[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICS, UNIVERSITY OF CHICAGO]

Molecular Compounds and their Spectra. II[1]

BY ROBERT S. MULLIKEN

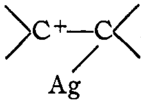
(1) A simple general quantum-mechanical theory is presented for the interaction of electron acceptors and donors (Lewis acids and bases) to form 1:1 or *n*:1 molecular compounds ranging from loose complexes to stable compounds. This puts into more accurate or more general form ideas which have been in frequent use for some time. The theory involves resonance between no-bond structures (A,B) and dative structures (A^-–B^+), where A is an acceptor atom, molecule, or ion and B is a donor atom, molecule, or ion. Two classes of donors (π, and *n* or onium, bases) and three classes of acceptors (π, *v* or vacant-orbital, and *d* or dissociative) are particularly considered; *i* (ionic) donors and acceptors are also mentioned. General and specific factors governing the strengths of interaction between acceptors and donors of various classes are deduced from the theory. (2) A special class of intense electronic absorption spectra characteristic of molecular compounds A·B, and non-existent for either partner A or B alone, is predicted. These are called charge-transfer spectra. (3) The forces which lead to complex-formation may be called charge-transfer forces. They may be of comparable importance to London's dispersion forces in accounting for van der Waals attractions. They have characteristic specific orientational properties of possible importance for the manner of packing of molecules in liquids, in molecular crystals, in heterogeneous systems, and in biological systems. They may also be important in adsorption. They should increase under compression and thus contribute to compressibilities. The effect of charge-transfer forces in lowering activation barriers for chemical reactions is briefly discussed. (4) The benzene–iodine and the $BX_3 \cdot NR_3$ types of molecular compound and the Ag^+ complexes are considered in detail. The characteristic absorption peak of the benzene–iodine and related complexes near λ3000, discovered by Benesi and Hildebrand, is identified with the predicted charge-transfer absorption. Its position and intensity are in good agreement with the theory. Theoretical considerations based on symmetries of quantum-mechanical wave functions often favor unsymmetrical geometrical configurations of molecular complexes. For example, they point to an off-axis position for the Ag^+ in the Ag^+–benzene complex, a result which is supported also by empirical evidence.

I. Introduction

The appearance in many cases of strong color on bringing together two colorless or nearly colorless organic compounds is well known. The effect is generally attributed to a loose reversible association ("molecular compound" or "molecular complex") of the original molecules in a definite ratio, most often 1:1. Equilibrium constants, heats of formation and other thermodynamic data for many such complexes have been established.

There is similar and other evidence for complexes between inorganic and organic molecules; for example, between halogen molecules and organic compounds,[2] and between Ag^+ and aromatic or unsaturated compounds.[3,4] Finally, such compounds as $R_3N \cdot BX_3$ may be viewed[5] as colorless molecular complexes of unusually high stability.

Many authors have discussed the structure of molecular complexes. For stable compounds like $R_3N \cdot BF_3$, the dative bond structure R_3N^+–B^-F_3 is generally accepted. Likewise, the view that a molecular complex is the result of the combination of an electron donor or base, say B, with an electron acceptor or Lewis acid,[44] say A, is widely held.

Notable contributions to the theory of molecular complexes have been made by Weiss[6] and by Brackmann.[5] Some of Dewar's ideas,[7] particularly on π complexes, are relevant. So also is Pauling's 1938 suggestion[3] that the $C_2H_4 \cdot Ag^+$ complex is made stable by resonance between a predominant no-bond structure and structures of the type .

Finally, a 1942 note by Woodward,[8] in which he advanced the idea of an "*intermolecular semi-polar bond*" in molecular complexes, comes close to the theme of the present paper; Woodward also refers to similar work by Bateman.

Neither Weiss's nor Brackmann's views appear acceptable *in toto*, but a selection and combination of their ideas with some extensions appears to lead to a satisfactory theory. This will be given below, including an explanation of the colors of molecular complexes and related phenomena, matters not treated satisfactorily by previous writers.

Weiss proposed that all molecular complexes have an essentially ionic structure B^+A^-, and pointed out that a *low ionization potential* for the base B, and a *high electron affinity* for the Lewis acid A, should then favor a stable complex. He attributed the color of molecular complexes to intense charge-resonance spectra arising within the ions in the complex.

Brackmann attributed molecular complex formation to "complex resonance," meaning quantum-mechanical resonance between a no-bond structure and a structure with a bond between the two partners A and B, but made no clear statement about ionic character in the latter structure. Brackmann insisted that (assuming colorless partners) the complex *as a whole* determines the color, that is, that the light absorption causing color is not localized in one of the partners. This is an important and, according to the present analysis, an essentially correct idea. Brackmann also emphasized that reversible formation of a resonance complex, by reducing the activation barrier, may often be a preliminary step in an irreversible chemical reaction.

The writer recently[2d] discussed the structure of

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(2) (a) H. A. Benesi and J. H. Hildebrand, THIS JOURNAL, **70**, 2382 (1948); **71**, 2703 (1949); (b) T. M. Cromwell and R. L. Scott, *ibid.*, **72**, 3825 (1950); (c) R. M. Keefer and L. J. Andrews, *ibid.*, **72**, 4677, 5170 (1950); **73**, 462 (1951); (d) R. S. Mulliken, *ibid.*, **72**, 600 (1950).

(3) S. Winstein and H. J. Lucas, *ibid.*, **60**, 836 (1938); 1:1, 2:1, and 1:2 Ag^+ complexes with ethylene, benzene, etc.

(4) L. J. Andrews and R. M. Keefer, *ibid.*, **71**, 3644 (1949); **72**, 3113, 5034 (1950).

(5) W. Brackmann, *Rec. trav. chim.*, **68**, 147 (1949).

(6) J. Weiss, *J. Chem. Soc.*, 245 (1942), and to some extent later papers.

(7) M. J. S. Dewar, *Nature*, **156**, 784 (1945); *J. Chem. Soc.*, 406, 777 (1946); "The Electronic Theory of Organic Chemistry," Oxford Clarendon Press, London, 1949.

(8) R. B. Woodward, THIS JOURNAL, **64**, 3058 (1942).

the complexes formed by halogen molecules (X_2 or XY) with aromatic (Ar) and other solvents, in terms of resonance between a predominant no-bond structure (Ar, X_2) and small admixtures of structures of the type ($Ar^+–X_2^-$). As was shown by Benesi and Hildebrand and others, the Ar·I_2 complexes, in addition to visible absorption attributable to the I_2 in the complex, have an intense characteristic ultraviolet peak near λ 3000.[2] This the writer at first attributed to a modified Ar absorption, but later, in a "Note added in Proof," to an Ar → X_2 electron-transfer process,[2d] in harmony with Brackmann's idea that any complex should have a characteristic absorption of its own.

The present paper develops this idea further as part of a general discussion of the structure of complexes and compounds between Lewis acids and bases, and of related matters. Because of the great variety and complexity of actual molecular situations, the discussion should be regarded at many points as approximate and tentative.

II. Structure and Charge-transfer Spectra of Molecular Complexes

The viewpoint indicated in Section I can be put into quantum-mechanical form by writing the wave function of the ground state N of any molecular compound A·B as

$$\psi_N = a\psi_0 + b\psi_1 + \cdots \qquad (1)$$

The acceptor A and donor B may in general be any suitable pair chosen from atoms, atom-ions, molecule-ions, molecules, or perhaps even solids, but in the present section with the limitation that both are in totally symmetrical singlet electronic ground states.[9]

In Eq. (1), ψ_0 is (with respect to covalent bonding at least) a "*no-bond*" wave function ψ(A,B). It has the form

$$\psi_0 = \psi(A,B) = \mathcal{A}\psi_A\psi_B + \cdots \qquad (2)$$

where $\mathcal{A}$ denotes that the product $\psi_A\psi_B$ of the wave functions of A and B is to be made antisymmetric in all the electrons, and the terms indicated by + · · · · represents such small modifications[10] as might be expected from hitherto recognized types of of polarization effects. In Eq. (1), ψ_1 is a "dative" wave function corresponding to *transfer of an electron* from B to A accompanied by the establishment of a (usually weak, because of the distance between A and B) covalent bond between the odd electrons in A^- and B^+. That is

$$\psi_1 = \psi(A^- - B^+) + \cdots \qquad (3)$$

where the + · · · again indicates small modifying terms.[10]

In Eq. (1), the + · · · indicates additional terms $c\psi_2 + \cdots$.[11] However, in the present Section ψ_N will be approximated by the sum of the first two terms alone. If ψ_N is then normalized so that $\int\psi_N^2\,dv = 1$, the coefficients a and b are related by

$$\left.\begin{array}{l} a^2 + 2abS + b^2 = 1 \\ \text{where} \quad S \equiv \int\psi_0\psi_1 dv \end{array}\right\} \qquad (4)$$

We next consider force and energy relations. For loose complexes, second-order perturbation theory will give an adequate approximation. Then[12]

$$\left.\begin{array}{l} W_N \equiv \int\psi_N H\psi_N\,dv \approx W_0 - \dfrac{(H_{01} - SW_0)^2}{(W_1 - W_0)} + \cdots \\ \quad\text{where} \quad W_0 \equiv \int\psi_0 H\psi_0\,dv;\ W_1 \equiv \int\psi_1 H\psi_1\,dv \\ \qquad\qquad\quad H_{01} \equiv \int\psi_0 H\psi_1\,dv \end{array}\right\} \qquad (5)$$

H is the *exact* Hamiltonian operator for the entire set of nuclei and electrons. W_0 is equal to the sum of the separate energies of A and B, modified by any energy of attraction arising from ionic, ion-dipole, dipole-dipole, hydrogen bridge, London dispersion, or classical-type polarization forces, also by any energy of repulsion arising from exchange repulsion forces. W_1 has a similar meaning, but includes also attraction energy of ionic and covalent bonding.

The *resonance energy* in the ground state due to interaction of ψ_1 with ψ_0 is now given by $W_0 - W_N$ of Eq. (5). This should be large if $(H_{01} - SW_0)^2$ is large, which in general is true only if ψ_0 and ψ_1 overlap strongly (and are of the same symmetry—see below) and if $W_1 - W_0$ is reasonably small. The *energy of formation* of the complex is

$$Q = (W_A + W_B) - W_N = (W_A + W_B - W_0) + (W_0 - W_N) \qquad (6)$$

The *charge-transfer forces* corresponding to the resonance energy may either be *assisted* or *opposed* by the forces of familiar type mentioned above, according as $W_A + W_B \gtrless W_0$.

In using Eq. (6) for an actual molecular complex, it is necessary to take values of H_{01}, W_1, W_0 appropriate to the actual geometrical configuration of the complex in equilibrium (or with only its zero-point vibration energy) in its ground state. However, Eq. (5) and (6) can of course *also* be used for other configurations, for example, in constructing a curve or surface showing how W_N changes as two separated molecules A and B approach each other.

Second-order perturbation theory yields the following approximate relation for the coefficients in Eq. (1)[12]

$$\rho \equiv b/a \approx -(H_{01} - SW_0)/(W_1 - W_0) \qquad (7)$$

Eq. (4) can then be used to get a and b individually.

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(9) If A or B is an atom or atom-ion, this means a *closed-shell* electronic structure in ordinary terminology. If A or B is a molecule or molecule-ion, this also means a closed-shell structure if the description is given in terms of *molecular orbitals*. If, however, the description is given in terms of *atomic orbitals*, it means that all valence electrons are paired in electron-pair bonds.

(10) It will be convenient to consider these well-recognized effects as included in ψ_0 of Eq. (2) or ψ_1 of Eq. (3), in order to distinguish them from the effect of the interaction between ψ_0 and ψ_1. Strictly speaking, these two kinds of effects are not always entirely independent; thus if A and B in ψ_0 are oppositely charged ions, some part of their mutual polarization is expressed by the terms in ψ_1 in Eq. (1).

(11) If A and B are neutral molecules, a term ψ_2 of structure $A^+–B^-$ (B acting as acid and A as base) may be of appreciable importance. A second excited state ψ_F usually somewhat higher than ψ_E of Eq. (2) may then be important for the spectrum of the complex; ψ_E and ψ_F as well as ψ_N will then be mixtures of ψ_0, ψ_1 and ψ_2. Frequently also, further terms of structure $A^-–B^+$ derived from low excited states of A^- or sometimes of B^+ may be of appreciable importance (see *e.g.*, ref. 34).

