ture hydrogen-bonded form at 25°. There is a corresponding decrease of 38 cm.$^{-1}$ and a considerable broadening of the asymmetric vibrational peak under these conditions. If the visible absorption spectrum of the high temperature hydrogen-bonded form is obtained at 100°, which is above or at least near the transition temperature, this difference in the symmetrical vibration frequency is not observed.

It does not appear possible to conclude from this analysis whether the observed hydrogen bonding to the actinide(VI) tetrachloro complex is to the oxygen of the MO_2 entity or to chloride. The fact that no corresponding spectral evidence for hydrogen bonding was observed in studies of alkylammonium salts of the $UO_2(NO_3)_3^-$ complex[13,25,32] tends to make the chloride suspect as the hydrogen bond acceptor but cannot be considered proof of this. It is difficult to say whether hydrogen bonding, if it does occur, would have a significant effect on the absorption spectra of chloro complexes of the type MCl_x^{-x+m}, in which the spectra are due to electronic transitions and the M–O vibrational effects are absent.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
NORTHWESTERN UNIVERSITY, EVANSTON, ILLINOIS

Partial Ionic Character of Metal–Chlorine Bonds[1]

BY RALPH G. PEARSON AND HARRY B. GRAY

Received October 17, 1962

Several simple "ionic" models for the bonding in metallic chlorides are tested. These include the hard sphere ion model, the polarizable sphere, and a localized molecular orbital model with partial covalent bonding. van der Waals' repulsions are included. All integrals are evaluated from experimental data. In the MO model the coulomb integrals are considered as functions of x, the fractional "ionic character" of each bond. Binding energies can be calculated about equally well by either the covalent bonding or polarization approach. It seems feasible to develop a semi-empirical MO method in inorganic chemistry for both absolute (binding) energies and relative (spectroscopic) energies. The best value of x was found for each system and the resulting ionicities of 50–90% appear reasonable. Other criteria for x such as the equalization of electronegativities and the principle of electroneutrality are criticized.

Inorganic chemistry is in great need of a theory of binding which enables heats of reaction, activation energies, and similar quantities to be estimated. Recent advances such as crystal field, or ligand field, theory have emphasized differences in energy between ground and excited states only. Also the electron distribution pattern in inorganic systems is of great interest. No experimental or theoretical method is known which gives a reasonably exact answer to the electron distribution problem in any cases but the simplest.

It is very common to adopt a conceptual approach in which the various bonds of a molecule or complex ion are ascribed different degrees of "ionic" and "covalent" character.[2] It is well known that such terms as "per cent ionic character" have no precise meaning except in terms of a model. Nevertheless the concept is useful and interesting.

In this paper we will consider the bonding in a number of metallic chlorides. One chief interest is to try to evaluate the ionicity of such compounds. Bonding energies also have been calculated to compare with experimental results. The ionic character is calculated by means of a localized, two-center molecular orbital method, *e.g.*

$$\psi_{MO} = \phi_a + \lambda\phi_c \qquad (1)$$

where ϕ_a is an atomic orbital of a valence electron on the chlorine atom, ϕ_c is an atomic orbital on the metal atom, and λ is a mixing coefficient. If x is defined as the fractional charge (negative) on the chlorine atom, and if overlap is neglected, then it follows that

$$x = \frac{1 - \lambda^2}{1 + \lambda^2} \qquad (2)$$

$100x$ is also the per cent ionic character of the bond.

Since many of these metal chlorides are certainly very ionic, the hard sphere ion model and the polarized ion model also have been tested. Many such calculations already have been made, especially for the alkali chlorides.[3]

For the sake of completeness and to ensure the use of consistent experimental data, the calculations were repeated even for cases already in the literature. Good agreement was generally found with the earlier calculations. It should be noted that all results refer to

---

(1) Presented in part at the Seventh International Conference on Coordination Chemistry, Stockholm, June, 1962.

