"Absolute" Lewis acid or base strength is defined as the power to donate or attract electrons governed by inductive and resonance effects but uncomplicated by the steric effects which plague the other measurements of Lewis acid and base strengths. Using δ_K values of amines or ethers and BY_3 molecules, one can predict on the basis of electron donating effects which pairs of molecules should be able to form donor-acceptor bonds and what the relative bond strengths should be. If a pair $D\text{-}BY_3$ should form a donor–acceptor bond on the δ_K basis, but does not or forms only a weak bond defined in terms of the equilibrium constant, K_P, for the reaction

$$D{\cdot}MX_3(g) \rightleftarrows D(g) + MX_3(g)$$

then one can also derive a measure of the steric effect.

In later papers the authors will discuss δ_K values in unsaturated compounds, substituted aliphatic compounds and aromatic compounds and the relation of δ_K values to the field of donor–acceptor bonding.

[CONTRIBUTION FROM THE DEPARTMENTS OF PHYSICS AND CHEMISTRY, THE UNIVERSITY OF TEXAS, AUSTIN, TEXAS]

Acceptor Infrared Band Intensities in Benzene–Halogen Charge-transfer Complexes[1]

BY E. E. FERGUSON AND F. A. MATSEN

RECEIVED JULY 20, 1959

The previously developed "electron vibration" mechanism for the enhancement of intensity of molecular vibration bands in charge-transfer complexes is extended to a calculation of the halogen stretching mode intensities in the complexes of I_2, Br_2 and Cl_2 with benzene. The simultaneous enhancement by a "permanent dipole" mechanism also is treated.

Introduction

In a previous paper[2] it was proposed that the enhancement of the intensities of molecular vibration bands in charge-transfer complexes is due to a change in amount of charge transferred from donor to acceptor during molecular vibration. This change is a consequence of the change in vertical ionization potential (for donor bands) or vertical electron affinity (for acceptor bands) during the molecular vibrations. The mechanism might appropriately be called an "electron-vibration" spectrum, since infrared absorption is due to electron motion rather than to the motion of differently charged nuclei. With the electron-vibration model the direction of dipole moment change can be perpendicular to the directions of motion of nuclei involved in the vibration. In the previous paper,[2] a calculation of the intensity enhancement of the symmetric ring breathing vibrational mode of benzene complexed with iodine was shown to be in reasonable agreement with the observed value. In the present report is presented a similar calculation for the acceptor stretching mode intensity in the benzene complexes.

Theory

The Mulliken[3] charge-transfer theory assumes a wave function for the ground state of a weak complex

$$\Psi_c \sim \Psi_0 + b\Psi_D \tag{1}$$

where Ψ_0 and Ψ_D are the wave functions for no-bond and dative states, respectively. Neglecting overlap, the dative coefficient is

$$b = \frac{H_{OD}}{W} \tag{2}$$

where $H_{OD} = \int \Psi_0 H \psi_D d\tau$, and $W = I - (A + C)$; I, A and C are the ionization potential of the donor, electron affinity of the acceptor and the coulomb and other energy terms, respectively. The dipole moment of the complex is

$$\mu_c = b^2\mu_D \tag{3}$$

where μ_D is the moment of the complex in the zero order dative state. The binding energy is (neglecting repulsive and dispersion forces which tend to cancel)

$$E_c \cong b^2W \tag{4}$$

The ultraviolet absorption frequency is

$$h\nu_{uv} = W(1 + 2b^2) \sim W \tag{5}$$

The values of b conforming to (3), (4) and (5) are listed in Table I.

TABLE I

DATIVE COEFFICIENT, BENZENE–IODINE COMPLEX

$b = 0.17$	Dipole moment	$\mu_c = 0.72D$	ref. 3 (with $S = 0.1$)
.21	Dipole moment	$\mu_c = 0.72D$	with $S = 0$
.286	Dipole moment	$\mu_c = 1.80D$	G. Kortüm and H. Walz, *Z. Elektrochem.*, **57**, 73 (1953)
.13	Binding energy	$\Delta H = -0.057$	e.v., T. M. Cromwell and R. L. Scott, THIS JOURNAL, **72**, 3825 (1950)
.37	Ultraviolet spectra		S. H. Hasting, J. L. Franklin, J. Schiller and F. A. Matsen, THIS JOURNAL, **75**, 2900 (1953)