(12) Equations (5), (7), (10) and (11) are generalizations of familiar expressions. They may be derived by, for example, following the procedure used by H. Margenau and G. M. Murphy, "The Mathematics of Physics and Chemistry," Van Nostrand Co., Inc., New York, N. Y., 1943, in obtaining Eq. (11-106) and (11-108); modified, however, by starting from the secular equation (11-97) instead of (11-104).

An essential requirement in Eq. (1) is that ψ_1 shall be of the same group-theory species as ψ_0; otherwise H_{01} and S are zero and there is no resonance. This means usually that ψ_1 must be (1), of the same spin type as ψ_0; (2) of the same orbital species under the group-theoretical classification corresponding to the over-all symmetry of the complex as a whole. With our supposition that ψ_A and ψ_B in Eq. (2) are both totally symmetrical singlet states,[9] ψ_0 is necessarily also a totally-symmetrical singlet state of the symmetry of the complex, and ψ_1 must then be of this same type. Requirement (1) may be somewhat relaxed in the case of heavy atoms (*e.g.*, iodine) with very strong spin-orbit coupling; but in this event, ψ_1 must definitely be of the same *spin-orbit* species as ψ_0.

If the complex has no over-all symmetry, requirement (2) vanishes. However, unless ψ_1 is of the same group-theory species as ψ_0 under the species-classification of whatever *approximate* symmetry exists in the neighborhood of the A–B interaction zone, $H_{01} - SW_0$ will still be too small to yield a stable complex.

The symmetry requirements just stated should often be important in determining the geometrical arrangement of the partners in a complex. Thus if for a particular geometrical configuration the lowest-energy state of A^-–B^+ is of a different group-theory species than ψ_0, one must go to an *excited* state of A^-–B^+ to find an acceptable ψ_1. Because of the inverse proportionality of the resonance energy to $W_1 - W_0$ (see Eq. (5)), the situation just described is unfavorable for a stable complex. However, there may then exist a different geometrical configuration whose symmetry permits ground-state A^-–B^+ to interact with ψ_0 and thus to serve as ψ_1. If so, then, other things being equal, this geometrical configuration will be favored for the actual complex. Several examples of the application of these considerations are described in a previous paper[2d] and in the later sections of the present paper.

Aside from the symmetry considerations just presented, no theoretical analysis of the magnitudes to be expected in various cases for $H_{01} - SW_0$ will be attempted here. Suffice it to say that it is theoretically reasonable in general to expect $H_{01} - SW_0$ to be of adequate size to account for the observed phenomena in terms of the present theory. Conversely, estimates[2d] of other forces[10] to which complex-formation has often been attributed indicate these to be of inadequate size, particularly in such cases as Bz·I_2 where the component molecules do not possess even dipole fields.

If A·B is a loose complex between closed-shell systems, with little overlapping between A and B, the covalent bond in the ψ_1 structure A^-–B^+ is necessarily weak. It must then be formulated in accordance with Heitler–London theory. However, the bond need not necessarily be interatomic, that is, between electrons of two specific atoms. It may instead be intermolecular; or between an atomic and a molecular electron. Thus, for example, if B is Bz (benzene), the odd electron in B^+ which is to form a bond may most conveniently be described as occupying an MO (molecular orbital) of the benzene ring as a whole—one of the πMO's. (This is the viewpoint used by Dewar[7] in speaking of π complexes.) Then if, for example, A is I_2, the odd electron in A^- may similarly be described as occupying an MO of I_2^-. In this case we have an intermolecular electron-pair bond.[13] In the Bz·Ag^+ complex the bond in ψ_1 (structure Bz^+–Ag) is between a Bz^+ electron in an MO and an Ag electron in an AO.

In more stable complexes or compounds such as $BF_3 \cdot NR_3$ or R_3NO, the electron-pair bond in ψ_1 (in these cases ψ_1 is probably lower in energy than ψ_0) is to a large extent localized between the N and B atoms or the N and O atoms, respectively.

For tight complexes or stable compounds, Eq. (5), (7) are no longer more than qualitatively correct.[14] A fairly good approximation can then be obtained if Eq. (1) is replaced entirely by an MO description for the complex or molecule as a whole, including a rather strongly polar N–B or N–O bonding MO occupied by two electrons. For *loose* complexes, such an MO description in terms of MO's of the complex as a whole would not be a good approximation.

In loose molecular complexes we expect $a^2 >> b^2$ in Eq. (1). In compounds such as $BX_3 \cdot NR_3$ or R_3NO, a and b should be more nearly equal, probably with $b^2 > a^2$.

If the ground state electronic wave function is given by Eq. (1), it necessarily follows that there exists an *excited state* function ψ_E of the form

$$\psi_E = a^*\psi_1 - b^*\psi_0 + \cdots \quad (8)$$

with $a^* \approx a$, $b^* \approx b$. In the present Section, ψ_E will be approximated by the first two terms on the right of Eq. (8).[11] Then, corresponding to Eq. (4),

$$a^{*2} - 2a^*b^*S + b^{*2} = 1 \quad (9)$$

In the approximation of second-order perturbation theory, the following relations hold[12]

$$W_E = W_1 + \frac{(H_{01} - SW_1)^2}{(W_1 - W_0)} + \cdots \quad (10)$$

$$-\rho^* = b^*/a^* = -(H_{01} - SW_1)/(W_1 - W_0) \quad (11)$$

The existence of an *intense absorption spectrum* corresponding to the transition $\psi_N \rightarrow \psi_E$ can be predicted, and its total absolute intensity[15] approximately computed. Since if $a^2 >> b^2$, ψ_N has nearly pure no-bond character and ψ_E nearly pure ionic character, the spectrum associated with the transition may then be called an *intermolecular charge-*

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(13) Alternatively, one may speak of a bond between a particular carbon atom π electron and a particular iodine atom electron, but if so, it is necessary to use a cumbersome description in terms of resonance among numerous bond-structures of this type.

(14) The predictions made about state E and the N → E transition in this Section should therefore for $F_3B.NMe_3$ and similar stable complexes be regarded with some reserve. The non-localized MO viewpoint suggests that E may (for the equilibrium R of $F_3B.NMe_3$) be a rather high-energy state, in which case it may exist only in mixture with several other excited states.

(15) The spectrum $\psi_N \rightarrow \psi_E$ should in general appear as a broad band or group of bands. The present computation refers to the total integrated absorption intensity, as discussed by R. S. Mulliken, *J. Chem. Phys.*, **7**, 14 (1939); see Mulliken and Rieke, "Reports on Progress in Physics, of the Physical Society, London," Vol. VIII, p. 231, 1941, for some corrections.

transfer spectrum: light absorption causes an electron to jump from B to A.[16]

It will be noted that the predicted charge-transfer spectrum is characteristic of the molecular complex A.B as such, and cannot be attributed to either of the partners A or B, being in this respect in agreement with one of the ideas advanced by Brackmann. Additional, *intramolecular*, spectra of A and B, more or less modified by their association, are of course also to be expected.

Frequently, intramolecular and charge-transfer spectra may overlap, or sometimes also interfere quantum-mechanically (that is, their excited states may partially mix). In such cases, it may not be possible to identify charge-transfer spectra unambiguously or uniquely.

To obtain the predicted intensity[15] of the charge-transfer absorption, the quantum-mechanical dipole moment μ_{EN} of the transition may first be computed. This is given by

$$\mu_{EN} = -e\int\psi_E\Sigma \mathbf{r}_i\psi_N\,dv \qquad (12)$$

where $\mathbf{r}_i$ is the vector distance of the i^{th} electron from any convenient origin.[17] Using Eqs. (1) and (8), Eq. (12) gives

$$\mu_{EN} = a^*b\mu_1 - ab^*\mu_0 + (aa^* - bb^*)\mu_{01} \qquad (13)$$

where

$$\mu_1 \equiv -e\int\psi_1\Sigma \mathbf{r}_i\psi_1\,dv \qquad (14)$$

$$\mu_0 \equiv -e\int\psi_0\Sigma \mathbf{r}_i\psi_0\,dv \qquad (15)$$

$$\mu_{01} \equiv -e\int\psi_1\Sigma \mathbf{r}_i\psi_0\,dv \qquad (16)$$

From the orthogonality condition $\int\psi_N\psi_E dv = 0$ and Eqs. (1) and (8), the following relation is obtained

$$\left.\begin{aligned}(a^*b - ab^*) &= -(aa^* - bb^*)S\\ \text{where}\quad S &\equiv \int\psi_0\psi_1\,dv\end{aligned}\right\} \qquad (17)$$

Making use of Eq. (17), Eq. (13) can be rewritten in the convenient form

$$\mu_{EN} = a^*b(\mu_1 - \mu_0) + (aa^* - bb^*)(\mu_{01} - S\mu_0) \qquad (18)$$

As we shall see below, the term in $\mu_1 - \mu_0$ is the main one.[18] The magnitude of $\mu_1 - \mu_0$ is easily estimated; it is essentially the change in the ordinary permanent dipole moment which would be produced by displacing one electron from a particular orbital in B to a particular orbital in A, with the nuclei held fixed.[17] Letting $\mathbf{r}_B$ and $\mathbf{r}_A$ denote the average positions of the electron in the B or A orbital, respectively, then $\mu_1 - \mu_0$ is, at least very nearly, $-e(\mathbf{r}_A - \mathbf{r}_B) = e(\mathbf{r}_B - \mathbf{r}_A)$. Thus $(\mu_1 - \mu_0)$ should be of the order of magnitude of 10 debye units. The magnitude of the factor a^*b should be between 0.1 or 0.2 and 0.7 in all molecular complexes sufficiently stable to be detected (see discussion of the benzene–iodine complex in Section III below).

In evaluating μ_{01}, it will be sufficient for present purposes to use approximations for ψ_0 and ψ_1. If we describe the structure of each partner in terms of MO's of that partner, the process $\psi_0 \rightarrow \psi_1$ involves the jump of one of a pair of outer electrons, initially occupying an MO ϕ_B, in B, into a previously unoccupied MO ϕ_A in A. This occurs in such a way that the second electron, left in ϕ_B, remains paired to the electron now in ϕ_A, but now by a covalent bond. (If one or both partners are atoms, read AO instead of MO.) On substituting the expressions for ψ_0 and ψ_1 conforming to these specifications into Eq. (16), and integrating, one finds, to a close approximation[19]

$$\left.\begin{aligned}&\mu_{01} - S\mu_0 \approx eS(\bar{\mathbf{r}}_B - \bar{\mathbf{r}}_{AB})\\ &\text{where}\quad \mathbf{r}_B \equiv \int\phi_B\mathbf{r}\phi_B\,dv;\ \ S_{AB}\bar{\mathbf{r}}_{AB} \equiv \int\phi_A\mathbf{r}\phi_B d\tau\\ &S \equiv \int\psi_0\psi_1\,dv \approx 2^{1/2}(1 + S^2{}_{AB})^{-1/2}S_{AB};\ \ S_{AB} \equiv \int\phi_A\phi_B d\tau\end{aligned}\right\} \qquad (19)$$

In Eq. (19), $\bar{\mathbf{r}}_{AB}$ is the average position of an electron having a charge distribution of the form of the overlap of the MO's ϕ_A and ϕ_B, and is therefore located between $\mathbf{r}_B$ and $\mathbf{r}_A$. In Eq. (19), S of Eq. (4) or (17) has been approximately evaluated in terms of the overlap integral S_{AB} of the MO's ϕ_A and ϕ_B.

Putting the first of Eqs. (19) into Eq. (18), with $\mu_1 - \mu_0 \approx e(\bar{\mathbf{r}}_B - \bar{\mathbf{r}}_A)$ as discussed above, one obtains

$$\mu_{EN} = a^*be(\bar{\mathbf{r}}_B - \bar{\mathbf{r}}_A) + (aa^* - bb^*)eS(\bar{\mathbf{r}}_B - \bar{\mathbf{r}}_{AB}) \qquad (20)$$

In case the molecular complex has an axis of symmetry running through the centers of ϕ_A and ϕ_B, then both terms in Eq. (20), and so μ_{EN}, are directed along that axis. The first term is directed from A toward B, and if $a > b$ the second is directed likewise and the two terms add. For loose complexes ($a^2 >> b^2$) the first term is much the larger, mainly because of the smallness of S if ϕ_A and ϕ_B do not overlap strongly.[18]

To obtain the total intensity of the $N \rightarrow E$ absorption in terms of the so-called oscillator strength f of the transition, one may use

$$f = (4.704 \times 10^{-7})\bar{\nu}(\mu_x{}^2 + \mu_y{}^2 + \mu_z{}^2) \qquad (21)$$

where μ_x, μ_y, μ_z here refer to the x, y and z components of the vector μ_{EN} *in debye units*, and $\bar{\nu}$, *in cm.*$^{-1}$, is a suitably weighted average wave number over the $N \rightarrow E$ band or bands (roughly the value of ν at the peak of intensity).[15]

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(16) The intermolecular charge-transfer spectra discussed here are related to the *interatomic charge-transfer* spectra discussed by R. S. Mulliken (*J. Chem. Phys.*, **7**, 20 (1939) and later papers; see especially Mulliken and Rieke, Ref. 15). For a review on electron-transfer spectra, see E. Rabinowitch, *Rev. Modern Phys.*, **14**, 112 (1942). One of the earliest recognized types is that involved in the photographic process: $[\mathrm{Ag^+Br^-}] \rightarrow [\mathrm{AgBr}]$ (Lenard, 1909; Fajans, 1922).

