|\mathbf{x}_1\mathbf{x}_2\ldots\mathbf{x}_N), \quad (29)$$

for arbitrary values of the parameters $\boldsymbol{\alpha}_1, \boldsymbol{\alpha}_2, \ldots \boldsymbol{\alpha}_N$. In a two-electron system, the second-order density matrix must therefore be varied subject to the condition (29) for $N = 2$, which is a rather severe restriction. It remains to investigate the auxiliary conditions which may exist for many-electron systems with $N \geq 2$.

There seems to be no question that the density matrix formalism renders a considerable simplification of the quantum theory of many-particle systems. It emphasizes such points as are of essential physical and chemical interests, and it avoids such concepts and ideas, which are of a more artificial or conventional type, as for instance different types of basic orbitals. However, the orbital idea itself is certainly useful, and we will now discuss how it may be preserved and utilized in connection with the density matrices.

(h) **Natural Spin-orbitals.**—The idea of the existence of certain spin-orbitals is of essential importance in describing atomic and molecular systems, since it gives a high degree of simplicity and visuality to the theoretical explanation of a great deal of physical and chemical experimental experience. The idea goes back to classical quantum mechanics, where it was assumed that each electron occupies its own fully specified quantum state, and we will now discuss whether it is possible to maintain this basic idea also in a more exact theory taking the interelectronic repulsion and correlation into full account.

Another reason for the introduction of spin-orbitals is of a more mathematical nature and depends on the fact that, if we introduce a complete orthonormal set of one-electron functions $\psi_k(\mathbf{x})$, it is possible to expand an arbitrary antisymmetric wave function $\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots \mathbf{x}_N)$ as an infinite sum of Slater determinants built up from this set

$$\Psi(\mathbf{x}_1,\mathbf{x}_2,\ldots\mathbf{x}_N) = \sum_{\mathrm{K}} C_{\mathrm{K}}\Psi_{\mathrm{K}}(\mathbf{x}_1,\mathbf{x}_2,\ldots\mathbf{x}_N), \\ \Psi_{\mathrm{K}}(\mathbf{x}_1,\mathbf{x}_2,\ldots\mathbf{x}_N) = (N!)^{-1/2}\det\{\psi_{k_1}, \psi_{k_2}, \ldots\psi_{k_N}\} \quad (30)$$

where the sum should be taken over all ordered configurations K, *i.e.*, over all selections of N indices $k_1 < k_2 < \ldots < k_N$. The coefficients C_{K} for an eigenfunction may in principle be determined by the variation principle, which leads to the linear system (14) and the secular equation 15; this is the method we have previously mentioned under the name of "configurational interaction." In the different approaches to a molecular quantum theory, one has hoped to obtain good accuracy with only one or a few terms included in the expansion (30) and, for this purpose, one has chosen different basic sets of spin-orbitals: atomic orbitals, molecular orbitals and so on. A survey is given in Fig. 5, showing also the main advantages of the different descriptions.

If the basic set is not properly chosen, the series of determinants in (30) may be very slowly convergent with a corresponding difficulty in interpreting the results. In this connection, it seems therefore natural to ask whether there exists any basic set of spin-orbitals $\chi_k(\mathbf{x})$ which leads to the most "rapid convergency" in the expansion of the wave function $\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots \mathbf{x}_N)$ for a specific state.[25] The answer may be found by a consideration[26] of the first-order density matrix defined by (21) for $p = 1$

$$\Gamma(\mathbf{x}'_1|\mathbf{x}_1) = N\int\Psi^*(\mathbf{x}'_1\mathbf{x}_2\ldots\mathbf{x}_N)\Psi(\mathbf{x}_1\mathbf{x}_2\ldots\mathbf{x}_N)\,dx_2\ldots dx_N \quad (31)$$

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[23] R. McWeeny, *Proc. Roy. Soc.* (*London*), **A235**, 496 (1956).

[24] J. E. Mayer, *Phys. Rev.*, **100**, 1579 (1955).

[25] J. C. Slater, *ibid.*, **81**, 385 (1951).

[26] P. O. Löwdin, *ibid.*, **97**, 1474 (1955).

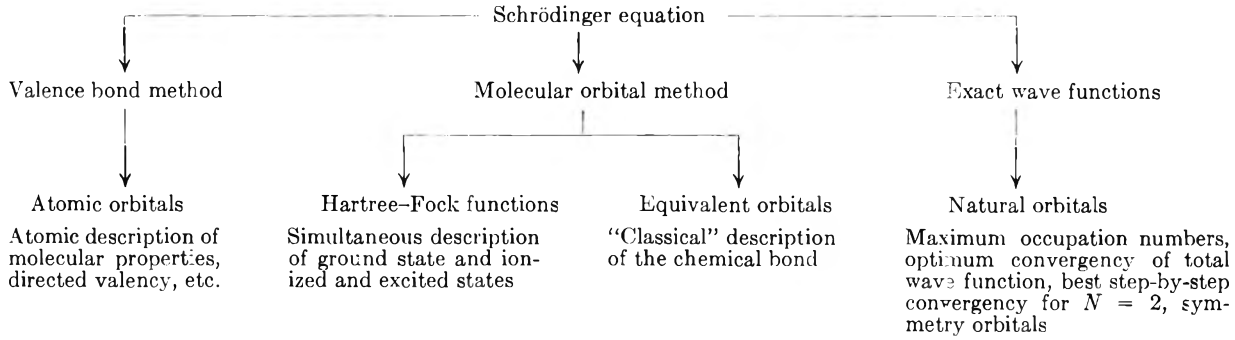

Fig. 5.—Development of the orbital idea in quantum chemistry.

By using the arbitrary complete orthonormal set $\psi_k(\mathbf{x})$, this matrix may be expressed in the form

$$\Gamma(\mathbf{x}'_1|\mathbf{x}_1) = \sum_{kl} \psi^*_k(\mathbf{x}'_1)\psi_l(\mathbf{x}_1)\gamma_{lk} \qquad (32)$$

where the coefficients γ_{lk} form an hermitean matrix, which may be found from the coefficients C_K by substituting (30) into (31). For the diagonal elements, we obtain the simple formula

$$\gamma_{kk} = \sum_{K}^{(k)} |C_K|^2 \qquad (33)$$

where the summation should be carried out over all configurations K containing the specific index k. The element γ_{kk} may be interpreted as the *occupation number* for the spin-orbital $\psi_k(\mathbf{x})$, and we note that it depends only on the given state characterized by $\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots \mathbf{x}_N)$ and the orbital $\psi_k(\mathbf{x})$ under consideration. By combining (31) and (32), we obtain the explicit formula

$$\begin{aligned}\gamma_{kk} &= \int \psi_k(\mathbf{x}'_1)\Gamma(\mathbf{x}'_1|\mathbf{x}_1)\psi^*_k(\mathbf{x}_1)dx'_1dx_1 = \\ &= N\int \psi_k(\mathbf{x}'_1)\Psi^*(\mathbf{x}'_1\mathbf{x}_2\ldots\mathbf{x}_N)\psi^*_k(\mathbf{x}_1)\Psi(\mathbf{x}_1\mathbf{x}_2\ldots\mathbf{x}_N) \\ &\qquad dx'_1dx_1dx_2\ldots dx_N \qquad (34)\end{aligned}$$

The occupation numbers γ_{kk} have simple properties. The normalization condition (5) gives $\Sigma_K |C_K|^2 = 1$, and (33) leads then to the inequality

$$0 \leqq \gamma_{kk} \leqq 1 \qquad (35)$$

showing that there is never more than one electron in any chosen spin-orbital. This theorem follows from the antisymmetry property and is an expression for Pauli's exclusion principle. In the naive formulation of this principle, each spin-orbital could be occupied by a full electron which then would exclude any other electron from entering the same orbital. This model has the advantage of a high degree of physical visuality, and, in order to approach it as much as possible, we will now introduce the basic orthonormal set $\chi_1, \chi_2, \chi_3, \ldots$ which has *maximum occupation numbers*.

Let $\mathbf{U}$ be the unitary matrix which brings the hermitean matrix γ_{lk} to diagonal form

$$\mathbf{U}^+\gamma\mathbf{U} = \mathbf{n} = \text{diagonal matrix} \qquad (36)$$

Introducing the set χ by the matrix formula $\chi = \psi\mathbf{U}$ or

$$\chi_k = \sum_\alpha \psi_\alpha U_{\alpha k} \qquad (37)$$

we obtain $\gamma = \mathbf{UnU}^+$, $\psi = \chi\mathbf{U}^+$, and finally

$$\Gamma(\mathbf{x}'_1|\mathbf{x}_1) = \sum_k \chi^*_k(\mathbf{x}'_1)\chi_k(\mathbf{x}_1)n_k \qquad (38)$$

The basic set χ defined by (37) has thus the occupation numbers n_k, and the extremum properties follow then immediately from the fact that $n_1, n_2, n_3, \ldots$ (with $n_1 \geq n_2 \geq n_3 \ldots$) are the *eigenvalues* of the matrix γ_{lk}.

The functions $\chi_1, \chi_2, \chi_3, \ldots$ will in the following be called the *natural spin-orbitals* associated with the state under consideration. The first function χ_1 is the spin-orbital which has the highest occupation number possible, the second function χ_2 has the same property within the class of orbitals orthogonal to χ_1, the third function has the same property within the class of orbitals orthogonal to χ_1 and χ_2, etc.

If the relation $\psi = \chi\mathbf{U}^+$ is substituted into (30), we obtain an expansion of Ψ into configurations of the natural spin-orbitals

$$\Psi(\mathbf{x}_1,\mathbf{x}_2,\ldots\mathbf{x}_N) = (N!)^{-1/2}\sum_{\mathrm{K}} A_K \det\{\chi_{k1}, \chi_{k2}, \ldots \chi_{kN}\} \qquad (39)$$

which will be called the *natural expansion*. This series is characterized by a most "rapid convergency" in the following sense: according to an elementary theorem[27] for the eigenvalues of an hermitean matrix, the sum of the r highest eigenvalues is always larger than the sum of any r diagonal elements, which gives

$$\sum_{k=1}^{r} n_k \geq \sum_{k=(1)}^{(r)} \gamma_{kk} \qquad (40)$$

By using (33) and (39), we then obtain

$$\sum_{k=1}^{r}\sum_{\mathrm{K}}^{(k)} |A_K|^2 \geq \sum_{k=(1)}^{(r)}\sum_{K}^{(k)} |C_K|^2 \qquad (41)$$

which expresses the optimum convergency property of the natural expansion.

The natural spin-orbitals are *symmetry orbitals*. This important property may be used for separating the σ- and π-electrons in an exact theory for the conjugated organic compounds, for an exact formulation of the band theory for crystals, etc.

The case of two electrons ($N = 2$) is of particular importance for the understanding of the chemical bond and has been analyzed in greater detail.[28] It has been shown that, in this case, the natural expansion of the total wave function $\Psi(\mathbf{x}_1, \mathbf{x}_2)$ has another important optimum convergency property in addition to (41). If the natural expansion is interrupted after r terms the renormalized function

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(27) This theorem is easily derived from the separation theorems given *e.g.*, in J. K. L. MacDonald, *Phys. Rev.*, **43**, 830 (1933).

(28) P. O. Löwdin and H. Shull, *ibid.*, **101**, 1730 (1956).

Ψ_r has the smallest total quadratic deviation from the exact solution.

$$\int |\Psi - \Psi_r|^2 \, dx_1 dx_2 \qquad (42)$$

of all functions built up by configurations selected from a finite basic set $\psi_1, \psi_2, \ldots \psi_r$ of order r. The result implies that χ_1 is closely related to but not identical with the corresponding Hartree–Fock function.

Detailed calculations on the ground state of the helium atom have given the following occupation numbers for the first three natural spin-orbitals

$$n_1 = 0.99562, n_2 = 0.00431, n_3 = 0.00007 \qquad (43)$$

The result shows how the coulomb repulsion is breaking up the closed shell $(1s)^2$, since it is energetically cheaper to have a small fraction of the electron in χ_1 excited to the higher spin-orbitals χ_2 and χ_3. Similar calculations for the ground state of the hydrogen molecule are now in progress, and we hope that they will lead to a simple but at the same time accurate treatment of the covalent bond.

The measurements in modern chemistry are now so refined that a very high degree of accuracy is needed in the corresponding theories. In quantum mechanics good methods have been worked out for determining eigenvalues, *i.e.*, total energies E, but unfortunately the chemists and physicists are usually measuring only energy differences ΔE which are very small fractions of the total quantities. This implies that rough models are no longer sufficient and that, in many cases, not even the Hartree–Fock scheme has a high enough accuracy. The problem of the electronic correlation has thus become of great importance, but it seems as if the introduction of density matrices and natural spin-orbitals would prevent the theory from becoming too complicated in its mathematical form to be given a simple physical and chemical interpretation.

Goal of Quantum Chemistry.—It is sometimes said that a theoretician is a person who knows how to solve a problem, but who cannot do it. This remark is certainly true concerning the quantum chemists since it is pointed out above that we know several ways of solving the many-electron Schrödinger equation in principle, but that there are large difficulties in carrying out these solutions. The difficulties are therefore transformed from the purely mathematical plane to a plane where both mathematics and numerical technique are involved. Unfortunately this does not mean that the problem has been solved or even essentially simplified, since numerical technique is a domain which requires just as much ingenuity as pure mathematics. The development of the modern electronic computers may here be of fundamental importance.

The problems involved in quantum chemistry are comparatively hard, and the scientists working within this field have therefore found it desirable to arrange a series of international conferences in order to get a common attack on all these problems (Shelter Island 1951, Nikko 1953, Stockholm-Uppsala 1955, Austin 1955). The arrangements of these symposia have greatly helped the development of molecular theory, but, since there is an extremely small number of quantum chemists in relation to the total number of chemists, it will probably take a considerable time before even the more fundamental problems of chemistry have been thoroughly treated by quantum mechanical methods. Today there is therefore no answer to the question whether the above-mentioned drastic extrapolation from $N = 2$ to an arbitrary N is justified or not, but so far there have not been any essential objections to it, and we have thus good reasons for believing that the many-electron Schrödinger equation in configuration space is the correct basis for the description of molecular or solid-state systems.

There seems to be a rather long way to go before we reach the mathematical goal of quantum chemistry, which is to be able to predict accurately the properties of a hypothetic polyatomic molecule before it has been synthesized in the laboratories. The aim is also to obtain such knowledge of the electronic structure of matter that one can construct new substances having properties of particular value to mankind. To learn to think in terms of electrons and their quantum mechanical behavior is probably of greater technical importance than we can now anticipate. We have further shown that quantum mechanics is necessary to understand the covalent bond, and there is certainly no doubt that the tool of quantum mechanics will appear to be more and more fundamental for the discussion of chemical problems in general. It seems therefore urgent to incorporate the language and technique of quantum mechanics in the domain of chemistry, and particularly to find the correct electronic interpretations of the ordinary chemical phenomena. Many important qualitative and quantitative problems remain here to be solved.

THE SOLVENT EXTRACTION BEHAVIOR OF INORGANIC COMPOUNDS.[1]
II. GENERAL EQUATIONS

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A general expression is obtained for the distribution quotient, D, of a metal halide between an aqueous hydrohalic acid phase and an organic solvent. Cationic, neutral, anionic, and polymeric (associated) metal halide species are considered. The variations in this quotient with changes in concentration of the halide ion, of the hydrogen ion, of other halide salt, and of other strong acid, as well as of total metal halide, are also given. With increasing concentration of one of these substances, the value of D varies in such a way as to favor that phase in which the average metal-containing species contains more of that substance, *i.e.*, more metal, halide or hydrogen ion. But even when the same metal halide species exists in both phases, D may still vary through a "common ion" effect. For example, D may vary with total metal concentration even when only the same ionic metal-containing species exists in both phases, if another substance with a common ion is present, and the common ion from it dominates one, but only one, phase.

In a previous paper[2] the gross extraction behavior of molybdenum(VI) from aqueous acid solutions into a variety of organic solvents has been discussed and four processes involved in such acid–metal halide extraction systems have been suggested. These are (1) association and polymerization of the metal species in either, or both, phases, and consequent dependence of the extraction on the metal ion concentration; (2) possible acid ionization of the metal species, and hence dependence of the extraction on hydrogen ion and thus on all other acid species present; (3) complex formation with halide ion, and consequent dependence of the extraction on halide ion concentration and thus on all other species present capable of dissociating into such ions; (4) solvation and hydration in the two phases, and consequent dependence on the specific nature of the solvent. The purpose of this paper is to give general equations applicable to such systems, and to discuss various possible special cases. A treatment of the problem has recently been given by Irving, Rossotti and Williams,[3] but with a different formulation, and a quite different interpretation of the results. The present treatment follows that suggested by J. Saldick,[4] and represents an extension to a more general system and a physical interpretation.[5] Two papers to follow will treat the first three factors above in greater detail using the molybdenum(VI) system specifically as an illustration. The effects of solvation and of the specific nature of the solvents cannot be handled mathematically and will be ignored in this paper, but these will be treated in a qualitative manner in the papers dealing with actual extraction systems. The justification for this procedure is that actual systems do show the effects predicted by the equations derived below, and that variation in the extraction behavior with a change in organic solvent can be predicted qualitatively from a knowledge of certain of the properties of the solvents.

An ideal system of two completely immiscible phases, an aqueous hydrohalic acid and an organic solvent, and a minimum number of representative examples of cationic, neutral and anionic metal-containing species will be considered. As components we shall take the metal halide, MX,[6] the hydrogen halide, HX, a non-complexing acid, HZ, and an inert halide salt, AX, with the following possible species present in each phase

Aqueous phase: M^+, MX, MX_2^-, HMX_2, M_2X_2, H^+, X^-, Z^-, A^+

Organic phase: M^+, MX, MX_2^-, HMX_2, M_2X_2, AMX_2, H^+, X^-, Z^-, A^+, HX, HZ, AX

M^+, MX and MX_2^- represent typical cationic, neutral and anionic metal-containing species, respectively; HMX_2 represents a species which is a weak acid, or an ion pairing between H^+ and MX_2^- in the organic solvent; M_2X_2 represents a dimeric (polymeric) species, but also in the organic phase stands for ion-triplets and higher ion associations; AMX_2, HX, HZ and AX in the organic phase represent neutral species, either true molecules or ion-pairs.

The partition of the metal halide between the two phases is given by the distribution quotient, D

$$D = \frac{\text{metal concn. in organic phase}}{\text{metal concn. in aqueous phase}}$$

$$D = \frac{(M)_0 + (MX)_0 + (MX_2)_0 + (HMX_2)_0 + (AMX_2)_0 + 2(M_2X_2)_0}{(M) + (MX) + (MX_2) + (HMX_2) + 2(M_2X_2)} \qquad (1)$$

where $(\ )_0$ represents concentration in the organic phase and $(\ \ )$ that in the aqueous phase. Leaving out charges on the ions for simplicity, the distribution of the species M^+ between the phases can be represented by the expression

$$\alpha_{MX}(M)(X) = (M)_0(X)_0$$

where α is the concentration "constant" for the equilibrium involved. Similarly

$$\begin{aligned}
\alpha_{H,MX_2}(H)(MX_2) &= (H)_0(MX_2)_0\\
\alpha_{A,MX_2}(A)(MX_2) &= (A)_0(MX_2)_0\\
\alpha_{HX}(H)(X) &= (H)_0(X)_0\\
\alpha_{HZ}(H)(Z) &= (H)_0(Z)_0\\
\alpha_{AX}(A)(X) &= (A)_0(X)_0
\end{aligned} \qquad (2)$$

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[1] Supported in part by the joint program of the Office of Naval Research and the Atomic Energy Commission. The right to reproduce in whole or in part is granted to the U. S. Government.

[2] I. Nelidow and R. M. Diamond, THIS JOURNAL, **59**, 710 (1955).

[3] H. Irving, F. J. C. Rossotti and R. J. P. Williams, *J. Chem. Soc.*, 1906 (1955).

[4] J. Saldick, Abstracts of the 126th National Meeting of the American Chemical Society, New York, N. Y., September, 1954.

[5] Saldick has since published a more detailed treatment, J. Saldick, THIS JOURNAL, **60**, 500 (1956), but not for as general a system as in the present work.

[6] The choice of unipositive M^+ as the metal ion is for simplicity's sake and not to indicate that unipositive ions extract easily. They do not. For reasons to be discussed in a later paper, certain complex ions of some tripositive and dipositive metals extract most readily.

and for the association equilibria in the aqueous phase

$$\begin{aligned} &\beta_{\mathrm{MX}}(\mathrm{M})(\mathrm{X}) = (\mathrm{MX}) \\ &\beta_{\mathrm{MX_2}}(\mathrm{M})(\mathrm{X})^2 = (\mathrm{MX_2}) \\ &\beta_{\mathrm{M_2X_2}}(\mathrm{M})^2(\mathrm{X})^2 = (\mathrm{M_2X_2}) \\ &\beta_{\mathrm{H.MX_2}}(\mathrm{H})(\mathrm{MX_2}) = (\mathrm{HMX_2}) \end{aligned} \qquad (3)$$

and for the association equilibria in the organic phase

$$\begin{aligned} &\delta_{\mathrm{MX}}(\mathrm{M})_0(\mathrm{X})_0 = (\mathrm{MX})_0 \\ &\delta_{\mathrm{H.MX_2}}(\mathrm{H})_0(\mathrm{MX_2})_0 = (\mathrm{HMX_2})_0 \\ &\delta_{\mathrm{A.MX_2}}(\mathrm{A})_0(\mathrm{MX_2})_0 = (\mathrm{AMX_2})_0 \\ &\delta_{\mathrm{M_2X_2}}(\mathrm{M})_0{}^2(\mathrm{X})_0{}^2 = (\mathrm{M_2X_2})_0 \end{aligned} \qquad (4)$$

so

$$D = \frac{\left(\begin{aligned} &\alpha_{\mathrm{MX}}(\mathrm{M})\frac{(\mathrm{X})}{(\mathrm{X})_0} + \delta_{\mathrm{MX}}\alpha_{\mathrm{MX}}(\mathrm{M})(\mathrm{X}) + \alpha_{\mathrm{H.MX_2}}\beta_{\mathrm{MX_2}}(\mathrm{M})(\mathrm{X})^2\frac{(\mathrm{H})}{(\mathrm{H})_0} + \delta_{\mathrm{H.MX_2}}\alpha_{\mathrm{H.MX}}\beta_{\mathrm{M_2X}}(\mathrm{H})(\mathrm{M})(\mathrm{X})^2 + \\ &\qquad \delta_{\mathrm{A.MX_2}}\alpha_{\mathrm{A.MX_2}}\beta_{\mathrm{MX_2}}(\mathrm{A})(\mathrm{M})(\mathrm{X})^2 + 2\delta_{\mathrm{M_2X_2}}\alpha^2{}_{\mathrm{MX}}(\mathrm{M})^2(\mathrm{X})^2 \end{aligned}\right)}{(\mathrm{M}) + \beta_{\mathrm{MX}}(\mathrm{M})(\mathrm{X}) + \beta_{\mathrm{MX_2}}(\mathrm{M})(\mathrm{X})^2 + \beta_{\mathrm{H.MX_2}}\beta_{\mathrm{MX_2}}(\mathrm{H})(\mathrm{M})(\mathrm{X})^2 + 2\beta_{\mathrm{M_2X_2}}(\mathrm{M})^2(\mathrm{X})^2} \qquad (5)$$

From this expression it can be seen that, if the average metal-containing species in the organic phase has more hydrogen, metal or halogen than the average metal-containing species in the aqueous phase, the value of D will increase with increasing (H), (M) or (X), respectively, and decreasing $(\mathrm{H})_0$ or $(\mathrm{X})_0$. D will decrease with increasing (H), (M) or (X) and decreasing $(\mathrm{H})_0$ or $(\mathrm{X})_0$ if the average metal-containing species in the organic phase has less hydrogen, metal or halogen than that in the corresponding aqueous phase. Furthermore, since the concentration of hydrogen, metal or halide ion involved is the total concentration in that phase, from whatever source, a variation in D may result even when the average metal-containing species in the two phases are the same. For if the metal halide species involved are ionic, D may depend upon the concentration of $\mathrm{M^+}$, $\mathrm{H^+}$ or $\mathrm{X^-}$, or even on foreign ions (such as $\mathrm{A^+}$ and $\mathrm{Z^-}$ in the present system), through what shall hereafter be called a common ion effect. This is true whenever the co-ion of an ionic metal-containing species is also the co-ion of some other species present in excess in one, either one, but only one, of the phases. For example, D may depend on (M) even though no dimers are present in either phase. If the only metal-containing species is $\mathrm{M^+}$ in both phases, an inverse dependence of D on $(\mathrm{M})^{1/2}$ would result if the acid HX were very soluble and highly dissociated in the aqueous phase and very little so in the organic phase, *i.e.*, $(\mathrm{M}) << (\mathrm{H}) \approx (\mathrm{X})$ and $(\mathrm{X})_0 \approx (\mathrm{M})_0 >> (\mathrm{H})_0$. Conversely, if HX were very soluble and highly dissociated in the organic phase and poorly so in the aqueous phase, so that $(\mathrm{X}) \approx (\mathrm{M}) >> (\mathrm{H})$ and $(\mathrm{M_0}) << (\mathrm{H})_0 \approx (\mathrm{X_0})$, D would vary directly with $(\mathrm{M})^{1/2}$, not inversely. Such behavior follows from $\alpha_{\mathrm{MX}}(\mathrm{M})(\mathrm{X}) = (\mathrm{M})_0 \cdot (\mathrm{X})_0$ with either (X) or $(\mathrm{X_0})$, but not both, a constant by virtue of being furnished in large excess by another substance, $\mathrm{H^+X^-}$. This effect does not require that the $\mathrm{H^+X^-}$ exist in both phases, in fact, the effect would be maximal if $\mathrm{H^+X^-}$ did not exist in one phase. If there were no ionized HX in the organic phase, the metal distribution quotient would show an inverse dependence on $(\mathrm{M})^{1/2}$ at all concentrations up to where the aqueous $\mathrm{M^+X^-}$ concentration approached that of the $\mathrm{H^+X^-}$.

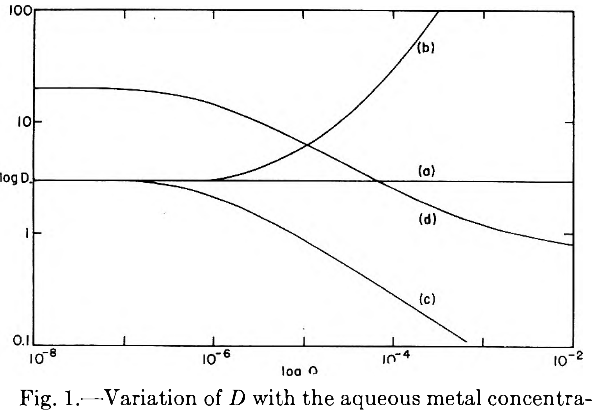

Fig. 1.—Variation of D with the aqueous metal concentration, Q: (a) no dimers present in either phase, and no ionic metal-containing species in the organic solvent, only MX and $\mathrm{HMX_2}$ in the organic phase, and $\mathrm{M^+}$, MX, $\mathrm{MX_2^-}$, $\mathrm{HMX_2}$ in the aqueous one; (b) same species as in (a), but dimers also allowed in the organic phase; (c) same species as in (a) but dimers in the aqueous phase; (d) same species as in (a), but $\mathrm{MX_2^-}$ also possible in the organic phase and $\alpha_{\mathrm{H.MX_2}} \gg \alpha_{\mathrm{HX}}$.

The distribution ratio for $\mathrm{M^+X^-}$ is similarly dependent upon the concentration of any other substance which has the co-ion $\mathrm{X^-}$ (represented in this model system by $\mathrm{A^+X^-}$). But it is also dependent on the concentration of substances which have no common ion with $\mathrm{M^+X^-}$, but contain a cation common to a substance which does contain $\mathrm{X^-}$ (illustrated by $\mathrm{H^+Z^-}$ in our model system). A similar situation occurs for the anionic metal-containing species, $\mathrm{MX_2^-}$. Obviously this can lead to a complicated dependence of D on a variety of ions.

To show this dependence explicitly, the concentrations of hydrogen and halide ions in the organic phase, $(\mathrm{H})_0$ and $(\mathrm{X})_0$, must be expressed in terms of aqueous phase variables. Hydrogen ion occurs in the organic phase through the dissociation of HX, HZ and $\mathrm{HMX_2}$, halide ion through the dissociation of HX, MX and AX. To eliminate $(\mathrm{H})_0$ and $(\mathrm{X})_0$ from eq. 5, use may be made of eq. 2 and the requirement of electrical neutrality in the organic phase

$$(\mathrm{H})_0 + (\mathrm{A})_0 + (\mathrm{M})_0 = (\mathrm{X})_0 + (\mathrm{Z})_0 + (\mathrm{MX_2})_0$$

$$(\mathrm{H})_0 + \frac{\alpha_{\mathrm{AX}}}{\alpha_{\mathrm{HX}}}(\mathrm{A})\frac{(\mathrm{H})_0}{(\mathrm{H})} + \frac{\alpha_{\mathrm{MX}}}{\alpha_{\mathrm{HX}}}(\mathrm{M})\frac{(\mathrm{H})_0}{(\mathrm{H})} = \alpha_{\mathrm{HX}}(\mathrm{X})\frac{(\mathrm{H})}{(\mathrm{H})_0} + \alpha_{\mathrm{HZ}}(\mathrm{Z})\frac{(\mathrm{H})}{(\mathrm{H})_0} + \alpha_{\mathrm{H.MX_2}}(\mathrm{MX_2})\frac{(\mathrm{H})}{(\mathrm{H})_0}$$

giving

$$(\mathrm{H})_0 = \sqrt{\alpha_{\mathrm{HX}}}\,(\mathrm{H})\sqrt{\frac{\alpha_{\mathrm{HX}}(\mathrm{X}) + \alpha_{\mathrm{HZ}}(\mathrm{Z}) + \alpha_{\mathrm{H.MX_2}}\beta_{\mathrm{MX_2}}(\mathrm{M})(\mathrm{X})^2}{\alpha_{\mathrm{HX}}(\mathrm{H}) + \alpha_{\mathrm{AX}}(\mathrm{A}) + \alpha_{\mathrm{MX}}(\mathrm{M})}} \qquad (6)$$

$$(\mathrm{X})_0 = \sqrt{\alpha_{\mathrm{HX}}}\,(\mathrm{X})\sqrt{\frac{\alpha_{\mathrm{HX}}(\mathrm{H}) + \alpha_{\mathrm{AX}}(\mathrm{A}) + \alpha_{\mathrm{MX}}(\mathrm{M})}{\alpha_{\mathrm{HX}}(\mathrm{X}) + \alpha_{\mathrm{HZ}}(\mathrm{Z}) + \alpha_{\mathrm{H.MX_2}}\beta_{\mathrm{MX_2}}(\mathrm{M})(\mathrm{X})^2}}$$

With the substitution of these two expressions in eq. 5

$$D = \frac{\dfrac{\alpha_{MX}}{\sqrt{\alpha_{HX}}}(M)\sqrt{\dfrac{\alpha_{HX}(X) + \alpha_{HZ}(Z) + \alpha_{H.MX_2}\beta_{MX_2}(M)(X)^2}{\alpha_{HX}(H) + \alpha_{AX}(A) + \alpha_{MX}(M)}} + \delta_{MX}\alpha_{MX}(M)(X) + \dfrac{\alpha_{H.MX_2}\beta_{MX_2}}{\sqrt{\alpha_{HX}}}(M)(X)^2\sqrt{\dfrac{\alpha_{HX}(H) + \alpha_{AX}(A) + \alpha_{MX}(M)}{\alpha_{HX}(X) + \alpha_{HZ}(Z) + \alpha_{H.MX_2}\beta_{MX_2}(M)(X)^2}} + \delta_{H.MX_2}\alpha_{H.MX_2}\beta_{MX_2}(H)(M)(X)^2 + \delta_{A.MX_2}\alpha_{A.MX_2}\beta_{MX_2}(A)(M)(X)^2 + 2\delta_{M_2X_2}\alpha^2_{MX}(M)^2(X)^2}{(M) + \beta_{MX}(M)(X) + \beta_{MX_2}(M)(X)^2 + \beta_{H.MX_2}\beta_{MX_2}(H)(M)(X)^2 + 2\beta_{M_2X_2}(M)^2(X)^2} \quad (7)$$

Consider now the variation of D with changes in the concentration of the various aqueous ions. This can perhaps best be seen by taking the partial derivatives of the logarithm of D with respect to the logarithms of the concentrations of the ions of interest, especially since the experimental data to be presented in following papers is most readily displayed in this fashion.

1. Variation of D with Metal Concentration.—Let the denominator in eq. 7, the metal concentration in the aqueous phase, be Q, the numerator be P, so that $D = P/Q$. Then

$$\frac{\partial \log D}{\partial \log Q} = \frac{\partial \log P}{\partial \log (M)} \Big/ \frac{\partial \log Q}{\partial \log (M)} - 1 = \frac{(M)}{P}\frac{\partial P}{\partial (M)} \Big/ \frac{(M)}{Q}\frac{\partial Q}{\partial (M)} - 1 =$$

$$\frac{(f^\circ_{M^+} - f^\circ_{MX_2^-})\dfrac{1}{2}\left(\dfrac{\alpha_{H.MX_2}(MX_2)}{\alpha_{HX}(X) + \alpha_{HZ}(Z) + \alpha_{H.MX_2}(MX_2)} - \dfrac{\alpha_{MX}(M)}{\alpha_{HX}(H) + \alpha_{AX}(A) + \alpha_{MX}(M)}\right) + f^\circ_{M_2X_2} - f_{M_2X_2}}{1 + f_{M_2X_2}} \quad (8)$$

The $f°$'s are the fractions of the total metal concentration in the organic phase represented by the species indicated by subscripts, and the f's are the fractions of the total aqueous metal concentration represented by the species similarly indicated. The $f°$'s and f's are, of course, themselves functions of the concentrations of H^+, M^+, A^+, X^-, Z^-, *i.e.*

$$f^\circ_{M^+} = \frac{\alpha_{MX}}{\sqrt{\alpha_{HX}}}(M)\sqrt{\frac{\alpha_{HX}(X) + \alpha_{HZ}(Z) + \alpha_{H.MX_2}(MX_2)}{\alpha_{HX}(H) + \alpha_{AX}(A) + \alpha_{MX}(M)}} \Big/ P$$

From (8) it can be seen that if the only species present in the organic phase are neutral molecules and there are no dimers in either phase ($f^\circ_{MX} + f^\circ_{HMX_2} = 1, f^\circ_{M_2X_2} = f_{M_2X_2} = 0$), the plot of log D *vs.* log Q will be a straight line of zero slope (Fig. 1a). If dimers can exist in the organic phase, $\partial \log D/\partial \log Q = f^\circ_{M_2X_2}$ and a plot of log D *vs.* log Q will be a curve with a slope going from 0 at very low Q to $+1$ at high Q where $f^\circ_{M_2X_2} \rightarrow 1$, that is, where the metal-containing species is predominantly in the dimeric form (Fig. 1b). Of course, a larger slope would result from higher order polymerization or ion association in the organic phase. In the specialized system chosen here, $(M_2X_2)_0$ stands for not only true molecular dimerization (polymerization), but also ionic association in the organic phase (of low dielectric constant), leading to clusters containing more than one metal atom, *i.e.*, ion triplets, quadruplets, etc. Such association has indeed been observed in the extraction of $H^+FeCl_4^-$ and $H^+GaCl_4^-$ into certain ethers, and does contribute to an increase in D with increasing (M).[7]

On the other hand, if dimers can exist only in the aqueous phase, the slope of the plot of log D *vs.* log Q will go from zero at low Q to $-1/2$ at high Q where $f_{M_2X_2} \rightarrow 1$ (Fig. 1c). If dimers exist in both phases, the slope will have a value between $+1$ and $-1/2$, depending upon which phase has dimers for the greater fraction of its metal-containing species.

If no dimers exist, but there are ionic metal halide species in the organic phase ($f^\circ_{M_2X_2} = f_{M_2X_2} = 0, f^\circ_{M^+}$ or $f^\circ_{MX_2^-} \neq 0$) and another ionic substance with a common ion is present, *i.e.*, H^+X^-, H^+Z^-, A^+X^-, a dependence of D on Q may still show up. As a simple example, consider the change in D for the distribution of the single metallic species HMX_2, between water and an organic phase, with a hydrohalic acid, HX, at a much larger concentration simultaneously present and distributing between the two phases. The aqueous phase then contains H^+, MX_2^- and X^-, while the organic phase has H^+, MX_2^-, X^-, and also undissociated HX and HMX_2. At very low metal concentrations the hydrogen ion concentration in both phases is determined by the distribution and dissociation of the HX, since it is in overwhelming amounts. Here a plot of log D *vs.* log Q will be a horizontal straight line. As the metal ion concentration is increased, a point will be reached at which the amount of H^+ brought into the organic phase by the MX_2^- will be comparable to that extracting with the X^-; this increase in $(H)_0$ common to both anions represses the extraction of both X^- and MX_2^-, and the value of D will begin to decrease. When $(MX_2)_0 >> (X)_0$, or $\alpha_{H.MX_2}(MX_2) >> \alpha_{HX}(X)$, the slope of log D *vs.* log Q approaches $-1/2$. But the increase in $(H)_0$ also increases the fraction of metal-containing species in the organic phase present as associated HMX_2, so eventually D becomes independent of Q again. A plot of log D *vs.* log Q illustrating this behavior is shown in curve d, Fig. 1. Obviously the metal concentrations at which D begins to decrease and then becomes constant again depend upon the relative acid strengths, concentrations, and distribution of HX and HMX_2, and upon the nature of the organic solvent. The stronger the acid HMX_2 is, and the weaker and less soluble in the organic phase that HX is, the lower the value of Q where D begins to decrease and the higher the value of Q before D becomes constant. Conversely, the weaker HMX_2 is, and the stronger and more soluble in the organic phase that HX is, the higher the value of Q at which D begins to decrease and the sooner D achieves constancy again.

If the concentrations of the acid species in the organic phase are known, the plot of log D *vs.* log Q will then give information as to the relative acid

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[7] (a) R. J. Myers and D. E. Metzler, *J. Am. Chem. Soc.*, **72**, 3772 (1950); (b) N. H. Nachtrieb and R. E. Fryxell, *ibid.*, **74**, 897 (1952).

strengths in that solvent. The type of behavior illustrated by curve d, Fig. 1, is to be expected with oxygenated, non-water-like (non-alcoholic) organic solvents of moderate dielectric constant. If the dielectric constant is low, association (ion-pairing) will be enhanced to the point where practically only HMX_2 exists in the organic phase and no variation of D will occur, (right-hand horizontal region, curve d, Fig. 1). If the dielectric constant of the organic solvent is high, approaching that of water, there will be little ion association, but the hydrohalic acid, HX, present in the aqueous phase in much higher concentration than the metal, will probably become quite soluble and dissociated in the organic phase and will furnish the major portion of the hydrogen ions there, too, for all reasonably obtainable concentrations of metal.[8] Thus again there would result no variation of D with Q (left-hand horizontal region, curve d, Fig. 1).

The addition of a third acid to a system which originally shows the behavior illustrated by curve d, Fig. 1, may also cause D to become invariant with Q. If the acid added, HZ, is stronger and more soluble in the organic phase than HMX_2, even the addition of small amounts will furnish more hydrogen ion to the organic phase than does HMX_2 (and HX). This common ion suppresses the extraction of MX_2^-, leaving only associated HMX_2 in the solvent, and the distribution of this species is, of course, independent of Q, yielding a low, constant value of D.

Since in the molybdenum(VI) systems studied experimentally, the total concentration of metal-containing species is much smaller than that of the HX in the aqueous phase, the partial derivative $\partial \log D/\partial \log Q$ has physical significance and can be obtained readily from experimental plots. However, under these conditions it is not easy to experimentally obtain $\partial \log D/\partial \log (X)$, $\partial \log D/\partial \log (H)$, $\partial \log D/\partial \log (Z)$ or $\partial \log D/\partial \log (A)$ individually, for one cannot increase the concentration of one of these ions (present in large amounts) without simultaneously increasing the concentration of an oppositely charged ion or decreasing the concentration of a similarly charged ion an equal amount. But one can determine the variation of D with such simultaneous variations in the concentrations of pairs of ions, and three such cases which have been measured for the molybdenum(VI) system are discussed in the next three sections.

2. Variation of D with Concentration of H^+X^- (represented by [HX]) at Constant (Z) and (A).—It can be seen from eq. 7 that whether D increases or decreases with increasing concentration of H^+X^- depends primarily upon whether the average metal-containing species in the organic or in the aqueous phase contains the larger number of hydrogen plus halide ions. But again, as in the variation with Q, even when the same species predominates in both phases, there may still be a dependence on [HX] through a common ion effect. The requirements are that the metal-containing species be ionic, and that H^+X^-, with the same co-ion, be present in much larger concentration in either one, but only one, of the two phases.

$$\frac{d \log D}{d \log [HX]} = \frac{[HX]}{(H)}\frac{\partial \log D}{\partial \log (H)} + \frac{[HX]}{(X)}\frac{\partial \log D}{\partial \log (X)}$$

$$= (f^\circ_{M^+} - f^\circ_{MX_2^-})\frac{1}{2}\left(\frac{\frac{[HX]}{(X)}\alpha_{HX}(X) + 2\alpha_{H.MX_2}\beta_{MX_2}(M)(X)^2}{\alpha_{HX}(X) + \alpha_{HZ}(Z) + \alpha_{H.MX_2}\beta_{MX_2}(M)(X)^2} - \frac{\frac{[HX]}{(H)}\alpha_{HX}(H)}{\alpha_{HX}(H) + \alpha_{AX}(A) + \alpha_{MX}(M)}\right) +$$
$$\frac{[HX]}{(X)}(2f^\circ_{MX_2^-} + f^\circ_{MX} + 2f^\circ_{HMX_2} + 2f^\circ_{M_2X_2} - f_{MX} - 2f_{MX_2^-} - 2f_{HMX_2} - 2f_{M_2X_2}) + \frac{[HX]}{(H)}(f^\circ_{HMX_2} - f_{HMX_2}) \quad (9)$$

Several cases may be distinguished. Consider that only HX([HX] = (H) = (X)) and the following metal halide species exist in the two phases. First, if only the neutral molecule MX exists in the organic phase, but both M^+ and MX are possible in the aqueous phase, the plot of log D *vs.* log [HX] would start with a slope of +1 when M^+ is the principal metal-containing aqueous species, and then decrease to zero at higher values of [HX] when MX becomes predominant. This behavior is illustrated in curve a, Fig. 2. If MX_2^- and/or M_2X_2 can also exist in the aqueous phase, the value of the slope will decrease to −1 when they become important at high [HX] (curve b, Fig. 2). If the undissociated species, HMX_2, and/or the dimer, M_2X_2, also exist in the organic phase, D may not decrease at all, but may continue to increase with increasing [HX], depending upon the relative fractions of the species present.

If M^+ is the only metal-containing species in either phase, but excess (HX) is present in the aqueous one, the plot of log D *vs.* log [HX] will have a finite slope of $+^1/_2$ as long as $(M)_0 >> (H)_0$ or $\alpha_{MX}(M) >> \alpha_{HX}(H)$. At high [HX] where $(M)_0 << (H)_0$ or $\alpha_{MX}(M) >> \alpha_{HX}(H)$, that is, where $H^+ >> M^+$ in both phases, the plot of log D *vs.* log [HX] levels off to zero slope. If other aqueous phase species are allowed, the slope will become negative, reaching a value of −2 when MX_2^- becomes the principal aqueous metal-containing species at high [HX] (curve c, Fig. 2). However, as can be seen from eq. 7 and 9, the values of D and of d log D/d log [HX] also depend, again through a common ion effect, upon the concentration, strength and distribution of any other strong acid or halide salt that may be present.

If MX_2^- is the only metal-containing species present in the organic phase, but all are possible in the aqueous phase, D will initially increase with increasing [HX]. The slope of the plot of log D *vs.* log Q depends upon the relative amounts of hydrogen ion in the organic phase furnished by HX and HMX_2, $+^3/_2$ if $(H)_0 \approx (MX_2)_0 >> (X)_0$ or +2 if

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[8] This is not to imply that the dielectric constant of the organic solvent is the all powerful factor. Only oxygenated solvents, or those containing basic nitrogens, etc., are being considered here, *i.e.*, ethers, esters, ketones, nitriles and alcohols, as in ref. 2 it was shown that these alone extract molybdenum(VI). Ethylene dichloride and *o*-dichlorobenzene have dielectric constants higher than some of the oxygenated solvents used and show negligible extraction. This seems to be a general phenomenon in ionic metal halide-acid halide extraction systems, and points up the importance of solvation of the metallic species and/or the hydrogen ion in the organic phase, that is, the requirement of a basic atom in the organic molecule capable of further coordination.

$(MX_2)_0 << (X)_0 \approx (H)_0$. Log *D* will reach a maximum, and then, at high [HX], decrease with a slope approaching, again as $(MX_2)_0 >> (X)_0$ or $(MX_2)_0 << (X)_0$, $-1/2$ or 0 if MX_2^- is the principal metal-containing species in the aqueous phase, $-3/2$ or -1 if HMX_2 is the principal one (curve d, Fig. 2). The values of *D* and of d log *D*/d log [HX] also depend upon the amounts of HZ and AX present. If the strong acid HZ is added to the system, the values of *D* will be smaller, but the initial slope of the plot of log *D vs.* log [HX] will be larger, the maximum in the curve will be at a higher halide concentration, and the subsequent decrease at still higher [HX] will be gentler. This behavior is due to the fact that the hydrogen ion extracting with the Z^- represses the extraction of the MX_2^-; a high concentration of $(MX_2)_0$ or $(X)_0$ will, of course, diminish the effect of HZ. On the other hand, the addition of AX instead of HZ to this system will make the initial value of *D* higher and the slope of log *D vs.* log [HX] less positive, through the presence of the extra A^+ co-ion for the MX_2^- in the organic phase.

3. Variation of *D* with [HX] when HZ is Present to Keep the Ionic Strength Constant, *i.e.*, when (X) + (Z) = (H) = Constant.—

$$\frac{d \log D}{d \log [HX]} = \frac{\partial \log D}{\partial \log (X)} - \frac{(X)}{(Z)} \frac{\partial \log D}{\partial \log (Z)} = (f^\circ_{M^+} - f^\circ_{MX_2^-}) \frac{1}{2} \frac{\alpha_{HX}(X) + 2\alpha_{H,MX_2}(MX_2) - \alpha_{HZ}(X)}{\alpha_{HX}(X) + \alpha_{HZ}(Z) + \alpha_{H,MX_2}(MX_2)} + 2f^\circ_{MX_2^-} + f^\circ_{MX} + 2f^\circ_{HMX_2} + 2f^\circ_{M_2X_2} - f_{MX} - 2f_{MX_2^-} - 2f_{HMX_2} - 2f_{M_2X_2} \quad (10)$$

D will increase or decrease with increasing (X) and decreasing (Z) as the average metal-containing species in the organic or in the aqueous phase, respectively, involves more X (species involving Z are not being considered here, but extension of the equations to include them is obvious). For example, if only MX exists in the organic phase but all of the metal halide species considered are possible in the aqueous phase, the slope of the plot of log *D vs.* log [HX] will initially be +1 at low [HX] where M^+ is the principal metal-containing species in the aqueous phase. Log *D* will reach a maximum, d log *D*/d log [HX] = 0, when MX becomes the principal aqueous phase metal-containing species, and then log *D* will decrease with a slope approaching −1 as MX_2^- (or HMX_2 and/or M_2X_2) becomes the dominant species at high [HX] (curve a, Fig. 3). If HMX_2 also exists in the organic phase, the initial rise of log *D* may be steeper, the slope tending to +2 as $f^\circ_{HMX_2} \rightarrow 1$, but eventually becoming zero at high [HX], that is, *D* becomes a constant, when MX_2^- (or HMX_2 and/or M_2X_2) becomes the principal aqueous phase metal-containing species.