(2) Recent work which may be referred to includes (a) J. K. Wilmshurst, *J. Chem. Educ.*, **39**, 132 (1962); (b) H. Shull, *J. Am. Chem. Soc.*, **82**, 1287 (1960); (c) L. E. Orgel, "An Introduction to Transition-Metal Chemistry," Methuen, London, 1960, Chapter 8; (d) J. Hinze, M. A. Whitehead, and H. H. Jaffé, *J. Am. Chem. Soc.*, **85**, 148 (1963); (e) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, Chapter 3.

(3) (a) E. S. Rittner, *J. Chem. Phys.*, **19**, 1030 (1951); (b) Y. P. Varshni, *Trans. Faraday Soc.*, **53**, 132 (1957); (c) A. A. Frost and J. H. Woodson, *J. Am. Chem. Soc.*, **80**, 2617 (1958); (d) K. S. Krasnov, *Izv. Vysshykh Ucheb. Zavedenii, Khim. i Khim. Tekhnol.*, **4**, 38 (1961); *Chem. Abstr.*, **55**, 15024e (1961); (e) A. Buchler, W. Klemperer, and A. G. Emslie, *J. Chem. Phys.*, **36**, 2499 (1962); (f) D. Cubicciotti, *J. Phys. Chem.*, **65**, 1058 (1961); (g) T. E. Brackett and E. B. Brackett, *ibid.*, **66**, 1542 (1962).

gaseous molecules. Thus the energies calculated refer to dissociations such as

$$MCl_n(g) \rightleftharpoons M^{n+}(g) + nCl^-(g) \qquad (3)$$

Hard Sphere Ion Model.—The molecule is assumed to be made of spherical, non-polarized ions. The potential energy function per bond is written as

$$E = -\frac{f}{R} - \frac{d}{R^6} + be^{-aR} \qquad (4)$$

The first term is the coulomb energy. The last two represent van der Waals' attraction (London energy) and repulsion, respectively. The Buckingham potential[4] is used for the latter terms. The coulomb term is a sum of all the attractions and repulsions divided by the number of bonds. R is the internuclear separation in Ångstrom units. The value of f is 1.00 for a diatomic molecule, 1.75 for a linear triatomic, 2.44 for a trigonal planar tetraatomic, and 3.08 for a tetrahedral pentaatomic molecule. These numbers are calculated as shown by $CaCl_2$ as an example. The attractive energy is $-2(2e^2/R)$, where R is the calcium–chlorine bond distance and e is the charge of the electron. The repulsion between the two chlorine atoms is $e^2/2R$. The algebraic sum is $-3.50e^2/R$ and the coefficient of e^2/R is divided by two to give 1.75 as the value of f. The energy in electron volts is obtained directly if R is in Ångstrom units and if f/R is multiplied by $14.43 = (4.8 \times 10^{-10}\text{ e.s.u.})^2 \times 10^8$ Å./cm. $\times\ 6.24 \times 10^{11}$ e.v./erg.

The constants a, b, and d were evaluated from virial coefficient data using the rules of Mason[5] and the data of Mason and Rice[4] and Whalley and Schneider.[6]

Table I shows the values of R used for the various metal chlorides and the source of the data. Where no data exist, the Schomaker–Stevenson[7] equation was used to calculate R. Table I also shows the sum of the repulsion and London energies from the data given by ref. 4 and 6. The values from 6 were used in preference to those from 4 where differences existed. Corrections for the differences in ion sizes and the sizes of the corresponding inert gases were considered, according to the discussions of Pauling[8] and Lennard-Jones.[9] While it was found that the changes in energy produced by this correction were small, they have been included in the final results for the non-transition metal chlorides. For the transition metal chlorides which do not have inert gas shells, repulsive and attractive energies were only estimated roughly as being about the same as for $ZnCl_2$, which was assumed to approximate an Ar–Ar interaction.