(17) Equation (12) is based on the usual assumption that the positions of the nuclei do not change during the electronic transition N → E. According to the Franck-Condon principle, this introduces but minor errors into the computed total absolute intensity (see Mulliken, and Mulliken and Rieke, ref. 15, for detailed analysis). Note that because of the rigorous orthogonality of the (true exact) wave functions ψ_E and ψ_N, μ_{EN} is independent of the origin of coördinates for the $\mathbf{r}_i$, and (when the assumption mentioned above is used) does not involve the nuclear coördinates. Note that throughout Eqs. (12)–(20), all the μ's, like the $\mathbf{r}$'s, are *vector quantities*.

(18) In the "Note added in Proof," on p. 605 in ref. 2d, it was erroneously assumed that the first term was less important than the second.

(19) The evaluation proceeds by taking ψ_0 and ψ_1 as antisymmetrized MO-product functions as follows (*cf.* R. S. Mulliken, *J. Chem. Phys.*, **8**, 234 (1940), Section III, for notation and a similar discussion; the MO's of the two *molecules* A and B play the same role in the present case as the AO's of the two *atoms* in the discussion cited):

$$\psi_0 \approx \mathfrak{N}_0(n!)^{-1/2}\sum_P(-1)^P\,P\phi_B\alpha(1)\phi_B\beta(2)\phi_3\alpha(3)\cdots\phi_n\beta(n)$$

$$\psi_1 = 2^{-1/2}(1 + S^2{}_{AB})^{-1/2}(\psi_1 + \psi_{11})$$

$$\psi_1 \approx \mathfrak{N}_1(n!)^{-1/2}\sum_P(-1)^P\phi_B\alpha(1)\phi_A\beta(2)\phi_3\alpha(3)\cdots\phi_n\beta(n)$$

$$\psi_{11} \approx \mathfrak{N}(n!)^{-1/2}\sum_P(-1)^P\phi_A\alpha(1)\phi_B\beta(2)\phi_3\alpha(3)\cdots\phi_n\beta(n)$$

The normalizing factor in the expression for ψ_1 is obtained in the usual manner (see Eq. (19) for definition of S_{AB}); n is the total number of electrons in the complex; $\phi_1\cdots\phi_n$ are A and B MO's occupied by electrons which remain undisturbed during the process $\psi_0 \rightarrow \psi_1$. (Actually ϕ_1 and ϕ_4, and so on, are identical in pairs, but the electrons occupying them differ in spin —α or β.)

Substituting the above expressions for ψ_0 and ψ_1 into Eq. (16), one obtains (aside from certain factors including $\mathfrak{N}_0\mathfrak{N}_1$ which on multiplying together yield a factor of 1, either exactly or very nearly: compare the reference cited above) the following

$$\mu_{01} = -Se(\bar{\mathbf{r}}_B + \bar{\mathbf{r}}_{AB} + \bar{\mathbf{r}}_3 + \cdots \mathbf{r}_n)$$

In this expression, S means $2^{1/2}(1 + S^2{}_{AB})^{-1/2}S_{AB}$ (*cf.* Eq. (19)); the near or exact equality of S of Eq. (17) to this is readily obtained for the case that ψ_0 and ψ_1 are as given above. Now it is readily seen that if ψ_0 is as given above, μ_0 is given by

$$\mu_0 = -e(\bar{\mathbf{r}}_B + \bar{\mathbf{r}}_B + \bar{\mathbf{r}}_3 + \cdots \bar{\mathbf{r}}_n)$$

from which and the expression just given for μ_{01}, the first of Eqs. (19) follows at once.

Here it is important to point out that, since Eqs. (1) and (8) give in general only somewhat rough approximations for ψ_N and ψ_E,[11] Eq. (20)–(21) are correspondingly rough. However, it would seem that they should in general be reliable as to order of magnitude. The most essential fact is that they predict high intensities for N → E transitions even in loose complexes.

* * * *

The preceding discussion can be extended to n:1 molecular complexes, provided they are loose so that one resonance structure is predominant. Eq. (1) may then be generalized to

$$\psi_N = a\psi_0 + \Sigma b_i\psi_i + \cdots \qquad (22)$$

provided $a^2 > \Sigma b_i^2$. Thus for a complex A·B·A or B·A·B (for example, B = benzene, A = Ag^+ or I_2), provided the two A's are in equivalent locations with respect to the B or the two B's with respect to the A, we have

$$\psi_N = a\psi_0 + b(\psi_1 + \psi_1') + \cdots \qquad (23)$$

In Eq. (23), ψ_0 is a no-bond structure and ψ_1 and ψ_1' are structures $A{\cdot}B^+{-}A^-$ and $A^-{-}B^+{\cdot}A$ or $B^+{-}A^-{\cdot}B$ and $B{\cdot}A^-{-}B^+$.

The resonance energy for a loose n:1 complex should be given approximately by a sum of terms of the form of $W_0 - W_N$ of Eq. (5), one for each ψ_i in Eq. (22). For a 1:2 or 2:1 complex this means merely multiplying the result of Eq. (5) by a factor 2. More accurately, there will be a saturation effect diminishing somewhat the resonance energy of an n:1 complex, but this should not become important as long as Σb_i^2 is sufficiently small compared with a.[2] Repulsions between the different A's attached to a single B, or the B's attached to an A, may cause a further diminution.

From the empirical fact that molecular compounds of the same 1:1 composition for which there may be evidence in solution often appear also as crystalline solids, it seems probable that charge-transfer forces operate in more or less localized fashion in much the same way in such solids (which may also be regarded as n:n complexes, n exceedingly large) as in 1:1 or n:1 complexes in vapor or solution. However, no attempt at a theoretical analysis will be made here.

Another situation to which it seems probable that the present theory can in many cases be extended is that of an electron acceptor or donor adsorbed on or reacting with a metal or solid, the latter then acting as an electron donor or acceptor, respectively.

III. The Benzene–Iodine and Related Loose Complexes

The preceding discussion can be clarified by discussion of the benzene–iodine complex. As Benesi and Hildebrand have shown,[2] this has an intense characteristic absorption near λ 2900. It will be convenient to begin by computing the f value for this absorption on the hypothesis that it is an intermolecular charge-transfer spectrum.

If we assume the most compact and most probable model,[2d] with the iodine molecule resting on the benzene molecule with its axis parallel to the plane of the benzene and its center on the sixfold axis of the benzene, then μ_{EN} lies along the latter axis. Calling this the z axis, Eq. (20) becomes

$$\mu_{EN} = a^*be(\bar z_B - \bar z_A) + (aa^* - bb^*)eS(\bar z_B - \bar z_{AB}) \qquad (24)$$

Here benzene is the donor (B) and iodine the acceptor (A),[2a–d] and $\bar z_A$ and $\bar z_B$ are evidently the z values of points on the z axis near the centers of the two molecules. Allowing for some compression by the attractive forces forming the complex, $\bar z_B - \bar z_A$ may be estimated[2d] as 3.4 Å. and $\bar z_B - \bar z_{AB}$ as 1.7 Å. The value of S is very uncertain, but 0.1 seems reasonable.[20]

We next need values of a, a^*, b and b^*. That of b can be estimated to be roughly 0.17 from the dipole moment μ_N of the benzene–iodine complex, as determined from Fairbrother's data.[21] From this and the assumed value of S one obtains

$$a = 0.97,\ a^* = 0.99,\ b^* = 0.27$$

substituting in Eq. (22), one obtains

$$\mu_{EN} = (2.69 - 0.75) = 3.45\ D$$

The two terms 2.69 and 0.75 correspond, respectively, to the first and second terms in Eq. (24). From this value of μ_{EN}, together with $\nu = 3.36 \times 10^4$,[2a] and using Eq. (21), one obtains $f = 0.19$. The observed value[22,23] is 0.30. The agreement is satisfactory in view of uncertainties in both the theoretical and observed values.

The above b value of 0.17, giving $b^2 = 0.028$, corresponds to 2.8% of ionic character in state N.

For further understanding, Fig. 1 has been constructed to indicate how the energies $W_N(R)$ and $W_E(R)$ of states N and E may vary with the distance R between the centers of the benzene and iodine molecules, and how $W_N(R)$ and $W_E(R)$ may have arisen as the result of a resonance interaction between states ψ_0 and ψ_1 of Eq. (2) with respective energies $W_0(R)$ and $W_1(R)$. The energy $W_N(\infty) = W_0(\infty)$ is taken as zero. $W_0(R)$ corresponds to constant energy with decreasing R down to 3.7 Å., then a slight dip (dispersion force attraction), then a pronounced rise (exchange

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(20) Note that $S = 2^{1/2}(1 + S^2_{AB})^{-1/2}S_{AB}$ by Eq. (19). In ref. 2d, "an upper limit for reasonable estimates of S_{AB} [there called S] appears to be about 0.1–0.2."

(21) First the value $\mu_N = 0.72\ D$ is obtained by the method indicated in footnote 19 of ref. 2d, revised in accordance with ref. 2b to the basis that iodine in pure benzene is 70% complexed. Now theoretically, if ψ_N is given by Eq. (1)—see also Eq. (15), (16)—we have

$$\mu_N = \int \psi_N M \psi_N\, dv = a^2\mu_0 + b^2\mu_1 + 2ab\mu_{01}$$

But $\mu_0 = 0$, and using Eq. (19) for μ_{01}, with $\bar z_B - \bar z_{AB} = \frac{1}{2}(\bar z_B - \bar z_A)$ in accordance with the values of $\bar z_B - \bar z_{AB}$ and $\bar z_B - \bar z_A$ assumed above, and putting $\mu_1 = e(\bar z_B - \bar z_A)$, we have $2\mu_{01} = S\mu_1$. Hence

$$0.72 = \mu_N = (b^2 + abS)\mu_1 = (b^2 - 0.1b)\mu_1 = 16.33(b^2 - 0.1b)$$

if we put $a = 1$ (nearly enough correct), $S = 0.1$, and $\mu_1 = e(\bar z_B - \bar z_A) = 16.33\ D$, using the values of S and $(\bar z_B - \bar z_A)$ assumed in the text above. From this, $b = 0.17$. However, mainly because of its strong dependence on the uncertain quantity S, this value of b cannot be considered reliable.

(22) An unpublished f value of 0.21 per mole of *total* I_2 in benzene by Green and Rees, quoted by N. S. Bayliss (*J. Chem. Phys.*, **18**, 292 (1950)) is probably the most reliable (see ref. 2, Table II, for summary of earlier data). Assuming that this f value comes only from the 70% of the I_2 which is associated (*cf.* ref. 21), the f value for the complexed molecules is 0.30.

(23) The observed value[22] is measured in benzene solution, whereas the computed value is applicable to isolated molecules, as in a vapor. However, experience indicates that actually there may be little difference between vapor and solution f values (*cf.* L. E. Jacobs and J. R. Platt, *J. Chem. Phys.*, **16**, 1137 (1948), including references to earlier work).