A change in (X) and (Z) may also affect the distribution of any ionic species through the common ion effect described earlier. If HZ is not soluble in the organic solvent or does not ionize appreciably there, that is, $\alpha_{HX} >> \alpha_{HZ}$, HZ will have little effect other than determining the initial slope of log *D vs.* log [HX]; the rest of the curve will behave as $\partial \log D / \partial \log (X)$. For example, if M^+ is the principal metal-containing species in the organic phase, a plot of log *D vs.* log [HX] will start out with zero slope, rise to a maximum, and then decrease with a slope approaching $-3/2$ as MX_2^- becomes the most important metal-containing species in the aqueous phase. If MX_2^- is the principal metal-containing species in the organic phase, a plot of log *D vs.* log [HX] for $\alpha_{HZ} << \alpha_{HX}$ will start out with an initial slope of +2 which immediately decreases. Log *D* will reach a maximum and then decrease with a slope approaching $-1/2$ when MX_2^- becomes the important metal-containing aqueous phase species (curve b, Fig. 3).

Depending upon the nature of HZ and upon that of the organic solvent, however, HZ may be more soluble and more dissociated in the organic phase than HX, that is, $\alpha_{HZ} >> \alpha_{HX}$, and then the presence of HZ will greatly change *D* for M^+ or MX_2^-. As an illustration, HZ will repress the extraction of MX_2^- into the organic phase through the increase in concentration of the common $(H)_0$. For, from $\alpha_{H,MX_2}(H)(MX_2) = (H)_0(MX_2)_0$, keeping (H) and (MX_2) constant, an increase in $(H)_0$ requires a decrease in $(MX_2)_0$. A plot of log *D vs.* log [HX] would start with an initial slope of +2 and rise with the slope increasing to the value $+1/2\,(\alpha_{HZ}/\alpha_{HX})$ at high [HX] (curve c, Fig. 3).

Similarly, the presence of H^+Z^- in the organic phase may affect the distribution of cationic species through the resulting changes in $(X)_0$. For with $\alpha_{HZ} >> \alpha_{HX}$, the plot of log *D vs.* log [HX] for M^+ will not initially rise, (as when $\alpha_{HZ} << \alpha_{HX}$) but will decrease with a slope approaching $-1/2\,(\alpha_{HZ}/\alpha_{HX}) - 2$ at high [HX] when MX_2^- becomes the dominant metal-containing species in the aqueous phase.

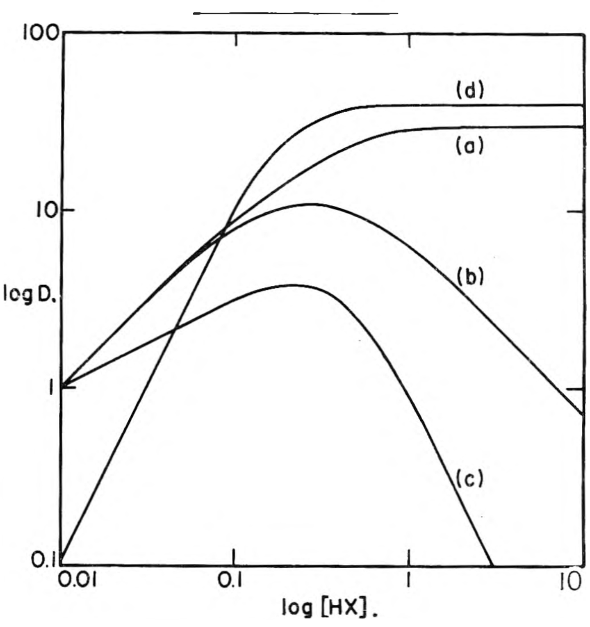

Fig. 2.—Variation of *D* with HX concentration when (HZ) = (AX) = 0: (a) only MX in the organic phase, M^+ and MX in the aqueous one; (b) only MX in the organic phase, M^+, MX, MX_2^-, M_2X_2 in the aqueous one; (c) only M^+ in the organic phase, M^+, MX, MX_2^-, M_2X_2 in the aqueous one; (d) MX_2^- in the organic phase, M^+, MX, MX_2^-, M_2X_2 in the aqueous one.

4. Variation of *D* with [HX] When AX is Present to Keep the Ionic Strength Constant, That is, (H) + (A) = (X) = Constant.—

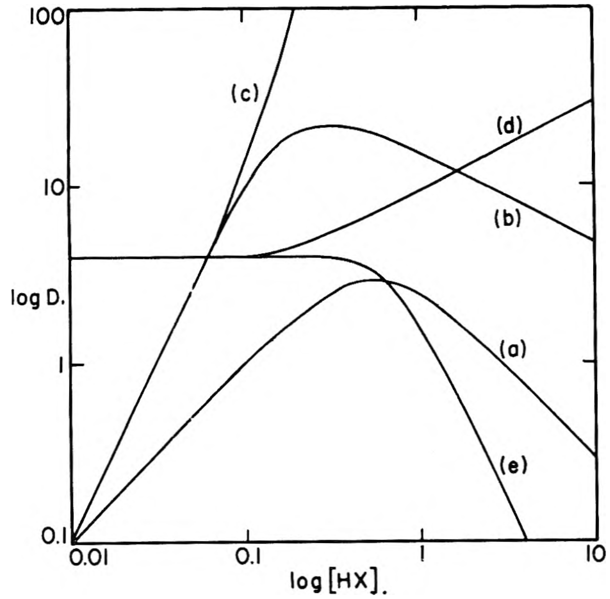

Fig. 3.—Variation of D with HX concentration when either HZ (curves a, b, c) or AX (curves d, e) is also present to keep the ionic strength constant; (a) only MX in the organic phase, M^+, MX, MX_2^-, M_2X_2 in the aqueous phase; (b) only MX_2^- in the organic phase, all species in the aqueous phase, as in (a), and $\alpha_{HZ} \ll \alpha_{HX}$; (c) same as in (b), but with $\alpha_{HZ} \gg \alpha_{HX}$; (d) only MX_2^- in the organic phase, all species in the aqueous phase, as in (a), with $\alpha_{AX} \ll \alpha_{HX}$; (e) same as in (d), but with $\alpha_{AX} \gg \alpha_{HX}$

$$\frac{d \log D}{d \log [HX]} = \frac{\partial \log D}{\partial \log (H)} - \frac{(H)}{(A)} \frac{\partial \log D}{\partial \log (A)} =$$

$$(f^\circ{}_{M^+} - f^\circ{}_{MX_2^-}) \frac{1}{2} \frac{\alpha_{AX}(H) - \alpha_{HX}(H)}{\alpha_{HX}(H) + \alpha_{AX}(A) + \alpha_{MX}(M)} \quad (11)$$

$$+ f^\circ{}_{HMX_2} - f_{HMX_2} - \frac{(H)}{(A)} f^\circ{}_{AMX_2}$$

There is no effect on D when AX and HX are interchanged if only MX or M_2X_2 exists in the organic phase (all possible metal-containing species allowed in the aqueous phase other than HMX_2). If HMX_2 and AMX_2 are also allowed in the organic phase, D will increase or decrease with increasing [HX] depending upon which one is the more soluble in the solvent, that is, whether $\alpha_{H,MX_2}\delta_{H,MX_2}$ is larger or smaller than $\alpha_{A,MX_2}\delta_{A,MX_2}$.

If M^+, or MX_2^-, is the principal metal-containing species in the organic phase, the presence of AX may increase or decrease the value of D, depending upon the relative magnitudes of α_{AX} and α_{HX}, through the common ion effect. If $\alpha_{AX} << \alpha_{HX}$, the D for M^+ is larger, and that for MX_2^- is smaller, for an aqueous phase with AX than for one with HX. The plot of log D *vs.* log [HX] starts with a slope of zero for M^+ and falls off to a final slope of $-{}^1/_2$; for MX_2^- it starts with zero slope and rises to approach the limiting slope of $+{}^1/_2$ at pure HX (curve d, Fig. 3). If $\alpha_{AX} >> \alpha_{HX}$, the situation is reversed; the D for M^+ is smaller, and that for MX_2^- is larger, from AX than from HX solutions, and the plot of log D *vs.* log [HX] starts with zero slope for either ion, and rises to a limiting slope of $+{}^1/_2(\alpha_{AX}/\alpha_{HX})$ for M^+ or falls to the value $-{}^1/_2(\alpha_{AX}/\alpha_{HX})$ for MX_2^- at high (pure) HX (curve e, Fig. 3).

Evidence exists for the "common ion" effect on the distribution quotient, D, discussed in this paper, and some of this will be presented in the following paper. This effect is a major difference between the present work and the general equations for solvent extraction presented by Irving, Rossotti and Williams,[3] and is an important one. Neglect of this effect by the latter authors invalidates much of their interpretation of their experimental results with the indium bromide–hydrobromic acid–methyl isobutyl ketone system,[9] as their data lead to the conclusion that they are observing just this effect, and not dimerization of the indium species in the aqueous phase as they suggest.

It should also be re-emphasized that the equations derived above are for an idealized system in which no changes are assumed to occur in the natures of the organic and aqueous phases caused by the variations of concentrations described above. That is, the two phases, organic and aqueous acid, are always considered as immiscible liquids which keep their original individual properties throughout the changes considered above, and hence the constants of eq. 2, 3 and 4 are constant. Actually, of course, real two-phase systems are not so ideal, and allowance must be made not only for their mutual solubility, but more importantly, for the changes in mutual solubility, phase volumes, dielectric constants, solvation of species, etc., which occur under the concentration changes considered. Unfortunately, these solvent effects cannot be so easily expressed in mathematical form as the direct effects of changes in concentrations given in this paper, so they will be considered qualitatively, as corrections to the behavior of ideal systems, when treating real systems in the following papers. If the solvent–aqueous acid system is properly chosen, these corrections may actually be small and the equations do seem to hold. If the system is such as to have large solvent corrections, when varying the concentrations of X^-, H^+, Z^-, A^+, the effects may greatly change the predictions of the equations developed here, but in a manner which also can be predicted, though only qualitatively.

[9] H. Irving and F. J. C. Rossotti, *J. Chem. Soc.*, 1927 (1955), and 1938 (1955).

THE SOLVENT EXTRACTION BEHAVIOR OF INORGANIC COMPOUNDS.[1] III. VARIATION OF THE DISTRIBUTION QUOTIENT WTIH METAL ION CONCENTRATION

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The metal ion concentration dependence of the distribution quotient expression previously derived[2] has been tested for molybdenum(VI) at concentrations from 10^{-9} to 10^{-2} M distributing between aqueous HCl, HBr and mixed HCl–HNO_3 and HBr–$HClO_4$ acids and the following oxygenated organic solvents: diethyl, β,β'-dichlorodiethyl and dibutyl ethers, methyl isobutyl and methyl amyl ketones and 2-ethylhexanol. These results are interpreted in terms of the expression derived for $\partial \log D/\partial \log Q$ and show that both polymerization of the metal-containing species and the "common ion" effect can cause a variation of D with molybdenum(VI) concentration. Some information on the molybdenum(VI) species is also obtained. It is shown that polymeric forms can exist in the aqueous solutions at hydrohalic acid concentrations below 6 M (and $<10^{-1}$ M molybdenum), but no appreciable amount of monomeric cations is present; the main species are apparently the anions of acids stronger than HCl.

The preceding paper[2] has derived expressions for the distribution quotient, D

$$D = \frac{\text{metal conc. in organic phase}}{\text{metal concn. in aqueous phase}} = \frac{P}{Q}$$

for the extraction of a metal into an organic solvent from a hydrohalic acid solution and for the variation in D with changes in concentration of the aqueous metal species, of the hydrogen halide, and of other strong acids or halide salts possibly present. The study of the dependence of D on the metal concentration is a most favorable one for investigating the validity of the equations, as in such a study the solvent effects, which have not been taken into account in deriving the equations, can be held constant. The results also allow a comparison to be made between these equations and those proposed by Irving, Rossotti and Williams.[3] In the present paper the dependence of D on the equilibrium aqueous molybdenum(VI) concentration when varied from 10^{-9} to 10^{-2} M in solutions from 2 to 12 M in hydrochloric acid, or sometimes from 2 to 8 M in hydrobromic acid, or in HCl–HNO_3 or HBr–$HClO_4$ mixtures is given. The organic solvents used are diethyl, β,β'-dichlorodiethyl and dibutyl ethers, methyl isobutyl and methyl amyl ketones and 2-ethylhexanol.

Consideration of the types of molybdenum(VI) species to be expected in these phases will allow specialization and simplification of the pertinent equations. It is usually considered that the predominant molybdenum(VI) species in aqueous solutions of pH > 7 is $MoO_4^{=}$.[4] Lowering the pH causes the formation of polymeric species[5]; some, such as the paramolybdate ion, $Mo_7O_{24}^{6-}$, are well characterized.[6] Around pH 0.9 the isoelectric point occurs,[7] and precipitation of hydrous MoO_3 takes place. Increasing the acidity still further results in solution of the oxide precipitate if the acid used has an anion such as sulfate or chloride which forms complex ions with metals; perchloric acid is not very effective in dissolving MoO_3. There have been suggestions that the resulting acid solutions contain the cation MoO_2^{++}, similar to the UO_2^{++} ion, or even MoO^{++++}, but there is little evidence for the existence of such ions. Resin-exchange studies performed in the course of the present work showed little or no absorption of molybdenum(VI) by a cation resin (Dowex-50) from solutions 1–12 M in HCl or 1–6 M in HBr, HF, H_2SO_4 or HNO_3, while anion-exchange resin (Dowex-1) gave marked absorption from the same solutions. Only solutions 1–6 M in $HClO_4$ showed very low distribution quotients for the anion resin and some slight absorption on cation resin. These results indicate that if cationic molybdenum(VI) species exist in these solutions (other than perchloric), the species are probably polymeric and large. Except in the perchloric acid solutions, however, there must be anionic species small enough to exchange. Dimeric species have been suggested for both molybdenum(V) and molybdenum(VI) in hydrochloric acid solutions below 6 M in concentration,[8] and the monomer–dimer equilibrium has been demonstrated for the former. In 2 M HCl, 0.2–0.3 M molybdenum(V) is predominantly dimeric, but with increasing HCl concentration the equilibrium shifts in favor of the monomer so that in 6 M HCl, the monomer predominates.[9] Such behavior seems to indicate that the dimer contains more oxygen or less chorine, or both, than the monomer. No proof of such a monomer–polymer equilibrium has yet been given in the molybdenum(VI)– HCl system, but evidence for it comes from the results of the present work. Since the formula of this proposed polymer is not known, it will be assumed, as in the molybdenum(V) case, to be a dimer and will be represented by the symbol G in the following equations.

Previous work[10] has shown that the species extracting into diethyl and diisopropyl ethers from 3,

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[1] Supported in part by the joint program of the Office of Naval Research and the Atomic Energy Commission.

[2] R. M. Diamond, THIS JOURNAL, **61**, 69 (1957).

[3] H. Irving, F. J. C. Rossotti and R. J. P. Williams, *J. Chem. Soc.*, 1906 (1955).

[4] H. J. Emeléus and J. S. Anderson, "Modern Aspects of Inorganic Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1954, p. 215.

[5] G. Jander, *Z. anorg. Chem.*, **194**, 383 (1930).

[6] (a) J. Sturtevant, *J. Am. Chem. Soc.*, **59**, 630 (1937); (b) I. Lindqvist, *Acta Chem. Scand.*, **2**, 88 (1948).

[7] G. Carpeni, *Bull. soc. chim. France*, **14**, 496 (1947).

[8] (a) A. R. Tourky and H. K. El-Shamy, *J. Chem. Soc.*, 140 (1949); (b) H. K. El-Shamy and A. M. El-Aggan, *J. Am. Chem. Soc.*, **75**, 1187 (1953).

[9] L. Sacconi and R. Cini, *ibid.*, **76**, 4239 (1954). Actually, this experiment does not rule out the possibility that the dimer is really a higher polymer.

[10] L. Nelidow and R. M. Diamond, THIS JOURNAL, **59**, 710 (1955).

6 or 9 M HCl or 6 M HBr solutions have the composition $MoO_2X_2(H_2O)_y(Ether)_z$, where X is Cl or Br. Conductivity studies[11] on the ether extracts indicate that the molybdenum-containing species is either molecular or, if ionic, highly ion-paired in these solvents of low dielectric constant. The same empirical formula holds for the molybdenum(VI) species extracted into β,β'-dichlorodiethyl ether from 9 M HCl or from 7.5 M LiCl–2.5 M HCl, but conductivity studies in this solvent, as well as in methyl isobutyl and methyl amyl ketones, indicate that the molybdenum-containing species is no longer mainly ion-paired, at least not as much as HCl, although more so than perchloric acid. Also, since other metal halides which extract into oxygenated organic solvents from aqueous hydrohalic acid solutions do so as the anions of acids stronger than HCl, *i.e.*, $HFeCl_4$, $HAuCl_4$, $HGaCl_4$, $HTlCl_4$ $HInBr_4$, etc., it is plausible to ascribe the ionization of the molybdenum species to an acid ionization into $H^+_{solvated}$ and a molybdenum containing anion, possibly $MoO_2(OH)X_2(H_2O)^-$ or $MoO_2(OH)X_2(Ether)^-$, which shall be represented by the symbol A^-. The anion-exchange resin work briefly mentioned above shows that anionic molybdenum species also exist in the aqueous phase, and these include, as is to be expected, dihalide species of the form represented by A^-.[12] Since solid compounds of the type $M[MoO_2Cl_3(H_2O)]$ and $M_2[MoO_2Cl_4]$ ($M = NH_4^+$, K^+, Rb^+, Cs^+) can be precipitated from solutions,[13] the existence in aqueous solution of anionic species containing three and four halogen atoms and carrying a dinegative charge is possible; such anions will be represented by the symbol $B^=$.

Since it is not known whether the molybdenum dimer present in solutions less than 6 M in HCl dissociates directly to form anionic species or also is in equilibrium with a neutral monomer, the possibility of the latter will also be considered for completeness. It will be given the symbol N, although its existence in moderate amounts, or lack of existence, does not change the results to be described. Then the possible species to be considered in the aqueous and organic phases, including the hydrohalic acid, HX, and the possible presence of a foreign strong acid, HZ, are

Aqueous phase: G, N, A^-, $B^=$, H^+, X^-, Z^-
Organic phase: N, A^-, H^+, X^-, Z^-, HA, HX, HZ[14]

In the organic phase, the last three entities may be true molecular species, but, except for possibly HX, are most likely ion-pairs. Higher ion associations such as ion-triplets, quadruplets, etc., are also possible,[15] but apparently are not important in the molybdenum concentration range up to 10^{-2} M covered in this work. So the molybdenum distribution quotient can be expressed as

$$D = \frac{(N)_0 + (A)_0 + (HA)_0}{2(G) + (N) + (A) + (B)} \tag{1}$$

where ( )$_0$ and ( ) indicate concentration of the enclosed species in the organic and aqueous phase, respectively, and charges on ions are not being shown. Using the notation of reference 2 and the derivations given there one obtains[16]

$$D = \frac{\alpha_N (N) + \alpha_{HA} \dfrac{(H)(A)}{(H)_0} + \alpha_{HA}\delta_{HA} (H)(A)}{2(G) + (N) + (A) + (B)} \tag{2}$$

and in terms of aqueous concentrations

$$D = \frac{\alpha_N (N) + \dfrac{\alpha_{HA}}{\sqrt{\alpha_{HX}}} (A) \sqrt{\dfrac{\alpha_{HX} (H)}{\alpha_{HX} (X) + \alpha_{HZ} (Z) + \alpha_{HA} (A)}} + \alpha_{HA}\delta_{HA} (H)(A)}{2(G) + (N) + (A) + B)} = \frac{P}{Q} \tag{3}$$

In this paper we are concerned with the variation of D caused by variations in the molybdenum(VI) concentration. The experimental data will be presented in graphs of log D *vs.* log Q and compared with the expression derived from eq. 3

$$\frac{\partial \log D}{\partial \log Q} = \frac{\partial \log P}{\partial \log (A)} \frac{\partial \log (A)}{\partial \log Q} - \frac{\partial \log Q}{\partial \log Q}$$
$$= \frac{(A)}{P} \frac{\partial P}{\partial (A)} \bigg/ \frac{(A)}{Q} \frac{\partial Q}{\partial (A)} - 1$$
$$= \frac{-{}^1\!/_2 f^\circ_{A^-} \left[\dfrac{\alpha_{HA} (A)}{\alpha_{HX} (X) + \alpha_{HZ} (Z) + \alpha_{HA} (A)} \right] - f_G}{1 + f_G} \tag{4}$$

where $f^\circ_{A^-}$ is the fraction of organic phase molybdenum present as A^- and f_G is the fraction of aqueous phase molybdenum present as G, *i.e.*

$$f_G = \frac{2(G)}{Q} = \frac{2\beta_G (A)^2 g''(H,X)}{Q}$$

Experimental

Tracer and Reagents.—The radioactive tracer used was 6.7 hour Mo^{93m}. It was produced by irradiating Nb^{93} metal foil with deuterons in the Massachusetts Institute of Technology cyclotron and separating carrier-free Mo^{93m} from the target. The niobium metal contained 0.004% molybdenum, which determined the lower limit on the concentration of molybdenum usable in the extraction experiments. Samples of the tracer were followed for decay over a several week period, so that the amount of long-lived (non-extracting) impurity present at the time of the distribution experiments could be determined. It was negligible during the course of the experiments.

Reagent grade nitric, hydrochloric, hydrobromic and perchloric acids were used without further treatment, as were reagent grade diethyl ether and C.P. dibutyl ether, methyl isobutyl and methyl amyl ketones, and practical grade 2-ethylhexanol. In contrast to these solvents, two different samples of C.P. β,β'-dichlorodiethyl ether were used, and were found to give different distribution quotients. Both samples were distilled under reduced pressure and a

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(11) R. M. Diamond, unpublished results.

(12) H. M. Neumann and Nancy C. Cook, Abstracts of the 129th Meeting of the American Chemical Society, Dallas, Texas, April, 1956.

(13) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. XI, Longmans, Green and Co., London, 1931, p. 632.

(14) On purely electrostatic grounds, small polynegative ions, represented by $B^=$, are not expected to extract significantly into these organic solvents of moderately low dielectric constants and actually dinegative ions such as $ZnCl_4^=$ and $CoCl_4^=$ do not extract appreciably while the similar uninegative ions $FeCl_4^-$, $AuCl_4^-$, $GaCl_4^-$, $TlCl_4^-$, $InBr_4^-$ do.

(15) (a) R. M. Fuoss and C. A. Kraus, *J. Am. Chem. Soc.*, **55**, 2387 (1933); (b) N. H. Nachtrieb and R. E. Fryxell, *ibid.*, **70**, 3552 (1948); **74**, 897 (1952); (c) R. J. Myers and D. E. Metzler, *ibid.*, **72**, 3772 (1950).

(16) The relationships needed in this case are $\alpha_N(N) = (N)_0$ $\alpha_{HX}(H)(X) = (H)_0(X)_0$, $\alpha_{HZ}(H)(Z) = (H)_0(Z)_0$, $\alpha_{HA}(H)(A) = (H)_0(A)_0$, $\delta_{HA}(H)_0(A)_0 = (HA)_0$, $\beta_B(A)g(H,X) = (B)$, $\beta_N(A)g'(H,X) = (N)$, $\beta_G(A)^2g''(H,X) = (G)$, and $(H)_0 = (X)_0 + (Z)_0 + (A)_0$, where α, β, δ are concentration constants and g. g'. and g'' are functions of (H) and (X) but not (A).

similar two degree cut taken, but these cuts still yielded unchanged, differing, quotients. The cause of this is not known and only the results with the better extracting ether are presented. (The shape of log D vs. log Q plots are similar for the two, differing only in magnitude of D.) The various molybdenum(VI) solutions were prepared by weighing out reagent grade $Na_2MoO_4 \cdot 2H_2O$ into the appropriate volume of acid to make a 0.100 M solution. From these solutions aliquots were taken and diluted with more of the acid, and the process repeated down to 10^{-6} M molybdenum. Lower concentrations were obtained using the tracer alone.

Procedure.—Five or ten milliliters of aqueous acid were added to equal volumes of the organic solvents in 2 oz. glass-stoppered bottles. (The solvents were not pre-treated with the aqueous acids.) The tracer was added in a volume of 5–20 mcl., and the bottles were shaken for 40 minutes on a mechanical shaker. (Distribution quotients determined after 5, 10, 20, 40, 80 minutes, and 6 and 20 hours, showed that constant values were obtained in less than 20 minutes.) The bottles were then allowed to stand for 10–20 minutes; satisfactory phase separation usually occurred immediately, but for a few difficult cases the mixture was centrifuged. These experiments were all performed in an air-conditioned room at a temperature of 21 ± 1°. Two-milliliter aliquots from each phase were then pipetted into screw-cap vials and γ-counted using a well-type NaI(Tl) scintillation counter. The ratio of the counting rate, corrected for background, of the sample from the organic phase to that from the aqueous phase gives directly the value of the distribution quotient, D, of molybdenum(VI) between the two phases. Duplicate trials showed that reproducibility was usually 5% or better; exceptionally difficult systems might show differences as large as 20%, but these were rare.

Results and Discussion

The experimental results for the changes in the distribution quotient, D, with variation in the total aqueous molybdenum(VI) concentration, Q, for extraction from various aqueous acid solutions into the solvents are given in Figs. 1–5. The data are plotted as curves of log D vs. log Q for a variation of Q from 10^{-9} to 10^{-2} M, and for a variety of HCl and HBr concentrations, as well as for some mixed $HCl-HNO_3$ and $HBr-HClO_4$ solutions.

From eq. 3 it can be seen that the only species which can lead to a change of D with variation of the aqueous molybdenum concentration are the dimer, G, in the aqueous phase and the anion, A^-, in the organic phase. If a dimer can exist in the aqueous phase, its formation with increasing molybdenum concentration should cause a decrease in D which is independent of the nature of the organic solvent, being an aqueous phase phenomenon. This decrease should be of the form $\partial \log D/\partial \log Q = -f_G/(1 + f_G)$, with a limiting slope of $-^1/_2$ when $f_G \rightarrow 1$ at high Q. (The slope would have a somewhat larger negative value if higher polymers are involved, *i.e.*, $-^2/_3$ for trimers and -1 for very high polymeric species.) On the other hand, if no dimer exists but the anionic species, A^-, occurs in the organic phase, $\partial \log D/\partial \log Q$ would take the form $-^1/_2 f°_{A^-} \alpha_{HA}(A)/[\alpha_{HA}(A) + \alpha_{HX}(X) + \alpha_{HZ}(Z)]$ and so would depend on the nature of the organic solvent through the different relative solubilities and ionization of HA, HX and HZ in the organic phase when shaken with the same initial aqueous solution. Thus the "common ion" effect described in the preceding paper can be differentiated from the effect of aqueous phase polymerization.

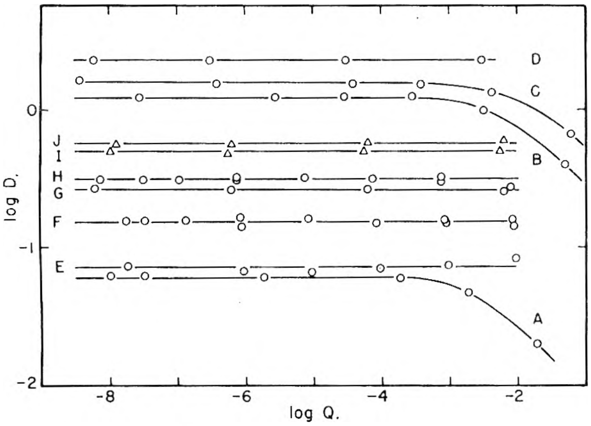

Fig. 1.—Plot of log D vs. log Q (equilibrium aqueous molybdenum concentration) for diethyl ether and (initial concentrations) 2.0 M HCl, A; 3.1 M $HCl-1.0$ M HNO_3, B; 4.1 M HCl, C; 7.1 M HCl, D; for dibutyl ether and 8.1 M HCl, E; 10.1 M HCl, F; 9.0 M $HCl-2.0$ M HNO_3, G; 11.9 M HCl, H; 5.8 M $HBr-1.0$ M $HClO_4$, I; 7.7 M HBr, J.

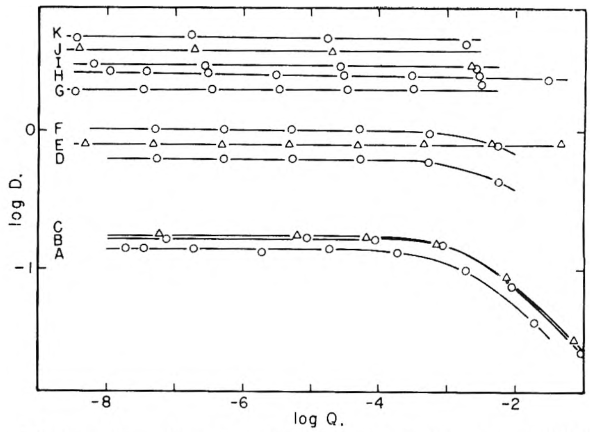

Fig. 2.—Plot of log D vs. log Q for 2-ethylhexanol and 2.0 M HCl, A; 2.0 M HBr, B; 1.5 M $HBr-0.5$ M $HClO_4$, C; 3.1 M $HCl-1.0$ M HNO_3, D; 9.0 M $HCl-2.0$ M HNO_3, E; 4.1 M HCl, F; 11.9 M HCl, G; 10.1 M HCl, H; 7.1 M HCl, I; 5.8 M $HBr-1.0$ M $HClO_4$, J; 7.7 M HBr, K.

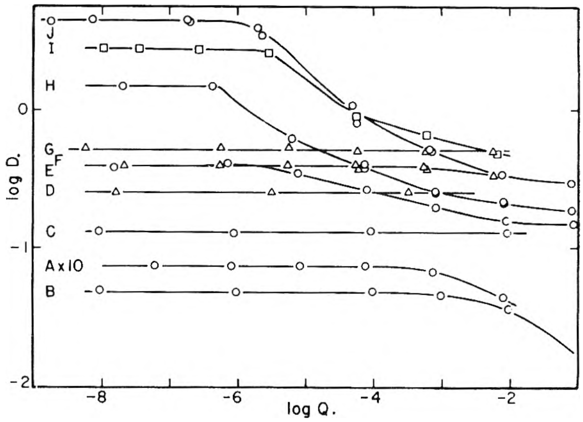

Fig. 3.—Plot of log D vs. log Q for DDE and 3.1 M $HCl-1.0$ M HNO_3, A (the D-values have been multiplied by 10); 4.1 M HCl, B; 6.2 M HCl, C; 4.0 M $HCl-2.4$ M HNO_3, D; 7.1 M HCl, E; 6.1 M $HCl-2.0$ M HNO_3, F; 9 M $HCl-2.0$ M HNO_3, G; 8.1 M HCl, H; 11.9 M HCl, I; 10.1 M HCl, J.

Consider first the solvents, diethyl and dibutyl ethers, representative of the aliphatic ethers. These two solvents have low dielectric constants, 4.34 at 20° and 3.06 at 25°, respectively,[17] so that small and moderate sized ions extracting into them

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[17] A. A. Maryott and E. R. Smith, "Tables of Dielectric Constants of Pure Liquids," National Bureau of Standards Circular 514, 1951.

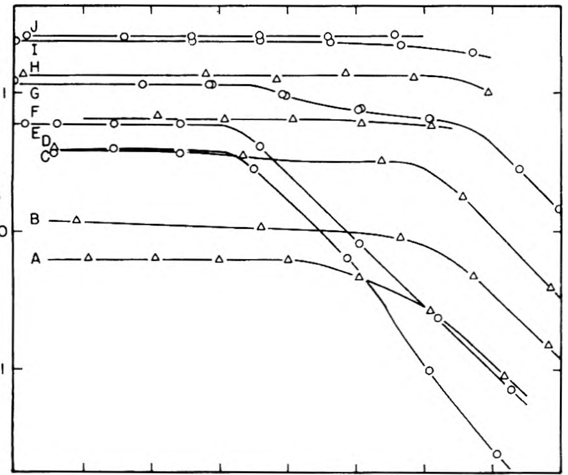

Fig. 4.—Plot of log D *vs.* log Q for methyl isobutyl ketone and 1.6 M HCl–0.4 M HNO_3, A; 3.2 M HBr–1.0 M $HClO_4$, B; 1.2 M HCl, C; 4.3 M HBr, D; 2.0 M HCl, E; 3.1 M HCl–1.0 M HNO_3, F; 4.1 M HCl, G; 4.6 M HCl–1.5 M HNO_3, H; 6.2 M HCl, I; 8.1 M HCl, J.

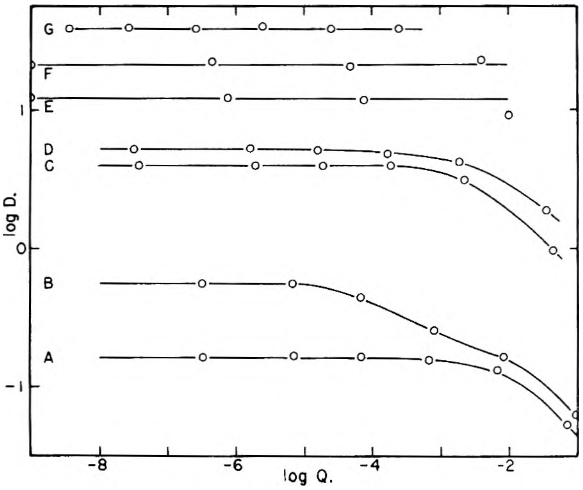

Fig. 5.—Plot of log D *vs.* log Q for methyl amyl ketone and 1.5 M HCl–0.5 M HNO_3, A; 2.0 M HCl, B; 3.1 M HCl–1.0 M HNO_3, C; 4.1 M HCl, D; 7.5 M HCl–2.0 M HNO_3, E; 10.1 M HCl, F; 8.1 M HCl, G.

will largely form ion-pairs except at vanishingly small concentrations. The term in (A) in the numerators of eq. 3 and 4 will thus be negligible, so that any molybdenum concentration dependence of D will have to come from the presence of the dimer. The dimer is expected to exist at low HCl concentrations and, in fact, the curve of log D *vs.* log Q for 2 M HCl and diethyl ether (Fig. 1) is flat from 10^{-8} to 10^{-4} M Q, and then D does begin to decrease, the slope reaching a value of about $-{}^{1}/_{2}$. Similarly, the curve for 4 M HCl is flat from 10^{-8} to beyond 10^{-3} M Q, and then again shows a decrease. The fact that the decrease starts at a higher equilibrium molybdenum concentration in 4 M HCl than in 2 M HCl indicates that the monomer–dimer equilibrium involves hydrogen and chloride ions, as suggested earlier. On going to higher HCl concentrations, the formation of the dimer requires still higher molybdenum concentrations and so the curve for 7 M HCl is flat from 10^{-8} to 10^{-2} M. Changing to dibutyl ether at 8 M HCl again yields a flat curve, as expected, as does 10 and 12 M HCl and 8 M HBr.

A check on the above reasoning is obtained by studying the concentration dependence of D when a foreign strong acid, $HClO_4$, or HNO_3, is present. Since the extraction of molybdenum(VI) from $HClO_4$ or HNO_3 solutions alone is small, the assumption that no appreciable amounts of new extractable molybdenum-containing species have been created is reasonable. Then, except with the anionic species, A^-, the presence of the foreign acid will have little effect on the distribution, lowering the value of D perhaps, but leaving the shape of the log D *vs.* log Q plots relatively unchanged, including the decrease due to formation of the dimer. If the added acid is more soluble and highly ionized in the organic solvent than HCl, it will, however, have an effect on the extraction of A^- as seen by the term in $\alpha_{HZ}(Z)$ in eq. 3 and 4; the added acid will repress the extraction of A^- through the common ion effect described in ref. 2 and D will become small and independent of Q.

Experimentally, the plot for 3 M HCl + 1 M HNO_3 and diethyl ether is very similar to the 4 M HCl plot, except for having slightly smaller values of D. In particular, D still decreases above 10^{-4} M Q, indicating that the decrease is due to the formation of molybdenum dimers (polymers) in the aqueous phase. The curves from 9 M HCl–2 M HNO_3 and 6 M HBr–1 M $HClO_4$ and dibutyl ether are flat from 10^{-8} to 10^{-2} M Q and practically unchanged by the addition of the HNO_3 or $HClO_4$; the latter acids have little effect on the distribution of the H^+A^- ion-pairs existing as the predominant molybdenum-containing species in the ether.

Next, consider extraction into 2-ethylhexanol. This solvent has a higher dielectric constant than diethyl and dibutyl ethers and with its OH group is more water-like in its solvating abilities. HCl extracts into 2-ethylhexanol quite well, and is much more highly ionized there than in the two ethers, as is indicated by conductivity studies.[11] So in this solvent, representative of the higher, immiscible alcohols, the fraction f°_{HA} might be expected to be smaller and $f^{\circ}_{A^-}$ larger, than with the ethers, but there will also be much more ionized HCl dominating the organic phase.

The experimental results are shown in Fig. 2. With 2 M HCl log D is constant from 10^{-8} to 10^{-4} M Q and then decreases. This curve is superposable on that for 2 M HCl and diethyl ether by a translation along the ordinate axis, as it must be if the decrease is due, as suggested, to a common aqueous phase phenomenon, namely dimerization. The same is true of the 4 M HCl plot which is similar to the 4 M HCl and diethyl ether curve. The 2 M HBr plot for 2-ethylhexanol also shows a decrease at high Q due to molybdenum(VI) dimerization. From the diethyl ether results at 7 M HCl, no decrease of D due to dimerization is expected up to 10^{-2} M Q with 2-ethylhexanol and 7 M HCl and none is found. But the two situations are nevertheless somewhat different. In the former solvent, the molybdenum(VI) and HCl species exist predominantly as ion-pairs, $f^{\circ}_{A^-} << 1$ and hence, as seen in eq. 4, there can be no molybdenum concentration dependence. In 2-ethyl hexanol, these species are much more highly dissociated, as indicated by conductivity studies,[11] but even though $f°_{A^-}$ may not be very small, the hydrogen ion furnished by the HCl in the organic phase is much greater than that extracting with the A^-, at least up to 10^{-1} M Q. This large and constant hydrogen ion concentration keeps the value of D constant, as can be seen in eq. 4 with $\alpha_{HX}(X) >> \alpha_{HA}(A)$. For this reason no dependence is found, from 10^{-9} to 10^{-2} M Q, for 10 or 12 M HCl or 8 M HBr with 2-ethylhexanol. The decrease in magnitude of D in going above 7 M HCl (which also occurs with diethyl ether) is due to the increasing miscibility of the two phases and will be discussed more fully in a later paper.

The addition of HNO_3 to the HCl and of $HClO_4$ to the HBr systems does not change the shape of the log D *vs.* log Q plots. The retention of the decrease of D with Q in these mixed acid systems below 6 M in concentration again shows that dimerization in the aqueous phase occurs at these acid concentrations.

Next, consider the results with β,β'-dichlorodiethyl ether, hereafter indicated by DDE. DDE has a much higher dielectric constant (21.2 at 20°[17]) and much smaller mutual solubility with aqueous solutions than diethyl ether. Measurable distribution ratios cannot be obtained readily with DDE at 2 M HCl, but the plot of log D *vs.* log Q for 4 M HCl is again similar to those for diethyl ether and for 2-ethylhexanol as to shape, requiring only a translation along the ordinate axis for all three to become superposable, Fig. 3. The 3 M HCl + 1 M HNO_3, curve also has the same shape, again indicating the presence of molybdenum dimer above 10^{-3} M Q. The log D plot for 6 M HCl is flat from 10^{-8} to 10^{-2} M Q, dimerization requiring a still higher molybdenum concentration at this hydrochloric acid molarity. A gentle decrease in log D beginning around 10^{-6} M Q shows in the 7 M HCl plot, and is more marked at 8 M HCl and still more so at 10 M. The 12 M HCl curve lies below the 10 M curve at low Q and above it at high Q but still shows a marked decrease in D with increasing equilibrium aqueous molybdenum concentration above 10^{-6} M.

The variation in D with Q observed with DDE and HCl solutions above 6 M in concentration cannot be ascribed to dimer formation in the aqueous phase, as similar results do not occur with dibutyl ether or 2-ethylhexanol. Conductivity measurements show that the DDE phase in contact with such aqueous acid solutions is much more highly conducting than the corresponding dibutyl ether phase, and that when molybdenum(VI) is also initially present in the aqueous phase to the extent of $\sim 10^{-2}$ M, the conductivity is increased still further with DDE, though not appreciably with 2-ethylhexanol.[11] These results suggest that appreciable amounts of unassociated molybdenum(VI) ions exist in the DDE phase under these conditions and, in fact, in larger concentration than the chloride ions from extracted and dissociated HCl. This gives the necessary condition for the occurrence of the "common ion" effect on D, namely, that the hydrogen ion from the HCl dominates in one phase, the aqueous, while that from the molybdenum(VI) species dominates in the other, the organic phase. Of course, when the total molybdenum(VI) concentration is very small, the hydrogen ion in the DDE phase also comes predominantly from ionization of extracted HCl, and log D should have a constant value independent of Q. As Q is increased, there comes a point at which the hydrogen ion furnished by the molybdenum(VI) extracted into the DDE becomes comparable to that from the HCl there, and then the two species interfere with each others' extraction through their common hydrogen ions, both of their distribution quotients decreasing. If A^- is the only molybdenum(VI) species present in the DDE and there is no foreign acid present, the limiting slope of the log D *vs.* log Q plot would be $-{}^1/_2$, as can be seen from eq. 4 with $f°_{A^-} = 1, f_G = (Z) = 0, \alpha_{HA}(A) >> \alpha_{HX}(X)$. Actually, A^- is not the only species; with increasing molybdenum(VI) concentration in the organic phase, the proportion of HA increases, where HA is either an ion-pair or true molecular species, and so the curve of log D *vs.* log Q levels off again to zero slope at high Q when $f°_{HA}$ becomes large compared to $f°_{A^-}$. Such behavior should result in the sigmoid-type curve actually observed with DDE for HCl concentrations above 6 M.

That the decrease in D observed with DDE at HCl concentrations above 6 M is due to a common ion effect in the organic phase and not to dimerization in the aqueous phase can be shown by adding another strong acid to the system. As has already been discussed and illustrated, such an addition does not change the shape of the log D *vs.* log Q plot when the variation in D is due to dimerization. If, however, the variation is due to a common ion effect with hydrogen ion from the metal-containing species dominating in the organic phase, the addition of a highly soluble and dissociated acid to that phase will repress the extraction of the metal-containing anion, decreasing the value of D and making it independent of Q. This corresponds to the term $\alpha_{HZ}(Z)$ in eq. 3 and 4 becoming large and making D and $\partial \log D/\partial \log Q$ small and independent of molybdenum(VI) concentration. These are exactly the results observed upon adding HNO_3 to the DDE systems greater than 6 M in HCl (Curves F and G, Fig. 3).

More difficult to explain is why the DDE systems do not show this behavior at HCl concentrations below 7 M, but have constant log D curves, except for the decrease due to dimerization above 10^{-3} M Q. This may be due to the extraction, in this HCl concentration range, of a monomeric neutral species (symbolized by N, in eq. 3 and 4) whose distribution is, of course, independent of Q. But there is no difference in the ultraviolet spectrum of the molybdenum(VI) species extracting into DDE from 3 to 10 M HCl, so the change in the nature of the species is not likely to be marked. Possibly the reason for the constancy in D is that below 6 M HCl the hydrogen ions extract as H_3O^+ and that above 6 M HCl there is an increasing amount of hydrogen ions in the organic phase as ether oxonium ions due to the decreasing availability of water for solvation. The hydronium ions are smaller and so ion-pair more readily, and not until an appreciable amount of oxonium ions are produced are the ionic effects possible. Perhaps a similar change in the solvation of the molybdenum(VI) anion also occurs, *i.e.*

$$MoO_2(OH)Cl_2(H_2O)^- \longrightarrow MoO_2(OH)Cl_2(Ether)^-$$

In any case, it seems evident that the decrease in D with increasing Q observed at 10 M HCl and below 4 M HCl are due to different causes, the former to a common ion effect and the latter to polymerization in the aqueous phase. The studies on methyl isobutyl and methyl amyl ketones further support this conclusion. These solvents have a lower dielectric constant (13.1 at 25° and 11.9 at 20°, respectively[17]) than DDE, but their oxygens appear able to coördinate more readily with hydrogen ion and other ionic species so that extraction occurs to a greater extent. A very marked dependence of D on Q is evident with methyl isobutyl ketone at 1.2 and 2 M HCl (curves C and E, Fig. 4). Starting at about $Q = 10^{-6}$ M, D falls by a factor of $\sim$100 by $Q = 10^{-2}$ M. However, when HNO_3 is added, the value of D at low Q is decreased greatly and becomes constant up to 10^{-4} M Q. The HNO_3, which is quite soluble in the methyl isobutyl ketone, furnishes much more hydrogen ion to the organic solvent than the molybdenum species, (which in turn furnishes more than the HCl, as indicated by conductivity measurements[11]) and so represses the molybdenum extraction. At a high enough value of Q, a decrease due to molybdenum(VI) dimerization should, and does, start. This result shows that the major part of the decrease observed with 2 M HCl alone is due to the common ion effect. But by 10^{-3} M Q most of the molybdenum(VI) is in the ion-paired form, HA; the decrease which occurs beyond 10^{-3} M Q is due to the aqueous phase dimerization of molybdenum(VI). This latter decrease does not overlap the "common ion" decrease, for the slope of the log D *vs.* log Q plot remains $-1/2$ all the way up to 10^{-2} M Q, and, for both processes occurring simultaneously, a slope of $-3/4$ would be expected as can be seen from eq. 4. The 1.2 M HCl curve does show a slight region of overlap (possibly experimental error) but the two regions of decrease are better separated in the 4 M HCl curve; there is a small decrease from 10^{-6} to 10^{-4} M Q and another starting at about 10^{-3} M Q. The latter decrease is similar to those observed with 4 M HCl and DDE, diethyl ether and 2-ethylhexanol, and this decrease is not eliminated when HNO_3 is added to the system, showing it to be due to aqueous phase dimerization. However, the first small decrease in log D is eliminated by HNO_3, indicating that this decrease is due to the common ion effect. The reason for the smallness of the effect at 4 M HCl is that with increasing HCl concentration, the amount of HCl extracting into the ketone goes up rapidly, so that there is a larger amount of hydrogen ion in the solvent from non-molybdenum(VI) sources, and a larger degree of ion-pairing of the molybdenum(VI) species. Thus the 6 M HCl curve is flat from 10^{-9} to 10^{-4} M Q and with only a slight decrease thereafter, while the 8 M HCl curve is flat as far as measured to 10^{-3} M Q and has the same D as the 6 M HCl curve. Actually the D with 7 M HCl is larger, but above this HCl concentration the increasing amount of hydrogen ion brought into the ketone by extracted HCl represses the molybdenum anion extraction so much that its D decreases as well as becoming independent of Q in the concentration range studied. This result is also indicated by conductivity measurements[11]; methyl isobutyl ketone equilibrated with 8 M HCl has a fairly high conductivity which is not increased significantly when the aqueous solution is also made 10^{-2} M in molybdenum. However, the addition of HNO_3 or $HClO_4$ does increase the conductivity and also causes a decrease in the distribution quotient of molybdenum.

The greater solubility of HBr over HCl in methyl isobutyl ketone swamps out the decrease in D due to the common ion effect at a lower acid concentration when using HBr, so the log D curve for 4.4 M HBr is essentially flat from 10^{-8} to 10^{-4} M Q after which the decrease in D due to dimerization sets in. As expected, the curve retains its shape, though moved to lower values of D, when $HClO_4$ is added.