Calculation of B

The integrated intensity of an infrared absorption band is given by

$$B = \frac{N\pi}{3c^2}\left(\frac{\partial\mu}{\partial Q}\right)^2 \tag{6}$$

Here N is the absorber concentration. From (3)

$$\frac{\partial\mu}{\partial Q} \cong \frac{\Delta\mu_c}{\Delta Q} = \mu_D 2b\,\frac{\Delta b}{\Delta Q} \tag{7}$$

Using (2) and (3), assuming H_{OD} is approximately constant and setting $W \sim h\nu_{uv}$ (7) becomes

$$\frac{\Delta\mu_c}{\Delta Q} = \frac{2\mu_D b^2}{h\nu_{uv}L}\left(\frac{\Delta W}{\Delta r}\right) \tag{8}$$

where L relates the normal coördinate to the symmetry coördinate. $L = \sqrt{\text{reduced mass}}$, for a diatomic molecule.

---

[1] This research was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

[2] E. E. Ferguson and F. A. Matsen, *J. Chem. Phys.*, **29**, 105 (1958).

[3] R. S. Mulliken, THIS JOURNAL, **74**, 811 (1952).

Estimation of ΔW

To estimate ΔW it is assumed that the change in complex energy is due to a change in ionization potential (for donor vibrations) or electron affinity (for acceptor vibrations) during vibration.

For the totally symmetric stretching donor band the variation in ionization potential of benzene during vibration is the variation in the vertical distance from the ground state potential curve to that of the ionic state, as deduced from the vibrational frequencies for the ground state and for the benzene ion. Actually, the vibrational frequencies of a highly excited Rydberg state (within a few tenths of a volt of ionization) rather than those of the ion, were used in the calculation. With $\Delta\mu$ so calculated, the infrared absorption intensity was computed and found to agree well with experiment. For the acceptor band such data are not available, so that it is necessary to obtain $\Delta\mu$ by other means.

The ΔW for the I_2 band in the $Bz \cdot I_2$ complex in the zero order state (isolated I_2) is the change in vertical electron affinity of I_2 during the iodine vibration. The vertical electron affinity is the vertical difference in the potential energy *versus* internuclear distance curves for I_2 and I_2^-. The vertical electron affinity of I_2 is to the harmonic oscillator approximation

$$A = A_e + \frac{1}{2}K(r - r_e)^2 - \frac{1}{2}K^-(r - r_e^-)^2 \qquad (9)$$

where A_e is the equilibrium electron affinity, K and K^- and r_e and r_e^- are force constants and equilibrium distances in I_2 and I_2^-, respectively. Then

$$\left(\frac{dA}{dr}\right)_{r_e^c} = K(r_e^c - r_e) - K^-(r_e^c - r_e) \qquad (10)$$

where r_e^c is the equilibrium internuclear separation for the I_2 molecule in the complex.

Approximate potential energy curves for I_2, I_2^- and I_2^c are given in Fig. 1. The repulsive part of the I_2^- curve is obtained from the electron energy dependence of the cross section for the process[4,5]

$$e + I_2 \longrightarrow I + I^- \qquad (11)$$

These data clearly show that I_2 has a zero or a negative vertical electron affinity and that an increased separation must occur before the usually quoted equilibrium value

$$A_{I_2} \geqslant A_{I^-} - D_{I_2} = 1.8 \text{ e.v} \qquad (12)$$

(see Table III) is attained. Nothing decisive can be said about the intermediate part of the I_2^- potential except that it is believed to have at most a shallow minimum, that is, $K^- < K$.[6a] Since the contribution of the second term in eq. 10 cannot be estimated and since it may be small, the term is arbitrarily neglected. The possible effect of this neglect is discussed below. Then

TABLE II

X_2	ν, cm.$^{-1}$	ν_c, cm.$^{-1}$	r_e, Å.	L^2, amu.	ν_{uv}, ergs	b^f
Cl_2	557	531^a	1.99	18	7.2×10^{-11c}	0.18
Br_2	321	305^a	2.28	40	6.8×10^{-11d}	.34
I_2	213	204^b	2.67	63.5	6.8×10^{-11e}	.37

[a] W. B. Person, R. E. Erickson and R. E. Buckles, *J. Chem. Phys.*, **27**, 1211 (1957). [b] E. K. Plyler and R. S. Mulliken, THIS JOURNAL, **81**, 823 (1959). [c] L. J. Andrews and R. M. Keefer, *ibid.*, **73**, 462 (1951). [d] R. M. Keefer and L. J. Andrews, *ibid.*, **72**, 4667 (1950). [e] H. A. Benesi and J. H. Hildebrand, *ibid.*, **71**, 2703 (1949). [f] Calculated from eq. 22 using data in Table III.