TABLE I

PARAMETERS USED IN CALCULATIONS

Molecule	R, Å.[a]	van der Waals' e.v.[d]	$CFSE$, e.v.[g]	$VSPE$, e.v.[h]	-2β, e.v.[j]
LiCl	2.02	0.59[e]	...	0	2.02
NaCl	2.36	.59[e]	...	0	1.69
KCl	2.67	.77	...	0	1.38
RbCl	2.79	.70	...	0	1.32
CsCl	2.91	.73	...	0	1.26
$BeCl_2$	1.74 (1.75)[b]	.80[e]	...	3.22	3.60
$MgCl_2$	2.18 (2.18)[b]	.80[e]	...	3.13	(3.45)
$CaCl_2$	2.54 (2.51)[b]	.80[e]	...	2.17	2.88
$SrCl_2$	2.70 (2.67)[b]	.54	...	2.04	(2.78)
$BaCl_2$	2.77 (2.82)[b]	.73	...	1.74	(2.57)
$ZnCl_2$	2.12 (2.05)[b]	1.40	...	4.47	4.11
$CdCl_2$	2.24	1.82	...	4.21	3.94
$HgCl_2$	2.28	1.76	...	5.44	4.45
$AlCl_3$	2.10[c]	0.66[e]	...	5.13	3.80
$TiCl_4$	2.21	1.48	...	1.65[i]	2.42
$TiCl_2$	2.16[b]	2.00[f]	1.80	0.81[i]	2.42
$CrCl_2$	2.03[b]	2.00[f]	1.34	0[i]	1.64
$MnCl_2$	2.02[b]	2.00[f]	0.0	2.11[i]	3.07
$FeCl_2$	2.04[b]	2.00[f]	0.76	0.86[i]	2.44
$CoCl_2$	2.03[b]	2.00[f]	1.40	0.43[i]	2.06
$NiCl_2$	2.03[b]	2.00[f]	0.91	0.25[i]	1.88

[a] Experimental values from "Tables of Interatomic Distances and Configurations in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958, L. E. Sutton, Ed. [b] Calculated values. The figures in parentheses are recent experimental values from P. A. Akishin and V. P. Spiridonov, *Kristallografiya*, **2**, 475 (1957). [c] Value for Al–Cl in Al_2Cl_6 (non-bridging Cl). [d] From ref. 6 unless otherwise indicated. [e] From ref. 4. [f] Estimated, see text. [g] See ref. 10 and 11; d-orbital separations for the divalent transition metal chlorides are estimated as proportional to the known separations for $CuCl_2$; the proportionality constants are assumed to follow the known variances of Δ for octahedral hydrates. [h] Spectroscopic data from C. E. Moore, "Atomic Energy Levels," Natl. Bur. Std. Circ. 467, Washington, D. C., 1949 and 1952. [i] Promotional energy to lowest sd^3 ($TiCl_4$) and sd^n (MCl_2) orbital configurations. [j] Data for alkali metals from standard references. For Be and Ca, from G. Ehrlich, *J. Chem. Phys.*, **31**, 1111 (1959); other alkali earths (in parentheses) are estimated. Zn, Cd, and Hg from T. A. Allen, *ibid.*, **26**, 1644 (1957). Data for remaining metals according to method of Allen in that one sixth of ΔH_{sub} of metal is taken as single metal–metal bond energy. Heats of sublimation are from D. R. Stull and G. C. Sinke, "Thermodynamic Properties of the Elements," Advances in Chemistry Series, No. 18, American Chemical Society, Washington, D. C., 1956.

Also for the MCl_2 transition metal complexes, corrections for crystal field stabilization[10,11] were made using the single electron orbital separations obtained experimentally for gaseous $CuCl_2$ by Hougen, LeRoi, and James.[12] The crystal field stabilization energy used is given in Table I. These figures may be compared with other, direct data on linear transition metal complexes from the recent literature.[13] The molecules all are assumed spin-free because of the weak crystal field of chloride ion. All the divalent metal chlorides were assumed to be linear.