Curves similar to those obtained with methyl isobutyl ketone are given by methyl amyl ketone, Fig. 5. Due to the more hydrocarbon-like nature and larger molar volume of the latter, the value of D is lower at low HCl concentrations (larger ketones such as diisobutyl ketone have still smaller quotients[10]) but is higher at high HCl concentrations. (Aqueous HCl is less soluble in methyl amyl ketone than in methyl isobutyl ketone, so the maximum value of D occurs above 8 M HCl.) The 2 M HCl plot shows a decrease in D above 10^{-5} M Q and again the addition of HNO_3 lowers D and eliminates the first part of the decrease, but leaves that due to dimerization. With increasing extraction of HCl at higher aqueous HCl concentrations and increased ion-pairing in the organic phase, the decrease due to the common ion effect becomes smaller and has almost vanished at 4 M HCl, although that due to dimerization still remains above 10^{-3} M Q, as shown by the addition of HNO_3. At 8 and 10 M HCl the dimerization process has moved to higher molybdenum(VI) concentrations than are covered in the present investigation, and so much HCl is extracting that flat curves are obtained for the log D plots from 10^{-9} to 10^{-2} M Q and the value of D passes through a maximum and is decreasing by 10 M HCl.

The fact that with increasing HCl concentration some solvents show a greatly increasing solubility for HCl (noticeable phase volume changes occur with diethyl and diisopropyl ethers and with methyl isobutyl ketone) indicates that one of the primary assumptions made in deriving the extraction equations in the preceding paper, that of two "ideal" immiscible phases, is often not realized in actual systems. However, in a study of the variation of D with *metal ion concentration*, as in the present paper, any deviations from the ideal case are constant for a particular curve, so that the equation derived for $\partial \log D/\partial \log Q$ should hold. The results presented do lead to a ready explanation from eq. 4; they show that there are two[18] possible processes leading to a variation of D with increasing metal concentration, and that these processes can be differentiated. If the shape of the plot of log D *vs.* log Q is the same in different solvents and remains essentially unchanged when a strong acid, more soluble and dissociated in the solvent than HCl, is added to the system, the cause of the decrease in D is polymerization of the metal species in the aqueous phase. If the shape of the plot depends upon the nature of the solvent and D is decreased to a low constant value upon the addition of the strong foreign acid, the dependence of D on metal concentration is due to the common ion effect, *i.e.*, the domination of the organic phase by the metal anions and of the aqueous phase by the halide ions.

The extraction equations derived by Irving, Rossotti and Williams[3] ignore the effects of ionic equilibria suggested by Saldick[19] and extended in the preceding paper,[2] and so when in their experimental work on the extraction of $InBr_3$ into methyl isobutyl ketone, they observe a decrease in D with increasing metal concentration they are forced to ascribe this decrease to dimerization of the indium species in the aqueous phase. However, the extreme sensitivity of their distribution quotients to the presence of perchlorate and nitrate ions, that is, to $HClO_4$ and HNO_3 which extract into the ketone much better than HCl, shows that the variations in D that they observe are not due to aqueous phase dimerization but to the common ion effect. The indium extracts as the anion $InBr_4^-$ and furnishes to the ketone phase much more H^+ than does the HBr which extracts, but the reverse situation is true in the aqueous phase, where far more H^+ comes from the HBr. This is the necessary condition for the common ion effect, and a dependence of D on $Q^{-1/2}$ should result. Indeed, this behavior should be general for metal halide–hydrohalic acid–oxygenated organic solvent systems where the extracting metal-containing species is a stronger acid than the hydrohalic acid involved and the organic solvent has a dielectric constant high enough to permit ionization but low enough to enable differentiation of the acids. In fact, such a dependence of D on the metal concentration has also been observed with DDE and $InBr_3$, $GaCl_3$, $TlCl_3$ and $AuCl_3$.[20]

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[18] In the general case there are three possible processes. Multiple ion association such as ion-triplets, quadruplets, etc., in low dielectric constant solvents such as the aliphatic ethers and the esters will lead to an increase in D with increasing metal concentration at relatively high metal concentrations and this behavior has been observed in several systems, *cf.* ref. 15. In the molybdenum concentration range investigated in this work, this effect was not noticeable.

[19] J. Saldick, Abstracts of the 126th Meeting of the American Chemical Society, New York, N. Y., September, 1954, and *J. Phys. Chem.*, **60**, 500 (1956).

[20] R. H. Herber, W. E. Bennett, D. R. Bentz, L. C. Bogar, R. J. Dietz, Jr., G. S. Golden and J. W. Irvine, Jr., Abstracts of the 126th Meeting of the American Chemical Society, New York, N. Y., September, 1954.

THE OXIDATION OF CARBON BY NITROUS OXIDE[1]

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The reaction of nitrous oxide with ashless carbon surfaces is first order with respect to N_2O over almost the entire course of the reaction in the temperature range 400–650°. A dynamic (circulating gas) reaction system has been used. The rate constant appears to decrease somewhat with increasing initial N_2O pressure. Carbon–oxygen surface complexes increase the rate on Graphon (a carbon black) but have a slight inhibitory effect on Su-60 (a charcoal). Repeated high temperature H_2-treatments of the carbon, alternating with oxidation by N_2O, greatly increase the reactivity of the Graphon surface, but have no effect on the Su-60 surface. The activation energies are about 42 kcal./mole for Su-60 and about 68 kcal./mole for Graphon. The reaction mechanism appears to be simply a rapid oxidation of the active part of the surface by N_2O to form carbon–oxygen complexes and N_2, followed by further slow reaction of N_2O with these complexes to produce CO_2 and more N_2. The results are at variance with previously published work and reasons for this are suggested in the Discussion.

In the course of the work reported[2] concerning the catalytic oxidation of CO by N_2O on carbon surfaces it became evident that the reaction of N_2O itself with these same carbon surfaces was at variance with the description given earlier by Strickland-Constable.[3,4] This reaction has now been studied more extensively and it is the purpose of this paper to give new information about the reaction and to point out and explain the differences between this and the earlier work.

Experimental

Two types of carbon were used in this study: one a black and the other a charcoal.

Graphon.—A partially graphitized carbon black (supplied through the courtesy of the Godfrey L. Cabot Co.) was made by heating Spheron Grade 6 (a medium processing channel black) to approximately 3000° in an electric furnace. The surface area is about 80 sq. m. per g. and its ash content is about 0.02%.

Su-60.—A sugar charcoal of extremely low ash content was prepared, starting with Confectioners AA sugar furnished through the courtesy of the California and Hawaiian

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[2] R. N. Smith and J. Mooi, THIS JOURNAL, **59**, 814 (1955).

[3] R. F. Stickland-Constable, *Trans. Faraday Soc.*, **34**, 1374 (1938).

[4] D. G. Madley and R. F. Strickland-Constable, *ibid.*, **49**, 1312 (1953).

Sugar Refining Corporation. This sugar was used because it had an ash content of 0.0008%. After activation[2] this charcoal had a BET area of 1020 sq. m. per g., using ethyl chloride, and its ash content was less than 0.005%.

Nitrous Oxide.—This was obtained from the American Medical Gas Co. and used from the cylinder without further purification. Precautions were taken to prevent contamination on removal from the cylinder. The analytical method used in this study showed this gas to be pure N_2O.

The analytical methods, apparatus and reaction system are the same as those previously described,[2] except that the soda lime tube was omitted from this study. In essence, the reaction system provides for the continuous circulation of N_2O through a heated bed of carbon, and a manometric measure of the rate of the reaction.

Results

The experimental results are summarized in Tables I, II, III and IV. A few typical runs are plotted in Figs. 1 and 2 in order to show how closely the runs follow a linear plot and over what fraction of the reaction. They also show graphically the relative effects of initial nitrous oxide pressure and H_2 treatment *vs.* surface oxidation. These tables and figures will be referred to as needed in the Discussion.

Table I

First-order Rate Constants with Su-60

H = hydrogen treated surface, O = oxide surface

Type of surface[a]	Initial N_2O pressure, mm.	k, min.$^{-1}$ g.$^{-1}$
	T = 400°	
H	66.5	3.5×10^{-6}
	T = 500°	
H	73.6	5.29×10^{-3}
O	27.2	2.91×10^{-3}
O	27.8	2.83×10^{-3}
O	78.8	2.58×10^{-3}
O	78.8	2.78×10^{-3}
O(5)	346.8	1.91×10^{-3}
	T = 550°	
H(3)	69.2	2.39×10^{-2}
H	74.4	2.25×10^{-2}
O	29.4	2.42×10^{-2}
O	76.2	1.89×10^{-2}
O	78.8	1.68×10^{-2}
O(4)	83.0	1.96×10^{-2}
O	312.2	1.43×10^{-2}
	T = 600°	
H	64.4	7.44×10^{-2}
H	72.4	5.80×10^{-2}
O(1)	31.0	7.18×10^{-2}
O	73.6	6.82×10^{-2}
O(2)	76.2	5.87×10^{-2}
O	81.8	4.30×10^{-2}
O	333.8	3.80×10^{-2}
O	343.4	3.11×10^{-2}

[a] No. in ( ) refers to curve in Fig. 1.

Table II

First-order Rate Constants with Graphon

H = hydrogen treated surface; O = oxide surface

Type of surface[a]	Initial N_2O pressure, mm.	k, min.$^{-1}$ g.$^{-1}$
	T = 400°	
O	100.5	9.77×10^{-7}
	T = 500°	
H	68.8	3.43×10^{-5}
O	75.0	3.36×10^{-5}
	T = 550°	
H	63.4	3.10×10^{-4}
O	76.0	1.81×10^{-4}
O(5)	76.4	2.01×10^{-4}
	T = 600°	
H	66.6	8.18×10^{-4}
O	32.4	14.40×10^{-4}
O	79.8	7.87×10^{-4}
O	83.2	9.00×10^{-4}
O	83.6	12.00×10^{-4}
O	84.4	8.82×10^{-4}
O(4)	193.8	12.00×10^{-4}
O	372.4	11.70×10^{-4}
	T = 650°	
H	71.2	2.17×10^{-3}
O(1)	33.0	5.85×10^{-3}
O(2)	81.2	4.51×10^{-3}
O	83.8	4.75×10^{-3}
O	178.8	4.51×10^{-3}
O(3)	185.8	3.66×10^{-3}
O	365.2	3.43×10^{-3}
O	369.4	3.15×10^{-3}
O	375.4	2.90×10^{-3}

[a] No. in ( ) refers to curve in Fig. 2.

Table III

Effect on Rate Constant of Increasing Surface Oxidation of Graphon at 650°

Each reaction period is 45 min. long and separated from the next by a 15 min. pumping interval. The initial pressure of the fresh N_2O sample is given for each period. A H_2 treated surface was used at the beginning of the first interval.

Reaction period	Initial N_2O pressure, mm.	k, min.$^{-1}$ g.$^{-1}$
1	85.7	2.06×10^{-3}
2	86.7	2.12×10^{-3}
3	86.1	2.74×10^{-3}
4	86.7	2.90×10^{-3}
5	86.5	3.73×10^{-3}
6	86.4	4.30×10^{-3}

Table IV

Effect on Rate Constant of Repeated Hydrogen Treatment of Graphon Surface

No. of H_2 treatments	Initial N_2O pressure, mm.	k, min.$^{-1}$ g.$^{-1}$
1	79.8	2.15×10^{-4}
2	78.4	4.95×10^{-4}
3	79.6	6.44×10^{-4}
6	66.6	8.18×10^{-4}

Discussion

In the following discussion it will be well to bear in mind the significant experimental differences in this and earlier studies. Strickland-Constable's work was done with coconut charcoals containing considerable ash (1.8% in one case[4] and an unspecified amount in the other[3]) and with surfaces which had been "reproducibly" oxidized by 6 to 12 additions of N_2O. The reactions were carried out in a static system and followed by pressure changes; in the later paper[4] additional information was furnished by microgas analysis. In the present work an "ashless" carbon black and charcoal were used, the effect of both "clean" and "oxidized" surfaces was studied, and the reaction was carried out in a dynamic (circulating) system and followed by pressure changes; microgas analysis was also used as an adjunct. The important features of the reaction are reported separately below.

Order of Reaction.—In plotting log P_{N_2O} *vs.* t, a straight line plot is usually obtained for each run for the first 95% of the reaction; see Figs. 1 and 2. This indicates that all but the last bit of each run is strictly first order with respect to N_2O pressure. This last bit of reaction is unpredictable in nature and may be caused by some unknown and uncontrolled experimental variable, or it may have something to do with the fact that the CO_2 and N_2 pressure is over 70 times greater than the N_2O pressure at this point and soon thereafter becomes overwhelmingly greater. Strickland-Constable states that this reaction is first order with respect to N_2O "throughout the major part of the run," but examination of his data shows that in his experiments this first-order characteristic was not demonstrated until after about half the reaction had occurred. In fact, the data of his seven experiments (Strickland-Constable's[4] Figs. 2, 3 and 4) give excellent linear second-order plots ($1/P_{N_2O}$ *vs.* t for Fig. 2, and dP/dt *vs.* $P^2_{N_2O}$ for Figs. 3 and 4) for a little more than the first half of the reaction; the remaining half of the reaction gives a linear first-order plot (log P_{N_2O} *vs.* t for Fig. 2, and dP/dt *vs.* P_{N_2O} for Figs. 3 and 4). Further discussion of this difference will be given in the discussion of the reaction mechanism.

Reproducibility of Results.—The rate for a given run is unquestionably first order. The rate constants obtained from different runs under the same conditions of temperature, pressure and surface show some fluctuation. This is evident from Tables I and II. The reproducibility is of the same order as that obtained by Strickland-Constable.

Effect of N_2O Pressure.—With Su-60 there appears to be an increase in k as the *initial* nitrous oxide pressure decreases. In some instances there seems to be as much as a twofold change in k for a 10-fold change in the initial pressure. Because of the non-reproducibility of the runs it is not possible to make a precise statement of this fact, but there is no question about the general effect. Strickland-Constable also observed this effect, but to a greater degree than observed here. In his more recent paper his calculations were based on the rate constants for the last half of the reaction. It is interesting to note that during the course of the reaction k is unaffected by the changing N_2O pressure. It is also unaffected by the presence of CO_2 and N_2, for by the time a given reaction is 80% completed the pressure of products is six times that of the remaining N_2O, yet k is the same as at the start. These facts can mean only that immediately after addition of N_2O to the surface a state of surface oxidation is produced which, in addition to the changing N_2O pressure, determines the subsequent rate of the reaction. The "state of oxidation" is somehow determined by the initial N_2O pressure,

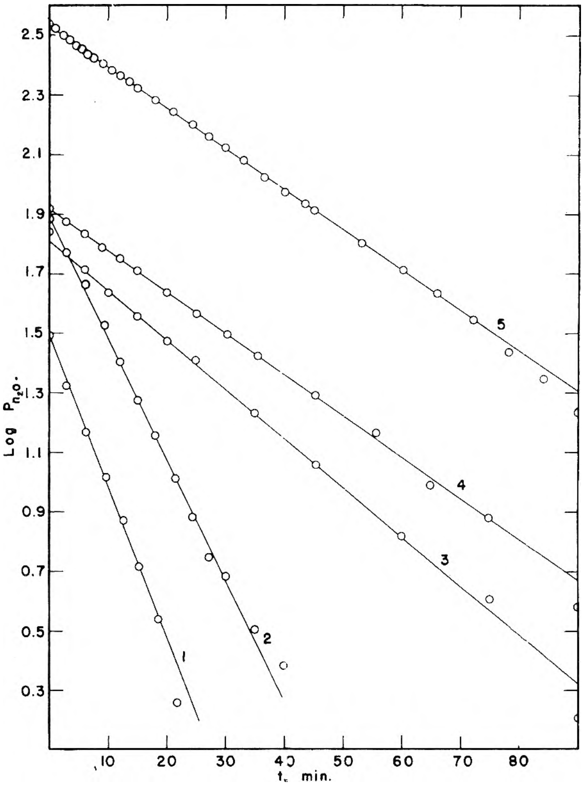

Fig. 1.—Typical first-order rate plots for Su-60: (1) and (2) oxidized surface at 600°; (3) H_2 treated surface at 550°; (4) oxidized surface at 550°; (5) oxidized surface at 500°. Multiply abscissa by 10 for correct time scale for curve 5.

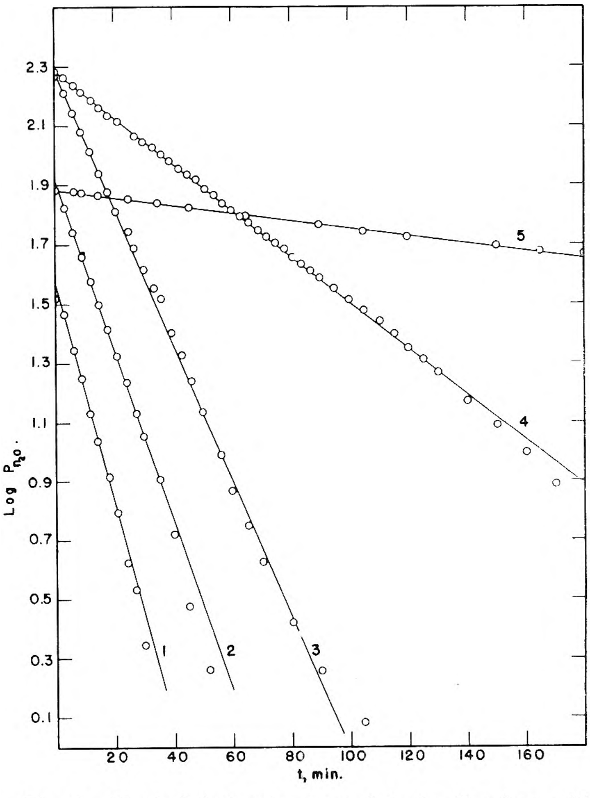

Fig. 2.—Typical first-order rate plots for Graphon with oxidized surface: (1), (2) and (3) at 650°; (4) at 600°; (5) at 550°.

but it is not the same as the "labile oxide" postulated by Strickland-Constable (*vide infra*).

Effect of Carbon–Oxygen Surface Complexes.—Table II shows that with Graphon the reaction rate is higher on the oxidized surface than on the H_2 treated surface. This information indicates that the stable carbon–oxygen surface complexes are important as intermediates in the reaction of N_2O with carbon. To emphasize this point note the runs in Table III in which successive fresh portions of N_2O, separated by 15-minute pumping periods, were added and allowed to react for 45 minutes. After 6 hours and six different N_2O samples at the same initial pressure the reaction rate had doubled. This additional surface oxidation over a period of time is very slow compared to the rate at which N_2O reacts with the surface to form N_2 and CO_2. Consequently the rate constant is but slightly affected during the course of any one run and each run was cleanly first order.

Table I shows that in the case of Su-60 the reaction rate is slightly higher on the hydrogen treated surface than on the oxidized surface. In the case of Su-60, then, it appears that extensive surface oxidation so stabilizes a small per cent. of the active oxygen complexes that they are no longer reactive to N_2O. These results with Graphon and Su-60 are especially striking when one realizes that Strickland-Constable observed that "when a fresh sample of charcoal was used, the rate of successive runs fell off from run to run, to attain a constant value only after half a dozen runs or more had taken place, after which the rate was reasonably constant."

Effect of Repeated Hydrogen Treatment.—Repeated H_2 treatment, alternating with oxidation by N_2O, has a marked effect on increasing the surface activity of Graphon for the reaction when it occurs on hydrogen treated surfaces; it has little effect on the reaction rate on an oxidized surface. This is shown in Table IV. Repeated H_2 treatment of Su-60 surfaces has no apparent effect. Similar behavior was observed[2] for the catalytic oxidation of CO by N_2O; repeated H_2 treatment greatly increased the catalytic activity of Graphon, but had no effect on Su-60. It is evident that active sites for both the N_2O reaction and the CO oxidation by N_2O are created by H_2 treatment of Graphon.

Effect of Temperature.—One of the most impressive differences between this work and that of Strickland-Constable is the temperature required for a reasonable reaction rate. In his earlier paper, Strickland-Constable gives no surface area for his charcoal, but assuming the area to be of the same order of magnitude as for Su-60 and converting his value of k to a per gram basis, one sees that his lot III has rate constants at 400° that are almost as large as Su-60 has at 600°. His lot I has rate constants about one-sixth of those for lot III (lots I and III are different samples from the same bottles.) In his second paper, Strickland-Constable studied the reaction at 320° and obtained a rate constant of about 10^{-3} min.$^{-1}$ g.$^{-1}$ at a pressure of about 100 mm. Su-60 must be heated to almost 500° in order to have a comparable rate. At 300°, Su-60 undergoes a certain amount of surface oxidation and then will no longer react. This was checked by CO_2 and N_2 analyses of a fresh N_2O sample which was circulated for 14 hours in contact with a N_2O-oxidized sample whose surface had been oxidized at 300°. H_2 Treated Graphon, even after 24 hours contact at 300°, does not produce a measurable amount of N_2 or CO_2.

The data in Tables I and II for the reaction occurring on oxidized surfaces at initial N_2O pressures of about 70 to 80 mm. yield activation energies of about 42 kcal./mole on Su-60 and about 68 kcal./mole on Graphon. These values are considerably higher than the 30 kcal./mole found by Strickland-Constable for his charcoals.

Effect of Ash.—The most reasonable way to explain the difference in reactivity between Strickland-Constable's charcoals and those used here is to ascribe Strickland-Constable's greater activity to the promoting effect of the ash present (1.8%) in his samples. Concerning his samples, Strickland-Constable states that "a commercial activated charcoal as such was used for this research rather than an artificially de-ashed charcoal, since the de-ashing process reduces the activity by a large factor, and it was feared that the chemically active surface would be too small to measure." If this is true, the rates described in this paper are more truly representative of the reaction between N_2O and carbon, while Strickland-Constable's results would show the catalytic action of ash on this reaction. The de-ashing process itself is not responsible for the lowered activity of Su-60 and Graphon, for the low ash here is due to the initial preparation of the samples and not to a subsequent de-ashing treatment.

The Reaction Mechanism.—To explain his experimental results Strickland-Constable postulates the mechanism

$$N_2O + C = \text{"labile oxide"} + N_2 \qquad (1)$$

$$N_2O + \text{"labile oxide"} = CO_2 + N_2 \qquad (2)$$

He states that "there is formed very rapidly a complete layer of the labile oxide (in addition to any stable oxides). The layer is complete in the sense that all sites which are capable of reacting are covered" . . . . . and "since (1) is very rapid, the over-all rate of reaction will depend on the rate of (2) and will therefore be first order with respect to N_2O." He supports this mechanism by analyses which show that during the course of the reaction the total oxygen which is present in the gaseous phase is not equal to that initially present in the added N_2O. He calls this missing oxygen (which is quite distinct from the stable oxides with which the surface is already saturated) the "labile oxide" or the "undesorbed CO_2." The latter name is used because at the end of a run all of the missing oxygen can be recovered as CO_2 or N_2O by pumping, without raising the temperature. He makes the additional statement that "it is necessary to make the further assumption that the total surface available for reaction is limited: then the falling off in value of the first order "constant" in the early stages of each run can be explained as due to the progressive blocking of part of this surface by the undesorbed CO_2."

At this point Strickland-Constable is actually in a dilemma; his analytical data show that the "labile oxide" is not formed "very rapidly" but actually builds up steadily during the first quarter of the reaction and then levels off at some concentration determined by the initial N_2O pressure. Since the "labile oxide" is the postulated intermediate important to the slow step of his mechanism the observed rate constant should actually increase during the first quarter of the reaction. At the same time, he finds it necessary to use this all-important intermediate as an agent to block reactive sites to account for the observed decrease in initial rates. If there is no "labile oxide" initially (as indicated by analysis), then step (2) must be very unimportant at the beginning—and as the reaction proceeds it must become less important as the reaction sites are blocked off; yet CO_2 *is* produced.

Strickland-Constable ruled out the possibility of the missing oxygen being merely adsorbed CO_2 and N_2O with an experiment at 328° in which he added, separately, equal volumes of N_2, CO_2 and N_2O and measured the resulting equilibrium pressures. He found the CO_2 and N_2O equilibrium pressures to be a little less than the equilibrium N_2 pressure and from the relative adsorbabilities concluded that "assuming that N_2 is not adsorbed, then the amounts of CO_2 and N_2O that are adsorbed are small, and not nearly enough to account for the amount of missing oxygen observed in the oxidation experiments."

It is interesting to examine these data with some care. Strickland-Constable states that the volume of his reaction bulb is 500 ml. and that, referring to his drawing, the "two bulbs S_2 and S_1 are for measuring out the N_2O or other gas before adding it to the carbon." He does not give the volumes of S_1 and S_2, but using his data for N_2 before and after expansion and assuming that no N_2 was adsorbed, one can calculate the combined volume to be 134 cc. In this and other calculations here it was assumed that room temperature was 25° (the reaction bulb was given as 328°). Further information from Strickland-Constable's data concerning the amounts of N_2O and CO_2 adsorbed is given in Table V.

TABLE V

THE ADSORBABILITY OF N_2O AND CO_2 ON STRICKLAND-CONSTABLE'S CHARCOAL

(Wt. of sample = 12 g.; temp. of reaction bulb = 328°; temp. of S_1 and S_2 assumed = 25°)

	CO_2	N_2O
Pressure in S_1 and S_2, mm.	647	646
Pressure in reaction bulb, mm.	345	344
Moles of gas added	4.67×10^{-3}	4.67×10^{-3}
Moles of gas not adsorbed	4.61×10^{-3}	4.60×10^{-3}
Moles of gas adsorbed	6.0×10^{-5}	7.0×10^{-5}
Moles of gas adsorbed (expressed as O atoms)	12.0×10^{-5}	7.0×10^{-5}
O atoms adsorbed, cc. at S.T.P. per g. of charcoal	0.22	0.13
Pressure of missing oxygen atoms, mm.	9.0	5.2

In addition to this recalculation, an experiment was conducted in which 12 g. of a commercial coconut charcoal of about 1000 m.²/g. out-gassed at 300° for 12 hours, was exposed to a known volume of helium. In each case the equilibrium pressure was essentially 300 mm. Relative to helium, N_2 was found to be adsorbed to the extent of 7.76×10^{-5} mole. If this charcoal was at all comparable to the one used by Strickland-Constable, one should then increase the amount of each of the adsorbed gases given in Table V by 7.76×10^{-5} mole to give a total of 13.8×10^{-5} mole of CO_2 and 14.8×10^{-5} mole of N_2O. This in turn corresponds to 0.51 cc. (S.T.P.) of O atoms adsorbed per gram or to a pressure of 20.6 mm. of "missing oxygen" for CO_2, and to 0.27 cc. (S.T.P.) per gram or to 11.1 mm. pressure of O atoms for N_2O. Thus the adsorption of these two quantities of gases is somewhat more than enough to account for the "missing oxygen" observed by Strickland-Constable during the course of a reaction with an initial N_2O pressure of 345 mm. Admittedly, several approximations were used in this calculation, and the final values are rough, but when they are considered along with the additional facts that the missing oxygen can always be quantitatively desorbed by pumping (without heating), that CO_2 has negligible effect on the reaction rate, and that the amount of missing oxygen comes as the small difference between two large experimental values, it seems reasonable to conclude that the missing oxygen is merely adsorbed CO_2 and N_2O. This same conclusion makes it unnecessary to postulate a "labile oxide" intermediate in the reaction mechanism.

Strickland-Constable's remaining difficulty, the change from a second-order reaction to a first-order reaction when the reaction is about half completed, seems best explained by considering the circumstance of 12 g. of carbon in a 500-ml. vessel in a static system. Initially the reaction will be rapid, but as the N_2O in the vicinity is consumed, the reaction slows as it becomes necessary for N_2O to diffuse through the reaction products to reach the carbon. Perhaps the rate-determining factor in a static system is ultimately the diffusion process, the rate being determined by the N_2O concentration (and hence an observed first-order reaction in the latter stages of the reaction).

A simple mechanism which will account for the experimental results in the present study is

$$N_2O + C = (CO) + N_2 \qquad (3)$$

$$N_2O + (CO) = CO_2 + N_2 \qquad (4)$$

where (CO) is a stable carbon–oxygen surface complex. Step 4 is the slower, rate-determining step. This mechanism is in agreement with the fact that stable surface oxides are formed. Direct analytical results[5] show that Graphon exposed to N_2O for three hours at 500° picks up 0.013% oxygen, and that Su-60 under the same conditions picks up 1.21% oxygen. If the rate constants in Tables I and II are converted to a unit area basis instead of a unit weight basis, it will be observed that the Su-60 surface is about 7 times more active than the Graphon surface. This is in keeping with the fact that the analytical results show about 7 times more

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[5] R. N. Smith, J. Duffield, R. A. Pierotti and J. Mooi, THIS JOURNAL, **60**, 495 (1956).

oxygen on the surface of the Su-60 than on the Graphon. Table III shows the doubling of the reaction rate resulting from increased surface oxidation over a period of six hours. The somewhat slower rate of reaction on the oxide surface than on the H_2 treated surface of Su-60 indicates that with extended surface oxidation some of the reactive complex sites which are formed immediately after addition of N_2O must be converted to unreactive complex sites.

STRESS ACTIVATED LUMINESCENCE IN X-IRRADIATED ALKALI HALIDE CRYSTALS

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The luminescence caused by stressing crystals of potassium bromide, sodium chloride, and lithium fluoride containing F-centers produced by X-rays has been investigated in the region of plastic flow. Light output was measured under varying conditions of irradiation time and strain rate. Rate of light output shows a linear dependence on strain rate (from 12.1 to 116 per cent./min.) for all three materials. It is shown that a process by which F-center electrons are excited to the conduction band by thermal spikes associated with the movement of dislocations, with subsequent recombination with a vacancy or a halogen atom, can account for the experimental observations.

In the course of a study on the effect of irradiation on transient creep of alkali halides done at this Laboratory,[2] it was observed that relatively intense visible light was emitted from irradiated crystals during compression. Such a phenomenon has been observed previously in irradiated alkali halides when they were compressed or otherwise mechanically worked.[3–5]

It has been shown that the application of stress to X-rayed crystals causes bleaching.[6–8] This would suggest that the rate of recombination of trapped halogen atoms and electrons is considerably increased by external stress. Studies of the effect of stress on the conductivity of sodium chloride[9,10] lead to the conclusion that the observed increase is the result of either vacancy generation or the freeing of electrons by the motion of dislocations.[11,12]

In this investigation the luminescence caused by compressing single crystals of sodium chloride, potassium bromide and lithium fluoride containing F-centers produced by X-rays was studied in the region of plastic flow in order to elucidate the mechanism. The rate of light emission was measured as a function of strain, strain rate, irradiation time and temperature. In addition, the general characteristics of the emission spectra were determined.

Experimental

Sodium chloride, potassium bromide and lithium fluoride specimens were cleaved to 4 × 4 × 10 mm. from larger optical grade single crystals which were obtained from the Harshaw Chemical Company. Six specimens were used for each strain-light output curve in order to average out individual crystal variations. The specimens were packed in crushed salt from the same stock and heated for at least four hours at 100° below the melting point. This heat treatment was found to yield sufficiently reproducible data. The specimens were then quenched to room temperature in a stream of air, separated from the crushed material and placed in a desiccator. The crystals were used within a few hours after quench.

The specimens were irradiated in a light-tight aluminum foil container (1 mil thickness) which was rotated by a four r.p.m. clock motor around an axis normal to the X-ray beam. Irradiations were made with a Machlett AEG-50 T tube with a tungsten target and a beryllium window. The tube was operated at 50 KV. and 30 ma. providing about 72,000 Roentgen per hour at the point of irradiation.

The irradiation times used in the investigation of variation of light output with strain rate were one minute for KBr, 2.5 minutes for NaCl and ten minutes for LiF. For experiments at constant strain rate, crystals were irradiated from one minute to two hours for all three materials. After irradiation, the crystals were placed in the compression apparatus in room light. Each specimen was exposed to room light for 0.7 minute and kept in the dark for one minute before compression. This procedure was found to adequately eliminate any excitation effects due to room light.

A small tensile machine was modified for compression tests. The upper head of the tester was replaced with a proving ring and linear differential transformer to allow measurement of force during compression. The linear differential transformer was connected to an electronic micrometer whose output was recorded on one channel of a recorder. The specimen was placed on the lower ram which protruded up into a reflecting chamber consisting of several front silvered mirrors arranged to direct the light from the specimen onto two 1P28 phototubes. These phototubes were connected to an amplifier and the output was recorded on the other channel of the recorder. A constant fraction of the light from a crystal was measured in every experiment since the geometry was constant. The useful phototube range was 2300 to 5800 Å.[13] The approximate light intensity as seen by the phototubes for the maximum luminescence observed was 1.8 μ lumens for KBr, 0.16 μ lumen for NaCl and 0.07 μ lumen for LiF. The measurements were reliable to a reading of 0.001 μ lumen.

The total strain introduced during an experiment was about 15% in the direction of the long axis.

The general characteristics of the luminescence spectra were determined by placing various gelatine Wratten filters in front of the phototubes. The filters used were Wratten O, 1A, 2B, 8K2, 15G and 22. Calibration of the proving ring was done by loading with weights, and it was found to be

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(1) Chemistry Department, Iowa State College, Ames, Iowa.

(2) R. A. Lad and F. I. Metz, *J. Mech. Phys. of Solids*, **4**, 28 (1955).

(3) J. Trinks, *Wien. Ber.*, [IIa] **147**, 217 (1938).

(4) F. Urbach, *ibid.*, **139**, 353 (1930).

(5) F. G. Wick, *J. Opt. Soc. Am.*, **29**, 141 (1939).

(6) A. Smekal, *Z. Ver. Deut. Ing.*, **72**, 667 (1928).

(7) H. J. Schroder, *Z. Physik*, **76**, 608 (1932).

(8) I. S. Jacobs, *Phys. Rev.*, **93**, 993 (1954).

(9) Z. Gyulai and D. Hartley, *Z. Physik*, **51**, 378 (1928).

(10) Z. Gyulai and J. Boros, *Math. Naturw. Anz. ung. Acad. Wiss.*, **59**, 115 (1940).

(11) W. W. Tyler, *Phys. Rev.*, **86**, 80 (1952).

(12) F. Seitz, *ibid.*, **80**, 239 (1950).

(13) R. W. Engstrom, *J. Opt. Soc. Am.*, **37**, No. 6, 420 (1947).

linear up to 10 kilograms, the largest load reached in the experiments. The linearity of the phototubes and recording circuits was verified. The rate of straining was changed by shifting belts onto different steps of a set of cone pulleys. Experiments were performed at strain rates from 12.1 to 116%/min. Strain rate was found to be constant during a run by checking with a dial indicator and stop watch.

For determination of the temperature dependence of the light output, crystals were maintained at various temperatures (±0.2°) during compression. This was achieved by passing helium through a coil submerged in a Dry Ice–acetone bath and then electrically heating the gas to the required temperature. Several small jets of gas were directed over the faces of the crystals. The temperature range covered was from 10 to 30°.

With the procedure outlined above the data were reproducible to ±5%.

Results and Discussion

The rate of light emission as a function of compressive strain is shown in Fig. 1 for potassium bromide, lithium fluoride and sodium chloride for several strain rates. After a small induction time, the rate of light emission for all three materials was found to increase rapidly up to a strain of about 5%. The induction period was attributed to the time required for the crystal ends to adjust to the apparatus, and the subsequent rise was attributed to the time required for the transition from elastic to plastic deformation. In order to avoid complications due to these effects, all the following discussion will be restricted to the experimental region beyond 5% strain. It can be seen that for potassium bromide and lithium fluoride the rate of light emission becomes constant in the range greater than 5% strain. However, in the case of sodium chloride, the rate decreased continuously after this point. No explanation of this difference in behavior is as yet available. It should also be mentioned that if at any time during an experiment the compression was interrupted, the luminescence decayed to zero in less than one second. On resuming compression, the light output rose again to its original value with equal rapidity.

The rate of light output is directly proportional to strain rate for all three materials. This is true for sodium chloride provided the rates are compared at values of constant strain. These results are shown in Fig. 2.

The dependence of the rate of light emission on irradiation time is shown in Fig. 3. Sodium chloride and potassium bromide show a saturation effect, while for lithium fluoride the rate is still increasing up to 120 minutes of irradiation.

Experiments carried out between 10 and 30° indicated that the effect of temperature on the rate of light emission is small. The activation energies calculated from the plots of log (rate) against $1/T$, as shown in Fig. 4 were less than 0.05 e.v.

The luminescence spectra for all three materials showed two peaks with maxima in the vicinity of 3500 and 4500 Å. In each case, the shoulder on the short wave length side of the 3500 Å. peak was considerably greater than the shoulder on the long wave length side of the 4500 Å. peak. Because of the crudeness of these measurements the precise position of the two maxima are in doubt; however, the spectra suggest that at least two processes occur during compression which result in luminescence. The ratio of the intensities of the high

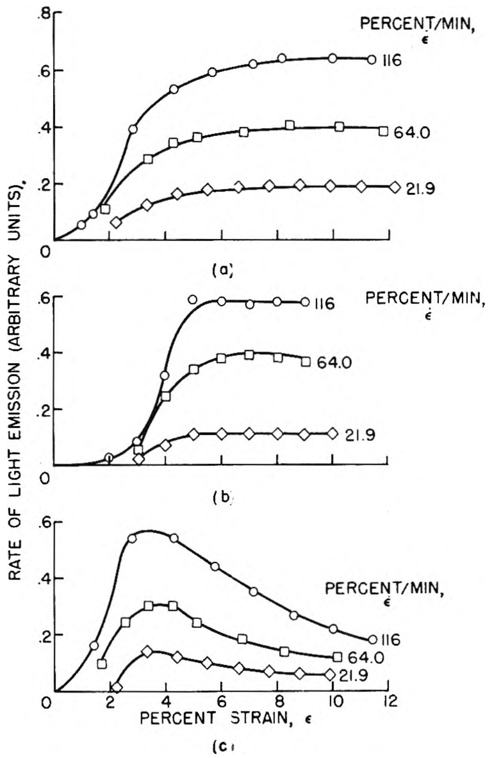

Fig. 1.—Dependence of rate of light emission on strain: (a) potassium bromide; irradiated for one minute; (b) lithium fluoride; irradiated for ten minutes; (c) sodium chloride; irradiated for 2.5 minutes.

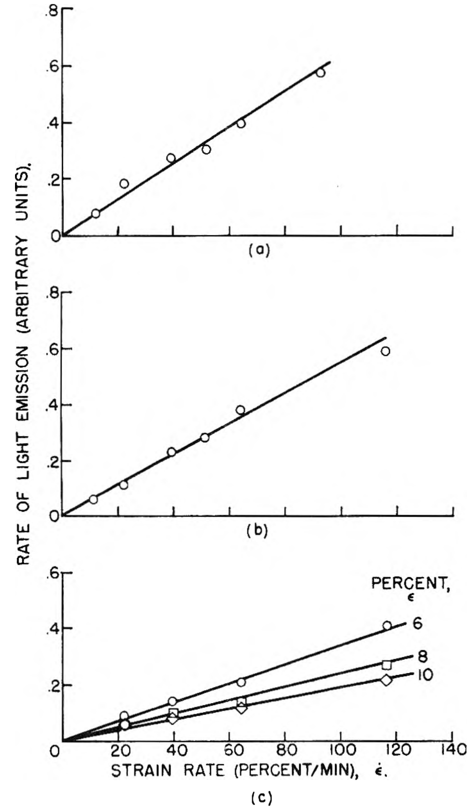

Fig. 2.—Dependence of rate of light emission on strain rate: (a) potassium bromide; irradiated for ten minutes; (c) sodium chloride; irradiated for 2.5 minutes.

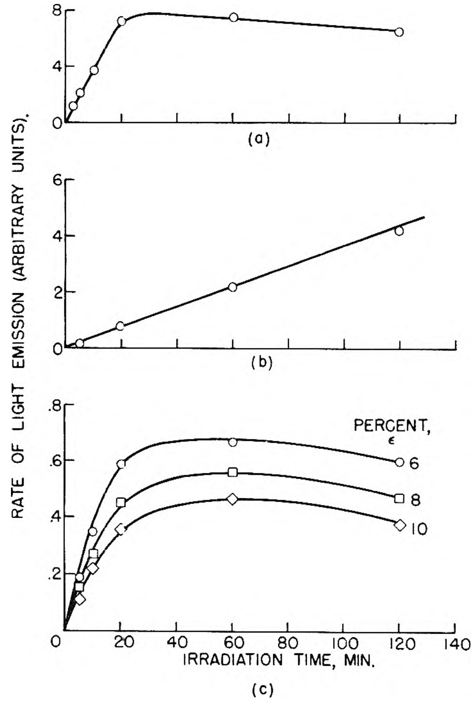

Fig. 3.—Dependence of rate of light emission on irradiation time: (a) potassium bromide; (b) lithium fluoride; (c) sodium chloride. All crystals were strained at 64%/min.

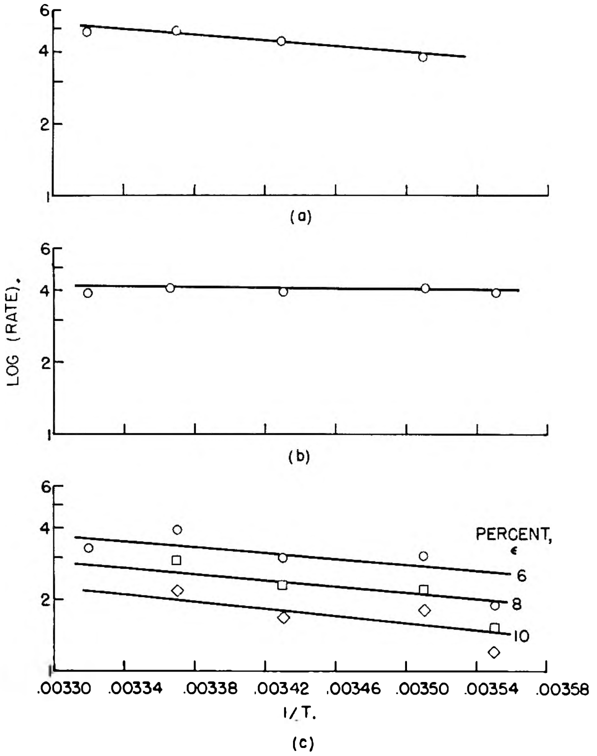

Fig. 4.—Temperature dependence of the rate of light emission: (a) potassium bromide irradiated for one minute; (b) lithium fluoride irradiated for ten minutes; (c) sodium chloride irradiated for 2.5 minutes. All crystals were strained at 64%/min.

wave length peak to the low wave length peak increased by about 80% for KBr and NaCl during the experiment. The reverse was true for LiF.

The absorption spectra were also measured in the wave length rate of 2100 to 10,000 Å. Comparison of irradiated crystals before and after compression showed no significant difference in the spectra. It may be concluded, therefore, that the average F-center concentration did not change measurably during compression. At most, only 3×10^9 photons/sec. were measured during the compression experiment. If only one emitted photon in a thousand were counted, and if the experiment ran 100 seconds, an upper limit of 10^{14} photons were emitted. Since the F-center concentration is of the order of 10^{17} per cm.,[3] the emission processes could not significantly alter the F-center concentration.

Reasonable processes which may result in the emission of light are the recombination of electrons with halogen atoms or vacancies. Three mechanisms which may be involved in such processes are the following: (1) recombination of halogen atoms and F-centers as the result of normal diffusion. The increased number of vacancies during strain would increase the diffusion rate and thereby lead to an increase in luminescence. (2) Tunneling of electrons from F-centers to holes. The recombination of F-centers and holes may be imagined to take place by a tunneling process as described by Dexter.[14]

Since the probability of tunneling increases with increasing vacancy concentration, it is expected that the excess vacancies produced by strain would enhance the tunneling rate. Thus the effective transport of F-centers through the crystal, and their recombination with holes, would be increased by plastic strain. (3) Excitation of F-center electrons to the conduction band. Excited electrons could then recombine with halogen atoms or combine with vacancies to re-form F-centers. The energy for the excitation could arise from thermal spikes resulting from the motion of dislocations during strain.[12]

The experimental observations indicate that neither tunneling nor diffusion is important in contributing to the light emission. The fact that luminescence decays very rapidly when compression is interrupted and that the rate of emission is directly proportional to the strain rate shows that the rate-determining step is accelerated only while the crystal is being strained. Mechanisms 1 and 2 depend on the presence of vacancies produced by moving dislocations and should therefore lead to a rate of light emission that increases with increasing strain and decays only slowly when the compression is interrupted. Also, if a diffusion process were operative, the activation energy required would be of the order of 0.5 e.v. The observed activation energy is less than this by at least an order of magnitude, so that a diffusion mechanism is unlikely.

Furthermore, if mechanisms 1 and 2 were operative, the rate of light emission would be proportional to the square of the F-center concentration since the number of F-centers is equal to the number of halogen atoms. However, if mechanism 3 is rate determining, the rate of light emission should depend only on the F-center concentration. Assuming a constant scale factor which takes into

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[14] D. L. Dexter, *Phys. Rev.*, **93**, 985 (1954).

account differences in irradiation procedure, it is possible to compute the relative F-center concentration from irradiation time using the data of Mador, Wallis, Williams and Herman.[15] Then, if the rate of light emission is first order, the ratio of the rate to F-center concentration should be constant. This is shown to be the case for sodium chloride in Table I. The above-mentioned investigators also found a linear increase in surface F-center concentration with irradiation time for lithium fluoride; Fig. 3 shows a similar linear relationship of the rate with irradiation time in these experiments.

TABLE I

Ratio of the rate of light emission, Å., to the F-center concentration C_0 in the first 0.2 mm. of the surface layer for sodium chloride strained at 64%/min.

Irradiation-time, min.	Å./C_0 × 10^{15} (arbitrary units) $\epsilon = 6\%$	$\epsilon = 8\%$	$\epsilon = 10\%$
5	1.2	0.91	0.68
10	1.3	0.96	0.79
20	1.4	1.0	.84
60	0.96	0.90	.75

Mechanism 3, in which the rate-determining step is the excitation of an electron from an F-center to the conduction band by a thermal spike, is the only one of those proposed which can account for all the experimental observations. This process depends directly on the strain rate rather than the strain, and predicts that the luminescence would decay rapidly on interruption of compression. Also, since the probability of exciting an electron from the F-center to the conduction band depends on the thermal spike rather than on the average temperature of the crystal, the temperature coefficient of the excitation process should be quite small. This mechanism leads directly to a spectrum of emitted light containing two peaks The excited electron in the conduction band can combine with either a vacancy or a halogen atom to give an F-center or a negative ion, thereby giving off light at two different energies.

Acknowledgment.—The authors wish to express gratitude to Dr. R. A. Lad for many valuable suggestions made during the course of this investigation.

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[15] I. L. Mador, R. F. Wallis, M. C. Williams and R. C. Herman, *Phys. Rev.*, **96**, 617 (1954).

RATES OF ISOMERIZATION OF TRIETHYL PHOSPHITE TO DIETHYL ETHYL PHOSPHONATE IN THE PRESENCE OF ETHYL IODIDE

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Rates of the isomerization reactions have been determined by continuous density measurements at 90, 100 and 110° over a concentration range from 10 to 56 mole % ethyl iodide. The initial 60–70% of the reaction was found to be zero order with respect to triethyl phosphite and first order with respect to ethyl iodide. Initial specific reaction rate constants have been expressed as functions of concentration. The over-all composition–time curves resemble in shape those for an autocatalytic process. The experimental results over the entire temperature composition range studied have been found to be satisfactorily expressed in terms of concentrations by means of a single equation proposed much earlier by Zawidzki and Staronka.[1]

The reaction investigated is commonly indicated by the over-all equation

$$P(OC_2H_5)_3 + C_2H_5I \longrightarrow C_2H_5P(O)(OC_2H_5)_2 + C_2H_5I$$

The general reaction was first described by Michaelis and Kaehne[2] and was studied extensively by Arbuzov[3] who showed the general nature of the reaction and proposed a possible mechanism. The general mechanism proposed by Arbuzov postulates two steps for the reaction: the formation of a phosphonium halide intermediate followed by its decomposition into the products

$$P(OR)_3 + R'X \longrightarrow R'P(OR)_3{}^+X^-$$
$$R'P(OR)_3{}^+X^- \longrightarrow R'P(O)(OR)_2 + RX$$

Intermediates, which are condensation products of triphenyl phosphite with alkyl halides, have been isolated by Arbuzov[3] and by others.[4] They have the expected empirical formulas and have been assigned structural formulas corresponding to phosphonium halides. Landauer and Rydon,[4] however, have indicated that these phosphonium halides are rather unusual since they precipitate silver iodide quite slowly from silver nitrate solutions.[5] In reactions involving trialkyl esters of phosphorous acid, no intermediate has been isolated, presumably due to their very transient existence and low stability under experimental conditions. In the absence of a better alternative mechanism, more recent investigators[6] apparently agree that the reaction follows the general course proposed by Arbuzov.