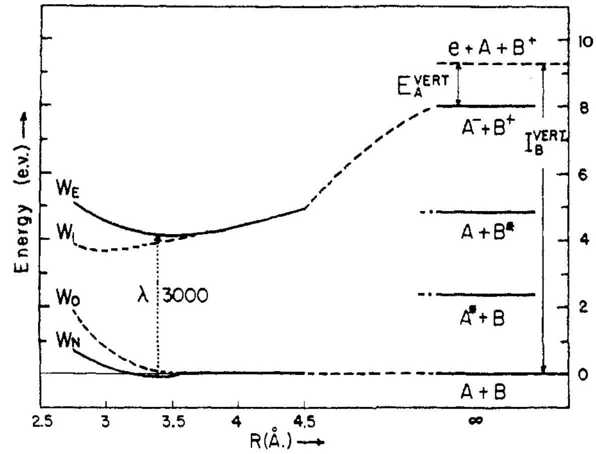

Fig. 1.—Some potential energy curves $W(R)$ for the benzene-iodine complex as a function of the distance R between the centers of the two molecules, assuming Model R described in Section III of the text. Close to the curve W_E there should be a second curve coming also from $A^- + B^+$ (see text). Additional curves (not drawn in) come from $A^* + B$, $A + B^*$, etc.

repulsions). But at the smaller R values resonance between ψ_0 and ψ_1 depresses W_0 to become W_N and raises W_1 to become W_E. This interaction is expected now to increase rapidly with decreasing R because of increase of H_{01}^2 and, to a lesser extent, decrease of $W_1 - W_0$, in Eq. (5). Figure 1 was drawn by first sketching in W_0 on the basis of qualitative considerations, then W_1 using roughly quantitative considerations now to be detailed, then drawing W_N and W_E on the basis of the expectations just outlined.[24]

The W_1 curve was based on the following: (1) For $R = \infty$, the energy is higher for $A^- + B^+$ than for $A + B$ (see Fig. 1) by the amount

$$I_B^{\text{vert}} - E_A^{\text{vert}}$$

I_B^{vert} and E_A^{vert} are the ionization energy of the benzene molecule and the electron affinity of the iodine molecule, for *vertical processes*. For benzene, I_B is 9.24 e.v., and I_B^{vert} must be practically the same.[25] For iodine, E_A^{vert}, which should be considerably less than E_A, has been estimated as 1.8 e.v.[26] (2) As A^- and B^+ approach, $W_1(R)$ drops because of the Coulomb attraction energy e^2/R until perhaps $R = 3.4$ Å. (3) At sufficiently small R values, covalent binding between the odd electron on I_2^- and that on Bz^+ should lower the energy somewhat further[25] (perhaps 0.3–0.5 e.v.), but also, (4), exchange repulsions set in between the closed shells of electrons in the two molecules, and finally predominate, causing $W_1(R)$ to rise again. $W_1(R)$ in Fig. 1 for $R < 3.3$ Å. has been drawn in qualitative agreement with considerations (3) and (4).[26]

One expects some modification in the magnitudes of effects (1) and (2) if the molecules approach not in the vapor state, but in solution. A quantitative treatment would require an elaborate analysis, but for a non-ionizing medium of low dielectric constant, a rough consideration indicates that the modifications required may not be large. They have been ignored in constructing Fig. 1, which is intended only to be illustrative. A further correction, also ignored, would allow for the fact that the positive and negative charges on Bz^+ and I_2^-, respectively, are not concentrated at the centers of the two molecule-ions.

By the Franck–Condon principle, the peak frequency ν_{NE} of the N → E absorption should correspond closely to $W_E - W_N$ measured *vertically up* at the R value (assumed in Fig. 1 to be 3.4 Å.) of the minimum of curve W_N. Curve W_E in Fig. 1 was adjusted to make ν_{NE} agree with the observed value of 33,600 cm.$^{-1}$ (4.17 e.v.). This was done using items (1)–(4) stated above for curve W_1, except that I_A^{vert} was taken as 1.2 e.v.[26]; W_E at 3.4 Å. was taken 0.15 e.v. above W_1.[27] The minor numerical adjustments made here are not unreasonable. This and the satisfactory agreement noted above between observed and computed f values give considerable support to the essential validity of the present theory in explaining the λ 2900 absorption.

A brief consideration of the expected complete absorption spectrum of $Bz{\cdot}I_2$ is now in order. In general for a complex A·B this should include: (a) absorption characteristic of A and B; (b) several charge-transfer spectra, corresponding to various excited states of B^+ and A^-. At the right of Fig. 1 ($R = \infty$), energy levels are shown for the two lowest spectroscopically important excited states of $I_2 + Bz$. In the free molecules, these give rise to absorption near λ 5200 (I_2) and near λ 2600 (Bz).[2] In the complex, absorption occurs[2] with a maximum near λ 5000. The slight shift from λ 5200 for free I_2 to λ 5000 for I_2 in the complex tells us that the distance between the $W(R)$ curves drawn from A + B, *i.e.*, W_N, and from A* + B (not shown in Fig. 1) increases by about 0.1 e.v. in going from $R = \infty$ to $R = 3.4$ Å., and means that A* + B has slightly less tendency to form a complex than A + B. Location of an additional absorption by $Bz{\cdot}I_2$ near λ 2600 corresponding to λ 2600 of benzene would be of considerable interest.[28]

Thus far, the *resting* model, R (see second paragraph of this Section) has been assumed. Arguments for this will now be given, also some necessary details about the electronic structures of Bz^+ and I_2^-. First, axes x and y may be taken in the benzene plane as indicated in Fig. 2, with z up from this plane. Next, it is necessary to notice certain sub-types of model R: namely R_x and R_y, with iodine axis parallel to x or y axis, respectively, both with symmetry C_{2v}; and intermediate models with symmetry C_2. These sub-types probably differ very little in energy and spectroscopic properties, even in methylated benzenes (*cf.* p. 604 of ref. 2d).

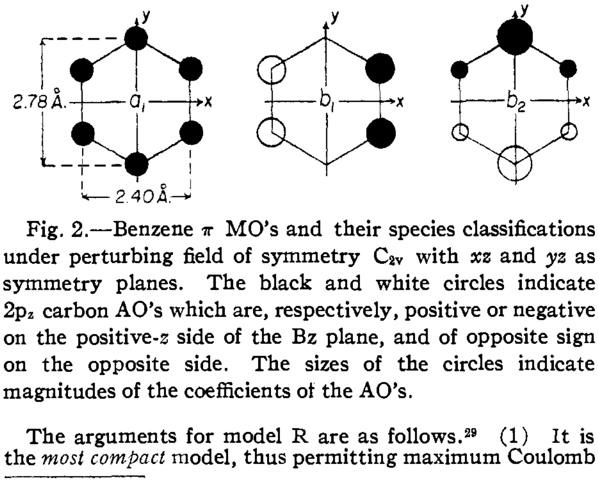

Fig. 2.—Benzene π MO's and their species classifications under perturbing field of symmetry C_{2v} with xz and yz as symmetry planes. The black and white circles indicate $2p_z$ carbon AO's which are, respectively, positive or negative on the positive-z side of the Bz plane, and of opposite sign on the opposite side. The sizes of the circles indicate magnitudes of the coefficients of the AO's.

The arguments for model R are as follows.[29] (1) It is the *most compact* model, thus permitting maximum Coulomb

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[24] The heat of association of $Bz{\cdot}I_2$ is about 1.4 kcal. as determined by Cromwell and Scott[2b] from equilibrium data in solution.

[25] See discussion of models beginning four paragraphs below for some further details.

[26] See Ref. 2d, footnote 25. Actually, the value 1.2 e.v. was used so as to raise curve W_1 in Fig. 1 to fit the observed ν_{NE}. Without changing E_A^{vert} from 1.8 e.v., a similar adjustment could have been made by assuming a greater exchange repulsion (larger effect 4) for W_1 than for W_0, attributable to the larger size of I_2^- in ψ_1 than of I_2 in ψ_0,

[27] By second-order perturbation theory, if ν_{NE}, and b of Eq. (1), are known, then the vertical frequency ν_{01} can be computed; further, the energy intervals $W_E - W_1$ and $W_0 - W_N$ should be nearly equal [*cf.* Eq. (4), (5), (7), (10)]. The result given in the text was obtained in this way.

[28] This transition appears to have been found in recent work in this Laboratory; see J. S. Ham, J. R. Platt and H. M. McConnell, *J. Chem. Phys.*, **19**, 1301 (1951). In ref. 2d, the writer at first attributed the λ 2900 absorption to modified λ 2600 absorption by the Bz in the complex, but then in a "Note added in Proof" suggested a charge-transfer process as a possible alternative.[18] Bayliss (*cf.* *J. Chem. Phys.*, **18**, 292 (1950)) attributed it to a modification of the intense I_2 absorption near λ 2000 by action of the solvent.

[29] See also ref. 2d, noting, however, that some of the arguments for model R (there called Model I) under the assumption that λ 2900 is a Bz absorption are now no longer valid.

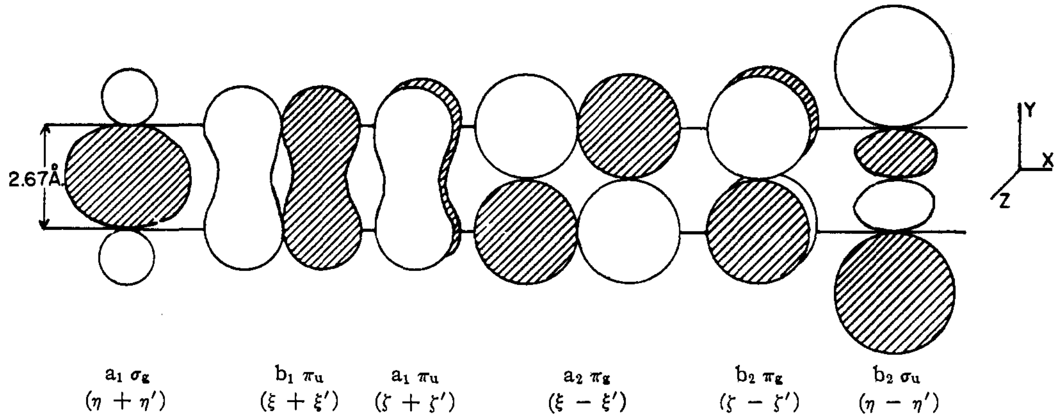

Fig. 3.—Semi-schematic drawing of forms of outer shell iodine (I_2 or I_2^-) MO's under perturbing field of symmetry C_{2v} for R_y model of Bz·I_2, with *xz* and *yz* as symmetry planes. Shaded and unshaded volumes in the orbitals indicate positive and negative regions, respectively. Inner nodes are omitted. The characterizations in parentheses correspond to Eq. (25).

attraction energy in W_1. (2) ψ_0 is the totally symmetrical singlet (${}^1A_1$) type, and (see Section II, sixth and eighth paragraphs) ψ_1 has to be of the same type. For model R, this condition can be satisfied using ground-state Bz^+ and I_2^-.

The lowest ionization potential of Bz involves removal of an electron from a π MO. There are three of these in Bz, each occupied by two electrons. Their forms may be approximated by suitable linear combinations (see Fig. 2) of carbon atom $2p_z$ AO's. The MO's b_1 and b_2 in Fig. 2 are of equal ionization energy (9.24 volts, the minimum ionization potential of Bz) in free benzene, while a_1 is less easily ionized. (The notation assumes model R_x or R_y.) Removal of one electron from the b_1 or b_2 MO gives, respectively, a ${}^2B_1$ or a ${}^2B_2$ state of Bz^+.

The six outer shell MO's of I_2 or I_2^-, in the forms they should assume in model R_y, may be approximated (normalization factors are omitted)[30] as

$$\left.\begin{aligned} a_1\sigma_g &\approx \eta + \eta'; & a_2\pi_g &\approx \xi - \xi' \\ b_1\pi_u &\approx \xi + \xi'; & b_2\pi_g &\approx \zeta - \zeta' \\ a_1\pi_u &\approx \zeta + \zeta'; & b_2\sigma_u &\approx \eta - \eta' \end{aligned}\right\} \tag{25}$$

Here ξ, η, ζ refer to 5p iodine atoms AO's with their axes, respectively, parallel to *x*, *y* and *z* and their positive ends suitably chosen (see Fig. 3). For each MO in (25), the first symbol gives the classification under the C_{2v} symmetry of model R_y of Bz·I_2, the second that for the isolated iodine molecule ($D_{\infty h}$ symmetry).[31] In the latter, the two π_u forms are equal in energy, as are also the two π_g forms.

The iodine molecule in its ground state has two electrons in each of the MO's of Fig. 3 except the strongly antibonding $b_2\sigma_u$, which is empty.[31] In the ground state of I_2^-, the odd electron goes into the $b_2\sigma_u$ MO, giving a ${}^2B_2$ state.[32] The required ${}^1A_1$ state of Bz^+–I_2^- to serve as ψ_1 for model R_y can be obtained if and only if the Bz^+ is also in its ${}^2B_2$ state.[30,33,34] It will be noted further that this combination permits favorable overlapping between the odd electrons in the Bz^+ b_2 MO and the I_2^- b_2 MO, to form the indicated weak Bz^+–I_2^- bond.[30,32]

Several additional models for Bz·I_2 will now be examined to see why they are less probable than model R. They are also of interest because analogous models may be set up for Bz·Ag^+ (see Section VI) and other Bz complexes, with relative stabilities depending on the electronic structure and the geometry of the acceptor involved. They or their analogs are of further interest as possible activated states or reaction intermediates for substitution reactions.[35]

Model E, the *edgewise model*, has the I_2 axis parallel to the Bz sixfold axis but located alongside one edge (model E_x) or corner (E_y) of the Bz ring. The symmetry is C_{2v} in either case For models E just as for Models R, a ψ_1 satisfying the symmetry requirements can be obtained from ground-state Bz^+ and I_2^-. However, the Bz^+ and I_2^- charge centers are a little farther apart now (especially for E_y), making $W_1 - W_0$ somewhat larger, so that Models E should probably be somewhat less stable than Model R (*cf.* Eq. 5).