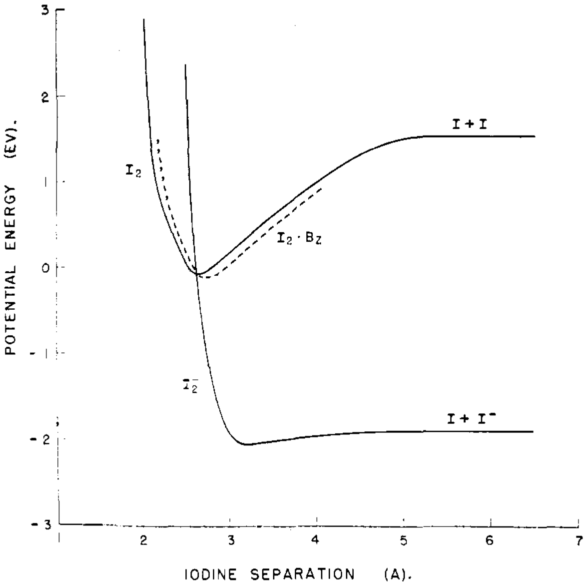

Fig. 1.

TABLE III

X_2	K,^{a} cm. moles	E, e.v.	A_x,^{c} e.v.	D_{x_2},^{d} e.v.	A_{x_2}, e.v.
Cl_2	0.33	0.014^b	3.8	2.5	$\geqslant 1.3$
Br_2	1.04	.044^b	3.6	2.0	$\geqslant 1.6$
I_2	1.72	.057^e	3.1	1.5	$\geqslant 1.8$

[a] L. J. Andrews and R. M. Keefer, THIS JOURNAL, **72**' 462 (1951). [b] Calculated from eq. 23 and the value for I_2. [c] F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, Inc., New York, N. Y., 1957, p. 149. [d] G. Herzberg, "Spectra of Diatomic Molecules," Van Nostrand, New York, N. Y., 1950. [e] See Table I.

$$\left(\frac{dA}{dr}\right)_{r_e^c} \cong K(r_e^c - r_e) \qquad (13)$$

From Badger's rule[7]

$$r_e^c - r_e = \frac{r_e}{\nu_c^{1/2}}(\nu^{1/2} - \nu_c^{1/2}) \qquad (14)$$

For a diatomic molecule

$$K = 4\pi^2 L^2 \nu^2 \qquad (15)$$

Substitute (14) and (15) into (13) and set $\nu \sim \nu_c$ in the denominator

$$\frac{\Delta A}{\Delta r} = 4\pi^2 L^2 \nu^2 r_e \frac{\nu^{1/2} - \nu_c^{1/2}}{\nu^{1/2}} \qquad (16)$$

Substitute (16) into (8) since $dA/dr = -dW/dr$

$$\frac{\Delta\mu}{\Delta Q} = \frac{8\pi^2 \mu_D b^2 L \nu^2 r_e}{h\nu_{uv}} \left(\frac{\nu^{1/2} - \nu_c^{1/2}}{\nu^{1/2}}\right) \qquad (17)$$

---

(4) R. Buchdahl, *J. Chem. Phys.*, **9**, 146 (1941).

(5) M. A. Biondi and R. E. Fox, *Phys. Rev.*, **109**, 2005, 2008, 2012 (1958).

(6) This belief is fostered by the following: (1) In the m.o. description the added electron must go into an antibonding orbital. This may imply that $D_{I_2^-} \sim (1/2)D_{I_2}$. (2) The electron impact data indicates $r_e(I_2^-) > r_e(I_2)$ and a large separation usually is associated with a weak bond. For benzene (ref. 2) $r_e^c \sim r_e$ as is evidenced by the fact that the frequency of the vibration (992 cm.$^{-1}$) is unchanged in the complex.