Kinetic measurements on this reaction had been performed by Zawidski and Staronka[1] and by Staronka.[6] The original publication of Zawidski

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[1] J. Zawidzki and W. Staronka, *Anzeiger Akad. Wiss. Krakau A.*, 319 (1915); *Abhand. Akad. Wiss. Krakau*, **55**, 101 (1915); *via C. A.*, **11**, 2294 (1917).

[2] A. Michaelis and R. Kaehne, *Ber.*, **31**, 1048 (1898).

[3] A. E. Arbuzov, *J. Russ. Phys. Chem. Soc.*, **42**, 395 (1910); **38**, 161, 293, 687 (1906); *Ber.*, **38**, 1171 (1905).

[4] S. R. Landauer and H. N. Rydon, *J. Chem. Soc.*, 2224 (1953).

[5] Since this reaction was carried out in a solution of ethanol, with which triphenyl phosphite methiodide was shown to react rapidly to form ethyl iodide, the slow precipitation of AgI may neither prove nor disprove the ionic character of the methiodide.

[6] W. Staronka, *Roczniki Chim.*, **7**, 42 (1927); *via C. A.*, **22**, 1264 (1928).

and Staronka[1] has not been available. They made measurements at 85 and 95°, and agreed with Arbuzov's mechanism. They also postulated that the speed of the reaction was autocatalytically accelerated by the diethyl ethylphosphonate product. A rate equation was presented, which was claimed to incorporate in a quantitative manner all the data observed. This equation, after slight modification, has also been tested successfully in the present work.

Staronka[6] later postulated that the shape of the composition–time curves for the isomerization reaction were caused by changes of the reaction medium rather than by autocatalysis.

Pudovik[7] has discussed the kinetics of this reaction. He also supports Arbuzov's idea of a phosphonium halide intermediate and believes the intermediate to be of an ionic character.

Kosolapoff[8] observed rates of reactions between triethyl phosphite and *n*-butyl bromide by measuring the quantities of ethyl bromide which distilled from the reaction mixture. The shapes of the curves obtained suggested that the reactions were of a complex nature and no numerical rate constants were presented.

The present investigation may be regarded as an extension of the work of Zawidski and Staronka.[1] The experimental work, however, was completed before any reference to the older work had been found.

Experimental

Materials.—The reagents used were triethyl phosphite and ethyl iodide.

The triethyl phosphite used was a Victor Chemical product. Purification of this reagent was accomplished by refluxing the triethyl phosphite with metallic sodium for 3 to 4 hours *in vacuo* to remove diethyl phosphonate. The material was then distilled twice at reduced pressure (48–50 mm.), and the distillate collected between 75 and 76°. The triethyl phosphite was stored under a dry nitrogen gas atmosphere in black bottles.

The ethyl iodide was prepared, purified and stored according to approved and well established procedures.[9]

Apparatus and Procedure.—The apparatus consisted of a specially designed reaction flask, a stirrer, a calibrated glass bob suspended from an analytical balance by means of 34 gage silver wire and a constant temperature bath. The reaction flask was designed as a combination U and H tube constructed of glass tubing and standard tapered ground glass joints. A stirrer, made from 6 mm. glass rod was introduced vertically into the reaction mixture through a gas-tight stirrer bearing placed on the upper end of one of the legs of the reaction flask. The calibrated glass bob, immersed in the reaction mixture, was suspended from an analytical balance permanently mounted directly above the other leg of the reaction flask. The suspension wire passed through a reflux condenser directly attached to the reaction flask. The flask was enclosed in an oil-filled thermostat held at constant temperature with variations less than ±0.1°.

To perform an experiment, a weighed amount of triethyl phosphite was introduced into the reaction flask which had been flushed previously with dry nitrogen. Adequate time was allowed for the temperature of the ester to attain thermal equilibrium. At this time a weighed quantity of ethyl iodide was introduced quickly. The starting time of the reaction was taken as the time at which one-half of the ethyl iodide had drained into the reaction flask. The complete drainage time was usually less than 45 seconds. The initial temperature of the mixture showed a tendency to rise due to exothermic effects. This had to be compensated by adding the iodide at a lower temperature, designing the reaction flasks with a large surface, and using efficient stirring. The specific volumes of the reacting mixture were determined periodically by observing the variation in weight of the calibrated bob immersed in the solution. The reaction mixture was stirred continuously except during the brief periods required to obtain density values. The number of weighings performed was dependent upon the rate of reaction. Usually weighings were taken at approximately equal intervals during the first two half-lives of the reaction, and less frequently during the third and fourth half-life. After the fourth half-life the weighings were continued, however, until no further changes could be detected over a period of an hour.

Discussion of Results

As mentioned previously, the rates of reaction were followed by measuring the changes in specific volume of the reacting mixture. During the initial phases of the investigation, it was observed that the specific volumes at 30° of mixtures of triethyl phosphite and diethyl ethyl phosphonate were linear with the mole fraction of either constituent. The linearity persisted in the presence of ethyl iodide throughout the concentration range investigated. In the case of ternary mixtures, the specific volumes were plotted *versus* the ratio of the number of moles of diethyl ethylphosphonate to total number of moles of esters. No deviation from linearity greater than 0.05% was detected, even as the concentration of ethyl iodide was increased to 50 mole %.

The fraction of triethyl phosphite converted to diethyl ethylphosphonate was calculated from the relation

$$\alpha = \frac{V_0 - V_t}{V_0 - V_\infty}$$

Where V_0, V_t and V_∞ refer to the specific volumes of the reacting mixture at times zero, t and "infinite." The initial specific volume could not be measured directly due to incomplete mixing and rapidity of reaction. The value of V_0, however, could be determined satisfactorily by extrapolation to zero time of the function log $(V_t - V_\infty)$.

The specific volumes were measured to 0.0001 cc. and were probably internally consistent to better than 0.001 cc. This constitutes an estimated average uncertainty in the determination of α not greater than ±10% of the indicated value.

Experimental measurements were performed at 90, 100 and 110°. The results are summarized in Table I where rounded values of the fractional lives of the reaction, concentrations and temperatures are tabulated. Typical experimental results are also shown graphically in Fig. 1. At the same temperature, the degree of duplication at similar concentrations and fractional life appears to be within ±10%.

The appearance of the composition–time curves is rather striking and several observations can be made by simple inspection. During the first 60% of the reaction, the reaction rate appears to be of zero order with respect to the concentration of ester and first order with respect to the concentration of ethyl iodide. If these observations are approximately correct, there should be a linear correlation between the periods of half-life and the parame-

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(7) A. N. Pudovik, *Doklady Akad. Nauk. SSSR*, **84**, 519 (1952); *via C. A.*, **47**, 3227 (1953).

(8) G. M. Kosolapoff, *J. Am. Chem. Soc.*, **66**, 109 (1944).

(9) A. H. Blatt, "Organic Syntheses," Coll. Vol. II, John Wiley and Co., New York, N. Y., 1943, p. 390.

TABLE I

FRACTIONAL LIFE PERIODS OF ISOMERIZATION REACTION (MINUTES)

Temp., °C.	Mole % C_2H_5I	Fraction of ester isomerized 0.10	0.20	0.30	0.40	0.50	0.60	0.70
90°	56.0	14	33	52	72	92	112	136
	50.0	19	41	62	85	107	129	158
	50.0	21	44	67	89	112	135	158
	37.5	30	64	96	129	161	192	
	25.2	62	120	167	212	257	304	
	24.9	51	105	158	212	255	318	
100°	37.6	15	30	45	60	75	90	108
	37.5	15	30	45	60	75	89	105
	30.0	22	43	64	85	106	127	148
	25.0	28	54	78	103	128	152	177
	25.0	26	52	78	103	129	155	182
	12.5	65	128	191	255	317		
110°	24.8	14	27	41	54	68	82	96
	20.0	22	40	57	73	89	106	124
	15.0	27	51	75	99	124	148	173
	10.0	44	90	126	160	194	227	264

ter (n_{A_0}/n_c) where n_{A_0} denotes the initial number of moles of triethyl phosphite and n_c the moles of ethyl iodide. This correlation is shown in Fig. 2.

Specific reaction rate constants for the initial 60% of the reaction as functions of the initial concentrations of the reactants are readily expressed by a general equation of the form

$$k = \frac{(n_{A_0}/n_c)}{b + m(n_{A_0}/n_c)} \qquad (1)$$

where b and m are constants related to the intercepts and slopes of the linear correlations given in Fig. 2. Table II lists the numerical values of the particular constants.

TABLE II

INITIAL SPECIFIC REACTION RATE CONSTANT (NUMERICAL VALUES OF CONSTANTS FOR EQ. 1)

Temp., °C.	b, min.	m, min.
90	58	157
100	0	87.6
110	14	42.5

No particular theoretical significance has been attached to the above equation other than that it represents a convenient and concise means of expressing the experimental results for the first 60% of the reaction. The average deviation between the calculated and experimental values of α is less than ±10% of the experimental value.

Regardless of the actual mechanism of the reaction, it was considered of interest to attempt to derive a rate equation that would give the over-all shape of the experimental time–composition curves. Using a simple model where a reactant A changes to a product B in the presence of a catalyst C and assuming the product to be also a catalyst, one can write the scheme

$$A + C \xrightarrow{k_1} AC$$

$$AC \xrightarrow{k_2} B + C$$

$$A + B \xrightarrow{k_3} 2B$$

Assuming $k_2 >> k_1$ and a steady-state concentra-

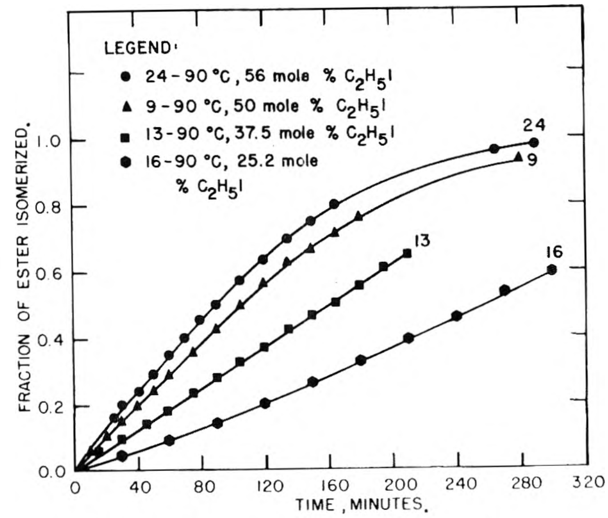

Fig. 1.—Progress of isomerization reaction.

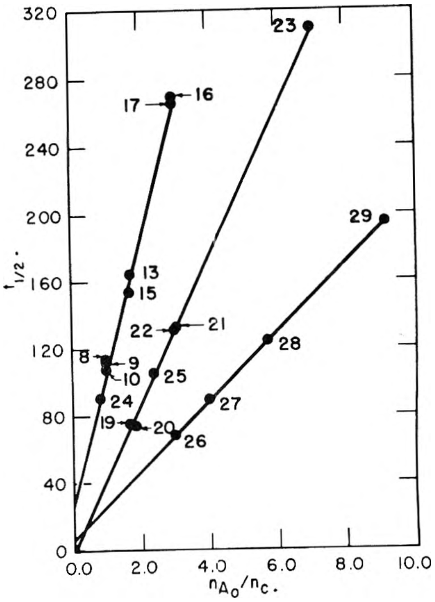

Fig. 2.—Period of half-life as a function of initial concentration ratio.

tion of the intermediate AC, rate equation (2) is derived easily

$$\frac{d\alpha}{dt} = k_1[c][1 + \left(\frac{k_3}{k_1}\right)\left(\frac{n_{A_0}}{n_c}\right) \alpha] (1 - \alpha) \qquad (2)$$

Equation 2 has the necessary properties to give, upon integration, α *vs.* t curves of shape similar to the experimental, provided the proper values of k_1 and k_3 are used. The authors, however, did not test eq. 2 as at this stage they found the abstract of the work of Zawidski and Staronka[1] performed some 40 years earlier at 85 and 95° on the same system. These investigators proposed a remarkably similar equation

$$\frac{d\alpha}{dt} = k\left(\frac{n_c}{n_{A_0}}\right)\left[1 + \frac{n'\alpha}{(A_0)}\right](1 - \alpha) \qquad (3)$$

where $n' = n_{A_0}/(0.2\, n_{A0} + 0.185\, n_c)$ is a "numerical factor," to correlate their experimental findings. According to the abstract, "by means of this equation not only are the results of the velocity measurements exactly represented but also all the related phenomena are quantitatively expressed by it."

Equation 3 as written appeared to the writers to be dimensionally inconsistent, perhaps due to a typographical error in the abstract. The equation was modified and rewritten as

$$\frac{d\alpha}{dt} = k\left(\frac{n_c}{n_{A_0}}\right)(1 + n'\alpha)(1 - \alpha) \qquad (4)^{10}$$

and integrated to obtain

$$\left(\frac{1}{n' + 1}\right) \ln \left(\frac{1 + n'\alpha}{1 - \alpha}\right) = k\left(\frac{n_c}{n_{A_0}}\right) t \qquad (5)$$

Equation 5 was tested graphically by plotting ln $(1 + n'\alpha)/(1 - \alpha)$ *vs.* t from the experimental results.

Typical curves are shown on Fig. 3 for four experiments at 100°. It may be observed that the agreement is quite consistent with the degree of experimental precision.

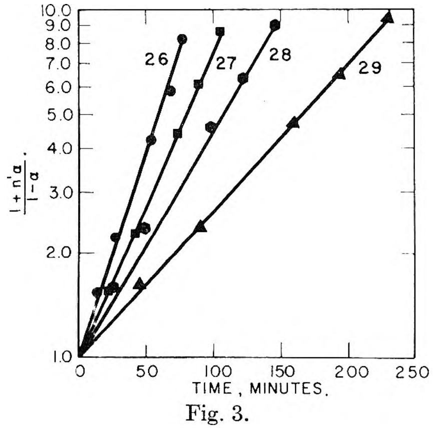

Fig. 3.

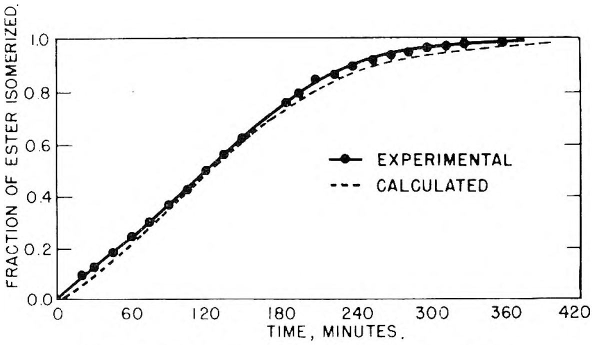

Fig. 4.—Progress of isomerization reaction.

Specific reaction rate constants were obtained from the slopes of curves similar to those in Fig. 3. Some typical results are summarized in Table III.

Table III

Specific Reaction Rate Constants from Eq. 5

Temp., °C.	Mole % ethyl iodide	(n_c/n_{A_0})	n'	k (10^{+3}) (min.$^{-1}$)
90	50.0	1.000	2.60	4.04
	37.5	.600	3.21	4.00
	25.0	.333	3.83	4.04
100	37.5	.600	3.21	8.75
	25.0	.333	3.83	8.32
	12.5	.143	4.32	8.29
110	24.8	.330	3.79	16.4
	20.0	.250	4.06	16.1
	15.0	.176	4.30	16.1
	10.0	.111	4.53	15.9

The tabulated results show surprisingly good correlation at the three temperatures studied and throughout the entire concentration range investigated. Furthermore, eq. 5 holds not only for initial rates but throughout the entire life of the reaction as shown in Fig. 4.

The temperature dependence of the rates of reaction corresponds to a process with an energy of activation of approximately 19600 cal. Zawidski and Staronka obtained a "temperature coefficient of the velocity constant" to be 2.168 for their experiments at 95 and 85°. The ratios of the average k's obtained in this investigation are 2.10 at 100–90° and 1.91 at 110–100°, which are in good agreement with the earlier value.

Although one of the objectives of kinetic studies of this kind is to arrive at the mechanism of the reaction, we do not believe that sufficient experimental data have been collected to justify such an attempt. However, additional investigations of this type should reveal eventually the true course of the reaction.

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(10) Even though eq. 2 and 4 are similar, they are not identical. Although attempts were made to derive eq. 4 from theoretical considerations, we were unable to do so.

THE TIME LAG IN DIFFUSION*

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Contribution from the Department of Chemistry, University of Southern California, Los Angeles, Cal.

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Explicit expressions for the time lag in linear diffusion of a gas or vapor through a membrane with concentration dependent diffusion coefficient are obtained without explicitly solving the diffusion equations. Generalizations of the method used to obtain the time lag are indicated. The use of the derived relations is sketched by applying them to several cases of physical interest.

Introduction

If one is measuring the rate of flow of a gas (or any other solute) through a membrane (or thin slab of material) in which the gas dissolves there will be an interval from the moment the gas comes into contact with the membrane until it emerges at a constant rate on the other side. By analyzing stationary and non-stationary states of flow it is possible to measure the diffusion constant, the permeability constant and the solubility of the gas in the membrane. By solving an appropriate diffusion equation in the case that the diffusion coefficient of the gas is a constant, D_0, a simple algebraic expression is obtained by direct calculation[2] which determines the intercept L, the so-called time lag, in terms of D_0, the thickness of the membrane l and the concentrations at the boundaries of the membranes, which the transmitted gas pressure–time curve makes on the axis of time. This experimental technique has proven in many instances to be a very valuable one in elucidating the diffusion constants of gases in both metals and non-metals.[2]

Unfortunately in many physical systems of current interest the diffusion coefficient is not a constant but the (differential) diffusion coefficient at a given place and time in the membrane, D, is a function of the concentration, c, at the given place and time, *i.e.*, $\mathfrak{D} = \mathfrak{D}(c)$. The form of this function is often known to a sufficient approximation. Among such systems can be found those involving organic vapors diffusing through various polymer membranes.[3–5] In such cases the formulas for the time lag given in Barrer[2] (calculated on the assumption of a constant diffusion coefficient) no longer apply. The difficulty in extending the method used in that reference to obtaining the time lag for a concentration dependent diffusion coefficient is that it requires explicit knowledge of the concentration of the diffusing species throughout the membrane for all times which can be obtained only by solving the appropriate Fickian diffusion equation. In most instances of physical interest such solutions are unknown and because of the non-linearity of the equation no general techniques for finding such solutions are known. Indeed attempts have been made to find L roughly from approximate solutions of the diffusion equation obtained by perturbation methods.[4]

The Time Lag.—In this paper we will derive our explicit expressions for the time lag which apply also to systems with a concentration dependent diffusion coefficients without explicitly solving the diffusion equation. In view of our own interest in the permeation of gases and vapors through high polymer membranes we will choose a simple experimental arrangement which is often used to study these systems.[4,5] In doing this we lose little of generality since other arrangements can be handled just as easily by the method developed. We imagine the left membrane surface in contact with a reservoir of the gas or vapor at some fixed pressure, while the right membrane surface is in contact with essentially a vacuum. The gas or vapor dissolves at the left membrane surface at $x = 0$ to give a concentration c_0 then undergoes activated diffusion to the right membrane surface at $x = 1$ where it evaporates and is immediately removed from contact with the membrane surface so that the concentration at $x = 1$ is zero. The membrane is assumed to be sufficiently thin so that diffusion occurs only along the x-axis.

If $c(x; t)$ denotes the concentration of the gas at a distance x from the left membrane surface at time t then the appropriate boundary value problem is completely specified by

$$\frac{\partial c}{\partial t} - \frac{\partial}{\partial x}\left\{\mathfrak{D}(c)\frac{\partial c}{\partial x}\right\} = 0 \text{ in } 0 < x < 1,\ t > 0 \quad (1)$$

with

$$\begin{aligned} c(x;0) &= 0 \text{ for } x > 0, \text{ (with } c(0;0) \text{ bounded)} \\ c(0;t) &= c_0 \text{ for } t > 0 \\ c(1;t) &= 0 \text{ for } t > 0 \end{aligned}$$

The differential diffusion coefficient $\mathfrak{D}(c)$ is assumed to be a given, single-valued, at least once continously differentiable function of c and x. For example for the diffusion of paraffins in rubber[4] $\mathfrak{D}(c) = D_0(1 + bc)$ while for the diffusion of paraffins in polyisobutylene[6] $\mathfrak{D}(c) = D_0 \exp(bc/2)(1 + bc/2)$ where b is a constant depending only on the temperature and the chemical make-up of the diffusion system. In all cases investigated a steady state in the flow of the gas or vapor is finally attained, *i.e.*

$$\lim_{t \to \infty} c(x;t) = c_s(x) \quad (2)$$

where $c_s(x)$ is the solution of eq. 1 with $\partial c/\partial t = 0$, *viz.*

$$\frac{\partial}{\partial x}\left\{\mathfrak{D}(c_s)\frac{\partial c_s}{\partial x}\right\} = 0 \text{ in } 0 < x < 1 \quad (3)$$

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* This research was supported by the United States Air Force Office of Scientific Research of the Air Research and Development Command under contract no. AF 18 (603) 122.

[1] Bell Telephone Laboratories, Murray Hill, N. J.

[2] For details of such a calculation refer to R. M. Barrer, "Diffusion In and Through Solids," Cambridge at the University Press, 1951, p. 18 ff.

[3] R. J. Kokes and F. A. Long, *J. Am. Chem. Soc.*, **75**, 6142 (1953).

[4] A. Aitken and R. M. Barrer, *Trans. Faraday Soc.*, **51**, 116 (1955).

[5] R. Waack, N. H. Alex, H. L. Frisch, V. Stannett and M. Szwarc, *Ind. Eng. Chem.*, **47**, 2524 (1955).

[6] S. Prager and F. A. Long, *J. Am. Chem. Soc.*, **73**, 4072 (1951).

with

$$c_s(0) = c_0 \qquad\qquad c_s(1) = 0$$

In what follows we shall assume that $\mathfrak{D}(c)$ is such that eq. 2 holds.

In Appendix I we show that the time lag L is given by

$$L = \frac{\int_0^1 \int_x^1 c_s(z)\mathrm{d}z\, \mathrm{d}x}{\int_0^{c_0} \mathfrak{D}(u)\mathrm{d}u} = \frac{\int_0^1 x\, c_s(x)\, \mathrm{d}x}{\int_9^{c_0} \mathfrak{D}(u)\, \mathrm{d}u} \tag{4}$$

where the steady-state concentration $c_s(x)$ can in principle always be explicitly found as a solution of the quadrature

$$\int_{c_s}^{c_0} \mathfrak{D}(u)\, \mathrm{d}u = \frac{x}{1} \int_0^{c_0} \mathfrak{D}(u)\, \mathrm{d}u \tag{5}$$

In view of eq. 5 one may rewrite eq. 4 in terms of quadratures of $\mathfrak{D}(c)$ only as

$$L = \frac{l^2 \left\{ \int_0^{c_0} w\, \mathfrak{D}(w) \left[\int_w^{c_0} \mathfrak{D}(u)\, \mathrm{d}u \right] \mathrm{d}w \right\}}{\left[\int_0^{c_0} \mathfrak{D}(u)\, \mathrm{d}u \right]^3} \tag{6}$$

showing that L is a function only of l, c_0 and the constant parameters of $\mathfrak{D}$, *i.e.*, D_0 and b in the foregoing examples. Since the functional form of $\mathfrak{D}(c)$ is known the measurement L for various values of c_0 determines the constant parameters of $\mathfrak{D}$ and hence $\mathfrak{D}$ itself.

Applications and Discussion.—To illustrate the use of eqs. 4–6 we will apply them to two cases which have been discussed in the literature.

Case 1:

$$\mathfrak{D}(c) = D_0 \text{ a constant}$$

We find from eq. 5 that

$$c_s(x) = c_0 \left(1 - \frac{x}{l}\right)$$

and substituting this result into eq. 4, noting that

$$\int_0^{c_0} \mathfrak{D}(u)\, \mathrm{d}u = D_0 c_0$$

we obtain for L the known result[2]

$$L = l^2/6D_0 \tag{7}$$

Case **2**:

$$\mathfrak{D}(c) = D_0(1 + bc)$$

Again from eq. 5 we find that

$$c_s(x) = \frac{1}{b} \left\{ -1 + \left[1 + (2bc_0 + b^2c_0^2)\left(1 - \frac{x}{l}\right)\right]^{1/2} \right\}$$

$$= \frac{1}{b} \left\{ bc_0 u + \frac{1}{2} b^2c_0^2(u - u^2) + \frac{1}{2} b^3c_0^3(u^3 - u^2) + \frac{1}{8} b^4c_0^4(6u^3 - u^2 - 5u^4) + 0(b^5c_0^5) \right\};\ u = 1 - \frac{x}{l}$$

Substituting this $c_s(x)$ into eq. 4 we find the exact L in this case

$$L = \left\{ \frac{4A^{5/2} - (4A + 6Bl)(A - Bl)^{3/2}}{15B^2} - \frac{l^2}{2} \right\} \Big/ D_0(A - 1)/2 \tag{8}$$

with

$$A = 1 + 2b\left(c_0 + \frac{1}{2} bc_0^2\right)$$

$$B = \frac{2b}{l}\left(c_0 + \frac{1}{2} bc_0^2\right)$$

In order to compare this result with Aitken and Barrer's[4] approximate value of L obtained from an approximate solution of the diffusion equation we expand eq. 8 in powers of b or preferably substitute the series expansion for $c_s(x)$ in eq. 4 to obtain

$$L = \frac{l^2}{6D_0} \left\{ \left(\frac{1 + \frac{1}{4} bc_0}{1 + \frac{1}{2} bc_0} \right) - \frac{b^2c_0^2}{10} \left(\frac{1 - \frac{3}{8} bc_0}{1 + \frac{1}{2} bc_0} \right) + 0\left(\frac{b^4c_0^4}{1 + \frac{1}{2} bc_0} \right) \right\} \tag{9}$$

This agrees well with Aitken and Barrer's result for small b

$$L \sim \frac{l_2}{6D_0} \left(\frac{1 + \frac{1}{4} bc_0}{1 + \frac{1}{2} bc_0} \right) \tag{10}$$

The method developed in the appendix to this paper applies to other diffusion problems with different symmetries and boundary conditions (see *e.g.*, Appendix II). A variant can even be applied to the study of time lags of the more general Smoluchowski equation. The author is indebted to his wife for the series expansion, eq. 9, and to Dr. W. Noll of the Department of Mathematics, University of Southern California, for his interest in this problem.

Appendix I

We shall derive eqs. 4 and 5. From eq. 3 we find (on integration) that there exists a constant q_s such that

$$\mathfrak{D}(c_s) \frac{\partial c_s}{\partial x} = q_s = \left[\mathfrak{D}(c_s) \frac{\partial c_s}{\partial x} \right]_{x=1} \tag{11}$$

Integrating eq. 11 over x from l to 0 we find

$$\int_0^l \mathfrak{D}(c_s) \frac{\partial c_s}{\partial x}\, \mathrm{d}x = q_s l = \int_{c_s0}^{c_s(l)} \mathfrak{D}(c_s)\, \mathrm{d}c_s = -\int_0^{c_0} \mathfrak{D}(u)\, \mathrm{d}u$$

Hence

$$-q_s = \frac{1}{l} \int_0^{c^0} \mathfrak{D}(u)\, \mathrm{d}u \tag{12}$$

The total flow of gas (per unit volume through the right membrane surface) up to time t at steady state is given by

$$Q_s(t) = -\int_0^t q_s \mathrm{d}t = \frac{t}{l} \int_0^{c_0} \mathfrak{D}(u)\, \mathrm{d}u \tag{13}$$

Similarly for the non-steady state flow there exists a flux function $q = q(t)$ given by

$$q(t) = \left[\mathfrak{D}(c) \frac{\partial c}{\partial x} \right]_{x=1}$$

such that the total flow time t is given by the analog of eq. 13

$$Q(t) = -\int_0^l q(t)\, \mathrm{d}t \tag{14}$$

To find $Q(t)$ integrate both sides of eq. 1 over x from l to x

$$\int_x^l \frac{\partial c(z;t)}{\partial t}\, \mathrm{d}z - q(t) + \mathfrak{D}(c) \frac{\partial c}{\partial x} = 0$$

Integrating this equation again over x from l to 0 we find on rearranging

$$-q(t) = \frac{1}{l} \left\{ \int_0^{c_0} \mathfrak{D}(u)\, \mathrm{d}u - \int_0^l \int_x^l \frac{\partial c(z;t)}{\partial t}\, \mathrm{d}z\, \mathrm{d}x \right\} \tag{15}$$

Finally integrating over t from 0 to t we find

$$
\begin{aligned}
Q(t) &= \frac{1}{l}\left\{t\int_0^{c_0}\mathfrak{D}(u)\,\mathrm{d}u - \int_0^t\int_0^l\int_x^l \frac{\partial c(z;t)}{\partial\tau}\,\mathrm{d}z\,\mathrm{d}x\,\mathrm{d}\tau\right\} \\
&= \frac{1}{l}\left\{t\int_0^{c_0}\mathfrak{D}(u)\,\mathrm{d}u - \int_0^l\int_x^l\int_0^t \frac{\partial c(z;\tau)}{\partial\tau}\,\mathrm{d}\tau\,\mathrm{d}z\,\mathrm{d}x\right\} \\
&= \frac{1}{l}\left\{t\int_0^{c_0}\mathfrak{D}(u)\,\mathrm{d}u - \int_0^l\int_x^l c(z;t)\,\mathrm{d}z\,\mathrm{d}x\right\}
\end{aligned}
$$

or

$$Q(t) = Q_s(t) - \frac{1}{l}\int_0^l\int_x^l c(c;t)\,\mathrm{d}z\,\mathrm{d}x \qquad (16)$$

Now L is defined[2] by the fact that the asymptote to $Q(t)$, $Q_a(t)$ is given by

$$Q_a(t) = \frac{1}{l}\int_0^{c_0}\mathfrak{D}(u)\,\mathrm{d}u\,\{t - L\} \qquad (17)$$

since $\mathrm{d}Q_s(t)/\mathrm{d}t = \int_0^{c_0}\mathfrak{D}(u)\,\mathrm{d}u/l$. Hence on comparing eqs. 17 and 16 we find

$$
\begin{aligned}
L &= \lim_{t\to\infty}\frac{1}{\left(\int_0^{c_0}\mathfrak{D}(u)\,\mathrm{d}u\right)}\int_0^l\int_x^l c(z;t)\,\mathrm{d}z\,\mathrm{d}x \\
&= \int_0^l\int_x^l c_s(z)\,\mathrm{d}z\,\mathrm{d}x\Big/\int_0^{c_0}\mathfrak{D}(u)\,\mathrm{d}u \qquad (18)
\end{aligned}
$$

by virtue of eq. 2. Integration by parts of the numerator of eq. 18 gives us then the desired eq. 4. $c_s(z)$ incidentally is found by substituting eq. 12 into eq. 11 and subsequent integration over x from x to 0 to give eq. 5.

So far nothing has been said as to the nature of $\mathfrak{D}$ in order that eq. 2 applies. This certainly is the case if

$$
\begin{aligned}
&\lim_{t\to\infty} c(x;t) \longrightarrow a(x) < \infty \\
&\lim_{t\to\infty} \frac{\partial c}{\partial x}(x;t) \longrightarrow b(x) < \infty \qquad (19) \\
&\lim_{t\to\infty} \frac{\partial^2 c}{\partial x^2}(x;t) \longrightarrow f(x) < \infty
\end{aligned}
$$

uniformly. For then by virtue of eq. 1

$$\lim_{t\to\infty}\frac{\partial c(x;t)}{\partial t} \longrightarrow h(x) < \infty$$

uniformly. All we have to show now is that $h(x) = 0$. To see this consider the graph of $c(x;t)$ *versus* t for a fixed value of x. If $c(x;t)$ is bounded then two cases can only arise: (a) c oscillates as $t \to \infty$ or (b) c approaches an asymptotic value, say $a(x)$ with vanishing slope as $t \to \infty$. The first case is excluded by hypothesis hence

$$\lim_{t\to\infty}\frac{\partial c}{\partial t} = 0$$

and eq. 2 follows. Actually eq. 19 are certainly too prohibitive and there should exist weaker conditions in order that eq. 2 applies.

Appendix II

The same method also can be applied to the calculation of L for a diffusion problem with more general boundary conditions, *e.g.*, eq. 1 with $c(x;0) = a$, $c(0;t) = c_0$ and $c(l;t) = c_1$. We find

$$L = \frac{\int_0^l x[c_s(x) - a]\,\mathrm{d}x}{\int_{c_1}^{c_0}\mathfrak{D}(u)\,\mathrm{d}u} \qquad (20)$$

with $c_s(x)$ a solution of the quadrature

$$\int_{c_s(x)}^{c_0}\mathfrak{D}(u)\,\mathrm{d}u = \frac{x}{l}\int_{c_1}^{c_0}\mathfrak{D}(u)\,\mathrm{d}u \qquad (21)$$

Combining eqs. 21 and 22 we can write

$$L = l^2\,\frac{\left[\int_{c_1}^{c_0}\mathrm{d}u\,\mathfrak{D}(u)\,(u - a)\int_u^{c_0}\mathrm{d}w\,\mathfrak{D}(w)\right]}{\left[\int_{c_1}^{c_0}\mathrm{d}u\,\mathfrak{D}(u)\right]^3} \qquad (22)$$

FLUORINE MAGNETIC RESONANCE STUDIES OF SOME SOLID FLUOROETHANES[1]

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Received August 8, 1956

The fluorine magnetic resonance line shapes have been observed in solid $CFCl_2CFCl_2$, CF_2ClCF_2Cl, CF_2BrCF_2Br and CF_2BrCCl_2Br. The second moments of the absorption at liquid nitrogen temperatures show that $CFCl_2CFCl_2$ exists mainly in the *gauche* form while CF_2ClCF_2Cl and CF_2BrCF_2Br are probably in the *trans* form. The temperature dependence of the line widths is reported; the results demonstrate the occurrence of restricted molecular reorientations in the solids, particularly in $CFCl_2CFCl_2$ and CF_2BrCCl_2Br.

The rotational isomerism of $CFCl_2CFCl_2$ was investigated by Kagarise and Daasch[3] who observed the infrared and Raman spectra of the gas, liquid and solid. The spectra were found to be independent of the state of the sample which would be the case if only one isomer were present, most likely the *trans* form, or if two isomers coexisted, with a very small energy difference in all states; but a choice could not be made between the two possibilities. The success of proton magnetic resonance[4] studies of the molecular forms[5] of solid $CHCl_2$-$CHCl_2$ and $CHBr_2CHBr_2$ suggested that a similar approach be made to $CFCl_2CFCl_2$, using the fluorine nuclear magnetic resonance

(1) Assisted in part by the U. S. Office of Naval Research and by a Grant-in-Aid from E. I. du Pont de Nemours and Co.

(2) Research Scholar under the Smith–Mundt and Fulbright Acts; on leave of absence from Tokyo College of Science.

(3) R. E. Kagarise and L. W. Daasch, *J. Chem. Phys.*, **23**, 113 (1955).

(4) An excellent introduction to the field is given by E. R. Andrew, "Nuclear Magnetic Resonance," Cambridge Univ. Press, Cambridge, 1956.

(5) M. Takeda and H. S. Gutowsky, *J. Chem. Phys.*, **26**, in press (1957).

Table I

Calculated Second Moments in Gauss^2 of the Fluorine Magnetic Resonance Absorption and Experimental Values at Liquid Nitrogen Temperature for Solid Powder Samples

	$CFCl_2CFCl_2$		CF_2ClCF_2Cl		CF_2BrCF_2Br		CF_2BrCCl_2Br	
Calcd.	*trans*	*gauche*	*trans*	*gauche*	*trans*	*gauche*	*trans*	*gauche*
F–F	0.17	0.75	3.81	4.38	3.81	4.38	2.89	2.89
F–X	.08	.07	0.04	0.03	0.21	0.20	0.23	0.21
inter.	.30	.65	1.40	0.84	1.73	1.17	0.73	0.75
Total[a]	.55	1.47	(3.85)	(4.41)	(4.02)	(4.58)	(3.12)	(3.10)
Obsd.	1.40 ± 0.1		5.25 ± 0.1		5.75 ± 0.4		3.85 ± 0.1	

[a] Values in parentheses include only intramolecular contributions to the broadening; the intermolecular values in these cases are obtained by difference from the observed second moments.

The two fluorine nuclei are the only important magnetic species in the molecule so the broadening by the nuclear magnetic fields of the fluorine resonance in the "rigid lattice" solid is significantly greater in the *gauche* than in the *trans* form. Using the second moment of the absorption line as a quantitative measure of the dipolar broadening, the intramolecular contribution for a powder sample of $CFCl_2CFCl_2$ is[4,5]

$$\Delta H_2{}^2 = 317r^{-6}{}_{F-F} + 7.08 \sum_{Cl} r^{-6}{}_{F-Cl} \qquad (1)$$

The summation is taken over the distances, r, in Å., between one of the fluorine nuclei and all four chlorine nuclei in the molecule. The results of the calculations are given in Table I. Tetrahedral bond angles were assumed and bond distances[6] used were C–C, 1.54; C–Cl, 1.78; and C–F, 1.34 Å.

The *inter*molecular contributions to the second moment could not be calculated accurately because of the lack of any structural data on the solid. However, the estimates given in Table I were made by multiplying the approximate values calculated[5] for $CHCl_2CHCl_2$ by $r^6{}_H/r^6{}_F$, the ratio of the van der Waals radii (1.2/1.35) of hydrogen and fluorine. This gives a lower limit to the broadening as it assumes that all internuclear distances, between adjacent molecules, are larger than in $CHCl_2CHCl_2$ by the same scale factor. Certainly, some will increase by a smaller fraction.

An empirical check on the *inter*molecular broadening in $CFCl_2CFCl_2$ was made by comparing the second moments of the fluorine resonance observed in CF_2ClCF_2Cl, CF_2BrCF_2Br and CF_2BrCCl_2Br with the intramolecular second moments calculated with the appropriate modification of eq. 1. The results are given also in Table I; a value of 1.91 Å. was used for the C–Br distance. The observations on the tetrafluoro compounds also bear upon the configuration of these molecules in the solid state. The widths of the resonances were observed as a function of temperature for all four compounds to establish whether or not the molecules are in rigid lattices at liquid nitrogen temperature. The partial narrowing of the absorption at higher temperatures demonstrates the occurrence of restricted molecular reorientations in the solids.

Experimental

The fluorine magnetic resonances were observed at a fixed radiofrequency of about 25.25 Mc., as a function of applied magnetic field, with the spectrometer, narrow-band system and recorder, and the cryostat described previously.[7] The apparatus records the first derivative of the absorption. The line shapes observed correspond to simple bell shaped curves; they are very similar to those given[5] for the proton resonance in $CHCl_2CHCl_2$ and $CHBr_2CHBr_2$, so none are reproduced here. Line widths, δH, defined as the separation in gauss between the maximum and minimum of the recorded derivative, are plotted against temperature in Fig. 1. Table I lists the second moments obtained by numerical integration of several of the curves observed at −190°, 5 for $CFCl_2CFCl_2$, 3 for CF_2BrCF_2Br and 2 for each of the other compounds.

The samples of $CFCl_2CFCl_2$, CF_2ClCF_2Cl and CF_2BrCF_2Br were very kindly furnished by Dr. J. M. Hamilton of the Jackson Laboratory, E. I. du Pont de Nemours and Co. The sample of CF_2BrCCl_2Br was purchased from Peninsular ChemResearch Co., Inc. The samples were used as received; the sample volumes in these experiments were about 0.7 ml.

Discussion

Rotational Isomers.—The line width *versus* temperature plots in Fig. 1 suggest that at −190°, the lower temperature limit, the samples have just reached the "rigid lattice" widths. For $CFCl_2CFCl_2$, the observed second moment of 1.40 ± 0.01 gauss^2 is much closer to the value 1.47 gauss^2 calculated for the *gauche* form than the 0.55 value for the *trans* form. However, the estimate of 0.65 gauss^2 for the *inter*molecular broadening may be low so that the possibility of the sample containing some *trans* molecules is not excluded. It is certain that the sample is not pure *trans*. Moreover, no differences outside of experimental error were found between the spectra of a quick frozen and an annealed sample.

The *intra*molecular second moments calculated for CF_2ClCF_2Cl and CF_2BrCF_2Br are about 0.55 gauss^2 larger for the *gauche* than for the *trans* form. This difference is large enough to differentiate between the rotational isomers if reliable values were available for the *inter*molecular broadening. A good approximation to the latter can be obtained by considering the results for CF_2BrCCl_2Br. The *intra*molecular broadening calculated for the *trans* and *gauche* forms of this compound is the same (3.12 and 3.10), so the difference of about 0.75 gauss^2 between these values and the observed second moment of 3.85 ± 0.1 gauss^2 is the *inter*molecular broadening.

Most of the broadening in the compounds arises from the F–F interactions. The volume concentration of fluorine nuclei in CF_2ClCF_2Cl and CF_2BrCF_2Br is about twice as great as in CF_2BrCCl_2Br, so the *inter*molecular broadening in the tetrafluoroethanes should be about 1.5 gauss.^{2} In this manner, the data in Table I lead to the suggestion that both CF_2ClCF_2Cl and CF_2BrCF_2Br occur predominantly as the *trans* form in the low temperature

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(6) R. L. Livingston and D. H. Lyon, *J. Chem. Phys.*, **24**, 1283 (1956).

(7) H. S. Gutowsky, L. H. Meyer and R. E. McClure, *Rev. Sci. Instr.*, **24**, 644 (1953).

solid. This agrees with a study of the vibrational spectra of CF_2BrCF_2Br which showed[8] the *trans* form to be about 900 cal. more stable than the *gauche*, in the liquid and vapor states. Similar line width considerations suggest a value of about 0.75 gauss[2] for the *inter*molecular broadening in $CFCl_2$-$CFCl_2$ and supports the view that the molecular form is mainly *gauche*.

Molecular Reorientations.—The temperature dependence of the line widths shows[9] that the molecules of all four fluoroethanes undergo low frequency reorientations in the solid. $CFCl_2CFCl_2$ and CF_2BrCF_2Br, in particular, have line widths only a few tenths of a gauss wide down to temperatures about 75° below their melting points. In order for the absorption to be this narrow, the molecules must be reorienting about at least two axes, with frequencies greater than 5 kc. at the temperatures where the absorption begins to broaden. The same two compounds also have resonances with an intermediate width of 1 gauss for considerable temperature intervals about $-100°$.

The molecules must be reorienting in some restricted fashion to give line widths of the intermediate width found. The contribution to the second moment by the dipolar interactions between a pair of nuclei, at a fixed separation, is reduced[9] by a factor $\frac{1}{4}(3 \cos^2 \gamma - 1)^2$, where γ is the angle between the internuclear vector and the axis of rotation. For $CFCl_2CFCl_2$, the second moment found in the region of intermediate width is 0.18 gauss,[2] at $-146°$. Most of this no doubt comes from the *intra*molecular F–F interaction, in which case the molecules are rotating about an axis nearly perpendicular to the F–F vector. Inspection of a molecular model suggests that the axis bisects the F–F vector and the C–C bond, in the *gauche* form.

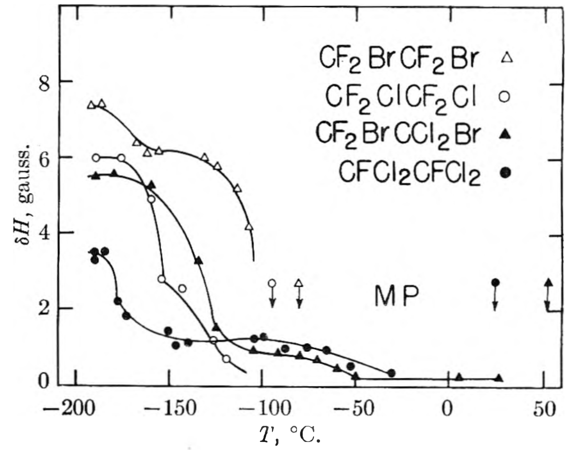

Fig. 1.—The temperature dependence of the fluorine magnetic resonance line widths. δH is the separation in gauss of the maximum and minimum of the derivative of the absorption.

For CF_2BrCCl_2Br, the second moment at $-125°$, where the absorption begins to broaden, is 0.6 gauss.[2] This again corresponds to rotation of the molecule about an axis perpendicular to the F–F vector in the molecule. In this case however the most likely axis is that joining the two bromine atoms, in the *gauche* form. At temperatures above $-125°$, the line narrows gradually; at $-105°$ the second moment is only 0.15 gauss,[2] which shows that some other type of motion is also beginning to occur.

The results for CF_2ClCF_2Cl and CF_2BrCF_2Br differ from the others in that neither has any appreciable temperature range in which restricted reorientations occur. There is a shoulder at $-145°$ on the curve for CF_2ClCF_2Cl which might very well be due to the molecules reorienting only about the axis passing through the chlorine nuclei, in the *trans* form.

(8) R. E. Kagarise and L. W. Daasch, *J. Chem. Phys.*, **23**, 130 (1955).

(9) H. S. Gutowsky and G. E. Pake, *ibid.*, **18**, 162 (1950).

COMPRESSIBILITY OF GRAPHITE–FERRIC CHLORIDE COMPOUNDS

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The compressibility coefficient of graphite–ferric chloride compounds has been measured at 30°. The compressibility of the compound is greater than that of pure graphite. An approximate relationship has been found which appears to represent the variation of the compressibility coefficient with density and composition of the lamellar compounds.

During the past few years the lamellar compounds of graphite have been the object of increasing attention. To gain further information regarding the nature of these compounds it seemed worthwhile to determine the compressibility coefficient of a typical compound of this type, *viz.*, graphite–ferric chloride.

According to Rüdorff, *et al.*,[1] who have made extensive studies of the graphite–ferric chloride systems, various compounds are formed depending on the temperature at which the reaction is allowed to take place and on the subsequent treatment of the product. In the present experiments using Ceylon graphite we have been able to produce all but one of the products described by Rüdorff, although the conditions for our preparations do not agree exactly with those of Rüdorff.

The graphite–ferric chloride compounds for the present experiments were prepared by heating anhydrous ferric chloride and powdered graphite (80–100 mesh) in a Pyrex glass pressure tube at a known temperature for 48 hours, after which the excess ferric chloride was removed by sublimation A small sample of this initial product was taken for analysis; the bulk of the product in each case was

(1) W. Rüdorff, *Z. anorg. allgem. Chem.*, **243**, 383 (1941); **254**, 319 (1947); W. Rüdorff and G. Rüdorff, *Ber.*, **80**, 417 (1947); W. Rüdorff and H. Schulz, *Z. anorg. allgem. Chem.*, **245**, 121 (1940).

washed generally with 10% hydrochloric acid until the washings showed only a faint test with thiocyanate. The washed product was dried at 120° for 4–5 hours and finally dried in a desiccator over phosphorus pentoxide. A sample of this washed product was also analyzed. Analysis of the graphite–ferric chloride products involved, first, the perchloric acid digestion of the sample, followed by determination of iron by means of standard dichromate solution.

Densities of the washed samples were found by means of a pycnometer for solids, using benzene for the filling liquid.

The compressibility of the graphite–ferric chloride samples was determined by the Richards procedure for the case of solids.[2] Certain details, however, may be noted: a piezometer for solids was constructed from Pyrex glass; the liquid filling the piezometer was purified benzene except in one experiment with graphite when water was employed; in the experiments the pressure was varied over the range of 100–300 kg./cm.^{2}, approximately; all density and compressibility measurements were carried out at 30.00 ± 0.01°. In the compressibility experiments the solid samples were in the form of fine powder or pellets prepared from the powder material. The pellets were not found to be satisfactory.