In both of models R_x and E_x, the I_2 axis lies in the *xz* plane of Fig. 2, but parallel or perpendicular to the *xy* plane in *R* and *E*, respectively. A third model (or range of models) with the I_2 axis still in the *xz* plane, but inclined to the *xy* plane, is intermediate between models E_x and R_x.[30] This *oblique* model O_x has symmetry C_s. It seems likely that models R_x and E_x both correspond to distinct energy minima (with that of R_x the lower) relative to moderate deformations (except rotations of R_x to R_y). If so, model O_x would correspond to a mild energy maximum between these two minima. In contrast to the case of Bz·I_2, the analogs of models R and E for Bz·Ag^+ (Section VI) probably correspond to energy maxima, with minimum energy for the analog of Model O_x. Model O_y, intermediate between R_y and E_y may be important for substitution reactions (see later paper[35a]). Two further

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(30) For model R_x, the labels b_1 and b_2 in Eq. (25) and Fig. 3 and the axes *x* and *y* in Fig. 3 would be exchanged, and the ground state of I_2^- would be of species ${}^2B_1$. This combined with ${}^2B_1$ of Bz^+ would then give ψ_1. The weak Bz^+–I_2^- bond in ψ_1 for the R_x model would be between a b_1 electron of Bz^+ and a $b_1\sigma_u$ of I_2^-.[12]

(31) See ref. 2d, Section II.

(32) In addition, I_2^- must have five low-energy unstable excited states, some of which are of possible interest for Bz^+–I_2^- resonance structures. Each is obtained by putting two electrons into $b_2\sigma_u$ and taking one electron out of one of the other five MO's of Eq. (25). For each of models R_x and R_y,[30] the Bz^+–I_2^- bond in ψ_1 should be appreciably stabilized by some admixture[14] of structures involving two of these excited I_2^- states.

(33) This combination also gives a ${}^3A_1$ state. Further, the ${}^2B_1$ state of Bz^+ combined with the ${}^2B_2$ ground state of I_2^- gives a ${}^1A_2$ and a ${}^1A_2$ state. All these states must give *W*(*R*) curves with the same asymptote as W_E of Fig. 1, but lying somewhat above the latter (not shown in Fig. 1).

(34) For model Ry, I_2^- in its lowest excited state, which is of type ${}^2B_2$ with the odd electron in $b_2\pi_g$, can also interact with ${}^2B_2$ of Bz^+ to give a second acceptable ψ_1. Further, excited I_2^- of the type ${}^2B_1$ with the odd electron in $b_1\pi_u$ can interact with ${}^2B_1$ of Bz^+ to give a third acceptable ψ_1. No doubt those higher-energy ψ_1's contribute appreciably to the complete resonance structure of ψ_N. For model Rx, a similar pair of excited ψ_1's exists.

(35) The models here called R, L, E and A were called I, II, III and IV in ref. 2d.

(35a) Probably in *Proc. Nat. Acad. Sci.*

groups of models, with the iodine axis *lying* in the benzene plane, either pointing toward the center of the ring (L_x, L_y) or *tangential* to an edge or corner of the ring (T_x, T_y), are easily seen to be unfavorable for steric and/or symmetry reasons.

Finally, Model A, the *axial model*, with the I_2 axis coincident with the Bz sixfold axis and of symmetry C_{6v}, deserves mention. Although at first sight attractive,[2c] this model does not satisfy the symmetry requirements for ψ_1 unless *excited* I_2^- (excitation energy perhaps 2.5 e.v.)[32] or excited Bz^+ (excitation energy perhaps 4 or 5 e.v.) is used. Further, the mean separation between the charge centers in Bz^+ and I_2^- is greater here than for any of Models R, O or E. Thus Model A must very probably be ruled out.

Besides $Bz{\cdot}I_2$, numerous other related $Ar{\cdot}X_2$ and $Ar{\cdot}XY$ complexes have been studied, beginning with $Ms{\cdot}I_2$ (Ms = mesitylene).[2a,2c,2d] For $Ms{\cdot}I_2$ the visible I_2 absorption peak is at λ 4900 and the charge-transfer peak at λ 3330 as compared with λ 5000 and λ 2900, respectively, for $Bz{\cdot}I_2$; and the equilibrium constant of the complex is increased. All these facts are qualitatively in agreement with the theory in this paper. For Ms, I_B is about 1.1 e.v. less than for Bz;[2] hence, other things being equal, curve W_1 in Fig. 1 should be lower for $Ms{\cdot}I_2$ than for $Bz{\cdot}I_2$ by this amount. However, there are other changes: R should be smaller at equilibrium, curve W_N should have a deeper minimum, and the distance of curve W_E above W_1 should be increased. The last mentioned changes may well be the main reason why the shift in wave length of the ν_{NE} absorption peak is less than the predicted shift (to λ 4100) that one would obtain on the basis of the change in I_B alone. Less easily understandable is the fact that the ν_{NE} *intensity* for $Ms{\cdot}I_2$ is *less* than for $Bz{\cdot}I_2$, whereas Eq. (22) would tend[36] to indicate the contrary.

The spectroscopic and equilibrium constant data on other $Ar{\cdot}X_2$ and $Ar{\cdot}XY$ complexes,[2] while apparently all in general agreement with the present theory, show a number of interesting features worthy of further systematic experimental study and theoretical analysis. It seems probable that the geometrical arrangement corresponds to model R in all or most cases. The order of stability $ICl > I_2 > Br_2 > Cl_2$ for Bz complexes[2c] is understandable by charge-transfer theory except for $Bz{\cdot}ICl$, which would be expected to resemble $Bz{\cdot}Br_2$ in stability. This anomaly may perhaps be explained by additional, dipole polarization, forces exerted by the ICl, lying in an O rather than an R position.

The present conclusions differ from those tacitly adopted by other authors who, for complexes like $Bz{\cdot}I_2$, have indicated structures of partially BzI^+I^- character[37]; for example, Dewar[7] wrote $BzI^{\delta+}I^{\delta-}$. Polarization of this kind would be immediately excluded by symmetry except for a model with the two iodine atoms in non-equivalent positions, and as we have seen above, these models for $Bz{\cdot}I_2$ seem improbable. Moreover, even in such a model, for example Model A, the present analysis indicates that the polarization effect would consist only in a somewhat unequal distribution of negative charge over the two iodine atoms in the minor $Bz^+–I_2^-$ resonance component (ψ_1), with only extremely slight (quadrupole-quadrupole) polarization in the main ($Bz{\cdot}I_2$) component.[38]

If $Bz{\cdot}I_2$ could be dissolved in a sufficiently strongly ionizing medium, one might expect to obtain $(BzI)^+$ plus I^-, with predominantly $Bz^+–I$ structure in the positive ion.[39] A related case is that of iodine dissolved in pyridine (Py), an ionizing medium, where $(PyI)^+$ ions are present,[40] presumably in equilibrium with undissociated $Py{\cdot}I_2$.[41] The structure of the $(PyI)^+$ ions is doubtless predominately $Py^+–I$ with the iodine attached to the nitrogen atom of the pyridine.[42,43] With respect to predominant bond structure, this conclusion differs from that of previous authors, who speak of unipositive iodine in this and related compounds.[40]

IV. Factors Determining Lewis Acid and Base Strengths. Molecular Compounds as Reaction Intermediates

At this point it will be useful to draw some general conclusions from the discussion of $Bz{\cdot}I_2$ in Section III, particularly as to the factors determining Lewis acid and base,[44] or electron donor and acceptor,[45] strengths. For this purpose, Fig. 1 may be taken as typical for any Lewis acid–base pair A, B in which A and B are weakly-interacting neutral molecules in totally-symmetrical singlet states. The dissociation constants of A·B for a given B with different A's, or for a given A with different B's, are the natural measures of Lewis acid or base strengths. However, it must be kept in mind[44] that the strength of a (Lewis) acid is not quite a

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[36] Mainly by reason of increased b in Eq. (1), corresponding to the greater stability of $Ms.I_2$.

[37] In particular, see F. Fairbrother, *Nature*, **160**, 87 (1947), *J. Chem. Soc.*, 1061 (1948).

[38] In Model A, ψ_1 would be $Bz^+–I_2^-$ just as in Model R. However, this can be written as a combination of two structures $Bz^+–II^-$ and $\underbrace{\mathrm{Bz^{+}I^{-}I}}$, of which the latter would probably predominate in view of the weakness of the $Bz^+–I$ bond in the actual complex.

[39] The alternative structure Bz,I^+ is disfavored not only by its no-bond character but also because for good resonance with $Bz^+–I$, the I^+ would have to be in an excited singlet state.

[40] R. A. Zingaro, C. A. VanderWerf and J. Kleinberg, THIS JOURNAL, **73**, 88 (1951), and other references there cited.

[41] *Cf.* ref. 2d, footnote 26d.

[42] Ionization of Py may be effected either by removal of a π electron as for Bz, or of a lone-pair N atom electron, probably with nearly the same ionization energy. This gives a choice of two quite different ψ_1's for $Py{\cdot}I_2$, the one leading to a π-type complex as in benzene, the other to an onium-type complex. The latter is favored by the fact that it permits more strongly localized binding in $\psi_1(Py^+–I_2^-)$, and becomes *strongly* favored in an ionizing medium.

[43] The structure $Py^+–I$ would be favored over Py,I^+ for the same reasons[39] as $Bz^+–I$ over Bz,I^+ in $(BzI)^+$, but even more strongly because the N^+ in the Py^+ should be able to form a fairly strong localized bond to iodine without disturbing the aromatic π structure.

[44] G. N. Lewis, *J. Franklin Inst.*, **226**, 293 (1938). Lewis defined a basic molecule as "one that has an electron-pair that may enter the valence shell of another atom to consummate the electron-pair bond," an acid molecule as "one which is capable of receiving such an electron-pair into the shell of one of its atoms." The present viewpoint as embodied in Eq. (1), emphasizing partial transfer of one electron from base to Lewis acid with accompanying (weak or strong) interatomic or intermolecular dative bond formation, essentially translates Lewis's definition into quantum-mechanical terms but also (almost automatically, because of the form of Eq. (1)) broadens its scope considerably, although in a way consistent with the spirit of Lewis's viewpoint.

[45] For a valuable critical review on acids and bases, with considerable emphasis on terminology, see R. P. Bell, *Quart. Rev. Chem.*, **1**, 113 (1949).

unique absolute quantity, but depends appreciably on specific features of its interaction with the base with which it is paired.

Since the dissociation constant of any complex A·B is determined to a large extent by its heat of formation, attention may be turned to this quantity, which in turn should usually depend mainly on the resonance energy as given by Eq. (5).

If curve W_0 in Fig. 1 is fairly flat, $W_1 - W_0$ depends mainly on the location of curve W_1. Clearly W_1 is the lower, and so B the better base, the smaller is I_B^{vert}; and W_1 is the lower and so A the better acid, the larger is E_A^{vert}. I_B and E_A are, respectively, properties of B and A alone, and are of major importance[6,2d] for base or acid strength. The somewhat different quantities I_B^{vert} and E_A^{vert}, however, depend at least slightly on the equilibrium configuration of the complex.

For a given distance R between centers of A and B, the Coulomb energy in ψ_1 may depend considerably on the detailed charge distribution within B^+ and A^-, and on the orientation of A to B. Thus if the charges are largely localized on two neighboring atoms, as on the N and B atoms in $R_3B{\cdot}NR_3$ (*cf.* Section V), the Coulomb energy is greater than e^2/R, whereas if the charges are widely dispersed as in Ar·Nt (Ar = aromatic, Nt = nitrated aromatic), it is less than e^2/R. To a large extent these Coulomb attractions, as well as the covalent bonding and the exchange repulsions between A^- and B^+, may be broken down into additive contributions to acid and base strengths; but, in part, specific factors remain. Finally, *all* the energy effects associated with curve W_1 are affected by the properties of any medium in which the complex may be dissolved.