Frost and Woodson[3c] have shown that eq. 4 can be used to calculate values of R that correspond to the known equilibrium values. However, in this work the value of R was assumed known and energies were calculated. The results are given in Table II.

---

(4) See E. A. Mason and W. E. Rice, *J. Chem. Phys.*, **22**, 552, 843 (1954).

(5) E. A. Mason, *ibid.*, **23**, 49 (1955).

(6) E. Whalley and W. G. Schneider, *ibid.*, **23**, 1644 (1955).

(7) See E. S. Gould, "Inorganic Reactions and Structure," Henry Holt and Company, New York, N. Y., 1955, p. 143.

(8) L. Pauling, *J. Am. Chem. Soc.*, **50**, 1036 (1928).

(9) J. E. Lennard-Jones, *Proc. Roy. Soc.* (London), **A109**, 584 (1925).

(10) See F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, Chapter 2, for a discussion.

(11) P. George and D. S. McClure, *Progr. Inorg. Chem.*, **1**, 381 (1959).

(12) J. T. Hougen, G. E. LeRoi, and T. C. James, *J. Chem. Phys.*, **34**, 1670 (1961).

(13) R. A. Berg and O. Sinanoğlu, *ibid.*, **32**, 1082 (1960).

TABLE II

ENERGIES FOR THE REACTION $1/n\mathrm{MCl}_n(\mathrm{g}) \rightarrow \mathrm{M}^{n+}/n(\mathrm{g}) + \mathrm{Cl}^-(\mathrm{g})$ IN ELECTRON VOLTS

Molecule	E_{hs}	E_{pol}	E_{cov}	E_{exp}[a]	x
LiCl	6.57	7.06	7.03	6.70	0.89
NaCl	5.53	5.81	5.98	5.54	.87
KCl	4.63	5.03	4.96	4.88	.89
RbCl	4.46	4.79	4.76	4.72	.89
CsCl	4.23	4.57	4.53	4.51	.89
$BeCl_2$	13.71	16.65	15.02	14.64	.79
$MgCl_2$	10.79	11.85	12.25	11.77	.75
$CaCl_2$	9.22	9.69	10.30	10.05[b]	.80
$SrCl_2$	8.81	8.98	9.76	9.58[c]	.80
$BaCl_2$	8.39	8.70	9.16	8.94[c]	.84
$ZnCl_2$	10.51	12.33	12.95	13.00[d]	.63
$CdCl_2$	9.47	11.42	11.84	11.99[d]	.64
$HgCl_2$	9.33	11.19	12.68	13.05[d]	.54
$AlCl_3$	16.07	18.02	19.40	18.23[c]	.59
$TiCl_4$	18.66	21.98	23.72	23.56	.53
$TiCl_2$	...	12.25	12.29	11.59[d]	.83
$CrCl_2$	...	12.43	12.43	11.73[d]	.80
$MnCl_2$	...	11.12	11.74	11.74[d]	.79
$FeCl_2$	...	11.80	12.28	12.33[d]	.76
$CoCl_2$	...	12.59	12.95	12.33[d]	.73
$NiCl_2$	...	12.00	12.58	12.79[d]	.69

[a] Data from A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," Chapman and Hall, Ltd., London, 1953, and T. L. Cottrell, "The Strengths of Chemical Bonds," Butterworths, Ltd., London, 1958. [b] From R. A. Berg and O. Sinanoğlu, *J. Chem. Phys.*, **32**, 1082 (1960). [c] From data of Rossini, *et al.*, "Selected Values of Chemical Thermodynamic Properties," Natl. Bur. Std. Circ. 500, Washington, D. C., 1952. Heat of sublimation of $SrCl_2$ estimated as 62 kcal./mole. Heat of vaporization of $AlCl_3$ monomer taken as 30 kcal./mole from A. Smits and J. L. Meijering, *Z. physik. Chem.*, **B41**, 98 (1938). [d] From T. L. Allen, *J. Chem. Phys.*, **26**, 1644 (1957); see also ref. *b*.