The data pertaining to the preparation of the graphite–$FeCl_3$ samples are presented in Table I. Products Ia, Ib, IIa, IIb and III are believed to be similar to the compounds (72–56% $FeCl_3$) which Rüdorff obtained at 180–300°. From X-ray analysis Rüdorff deduced that in these compounds a layer of $FeCl_3$ appears between each layer of C atoms. Product IV is believed to be similar to Rüdorff's stage III compounds (37–30% $FeCl_3$) which he obtained at temperatures of 325–400°. For this type of compound Rüdorff adduced evidence to show that $FeCl_3$ is probably intercalated between every third layer of C atoms in the graphite. Our product III, incidentally, was the result of an unsuccessful attempt to prepare Rüdorff's stage II compound.

TABLE I

INFORMATION REGARDING PREPARATION OF GRAPHITE–$FeCl_3$ SAMPLES

	Conditions of preparation		% $FeCl_3$		Molecular ratio $FeCl_3$:C	
Product	Wt. graphite, g.	Temp., °C.	Un-washed product	Washed product	Un-washed product	Washed product
Ia	1–2	250–260	71.3	62.7	1:5.4	1:8.0
Ib	10	255		52.3		1:13
IIa	3	360	58.1	54.9	1:9.7	1:11
IIb	10	355	63.4	55.6	1:8.0	1:11
III	3	400-410		61.5		1:8.5
IV	10	450	39.3	33.6	1:21	1:26

TABLE II

DATA PERTAINING TO COMPRESSIBILITY MEASUREMENTS

Substance	Density	$\beta \times 10^6$	Molar $\beta \times 10^6$
Water	0.998	40.28	
Grahite[a]	2.27	3.39[c]	17.5
[b]	2.69	47.6[d]	
Graphite–$FeCl_3$ samples			
Ib[b]	1.92	13.04	124
IIb[e]	2.37	10.12	117
IV[e]	2.36	10.32	80

[a] Graphite in the form of 1.5 × 5 cm. cylinders cut from large pieces of Ceylon graphite. [b] Pellets 1 cm. in diameter formed by pressing 80–100 mesh powder in a pellet press. [c] Water was used as the piezometer filling fluid. [d] The high value obtained for the compressibility of the graphite pellets is believed to be the compressibility of the pellet itself rather than that of the graphite particles making up the pellet. Apparently the pellet was not penetrated by the liquid filling the piezometer even under pressure. [e] Loose powder.

A summary of the data pertaining to the compressibility experiments is given in Table II. The compressibility coefficient β is expressed as the contraction (cc.) in unit volume per unit of pressure (kg. cm.$^{-1}$). The footnotes to the table give further details regarding the compressibility experiments.

As might be expected the graphite–ferric chloride compounds are more compressible than graphite itself. When values of the molar compressibility of these compounds (defined as the compressibility of that amount of compound containing one gram-atom of carbon) are plotted against per cent. ferric chloride, the plotted points fall closely on a straight line. If this relationship is accepted as valid one can derive the expression

$$\frac{\beta}{d} = 1.46 + 14.0f - 15.5f^2$$

Here β is the compressibility coefficient; d, the density of the compound; and f, the fraction by weight of ferric chloride in the compound. β/d, of course, can be viewed as the compressibility of 1.0 g. of the compound. This equation represents our experimental data satisfactorily for values of f over the range 0–0.56. It is noteworthy that the right-hand expression approximates zero when $f = 1$, suggesting that the changes in β/d with variation in f is due primarily to changes in the compressibility of the graphite structure rather than to an effect directly attributable to the ferric chloride present in the compound.

Acknowledgment.—We wish to acknowledge the assistance given us by Dr. Fred D. Ayres at various occasions during this work.

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[2] T. W. Richards and W. N. Stull, Carnegie Inst. of Wash. Pub. No. 7 (1903); T. W. Richards and Grinnell Jones, *J. Am. Chem. Soc.*, **46**, 935 (1924).

ACTIVITY COEFFICIENTS IN MIXED ELECTROLYTE SOLUTIONS

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In three-component aqueous electrolyte systems in which one solute is known to obey Harned's rule, the activity coefficient of the second electrolyte solute and the osmotic coefficient for the mixture may be directly computed without further assumptions by the integration of fundamental cross differentiation relations. The method is applied to four hydrochloric acid–metal chloride systems. In every case, Harned's rule is approximately followed by the second electrolyte solute, but the deviations are significant.

Introduction

In many aqueous solutions of two electrolytes with a common ion, it is found that at constant total ionic strength, the logarithm of the activity coefficient of one solute is a linear function of the ionic strength of the second solute. This behavior has been most extensively studied by Harned[1–3] and his co-workers for aqueous solutions of hydrochloric acid and a metallic chloride; it has been observed as well in solutions of two different metallic chlorides by Owen and Cooke,[4] Robinson[5] and McCoy and Wallace.[6] Although such behavior is not universal,[7–9] it is sufficiently common in at least the simpler systems to justify further study and use.

In most systems thus far studied it has been possible to determine the activity coefficient of but one electrolyte solute. Thus, Harned has very carefully determined the activity coefficient of hydrochloric acid in the mixed solutions from electromotive force measurements. Although additional measurements of solvent water activity would permit the calculation of the activity coefficient of the second solute by means of the Gibbs–Duhem equation, it has rather been customary to assume a linear variation for the second solute and to compute the rate of variation with ionic strength fraction. Glueckauf[10] has proposed a sensitive test of the hypothesis which indicates for several systems that the assumption although invalid at low ionic strength becomes increasingly valid at high ionic strength. There is a need, therefore, for means of determining directly the activity coefficient of the second solute from measurements of the activity of one other component. This has been accomplished by McKay[11] and McKay and Perring[12] through the use of cross differentiation relations applied to vapor pressure measurements. It also may be accomplished if sufficiently extensive electromotive force measurements are available to define the activity coefficient of the first solute over the entire range of interest of both composition variables.

Derivation of Relations

The mean activity coefficients of two electrolyte solutes with a common ion are related by the fundamental cross differentiation equation

$$\nu_1 \left[\frac{\partial \log \gamma_1}{\partial m_2}\right]_{m_1} = \nu_2 \left[\frac{\partial \log \gamma_2}{\partial m_1}\right]_{m_2} \qquad (1)$$

in which m represents molality and ν and γ possess their usual significance.[13] The total ionic strength μ may be written as

$$\mu = \mu_1 + \mu_2; \; \mu_1 = k_1 m_1; \; \mu_2 = k_2 m_2 \qquad (2)$$

and

$$k_1 = \frac{\nu_1 z_{1+} z_{1-}}{2}; \; k_2 = \frac{\nu_2 z_{2+} z_{2-}}{2} \qquad (3)$$

where z represents the absolute value of the valence of the indicated ion.

If electrolyte solute 1 obeys Harned's rule, then

$$\log \gamma_1 = \log \gamma_{1(0)} - \alpha_{12}\mu_2 \qquad (4)$$

in which $\gamma_{1(0)}$ is the activity coefficient of electrolyte solute 1 in its own pure solution at the same total ionic strength μ as the mixed solution; $\gamma_{1(0)}$ and α_{12} are functions of μ only. This relation has been established at several different ionic strengths in each of a number of systems; in what follows it is supposed that the relation has been established over the entire range of ionic strength of interest, and α_{12} and $\gamma_{1(0)}$ are therefore known functions of μ over this range.

Equation 4 may be substituted in eq. 1 to yield

$$\nu_2 \left[\frac{\partial \log \gamma_2}{\partial m_1}\right]_{m_2} = \nu_1 k_2 \left[\frac{\mathrm{d} \log \gamma_{1(0)}}{\mathrm{d}\mu} - \alpha_{12} - \mu_2 \frac{\mathrm{d}\,\alpha_{12}}{\mathrm{d}\mu}\right] \qquad (5)$$

This is now integrated from zero to m_1 at constant m_2, under which restriction $\mathrm{d}m_1 = \mathrm{d}\mu/k_1$. The result is

$$\frac{\nu_2}{k_2}\left[\log \gamma_2 - \log \gamma_{2(0)}(\mu_2)\right] = \frac{\nu_1}{k_1}\left\{\log \gamma_{1(0)}(\mu) - \log \gamma_{1(0)}(\mu_2) - \int_{\mu_2}^{\mu} \alpha_{12}\,\mathrm{d}\mu - \mu_2\left[\alpha_{12}(\mu) - \alpha_{12}(\mu_2)\right]\right\} \qquad (6)$$

In eq. 6, γ_2 is the activity coefficient of electrolyte solute 2 in the mixed solution containing ionic strengths μ_1 and μ_2, respectively, of the two solutes, and $\gamma_{2(0)}(\mu_2)$ is that in a pure solution of solute 2

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[1] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1950, p. 459.

[2] H. S. Harned, THIS JOURNAL, **58**, 683 (1954).

[3] H. S. Harned and R. Gary, *J. Am. Chem. Soc.*, **76**, 5924 (1954); **77**, 1995, 4695 (1955).

[4] B. B. Owen and T. F. Cooke, *ibid.*, **59**, 2273 (1937).

[5] R. A. Robinson, *ibid.*, **74**, 6035 (1952); R. A. Robinson and C. K. Lim, *Trans. Faraday Soc.*, **49**, 1144 (1953); R. A. Robinson, *ibid.*, **49**, 1147, 1411 (1953).

[6] W. H. McCoy and W. E. Wallace, *J. Am. Chem. Soc.*, **78**, 1830 (1956).

[7] H. S. Harned and M. A. Cook, *ibid.*, **59**, 1890 (1937).

[8] R. A. Robinson and R. O. Farrelly, THIS JOURNAL, **51**, 704 (1947).

[9] O. D. Bonner and V. F. Holland, *J. Am. Chem. Soc.*, **77**, 5828 (1955).

[10] E. Glueckauf, H. A. C. McKay and A. R. Mathieson, *J. Chem. Soc.*, S 299 (1949); *Trans. Faraday Soc.*, **47**, 428 (1951).

[11] H. A. C. McKay, *Nature*, **169**, 464 (1952).

[12] H. A. C. McKay and J. K. Perring, *Trans. Faraday Soc.*, **49**, 163 (1953).

[13] Brackets or braces will enclose quantities to be multiplied; parentheses will be reserved to indicate functional dependence on ionic strength.

at ionic strength μ_2. The quantities $\gamma_{1(0)}(\mu)$ and $\gamma_{1(0)}(\mu_2)$ refer to pure solutions of solute 1 at the indicated ionic strengths.

Equation 6 may be rearranged with the help of eq. 3 to yield

$$\log \gamma_2 = \log \gamma_{2(0)}\ (\mu_2) + \frac{z_{2+}z_{2-}}{z_{1+}z_{1-}} \Big\{ \log \gamma_{1(0)}\ (\mu) - \log \gamma_{1(0)}\ (\mu_2) - \int_{\mu_2}^{\mu} \alpha_{12}\,\mathrm{d}\mu - \mu_2\,[\alpha_{12}(\mu) - \alpha_{12}(\mu)_2] \Big\} \quad (7)$$

Thus, if $\gamma_{1(0)}$, $\gamma_{2(0)}$ and α_{12} are known as functions of μ, it is possible by means of eq. 7 to compute γ_2, the activity coefficient of solute 2 in the mixed solution.[14] Within the limitations imposed by the experimental knowledge of $\gamma_{1(0)}$, $\gamma_{2(0)}$ and α_{12}, the results are as valid and as direct as those computed for $\gamma_{2(0)}$, for example, by means of the Gibbs–Duhem equation from measurements of vapor pressure or of freezing point depression.

It is often convenient to introduce as a composition variable the ionic strength fraction of solute 1; thus one may write

$$x = \mu_1/\mu = k_1m_1/\mu;\ 1 - x = \mu_2/\mu = k_2m_2/\mu \quad (8)$$

With this substitution eq. 7 becomes

$$\log \gamma_2 = \log \gamma_{2(0)}\ (\mu\,[1 - x]) + \frac{z_{2+}z_{2-}}{z_{1+}z_{1-}} \Big\{ \log \gamma_{1(0)}\ (\mu) - \log \gamma_{1(0)}\ (\mu[1 - x]) - \int_{\mu[1-x]}^{\mu} \alpha_{12}\,\mathrm{d}\mu - \mu[1 - x] \times [\alpha_{12}(\mu) - \alpha_{12}(\mu[1 - x])] \Big\} \quad (9)$$

The relationship between these expressions and those derived by Harned[3] is most clearly seen by considering the solvent activity in the mixed solution. The appropriate cross differentiation relation may be written in the form

$$-55.51 \left[\frac{\partial \ln a_w}{\partial m_1}\right]_{m_2} = \left[\frac{\partial}{\partial m_2}\,\phi_x \left[\frac{\nu_1}{k_1}\,\mu_1 + \frac{\nu_2}{k_2}\,\mu_2\right]\right]_{m_1} = \nu_1 \left[1 + \mu\left[\frac{\partial \ln \gamma_1}{\partial \mu}\right]_x\right] \quad (10)$$

Here ϕ_x is the practical osmotic coefficient for the mixed solution. After the substitution of eq. 4 and Bjerrum's relation between the activity and osmotic coefficients for electrolyte solute 1 in its own pure solution, this equation may be integrated to yield

$$\phi_x \left[\frac{\nu_1}{k_1}\,\mu_1 + \frac{\nu_2}{k_2}\,\mu_2\right] = \frac{\nu_2}{k_2}\,\mu_2\phi_2(\mu_2) + \frac{\nu_1}{k_1} \Big\{ \mu\phi_1(\mu) - \mu_2\phi_1(\mu_2) - 2.3\,\mu_2\,[\mu\alpha_{12}(\mu) - \mu_2\alpha_{12}(\mu_2)] \Big\} \quad (11)$$

in which ϕ_1 and ϕ_2 are the osmotic coefficients of solutes 1 and 2, respectively, in their pure solutions at the indicated ionic strength.

Now if Harned's rule holds as well for solute 2, that is, if

$$\log \gamma_2 = \log \gamma_{2(0)} - \alpha_{21}\mu_1 \quad (12)$$

then Harned[3] has shown that

$$\phi_x \left[\frac{\nu_1}{k_1}\,\mu_1 + \frac{\nu_2}{k_2}\,\mu_2\right] = \frac{\nu_2}{k_2}\,\mu\phi_2 + \mu_1 \left[\frac{\nu_1}{k_1} - \frac{\nu_2}{k_2} - 2.3\,\frac{\nu_2}{k_2}\,\alpha_{21}\mu\right] + \frac{2.3}{2}\,\mu_1{}^2 \left[\frac{\nu_1}{k_1}\,\alpha_{12} + \frac{\nu_2}{k_2}\,\alpha_{21}\right] \quad (13)$$

In eq. 13 and eq. 14 to follow, ϕ_1, ϕ_2, α_{12} and α_{21} are all to be evaluated at ionic strength μ. If eq. 11 and 13 are to be identical at all values of μ and μ_2, it may be shown that

$$\frac{\nu_2}{k_2}\,\alpha_{21} = \frac{\nu_1}{k_1}\,\alpha_{12} - \frac{2}{2.3\mu}\left[\frac{\nu_1}{k_1}\,[\phi_1 - 1] - \frac{\nu_2}{k_2}\,[\phi_2 - 1]\right] \quad (14)$$

and

$$\frac{\nu_1}{k_1}\,\alpha_{12}(\mu) + \frac{\nu_2}{k_2}\,\alpha_{21}(\mu) = \frac{\nu_1}{k_1}\,\alpha_{12}(\nu_2) + \frac{\nu_2}{k_2}\,\alpha_{21}(\mu_2) \neq f(\mu) \quad (15)$$

The first of these two results is the usual expression for computing α_{21} from α_{12} and the osmotic coefficients; the second is the test of the linearity relations proposed by Glueckauf. Thus, eq. 7 and 11 permit the direct calculation of γ_2 and ϕ_x, and eq. 12 and 13 with 14 the approximate calculation by means of Harned's rule.

Applications

The wealth of careful experimental work done by Harned and his co-workers provides the best material for exploiting the relations here derived. Even so, in most instances the linear rule has been established at only a few different values of the ionic strength, and so α_{12} cannot be said to be very well known as a function of μ. It is necessary to use a suitable empirical expression for α_{12} and to limit the computations to the ionic strength range over which α_{12} is known. Thus if in a system α_{12} has been measured for $\mu_a \leqslant \mu \leqslant \mu_b$, at any particular ionic strength μ' in this range the accessible values of x are given by $0 \leqslant x \leqslant 1 - \mu_a/\mu'$. The upper limit on x may be increased to unity only if it is permissible to extrapolate the empirical expression for α_{12} to infinite dilution.

The equations have been applied to the data of Harned and Gary[3] at 25° for hydrochloric acid in solutions containing barium, strontium, aluminum or cerium chloride. The requisite values of $\gamma_{1(0)}$, $\gamma_{2(0)}$, ϕ_1 and ϕ_2 have been obtained by interpolation from values in the literature,[15] and the observed values of α_{12} have been incorporated in expressions of the form

$$\alpha_{12} = \frac{A}{\sqrt{\mu}} + B + C\,\sqrt{\mu} \quad (16)$$

which is suggested by the observed variation of α_{12} with μ in a number of systems.[16] Other empirical expressions which were tested and found to give negligibly different results over the allowed composition range were considered unsuitable for possible extrapolation.

The results of the calculations are given as the unprimed quantities in Tables I–IV for the four systems at the accessible compositions in each case. The primed quantities in the tables are the corresponding values of $\log \gamma_2$ or ϕ_x computed on the assumption that Harned's rule holds for the second electrolyte solute.

Discussion

As the tables indicate, the values of the activity and osmotic coefficients calculated by means of the

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(14) The advantage of vapor pressure measurements over electromotive force measurements as a means of determining all the activities in a mixed electrolyte solution lies in the fact that the integration of the cross differentiation relation may be carried from the reference state for the solutes (infinite dilution), and so independent data for $\gamma_{2(0)}$ are not necessary.

(15) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Academic Press, Inc., New York, N. Y., 1955, pp. 468–487.

(16) Ref. 1, pp. 468–469.

TABLE I

ACTIVITY AND OSMOTIC COEFFICIENTS IN HCl–BaCl$_2$ SOLUTIONS

$$\alpha_{12} = \frac{0.0184}{\sqrt{\mu}} + 0.0332 + 0.0135\sqrt{\mu}$$

	$\mu = 2$				$\mu = 3$			
x	log γ_2	log γ'_2	ϕ_x	ϕ_x'	log γ_2	log γ_2'	ϕ_x	ϕ_x'
0	−0.408	−0.408	0.886	0.886	−0.403	−0.403	0.934	0.934
0.05	.400	.400	.911	.910	.391	.390	.966	.966
.1	.392	.392	.933	.932	.378	.377	.996	.996
.15	.383	.383	.954	.952	.365	.364	1.023	1.024
.2	.373	.375	.975	.972	.352	.351	1.050	1.051
.25	.365	.367	.994	.990	.339	.338	1.075	1.075
.3	.356	.359	1.012	1.008	.326	.326	1.098	1.098
.35	.347	.350	1.027	1.024	.313	.312	1.121	1.121
.4	.338	.342	1.044	1.040	.300	.300	1.143	1.142
.45	.330	.334	1.058	1.054	.286	.287	1.164	1.163
.5	.322	.326	1.073	1.069	.272	.274	1.184	1.183
.55					.258	.260	1.203	1.202
.6					.244	.248	1.222	1.220
.65					.232	.234	1.240	1.238

TABLE II

ACTIVITY AND OSMOTIC COEFFICIENTS IN HCl–SrCl$_2$ SOLUTIONS

$$\alpha_{12} = \frac{0.0027}{\sqrt{\mu}} + 0.0541 + 0.0013\sqrt{\mu}$$

	$\mu = 3$				$\mu = 5$			
	log γ_2	log γ_2'	ϕ_x	ϕ_x'	log γ_2	log γ_2'	ϕ_x	ϕ_x'
0	−0.336	−0.336	1.009	1.009	−0.236	−0.236	1.193	1.193
0.05	.324	.324	1.038	1.036	.213	.214	1.231	1.232
.1	.311	.311	1.065	1.062	.189	.193	1.265	1.268
.15	.297	.299	1.090	1.085	.168	.171	1.298	1.302
.2	.283	.286	1.112	1.108	.147	.149	1.331	1.333
.25	.271	.274	1.133	1.128	.124	.128	1.362	1.363
.3	.258	.261	1.153	1.148	.100	.106	1.392	1.391
.35	.244	.249	1.172	1.166	.078	.084	1.420	1.418
.4	.230	.236	1.190	1.184	.056	.062	1.446	1.443
.45	.218	.223	1.207	1.201	.034	.041	1.471	1.467
.5	.206	.211	1.223	1.217	.011	.019	1.494	1.490
.55	.194	.198	1.237	1.232	+ .010	+ .003	1.516	1.512
.6	.182	.186	1.252	1.247	.032	.024	1.537	1.534
.65	.171	.173	1.265	1.262	.055	.046	1.558	1.554
.7					.075	.068	1.577	1.574
.75					.096	.089	1.596	1.594
.8					.115	.111	1.613	1.612

TABLE III

ACTIVITY AND OSMOTIC COEFFICIENTS IN HCl–AlCl$_3$ SOLUTIONS

$$\alpha_{12} = \frac{-0.0052}{\sqrt{\mu}} + 0.0674 - 0.0009\sqrt{\mu}$$

	$\mu = 3$				$\mu = 5$			
x	log γ_2	log γ_2'	ϕ_x	ϕ_x'	log γ_2	log γ_2'	ϕ_x	ϕ_x'
0	−0.480	−0.480	1.008	1.008	−0.352	−0.352	1.246	1.246
0.05	.462	.464	1.048	1.043	.318	.321	1.289	1.288
.1	.443	.447	1.084	1.073	.284	.291	1.327	1.326
.15	.424	.430	1.111	1.100	.253	.260	1.361	1.358
.2	.406	.413	1.136	1.123	.222	.229	1.394	1.388
.25	.389	.397	1.158	1.145	.188	.199	1.422	1.415
.3	.372	.380	1.177	1.164	.153	.168	1.450	1.440
.35	.355	.363	1.194	1.182	.121	.138	1.475	1.462
.4	.337	.347	1.210	1.199	.088	.107	1.496	1.484
.45	.321	.330	1.225	1.215	.057	.076	1.518	1.504
.5	.306	.313	1.240	1.230	.025	.046	1.536	1.523
.55	.289	.297	1.253	1.244	+ .003	.015	1.554	1.542
.6	.272	.280	1.265	1.257	.032	+ .015	1.569	1.559
65	.259	.263	1.277	1.270	.061	.046	1.585	1.576
.7					.087	.077	1.599	1.592
.75					.115	.107	1.614	1.608
.8					.139	.138	1.628	1.623

TABLE IV

ACTIVITY AND OSMOTIC COEFFICIENTS IN HCl–$CeCl_3$ SOLUTIONS

$$\alpha_{12} = -\frac{0.0202}{\sqrt{\mu}} + 0.1122 - 0.0051\sqrt{\mu}$$

	$\mu = 2$				$\mu = 3$			
x	log γ_2	log γ_2'	ϕ_x	ϕ_x'	log γ_2	log γ_2'	ϕ_x	ϕ_x'
0	−0.585	−0.585	0.847	0.847	−0.578	−0.578	0.914	0.914
0.05	.580	.581	.874	.871	.569	.571	.945	.940
.1	.575	.577	.895	.893	.558	.563	.974	.964
.15	.571	.573	.916	.914	.549	.555	.998	.988
.2	.566	.568	.937	.934	.540	.548	1.022	1.011
.25	.563	.564	.956	.953	.532	.540	1.045	1.034
.3	.558	.560	974	.971	525	.532	1.067	1.056
.35	.554	.555	.990	.988	.517	.525	1.088	1.078
.4	.549	.551	1.007	1.006	.509	.517	1.109	1.099
.45	.546	.547	1.023	1.022	.502	510	1.129	1.121
.5	.543	.543	1.038	1.039	.495	.502	1.150	1.142
.55					.488	.494	1.170	1.163
.6					.481	.487	1.190	1.184
.65					.476	.479	1.209	1.204

cross differentiation relations are but slightly different from those calculated on the assumption of Harned's rule for the metallic chloride. The differences, however, are considerably larger than the variations from linear behavior for the hydrochloric acid, for example, or the experimental uncertainties in the independent values for the separate pure solutions, or finally, the quite small variations arising from the use of different reasonable empirical expressions for α_{12}. That the particular choice of expression used for α_{12} is not itself responsible for the deviations from Harned's rule may be inferred from comparisons of the osmotic coefficients at compositions for which α_{12} is specifically known from experiment; for example, $\phi_x = 1.496$ and $\phi_x' = 1.484$ in the hydrochloric acid–aluminum chloride system at $\mu = 5, x = 0.4$, and in the hydrochloric acid–barium chloride system at $\mu = 2, x = 0.5$ the values are 1.073 and 1.069, respectively. The general consistency in the trend of calculated values in a given system at a specified total ionic strength further argues against random errors in the interpolations used to obtain $\gamma_{1(0)}$, $\gamma_{2(0)}$, ϕ_1 and ϕ_2 as the source of the deviations from Harned's rule.

Glueckauf's test was applied by Harned and Gary to their results in all four systems and it showed that Harned's rule does not hold precisely. This test, however, in its very nature is extremely sensitive; for these systems the left member of eq. 15 varies over the appropriate ionic strength ranges by from 7.7 to 44.4%, instead of remaining constant as required by the test, but still Harned's rule may be said to hold with only slight deviations. As Robinson[17] has pointed out, the effect of deviations from Harned's rule is much greater with respect to solute activity coefficients than with respect to solvent activity; the calculated vapor pressures of the solutions are not here presented because they differ so slightly from those computed by the approximate method.

The computed values of log γ_2 may be fitted to quadratic expressions as suggested by Robinson[17]; the coefficients of the quadratic terms are generally quite small. The deviations from linearity are in most cases rather less than the difference between the straight line determined by the computed values of log γ_2 and that required by the usual calculation of α_{12} through eq. 14. It may be concluded that the activity coefficients of the second electrolyte solute satisfy quite well a linear relation such as eq. 12, but the slope of the line is given less accurately by eq. 14, because the latter is based on the premise that Harned's rule holds precisely.

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[17] R. A. Robinson, in "Electrochemical Constants," National Bureau of Standards Circular 524, Washington, D. C., 1953, p. 171.

THE PREPARATION, DENSITIES, REFRACTIVE INDICES AND VISCOSITIES OF 1-AZIDOÖCTANE, 1-AZIDOHEPTANE, 1-AZIDOHEXANE AND 1-AZIDOPENTANE

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Contribution from the Research and Development Department, U. S. Naval Powder Factory, Indian Head, Maryland and from the Chemistry Department, University of Delaware, Newark, Delaware

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Four homologous 1-azidoalkanes have been prepared and characterized by analysis, boiling point and infrared absorption spectra (by Skinner and Wright). The densities and viscosities have been measured over the range 15 to 50°; refractive indices referred to the D-line of sodium have been measured from 15 to 35° (by Brown and Cary).

Henkel and Weygand's procedure[3] for the preparation of 1-azidohexane was modified in several particulars.

A solution of 45 g. (0.273 mole) of pure *n*-hexyl bromide in 200 cc. of methanol was heated with 22.5 g. (0.346 mole) of sodium azide and 30 cc. of water in a water-bath so as to maintain gentle reflux (75–80°). The oil separating was heavier than the medium but in 3 hours floated on the surface. After 15 hours 70 cc. of water was added to the ice-cold mixture which was now extracted four times with 60-cc. portions of a 1:1 mixture of ether and petroleum ether and once with 30 cc. of petroleum ether. The combined extract was extracted with 50 cc. of a solution of calcium chloride prepared from 160 g. of calcium chloride and 200 cc. of water. The ethereal layer was dried over calcium chloride and distilled, first to remove the solvent: Fractions I, 3.5 g. (10.8%), b.p. 60–65° (25.5 mm.); II, 29.7 g. (85.6%), b.p. 63–64° (25.5 mm.); residue, negligible. This procedure similarly gave a distillate free of bromide (alcoholic silver nitrate) in the case of 1-azidopentane and 1-azidoheptane. 1-Azidooctane contained a small amount of bromide. A mixture of this product (153 g.), 375 cc. of methanol, 22.5 g. of sodium azide and 30 cc. of water was then refluxed for 3 hours with mechanical stirring. The substance (147 g.), b.p. 99° (27 mm.), was now free from bromide.

Combined preparations of corresponding azides were fractionally distilled until the refractive indices were constant. The yields were more than 90%. The purified products had the following boiling points: C_5, 52° (40 mm.); C_6, 57.5° (19 mm.); C_7, 74° (18 mm.); C_8, 44° (0.70 mm.). The infrared absorption spectra were all similar, showing bands for the azide group as follows: 3.02 (w), 4.00 (w), 4.8 (s) and 7.9–8.0 (s).

TABLE II

DENSITIES, VISCOSITIES AND REFRACTIVE INDICES OF AZIDOALKANES

(Parenthetical values are those of Skinner and Wright)

	Density, g./ml. 1-Azido-				Viscosity, centipoises 1-Azido-				Refractive index n_D 1-Azido-			
t°	octane	heptane	hexane	pentane	octane	heptane	hexane	pentane	octane	heptane	hexane	pentane
15	0.8695	0.8704	0.8735	0.8790	1.2886	1.0240	0.8154	0.6509	1.4413	....	....	1.4292
20	.8658	.8663	.8688	.8740					1.4391	1.4357	....	....
	(.8651)	(.8667)	(.8693)	(.8730)					(1.4385)	(1.4351)	(1.4312)	(1.4266)
25	.8614	.8622	.8647	.8695	1.1039	.8877	.7190	.5885	1.4369	1.4337	1.4294	1.4248
30	.8571	.8579	.8600	.8642					1.4349	....	1.4273	....
35	.8531	.8535	.8551	.8598	.9618	.7790	.6361	.5187	1.4326	....	1.4251	1.4202
40	.8488	.8490	.8506	.8549								
45	.8446	.8445	.8464	.8500	.8382	.6901	.5712	.4697				
50	.8405	.8398	.8416	.8446								

The azides also gave a negative test for alcohol with ceric nitrate reagent. There was no explosive reaction when a drop was brought into contact with a red hot copper wire. No explosive reaction resulted when a drop was allowed to fall upon a red hot iron plate. A drop gave a vigorous evolution of gas by addition to concentrated sulfuric acid. They did not decolorize bromine in carbon tetrachloride.

Analyses by Mrs. P. P. Wheeler (microanalyst, USNPF) are summarized in Table I.

TABLE I

CARBON, HYDROGEN AND NITROGEN ANALYSES OF 1-AZIDOALKANES

Alkane	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
1-Azidopentane	53.1	53.2	9.8	9.6	37.1	36.0, 36.4
1-Azidohexane	56.7	57.1	10.3	9.6	33.0	32.5
1-Azidoheptane	59.5	60.2	10.7	10.7	29.8	29.8
1-Azidoöctane	61.9	62.8	11.0	11.1	27.1	28.0

Measurements were carried out in a water-bath controlled to 0.005° by a Sargent Thermonitor controller. The thermometers were calibrated with an NBS certified platinum resistance thermometer. Densities were measured with a 1-ml. pycnometer of the Lipkin type which was calibrated with purified benzene and with water.[4] Experimental values are recorded in Table II, except that densities of 1-azidoheptane determined at uneven temperatures were calculated to rounded temperatures by means of the least squares equation

$$d = 0.88218 - 7.545 \times 10^{-4}t - 1.8667 \times 10^{-6}t^2$$

which fitted the seven experimental points with an average deviation of 0.0002 unit. A modified Ostwald viscometer was used for determining viscosities.[5] In measuring refractive indices water from the controlled bath was pumped through a refractometer, Valentine No. 1091 (Abbe type), which had been calibrated with purified benzene, water and a standard glass plate.

Molar refractions were calculated and recorded in Table III with the contributions of the azide group to the molar refractivity at 20°, using as values for atomic refraction C = 2.418 and H = 1.100. In studying the contribution of the azide group to molar refractions of seven different com-

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(3) (a) K. Henkel and F. Weygand, *Ber.*, **76B**, 812 (1943); (b) P. A. Levene, A. Rothen and M. Kuna, *J. Biol. Chem.*, **120**, 777 (1937).

(4) M. R. Lipkin, J. A. Davison W. T. Harvey and S. S. Kurtz, Jr., *Ind. Eng. Chem., Anal. Ed.*, **16**, 55 (1944).

(5) M. R. Cannon and M. R. Fenske, *ibid.*, **10**, 297 (1938).

pounds J. C. Philip has found comparable values of 9.00, 9.00, 8.75, 8.95, 8.93, 8.75 and 8.91.[6]

TABLE III

CONTRIBUTION OF THE AZIDE GROUP TO MOLAR REFRACTION AT 20°

Azide	MR_D Brown and Cary	MR_D Skinner and Wright	$-N_3$ value Brown and Cary	$-N_3$ value Skinner and Wright
n-Octyl	47.174	47.15	9.130	9.08
n-Heptyl	42.593	42.52	9.167	9.09
n-Hexyl	37.909[a]	37.89	9.101	9.06
n-Pentyl	33.234[b]	33.25	9.044	9.07

[a] Extrapolated. [b] Interpolated.

The values obtained for viscosities of the azidoalkanes were checked by plotting the logarithm of the viscosity against the reciprocal of the absolute temperature. In each case the four points plotted fell in a straight line, the slopes of these lines increasing slightly with increasing molecular weight. It was found that all four straight lines converged to a common point at $1/T$ equal to 0.0013241, and that the slope of each line was a linear function of the number of carbon atoms. Thus one equation could fit the data for all four compounds. This equation is

$$\log_{10} \eta = \frac{45.867n + 205.66}{T} - 0.060727n - 1.38663$$

where n is the number of carbon atoms and η the viscosity in centipoises. The deviations of the experimental points from the straight line are shown in Table IV.

TABLE IV

COMPARISON OF OBSERVED AND CALCULATED VISCOSITIES

$t°$	100 $(\eta_{obs}/\eta_{calcd.})$ for 1-Azido- octane	heptane	hexane	pentane
15	100.30	99.92	99.81	99.95
25	100.12	99.76	100.12	101.54
35	100.68	99.89	99.91	99.80
45	100.37	99.85	100.45	100.09

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[6] J. C. Philip, *J. Chem. Soc.*, **101**, 1866 (1912).

THE THERMODYNAMICS OF BROMINATION OF TOLUENE AND THE HEAT OF FORMATION OF THE BENZYL RADICAL[1-3]

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The equilibrium constant for the reaction $C_6H_5CH_3(g) + Br_2(g) \rightleftarrows C_6H_5CH_2Br(g) + HBr(g)$ has been measured at 150° and found to be 7.2×10^4, equilibrium being approached from both sides. This gives $\Delta F_{(423° K.)} = -9.4$ kcal./mole. The entropy of $C_6H_5CH_2Br$ has been estimated from spectroscopic and other data as $S°_{298} = 90.8 \pm 1$; $S°_{423} = 102.2 \pm 1$ $\Delta S_{(423° K.)}$ is then 3.5 cal./mole-deg. Together with other known thermal data, this leads to $\Delta H°_f(C_6H_5CH_2Br) = 20.0 \pm 0.9$ kcal./mole and $\Delta H_{(298° K.)} = -8.0 \pm 0.9$ kcal./mole which compares well with another less precise measurement. This value is 6 kcal. greater than that derived from bond energies for $D(C_6H_5CH_2{-}H)$ and $D(C_6H_5CH_2{-}Br)$ assigned from kinetic studies. A review of the various kinetic studies which yield values for the heat of formation of $C_6H_5CH_2$ radicals shows a range of values from about 34 to 50 kcal./mole. Most of the data lie in the range 38–44 kcal./mole and it is felt that this latter is probably closest to the true value. This leads to a bond dissociation energy for toluene, $D(C_6H_5CH_2{-}H)$ of about 84 kcal./mole. Specific considerations are given of the pyrolyses of bibenzyl and toluene and it is concluded that despite the small amounts of decomposition permitted in the flow systems, secondary processes are still important and the interpretations of the data have been oversimplified. In the pyrolysis of $C_6H_5CH_3$, it is shown that entropy considerations favor the process $C_6H_5CH_3 \rightarrow C_6H_5 + CH_3$ in relation to $C_6H_5CH_3 \rightarrow C_6H_5CH_2 + H$ despite the larger activation energy of the former. Quantitative estimates of the relative rates of these two processes are in reasonable accord with the ratios of CH_4/H_2 experimentally observed.

Introduction

The bond dissociation energy of toluene, $D(C_6H_5{-}CH_2{-}H)$, has in recent years become a topic of considerable dispute. Szwarc,[4] from kinetic studies of the pyrolysis of toluene in a flow system, assigned it a maximum value of 77.5 kcal. Later Van Artsdalen and co-workers,[5,6] from studies of the thermal and photochemical bromination of toluene derived a value of 89.9 kcal. which, however, can at best be considered an upper limit. More recently Steacie, *et al.*,[7] repeated the pyrolysis studies on toluene in a flow system over an extended range of pressures and temperatures and found, contrary to Szwarc, that the kinetics were not first order and that the rates were sensitive to surface conditions and contact times. Although they refrained from assigning a bond dissociation energy they did point out that an Arrhenius plot of an assumed first-order rate constant, measured on a "conditioned" surface at constant contact times gave an activation energy of 90 kcal., which is to be contrasted to the value of 77.5 kcal. obtained by Szwarc using a similar kinetic calculation.

Schissler and Stevenson,[8] using mass spectroscopic measurements of the appearance potentials of the benzyl ion $(C_7H_7^+)$ from various toluene derivatives, together with other thermodynamic data and some assumed bond energies derived a value for

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[2] Presented at the Fall Meeting of the American Chemical Society, Atlantic City, New Jersey (September, 1956).

[3] Taken in part from the thesis of Jerry H. Buss, to be submitted to the Graduate School of the University of Southern California for the Ph.D. degree.

[4] M. Szwarc, *J. Chem. Phys.*, **16**, 128 (1948). The uncertainty in the activation energy is estimated by Szwarc somewhat conservatively as ±4 kcal.

[5] E. W. Swegler, H. A. Scheraga and E. R. Van Artsdalen, *ibid.*, **19**, 135 (1951).

[6] H. R. Anderson, H. A. Scheraga and E. R. Van Artsdalen, *ibid.*, **21**, 1258 (1953).

[7] H. Blades, A. T. Blades and E. W. R. Steacie, *Can. J. Chem.*, **32**, 298 (1954).

[8] D. O. Schissler and D. P. Stevenson, *J. Chem. Phys.*, **22**, 151 (1954).

$D(C_6H_5CH_3\text{–}H) = 77 \pm 3$ kcal. Lossing, *et al.*,[9] have, however, challenged the assumptions employed by Schissler and Stevenson and shown that in fact the available appearance potentials give at best the difference in bond dissociation energies of pairs of toluene derivatives, and cannot be used *per se* to fix unambiguously $D(C_6H_5CH_2\text{–}H)$. In a more recent paper[10] they have shown that the difference between the measured appearance potential of $(C_7H_7^+)$ from toluene and the measured ionization potential of the benzyl radical yields an upper limit for $D(C_6H_5CH_2\text{–}H) \leq 95$ kcal.

In view of these disagreements, and in addition of the weaknesses of the kinetic studies, it was felt that it would be desirable to obtain independent evidence relating to the bond dissociation energy. The method chosen was a study of the equilibrium

$$C_6H_5CH_3 + Br_2 \underset{2}{\overset{1}{\rightleftarrows}} C_6H_5CH_2Br + HBr \qquad (1)$$

The range of bond dissociation energies listed for toluene suggested that the equilibrium would be measurable if the true value were sufficiently high. If even crude values of the equilibrium constant, K_1, could be obtained at one temperature, the available methods for estimating the entropy of $C_6H_5CH_2Br$ would be good enough to yield a value for the heat of reaction, ΔH_1, with an uncertainty which might be better than that of the available data. Such a value would at least fix the differences in bond dissociation energies of $C_6H_5CH_3$ and $C_6H_5CH_2Br$ (those for Br_2 and HBr being known) and provide an independent piece of data for assessing the reliability of various proposed bond energies. The relations between K_1, ΔH_1 (at temperature T) and the relevant bond dissociation energies are given by

$$\Delta H_1 = \Delta F_1 + T\Delta S_1 = -RT \ln K_1 + T\Delta S_1 \quad (2)$$

$$D(C_6H_5CH_2\text{–}H) - D(C_6H_5CH_2\text{–}Br) = \Delta H_1 + D(HBr) - D(Br_2) \quad (3)$$

where the quantities on the right-hand side of the eq. 3 are either known, measurable or calculable from known data.

Experimental

A middle cut of Baker and Adamson (reagent grade) toluene, boiling from 110.1–111.0° (760 mm.) was put through two bulb-to-bulb isothermal distillations in a high vacuum line, the first $^2/_3$ of each sample being kept after degassing. The final sample was stored *in vacuo* in a Pyrex bulb sealed from the line by a stopcock.[11] Bromine (B and A, reagent grade also) was allowed to equilibrate with KBr for a week to remove chlorine and then purified by the same procedure.

Long capillaries were drawn from Pyrex tubing, one end sealed to a ground joint and the other end closed. Their volumes were calibrated by weighing mercury in them. They were cleaned with aqua regia, rinsed, cleaned again with cleaning solution, rinsed thoroughly with distilled water, attached to the vacuum line and evacuated ($\sim 10^{-6}$ mm.).

Samples of Br_2 and $C_6H_5CH_3$ were distilled into separate capillaries, the amounts being estimated volumetrically, and the capillaries were then sealed under vacuum. The exact amount of each reagent was determined by differences in weight of the capillaries, similar capillaries being used as tares. Two capillaries, one with Br_2 and one with $C_6H_5CH_3$ were then placed in a cleaned and rinsed Pyrex flask (~ 300 cc.) which was sealed to the vacuum line, evacuated to 10^{-6} mm. and sealed off.

The flask was then heated to 150° (±1°) in an air oven, withdrawn and the capillaries broken by shaking.[12] The flask was then put back in the oven (darkened for 96 hours[13]) after which the reaction was quenched by immersing a "tit" attached to the flask in liquid N_2. The flask was then sealed to a vacuum line and the products separated by bulb-to-bulb, isothermal distillation. An EtBr bath at −108° was used to separate HBr from Br_2. HBr was distilled into a calibrated capillary, weighed as previously described and finally dissolved in water (by breaking the capillary tips under water) and titrated with standardized NaOH.

A $CHCl_3\text{–}CCl_4$ bath at −33° was used to separate Br_2 which could be identified by color. It was permitted to react with Hg to give $HgBr_2$ which was weighed. A diethylene glycol bath at −10° was used to separate toluene which was distilled into a small volume where it could be measured accurately from its $P\text{–}V\text{–}T$ data.

The remaining material, presumably $C_6H_5CH_2Br$,[14] was then distilled at room temperature into a capillary and weighed. For experiments on the reverse reaction, HBr was prepared by allowing solid NaBr (reagent grade), kept in an evacuated flask to come in contact with sirupy H_3PO_4.[15] The HBr gas was passed through a tower containing anhydrone and indicating "drierite" and then put through several bulb-to-bulb distillations at −110°. It was measured into capillaries and weighed. Reagent grade $C_6H_5CH_2Br$ (Matheson, Coleman and Bell) boiled from 197–199° and had a specific gravity of 1.43 at 21° (literature 1.438^{22}_{0}). It was put through two bulb-to-bulb isothermal distillations at 0°, measured into capillaries and weighed. The procedure followed for observing the reverse reaction was essentially the same as that described for the forward reaction.

Results

The quantitative data for forward and reverse reactions are listed in Table I.

As can be seen in Table I, the quantities of HBr and $C_6H_5CH_2Br$ recovered in all experiments agree to better than 1% with the values expected from a material balance. As anticipated the Br_2 and $C_6H_5CH_2$ were the most difficult to measure in the products and consequently the errors in the determination of the equilibrium constant, K_1, arise for the major part from the uncertainties in these quantities. The average value from all runs for which explicit values for Br_2 were obtained is $K_1 = (7.2 \pm 0.7) \times 10^4$. This gives $-\Delta F_1$ (423°K.) = 9.4 ± 0.3 kcal., the spread being much smaller than that of any of the other relevant thermal data. The maximum spread about the mean is 12% which makes it rather difficult to calculate ΔH by measuring K at some other temperature.[16]

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[9] J. B. Farmer, I. H. S. Henderson, C. A. McDowell and F. P. Lossing, *J. Chem Phys.*, **22**, 1948 (1954).

[10] J. B. Farmer, F. P. Lossing, D. G. H. Marsden and C. A. McDowell, *ibid.*, **24**, 52 (1956).

[11] All stopcocks used were lubricated by silicone grease which was not attacked by Br_2, nor did it cause any difficulties attributable to adsorption.

[12] This was done in darkness to prevent photolysis. In later experiments the toluene capillary was broken first. This was accomplished by using larger diameter capillary and curving the end. This avoided the possibility of a liquid phase reaction.

[13] The data of Van Artsdalen, *et al.* (ref. 6), show this to be more than sufficient to reach equilibrium.

[14] No direct analysis was made. Less volatile products such as bibenzyl or $C_6H_5CHBr_2$ would not distil under these conditions. The best check on the $C_6H_5CH_2Br$ was the mass balance. In the earlier experiments it was found that a black, non-volatile, insoluble tar was formed, amounting to from 2–10% by weight of the total reactants. It was found that by cleaning the reaction flask in hot HNO_3 and rinsing carefully no tar would be formed.

[15] This was done through the rotation of a bent tube attached to the flask by a ground joint.

[16] It can in fact be shown that the measure of K with similar precision at a temperature 40° higher will not lead to a more precise value for ΔH than is obtained from estimates of the entropy—even neglecting the added difficulty of side reactions at the higher temperature.

TABLE I

Sample	$C_6H_5CH_3$[a] added	Br_2 added	HBr recovered		$C_6H_5CH_2Br$ Recvrd.	Br_2 Recvrd.	$C_6H_5CH_3$ Recvrd.	Calcd. equil. const. $K_1 \times 10^{-4}$
			By wt.	By titr.				
A_1[b]	1.04	1.02	1.01	1.03	1.03	<0.01	0.01	>1.0
A_2[b]	1.07	1.06	1.05	1.05	1.06	< .01	.01	>1.0
A_3	1.127	1.096	1.085	1.098	1.099	6×10^{-4}[c]	.0309	6.3
	HBr added	$C_6H_5CH_2Br$ added						
B_1	0.985	1.026	0.982	0.984	1.032	0.003[c]	0.0042	8.0
B_2	1.011	1.018	1.006	1.013	1.029	.003[c]	.0046	7.4
B_3	1.985	2.022	1.987	1.985	2.040	.007[c]	.0091	6.3
B_4	1.983	2.016	1.980	1.983	2.025	.006[c]	.0083	8.0
							Av. =	7.2 ± 0.7

[a] All amounts in millimoles. [b] Minimum values since the amount of Br_2 was only found to be less than 0.01. [c] Weighed as $HgBr_2$.

Two points are worthy of notice in the experimental results. One is the finding that there is no measurable tendency for secondary bromination of the $C_6H_5CH_2Br$ to produce either $C_6H_5CHBr_2$ or a ring substituted compound.[17] This seems to be in agreement with the results reported by Van Artsdalen, *et al.*[6] The second is the possibility of producing bibenzyl in this reaction. If it is formed in equilibrium with the system its appearance is unimportant. If it is produced in an irreversible fashion then it can be seen again that within the limits of our measurements its appearance is unimportant.

The Entropy of $C_6H_5CH_2Br$ and the Entropy of Bromination.—Third law data[18,19] are available for $C_6H_5CH_3$, HBr and Br_2 but not for $C_6H_5CH_2Br$. Its entropy, however, is readily estimated by standard procedures and is shown in Table II, together with values calculated by a similar method for $C_6H_5CH_3$.

The most serious error in these calculations lies in the estimates of internal rotation and vibration. At the upper temperature we estimate the maximum expected error as ±2 e.u. and a probable error of ±1 e.u. This leads to a maximum error in ΔF (423° K.) of less than 1 kcal. so that the estimates are about as good as the measurements of the equilibrium constant.