The forms of the W_0 and W_N curves may now be reconsidered more carefully. If A and/or B are "soft" molecules, curve W_0 rises less steeply than if both are "hard" molecules, and curve W_N then tends to have a deeper minimum. Hence, "softness" in A or B, respectively, should tend to make it a better acid or base. Two special cases may be mentioned. If there is a general softness in curve W_0 down to distances close to those of equilibrium in curve W_N, we may have an exothermic complex with no activation energy. If there is a hardness in curve W_0 at relatively large distances (for example as a result of steric hindrance) but this levels off or even relaxes at shorter distances, there may then be in curve W_N an activation barrier followed by a more or less deep energy minimum. The complex may then be either exothermic or endothermic. Even if moderately endothermic, it may then exist in appreciable concentration in equilibrium with its dissociation products. If strongly endothermic, it may be important as an "activated" complex.

In general, the many-dimensional surface which is the generalization of curve W_0 of Fig. 1 does not rise indefinitely in all directions when various atoms or groups in A and B are brought closer together. Instead, there exist activation energies for various chemical reactions. However, complex-formation depresses part and probably most of the many-dimensional surface W_N below W_0, and probably increasingly so as A and B are brought closer (increase of $H_{01}^2/(W_1 - W_0)$ in Eq. (5)). This should lower the activation barriers for some if not all possible chemical reactions between A and B. Thus complex-formation (especially if the complex is fairly tightly bound) may often be the precursor of a chemical reaction—an idea earlier set forth clearly by Brackmann[5] and doubtless others. Such a reaction may in many cases proceed so rapidly at ordinary temperatures that the reversible complex is never isolated.

As an example, it occurs to one that the observed benzene–halogen complexes may be intermediates in the halogenation of benzene.[2] This could be true without implying that halogenation necessarily proceeds over an activation barrier in the direction of the particular coördinate R in Fig. 1. Rather, it could proceed over a quite different barrier or "activated complex." The point is that much or all of the W_N surface, including this other barrier, may be lower than it would be without existence of a $Bz{\cdot}X_2$ complex.

V. Compounds of the $BX_3{\cdot}NR_3$ Type

In Section III and previously,[2d] several examples of loose molecular compounds between neutral closed-shell molecules have been discussed. As has already been indicated, the stable compounds $BR_3{\cdot}NR_3$ and the like can be understood in terms of the same general theoretical framework. However, there are important quantitative differences. Figure 4, for $BF_3{\cdot}NMe_3$ (Me = methyl), has been constructed to aid in understanding these. It must be emphasized that Fig. 4 is largely schematic.

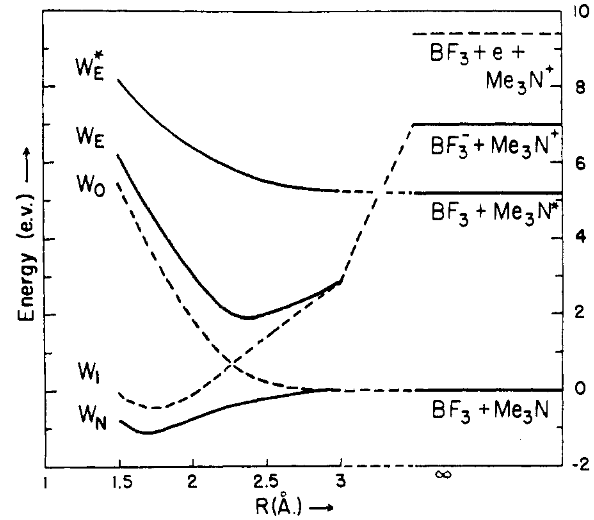

Fig. 4.—Schematic diagram of potential curves for the compound $BF_3{\cdot}NMe_3$ as a function of the distance R between the centers of the B and N atoms, with the remaining atoms so located at all R values as to minimize the energy *for curve* W_N. The diagram is largely qualitative. However, the position of the level $BF_3 + Me_3N^*$ is approximately correct, where Me_3N^* represents the first excited singlet state of Me_3N.

The energy curves in Fig. 4 are all intended to correspond to an adjustment of the shapes and dimensions of the BF_3 and NR_3 groups at each value of the B–N distance R to be such as to minimize the energy of W_N, but *not* of the other W curves. This preserves the relationship of *verticality* between the other curves and W_N, as is needed for an analysis of the interactions of ψ_0 and ψ_1 to give ψ_N and ψ_E, and for a discussion of the absorption spectra of $BF_3{\cdot}NMe_3$.

An important point is that if BF_3 and NMe_3 approach each other with their symmetry axes coincident, then the no-bond wave function ψ_0, and the dative structure $F_3B^--N^+Me_3$ formed from F_3B^- and N^+Me_3 in their respective ground states, are both totally symmetrical singlet states of the whole molecule. Thus ground-state $F_3B^--N^+Me_3$ can serve as ψ_1. It appears altogether probable that as R decreases from ∞, the two molecules approach with their axes always in coincidence. Further, as R decreases, the B atom must move out of the F_3 plane toward the N atom and the N atom also move toward the B atom, the tendency being to set up tetrahedral angles around both. This tendency would be fully realized in the equilibrium state of pure ψ_1, in which the charges and the covalent bond are largely localized on the B and F atoms. For pure ψ_0, the equilibrium geometry would be quite different, with some electrostatic attraction between the boron and nitrogen atoms at larger R values, but strong repulsion between the two molecules if R gets at all small. The actual ground state is expected to have a wave function and an equilibrium geometrical arrangement which are compromises between those of ψ_1 and ψ_0.

According to chemical experience, ψ_1 predominates in ψ_N ($b^2 > a^2$ in Eq. (1)). This implies a crossing of the curves W_0 and W_1 as shown in Fig. 4, and a resultant excited state curve W_E with a minimum at a large R value and a steep rise at smaller R. This should lead to a broad charge-transfer absorption spectrum in the ultraviolet.[14]

Besides W_N and W_E, Fig. 4 shows a $W(R)$ curve (marked W^*_E) for an excited singlet state of $BF_3 \cdot NMe_3$ related to the first excited singlet state of NMe_3. The latter, which gives rise to well-known absorption of NMe_3 near λ 2400, almost certainly corresponds to excitation of an electron from the lone pair of the nitrogen atom.[46] This lone pair becomes a B^--N^+ bonding pair in the molecule $BF_3.NMe_3$, with a resultant increase in the binding energy of its electrons, so that the corresponding λ 2400 absorption should shift strongly toward shorter wave lengths. The $W_E{}^*$ curve in Fig. 4 has been drawn to be in qualitative agreement with this expectation.

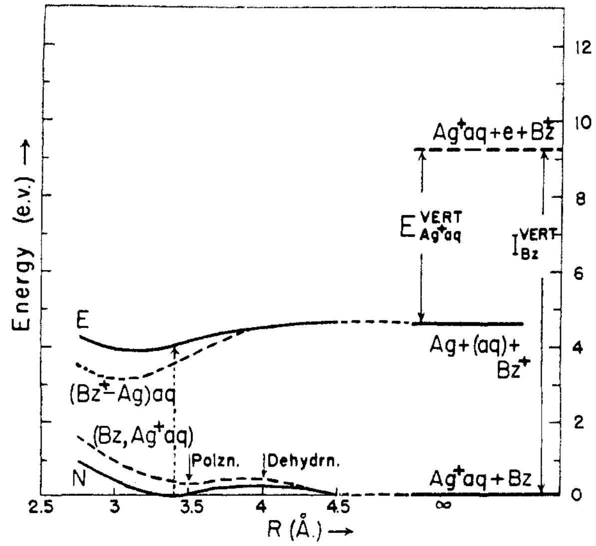

Fig. 5.—Predicted potential curves for the interaction of a benzene molecule with an Ag^+ ion in aqueous silver nitrate solution, as a function of the distance R in the model described in the text (qualitative only). At the right, Ag^+ aq. designates a hydrated Ag^+ ion, while Bz indicates a benzene molecule surrounded by solution. Bz^+ designates a benzene molecule ionized vertically, which in this case implies that the environing molecules are in the same positions and orientations as for curve N of the complex; and that the medium is *only electronically* polarized by the Bz^+.

VI. The Ag^+ Complexes

Examples of a type of complex in which one partner is an atom–ion are those formed[3,4] by Ag^+, acting as a Lewis acid, with ethylene, benzene, or related compounds as bases. Here the partners are totally symmetrical singlet structures[9] as before, and the theory of Section II is applicable. State ψ_0 has the no-bond structure (B, Ag^+) and ψ_1 the bonded structure B^+–Ag.

The Ag^+ complexes occur both in aqueous solutions, as for example when benzene is dissolved at low concentrations in aqueous $AgNO_3$, and in non-aqueous solutions, as when $AgClO_4$ is dissolved in benzene. In the former case, the NO_3^- ions may be assumed to be completely dissociated from the ions of Ag^+ or of $Ag^+ \cdot Bz$. In the latter, the ClO_4^- ions presumably remain attached to the Ag^+ or $Ag^+ \cdot Bz$ ions, but in a relatively passive role.

Let us consider the aqueous case, for which a *schematic* $W(R)$ diagram is given in Fig. 5. This is similar to Fig. 1, except for the following points. (1) The electron affinity of the Lewis acid here is much larger because the acid is a positive ion, the electron affinity being now the ionization potential of the silver atom. (2) But there is no e^2/R attraction in state ψ_1 or state E. (3) Allowance must be made for sizeable solvation and polarization effects.

In state ψ_0, as R decreases, we may imagine a Bz molecule to approach an Ag^+aq ion. As the Bz penetrates the hydration sphere surrounding the Ag^+, the ψ_1 curve may rise at first as water molecules are displaced, then fall somewhat as polarization of the Bz by the Ag^+ becomes appreciable (*cf.* Fig. 5). The resulting complex, probably endothermic if it were pure ψ_0, perhaps becomes thermoneutral or exothermic by resonance with ψ_1 giving ψ_N.

To permit correct adjudication of the resonance of ψ_1 with ψ_0, curve W_1 in Fig. 5 (labeled $(Bz^+-Ag)aq$), is drawn for the situation that all the nuclei, including those of immediately neighboring water molecules, are for each R value located at the positions they assume for curve W_N of the actual complex. The position of curve W at $R = \infty$ is determined using $I_{Bz}{}^{vert}$ and $E_{Ag+aq}{}^{vert}$. $I_{Bz}{}^{vert}$ is the ordinary I of Bz minus slight corrections; $E_{Ag+aq}{}^{vert}$ is the ordinary I of Ag (7.5 e.v.) minus a considerable correction (estimated as 2.9 e.v. in Fig. 5) corresponding to loss of hydration energy by, (a), displacement of some H_2O by Bz; (b), diminished attraction or change to repulsion for the remaining H_2O when Ag^+ becomes Ag without change in positions of these H_2O. At sufficiently small R, covalent bonding tends to lower W_1 somewhat. Finally, resonance interaction with ψ_0 leads to the N and E curves of Fig. 5.

Although Fig. 5 is only schematic, it is perhaps only fair to state that no intense ultraviolet charge-transfer spectrum, such as Fig. 5 would suggest, has yet been identified for $Bz \cdot Ag^+$.

For Bz in aqueous $AgNO_3$ solution, it is known that 2:1 complexes Ag^+BzAg^+ are present in appreciable amounts in addition to the predominant 1:1 complexes.[3,4]

A somewhat similar discussion could be given for the $Bz \cdot Ag^+ClO_4^-$ complex in benzene solution, with ClO_4^- more or less taking the place of the water in Ag^+aq.

A question of considerable interest for $Bz \cdot Ag^+aq$. and $Bz \cdot Ag^+ClO_4^-$ is the location of the Ag^+ with respect to the Bz ring. Previous writers[3,4] have made the plausible suggestion that the Ag^+ lies above the middle of the ring on its symmetry axis (Model A of Section III). This, however, is probably excluded by symmetry considerations very similar to those for Model A of $Bz \cdot I_2$. Since ψ_0 is of type $^1A_1$, ψ_1 will give no resonance unless it is also $^1A_1$. But since Bz^+ has a nodal plane through the

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(46) *Cf.* R. S. Mulliken, *J. Chem. Phys.*, **3**, 506 (1935).

symmetry axis (*cf.* Fig. 2 and Section III), an electronic state of Ag must be used which has a like plane. The lowest suitable state is a ^2P or ^2D state requiring about 4 e.v. excitation energy. This makes the energy of ψ_1 so high that resonance with ψ_0 is weakened (*cf.* Eq. (5)).