(7) R. M. Badger, *J. Chem. Phys.*, **2**, 128 (1934); **3**, 710 (1935).

Since Person, *et al.*,[8] have proposed the empirical relation

$$\frac{\Delta\mu}{\Delta Q} \propto \frac{\Delta K}{K} \tag{18}$$

to correlate their data on a number of charge-transfer complexes, it is of interest to note that

$$\frac{\nu^{1/2} - \nu_c^{1/2}}{\nu^{1/2}} \sim \frac{\Delta\nu}{2\nu} \sim \frac{\nu^2 - \nu_c^2}{4\nu^2} = \frac{\Delta K}{K} \tag{19}$$

However, the resemblance between (17) and (18) is only superficial since the coefficient of $(\Delta K/K)$ in (17) varies from complex to complex.

"Permanent" Dipole Intensity

The charge-transfer in the extent of b^2e from benzene to halogen is probably asymmetric with respect to the halogen molecule and consequently creates a "permanent" dipole μ_p in it. The change in this permanent dipole in the course of vibration also gives rise to infrared absorption.[9] The extent of the charge asymmetry cannot be determined *a priori* but the maximum dipole moment

$$\mu_p = b^2er/2 \tag{20}$$

obtainable is that in which all the charge is transferred to one halogen atom.[10] Then

$$\frac{\Delta\mu}{\Delta Q} = \frac{\Delta\mu_p}{L\Delta r} = \frac{b^2e}{2L} \tag{21}$$

This gives then a maximum value for the additional contribution to intensities due to "permanent" dipole contribution. Values calculated from eq. 21 are given in Table IV.

TABLE IV

X_2	*B* (darks) electr. vibr.	*B* perm. dipole	*B* total	*B* obsd.
Cl_2	57 (18)[d]	14 (1.3)[d]	71	153[a]
Br_2	102 (32)	8 (10.8)	110	425[b]
I_2	40 (12)	7 (0.7)	47	120[c]

[a] W. B. Person, R. E. Erickson and R. E. Buckles, ref. 8. [b] W. B. Person, R. E. Erickson and R. E. Buckles, *J. Chem. Phys.*, **27**, 1211 (1957). [c] E. K. Plyler and R. S. Mulliken, THIS JOURNAL, **81**, 823 (1959). [d] Values in parentheses assume a dative coefficient $b = 0.21$.

Calculations

The data used in the calculations are given in Table II. The largest (*i.e.*, the spectroscopic) value of b^2 is used for the benzene–iodine complex. The quantity b^2 for the other two complexes was obtained from the value for the iodine complex making use of equations 4 and 5. That is

$$\frac{b_1^2}{b_2^2} = \frac{E_1\nu_{uv_2}}{E_2\nu_{uv_1}} \tag{22}$$

E is known experimentally for the benzene–iodine complex. If it is assumed that the entropy of formation of the three complexes is constant

$$RT \ln \frac{K_1}{K_2} = E_1 - E_2 \tag{23}$$

so that the E's for the chlorine and bromine complexes can be obtained from the E for the iodine complex and the ratio of the equilibrium constants. Thus, while a spectroscopic value of b^2 is used, the variation in b^2 is obtained from the thermal values. The data are summarized in Table III. It may be noted that the calculated heats roughly parallel the electron affinity of the halogen molecule. The I_2 frequencies, 213 and 204 cm.$^{-1}$, for the vapor and complex state are taken from Plyler and Mulliken[11] and as pointed out these include the shift due to the inert solvent effect as well as that due to the loosening of the bond in the complex. The solvent effect is estimated to be no more than 1 or 2 cm.$^{-1}$ on the basis of the Kirkwood, Bauer-Magat relationship[12] $\Delta\nu = 10^{10}\frac{f}{a^3}\left(\frac{n^2-1}{2n^2+1}\right)$, where f is oscillator strength, (24) a, spherical cavity radius and n refractive index. Further support for this estimate is obtained from the observation by Person[8a] of a 6 cm.$^{-1}$ shift for the ICl band from vapor to the inert solvent CCl_4. The I_2 band has $^1/_7$ the intensity of the ICl band and accordingly should undergo by (24) a solvent shift smaller by the same factor, since the other factors in this relation do not vary appreciably.