Together with thermodynamic[18] and spectroscopic[20] data on HBr and Br_2 the entropy change for reaction 1 may now be computed as $\Delta S°_{423} = 3.5 \pm 2$ cal./mole°K. and $\Delta S°_{298} = 3.3 \pm 2$ cal./mole-°K. From the measured value of the equilibrium constant at 423°K. (Table I), we find $\Delta F°_{(423)} = -9.4 \pm 0.3$ kcal. Together with $\Delta S°_{423}$ this leads to $\Delta H°_{(423)} = -8.0 \pm 0.9$ kcal. with a maximum expected error of ±1.2 kcal. The value at 298°K. is the same within 0.1 kcal. Finally, $\Delta H°_f(C_6H_5CH_2Br) = 20.0$ kcal./mole.

TABLE II

CALCULATED ENTROPIES OF $C_6H_5CH_2Br$ AND $C_6H_5CH_3$[a]

		$C_6H_5CH_2Br$	$C_6H_5CH_3$	$C_6H_5CH_3$ (obsd.)[b,d]
$S_{trans.}$	(298)	41.31	39.46	39.46
	(423)	43.07	41.22	...
$S_{rot.}$[b]	(298)	30.67	26.95	27.1
	(423)	31.72	28.00	...
$S_{int. rot.}$[c]	(298)	7.94	2.18	2.2
	(423)	8.29	2.53	...
S_{vib}[e]	(298)	10.9	...	7.66
	(423)	19.1	...	15.1
S_{total}	(298)	90.8	...	76.4
	(423)	102.2	86.9	...

[a] All ideal gases at 1 atm., units in cal./mole°K. [b] $\sigma_e = 1$ for both $C_6H_5CH_3$ and $C_6H_5CH_2Br$. [c] $\sigma_i = 6$ for $C_6H_5CH_3$ and 2 for $C_6H_5CH_2Br$. Assumed free rotation for $C_6H_5CH_2Br$ and $C_6H_5CH_3$. No correction made for the angle between axes of C_6H_5 and CH_2Br groups so that $S_{int. rot.}$ may be slightly high on this account. [d] Observed values are those taken from the A.P.I. report (ref. 19) and K. S. Pitzer and D. W. Scott, *J. Am. Chem. Soc.*, 65, 803 (1943) for free rotation, also W. J. Taylor, D. D. Wagman, M. C. Williams, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **37**, 95 (1946). [e] These values have been estimated by assuming that $S_{vib}(C_6H_5CH_2Br) = S_{vib}(C_6H_5CH_3) + [S_{vib}(CH_2Br_2) - S_{vib}(CH_3Br)]$, values for the latter three substances being available. There is considerable justification for this type of analysis. See for example, W. F. Edgell and C. E. May, *J. Chem. Phys.*, 22, 1808 (1954).

Discussion

There are two independent values with which ours may be compared. In 1949 Skinner and Gellner[21] measured the heats of hydrolysis of $C_6H_5CH_2Br$ and $C_6H_5CH_2I$ in aqueous alcoholic solution. Together with relevant thermodynamic data and estimates, they derived values for the standard enthalpies of formation of 15.6 ± 3 and 26.4 ± 3 kcal./mole, respectively. Using more recent data[22] and better heats of vaporization[23] we have corrected their values to 18.4 ± 3 kcal. and 29.2 ± 3 kcal., respectively. The former is in excellent agreement with our own value of 20.0 kcal./mole quoted above.

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(17) This has some interesting kinetic consequences in regard to the relative rates of reaction of Br with benzyl bromide which would imply either that the rate of abstraction of Br is so much faster than H abstraction that the latter is not observed or else that if H abstraction does occur to form C_6H_5CHBr, then this radical will react with HBr to reform $C_6H_5CH_2Br$ + Br, much more rapidly than it will react with Br_2 to form $C_6H_5CHBr_2$.

(18) Selected Values of Chemical Thermodynamic Properties, National Bureau of Standards Circular 500, 1952.

(19) Selected Values of the Properties of Hydrocarbons, Am. Petrol. Inst. Project 44

(20) G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand and Co., New York, N. Y., 1950.

(21) O. H. Skinner and H. A. Gellner, *J. Chem. Soc.*, 1145 (1949).

(22) G. S. Parks, K. M. Manchester and L. M. Vaughan, *J. Chem. Phys.*, **22**, 2089 (1954), give the value of $\Delta H°_f(C_6H_5CH_2OH,S) = -38.5$ kcal./mole (−39.0 used by S. and G.).

(23) "Die Destillation unter vermindentum Druck im Laboratorium," Anschutz and Reitter, 2nd Ed. Bonn, Cohen, 1895. W. A. Felsing and S. A. Durban, *J. Am. Chem. Soc.*, **48**, 2885 (1926). From these vapor pressure data we compute $\Delta H_{vap} = 11.3$ kcal./mole for both $C_6H_5CH_2Br$ and $C_6H_5CH_2I$ (9 was used by S. and G.).

If we use eq. 3, ΔH_1 may be computed from the spectroscopic data[18] on HBr and Br_2 together with the bond dissociation energies measured kinetically by Szwarc, *et al.*[24,25] Correcting these values[26] to adapt them to thermodynamic usage we find that $\Delta H_{1(298)} = -14.9$ kcal./mole[27] which differs by 6.9 kcal. from our own value of -8.0 and by 5.3 kcal. from the value derived by us from the data of Skinner and Gellner. Both of these differences are outside the estimates of errors claimed by Szwarc[24] but within the limits estimated by us and others[7] for the kinetic studies.

If we take our revised value for the $\Delta H^\circ_f(C_6H_5CH_2I, g)$, the heat of iodination of toluene (gas phase) is computed as $+8.5$ kcal./mole. Once again, correcting Szwarc's values for the bond dissociation energies of $C_6H_5CH_2I$[28] and $C_6H_5CH_3$[27] we compute *via* eq. 3 a value of $+2.2$ which is 6.3 kcal. low. On the other hand the bond dissociation energies of $C_6H_5CH_2Br$ and $C_6H_5CH_2I$ are both compatible within 0.6 kcal. with the revised heats of formation of these two compounds. One may conclude, (a) the bond dissociation energies of both $C_6H_5CH_2Br$ and $C_6H_5CH_2I$ are correct and that for toluene is low by about 6 to 7 kcal., (b) the bond dissociation energy of toluene is correct but that for $C_6H_5CH_2Br$ and for $C_6H_5CH_2I$ is too high by about 6–7 kcal. (c) All three bond energies are in error. There is at present no way of deciding among these alternatives[29] although it appears very probable that the previously assigned bond energy of toluene is low.

The Heat of Formation of the Benzyl Radical.—In an effort to resolve the problem of the bond dissociation energy of toluene we have made a review of the experimental data on bond dissociation energies of benzyl derivatives, $C_6H_5CH_2R \rightarrow C_6H_5CH_2 + R$. Where data are available on the heats of formation of $C_6H_5CH_2R$ and R, the bond dissociation energy can be used to derive a value for the heat of formation of $C_6H_5CH_2(g)$. In Table III we summarize the values of $H^\circ_f(C_6H_5CH_2, g)$ currently available.[30] With the exception of the extreme values derived from $C_6H_5CH_2NH_2$, $C_6H_5CH_2COCH_3$ and $C_6H_5CH_2C_2H_5$,[31] the remaining values for some 6 compounds range between about 38 and 45 kcal./mole. On the basis of quantity one would be tempted to choose a value near 40 kcal. However, there are a sufficient range of values presented that one is inclined to look in some greater detail into the kinetic methods used to derive these values.

The Kinetics of Formation of Benzyl Radicals.—Horrex and Miles[32] found that the pyrolysis of bibenzyl in the range 630–780° gave products as shown by the equation

$$3(C_6H_5CH_2)_2 \longrightarrow 2C_6H_5CH_3 + C_6H_5CH{=}CHC_6H_5 + C_6H_5H + C_6H_5CH{=}CH_2$$

together with small amounts of H_2. The analyses were, however, only approximate and their experimental rate constants (which show a considerable spread in values) are based on a fixed stoichiometry (as given by the previous equation) between the amount of toluene produced and bibenzyl lost. A reasonable scheme for the decomposition is

$$C_6H_5CH_2CH_2C_6H_5 \underset{2}{\overset{1}{\rightleftarrows}} 2C_6H_5CH_2$$

$$C_6H_5CH_2 + C_6H_5CH_2CH_2C_6H_5 \xrightarrow{3} C_6H_5CH_3 + C_6H_5CH_2CHC_6H_5$$

$$C_6H_5CH_2CHC_6H_5 - \begin{array}{l} \xrightarrow{4} C_6H_5CH{=}CH_2 + C_6H_5 \\ \xrightarrow[4']{} C_6H_5CH{=}CHC_6H_5 + H \end{array}$$

Chain propagation

$$C_6H_5 + C_6H_5CH_2CH_2C_6H_5 \xrightarrow{5} C_6H_5H + C_6H_5CH_2CHC_6H_5$$

$$H + C_6H_5CH_2CH_2C_6H_5 \xrightarrow{5'} H_2 + C_6H_5CH_2CHC_6H_5$$

$$C_6H_5 + C_6H_5CH_2CHC_6H_5 \xrightarrow{6} C_6H_5H + C_6H_5CH{=}CHC_6H_5$$

Termination

$$C_6H_5CH_2 + C_6H_5CH_2CHC_6H_5 \xrightarrow{7}$$

$$H + \text{Olefins} \xrightarrow{8} \text{Radicals}$$

Transfer

This can give a reasonable accounting for the product distribution if we assume that $k_4 > k_4'$ and $k_3k_4 \approx k_1k_7$ in the range studied. Steacie, *et al.*,[7] have shown that H_2 becomes an important product in the bibenzyl pyrolysis at about 900° but also that it tends to a limiting value. This is also reasonable since we might expect $E_4' > E_4$ and the inhibition of H atoms by unsaturated products can account for the levelling off of H_2.

If we try to write from such a scheme a kinetic expression for the disappearance of bibenzyl, BB, then we find in a simplified case (neglecting 8, 2, 6)

$$\frac{-\mathrm{d(BB)}}{\mathrm{d}t} = [(k_4 + k_4')\frac{k_3}{k_7} + 2k_1](\mathrm{BB})$$

which is first order in (BB). However, the experimental first-order rate constant cannot be equated to k_1, although $2k_1$(BB) is the rate of production of $C_6H_5CH_3$.

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(24) M. Szwarc, *Chem. Revs.*, **47**, 75 (1950).

(25) M. Szwarc, B. N. Ghosh and A. H. Sehon, *J. Chem. Phys.*, **18**, 1142 (1950).

(26) We shall adopt the convention of equating the bond dissociation energy $D_T(R–X)$, with the enthalpy change ΔH_T for the reaction $R–X = R + X$ at the temperature T. For a fission reaction this gives $D_T(R–X) = E_F + RT$, where E_F = the activation energy for the unimolecular decomposition, it being assumed that for the reverse reaction, $E_R = 0$. In the work that follows we have corrected D_T to 298°K. by estimating ΔC_p, using classical values for translational and rotational heat capacities and estimates of the vibrational frequencies where these were not available.

(27) This derives from $D_{298}(C_6H_5CH_2–H) = 77.8$ kcal./mole and $D_{298}(C_6H_5CH_2–Br) = 51.3$ kcal., vibrational assignments being derived in part from K. S. Pitzer and E. Gelles, *J. Chem. Phys.*, **21**, 855 (1953).

(28) M. Szwarc, Thesis, Manchester Univ., 1947. $D_{298}(C_6H_5CH_2–I) = 40.3$ kcal./mole.

(29) Prof. M. Szwarc prefers (a), (private communication) and (b) is probably unlikely from considerations of the thermal stability of $C_6H_5CH_2I$.

(30) Where the data are kinetic we have made corrections to 298°K., using the procedure mentioned in footnote 26.

(31) Both $C_6H_5CH_2NH_2$ and $C_6H_5CH_2COCH_3$ are suspected by Szwarc of not being suitable compounds for the toluene carrier technique. The former in addition involves the use of questionable values for the $\Delta H^\circ_f(C_6H_5CH_2NH_2)$ and $\Delta H^\circ_f(NH_2)$. In the case of $C_6H_5CH_2COCH_3$, the kinetic data appear to us to be at least as good as for any of the other compounds studied. The objection of Szwarc[33] to the data on the basis of high frequency factors seems unfounded.

TABLE III

EXPERIMENTAL MEASUREMENTS OF THE HEAT OF FORMATION OF THE BENZYL RADICAL

Reaction	E_F, kcal.	ΔH_{298}, kcal.	$\Delta H^\circ_f(C_6H_5CH_2)$, kcal.	Ref. for secondary data used
$C_6H_5CH_2H \rightarrow C_6H_5CH_2 + H$	77.5[4]	77.8	37.8	4, 18, 19, Table II footnote *d*
$C_6H_5CH_2Br \rightarrow C_6H_5CH_2 + Br$	50.0[25]	51.3	43.0	18, 21, 22, 23, 27
			44.9	This paper
$C_6H_5CH_2I \rightarrow C_6H_5CH_2 + I$	39.0	40.3	44.0	18, 21, 22, 23, 27
$(C_6H_5CH_2)_2 \rightarrow 2C_6H_5CH_2$	48.0[28]	49.9	38.9	33, 34, 35
$C_6H_5CH_2COCH_3 \rightarrow C_6H_5CH_2 + COCH_3$	63[24,a]	64.6	47.4 (−8.3)	22, 24
			47.7 (−8.6)	22, 37
			49.1 (−10)	22, 38, 39, 40, 23
			50.3 (−11.2)	22, 36
$C_6H_5CH_2COCH_3 \rightarrow C_6H_5CH_2 + COCH_3$	68[41]	69.6	54.1(−10)	22 and av. from 4 values for acetyl radical
$C_6H_5CH_2NH_2 \rightarrow C_6H_5CH_2 + NH_2$	59[42]	60.5	30.1 (+42)	42–44, Table II, footnote *d*
			24.6 (+47.5)	Isoelectronic sequences
$C_6H_5CH_2CH_3 \rightarrow C_6H_5CH_2 + CH_3$	63.2[48]	64.5	39.6	19
$C_6H_5CH_2C_2H_5 \rightarrow C_6H_5CH_2 + C_2H_5$	57.5[45]	58.8	33.8	19, 45, 46
$C_6H_5CH_2\text{-}C_3H_7 \rightarrow C_6H_5CH_2 + n\text{-}C_3H_7$	65[47]	66.2	40.6	19, 47, 48
$C_6H_5CH_3 \rightarrow C_6H_5CH_2^+ + H + e^{-1}$ (AP)		95	55	8, 9, 10
$C_6H_5CH_2 \rightarrow C_6H_5CH_2^+ + e^{-1}$ (IP)				

[a] Value measured by Szwarc and Murawaki but never published. $\Delta H^\circ_f(C_6H_5CH_2COCH_3,l)$ has been measured by H. D Springall and T. R. White, *J. Chem. Soc.*, 2764 (1954), and by G. R. Nicholson, M. Szwarc and J. W. Taylor, *ibid.*, 2767 (1954). The value of Parks, *et al.*,[22] together with ΔH_{vap} = 13.5 kcal. gives $\Delta H^\circ_f(C_6H_5CH_2COCH_3,g)$ = −25.5 kcal. used by us. Values in parentheses in column 3 are the $\Delta H^\circ_f(CH_3CO)$ used.

If we accept such a formulation and the numerical results of Horrex and Miles a number of difficulties arise. Horrex and Miles find that $k_{exp} = 2 \times 10^9 \exp(-48{,}000/RT)$ so that the frequency factor of k_1 is $A_1 = (^1/_3)A_{exp} = 6.7 \times 10^8$ sec.$^{-1}$ However, the minimum calculable ΔS°_{298} for reaction 1 is 40 cal./mole °K. for a standard state of 1 atm. This in turn implies that the rate constant for the recombination of $C_6H_5CH_2$ radicals is about 30 l./mole-sec. (since it is assumed $E_2 = 0$) so that only about 1 in 10^{10} collisions between benzyl radicals leads to recombination. If verified this would turn out to be the most inefficient radical recombination reaction yet reported, far lower than one would predict from other known reactions of the $C_6H_5CH_2$ radical (including 3 above) or from considerations of some transition state.[49]

An even greater difficulty arises when we try to calculate the half-life of disappearance of $C_6H_5CH_2$ radicals *via* the principal reaction step 3. If we assume a typical value of 10^7 l./moles-sec. for A_3 and $E_3 \approx 9$ kcal./mole, then when BB = 0.2 mm. at 950°K., the half life for $C_6H_5CH_2 = 1/(k_3\text{BB}) \approx 3$ seconds. For contact times of 0.2–0.6 second, it is clear that all the $C_6H_5CH_3$ production is taking place outside the reaction furnace. Reducing E_3 to 4 kcal. only reduces this to 0.3 second which is still too long.[50] Reducing E_3 to zero raises serious difficulties with reaction 4 since the sum of the ΔE for 3 + 4 is fixed at a value of about 50 kcal. and if E_3 goes to zero then $E_4 \geqslant \Delta E_4$ will be in excess of the 48 kcal. proposed for E_1.[51]

Similar difficulties arise in the pyrolysis of toluene. For this system we can write a scheme

$$C_6H_5CH_3 \underset{12}{\overset{11}{\rightleftarrows}} C_6H_5CH_2 + H$$

$$C_6H_5CH_3 \underset{14}{\overset{13}{\rightleftarrows}} C_6H_5 + CH_3$$

$$H + C_6H_5CH_3 \text{ —}\begin{cases} \xrightarrow{18} C_6H_5 + CH_3 \\ \xrightarrow[15]{} H_2 + C_6H_5CH_2 \text{ (or } C_7H_7) \end{cases}$$

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(32) C. Horrex and S. E. Miles, *Disc. Faraday Soc.*, **10**, 187 (1951).

(33) *C. A.*, **48**, 8653b (1954).

(34) G. S. Parks, T. J. West, B. F. Naylor, P. S. Fujü and L. A. McClaine, *J. Am. Chem. Soc.*, **68**, 2524 (1946).

(35) N. F. H. Bright, *J. Chem. Soc.*, 624 (1951). Heat of sublimation of bibenzyl.

(36) F. B. Marcotte and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **74**, 783 (1952). $\Delta H_f^\circ(CH_3CO)$ = −11.2 kcal.

(37) D. H. Volman and W. N. Graven, *J. Am. Chem. Soc.*, **75**, 3111 (1953). $\Delta H_f^\circ(CH_3CO)$ = −8.6 kcal.

(38) M. Szware, *J. Chem. Phys.*, **23**, 2310 (1955). $\Delta H_f^\circ(CH_3CO)$ = −10 keal.

(39) T. Miyazawa, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **74**, 915 (1953).

(40) C. B. Miles and H. Hunt, THIS JOURNAL, **45**, 1346 (1941). ΔH_f°(acetone, l) = −52.0 kcal.

(41) Recently Szwarc and Taylor reported results of a repetition of the pyrolyses of biacetyl and benzyl methyl ketone. Using the new value of biacetyl and treating the data as before this leads to a heat of formation of the acetyl radical as −5.3 kcal./mole. The value given for benzyl methyl ketone used in conjunction with an approximate average of the four independent values for the heat of formation of the acetyl radical reported above yields the heat of formation of the benzyl radical as 54.1 kcal./mole. These values are in complete disagreement with the other values reported in this section and for this reason are left out of the discussion. The latter value for the benzyl radical is, however, added to the table for the sake of completeness.

(42) M. Szwarc, *Proc. Roy. Soc. (London)*, **A198**, 285 (1941). Values in parentheses are $\Delta H_f^\circ(NH_2)$ used. These data are somewhat suspect because of the uncertainty in $\Delta H_f^\circ(C_6H_5CH_2NH_2)$.

(43) M. S. Kharasch, *J. Research Natl. Bur. Standards*, **2**, 359 (1929). From Petit's combustion data and vapor pressure data[23] we calculate $\Delta H_f^\circ(C_6H_5CH_2NH_2, g)$ = +11.6 kcal.

(44) M. Szwarc, *J. Chem. Phys.*, **17**, 431 (1949).

(45) C. H. Leigh and M. Szware, *ibid.*, **20**, 403 (1952).

(46) H. C. Anderson and E. R. Van Artsdalen, *ibid.*, **12**, 479 (1944).

(47) C. H. Leigh and M. Szwarc, *ibid.*, **20**, 407 (1952).

(48) D. P. Stevenson, *Trans. Faraday Soc.*, **49**, 867 (1953).

(49) Such a low recombination rate also leads one to reconsideration of disproportionation reactions of the type: $2C_6H_5CH_2 \xrightarrow{9} C_6H_5\text{-}CH_3 + C_7H_8$ for which activation energies might not exceed 20 kcal. With a typical frequency factor of about $10^{-3}Z$ to $10^{-4}Z \sim 10^7$ l./mole-sec. this could provide a first-order competing path for the production of $C_6H_5CH_3$.

(50) When BB = 0.02 mm., even $E_3 = 0$ will not be sufficiently low.

(51) This difficulty has been discussed by B. G. Gowenlock. *Disc. Faraday Soc.*, **10**, 229 (1951).

$$CH_3 + C_6H_5CH_3 \xrightarrow{16} CH_4 + C_6H_5CH_2 \text{ (or } C_7H_7)$$

$$2C_6H_5CH_2 \xrightarrow{2} C_6H_5CH_2CH_2C_6H_5$$

$$C_6H_5 + C_6H_5CH_3 \xrightarrow{19} C_6H_5H + C_6H_5CH_2 \text{ (or } C_7H_7)$$

Szwarc[4] uses a more simple scheme in which he has omitted 12, 13, 14 and 19. It is clear that if Miles and Horrex' values are correct, then $C_6H_5CH_2$ never reaches a stationary state but simply accumulates in the gas. If $C_6H_5CH_2$ is permitted to reach a stationary state, as for example might occur in a static system, then reaction 12 can be shown to be an important chain ending process, particularly at high temperatures (>1000°K.) and low C_6H_5-CH_3 pressures.[52] These difficulties are well brought out in the work of Blades and Steacie[7] who showed the extreme sensitivity of the apparent first-order rate constant to contact times and total pressures, and who further showed that the products contained large amounts of dimethylbiphenyls.[53] This latter is to be expected at the high temperatures of the $C_6H_5CH_3$ pyrolysis experiments since the difference in activation energy of abstraction of H from either the ring or the CH_3 group of toluene is certainly not more than a few kcal. for H, C_6H_5 or CH_3 (reactions 15, 16, 19). At $T > 1000$°K. such differences cannot amount to more than a factor of 3–10 in the relative rates of abstraction from the different positions.[54] The effect of contact times and related secondary reactions is also clear when we consider that the rate of decomposition of bibenzyl is 500–1000 times greater than that of toluene. Consequently at contact times sufficient to produce 0.1% bibenzyl, its secondary rate of decomposition becomes equal to that of toluene.

A final point to consider in the interpretation is the relative rates of the two possible primary decomposition processes (Reactions 11, 13) to produce $C_6H_5CH_2 + H$ and $C_6H_5 + CH_3$, respectively. These have been suggested[7] as alternative sources of H_2 and CH_4. Szwarc has ruled out reaction 13 as a source of CH_4 on the grounds that it has a higher activation energy than 11 by about 15 kcal. so that if they both have similar frequency factors, 13 would be negligible. A second ground is that the H_2/CH_4 ratio would then be expected to show a much greater temperature variation than has been observed.

If, however, we assume that $D_{298}(C_6H_5\text{–}H) = 105$ kcal. (which would be rather high) and that $D_{298}(C_6H_5CH_2\text{–}H) = 84$ kcal., then the difference in ΔH_{298} for reactions 11 and 13 is only 8.8 kcal. and this difference is about 6.5 kcal. at 1100°K., *i.e.*

$$H + C_6H_5CH_2 \underset{11}{\overset{12}{\rightleftarrows}} [C_6H_5CH_3]^* \underset{14}{\overset{13}{\rightleftarrows}} C_6H_5 + CH_3 - 6.5 \text{ kcal. } (1100°\text{K.})$$

Reasonable estimates of the entropy change in the over-all reaction indicated above gives $\Delta S_{298} = 10.3$ cal./mole °K. and 6.7 cal./mole °K. at 1100°K. Then at 1100°K., $K_{\text{eq}} = (k_{12} \cdot k_{13})/(k_{11} \cdot k_{14}) = 1.5$ so that $k_{13}/k_{11} = 1.5\, k_{14}/k_{12}$. If instead of assuming that the frequency factors of 11 and 13 are the same, we assume that the rates of radical recombinations are the same, *i.e.*, $k_{14} = k_{12}$, then we see that at 1100°K. we might expect to obtain H and CH_3 at comparable rates of formation which would then be consistent with the observed rates of formation of H_2 and CH_4. This illustrates the importance of entropy changes in radical reactions, particularly reactions involving H atoms which have appreciably lower entropies than hydrocarbon radicals.[55]

This still, however, predicts a higher temperature coefficient for the ratio of production of CH_4/H_2 than is observed. If now we add an additional step to our reaction scheme, namely

$$C_6H_5CH_2 + CH_3 \xrightarrow{20} C_6H_5CH_2CH_3$$

then we can write for the stationary state ratios of production of CH_4 and H_2

$$\frac{d(CH_4)}{d(H_2)} = \left(\frac{k_{16}}{k_{15}}\right)^2 \frac{k_{13}}{k_{11}} \left[1 + \frac{k_{18}}{k_{15}} + \frac{k_{18}}{k_{15}}\frac{k_{11}}{k_{13}}\right] \left[1 + \frac{k_{20}}{k_{16}}\frac{(C_6H_5CH_2)}{(C_6H_5CH_3)}\right]^{-1}$$

which contains then a correction term in the denominator which is temperature sensitive and which tends to compensate for the temperature sensitivity of the ratio k_{13}/k_{11}. This seems a quite reasonable way of accounting for inhibited rates of formation of CH_4.[56]

It thus seems to us that the results from the flow systems which have been used for the pyrolysis studies have been subjected to considerable over-simplification, far more than is warranted by the evident complexity of the products. In addition serious problems in connection with the stationary state concentrations of radicals are involved in such flow systems so that the use of short contact times and consequent low amounts of over-all decomposition do not necessarily eliminate complications of secondary processes.

Serious difficulties are also present in the photochemical and thermal halogenation studies which make us reluctant to accept the kinetic data on bond energies which have been proposed by the writers in these fields. These will be discussed in a forthcoming publication.

Acknowledgment.—We would like to acknowledge the assistance of Dr. G. L. Vidale who helped us with those parts of the calculations which involved the use of vibrational spectra.

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[52] k_{12} can be estimated from the data of Szwarc since $k_{12} = k_{11}/K_{\text{eq}}$. The entropy change can be estimated as $\Delta S° \approx 27$ cal./mole°K. so that $k_{12} \approx 3 \times 10^8$ l./mole-sec. assuming $E_{12} = 0$.

[53] These authors also observed about 3–4% of anthracene among the products which would give additional weight to disproportionation reactions of $C_6H_5CH_2$ radicals producing $C_6H_4\text{–}CH_2$ which could be a reasonable precursor for anthracene.

[54] As an illustration of this, the differences in activation energies of $CH_3 + C_6H_5CH_3$ and $CH_3 + C_6H_5H$ is only 1 kcal. (E. W. R. Steacie, "Atomic and Free Radical Reactions," Vol. I, Reinhold Publ. Corp., New York, N. Y., 1955).

[55] Note that even had we assumed a value $D_{298}(C_6H_5CH_2\text{–}H) = 80$ kcal. which would be closer to Szware's value, then k_{13}/k_{11} would only be reduced by a factor of 4 at 1100°K. which is still in the proper range. If reaction 13 is unimportant either this way of analyzing the system is wrong or hydrogen plus benzyl is a much faster recombination than phenyl + methyl or else the whole analysis is incorrect which would have some important consequences in the theory of unimolecular decompositions. This indeed, however, may be true. These consequences will be discussed in a forthcoming publication.

[56] This would also be a reasonable precursor for the 7% of styrene which Blades and Steacie have observed among the products.

NOTES

A FUNCTION TO AID IN THE FITTING OF KINETIC DATA TO A RATE EQUATION

By Joseph H. Flynn

National Bureau of Standards, Washington 25, D. C.

Received May 7, 1956

A chemical reaction in which the rate is proportional to powers of the concentrations of a single reactant or several reactants present in stoichiometric concentrations may be reduced to the equation

$$\frac{dx}{dt} = k(1 - x)^n \qquad (1)$$

where x is the degree of advancement or extent of reaction, k is a constant that may include stoichiometric relationships and initial concentrations, and n is defined as the order.

A large number of chemical reactions that give a changing value for n (and k) when represented by equation 1 may better be represented by

$$\frac{dx}{dt} = \kappa(1 - x)^{\mu}(1 - \alpha x)^{\nu} \qquad (2)$$

where κ, α, μ, and ν may be considered in general as arbitrary parameters.

A few examples of reactions that are well represented by equation 2 are

(a) first-order reversible reactions ($\mu = 0$, $\nu = 1$, $\alpha > 1$)
(b) parallel reactions: one zero order and one first order ($\mu = 0$, $\nu = 1$, $1 > \alpha > 0$)
(c) parallel reactions: one first order and one second order ($\mu = 1$, $\nu = 1$, $1 > \alpha > 0$)
(d) hydrogen bromide formation ($\mu = {}^5/_2$, $\nu = -1$, $\alpha > 0$)
(e) many catalytic reactions ($\nu > 0$ for positively catalyzed reactions, and $\nu < 0$ for negatively catalyzed reactions. If a reaction is catalyzed by a reactant, $\alpha > 0$; if catalyzed by an intermediate or a product, $\alpha < 0$)
(f) reactions in which more than one reactant contributes to the order in proportion to a power of its concentration and one of these reactants is present in a non-equivalent concentration.

This paper describes an approximate method for estimating μ, ν, κ and α of equation 2 when inconstant values for n and k are obtained from the differential method.[1]

A plot of log dx/dt with respect to log $(1 - x)$ for data from a reaction whose kinetics follow equation 2 yields a curve with the slope, n_x, given by

$$n_x = \frac{d \log \frac{dx}{dt}}{d \log (1 - x)} = \mu + \frac{\alpha\nu(1 - x)}{1 - \alpha x} \qquad (3)$$

From equation 3 it follows that

$$\lim_{x \to 0} n_x = \mu + \alpha\nu \qquad (4)$$

$$\lim_{x \to 1} n_x = \mu \text{ (for } \alpha < 1)^2 \qquad (5)$$

and from equation 2 that

$$\lim_{x \to 0} \log \frac{dx}{dt} = \log \kappa \qquad (6)$$

Hence the parameters μ, ν, κ and α can be determined from the limiting characteristics of n_x and log dx/dt. The function θ

$$\theta = \frac{n_x - \mu}{\nu} = \frac{\alpha(1 - x)}{1 - \alpha x} \qquad (7)$$

defines a one-parametric family of curves which is useful in the determination of α, μ and ν. A set from this family is represented in Fig. 1. Such a set of θ *vs.* x curves may be used to estimate values of α, μ and ν to be used as guides for more precise curve fitting.

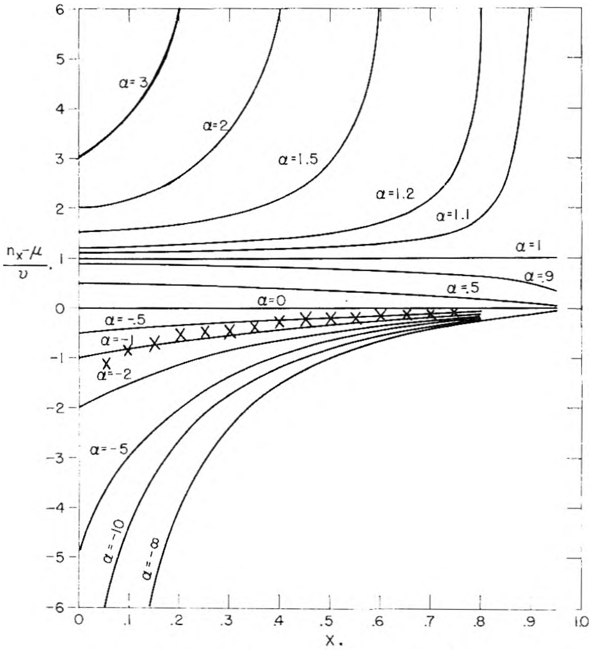

Fig. 1.—θ *vs.* x for various α.

An example to which this technique may be applied is the decomposition of $NaClO_2$ in acetic acid–sodium acetate buffer (pH 3.52, $\mu = 0.11$) at 40°. This reaction has been described as second order.[3] Careful reinvestigation of the kinetics of this reaction[4] indicated a curvature of the log dx/dt *vs.* log $(1 - x)$ plot from which values for n_x were obtained for $x = 0$ to 0.75. If it is assumed that $\theta = -(n_x - 1.5)$, then the points in Fig. 1 are obtained. Therefore, the reaction appears to be of an order less than two ($\mu = 1.5$) and is inhibited by a product ($\nu = -1$, $\alpha < 0$). Subsequent data from the determination of initial rates indicate an order with respect to initial concentration of approximately 1.69 and an inhibition by Cl^-, a product of the reaction.

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[1] For a description of Letort's extension of the differential method of van't Hoff, see K. J. Laidler "Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1950, pp. 15–18.

[2] The limit in equation 5 has no physical significance for $\alpha > 1$ as dx/dt = 0 when $x = 1/\alpha$, *e.g.*, a reversible reaction.

[3] H. F. Launer, W. K. Wilson and J. H. Flynn, *J. Research Natl. Bur. Standards*, **51**, 237 (1953).

[4] J. H. Flynn and W. L. Morrow, unpublished work.

THERMAL ISOTOPIC EXCHANGE BETWEEN ETHYL IODIDE AND MOLECULAR IODINE IN THE LIQUID PHASE[1]

By L. R. Darbee and G. M. Harris

Contribution from the Department of Chemistry of the University of Buffalo, Buffalo, N. Y.

Received July 10, 1956

Several investigators have reported experiments on the isotopic exchange reaction between iodine and ethyl iodide in the liquid phase.[2-5] On the whole, the results have been inconclusive insofar as determination of the kinetics of the process are concerned. The result of a further attempt to elucidate this mechanism is reported herewith.

Experimental

Purifications of Ethyl Iodide.—The best obtainable grades of a number of commercial ethyl iodides were treated to remove traces of impurities such as water, alcohol, iodine and hydrogen iodide. The "best" procedure, as judged from the results of preliminary experiments to be described below, was as follows: After successive washings with aqueous sodium thiosulfate and distilled water, the iodide was dried over anhydrous sodium carbonate, filtered through glass wool, and fractionated just prior to use in a 23 theoretical plate ceramic-packed column. A final trap-to-trap distillation preceded storage under vacuum.

Preparation of Radioactive Iodine.—Inactive solid iodine, purified as suggested by Pierce and Haenisch,[6] was added to aqueous carrier-free NaI^{131}. The mixture was acidified with H_2SO_4, and a small amount of C.P. inactive NaI added.[7] Iodide was oxidized to iodine with $KMnO_4$, the aqueous phase withdrawn and discarded, and the residual iodine containing nearly all the activity washed with water and dried by distillation through a glass wool–P_2O_5 mixture to storage under vacuum.[8]

Technique of Exchange Runs.—Active iodine was metered by vacuum technique into sample tubes containing measured quantities of carefully outgassed ethyl iodide cooled in liquid nitrogen. Series of identical sample tubes (lengths of 9 mm. Pyrex tubing) were sealed off under high vacuum, wrapped in aluminum foil to exclude light, and suspended in a thermostat maintained at the desired temperature to within ±0.05°, from which they were withdrawn singly at intervals for assay. Fixed aliquots of each sample were diluted to a standard volume with heptane[9] and placed in a 25-ml. erlenmeyer flask equipped with a metal collar enabling it to be positioned reproducibly over an inverted, cylindrically-shielded, end-window G/M tube. This count gave total activity. The heptane solution was then extracted with aqueous thiosulfate, enabling counts to be made of "inorganic" and "organic" activities. Low iodine concentrations in pure ethyl iodide solution were determined by its absorption in the 4700–4900 Å. region. Ethyl iodide at higher iodine concentrations required dilution of the mixture with known proportion of heptane before spectrophotometry. Beckman DU and DK2 spectrophotometers were employed. In experiments where ethanol was added, refractive index measurements, using a Bausch and Lomb "Abbe-56" Refractometer, gave ethanol concentrations with an error of less than 5 parts in 10000. Ethyl iodide/ethanol mixture refractive indices decrease linearly with ethanol content up to at least 0.4 *M* of ethanol.

Some competitive exchanges were carried out with mixtures of methyl, ethyl and propyl iodides Tests with labeled ethyl iodide proved that the three halides could be separated without inducing exchange of iodine between them by fractional distillation at atmospheric pressure in the ceramic-packed column already mentioned. For the exchange experiments, samples containing equal volumes of the alkyl halides[10] and the desired amount of radioactive iodine were distilled, outgassed and sealed off under vacuum as before. After several days in the thermostat, they were assayed for total, "organic" and "inorganic" activity as usual, the "organic" portion fractionated and the activities and refractive indices of successive 2-ml. aliquots determined. These measurements enabled calculation of total exchange and the proportion of the total for each halide, since the refractive indices gave the composition of each aliquot.

Results and Discussion

Since in all of this work the ethyl iodide was in large excess, the appropriate equation for *R*, the rate of exchange, is

$$R = -\frac{\ln (1 - f)}{t} \times 2(I_2) = \frac{0.693}{t_{1/2}} \times 2(I_2)$$

In some instances, *R* was obtained from the slope of $\ln(1 - f)$ *vs.* t plots, while in others a nomographic procedure was employed.[11] With iodine in the concentration range 10^{-4} to 10^{-2} mole/l., marked inconsistencies were observed which could not be eliminated entirely. It was found that the exchange rate varied greatly with the method of ethyl iodide purification. Any one product behaved fairly consistently, but exchange half-times under comparable conditions varied in the range from 2 to 12 days at 45° for different preparations. The most rigorously purified ethyl iodide exchanged least rapidly and gave the most coherent set of data, so was deemed the "best" as alluded to above.

On increasing the iodine concentration into the range 0.03 to 0.3 mole/l., and using only the "best" iodide, consistent runs under a wide variety of conditions became possible, with the results summarized herewith.

(1) At 61°, using various iodine concentrations in pure ethyl iodide, the rate of exchange was found to be proportional to the first power of the iodine concentration (see Fig. 1, curve A.) The curve of best fit gives the value $R = 0.09(I_2)$ mole/l./day.

(2) Exchanges were run at several other temperatures in the range 45 to 70°. The apparent activation energy of the process as determined from the usual linear Arrhenius plot is 19,500 cal./mole.

(3) The ethyl iodide concentration was varied by dilution with heptane. With (I_2) fixed at 6.5×10^{-2} mole/l., these data resulted at 61°

(C_2H_5I) (moles/l.)	2.5	6.2	7.4
$R \times 10^2$ (moles/l./day)	1.2	1.4	1.3

With (C_2H_5I) fixed at 6.2 moles/l. and (I_2) varied, the results at 61° were as shown in Fig. 1, curve B. It is clear that the exchange is independent of the ethyl iodide concentration in the range covered, and that it is first-order in iodine as before. How-

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(1) From the doctoral dissertation of L. R. Darbee, University of Buffalo, 1956. Complete text available from University Microfilms, Ann Arbor, Michigan.

(2) D. Hull, C. Shiflett and S. C. Lind, *J. Am. Chem. Soc.*, **58**, 535 (1936).

(3) P. F. D. Shaw and C. H. Collie, *J. Chem. Soc.*, 1217 (1949).

(4) R. Noyes, *J. Am. Chem. Soc.*, **70**, 2614 (1948).

(5) R. G. Badger, C. F. Chmiel and R. H. Schuler, *ibid.*, **75**, 2498 (1953); C. F. Chmiel, Master's Thesis, Canisius College, 1952.

(6) W. Pierce and E. Haenisch, "Quantitative Analysis," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1940, p. 203.

(7) This promoted reductions of $I^{131}O_3^-$, sometimes present in aged carrier-free solutions.

(8) Of several stopcock greases tried, "Ascolube" showed the greatest resistance to attack from and least tendency to dissolve iodine, and was used on all stopcocks and ground joints exposed to the halogen.

(9) Commercial heptane was purified by refluxing with iodine and fractional distillation.

(10) The corresponding concentration values are 5.35, 4.15 and 3.41 moles/l. for methyl, ethyl and propyl iodides, respectively.

(11) L. R. Darbee, *J. Chem. Phys.*, **23**, 1349 (1955).

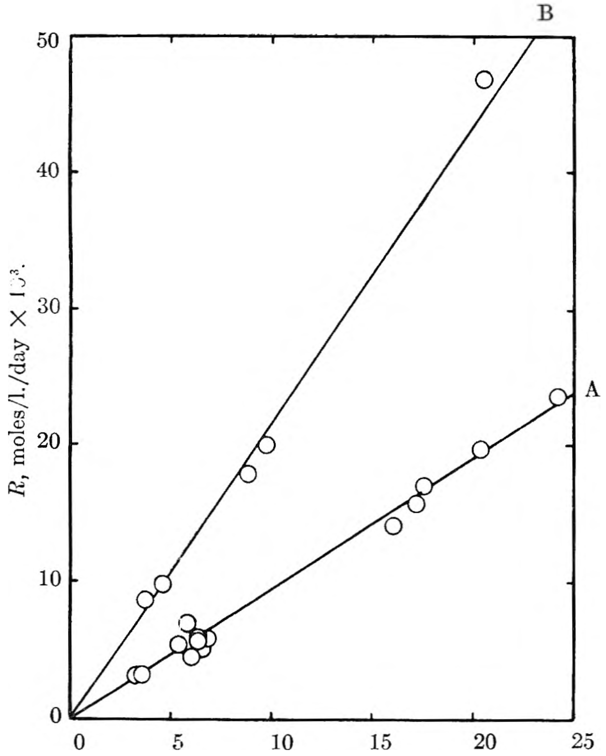

Fig. 1.—A, exchange in pure EtI at 61°; B, exchange in EtI–heptane mixture at 61°.

ever, the value $R = 0.20(I_2)$ obtained from curve B is more than double its previous magnitude. The reason for this discrepancy is unknown at present.

(4) Runs were made with ethanol contents varied up to about 0.15 mole/l., iodine being fixed at 4.25×10^{-2} mole/l. and the temperature at 61°. The rate of exchange always accelerated with time, leading to curvature in the $\ln(1 - f)$ *vs.* t plots. But the latter were reasonably linear in the early stages of exchange, and accurate initial rates were obtainable. These rates varied directly with alcohol content, and satisfy the relation

$$R = [0.08 + 0.9(\text{EtOH})]\ (I_2)\ \text{moles/l./day}$$

It is seen that the extrapolated R value for zero alcohol content is in reasonable agreement with the value obtained directly previously.

(5) The relative rates of exchange of methyl, ethyl and propyl iodides were determined by the competitive procedure already described. The data were

Elapsed time (days)	(I_2)	% Total exchange	Relative specific activities (counts/min./ml.)		
			MeI	EtI	PrI
3.0	0.22	49.5	8.5	1.0	0.74
17.0	.12	88.1	6.6	1.0	.64

The mathematical analysis of competitive exchange data has been published elsewhere.[12] It may be concluded that the R values for methyl, ethyl and propyl iodides are in the approximate ratio of their relative specific activities in the first experiment only, where the total exchange does not exceed 50%.

The mechanism of the exchange apparently involves a one-to-one ethyl iodide/iodine complex. With ethyl iodide in excess, a first-order dependence on iodine concentration is then quite reasonable.[13] The catalytic effect of the alcohol probably results from the rapid reduction of a fraction of the iodine to yield iodide ions, either by the alcohol itself or by some trace impurity in it. It is well known that I^- ions exchange rapidly with ethyl iodide.[14] The observed increase in the exchange rate with time no doubt occurs due to the further build-up of I^- concentration, due to subsequent slower reduction processes.[15]

Financial support of this research by the U. S. Atomic Energy Commission under Contract No. AT(30-1)-1578 is gratefully acknowledged.

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(12) L. R. Darbee, F. E. Jenkins and G. M. Harris, *J. Chem. Phys.*, **25**, 603 (1956).

(13) If exchange is by an association mechanism

$$C_2H_5I + I_2^* \rightleftarrows C_2H_5I \cdot I_2^* \rightleftarrows C_2H_5I^* + I_2$$

its rate will be given by

$$R = k\ (C_2H_5I \cdot I_2) = \frac{kK(C_2H_5I)_0(I_2)_0}{1 + K(C_2H_5I)_0}$$

Here K is the equilibrium constant of the complex-forming reaction and the zero subscripts indicate total concentrations of the two reactants, complexed and uncomplexed. Since ethyl iodide is in large excess, it is clear that for K of the order of only a few units, $R \cong k(I_2)_0$ as found experimentally. The low value of 0.37 has been reported for K at 25° (R. Keefer and L. Andrews, *J. Am. Chem. Soc.*, **74**, 1891 (1952)). However, their method of computation is subject to very large errors; also, the value was obtained on the basis of an initial assumption that a negligible fraction of the iodine is complexed. This assumption is contrary to the spectral evidence, since even a dilute ethyl iodide/iodine solution in heptane shows no strong absorption *peak* at 5250 Å., which it would be expected to do if most of the iodine were *not* associated with ethyl iodide.

(14) P. B. D. de la Mare, *J. Chem. Soc.*, 3196 (1955).

(15) A. Bagley, *Trans. Faraday Soc.*, **24**, 438 (1928).

STUDIES ON HOMOGENEOUSLY PRECIPITATED AND SUPPORTED PEROXIDES OF ZIRCONIUM, THORIUM AND OTHER POLYVALENT CATIONS[1]

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Peroxides of a number of tri- and tetravalent metal ions prepared by precipitation with internally generated hydroxide ion from the slow hydrolysis of urea in boiling water in the presence of hydrogen peroxide were studied as insoluble oxidants or adsorbant–oxidants for chromatographic-type column reactions: thorium, zirconium (hafnium), titanium, stannic and yttrium. Lanthanum peroxide was prepared by conventional precipitation with ammonium hydroxide in the presence of hydrogen peroxide after homogeneous precipitation produced a weakly reactive peroxide.

The peroxides of thorium and zirconium exhibited the most desirable chemical and physical properties, and retain their activity indefinitely in dry storage. Slow crystal growth during precipitation produces discrete but somewhat gelatinous particles which are easily washed and dried at 90–

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[1] Based upon a thesis submitted by Delbert E. Gantz in partial fulfillment of the requirements for the degree of Master of Science, Kansas State College, 1955.

100° to hard, glassy, non-porous masses. These particles, which can be ground and sieved to desired size, react as solid, insoluble hydrogen peroxide, and the oxidation of substances in solution takes place at the surface of the particles without the introduction of other substances into solution. One sample of 100–200 mesh zirconium peroxide remained under water in a column for seven months without loss of chemical activity or mechanical hardness.

The dried peroxides are insoluble in neutral solution. All of them oxidize iodide ion to iodine and thorium peroxide oxidizes bromide ion to bromine. Their physical properties are shown in Table I. X-Ray diffraction studies indicate nearly-amorphous structures for thorium and stannic peroxides, and amorphous structures for zirconium and lanthanum peroxides.

Zirconium peroxide was also prepared as a dispersion on starch, cellulose and adsorption alumina supports. Thorium peroxide was less desirable for this purpose, as it is less firmly bound to starch or cellulose, while titanium and lanthanum peroxides were not retained at all. The wide dispersion of zirconium peroxide on the surface of starch or cellulose molecules makes it especially effective as an oxidizing agent.

TABLE I

PHYSICAL PROPERTIES OF THE DRIED METAL PEROXIDES

	Color	Approx. dec. temp., °C.[a]
Thorium	Light blue-green	120
Zirconium	Colorless	140
Titanium	Light yellow	140
Stannic	Colorless	120
Yttrium	Light orange	155
Lanthanum	Colorless	150

[a] Obtained by observing particle breakdown and gas evolution of the sample contained in a capillary tube.

Experimental

Thorium Peroxide.—A solution containing 50.0 g. of thorium nitrate tetrahydrate, $Th(NO_3)_4 \cdot 4H_2O$, 80.0 g. of urea and 80.0 ml. of 30% hydrogen peroxide in 2 l. of distilled water was refluxed, with stirring, for one hour by which time the *p*H reached 7. A turbidity appeared as soon as heating started. The resultant precipitate was filtered immediately with suction, washed four or five times with hot water, and dried at 90° for 8–10 hours. The yield was 26.5 g.