The Polarizable Ion Model.—This calculation follows the earlier work of Garrick[10] and of Rittner.[3a] The potential energy function per bond is written as

$$E = -\frac{f}{R} - \frac{f^2\alpha}{2R^4\left(1 + \frac{n\alpha}{R^3}\right)} + \frac{B}{R^9} \tag{5}$$

where the first term is the same as for the hard sphere model. The second term is the polarization energy, assuming only polarization of chloride ion as being important. The polarizability of the chloride ion was taken as 3.0 Å.^{3}. The geometric factor n has the value zero for a diatomic molecule and 0.25, 1.01, and 1.15 for triatomic, tetraatomic, and pentaatomic molecules, respectively, if the geometry is regular.

The repulsive energy is now represented by the term in R^{-9}. Since the anion is grossly distorted, the inert gas parameters no longer can be used. The procedure is to set $(\partial E/\partial R)$ equal to zero and to evaluate B. Then E is calculated at the equilibrium value of R. The results are given in Table II.

Ionic Model with Covalent Bond Character.—The localized molecular orbitals of eq. 1 are used for each metal–chlorine bond, all assumed equal in a given molecule. If $\hat{H}$ is the one-electron Hamiltonian, then the energy of a pair of bonding electrons becomes

$$W = (1 + x)q_a + 2(1 - x^2)^{1/2}\beta + (1 - x)q_c \tag{6}$$

The anion and cation coulomb integrals are

$$q_a = \int \phi_a \hat{H} \phi_a d\tau \tag{7}$$
$$q_c = \int \phi_c \hat{H} \phi_c d\tau$$

The exchange integral is

$$\beta = \int \phi_a \hat{H} \phi_c d\tau \tag{8}$$

The atomic orbitals are normalized and the overlap integral is assumed to be zero, or negligible.

All of the above integrals are evaluated from empirical data, taking into account the important fact that they will be functions of x, the fraction of ionic character of the bond.[14] The problem is to estimate the energy of an electron in the field of the nuclei plus non-valence electrons, and the average field of the other valence electrons. For a diatomic molecule it is reasonable to set $q_c = -IP$, the ionization potential of the neutral metal atom. This ignores the possibility that the metal atom will simultaneously "hold" both valence electrons. In view of the high polarity of the bonds and because of correlation effects, this seems quite reasonable.

For the higher molecules it is necessary to allow for the simultaneous presence of several valence electrons on the cation and to use ionization potentials referring to the metal orbitals that are the ones used in bonding. For example, for the triatomic case

$$q_c = -xIP_2 - (1 - x)\frac{(IP_1 + IP_2)}{2} + \frac{VSPE}{2} \tag{9}$$

The meaning of eq. 9 is that for a fraction x of the time the metal ion has no valence electrons other than that to which q_c relates. Hence it is the second ionization potential, IP_2, relating to the process

$$\mathrm{M}^+(\mathrm{g}) \longrightarrow \mathrm{M}^{2+}(\mathrm{g}) + \mathrm{e} \tag{10}$$

which is relevant. For $(1 - x)$ of the time a second valence electron also is present. Thus the mean energy of the electrons, $(IP_1 + IP_2)/2$, is the proper quantity to use. It may be noted that the energy of the electron in the field of the electrons on the chloride ions is not included. This is because it is more convenient to count this interaction in computing the energy of the electron on the anion. Care must be taken not to count electron–electron repulsions twice.