Similar reasoning makes it improbable that the Ag^+ ion lies alongside the Bz in the latter's plane (*cf.* Model E of $Bz{\cdot}I_2$). For in this case a *second* nodal plane of the Bz^+, in the ring plane (xy plane of Fig. 2) gives ψ_1 a nodal plane in this same location, making it incapable of resonance with ψ_0 unless a ^{2}P or ^{2}D excited state of Ag is used in ψ_1.

However, if the Ag^+ is pulled to one side from the Bz symmetry axis, toward the region between but somewhat above two carbon atoms of the ring (symmetry C_s—*cf.* Model O_x of $Bz{\cdot}I_2$), fairly strong resonance of ψ_1 with ψ_0 may reasonably be expected.[47] In this orientation, one of the two states of Bz^+ (*cf.* Fig. 2) can give with Ag a totally symmetrical singlet as required for ψ_1.[48]

When the present work was presented at a recent meeting,[49] this model was proposed on the basis of the preceding arguments. In the discussion following, Professor R. E. Rundle stated that in unpublished work[50] on the crystal structure of $Bz{\cdot}AgClO_4$ (white crystals out of benzene solution) he had located the Ag^+ ions in exactly the position mentioned. In the crystal, each Ag^+ is located in this way with respect to *two* Bz, and each Bz is similarly located with respect to *two* Ag^+. Such a crystal is of course not the same thing as a 1:1 complex, but (*cf.* also the last paragraphs of Section III), a preliminary consideration of the symmetry requirements indicates that these may still operate mainly in a localized fashion to give approximately the same favored orientations (Model O) as for an isolated $Bz{\cdot}AgClO_4$.

Recent papers of Andrews and Keefer[4] show the following equilibrium constants K for 1:1 Ag^+ complexes in aqueous $AgNO_3$ solution: benzene, 2.4; toluene, 2.95; xylenes, 2.6–3.0; mesitylene, 1.8. The attainment of a maximum K for toluene and the xylenes and the low value for mesitylene would be difficult to understand if the Ag^+ were located as in Model A on the symmetry axis of the aromatic ring. But if it is located as in Model O, the observed K values are at once intelligible as the result of a balance between (*a*), a tendency toward increasing basicity with increasing number of methyl groups, and, (*b*), steric hindrance by methyl groups to attainment by the Ag^+ of one of its favored locations between two carbon atoms. Space models indicate that steric hindrance may well somewhat destabilize the two locations next adjacent to a methyl group. This leaves six "good" locations for benzene, four for toluene, three for *o*-xylene, two for *m*-xylene and *p*-xylene, none for mesitylene.

The reasoning just given is reinforced by the contrasting behavior of the halogen–aromatic complexes: their stability increases steadily from benzene to toluene to the xylenes to mesitylene. This is readily understood in terms of Model R for the $Ar{\cdot}I_2$ complex, where space models indicate no appreciable steric hindrance for any of the methyl-substituted benzenes.[2d]

VII. Further Examples and Further Discussion of the Interaction Strengths of Lewis Acids and Bases

The theory given in Section II is applicable to a wide variety of chemical entities A·B. In Section II, it was restricted to cases in which A and B are even-electron, closed-shell molecules, ions, or atoms.[9] A preliminary discussion of the factors governing the strengths of A and B as Lewis acids and bases has been given in Section IV. In Sections III, V and VI, examples of particular types of molecular complexes or compounds have been considered. The present Section is devoted to a generalization of the discussion, including the application of the theory of Section II to the case that A and B are odd electron entities, and to the case that they are identical. First, the closed-shell A and B types will be reviewed.

Two important classes of ***neutral-molecule*** bases are the weak π bases (unsaturated or aromatic hydrocarbons or amines, etc.), and the often strong n (or *onium*) bases (NR_3, OR_2, etc.).[51] For π bases, the donated electron in the dative structure $\psi_1(B^+–A^-)$ of Eq. (1) comes from a more or less bonding MO; for n bases, from a non-bonding MO occupied in the original base by a lone pair of electrons. Some molecules, for example pyridine[42] and acetone, have the possibility of functioning either as π or as onium bases.

Neutral-molecule Lewis acids or acceptors include π acceptors (nitroaromatic compounds, maleic anhydride, etc.), which combine especially with π bases or donors to form loose complexes,[52] and v (vacant-orbital) acceptors (BX_3, BR_3, AlX_3, SnX_4, etc.) which combine especially with n donors to form fairly stable compounds.

They also include the halogens, which combine with either π or n bases (*cf.* Section III and ref. 2d) to form loose complexes. Further, the hydrogen halides, although they are strong acids in the Brönsted sense,[45] act as weak Lewis acids rather like the halogens. The Lewis-acid character of the halogens and hydrogen halides is attributable to the incompletely satisfied electronegativity of their halogen atoms; and since the acquisition of a negative charge by halogen can take place, characteristically, only concurrently with a pronounced loosening of the covalent binding, these and other similar Lewis acids, *e.g.*, the alkyl halides, may be called *d* (*dissociative*) acids. Their weak acidity can become strong only by dissociation (into either

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(47) The distance R between centers of Ag^+ and Bz is larger in Model O than in Model A, but this is not of itself important here, in contrast to the case of $Bz{\cdot}I_2$, where minimum R makes W_1 lower because of the Coulomb attraction between Bz^+ and I_2^-.

(48) By similar reasoning, the most likely position for the Ag^+ in the Ag^+–ethylene complex[1] is directly above the center of the ethylene, on the twofold axis perpendicular to the plane of the latter.

(49) Reference 1.

(50) Now published: R. E. Rundle and J. H. Goring, THIS JOURNAL, **72**, 5337 (1950).

(51) This nomenclature is related to that of Dewar ("π complexes") and to that currently used by J. R. Platt and others in describing ultraviolet absorption spectra of unsaturated molecules ("π–π transitions" and "$n-\pi$ transitions"); M. Kasha, Faraday Society Discussions, 1950, No. 9, p. 14.

(52) See *e.g.*, J. Landauer and H. M. McConnell, THIS JOURNAL, **74**, in press (1952).

atoms or ions; this will be analyzed further in a later paper[35a]).[53]

The acid strengths of π acids also are often attributable mainly to the presence of unsatisfied electronegative atoms. In *v* acids, the presence of incompletely satisfied electronegative atoms, while not essential (consider *e.g.*, BMe_3,—Me-methyl), greatly increases acid strength (as *e.g.*, in BCl_3). This is understandable from the fact that the chlorine atoms withdraw negative charge from the boron atom, and so must increase the electron affinity *E* of the latter's vacant 2p orbital, thus increasing acid strength (*cf.* Section IV). However, halogen and similar atoms in BX_3 also at the same time feed some negative charge into the vacant orbital by a familiar resonance effect, thus tending to decrease its *E; but* apparently the *net* effect is usually to increase acid strength.[54]

Ionic (*i*) bases include X^-, CN^-, OH^-, etc. Atomic or ionic (*i*) Lewis acids include O, Ag^+, Li^+, H^+. (In the case of the O atom, an excited singlet state must be used.) Ionic acids or bases are necessarily accompanied by partner ions of opposite sign, which being themselves bases or acids, tend to neutralize the acids or bases which they accompany. This tendency is largely avoided only in ionizing media where after solvation of both ions the neutralizing partner is ionized away, or in the case that the partner ion (*e.g.*, K^+, a very weak Lewis acid, or ClO_4^- a very weak base[44]) is of large size and low charge.

As already suggested, it is possible to regard *odd-electron* systems A′ (*e.g.*, Cl, CN, OH, NH_2, C_2H_5) and B′ (*e.g.*, H, Na, NO, NO_2) as Lewis acids and bases for which the theory of Section II is applicable. (Primes are used here for odd-electron acids and bases to distinguish them from the more usual even-electron ones denoted by A and B.) The "complexes" A′·B′ are now usually stable compounds. The theory of the structure and charge-transfer spectra of such compounds is the same as for the complexes A·B, *provided* ψ_0 in Eq. (1) is taken to refer to a pure ionic structure $(A')^-(B')^+$ and ψ_1 to a pure covalent structure A′—B′.

However, even this modification of the previous treatment can be avoided if the basis of reference is shifted from the odd-electron entities A′ and B′ to a pair of even-electron entities A and B such that A is $(B')^+$ and B is $(A')^-$. For example, if B′ is Na or H and A′ is Cl, then A is Na^+ or H^+ and B is Cl^-. In terms of such a choice of A and B, the entire discussion in Section II is applicable, at least in its qualitative aspects. Just as in previous examples,[55] either ψ_0 or ψ_1 may predominate in the ground-state wave function ψ_N of Eq. (1). For example, $\psi_0(Na^+,Cl^-)$ predominates in diatomic NaCl, ψ_1(H–Cl) in HCl. For the excited-state function ψ_E, the relations are reversed. These simple diatomic examples illustrate how the (in general intermolecular) charge-transfer spectra N → E of Section II become identical in special cases with the more familiar interatomic charge-transfer spectra (N → V spectra).[56]

Returning to complexes and compounds between neutral molecules, it may be recalled from Section IV that the strength of any Lewis acid–base interaction is governed largely by the characteristics of the dative structure $\psi_1(A^-–B^+)$. Especially favorable are low ionization energy *I* of B and close approach between the centers of gravity of the charges on B^+ and A^-. High vertical electron affinity *E* for A is also helpful. Close approach between B^+ and A^- lowers the energy of ψ_1 both through increased Coulomb interaction and through strong covalent binding. Low energy of ψ_1, as well as close approach *per se*, favor strong resonance of ψ_1 with ψ_0.

In molecular compounds between *n* bases and *v* acids, conditions for close approach are especially favorable (see Sections IV, V). The relative binding strengths of different compounds of this type should depend largely on the *I* and the approachability of the base, and on the *E* and the approachability of the acid. According to H. C. Brown,[57] base strength, for BX_3, AlX_3 and the like as reference acids, decreases in each of the series $NR_3 > PR_3 > AsR_3 > SbR_3$; $OR_2 > SeR_2 > TeR_2$. In each series *I* decreases in the order given, tending to *increase* base strength, but at the same time the size of the onium atom increases, decreasing its approachability and tending to decrease base strength. If the latter effect predominates, Brown's result can be understood. Brown's observation that base strength varies in the order $NMe_3 > NH_3 > NF_3$ is readily understandable because *I* is considerably less for NMe_3 than for NH_3,[58] and would be expected to be less for NH_3 than for NF_3. (The observed diminished binding strength of compounds containing two bulky alkyl groups is of course also understandable, in terms of diminished approachability.) Likewise Brown's order of base strength $NR_3 > OR_2 > ClR$ is understandable because *I* is smaller for NR_3 than for OR_2.[58] Further, Brown's order of acid strength $BF_3 > BH_3 > BMe_3$ is understandable because *E* would be expected to decrease in this order[54] (see discussion in an earlier paragraph). It is not clear, however, why $AlMe_3$ should be a stronger Lewis acid than BMe_3 toward onium bases, as Brown reports.

An interesting case is that of borine carbonyl $OC·BH_3$, where a somewhat stable compound is formed in spite of the high *I* of CO (14.5 volts).

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[53] Actually, the functioning of the hydrogen halides and similar *d* acids as Lewis acids may be so weak as to be negligible, since ψ_1 must be high in energy (E^{vert} is probably *negative* for such molecules in loose complexes). It nevertheless makes sense to classify them as *d* acids in view of their behavior in strong solvents. See also R. Ferreira, *J. Chem. Phys.*, **19**, 794 (1951).

[54] H. C. Brown (see ref. 57) attributes the decreasing order of acid strength $BBr_3 > BCl_3 > BF_3$ to increasing resonance in this order; the anomalous weakness of $B(OMe)_3$—much weaker than BMe_3—he attributes likewise to this type of resonance.

[55] It should be noted that ionic binding now occurs in ψ_0 instead of in ψ_1. The case differs in this respect from that where A and B are neutral molecules.

[56] The case of charge-transfer spectra in molecules with homopolar bonds (H_2, C_2H_4, etc.)[16] corresponds to the special situation where A and B are identical (*cf.* Section VIII). For specific discussion of the states and spectra of diatomic molecules of the type here considered, see R. S. Mulliken, *Phys. Rev.*, **50**, 1017, 1028 (1936); **51**, 310 (1937).

[57] H. C. Brown, lecture at ONR-AEC-sponsored symposium at University of Chicago, Feb. 21–23, 1951; and numerous published papers, especially in THIS JOURNAL.