Anal. Ignition of the peroxide to the oxide, ThO_2, indicated 71.5% thorium. Ignition of the peroxide to drive off water, which was absorbed by anhydrous calcium sulfate and weighed, indicated 10.4% water (water of crystallization, water from hydrogen-bonded hydroxy groups or decomposed hydroperoxy groups). Oxygen, by difference (not released, or released as O_2 on ignition) 18.1%. Qualitative tests for aminoid nitrogen and nitrate ion were negative. Over-all composition: 71.5% thorium, 27.3% oxygen and 1.2% hydrogen, corresponding closely to an empirical formula of $Th_2O_{11}H_8$, which compares closely with the formula, ThO_5H_4 or $Th(OH)_3OOH$. Titration with standard thiosulfate solution of the iodine liberated by the reaction of thorium peroxide dissolved in dilute hydrochloric acid with excess iodide ion present showed 1.93 equivalents of peroxide oxygen per formula weight, or approximately one hydroperoxy group per thorium. The solubility of thorium peroxide in cold dilute hydrochloric acid suggests polymer formation through hydrogen bonding between hydroxy groups on adjacent thorium atoms, with an average of about three hydroxy groups per thorium entering into polymer formation.

Dye binding data shown in Table II indicate a deficiency of binding sites—hydroxy groups—per unit area of the surface of the thorium peroxide for strongly acidic functional groups. The surface of the thorium hydroxide particles evidently is rich in such sites. For dyes having only very weakly acidic functional groups, such as hydroxyl, strong binding of the dyes to thorium hydroxide may not occur. The thorium peroxide and thorium hydroxide were prepared and dried under similar conditions, with hydrogen peroxide omitted in the preparation of thorium hydroxide. The dye binding studies were made with 100–200 mesh particles, which had freshly exposed surfaces resulting from fracture of the larger masses obtained by grinding. These surfaces apparently do not alter appreciably with age. Oxidation of adsorbed dye by hydroperoxy groups proceeds very slowly and apparently is not a factor in determining the amount of dye initially adsorbed. Reaction of dyes with thorium ion was shown in a previous study to be dependent upon the type and number of functional groups on the dye anion, but independent of the type of dye.[2]

TABLE II

EXTENT OF DYE BINDING BY GRANULAR HYDROXIDES AND PEROXIDES OF THORIUM AND ZIRCONIUM[a]

Dyes[b]	Zr hydroxide	Zr peroxide	Th hydroxide	Th peroxide
Amaranth 3-SO_3^-, 1-OH 1-N=N-	Med. red	Med. red	Deep red	Pink
Indigo disulfonate 2-SO_3^-	Med. blue	Med. blue	Deep blue	Lt. blue
Orange II 1-SO_3^- 1-N=N-	Med. orange	Med. orange	Intense orange	Lt. orange
Aurin tricarboxylic acid 3-COOH, 3 -OH	Pale brown	Pale brown	Deep red	Lt. pink
Fluorescein 1 -COOH, 1 -OH	Bt. yellow	Bt. yellow	Pale orange	Yel. orange
p-Phenylazophenol 1 -OH, 1 -N=N-	Lt. yellow	Lt. yellow	Colorless	Lt. yellow
Indophenol (sodium 2,6-dichlorobenzenone), 1 -OH	Deep violet	Med. violet	Med. blue	Lt. violet

[a] 100–200 mesh. [b] Sodium or ammonium salts. Functional groups are listed by type and number.

Zirconium Peroxide.—A solution containing 50.0 g. of zirconyl chloride octahydrate, $ZrOCl_2 \cdot 8H_2O$, 50.0 g. of urea and 80.0 ml. of 30% hydrogen peroxide in 2 l. of distilled water was boiled under reflux in the apparatus described for the preparation of thorium peroxide. Turbidity first appeared approximately 45 minutes after boiling started, and the solution was boiled another 50 minutes, by which time the *p*H reached 7. The precipitate was filtered and washed as described above for thorium peroxide, and dried at 100° for 5–6 hours. The yield was 23.0 g.

Anal. Gravimetric determination by the cupferron method, and by ignition of the peroxide to form the oxide, both indicated 59.0% zirconium in the zirconium peroxide. Ignition of the peroxide to drive off water which was absorbed by anhydrous calcium sulfate and weighed indicated 15.7% water (water of crystallization, water from hydrogen-bonded hydroxy groups or decomposed hydroperoxy groups). Oxygen, by difference (not released, or released as O_2 on ignition) 25.3%. Qualitative tests for aminoid nitrogen, nitrate ion and chloride ion were negative. Over-all composition: 59.0% zirconium, 39.2% oxygen and 1.8% hydrogen, corresponding closely to an empirical formula of ZrO_4H_3, allowing for approximately 5% hafnium, which would increase the effective atomic weight of the zirconium. This indicates a more condensed structure than the formula, ZrO_5H_4 or $Zr(OH)_3OOH$, for zirconium monohydroperoxide.

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[2] J. L. Lambert and M. P. Grotheer, *J. Am. Chem. Soc.*, **77**, 1386 (1955).

No estimation of equivalents of oxidizing power was possible because zirconium peroxide could not be dissolved readily in acid solutions which would not oxidize or permit atmospheric oxidation of iodide ion. The difficult solubility in acids and the low proportion of oxygen and hydrogen to zirconium indicate extensive condensation of hydroxy groups to form Zr–O–Zr bonding.

Dye-binding data from Table II indicate a similar number of binding sites—hydroxy groups—per unit area of the surface of both the zirconium peroxide granules and the zirconium hydroxide granules. Both of these compounds were prepared under similar conditions and were 100–200 mesh in size, as mentioned in the description of the preparation of thorium peroxide. The number of binding sites per unit area for strongly acidic functional groups is definitely less for both zirconium peroxide and zirconium hydroxide than for thorium hydroxide, but more in each case than for thorium peroxide. This lessened adsorptive activity of the zirconium hydroxide for dye anions is apparently due to fewer hydroxy groups as a result of the condensation of hydroxy groups to form Zr–O–Zr type bonding.

Columns of 100–200 mesh zirconium peroxide oxidized iodide ion in solution to iodine approximately quantitatively in the range 0–15 p.p.m., determined spectrophotometrically as the blue starch–triiodide, I_3^-, complex,[3] when bromide ion was added to prevent adsorption of the iodine as a yellow band at the top of the column. Column activity was relatively short-lived, indicating that the oxidation reaction was principally a surface phenomenon. Attempts to regenerate the surface with 1% disodium ethylenediaminetetraacetate, 0.1 *N* hydrochloric acid or 3% hydrogen peroxide solutions were not very successful. Columns of thorium peroxide reacted in a similar manner.

Supported Zirconium Peroxide.—Zirconium peroxide was prepared as a dispersion on cellulose by treating filter paper (Whatman No. 42) with a 5% solution of zirconyl chloride octahydrate, $ZrOCl_2 \cdot 8H_2O$, blotting off the excess solution, drying at room temperature, and immersing in 3% hydrogen peroxide solution. Oxidation of iodide ion in solution was quantitative when the solution was passed through the paper. Drying seemed to alter the supported peroxide and make it slightly soluble.

When potato starch was used as the support, 30 g. of the starch was treated with 200 ml. of 10% zirconyl chloride solution for two minutes, filtered, washed and placed for three minutes in 3% hydrogen peroxide solution. The treated starch was partially dried with suction and finally air-dried. Solutions of 5% zirconyl chloride and 3% hydrogen peroxide can be mixed before treating the starch, with a satisfactory product resulting. The reactivity of the starch–zirconyl peroxide decreased only slightly after seven months' storage. A color is produced on the starch granules proportional to the concentration of iodide ion in solution—faint at 2.5 p.p.m. and of saturated intensity at 75 p.p.m.

Spot test papers for the detection of iodide ion were prepared by treating filter paper with 15% zirconyl chloride solution, drying, immersing in 3% hydrogen peroxide solution and drying. These papers were then immersed in 1% linear potato starch fraction (amylose) solution and dried. The sensitivity of the prepared papers decreased slightly after seven months' storage. The identification limit for the detection of iodide ion was 0.2 γ I^- in two drops of solution (approximately 0.1 ml.).

Zirconyl ion solutions react irreversibly with cellulose, probably by attachment of zirconyl ion through hydroxy groups on the glucose units. Filter paper treated with zirconyl ion solution retains the zirconium after ten washings with water, and forms zirconium peroxide on treatment with hydrogen peroxide. Thorium ion binds less firmly than zirconium. None of the other ions studied binds strongly to starch or cellulose.

Acknowledgment.—The authors wish to acknowledge the contribution of Dean Dragsdorf of the Department of Physics, Kansas State College, who examined most of the peroxides by means of X-ray diffraction.

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[3] J. L. Lambert, *Anal. Chem.*, **23**, 1247 (1951).

VAPOR PRESSURES OF SOME ALUMINUM ALKOXIDES

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As a start in the study of the physical and chemical properties of aluminum alkoxides, the vapor pressures of the liquids of the simpler members of the series have been determined from about 1 mm. to the temperature where decomposition is rapid. The ethoxide, propoxides and butoxides (except the *t*-butoxide) can be melted and distilled under reduced pressure. The isoteniscope described by Smith and Menzies[1] was used in the determination of vapor pressures. This method was chosen because it is probably the most reliable of the static methods, it does not involve some of the uncertainties of attaining equilibrium of the dynamic methods, and it is easier to keep the samples anhydrous than it would be with some of the dynamic methods. Since aluminum alkoxides have a strong affinity for water, producing aluminum oxide and the alcohol, great care was taken during preparation and handling to prevent contact with moisture. Table I summarizes the results, including the values of the constants *a* and *b* in the equation $\log p_{\text{mm.}} = a - b/T$, the heat of vaporization calculated from the constant *b*, the boiling point at 5 mm. pressure, and the entropy of vaporization at 5 mm. pressure. In this form the results can be compared with the data on aluminum alkoxides (except the isobutoxide) of Mehrotra[2] who determined vapor pressures by another method and of the vapor pressures of the titanium and zirconium alkoxides of Bradley, Mehrotra and Wardlaw.[3]

TABLE I

VAPOR PRESSURES OF ALUMINUM ALKOXIDES

	a	*b*	T_b (5 mm.), °C.	ΔH_v, kcal. mole^{-1}	ΔS_v, cal. deg.$^{-1}$ mole^{-1}	*a* (ref. 2)	*b* (ref. 2)
$Al(EtO)_3$	10.24	4410	189.0	20.2	43.7	11.8	5100
$Al(n\text{-}PrO)_3$	10.54	4880	222.7	22.3	45.0	12.6	6025
$Al(iso\text{-}PrO)_3$	11.88	4610	139.1	21.1	51.2	11.4	4240
$Al(n\text{-}BuO)_3$	10.91	5440	259.6	24.9	46.7	12.7	6540
$Al(iso\text{-}BuO)_3$	14.99	7280	236.2	33.3	65.4	..	...
$Al(sec\text{-}BuO)_3$	10.37	4260	167.3	19.5	44.3	11.3	4720

The aluminum ethoxide and isopropoxide were obtained from a commercial source (Eastman Kodak) while the other alkoxides were prepared by dissolving reagent grade aluminum foil in the alcohol using mercuric chloride as a catalyst. Starting with purified grades, the alcohols were distilled over calcium oxide through a 60 cm. Widmer column and fractions distilling within $^1/_2$ degree collected to prepare the alkoxides. The crude alkoxides were distilled once or twice at reduced pressure to obtain a clear colorless distillate and then distilled again at 1 to 2 mm. just before use. In some cases the alkoxide was distilled directly into the isoteniscope and in some cases it was collected in glass tubes sealed under vacuum. After solidifying, the tubes were broken and the isoteniscope loaded in a dry-box. Distillation apparently yields a pure product since the principal impurities are aluminum oxide which is non-volatile and the alcohol, which

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(1) A. Smith and A. W. C. Menzies, *J. Am. Chem. Soc.*, **32**, 1412 (1910).

(2) R. C. Mehrotra, *J. Indian Chem. Soc.*, **30**, 585 (1953).

(3) D. C. Bradley, R. C. Mehrotra and W. Wardlaw, *J. Chem. Soc.*, 2027, 4204, 5020 (1952); 2025 (1953).

(4) R. A. Robinson and D. A. Peak, THIS JOURNAL, **39**, 1125 (1935).

(5) W. C. Childs and H. Adkins, *J. Am. Chem. Soc.*, **45**, 3013 (1923).

passes off as a gas.[2,4,5] Some samples were analyzed for aluminum by dissolving in HCl or NaOH and precipitating with 8-hydroxyquinoline. Aluminum ethoxide, found (average of 4 samples) 16.76, theor. 16.63%; aluminum *n*-propoxide, found (average of 4 samples) 13.19, theor. 13.21%; aluminum isopropoxide, found (average of 6 samples) 13.15, theor. 13.21%; aluminum isobutoxide, found (average of 2 samples) 10.87, theor. 10.95%.

In use, the isoteniscope was placed in an oil-bath containing windows so that the levels in the U-tube could be observed. The oil-bath was equipped with suitable stirrers, heaters and a mercury expansion type thermoregulator. Temperature could be held constant to within 0.1° and did not vary by more than 0.02° within the bath. Temperatures were measured with a 2-junction copper–constantan thermocouple calibrated at the tin point and by comparison with two mercury thermometers having National Bureau of Standards calibrations. A very fine adjustment of pressure was made possible by the use of a pressure control system, and the pressure could be held constant automatically to better than 0.1 mm. by means of a sulfuric acid manostat which operated a solenoid valve. Below 7 mm. the pressure was measured with a small McLeod gage and above 7 mm. with a mercury manometer and cathetometer reading to 0.1 mm. Accuracy in temperature measurement is assumed to be at least 0.2° below 200° and 0.4° above 200°. Accuracy in pressure measurement is assumed to be at least 0.1 mm. below 5 mm. and 0.2 mm. above 5 mm.

The usual technique in using the isoteniscope was followed. At the beginning of each series of measurements the sample was refluxed in the isoteniscope and the volatile impurities allowed to escape the U-tube until constant readings were obtained on balancing the pressures. This required two to four hours. At least one-half hour was allowed at each of the other temperatures for attaining equilibrium and for testing. In many cases, after heating to the maximum in a series, the lower temperatures were checked again before admitting air so that many points are averages of two or more measurements. As the temperature was raised the rate of irreversible decomposition to give volatile products increased. The rate of production of volatile materials was always determined at each temperature by confining the vapors in the sample bulb and noting the increase in pressure. Vapor pressure measurements could be made within 30 seconds after allowing the vapor to bubble out of the sample bulb and measurements were discontinued when the rate of pressure increase was about one millimeter per minute. Measurements on each sample in Table II, except aluminum isopropoxide 1 and 2, were made in one period without letting air back into the isoteniscope.

One interesting result of these measurements is the time dependence found in the vapor pressure of aluminum isopropoxide. A number of careful experiments showed that when the temperature of aluminum isopropoxide is changed rapidly and then held constant an appreciable time is required for the attainment of the final equilibrium vapor pressure. If this alkoxide is allowed to reach equilibrium at one temperature and then raised to a higher temperature the vapor pressure increases, rapidly at first, and finally becomes constant in one to four hours. If the sample is lowered from a higher temperature to this same temperature the vapor pressure decreases and reaches the same equilibrium value as in the first case. This behavior is

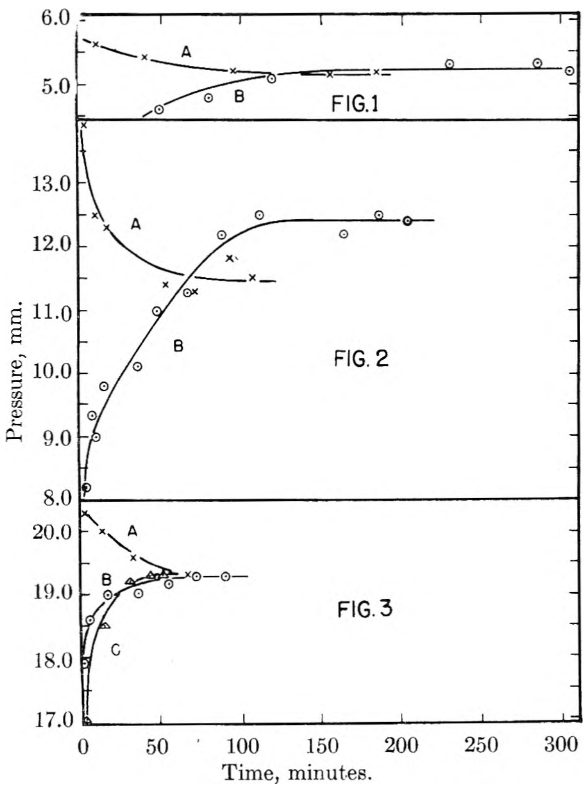

Fig. 1.—140.6°; A cooled from 159° in 35 minutes, B heated from 125° in 40 minutes.

Fig. 2.—155.1°; A cooled from 174 in 16 minutes, B heated from 132° in 8 minutes.

Fig. 3.—159.0°; A cooled from 175 in 20 minutes, B and C heated from 146° in 15 minutes.

TABLE II

OBSERVED AND CALCULATED VAPOR PRESSURES

Temp., °C.	Pressure, mm. Obsd.	Pressure, mm. Calcd.
Al(EtO)$_3$ sample 1		
157.5	0.9	1.0
171.1	2.0	2.1
179.9	3.1	3.2
192.0	5.8	5.8
218.0	21.1	18.4
232.7	35.3	33.8
237.8	41.3	41.1
Al(EtO)$_3$ sample 2		
180.0	2.5	3.2
201.8	8.6	9.1
222.8	21.1	22.5
233.9	32.2	35.2
250.0	57.7	65.5
Al(iso-PrO)$_3$ sample 1		
119.0	1.0	1.3
125.5	1.7	2.0
133.0	3.6	3.4
139.0	5.5	5.1
146.0	8.4	7.8
Al(iso-PrO)$_3$ sample 2		
127.0	2.2	2.3
142.5	7.1	6.3
158.0	15.8	15.4
170.5	32.5	36.7
Al(iso-PrO)$_3$ sample 3		
124.8	1.8	2.0
140.9	5.3	5.6
160.4	17.5	17.7
173.9	35.5	36.7
Al(iso-Pro)$_3$ sample 4		
132.2	2.7	3.2
155.1	12.0	13.3
173.5	33.5	36.0
Al(*n*-PrO)$_3$ sample 1		
206.4	1.8	1.9
217.7	3.2	3.3
227.2	4.9	5.0
239.4	9.4	8.6
252.3	14.5	14.6
Al(*n*-PrO)$_3$ sample 2		
202.4	1.5	1.5
217.1	2.8	3.1
237.4	7.5	7.9
254.6	15.8	16.0
266.3	26.8	25.4
Al(*n*-BuO)$_3$		
230.1	1.3	1.3
240.7	2.2	2.1
250.0	3.0	3.3
262.7	6.0	5.7
Al(iso-BuO)$_3$		
227.8	2.7	2.9
238.3	6.0	5.7
245.9	9.3	9.3
256.2	17.4	17.3
268.5	35.9	35.5
276.5	55.2	55.8
Al(*sec*-BuO)$_3$		
152.2	2.2	2.3
158.9	3.7	3.3
172.3	7.3	6.5
184.5	11.4	11.6
195.2	17.6	19.1

illustrated in Figs. 1, 2 and 3. It is not due to change of temperature since the sample has had time to reach the bath temperature before pressure measurements are started. It is not due to decomposition either since the same equilibrium value (within uncertainties due to impurities) can be reached from either side and since refluxing between measurements removes any decomposition products. This behavior is also found for other physical properties of aluminum isopropoxide and will be discussed in a later paper. It is also in agreement with some remarks made by Mehrotra[2] about changes of degree of association with aging. The possibility of time dependent behavior was examined in the other alkoxides. It was found to a slight extent in the propoxide and the *n*-butoxide only.

Table II shows the experimental data and compares it with the vapor pressure calculated from the constants in Table I. The deviation of the observed points from the smooth log *p* *vs.* $1/T$ plots are greater than the experimental error of temperature and pressure measurement and are probably due to the presence of impurities. Measurements at the higher temperatures are uncertain because of rapid decomposition. The discrepancy between data reported here and the data of Mehrotra is also greater than can be accounted for by temperature and pressure errors. The largest difference occurs with the isopropoxide and the *n*-butoxide. This is easy to understand in the case of the isopropoxide since failure to take into account its time dependent behavior could cause a large error in vapor pressure.

ELECTRICAL CONDUCTANCE IN MOLTEN SALT MIXTURES

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Some precise measurements of the equivalent electrical conductance of solutions of molten salts have been published recently.[1] Two of the systems studied, KCl/LiCl and KCl/NaCl, show pronounced minima in the graph of equivalent conductance *versus* mole fraction of KCl while the third, KCl/KI, shows a negative deviation from simple additivity of conductances. It is remarkable that the system with the greatest deviation from additivity of conductance, KCl/LiCl, displays zero volume change upon mixing, *i.e.*, the equivalent volume is a perfectly linear function of composition. The other two systems, where compound formation or solid solution is known to occur in the solid state, show very slight volume changes upon mixing.

Certain interesting features of the conductivity of these solutions may be seen when the data are presented in a different way.

The conductance of a solution of two salts is an extensive property which may be represented formally in terms of the "partial equivalent conductances" of the components.

$$\Lambda = n_1\bar{\Lambda}_1 + n_2\bar{\Lambda}_2$$

$$\Lambda_{eq} = x_1\bar{\Lambda}_1 + x_2\bar{\Lambda}_2$$

$$(\partial\Lambda/\partial n_i)_{T,n_k} = \bar{\Lambda}_i$$

where Λ_{eq} denotes the equivalent conductance, x_i the mole fraction and $\bar{\Lambda}_i$ the partial equivalent conductance of the ith component. The physical significance of $\bar{\Lambda}_i$ may be seen as follows: a pair of parallel plates is spaced one cm. apart and contains a very large amount of the appropriate mixture. One equivalent of a pure salt is added to the mixture between the plates. The increase in conductance is the partial equivalent conductance of the salt added at the composition of the mixture. These partial equivalent conductances are the quantities which are most meaningfully compared from one solution to another. Their calculation is facilitated by a construction similar to that given by Lewis and Randall[2] for volumes.

The partial equivalent conductance of one salt at vanishingly small concentration in a second salt is particularly interesting. It is a direct measure of the mobility of the added salt in the foreign salt. These limiting conductances have been computed from the data of Van Artsdalen and Yaffe and are presented in Table I. The important features brought to light are the following.

1. In all cases the limiting equivalent conductance of one salt in another salt is less than in the pure salt. Thus the partial equivalent conductance of LiCl is less in KCl than in LiCl and conversely the partial equivalent conductance of KCl is less in LiCl than in KCl.

TABLE I

PARTIAL EQUIVALENT CONDUCTANCES AT 800°, MHO CM.$^{-1}$

	$\bar{\Lambda}(x = 0)$	$\bar{\Lambda}(x = 1)$
NaCl	108.5	134.7
KCl	84.0	110.5
LiCl	75.5	197.5
KCl	−175	110.5
KI	78.8	108.0
KCl	77.3	110.5

2. The decrease in the equivalent conductance when a salt is dissolved in a second salt from its value in the pure salt, $[\bar{\Lambda}_i(x = 1) - \bar{\Lambda}_i(x = 0)]$, is larger the greater the difference in relative size of the ions of the different salts. Thus the depression for LiCl in KCl is greater than that for KCl in NaCl. Similarly the depression for KCl in LiCl is greater than for KCl in NaCl. The same effect appears to obtain for anions.

3. This effect is so pronounced in the case of KCl in LiCl that the addition of KCl to a large amount of LiCl actually decreases the total conductance. At the same time the partial molal volumes in this systems are ideal, so that no profound change in the quasi-lattice can have occurred.

4. It is possible to calculate the "heats of activation" for the separate partial equivalent conductances. The most interesting and probably the

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[1] E. R. Van Artsdalen and I. S. Yaffe, This Journal, **59**, 118 (1955).

[2] G. N. Lewis and M. Randall, "Thermodynamics," McGraw-Hill Book Co., New York, N. Y., 1953.

only significant ones are those for zero concentration. These were computed for the three systems mentioned and are presented in Table II.

TABLE II

APPARENT ACTIVATION ENERGIES FOR CONDUCTANCE AT 800°, KCAL.

	$\Delta\bar{H}(x = 0)$	$\Delta\bar{H}(x = 1)$
NaCl	4.95	2.8
KCl	5.75	3.6
LiCl	2.2	2.0
KCl	5.8	3.6
KI	6.6	3.5
KCl	3.5	3.6

The uncertainties estimated for the entries in both tables are rather large since there are insufficient data at low mole fractions to establish reliable slopes.

In order to further test these conclusions the data of Bloom and Heyman[3] and Bloom, *et al.*,[4] were converted into this form. These data are not as well suited for these calculations. Nevertheless, insofar as comparisons are possible, the conclusions listed above are valid for the 13 pairs of salts studied by these workers.[5]

It is a pleasure to acknowledge assistance from the Atomic Energy Commission (Contract AT 30-1 1938).

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[3] H. Bloom and E. Heyman, *Proc. Roy. Soc.* (*London*), **A188**, 392 (1947).

[4] H. Bloom, I. W. Kraggs, J. J. Molloy and D. Welch, *Trans. Faraday Soc.*, **49** (1953).

[5] $PbCl_2/CdCl_2$ may be an exception

CHARACTERISTIC PROPERTIES OF THORIUM OXIDE PARTICLES

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Thoria is of interest as a fertile fuel for the nuclear breeder reactor, as a starting material for thorium metal production and as a very high temperature ceramic. The pure oxide has a very high melting point (*ca.* 3200°), no reported allotropic transformation, and a high degree of chemical stability.

The most widely reported method for the preparation of high purity thorium oxide is the thermal decomposition of thorium oxalate. The mechanism by which thermal decomposition takes place has been quite widely investigated.[1-3] However, little work has been reported on the effect of the preparation variables on fundamental characteristics of the oxide product. Foex[4] investigated the rate of change in density as a function of firing temperature for thorium oxide prepared by the thermal decomposition of a hydrous oxide. This work is of interest since the density change was characteristically associated with crystallite growth for each firing temperature. Foex also observed that no sintering of particles seems to take place below 1000° and from this he surmised that growth occurred only among closely joined crystallites.

In this note the effects of oxalate precipitation temperature, calcination temperature and time upon the particle size, surface area and crystallite size of thorium oxide are presented.

Experimental

a. **Oxide Preparation.**—Thorium oxalate precipitates were prepared at 10, 40, 70 and 100° by dropwise addition of 1 *M* high purity oxalic acid to a vigorously stirred 1 *M* high purity thorium nitrate solution. The precipitates were digested at temperature for one hour, filtered, washed and finally dried at 110° for 24 hours.

An oxide was prepared from each of the four materials by calcining the dried oxalate in platinum crucibles at 375° for four hours and then at 400° for an additional 16 hours. The resulting oxides were used as stock materials. Ten-gram samples of each of the oxides were placed in small platinum crucibles and fired in a preheated furnace at 500, 650, 750 or 900° for a period of 24 hours.

For calcination time–temperature studies several one-gram samples of each oxide were put in small platinum crucibles and brought rapidly to temperature in a preheated furnace. At fixed time intervals samples were removed and quenched by partially immersing the crucibles in water.

6. **Oxide Characterization.**—Chemical analysis of the oxide products showed them to be extremely pure containing less than 100 p.p.m. each of Ca and $PO_4^{\equiv}$ and less than 50 p.p.m. each of $SO_4^{=}$, Cl^-, F^-, Fe, Cr, Ni, Pb, Ba, Mg, Na, K, Li, Si and total rare earths. Thermogravimetric gas adsorption data showed both water and carbon dioxide to be strongly adsorbed on the thoria surface and they were present in the oxide samples in amounts proportional to the specific surface areas. The oxides from the 400° calcinations contained as much as 1% carbonate and 0.4% water while those from the 900° calcination contained less than 0.2% of either. Firing the oxide in excess of 1000° was necessary to completely remove the water and carbon dioxide from the surface.

The shape, size and size distribution of the oxide particles were determined from electron micrographs and sedimentation particle size analysis. The method for sedimentation particle size analysis was developed at ORNL.[5] The oxide was activated by neutron irradiation, dispersed at <0.5 wt. % concentration in a 0.005 *M* $Na_4P_2O_7$ solution and allowed to settle past a scintillation counter connected to a count rate meter and a Brown recorder. The scintillation activity being proportional to thoria concentration was analyzed in the usual manner, using Stokes law, to give the size distribution data.

Specific surface areas were obtained by the BET method and the average crystallite sizes determined by X-ray diffraction line broadening using the equation

$$D_{av} = \frac{0.9\lambda}{\beta_{1/2} \cos \theta}$$

where λ is the wave length of the incident radiation, $\beta_{1/2}$ the corrected band width at half height, and θ the Bragg angle of diffraction.

Results and Discussion

Electron micrographs of the oxide products showed particles of the approximate size and shape of the original oxalate particles from which they were formed. The particles of oxide prepared from the 10° precipitated material were approximately 1 μ in size and appeared quite uniform; those from the 40° material 1 to 2 μ in size and less uniform. A marked increase in particle size was observed for the oxide particles prepared from the

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[1] C. L. Duval, "Inorganic Thermogravimetric Analysis," Elsevier Press, New York, N. Y., 1953, p. 496.

[2] R. Beckett and M. E. Winfield, *Aust. J. Sci. Res.*, **4**, 644 (1951).

[3] R. W. M. D'Eye and P. G. Sellman, *J. Inorg. Nuclear Chem.*, 143 (1955).

[4] Marc Foex, *Bull. soc. chim.* (*France*), [16] **55**, 231 (1949).

[5] G. W. Leddicotte, R. E. Druschel, H. H. Miller and J. P. McBride, "Particle Size Analysis by Radioactivation," ONRL-2160.

[6] H. P. Klug and L. E. Alexander, "X-Ray Diffraction Procedures for Polycrystalline and Amorphous Materials," John Wiley and Son, New York, N. Y., 1954, Chap. IX, p. 491.

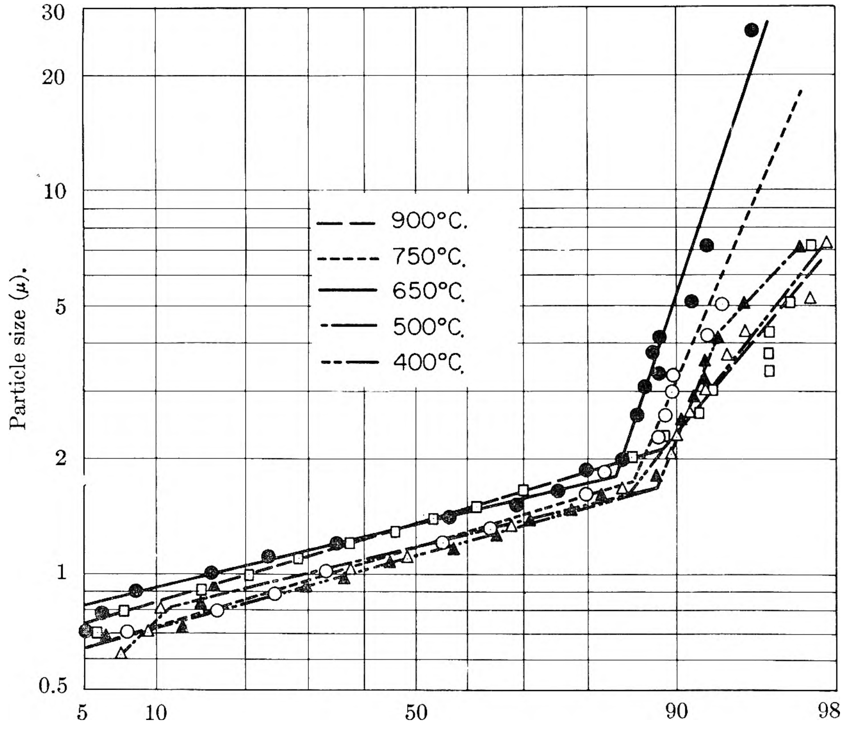

Fig. 1.—Sedimentation particle size distribution for thorium oxide prepared from 10° precipitated thorium oxalate.

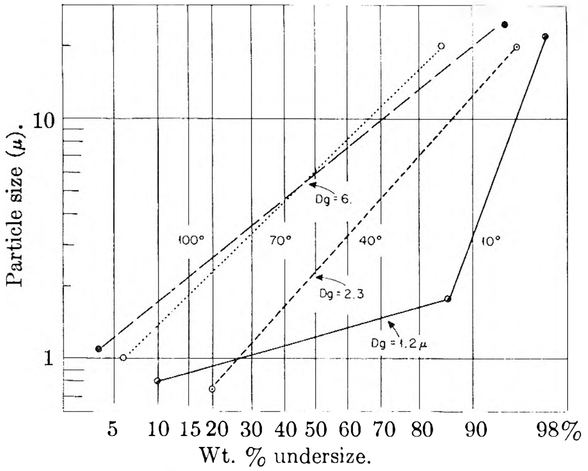

Fig. 2.—Particle size distribution *vs.* precipitation temperature.

70 and 100° precipitated materials which were 4–7 μ in size. No change in particle shape or size nor evidence of sintering was seen as the firing temperature was increased from 400 to 900°. Micrographs of shadow-cast oxides showed that the particles prepared from oxalate precipitated at 10° were cubical in shape with an edge-to-thickness ratio of about 3:2, and that those from the 100° material were platelets with an edge-to-thickness ratio of 6:1.

The geometric mean particle size, D_g, determined by sedimentation particle analyses was in good agreement with the data from the electron micrographs. Figure 1 shows the particle size distribution curves for the oxides prepared from the 10° precipitated oxalate. The close agreement between the size distribution data obtained with oxides prepared from the same oxalate precipitate but fired at the various temperatures is typical. Figure 2 shows composite size distribution curves for all the oxides. Of particular interest is the sharp dependence of the particle size on precipitation temperature. The shallow slope of the size distribution curve for the 10° oxide is indicative of its greater uniformity.

Specific surface areas were much larger than could be anticipated from the particle size and decreased with increasing firing temperatures (*cf.* Fig. 3). Crystallite sizes as measured by X-ray diffraction line broadening increased with increasing firing temperature (Fig. 4) and corresponded very closely to the particle sizes estimated from the specific surface areas. Since the micrographs and sedimentation data showed no size increase with increasing calcination temperature, the crystallite growth apparently is confined to the individual particles. This is in agreement with Foex[4] who postulated that crystallite growth was confined to groups of closely joined crystallites. Further evidence is seen in the fact that at 900° the crystallite size is smaller in the case of the smaller particle 10° material (550 Å.) than for the larger 100° material (775 Å.).

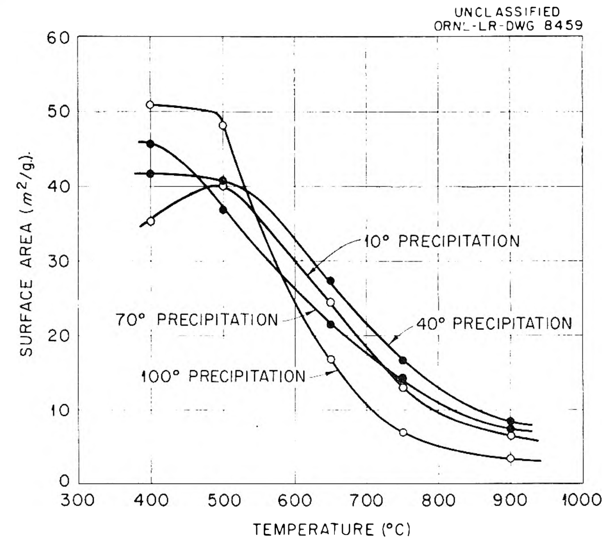

Fig. 3.—Effect of temperature upon the specific surface of thorium oxide.

All of these measurements agree with work on the thermal decomposition of oxalate by Beckett and Winfield.[2] These investigators concluded from electron micrographs of the oxide residues

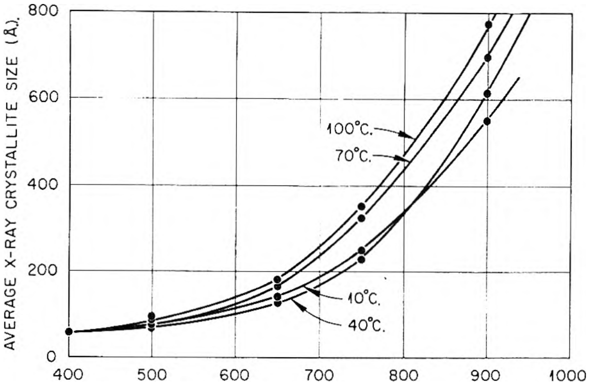

Fig. 4.—Effect of temperature upon the crystallite size of thorium oxide.

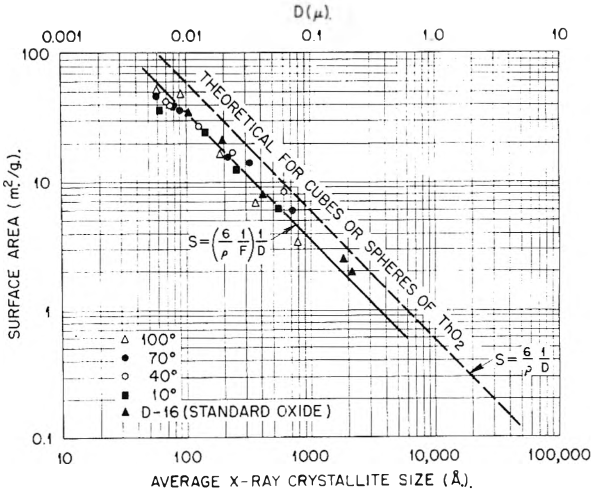

Fig. 5.—Relationship between average crystallite size and specific surface area for thorium oxide prepared by the thermal decomposition of thorium oxalate.

that the initial oxalate crystal imposes on the residual oxide a mosaic structure of thin, spongy microcrystalline laminae all oriented in very nearly the same direction. Apparently, as indicated above, when the firing temperature is increased an annealing and sintering process takes place between the crystallites in the interior of a particle with consequent decrease in the surface area.

What appears to be a fundamental relationship between the crystallite size and specific surface area is illustrated in Fig. 5 in which the X-ray crystallite sizes are plotted against the corresponding specific surface areas for several oxide products. The specific surface of a cube or sphere is related to an edge or diameter by the equation

$$S = 6/\rho\, D$$

where S is the area, ρ the density and D the edge or diameter. The data of Fig. 5 fit an equation of the form

$$S = \frac{6}{\rho D}\left(\frac{1}{F}\right)$$

where $1/F$ is a packing factor indicative of the relative crystallite surface area unavailable for nitrogen adsorption.

For S in m.²/g. and D in ångströms the average value of the SD product for all oxides was 3.6×10^3. This relation has been useful in calculating the approximate specific surface area of an oxide from the X-ray crystallite size which is much more readily obtained than is the surface area itself.

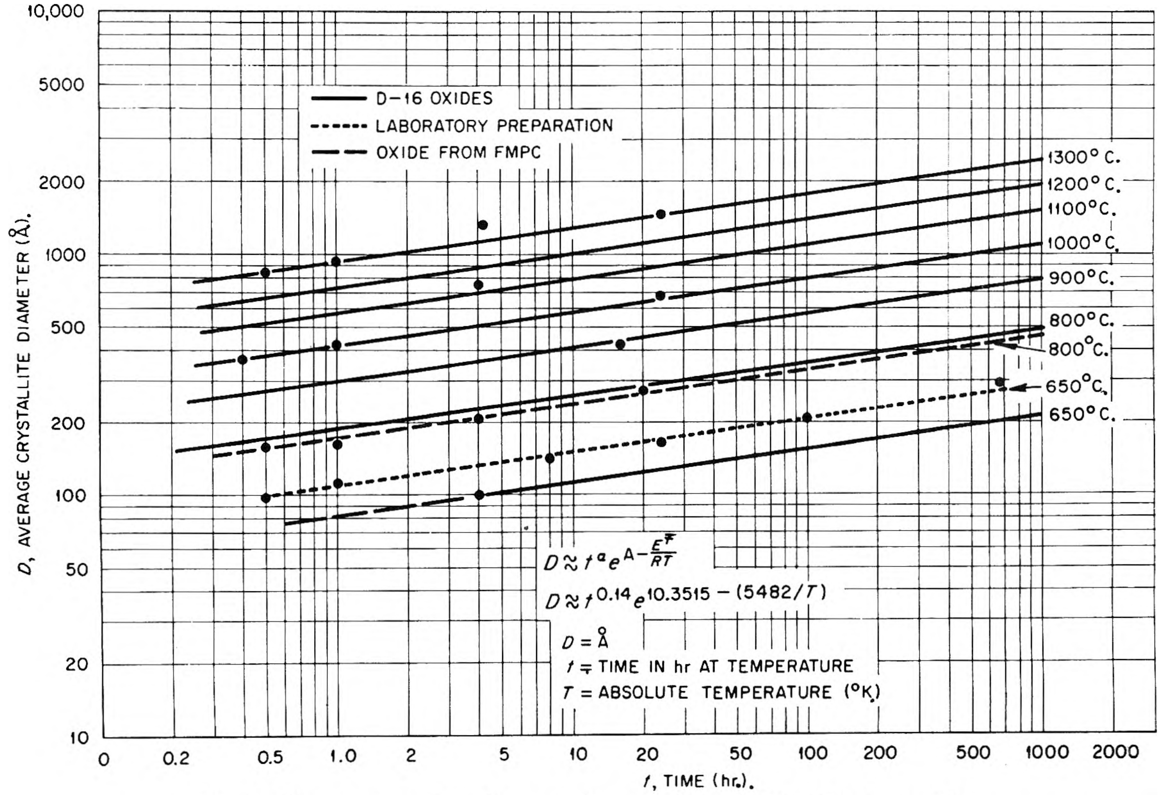

Fig. 6.—Temperature–time effects on the crystallite growth of thorium oxide.

While the crystallite size was determined primarily by the firing temperature, a relationship between crystallite size and firing time also was established. Log-log plots of crystallite size *versus* firing time for oxides at various firing temperatures are shown in Fig. 6. The growth curves fit an equation of the form

$$D = t^{\alpha}e^{A-B/T}$$

where D is the crystallite diameter, t the time and T the absolute temperature; α, A and B are constants.

The constant, α, appears to be characteristic of oxide prepared by the thermal decomposition of thorium oxalate. For D in ångströms and t in hours, α equals 0.14. The temperature dependent function, $e^{A-B/T}$ is typical for rate processes requiring an energy of activation, the constant B being equal to $\Delta H/R$ where ΔH is the heat of activation. The heat of activation was determined to be 10.97 kcal./g. mole. The low value is in accordance with growth taking place only among well ordered groups of crystallites. The intercept, A, being an entropy term is characteristic of a particular oxide preparation and must be determined for each new preparation.

Acknowledgment.—The authors wish to acknowledge the assistance of several members of the ORNL staff: T. E. Willmarth for the electron microscopy, G. W. Leddicotte for sedimentation particle size analyses, and R. M. Steele for the X-ray crystallite size determinations.

THE REACTION OF BORIC ACID WITH SOME PYRIDINE BASES

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It was reported recently by Astakhov, Elitsur and Nikolaev[1] that water could be extracted from orthoboric acid, H_3BO_3, by either pyridine or dioxane, leaving behind either metaboric acid, HBO_2, or pyroboric acid, $H_2B_4O_7$, depending on the temperature of extraction. Their claims were based on determination of the volume of hydrogen released by their solutions on treatment with calcium hydride, the gas being attributed solely to reaction with water extracted from the solid H_3BO_3. In an unsuccessful attempt to use such an extraction for the preparation of metaboric acid, it has been found that pyridine and its homologs react very readily with H_3BO_3. The apparent solubility of H_3BO_3 in dioxane and in pyridine has been determined and the solid phases have been examined by X-ray diffraction and by analytical methods. It was immediately apparent that the solid phase in equilibrium with the dioxane solution was unchanged H_3BO_3. Pyridine, on the other hand, reacts with boric acid to produce a stable solid salt. This product is presumably the same as the uncharacterized material reported a generation ago by Gebauer-Fülnegg and Riesenfeld,[2] who prepared it by extended heating of pyridine–boric acid mixtures.

Experimental

Materials.—Reagent grade orthoboric acid from several sources was employed without further treatment. The dioxane, 4-picoline, 2,3-lutidine and 2,4,6-collidine were pure grades from Matheson, Coleman and Bell, used without further treatment. The pyridine was Baker and Adamson reagent grade. The other pyridine bases and cyanuric acid were obtained from Eastman Organic Chemicals Department, Distillation Products Industries. The quinoline, isoquinoline and cyanuric acid were pure grades, used as received. The other materials were practical and technical grades which were subjected to a single distillation before use.

Solubility Determinations.—Orthoboric acid and the organic solvent were loaded into 2-oz. polyethylene bottles, the screwcaps sealed with paraffin. The bottles were rotated end-over-end in a constant temperature (±0.1°) water-bath for periods of one to five weeks. The two phases were separated by filtering rapidly at temperature. Two samples of each liquid phase were taken and made up to 50 ml. with the appropriate solvent. The boron content of each resulting solution was determined using a neutron absorption technique developed by Leddicotte, Brooksbank, and Strain of this Laboratory.[3] The method depends on the fact that the neutron density in a paraffin block containing a neutron source is greatly lowered by the presence of nuclides with high thermal-neutron absorption cross-sections. The apparatus consists of a $B^{10}F_3$-filled neutron detector, mounted coaxially in a 40-ml. Teflon cell. The cell is mounted within a block of paraffin containing also a Po–B neutron source. The time necessary for the detector to accumulate a fixed number of counts is proportional to the concentration of the high cross-section nuclide, in this case B^{10}. The apparatus was calibrated using known concentrations of H_3BO_3 in water. The method was used differentially to minimize errors due to the use of several different solvents. The results are shown in Table I.

TABLE I

APPARENT SOLUBILITY OF H_3BO_3 IN PYRIDINE AND IN DIOXANE

Temp., °C.	Solubility (moles H_3BO_3/l. of soln.) In pyridine	Solubility (moles H_3BO_3/l. of soln.) In dioxane
25.3	1.04, 1.08	0.213
32.5	1.13, 1.19	.234, .236
40.0	1.31	.266, .274

Crystalline Pyridine–Boric Acid Compounds.—The reaction of boric acid with pyridine and many of its homologs proceeds extremely rapidly. If pyridine is simply poured onto coarsely crystalline boric acid, the solid sinters immediately and must be crushed before complete reaction can be obtained. The product is independent of the reaction temperature in the range from 0 to 115°. Cursory study of the thermal stability of the pyridine compound shows that, at a pressure of 0.01 mm., it does not decompose appreciably until heated above about 120°. The vapor evolved appears to be principally water. The resulting solid is amorphous.

The crystalline compounds used for X-ray diffraction studies were generally prepared by loading boric acid and the appropriate base into a polyethylene bottle which was rotated end-over-end at 1 r.p.m. for several days at room temperature. The solid product was filtered and a portion was air-dried. X-Ray diffraction powder patterns were obtained on a Norelco diffractometer, using Ni-filtered, Cu Kα radiation (λ = 1.5418 Å.). Densities at room temperature were determined by toluene displacement in 25-ml. pycnometers. Aqueous solutions of the compounds were analyzed for boric acid by the usual mannitol method and for base by direct titration with standard acid. Tests using pyridine and boric acid solutions showed no interference of one substance with the analysis for the other. Karl Fischer analyses were carried out on methanol solutions, determining

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(1) K. V. Astakhov, A. G. Elitsur and K. M. Nikolaev, *Zhur. Obshchei Khim.*, **21**, 1753 (1951).

(2) E. Gebauer-Fülnegg and F. Riesenfeld, German Patent 482266 (Dec. 24, 1925).