The corresponding values of q_c for molecules MCl_3 and MCl_4 are given by the equations: tetraatomic

$$q_c = -x^2IP_3 - 2x(1 - x)\frac{(IP_3 + IP_2)}{2} - (1 - x^2)\frac{(IP_3 + IP_2 + IP_1)}{3} + \frac{VSPE}{3} \tag{11}$$

pentaatomic

$$q_c = -x^3IP_4 - 3x^2(1 - x)\frac{(IP_4 + IP_3)}{2} - 3x(1 - x)^2\frac{(IP_4 + IP_3 + IP_2)}{3} - (1 - x)^3\frac{(IP_4 + IP_3 + IP_2 + IP_1)}{4} + \frac{VSPE}{4} \tag{12}$$

The extension to MCl_5 and MCl_6 is obvious.

The valence state preparation energy, *VSPE*, is the

---

[14] This point has been discussed recently by J. Hinze and H. H. Jaffé, *J. Am. Chem. Soc.*, **84**, 540 (1962).

TABLE III

EXPRESSIONS FOR THE BEST VALUE OF x FOR DIFFERENT TYPE MOLECULES OBTAINED BY SETTING $\partial W/\partial x = 0$

Type molecule	Equation
Diatomic, MCl	$x = \frac{(IP_a + EA)/2 - IP_1 + 1/2R}{IP_a - EA - 2\beta/(1 - x^2)^{1/2} - 1/R}$
Triatomic, MCl_2	$x = \frac{(IP_a + EA)/2 - IP_1 + 1.75/2R + VSPE/2}{IP_a - EA - 2\beta/(1 - x^2)^{1/2} + (IP_2 - IP_1) - 1.75/R}$
Tetraatomic, MCl_3	$x = \frac{(IP_a + EA)/2 - IP_1 + 2.44/2R + VSPE/3}{\left(IP_a - EA - 2\beta/(1 - x^2)^{1/2} + 2(IP_2 - IP_1) + x(IP_1 + 2IP_2 + IP_3) - 2.44/R\right)}$
Pentaatomic, MCl_4	$x = \frac{(IP_a + EA)/2 - IP_1 + 3.08/2R + VSPE/4}{\left(IP_a - EA - 2\beta/(1 - x^2)^{1/2} + 3(IP_2 - IP_1) + 3x(IP_3 - 2IP_2 + IP_1) + x^2(IP_4 - 3IP_3 + 3IP_2 - IP_1) - 3.08/R\right)}$

energy required to promote an electron into a valence, or bonding, state.[15] These were calculated for sp, sp^2, and sp^3 valence states for MCl_2 and MCl_3 by formulas given by Moffitt.[16] For the transition metals, excluding zinc, the valence states were assumed to be sd and sd^3 for MCl_2 and MCl_4.

The coulomb integral q_a represents the energy of an electron in the field of the chlorine atom to which it belongs and the fields of the average charges of the other atoms. In all cases

$$q_a = -(1 - x)IP_a - x\,\frac{(IP_a + EA)}{2} - x\,\frac{f}{2R} \qquad (13)$$

IP_a is the ionization potential of the chlorine atom to the valence state ion, $s^2p_x{}^2p_y{}^2p_z{}^0$, and EA is the electron affinity of the chlorine atom. The probability that both electrons will be on the chlorine atom is x, and the average energy is $(IP_a + EA)/2$ plus the coulombic energy, which is $f/2R$ for one electron.

The exchange integral, β, is the most difficult to evaluate. The approximation finally used follows the original suggestion of Pauling and Sherman.[17] Thus β is taken as proportional to the geometric mean of the single bond energies, E_{aa} and E_{cc}, of chlorine and the metals

$$2\beta = -1.2(E_{aa}E_{cc})^{1/2} \qquad (14)$$

E_{aa} is the usual bond energy of Cl_2 and E_{cc} is the single bond energy of the gaseous molecule M_2, dissociating into valence state atoms. The factor of 1.2 allows 20% of the covalent bond energy in the molecules Cl_2 and M_2 to be cancelled by repulsion energy of the van der Waals' type.