Discussion

The electron vibration and permanent dipole mechanisms together appear to give a satisfactory description, with respect to both magnitude and order, of the charge-transfer enhancement of halogen infrared bands in benzene halogen complexes. The calculated intensities (see Table IV) are in each case low by a factor of three (or nine). A possible explanation lies in the approximation involved in dropping the second term in the change of electron affinity with internuclear separation (eq. 10). Since r_e^- is probably larger than r_e^c, the second term is of the same sign as the first. The factor of three could be accounted for if the neglected second term were 70% of the first.

It should be noted that the present theory does not require acceptor bands to be more intensified than donor vibration bands as has often been suggested. In fact, one might expect the situation to be generally reversed since donor vibration frequencies often exceed acceptor frequencies and hence the variations in ionization potential probably exceed variations in electron affinity. This prediction has been verified in the benzene–halogen complexes. The rather common impression that the donor bands are much weaker than acceptor bands probably arises from the manner of presentation of data in combination with the paucity of even crude numerical intensities. When an aromatic is saturated with iodine, the aromatic spectrum is slightly modified by the enhancement of a few weak (inactive) absorption bands[13,14] whose *relative* intensity is small. For such a spectrum 0.25 mm. is a suitable cell thickness. On the other hand, when one sees Cl_2, Br_2 or I_2 absorption in an otherwise clear spectral region, the relative intensity (relative to zero) is more impressive. In the

---

(8) (a) W. B. Person, R. E. Humphrey, W. A. Deskin and A. I. Popov, THIS JOURNAL, **80**, 2049 (1958). (b) W. B. Person, R. E. Humphrey and A. I. Popov, *ibid.*, **81**, 273 (1959). (c) W. B. Person, R. E. Erickson and R. E. Buckles, *ibid.*, **82**, 2444 (1960).

(9) Person, *et al.* (ref. 8), have discussed a model similar to this.

(10) From each atom subtract $b^2e/2$ charge, the subtraction causing no change in dipole moment. The dipole moment is then clearly $b^2er/2$.

(11) E. K. Plyler and R. S. Mulliken, THIS JOURNAL, **81**, 823 (1959).

(12) See N. S. Bayliss, *J. Chem. Phys.*, **18**, 292 (1950).

(13) E. E. Ferguson, *Spectrochimica Acta*, **10**, 123 (1957).

(14) W. Haller, G. Jura and G. C. Pimentel, *J. Chem. Phys*, **22**, 720 (1952).

$Bz{\cdot}I_2$ complex, for example, Plyler and Mulliken[11] used a 4 mm. cell to study I_2 absorption. The enhanced benzene bands in $Bz{\cdot}I_2$ complex at 992 and 850 $cm.^{-1}$ are measured to have intensities of roughly 200 and 400 darks, respectively, while the I_2 absorption in the same complex is indeed less, around 120 darks.[15]

A consideration which may be significant here is that part of the intensity of the $I_2{\cdot}Bz$ band must be due to solvent effects. That this can be important is shown by the data of Person, *et al.*,[8a] on ICl in various solvents. The vapor intensity is reported as 650 darks, while the intensity in the inert solvents CCl_4, *n*-heptane and *n*-hexane, are all around 1000 darks. The intensity in benzene is 1900 darks, but the Bz·ICl complex is considerably stronger (K = 4.76 cm. $moles^{-1}$) than the $Bz{\cdot}X_2$ complexes.

It is of interest to note that the "electronic vibration" intensity is large compared to the normal or "permanent dipole" contribution. The spectroscopic values of dative coefficient appear larger than those inferred from binding energy and dipole moment data. Using a lower dative coefficient would decrease the calculated intensities and hence lessen the agreement with experimental data.[16] However, the relative importance of the "electronic vibration" intensity to the "permanent dipole" intensity would increase with decreasing dative coefficient since the first goes as the square and the latter as the fourth power of the dative coefficient.

We wish to express our appreciation to Dr. R. E. Erickson, to our anonymous reviewer for a number of helpful suggestions and to Professor Person for sending us copies of his work before publication.

---

(15) In a previous paper (ref. 2) the 992 $cm.^{-1}$ benzene band in the benzene–iodine complex has been assigned an intensity of 770 ± 300 darks on the basis of a crudely measured peak intensity, an estimated normal half width and an assumed Lorentz shape. A recent direct measurement made in this Laboratory yields the value 190 ± 40 darks.