(3) W. A. Brooksbank, Jr., G. W. Leddicotte and J. E. Strain, AEC Report ORNL-1961 (unpublished).

water and boric acid together. Some samples were analyzed for carbon and hydrogen by conventional combustion methods.

The reaction of pyridine with cyanuric acid was carried out in the same way. A similar sintering effect was noted and an appreciable amount of heat was evolved.

Results and Discussions

The products of the reaction of the pyridine bases with H_3BO_3 are all white, non-hygroscopic crystalline solids, much softer than the original boric acid. They dissolve completely in methanol, forming methyl borate and water. All of the compounds dissolve in water, with complete hydrolysis, except for the piperidine derivative which is probably unhydrolyzed. The X-ray diffraction patterns obtained on these materials were characterized by large numbers of well-resolved lines at quite small diffraction angles (2ϑ), useful resolution being obtained only below about 40° (d >2.5 A.). In this range, 30 to 40 diffraction lines were observed for each compound. In the range $2\vartheta > 40°$, the lines were much weaker and very diffuse. The diffraction patterns obtained can all be described in terms of sets of orthorhombic lattice constants, listed in Table II. Using these constants, the calculated lattice spacings, d, agree with the observed values to within 1%, agreement to 0.5% being obtained for most lines. The possibility that one or more of these crystals may have symmetry less than orthorhombic is not completely excluded.

If the compounds of boric acid with 2,3- and 2,6-lutidine, 2,4,6-collidine and quinoline are washed with toluene, the densities are markedly increased (as might be expected, since the powders probably contain excess base) and the X-ray diffraction patterns are altered very extensively. In the other compounds, no changes occur in the diffraction patterns on washing with toluene, nor are the densities much altered. In each case where the X-ray pattern is altered, one set of lattice constants suffices to explain the results, the changes being attributed solely to alterations of intensities of important lines.

TABLE II

ORTHORHOMBIC LATTICE CONSTANTS FOR COMPOUNDS OF BORIC ACID WITH SOME PYRIDINE BASES[a]

Base	a (Å.)	b (Å.)	c (Å.)	Exptl. density (g./ml.)
Pyridine	16.9	17.7	14.6	1.47*
2-Picoline	17.0	18.5	16.1	1.22**
3-Picoline	17.9	18.6	15.1	1.38*
4-Picoline	17.2	18.2*	14.6	1.36
2,3-Lutidine	15.6	18.9	12.8	1.49*
2,4-Lutidine	17.6	22.4	16.4	1.25[b]
2,6-Lutidine	19.4	21.9	18.0	1.47[b]
2,4,6-Collidine	17.6	18.6*	14.6	1.20[b]
Quinoline	15.2	20.8	13.7	1.45[b]
Isoquinoline	16.2	17.2	12.5	1.22[b]
Piperidine	19.7*	25.5**	14.6	1.10[b]
Pyridine–cyanuric acid compound	16.0	21.7	17.5	....

[a] All lattice constants ±0.1 Å., except those indicated by *, ±0.2 Å. and by **, ±0.3 Å. Density values, ±0.01 g./ml., except those indicated by *, ±0.02 g./ml., and by **, ±0.03 g./ml. [b] These values determined only on toluene-washed samples.

Results of chemical analyses on several samples of the pyridine–boric acid compounds are presented in Table III. The formula $C_5H_5N\cdot 3HBO_2$ is believed to represent the ideal composition, although the last sample would be better represented by the formula $C_5H_5N\cdot 3HBO_3\cdot H_3BO_3$. Chemical analyses obtained on toluene-washed samples of each of the other compounds are presented in Table IV. It is clear from these analyses that, while most of the samples approximate to derivatives of metaboric acid (B_2O_3:H_2O::1:1), there is no simple formulation which will satisfy all of the analyses. Analyses of air-dried samples of the 2,4- and 2,6-lutidine compounds gave ratios, base:B_2O_3:H_2O, 1:1.4:0.89 and 1:0.49:1.5, respectively.

TABLE III

CHEMICAL COMPOSITION OF PYRIDINE–BORIC ACID COMPOUND COMPOSITION (WT. %)

Sample[a]	Carbon	Hydrogen	Boron	Pyridine	Water[b]
PB-15b	29.7	3.6	16.1	34.6	53.7
PB-15c	29.7	3.7	16.0	34.2	53.3
PB-15d	28.9	3.6	16.1	35.5	52.8
PB-15e	29.4	3.8	15.8	35.3	52.8
PB-17b	..	..	15.7	29.1	59.6
			Calculated		
$C_5H_5N\cdot 3HBO_2$	28.5	3.8	15.4	37.6	51.3

[a] The first four samples were freed of excess pyridine by drying to constant weight at room temperature at pressures ranging from 10 μ to atmospheric. The fifth sample (from a different batch) was thoroughly washed with toluene and air-dried. [b] Karl Fischer determination: includes water produced by reaction of sample with methanol.

TABLE IV

CHEMICAL COMPOSITION OF SUBSTITUTED PYRIDINE–BORIC ACID COMPOUNDS (TOLUENE WASHED)

Base	B_2O_3 (moles/mole of base)	H_2O[a] (moles/mole of base)
2-Picoline	2.1	3.5
3-Picoline	1.7	2.0
4-Picoline	1.3	1.4
2,3-Lutidine	2.8	4.6
2,4-Lutidine	2.4	3.1
2,6-Lutidine	12	33
2,4,6-Collidine	2.5	1.6
Quinoline	5.7	7.5
Isoquinoline	2.2	1.1
Piperidine[b]	2.4	1.4

[a] Karl Fischer method; corrected for B_2O_3 content. [b] Analyses corrected on assumption that piperidine is a strong base.

The most satisfying rationalization of the X-ray data is to interpret all of the compounds as being based ultimately on the layered structure of orthorhombic HBO_2 (III)[4] which has been reported[5] to be constructed of parallel sheets of $B_3O_6^{-3}$ ions, bound together in the plane by hydrogen bonds. The 17 to 19 Å. spacing found in all the compounds but two (Table II) is taken to be six times the interlayer spacing in HBO_2 (III) (3.12 Å.). Each pyridine ring has a unique direction, allowing three different orientations relative to a parallel B_3O_3 ring, which, taken with the fourfold symmetry re-

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(4) F. C. Kracek, G. W. Morey and H. E. Merwin, *Am. J. Sci.*, [5] **35A**, 143 (1938).

(5) H. Tazaki, *J. Sci. Hiroshima Univ.*, **A10**, 37, 55 (1940).

quired by the HBO_2 structure accounts for the presence of six layers per unit cell in the compounds as opposed to two layers in the original acid. The structure is then made up of alternate sheets of HBO_2 and organic base. The electronic structure of the $B_3O_6^{-3}$ ion is similar to that of the isoelectronic ion of cyanuric acid, $C_3N_3O_3^{-3}$, and the crystal structure of cyanuric acid[6] is very similar to that of HBO_2 (III). Pyridine has also been found to react readily with cyanuric acid, yielding a product with an X-ray diffraction pattern very similar to that of the pyridine–boric acid compound.

The chemical analyses may be rationalized by noting that the major deviations from metaborate composition are found where the bases have limited miscibility with water. There is thus insufficient solvent for all the water produced by reaction of the base with H_3BO_3, leading to products with more water than expected for metaborates. In a test of this idea, the reaction of H_3BO_3 was studied with a limited amount of pyridine. Analysis of the product showed a molar ratio, base: B_2O_3:H_2O of 1:3.5:7.9. Treatment of this product with additional pyridine produced a material of analysis very similar to those of the first four samples of Table III. The function of toluene seems to be removal of small amounts of base from the crystal, the excess HBO_2 being converted to H_3BO_3 by atmospheric moisture. Because of the composition variations resulting from toluene treatment as well as from the limited solvent properties of some of the bases, no clear-cut formulation can be given to most of the reaction products. It appears likely also that steric requirements of the larger organic molecules are incompatible with simple chemical formulations. This is believed to be the explanation of the apparent increase in relative amounts of B_2O_3 and H_2O as the base molecules increase in size.

Acknowledgments.—Grateful acknowledgment is made of the assistance of G. E. Klein, who prepared the X-ray diffraction patterns, of W. A. Brooksbank, Jr., who performed the neutron-absorption boron analyses and of L. C. Henley, who carried out most of the other boron and base analyses.

[6] C. Wiebenga and N. F. Moerman, *Nature*, **141**, 122 (1938); *Z. Krist.*, **99**, 217 (1938).

THE TERNARY SYSTEM SODIUM OXIDE–WATER–METHANOL[1]

By C. F. Boynton, J. F. Masi, P. E. Gallagher and R. E. Whan

Contribution from Callery Chemical Co., Callery, Pa.

Received August 30, 1956

In the course of fundamental research on solutions of sodium borates in aqueous methanol, the phase diagram for the system sodium oxide–water–methanol became desirable. As the work progressed there were indications that the adduct $NaOH \cdot CH_3OH$ was one of the solids in equilibrium with saturated liquid. Since this compound has not been reported in the literature, it was prepared in a vacuum system, identified by chemical analysis, and its X-ray diffraction pattern was obtained.

Experimental

Sodium oxide, purchased from A. D. Mackay, Inc., was found to be 99.4% Na_2O despite the fact that some of the particles were gray. It was not as hygroscopic as sodium hydroxide. Baker and Adamson reagent grade absolute methyl alcohol was used. Fisher Certified Reagent sodium hydroxide was used after the pellets were pulverized in a dry atmosphere. Sodium methoxide was prepared by Dr. Edgar F. Westrum, University of Michigan, and was found to be 100.0% $NaOCH_3$. No attempt was made to purify any of these materials.

A series of 20-g. samples was prepared by weighing appropriate amounts of sodium oxide, methanol and distilled water into a 50-ml. round-bottom Pyrex flask. It was found necessary to add the sodium oxide to the liquid very slowly, with shaking, while the mixture was cooled in a room temperature-bath. The flask was closed with a rubber stopper and agitated with a wrist-action shaker for at least 16 hours in a bath maintained at 25 ± 0.1°. Equilibration of several mixtures for longer periods up to 64 hours indicated that equilibrium was attained within 16 hours. The equilibrium mixture was filtered through a coarse fritted-glass funnel with the aid of dry nitrogen gas pressure. The solid was partially dried by quickly pressing it between sheets of absorbent paper. Samples of this solid residue, still slightly wet with mother liquor, and the saturated liquid were transferred to 1-ml. glass-stoppered weighing bottles for analysis.

Samples were titrated for sodium with 0.2 *N* hydrochloric acid to a brom cresol green end-point. Methanol was determined in duplicate by the method of Alexander, Bourne and Littlehale,[2] with certain modifications. Excess standard 0.1 *N* ceric ammonium nitrate containing 100 ml. of 15 *N* nitric acid per liter was added directly through the reflux condenser to the sample which was cooled in an ice-bath. The mixture was refluxed for ten minutes to oxidize the methanol to formic acid, then back titrated, while still hot, with standard 0.1 *N* ferrous ammonium sulfate containing 10 ml. of 36 *N* sulfuric acid per liter.

Sodium Hydroxide Methanolate.—A 0.3847-g. sample of sodium hydroxide was placed in a small bulb equipped with a ground joint. The bulb was attached to a vacuum system where it was directly connected to a mercury manometer and to a calibrated volume through a stopcock. Small portions of methanol were measured as a gas in the calibrated volume and then transferred to the sodium hydroxide bulb by condensation with a liquid nitrogen bath. After each addition of methanol the stopcock was closed, the bulb was warmed to 20° by means of a constant temperature water-bath, and the equilibrium pressure was recorded. For some points, as much as 24 hours was required to reach equilibrium. From the data, listed in Table I, it is evident that sodium hydroxide forms a monomethanolate with a dissociation pressure of 1 mm. at 20°. The slight displacement of the break from the 50 mole % value was undoubtedly due to impurities (*e.g.*, water) in the sodium hydroxide. At the pressure break the solid was removed from the tube. *Anal.* Calcd. for $NaOH \cdot CH_3OH$: Na, 31.9; CH_3OH, 44.5. Found: Na, 31.7; CH_3OH, 43.9. The compound is hygroscopic, and melts with decomposition at approximately 280°.

Further evidence for identifying this solid as the methanolate of sodium hydroxide rather than the hydrate of so-

Table I

Dissociation Pressures of Sodium Hydroxide Methanolate at 20°

Mole % methanol	Pressure, mm.	Mole % methanol	Pressure, mm.
9.4	0.3	39.1	1.2
17.5	0.7	43.1	0.9
24.4	1.1	46.8	1.0
29.9	1.4	49.6	23.3
34.9	1.0		

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[1] Presented at 129th American Chemical Society Meeting, Dallas, Texas, April 8, 1956.

[2] A. P. Alexander, P. G. Bourne and D. S. Littlehale, *Anal. Chem.*, **27**, 105 (1955).

dium methoxide, was obtained by adding water vapor to a weighed sample of sodium methoxide in the vacuum system until the mole % of water was about 40. The solid was then evacuated. The vapors which came off were trapped and identified as methanol by infrared analysis. A chemical analysis of the solid residue confirmed that most of the sodium methoxide had been converted to sodium hydroxide.

TABLE II

TERNARY SYSTEM SODIUM OXIDE–WATER–METHANOL AT 25°
COMPOSITION IN WEIGHT %

Satd. liquid Na_2O	Satd. liquid CH_3OH	Wet solid Na_2O	Wet solid CH_3OH	Extrapolated dry solid
18.6	81.4	35.5	..	
18.4	82.5	35.7	55.0	$NaOH\cdot CH_3OH$
18.2	79.1	35.7	54.5	$NaOH\cdot CH_3OH$
18.7	75.3	36.4	52.5	$NaOH\cdot CH_3OH$
20.2	68.7	35.7	51.6	$NaOH\cdot CH_3OH$
20.3	66.3	36.8	49.8	$NaOH\cdot CH_3OH$
20.6	65.6	35.8	48.2	$NaOH\cdot CH_3OH + 3NaOH\cdot 2H_2O\cdot CH_3OH$
20.5	65.5	37.0	40.4	$NaOH\cdot CH_3OH + 3NaOH\cdot 2H_2O\cdot CH_3OH$
20.8	64.5	38.1	35.7	$3NaOH\cdot 2H_2O\cdot CH_3OH$
21.4	60.8	..	..	$3NaOH\cdot 2H_2O\cdot CH_3OH$
22.3	54.7	36.8	34.6	$3NaOH\cdot 2H_2O\cdot CH_3OH$
22.8	50.3	38.7	31.0	$3NaOH\cdot 2H_2O\cdot CH_3OH$
24.6	44.7	42.1	24.3	$3NaOH\cdot 2H_2O\cdot CH_3OH$
25.6	39.3	43.5	22.8	$3NaOH\cdot 2H_2O\cdot CH_3OH$
26.7	32.5	43.4	21.5	$3NaOH\cdot 2H_2O\cdot CH_3OH$
26.8	29.0	42.3	20.4	$3NaOH\cdot 2H_2O\cdot CH_3OH$
28.4	24.2	42.7	19.2	$3NaOH\cdot 2H_2O\cdot CH_3OH$
29.6	18.3	43.0	16.3	$3NaOH\cdot 2H_2O\cdot CH_3OH$
30.8	13.4	43.2	14.8	$3NaOH\cdot 2H_2O\cdot CH_3OH$
32.5	7.9	42.6	11.9	$3NaOH\cdot 2H_2O\cdot CH_3OH$
33.8	4.3	44.2	12.0	$3NaOH\cdot 2H_2O\cdot CH_3OH$
35.3	1.7	41.8	8.7	$3NaOH\cdot 2H_2O\cdot CH_3OH$
37.3	0.7	43.8	10.0	$3NaOH\cdot 2H_2O\cdot CH_3OH$
39.4	0.24	44.6	10.1	$3NaOH\cdot 2H_2O\cdot CH_3OH$
40.0	0.13	46.4	5.0	$3NaOH\cdot 2H_2O\cdot CH_3OH + NaOH\cdot H_2O$
40.0	0.13	46.7	2.5	$3NaOH\cdot 2H_2O\cdot CH_3OH + NaOH\cdot H_2O$
40.0	0.13	48.0	0.99	$3NaOH\cdot 2H_2O\cdot CH_3OH + NaOH\cdot H_2O$
40.6	0	48.0	0	$NaOH\cdot H_2O$

TABLE III

X-RAY POWDER DIFFRACTION DATA

Characteristic lines and relative intensities $NaOH\cdot CH_3OH$	Characteristic lines and relative intensities $3NaOH\cdot 2H_2O\cdot CH_3OH$
4.92 (s)	3.64 (s)
4.11 (w)	3.25 (w)
3.58 (vs)	2.91 (m)
3.30 (m)	2.73 (m)
3.11 (w)	2.41 (vs)
2.86 (mw)	2.13 (mw)
2.72 (s)	2.00 (m)
2.57 (vs)	1.81 (m)
2.40 (w)	1.69 (s)
2.10 (w)	1.62 (m)
1.93 (s)	1.54 (vw)
1.81 (ms)	1.444 (w)
1.68 (w)	1.335 (mw)
1.63 (w)	1.199 (mw)
1.358 (w)	1.073 (mw)
	0.963 (vw)

Results and Discussion

Table II gives the compositions of the equilibrium mixtures at 25°. The last column indicates the formula of the extrapolated dry solid. Figure 1 shows the phase diagram for the ternary system sodium oxide–water–methanol at 25°. The two principal solubility curves intersect at the isothermally invariant point, 20.5 weight % sodium oxide and 65.5 weight % methanol. The greatest portion of the saturated liquid is in equilibrium with the solid $3NaOH\cdot 2H_2O\cdot CH_3OH$. A sample of this hydrate methanolate was prepared by the method of Smith,[3] and its X-ray powder diffraction pattern was compared with those of wet solid residues obtained in the phase study.

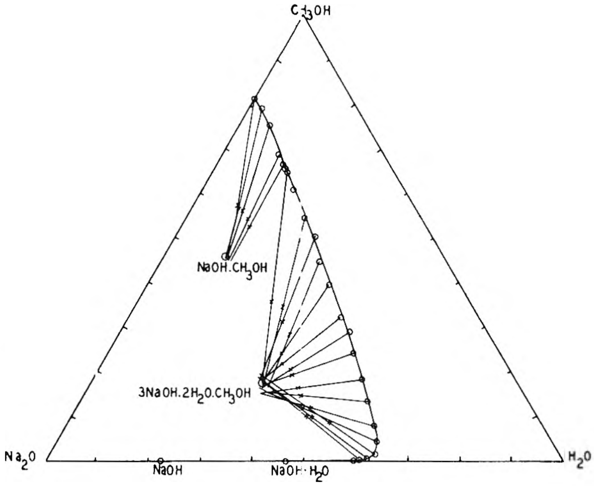

Fig. 1.—Isotherm for system sodium oxide–water–methanol at 25°, composition in weight per cent.

Another isothermally invariant point was found at 40.0 weight % sodium oxide and 0.13 weight % methanol, at which the saturated liquid is in equilibrium with both $3NaOH\cdot 2H_2O\cdot CH_3OH$ and $NaOH\cdot H_2O$.

The characteristic lines and their relative intensities in the X-ray powder diffraction patterns for two of the equilibrium solids are given in Table III. The sodium hydroxide methanolate has five strong lines, while the hydrate–methanolate has three different strong lines. With the aid of these standards an X-ray pattern of a wet solid residue could be used to confirm the identity of the extrapolated dry solid in equilibrium with saturated liquid at any given point on the solubility curves.

Acknowledgment.—The X-ray diffraction patterns were obtained by P. I. Henderson.

[3] D. F. Smith, U. S. Patent 2,418,372 (1947).

THE IONIC DISSOCIATION OF 2,4-, 2,6- AND 3,4-DICHLOROBENZOIC ACIDS IN WATER[1]

BY MARION MACLEAN DAVIS AND HANNAH B. HETZER

National Bureau of Standards, Washington 25, D. C.

Received September 17, 1956

No pK values are in the literature for dichlorobenzoic acids. Recently, in connection with stud-

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[1] This research was supported in part by the United States Air Force, through the Air Force Office of Scientific Research of the Air Research and Development Command under contract No. CSO-670-55-21.

ies of acidity in non-aqueous solvents, we needed approximate pK values for 2,4-, 2,6- and 3,4-dichlorobenzoic acids and obtained the respective experimental values 2.76, 1.82 and 3.64. The solubility of 2,6-dichlorobenzoic acid in water is great enough for satisfactory estimation of pK by potentiometric titration, but 3,4-dichlorobenzoic acid is so difficultly soluble in water that a spectrophotometric procedure had to be used. 2,4-Dichlorobenzoic acid is intermediate in solubility, and its pK was measured by both methods.

Values of pK can be calculated for the three acids by applying a generalization of Shorter and Stubbs.[2] These authors showed that the change in the free energy of ionization of benzoic acid produced by two or more substituents is generally very close to the algebraic sum of the effects of individual substituents, except in cases where substituents are present in both the 2,6- or the 2,3-positions. The calculated pK values, based on ionization data for benzoic acid and for *o*-, *m*- and *p*-chlorobenzoic acids, are 2.73, 1.68 and 3.65 for 2,4-, 2,6- and 3,4-dichlorobenzoic acids, respectively.[3] The results of our measurements support the generalization of Shorter and Stubbs, inasmuch as the experimental and calculated pK values are essentially the same in the cases of 2,4- and 3,4-dichlorobenzoic acids, but not in the case of 2,6-dichlorobenzoic acid. Evidently the first *ortho*-substituted chlorine atom is more effective than the second *ortho*-chlorine in enhancing the strength of benzoic acid.

Experimental

Materials.—**2,4-Dichlorobenzoic acid,** although of best available commercial grade, contained a reddish gummy impurity and had a strong odor. After three recrystallizations from aqueous ethanol, using decolorizing charcoal, and an additional crystallization from benzene, again using charcoal, the color and odor were removed, the melting point was 163–164°,[4] and the purity by potentiometric weight titrations in aqueous ethanol was 99.9%. A single titration of a saturated aqueous solution at 25° indicated a solubility equivalent to a little over 0.0025 M.

2,6-Dichlorobenzoic Acid.—α,α,2,6-Tetrachlorotoluene, the starting material, was hydrolyzed to the corresponding aldehyde by the prolonged action of concentrated sulfuric acid at about 55°.[5] The aldehyde was oxidized to the acid by heating with alkaline potassium permanganate. The crude product was recrystallized from cyclohexane, yielding long, flat, slender needles; after heating to 80° in a vacuum oven these melted at 143–144°.[4] The same melting point has been reported for specimens prepared from other starting materials.[6,7] The purity by potentiometric weight titrations in water was 99.9%.

3,4-Dichlorobenzoic acid,[8] after recrystallization from aqueous ethanol, using decolorizing charcoal, melted at 206–207°,[4] and a purity of a little over 99.8% was indicated by potentiometric weight titrations in aqueous ethanol. A single titration of a saturated aqueous solution at 25° indicated a solubility equivalent to about 2.9×10^{-4} M.

Potentiometric Measurements of pK.—Values believed to approximate closely the thermodynamic dissociation constants (expressed as pK) of 2,4- and 2,6-dichlorobenzoic acids were obtained by aqueous titrations at 25 ± 1°, using glass and saturated calomel electrodes[9] and standard sodium hydroxide approximately ten times as concentrated as the solution being titrated. 0.01 M solutions (100-ml. portions) of 2,6-dichlorobenzoic acid and 0.002 M solutions of 2,4-dichlorobenzoic acid were titrated. In the titration of 2,6-dichlorobenzoic acid the pH meter was adjusted using NBS standard potassium tetroxalate buffer (pH_s for 0.05 M solution equals 1.68 ± 0.01 at 25°), whereas in the titration of 2,4-dichlorobenzoic acid the adjustment was made using NBS standard potassium hydrogen phthalate (pH_s for 0.05 M solution equals 4.01 ± 0.01 at 25°). pH data at 0.5-ml. intervals, ranging from 0.5 to 5 ml., were used in the computations. The equation used in calculations of pK was[10,11]

$$pK = pH - \log \frac{[B^-] + [H^+]}{[HB] - [H^+]} + \frac{0.509\sqrt{\mu}}{1 + 1.32\sqrt{\mu}} \quad (1)$$

The pK values obtained in two titrations of **2,6-dichlorobenzoic acid** were $1.84 \pm 0.01_5$ and 1.82 ± 0.01. The latter value is thought to be the better one. A titration of **2,4-dichlorobenzoic acid** (120 ml.) using ~0.023 M alkali yielded the pK value 2.76 ± 0.03.[12]

Measurement of pK for 2,4- and 3,4-Dichlorobenzoic Acids by Combined Spectrophotometric and Potentiometric Measurements.—In calculating pK the following equation was used

$$pK = pH - \log([S]/[A]) \quad (2)$$

The measurement of pH was performed potentiometrically. The pH meter was adjusted before measurements with the most suitable buffer standard (phthalate or tetroxalate), and the temperatures of solutions during pH measurements were usually 25–25.5°. Well-buffered solutions gave pH values reproducible to at least ±0.01 unit. The term [S]/[A], which was determined spectrophotometrically, represents the ratio of the equilibrium concentrations of ionized and non-ionized acid (in moles per liter) present in a dilute solution maintained at a suitable pH by the addition of an appropriate buffer mixture of low ionic strength.[13] Spectral absorption measurements were made with a Beckman DU quartz spectrophotometer, using 1-cm. quartz cells in a cell box maintained at 25.00 ± 0.05°. Although no activity corrections were made, the solutions were so dilute that the results are believed to be close approximations to the thermodynamic pK values.

In the case of **3,4-dichlorobenzoic acid,** the stoichiometric concentration was $4 \times 10^{-5} M$,[14] and buffer mixtures of acetic acid and sodium acetate ranging from 5×10^{-4} M to 2×10^{-3} M in ionic strength were used. The [S]/[A] ratios in these solutions varied from about 0.6 to 1.5. Table I summarizes the results for 3,4-dichlorobenzoic acid. The average pK value is 3.64, either including or omitting the data for solutions having a temperature higher than 25.5° at the time of pH measurement.

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(2) J. Shorter and F. J. Stubbs, *J. Chem. Soc.*, 1180 (1949).

(3) Using more recent *thermodynamic* ionization data (see J. F. J. Dippy, *Chem. Rev.*, **25**, 151 (1939)), the corresponding calculated pK values are 2.72, 1.68 and 3.60.

(4) Melting points were determined using an ASTM thermometer maintained at 3-in. immersion.

(5) H. E. Fierz-David and L. Blangey, "Grundlegende Operationen der Farbenchemie," Springer-Verlag, Vienna, Austria, 1943, p. 156, lithoprinted by Edwards Brothers, Inc., Ann Arbor, Michigan, 1944.

(6) J. F. Norris and A. E. Bearse, *J. Am. Chem. Soc.*, **62**, 953 (1940).

(7) S. D. Ross, *ibid.*, **70**, 4039 (1948).

(8) The authors thank the Heyden Chemical Corporation for the gift of this material.

(9) The titration apparatus was similar to the one described by C. J. Penther and F. B. Rolfson, *Ind. Eng. Chem., Anal. Ed.*, **15**, 337 (1943).

(10) All of the symbols have their usual, well-known significance. The third term on the right is, of course, equal to log f, which in dilute solutions equals $-A\sqrt{\mu}/(1 + B'\sqrt{\mu})$; A and B are constants of the Debye–Hückel theory, and $B' = a_i B$. Following R. G. Bates (*Anal. Chem.*, **26**, 871 (1954)), a_i, the ion-size parameter, is assumed to have the average value 4.

(11) G. G. Manov, R. G. Bates, W. J. Hamer and S. F. Acree, *J. Am. Chem. Soc.*, **65**, 1765 (1943), in a tabulation of values of A and B, give $A = 0.509$ and $B = 0.329$ at 25°.

(12) Titrations of 0.002 M 2,4-dichlorobenzoic acid were also performed using ~0.047 M sodium hydroxide, but the titration curves had no satisfactorily linear portions. With 100-ml. and 175-ml. samples the pK values 2.69 ± 0.02 and 2.87 ± 0.02, respectively, were obtained.

(13) $[S]/[A] = (x - y)/(y - z)$, where x is the absorbance of any given stoichiometric concentration of the acid in question when present in the non-ionized form, z is the corresponding absorbance when the acid has become completely ionized, and y is the absorbance observed upon partial ionization of the acid.

(14) L. Doub and J. M. Vandenbelt, *J. Am. Chem. Soc.*, **77**, 4535 (1955), have reported spectral data for the ionized and non-ionized forms of 3,4-dichlorobenzoic acid in aqueous solution with which our results are in substantial agreement.

TABLE I

3,4-DICHLOROBENZOIC ACID

pH	Temp., °C.[a]	pK[b]	pH	Temp., °C.[a]	pK[b]
3.39	26.2	3.62	3.73	26.0	3.68
3.47	25.3	3.64	3.73	25.4	3.63
3.54	25.4	3.63	3.82	25.4	3.66
3.61	25.3	3.63	4.71[c]	28.0	3.64[d]

[a] Temperature of solution during measurement of pH. During absorbance measurements the temperature was 25.00 ± 0.05°. [b] Average result using spectral data for the 8 wave lengths 242, 243, 244, 246, 248, 250, 252 and 254 mμ (except where otherwise indicated) to calculate the term log ([S]/[A]). The deviation from the average value of this term was in all cases 0.01 or less. [c] No buffer was present. [d] Exclusive of results for 242 and 244 mμ. In this case the deviation from the average value for log ([S]/[A]) was 0.017.

In the attempt to determine experimentally the limiting spectral absorption curve for the non-ionized form of 2,4-dichlorobenzoic acid,[15] for which high concentrations of acid are needed, the absorption maximum of the principal band was found to shift gradually toward longer wave lengths, and the isosbestic point (which was near 229 mμ) was not sharp, just as others have frequently found for analogous cases. An absorption curve for the non-ionized acid was calculated, using eq. 2 and spectral data, taken at 2-mμ intervals in the range from 236 to 254 mμ inclusive, for each of five solutions which were maintained at different pH values by the addition of either sodium acetate plus acetic acid (of ionic strength about 5×10^{-4} M) or of hydrochloric acid (6×10^{-4} M to 4×10^{-3} M). Values of pK over the range 2.71 to 2.79 were substituted in the equation, and the best fit was found when the pK value assumed was 2.76. The calculated absorption curve differs very little from curves that were obtained for 5×10^{-5} M 2,4-dichlorobenzoic acid in the presence of about 0.48 to 0.96 M hydrochloric acid.[16] A few illustrative data and calculated pK values are given in Table II. In calculating the results given in the table the absorption curve obtained experimentally for 5×10^{-5} M 2,4-dichlorobenzoic acid in the presence of approximately 0.48 M hydrochloric acid was assumed to be the correct curve for the non-ionized form. The best experimental value of pK for 2,4-dichlorobenzoic acid, considering all the potentiometric and spectrophotometric data, appears to be 2.76, but because of the experimental uncertainties this value cannot be regarded as differing significantly from the calculated pK value.[17]

TABLE II

2,4-DICHLOROBENZOIC ACID

	λ = 240 mμ[a]		λ = 250 mμ[b]	
pH	Absorbance per cm.	pK	Absorbance per cm.	pK
2.43	0.389	2.74	0.250	2.71
2.78	.349	2.80	.212	2.78
2.92	.326	2.77	.189	2.76
3.23	.286	2.76	.151	2.75
3.38	.270	2.75	.134	2.72
	Av.	2.76	Av.	2.74

[a] The limiting absorbance found for the completely ionized acid, 5×10^{-5} M, was 0.223. The absorbance (0.470) of a solution approximately 0.48 M in hydrochloric acid was assumed to be that of completely non-ionic 2,4-dichlorobenzoic acid in computing the pK values given in this table. [b] The values used for completely ionic and non-ionic acid are 0.090 and 0.334, respectively.

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(15) The authors thank Maya Paabo for assistance in the spectrophotometric determination of pK for 2,4-dichlorobenzoic acid.

(16) Our spectral data for ionized and non-ionized 2,4-dichlorobenzoic acid are not in good agreement with results reported by Doub and Vandenbelt (see ref. 14). In our experiments, 5×10^{-5} M solutions of the acid had almost identical absorption curves in the pH range about 6 to 9 (the solutions being buffered with sodium acetate, borax, or borax plus boric acid). These curves, which were considered to be caused by the completely ionized acid, showed a flat plateau or step-out in the wave length region 224 to 230 mμ, instead of a band near 229 mμ, as reported by Doub and Vandenbelt. For non-ionized 2,4-dichlorobenzoic acid, instead of their "first primary band" at 232 mμ, with a molar absorbance index of about 7400, our calculated curve exhibits an absorption band near 240 mμ, having the approximate molar absorbance index 9500.

(17) There appears to be a similarly close agreement between the actual and calculated ionization constants for 2,4-dibromobenzoic acid (see footnote 2).

THE IONIC DISSOCIATION OF 2,6-DIMETHOXYBENZOIC ACID IN WATER[1]

BY MARION MACLEAN DAVIS AND HANNAH B. HETZER

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Received September 17, 1956

In view of the marked deficiency of published ionization data for aromatic acids with substituents in both the 2- and 6-positions, it seems worthwhile to report the pK value, 3.44, recently obtained for 2,6-dimethoxybenzoic acid at approximately 25° by a titration procedure.[2]

An ionic dissociation constant for the acid can be calculated by applying a generalization of Shorter and Stubbs.[3] These authors pointed out that the change in the free energy of ionization of benzoic acid, $\Delta(-RT \ln K)$, upon the introduction of two or more substituent groups is usually nearly the same as the algebraic sum of the effects of individual substituents, except for cases of substitution in both the 2- and 6- or the 2- and 3-positions, when marked discrepancies between the calculated and experimental values generally appear. They observed, moreover, that improved agreement between observed and calculated values of $\Delta(-RT \ln K)$ can be achieved by using in the computation the value of $\Delta(-RT \ln K)$ obtained experimentally for the corresponding di-*ortho*-substituted acid. Using ionization data for benzoic acid and for *o*-methoxybenzoic acid,[4] the calculated pK value for 2,6-dimethoxybenzoic acid is 3.99; a lower pK value (3.31), which is in closer agreement with our experimental value, results when the calculation is based on a published value for the acidic ionization of 2,4,6-trimethoxybenzoic acid[5] in conjunction with the ionization constant for *p*-methoxybenzoic acid.[4]

In the case of 2,6-dichlorobenzoic acid we found[2] that the experimental value of pK (1.82) exceeds the calculated value (1.68), indicating that the first

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(1) This research was supported in part by the United States Air Force, through the Air Force Office of Scientific Research of the Air Research and Development Command, under contract No. CSO-670-55-21.

(2) The equation used in the calculation of pK, was

$$pK = pH - \log \frac{[B^-] + [H^+]}{[HB] - [H^+]} + \frac{0.509\sqrt{\mu}}{1 + 1.32\sqrt{\mu}}$$

See also M. M. Davis and H. B. Hetzer, THIS JOURNAL, **61**, 123 (1957), footnotes 10 and 11.

(3) J. Shorter and F. J. Stubbs, *J. Chem. Soc.*, 1180 (1949).

(4) The ionization data used were values for the thermodynamic dissociation constants determined by Dippy and associates and summarized in Table I (3)-(a), J. F. J. Dippy, *Chem. Rev.*, **25**, 151 (1939).

(5) W. M. Schubert, R. E. Zahler and J. Robins, *J. Am. Chem. Soc.*, **77**, 2293 (1955).

ortho-substituted chlorine atom is more effective than the second *ortho*-chlorine in enhancing the strength of benzoic acid. In contrast to this, 2,6-dimethoxybenzoic acid appears to owe its enhanced strength more to the second than to the first *ortho*-methoxy group.

Experimental

To prepare 2,6-dimethoxybenzoic acid, *m*-dinitrobenzene was converted successively to 2-nitro-6-methoxybenzonitrile and 2,6-dimethoxybenzonitrile by essentially the procedures described in references 6 and 7. The latter compound was then saponified.[7a] The over-all yield by these procedures is low. After crystallization from benzene using decolorizing charcoal, followed by heating in a vacuum oven to about 80°, the acid melted at 187–188°.[8] The purity by potentiometric weight titrations was 99.1%. The most probable impurities are traces of 2,6-dimethoxybenzonitrile or the amide that results from its partial saponification.[7c] Either of these compounds would be inert during titrations.

In determining pK two independently prepared 0.01 M solutions (100-ml. portions) were titrated with standard sodium hydroxide approximately ten times as concentrated, using glass and saturated calomel electrodes,[9] and with precautions to exclude carbon dioxide. The temperature was in the range 25 to 26°. Preliminary adjustments of the apparatus were made using NBS standard potassium hydrogen phthalate. The pH data used in computing pK were those recorded at 0.5-ml. intervals from 0.5 to 5.0 ml. inclusive. Both titrations yielded the average pK value 3.44 ± 0.01.

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(6) A. Russell and W. G. Tebbens, *Org. Syntheses*, **22**, 35 (1942).

(7) (a) N. J. Cartwright, J. I. Jones and D. Marmion, *J. Chem. Soc.*, 3499 (1952); (b) C. A. Lobry de Bruyn, *Rec. trav. chim.*, **2**, 205 (1883); (c) F. Mauthner, *J. prakt. Chem.*, **121**, 259 (1929).

(8) Others have reported the melting points 186–187° (ref. 7a,c) and 187.5–188.5° (A. Kreuchunas, *J. Org. Chem.*, **21**, 368 (1956)). In the latter case the starting material was 2-methylresorcinol.

(9) The titration apparatus was similar to that described by C. J. Penther and F. B. Rolfson, *Ind. Eng. Chem., Anal. Ed.*, **15**, 337 (1943).

MAGNETIC STUDIES OF SOME COBALT COMPLEXES OF AMINO ACIDS AND PEPTIDES[1]

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Received August 23, 1956

It has been pointed out[2] that the assignment of configuration and state of coördination of complexes can be obtained from knowledge of the magnetic moments. A search of the literature shows however that of the cobalt complexes of amino acids and peptides, the magnetic moments of only the histidine complexes[2a,b] have been reported. As part of an extensive program on studies of metal complexes of amino acids and peptides carried on in this Laboratory,[3] therefore, this note presents the results on magnetic studies of some cobalt complexes of amino acids and peptides.

Experimental

Materials.—Oxidized glutathione was a Schwarz product and contained about 14% associated alcohol. The material was dried *in vacuo* at 56° to constant weight. The hexamminecobaltic chloride was prepared and recrystallized according to the method of Bjerrum and McReynolds.[4] All other chemicals were of reagent grade, and were used without further purification.

Magnetic Measurements.—The magnetic susceptibilities of the solutions were measured by the Gouy method at room temperature. The apparatus, consisting of a General Electric Isthmus Electromagnet and an Ainsworth microbalance, has been described previously.[5,6] The procedure and the method of calculating magnetic moments are similar to those used by Li, *et al.*,[3a] in their magnetic study of the nickel complexes of imidazole.

Results

Table I summarizes the results of the magnetic studies. It was found that cobalt solutions containing cysteinate and tris-(hydroxymethyl)-aminomethane became diamagnetic rapidly in the presence of air. For this reason, the cysteinate and tris- solutions were carefully degassed and measured under vacuum.

TABLE I

MAGNETIC MOMENTS IN AQUEOUS SOLUTION

Concn. of metal ion, M		Concn. of ligand, M		Magnetic moment, B.M.
$CoCl_2$ or $Co(NO_3)_2$,	0.057			5.02
$CoCl_2$,	.057	Glycylglycinate,	0.224	4.63
$Co(NO_3)_2$,	.007		.136	4.62[a]
$CoCl_2$,	.01	Triglycinate,	.05	4.85
	.007	Methionate,	.12	4.64
	.007	Oxidized glutathione,	.03	5.05
	.04	Cysteinate,	.12	3.86[b]
	.06	Tris-,	.30	4.80[b]
	.05	Ammonia,	1	4.92
	.07	Glycinate,	0.10	4.94
	.05	Imidazole,	.25	5.04
$Co(NH_3)_6Cl_3$,	.05			0
$NiCl_2$,	.005	Cysteinate,	.05	0

[a] After passing air or oxygen through the solution overnight, the magnetic moment drops to zero. [b] See text.

Discussion

It is seen from Table I that all the cobaltous complexes listed therein are paramagnetic and the moments indicate the presence of three unpaired electrons per molecule. The calculated spin moment for three unpaired electrons is 3.88, and this value is obtained for the cobaltous cysteinate complex only. The bonds in the cobaltous complexes listed in Table I therefore are all predominantly ionic. Li and White[7] have found from ion-exchange experiments that the highest order complexes of glycylglycinate and triglycinate are of the CoA_2 type, and have concluded that the coördination number of Co^{++} toward these peptides is four. Since the position of minimum potential energy for four ionic bonds is the tetrahedral arrangement, the configuration of the cobaltous complexes of the peptides is tetrahedral. On the other hand, it has

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(1) This investigation was supported by Grant No. NSF-G1926 from the National Science Foundation.

(2) (a) J. A. Hearon, D. Burk and A. L. Schade, *J. Natl. Cancer Inst.*, **9**, 337 (1949); (b) L. Michaelis, *Arch. Biochem.*, **14**, 17 (1947); (c) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940.

(3) (a) N. C. Li, T. L. Chu, C. T. Fujii and J. M. White, *J. Am. Chem. Soc.*, **77**, 859 (1955); (b) N. C. Li and R. A. Manning, *ibid.*, **77**, 5225 (1955); (c) J. M. White, R. A. Manning and N. C. Li, *ibid.*, **78**, 2367 (1956).

(4) J. Bjerrum and J. P. McReynolds, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 216.

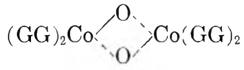
(5) T. L. Chu and S. C. Yu, *J. Am. Chem. Soc.*, **76**, 3367 (1954).

(6) T. L. Chu and T. J. Weismann, *ibid.*, **78**, 23 (1956).

(7) N. C. Li and J. M. White, unpublished data.

been shown[7,8] that the coördination number of Co^{++} toward cysteinate, ammonia and glycinate is six, so that the configuration of the cobaltous complexes of these is essentially octahedral. Hexamminecobaltic chloride and nickel(II) cysteinate $(NiCys_2)^{-2}$, ref. (3b), are diamagnetic, indicating that the configurations are covalent octahedral and covalent planar, respectively.

A cobalt–glycylglycine–oxygen complex was isolated and recrystallized by Gilbert, Otey and Price,[9] who obtained analytical data to show that the complex contained Co, glycylglycine (GG) and molecular oxygen in the molar ratio 2:4:1. Tanford, *et al.*,[10] postulated a structure of the complex to be



As seen from Table I, the magnetic moment of cobalt–glycylglycinate complex dropped from 4.6 to zero after passing air or oxygen through the solution overnight. This means then that the bonds in the oxygenated complex, which may be stated to be the d^2sp^3 octahedral configuration, are predominantly covalent; thus the nature of the bonds has changed upon oxygenation from essentially ionic to essentially covalent. Such a transition in bond nature with the formation of a binuclear oxygenated complex has also been observed on the oxygenation of histidine.[2a]

It has been shown[9] that $Co(cysteinate)_3^{-4}$ is oxidized to $Co(cysteinate)_3^{-3}$. The formation of Co(III) cysteinate complex from Co(II) cysteinate complex would be expected to take place more readily than the formation of a binuclear oxygenated complex, as in glycylglycinate. This has been experimentally observed.

In biochemical research, tris-(hydroxymethyl)-aminomethane has frequently been used as a buffer constituent.[3c] In view of our present experimental data, extreme precautions should be taken to exclude air, if cobaltous ion is to be used in the presence of tris-.

Acknowledgment.—The authors wish to thank the National Science Foundation for a research grant, and the Research Corporation for the use of a General Electric Isthmus Electromagnet.

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(8) A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., New York, N. Y., 1952.

(9) J. B. Gilbert, N. C. Otey and V. E. Price, *J. Biol. Chem.*, **190**, 337 (1951).

(10) C. Tanford, D. C. Kirk, Jr., and M. K. Cantooni, Jr., *J. Am. Chem. Soc.*, **76**, 5325 (1954).

COMMUNICATIONS TO THE EDITOR

MECHANICAL STABILITY OF COLLOIDAL DISPERSIONS

Sir:

A recent paper by Roe and Brass[1] on the mechanical stability of polystyrene lattices induces me to present now certain findings which were reported at the Symposium on Stability of Colloidal Dispersions held at the 110th Meeting of the American Chemical Society in Chicago, September, 1946.

I am again emphasizing, that none of the concepts on colloidal stability explain why dispersions generally stable if undisturbed, coagulate rapidly if the dispersion is subjected to mechanical action such as stirring, even at low speed.

The significant findings of Roe and Brass[1] that there is no apparent correlation between electrophoretic mobility and mechanical stability of K-palmitate stabilized polystyrene lattices is similar to the results of my investigations. I have studied K-laurate stabilized liquid and solid paraffin hydrocarbon dispersions, such as Nujol, hard paraffin wax and microcrystalline waxes in respect to their sensitivity to low speed stirring (60 r.p.m.), a much lower rate than that used by Roe and Brass (14,000 r.p.m.). In investigations of Freundlich, *et al.*,[2,3] similar results were reported.

No relationship was found between electrophoretic migration velocity and destabilization by stirring. The particle size of the emulsions was between 1–3 microns, *p*H 9.2–9.3. All of these remained stable for six months. The results are shown in Table I.

TABLE I

Dispersed phase	State	Migration Velocity (cm./volt sec. 10^{-5})	Coagulation (on stirring)
Nujol	Liquid	32	>14 days
Petrolatum	Liquid	32	>14 days
Microcrystalline wax	Solid	34	4 hours
Hard paraffin wax:			
at 25°	Solid	33	18 hours
at 60°	Liquid	34[a]	>14 days
with 10% toluene as solvent	Solid	32	>14 days

[a] Measured at room temperature.

Emulsions: 30 parts of 0.6 normal K laurate (*p*H 10.8) solution were premixed at 80° with 70 parts of the paraffin hydrocarbons and passed through a colloid mill. A thick paste formed on the spillway, and was collected over 40 parts of ice and agitated until it became homogeneous.

Stirring test: A paddle type stirrer was used of 6 cm. length and 2 cm. width; stirring rate, 60 r.p.m., a maximum linear velocity of 19 cm./sec.

Container: 200-ml. cylindrical closed with a water seal.

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(1) C. P. Roe and P. D. Brass, *Colloid Sci.*, **10**, 194 (1955).

(2) H. Freundlich and S. K. Basu, *Z. physik. Chem.*, **115**, 203 (1925).

(3) H. Freundlich and H. Kroch, *ibid.*, **124**, 155 (1926).

Size of the test sample: 150 ml.

Electrokinetic mobility: U-tube, moving boundary method was used.

Intermicellar liquid used to form the boundary was separated from the emulsions after coagulation by freezing.

Although the particle size was not quite uniform, the differences in the coagulation times on stirring are too large to be accounted for by particle size only.

Since then a large number of high polymer (polyvinyl acetate) dispersions have been examined and no correlation between storage and mechanical stability was found. Some dispersions which remained stable for several years could be coagulated by stirring (14,000 r.p.m.) in minutes and even seconds.

Previous investigations in this field were carried out by Freundlich and his school,[2] who found that, in the absence of a gas–liquid interface, coagulation by stirring does not take place, and by Heller.[4] The latter concluded that a critical zeta potential exists above which no mechanical coagulation takes place and that in the absence of a gas–liquid interface, mechanical coagulation can be induced by turbulent flow, when a deformation of the ionic layer around the particle occurs.

My investigations support those of Freundlich and now Roe and Brass's findings, that the zeta potential has no direct bearing on mechanical coagulation and that after termination of the stirring no further coagulation takes place.

Moreover, in our systems a weakening of the crystal lattice of the disperse phase by heat or solvent action produced mechanically stable dispersions, whereas the same material in the solid state was not stable.

With the experimental evidence available, no basis for a theoretical discussion of mechanical effects exists[5] and I have limited myself to present experimental results.

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[4] W. Heller and H. F. Roeder, *Trans. Far. Soc.*, **38**, 191 (1942); W. Heller, *Compt. rend.*, **198**, 1776 (1934), and **199**, 354 (1939).

[5] For example the results by H. L. Frisch, *J. Phys. Chem.*, **60**, 463 (1956).

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