[58] See for example W. C. Price, *Chem. Revs.*, **41**, 257 (1947); A. D. Walsh, *Quart. Rev. Chem.*, **2**, 73 (1948). For example, H_2O, 12.7, $(C_2H_5)_2O$, 10.2; NH_3, 10.8, $(CH_3)_3N$, 9.4; HCl, 12.84, C_2H_5Cl, 10.89. For π bases, ethylene 10.50, propylene 9.70; butadiene 9.07; benzene 9.24, toluene 8.92; naphthalene 8.3.

Here apparently a very favorable approachability situation balances the high I in the ψ_1 resonance structure $(OC)^+{-}B^-H_3$.[59]

The present theory also gives a tempting explanation of the ease with which gaseous carbon monoxide attacks solid ferrous metals. One may assume an initial attack involving strong development of a ψ_1 resonance structure $M^-{-}(CO)^+$, where M indicates solid metal; the CO functions as an M base, the metal as a v acid. On closer approach, the initial complex changes smoothly into a predominant M=C=O structure, while additional CO molecules attack until the gaseous carbonyl is released. But this is only speculative, and probably wrong.

As compared with the n bases, the π bases are in general aided by low I values (10.50 for C_2H_4, 9.24 for benzene, with considerably lower values[58] for methylated or conjugated compounds or larger-ring aromatics), but are much more limited as to approachability. Maximum approachability is to be expected between π bases and π acids, arranged (in the case of aromatics) with their planes parallel, so that the diffusely distributed positive charge in B^+ in $\psi_1(B^+{-}A^-)$ is as close as may be to the also diffusely distributed negative charge in A^-. For the association of aromatic π bases Ar with v acids like BR_3, the localized negative charge on the boron in B^-R_3 in $\psi_1(Ar^+{-}B^-R_3)$ is at a disadvantage for approach to the diffusely distributed positive charge in Ar^+. Taking $Bz{\cdot}BX_3$ as typical, there is an additional handicap: a symmetrical location of the BX_3 with its axis coincident with the Bz axis gives no resonance at all, for quantum-mechanical symmetry reasons similar to those which disfavor a symmetrical structure for $Bz{\cdot}Ag^+$(*cf.* Section VI); while the unsymmetrical location required (as in $Bz{\cdot}Ag^+$) for resonance may be hampered (more than for $Bz{\cdot}Ag^+$) by steric interference between the X_3 and Bz planes. The two unfavorable specific factors indicated may be adequate to explain why BX_3 and AlX_3 do not form complexes with aromatic bases.[60] On the other hand, pyridine,[42] undoubtedly acting as an n rather than as a π base, does form compounds with BX_3.

The iodine and other halogen molecules because of their simpler shape and the special nature of their electronic configuration should be more adaptable than BX_3, and indeed they apparently act as Lewis acids both toward π bases (Section III) and toward n bases such as R_2O and probably R_2CO, with in each case a different but always a compact geometrical configuration satisfying the symmetry requirements of that case.[2] The absence of known complexes of the halogens with certain bases is probably explainable by too great reactivity: interaction may pass rapidly through complex formation to irreversible chemical change.

VIII. Self-complexes, Intermolecular Forces and Compressibility

The limiting case where A and B are identical is of some interest. In this case, Eq. (1), (8) and (5) take[11] the special forms

$$\psi_N = a\psi_0 + b(\psi_1 + \psi_1') + \cdots \tag{1a}$$

$$\left.\begin{aligned}\psi_E &= c(\psi_1 - \psi_1') + \cdots \\ \psi_F &= a^*(\psi_1 + \psi_1') - b^*\psi_0 + \cdots\end{aligned}\right\} \tag{8a}$$

$$W_N = W_0 - \frac{2(H_{01} - SW_0)^2}{(W_1 - W_0)} + \cdots \tag{5a}$$

Here if ψ_1 is $A^-{-}B^+$, ψ_1' is is $A^+{-}B^-$. Comparing Eq. (5a) with Eq. (5), and referring also to Eq. (6), it is seen that very appreciable charge-transfer forces tending to form complexes must exist between like just as between unlike molecules. Empirically, however, it seems clear that these forces are generally weaker for like molecules. This may be understood by the fact that ordinarily if A is a strong Lewis acid, it is a weak base, and conversely. However, in some cases a strong base is at the same time a strong Lewis acid (*e.g.*, metals, where $I = E$, and polycyclic aromatic hydrocarbons), while in other cases (*e.g.*, rare gases, N_2, CH_4) a weak base is at the same time a weak Lewis acid.

The interaction of two Bz molecules may be considered as an example. One can approach this as the limiting case in a series $Me_nBz{\cdot}Bz(NO_2)_{n'}$ with n and n' decreasing to zero (Me_nBz = n-methylbenzene, $Bz(NO_2)_{n'}$ = n'-nitrobenzene). There is evidence[52] that very weak complexes of the indicated type exist, *e.g.*, for $n = 0$, $n' = 3$. One may surmise that in Bz·Bz itself, the forces, while not negligible, are too weak to give appreciable concentrations of Bz·Bz in the liquid at room temperature. To the extent that heats of formation are decisive, one might then suppose that these considerably exceed kT for larger values of $n + n'$, but fall below kT for Bz·Bz itself.

It may still be that in crystalline Bz, at least at low temperature, the charge-transfer forces are important in determining how the molecules are stacked. Considering a single pair Bz·Bz, if the two molecules were stacked with their axes coincident and their planes parallel, the symmetry would be D_{6h}. In ψ_1 and ψ_1' of Eq. (1a), ground-state Bz^+ and Bz^- would be of types $^2E_1$ and $^2E_2$, respectively. Now although the proper combination of these $(\psi_1 + \psi_1')$ gives rise to a very considerable number of states of Bz·Bz, no one of these is of the species $^1A_{1g}$ required for resonance with ψ_0. Hence a different stacking of the two Bz molecules is indicated. It seems likely that an arrangement obtained by sliding one Bz about half a ring diameter over the other would give maximum resonance.[61]

One thus sees that in pure liquids and molecular crystals, for example liquid benzene and crystalline benzene and naphthalene, charge-transfer forces should favor definite types of packing and definite orientations. They may thus afford an explanation of the way in which for example certain aromatic molecules are tilted at odd angles in their crystals.

The possibility emerges that charge-transfer forces may often share with London's well-known dispersion forces in accounting for the familiar van der Waals cohesive forces between molecules, especially in systems containing more than one component. Charge-transfer forces share with dispersion forces the property of approximate additivity: the fact that one molecule is bound to another does not prevent a third from being attracted,

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(59) W. Gordy, H. Ring and A. B. Burg. *Phys. Rev.*, **78**, 517 (1950), conclude that the no-bond structure contributes 40–50% to ψ_N, the structure $(OC)^+{-}(BH_3)^-$ about 30% (this includes the two structures $O^+{=}C{-}B^-H_3$ and $O{=}C^+{-}B^-H_3$).

(60) In the literature, it is sometimes indicated that molecular compounds $Ar{\cdot}BX_3$ or $Ar{\cdot}AlX_3$ *do* exist (see *e.g.* F. Briegleb, cited in footnote 26a of Ref. 2d), but according to H. C. Brown (see Brown, Pearsall and Eddy, THIS JOURNAL, **72**, 5347 (1950)), this is not true.

(61) It may be relevant that in crystalline graphite, exactly this sort of a displacement between successive planes is observed. Since each graphite plane is essentially a giant aromatic molecule (here with $I = E$), it seems possible that charge-transfer forces may be at least partially responsible.

steric factors permitting. (See the discussion of n:1 complexes at the end of Section II.) Dispersion-force attractions tend to be largest in orientations bringing maximum polarizabilities into play, while the orientational properties of charge-transfer forces, as shown in Sections II and III, are governed by considerations of quantum-mechanical symmetry of molecular wave functions. The two kinds of forces are thus different in this respect, and probably the sharpness of the orientational effect is stronger for the charge-transfer forces.

From what has preceded, it appears likely that charge-transfer forces may often be of the same order of magnitude as dispersion forces. Perhaps dispersion forces usually predominate for interactions between like molecules, but charge-transfer forces often in solutions and other systems in which molecules of different kinds are present together. Charge-transfer forces may well also be important in heterogeneous systems and in adsorption phenomena, and may afford new possibilities for understanding intermolecular interactions in biological systems. Definite conclusions about these points must, however, wait upon further investigations.

Even if it should turn out that charge-transfer forces are relatively unimportant for one-component liquids and crystals not under strong internal or external pressure, the theory indicates that if in any way a substance is sufficiently compressed, the charge-transfer forces should increase rather rapidly. (See here also the discussion of "hard' and "soft" molecules in Section IV.) Such compression might perhaps be effected by internal ionic forces in the case of a partially ionic crystal, by unusually strong dispersion or dipole forces, or by strong external pressure. The existence of charge-transfer forces should in general contribute considerably—in an anisotropic manner because of their strong orientational properties—to compressibilities. Here it is relevant to recall the studies of Gibson and Loeffler[61] who found marked shifts in the locations of the absorption spectra of aniline-polynitrobenzene and similar solutions under pressures of 1000 atmospheres; these are spectra which are attributable to the presence of very loose charge-transfer complexes.[62]

[62] R. E. Gibson and O. H. Loeffler, THIS JOURNAL, **61**, 2877 (1939); **62**, 1324 (1940).

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[CONTRIBUTION FROM THE LOS ALAMOS SCIENTIFIC LABORATORY]

Molar Volumes of Liquid Deuterium and of a 1:1 Mixture of Tritium and Deuterium, 19.5 to 24.5°K.[1]

BY EUGENE C. KERR

The molar volumes of liquid deuterium and of a 1:1 mixture of tritium and deuterium have been measured over a temperature range 19.5 to 24.5°K. The results deviate from fitted equations by about 0.2%.

The only previous determination of the molar volume of deuterium is that by Clusius and Bartholemé[2] who made eight measurements between 18.8 and 20.5°K. This report presents the results of molar volume measurements in the range 19.5 to 24.5°K. for pure deuterium and for a 50:50 atom per cent. mixture of deuterium and tritium.

Apparatus and Procedure.—The apparatus used consisted essentially of (1) a calibrated gas pipet and constant volume manometer to measure the amount of gas added to the condensing system, (2) a mercury "pusher" to compress the gas into the condensing system, (3) a small volume line leading to the pycnometer and including a Wallace and Tiernan differential pressure gage for measuring the system pressure, and (4) the pycnometer proper.

The pycnometer was connected to the filling line by a small glass capillary tube on which a fine mark was etched to define the liquid volume. The pycnometer volume to this mark was 0.06417 cm.^{3} and the capillary volume in the vicinity of the mark was 0.000360 cm.^{3}/mm.

A double compartmented dewar vessel containing liquid nitrogen and liquid hydrogen served as a cryostat for the apparatus. It was attached by means of a sliding seal so that the liquid hydrogen bath level could be maintained at a constant level with respect to the fiduciary mark on the pycnometer. Various temperatures were attained by varying the bath pressure up to 30 lb. gage pressure by an auxiliary pressure regulating device. Temperatures were measured by a strain-free platinum resistance thermometer which had been calibrated at the Bureau of Standards. Occasional temperature checks were made by comparing the resistance thermometer temperature with that obtained from the vapor pressure of the liquid hydrogen bath.

Molar volume measurements were made by adding successive small amounts of gas (measured in the gas pipet) to the condensing system until liquid was condensed in the pycnometer up to the vicinity of the calibration mark. The system was allowed to equilibrate for about 30 minutes and then the meniscus level with respect to the mark was noted by means of a cathetometer, the resistance thermometer current and potential were measured on a White double potentiometer, and the bath and system pressures were observed. A plot of the condensing system pressure as a function of the volume (NTP) of gas added gave the usual sharp break at the "dew point." The *difference* between the amount of gas required to fill the pycnometer with liquid to the calibration mark and that required to fill it with "dew-point" gas was taken as the true amount of gas required to fill the liquid density bulb.

The pycnometer volume was determined in the same manner except that pure hydrogen was used as a calibrating liquid, the data of Scott and Brickwedde[3] being used to establish the volume. The "noxious volume" of the gas in the connecting lines was determined by independent measurements as a function of the bath temperature in order to compensate for the uncertain part of the volume just above the bath level which was in a severe temperature gradient region.

The deuterium used contained 0.4 atom per cent. of protium as the only impurity determinable by the mass spectrograph. The tritium was originally 99.7% pure, but, once the 50:50 mixture was made up, a gradual increase in

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[1] This paper is based on work performed under University of California contract with the Atomic Energy Commission.

[2] K. Clusius and E. Bartholemé, *Z. physik. Chem.*, **B30**, 237 (1935).

[3] R. B. Scott and F. G. Brickwedde, *J. Research Natl. Bur. Standards*, **19**, 237 (1937).