(16) For example, using the value $b = 0.21$, calculated from the observed dipole moment (assuming the overlap integral $S = 0$ consistent with the other calculations here) would reduce the calculated intensity by a factor

$$\left(\frac{0.21}{0.37}\right)^2 = \frac{1}{3}$$

[Contribution from the Oak Ridge National Laboratory, Chemistry Division, Oak Ridge, Tennessee]

Anion Exchange Studies. XXXI. Adsorption of Zn(II) and Ga(III) from HCl Solutions in the Temperature Range 25 to 150°[1]

By Kurt A. Kraus and Richard J. Raridon[2]

Received November 30, 1959

Adsorption functions of Zn(II) and Ga(III) have been determined by the preloaded column technique in the temperature range 25 to 150° in HCl solutions. Large changes in adsorbabilities with temperature have been observed. Adsorbability of negatively charged complexes decreases rapidly with increasing temperature and for $GaCl_4^-$, $\Delta\bar{H}$ for the ion exchange reactions is *ca.* −14 kcal. (extrapolated to $m_{HCl} = 0$). The shape of the adsorption functions changes rapidly with temperature. From these changes one can deduce that the degree of complexing of Zn(II) and Ga(III) increases rapidly with temperature at constant chloride concentration. Attempts were made to estimate the average heats of the complexing reactions. While these are largely of a qualitative nature, one may conclude that with increasing temperature stability constants change in a direction which increases the preponderance of neutral species or of species of low absolute charge.

From the adsorption functions of metals, one may deduce[3,4] information regarding the extent of complexing of the metals in the aqueous phase. Because of the high intrinsic selectivities of anion exchangers for some complexes, substantial adsorption may occur even when the fraction of the metal in the form of negatively charged complexes is small and when the average charge of the dissolved metal is positive. In an earlier paper,[4] some of the techniques were discussed in detail which may be used for computation of the average charge of the metals from anion exchange data and of the fraction of the metal present as negatively charged complexes in the aqueous phase.

With the development[5] of relatively simple equipment for measurement of ion exchange equilibria as a function of temperature up to 200°, it became of interest to illustrate the use of the anion exchange techniques for study of complexing reactions at high temperatures. Zinc(II) and Ga(III) in HCl were chosen for illustration since these elements have been studied in considerable detail at room temperature.[4]

Experimental

1. Method and Equipment.—Adsorbabilities were determined by the "pre-loaded column technique" with the high temperature column equipment previously described.[5] In this method, a sample of resin, uniformly loaded with the ion whose adsorption is to be studied, is placed in the column. At proper flow rates, eluent passing through the column leaves it equilibrated with the lower layers of the bed whose composition does not materially change if the number of column volumes of solution passed through the column is

---

(1) This document is based on work performed for the U. S. Atomic Energy Commission at the Oak Ridge National Laboratory, Oak Ridge, Tennessee, operated by Union Carbide Corporation. Previous papers: (a) XXVIII, F. Nelson, *J. Polymer Sci.*, **40**, 563 (1959); (b) XXIX, F. Nelson and K. A. Kraus, *J. Chromatography*, **3**, 279 (1960); (c) XXX, F. Nelson, R. A. Day, Jr., and K. A. Kraus, *J. Inorg. & Nuclear Chem.* (in press).

(2) Based on work submitted by R. J. Raridon to Vanderbilt University in partial fulfillment of the requirement for a Ph.D. degree. Work carried out at Oak Ridge National Laboratory under sponsorship of the Oak Ridge Institute of Nuclear Studies.

(3) K. A. Kraus and F. Nelson, "Proceedings of the International Conference on the Peaceful Uses of Atomic Energy," Vol. VII, page 113, 131 (United Nations, 1956).

(4) K. A. Kraus and F. Nelson, "Anion Exchange Studies of Metal Complexes," in "The Structure of Electrolytic Solutions," Walter J. Hamer, Editor, John Wiley and Sons, Inc., New York, N. Y., 1959, p. 340.

(5) (a) K. A. Kraus, R. J. Raridon and D. L. Holcomb, *J. Chromatography* **3**, 178 (1960); (b) K. A. Kraus and R. J. Raridon, *J. Phys. Chem.*, **63**, 1901 (1959).