Table I shows the values used for the valence state preparation energies and the exchange integrals. Literature references also are given. All ionization potentials were taken from C. E. Moore, "Atomic Energy Levels," National Bureau of Standards Circular 467, 1949 and 1952. An electron affinity of 3.86 e.v. for Cl and a dissociation energy of 2.52 e.v. for Cl_2 were used.

Having expressed q_c and q_a as functions of x, eq. 6 then is differentiated with respect to x and $(\partial W/\partial x)$ set equal to zero. This fixes the value of x which gives the best energy of the system. Table III gives convenient formulas for calculating x by successive approximations for the various cases considered. The quantity $-W$ in eq. 6 refers to the process

$$MCl(g) \longrightarrow M^+(g) + Cl^+(g) + 2e \qquad (15)$$

and differs from the coördinate bond energy by the ionization potential and electron affinity of chlorine. Also (6) does not include any repulsion terms. A suitable repulsion energy was assumed to be the van der Waals' repulsion calculated from the hard sphere model and listed in Table I. Thus the energy per bond becomes

$$E = -W - (IP_a + E_a + be^{-aR}) \qquad (16)$$

It was not possible to find the minimum value of eq. 16 to evaluate R because the variation of β with distance is not known. Instead experimental values of R were used as before. The results of the final calculations for the energy and for x are given in Table II.

Discussion

As expected, an examination of the coördinate bond energies for the hard sphere model shows that it is only satisfactory for the alkali chlorides. The polarized ion model works surprisingly well, poor results being found only for $BeCl_2$, $HgCl_2$, and $TiCl_4$. These compounds are expected to be quite covalent and indeed the model with covalent bonding gives much better results. However, for $BeCl_2$ the error in both calculations is in the opposite direction from that of $HgCl_2$ and $AlCl_3$. The high bond energies calculated for $BeCl_2$ (and LiCl) probably are due in part to penetration effects. That is, this cation because of its small number of electrons penetrates to a considerable extent into the electron cloud of the anion. Thus the coulombic energy term is considerably overestimated. An extreme example of this phenomenon would be shown by the proton in HCl, for example.

The close correspondence, in most cases, between the energies calculated by means of the polarized ion model and the covalent model indicates that both of these are approximate ways of calculating the same thing, the distortion of the electron cloud of the anion in the field of the cation. The covalent model in principle is more reliable in that it is based on a quantum mechanical approach. The polarization model is, of

---

[15] J. H. Van Vleck, *J. Chem. Phys.*, **2**, 20 (1934); R. S. Mulliken, *ibid.*, **2**, 782 (1934).

[16] W. Moffitt, *Rept. Progr. Phys.*, **17**, 173 (1954).

[17] L. Pauling and J. Sherman, *J. Am. Chem. Soc.*, **59**, 1450 (1937).

course, much easier to use in actual calculations.[18] In any event, it is clear that a model using both polarization effects *and* covalent bonding would be inconsistent. This point has been recognized by many authors.

The results for the covalent–ionic MO model are good enough to offer hope that a semi-empirical molecular orbital method can be used for many inorganic compounds to calculate bond dissociation energies and total molecular energies. The MO theory has been fairly successful in calculating many *relative* properties of inorganic systems, for example, absorption spectra.[19] However the application of MO theory to bond energies has been small. This may be contrasted with the outstanding successes of the semi-empirical MO approach in organic chemistry.[20]

In the present work two center, localized MO's were used for purposes of convenience in that only a single parameter, x, entered into the calculations. There is no reason why MO theory in its more exact form cannot be used in a similar way. This would allow spectroscopic data to be used as part of the available empirical information. The additional labor of solving for several mixing coefficients would not be great. The dependence of these coefficients on the degree of ionicity would still be necessary.

The greatest uncertainty lies in the value of β, the exchange integral. For example, no account was taken of the undoubted variation of β with x. Also it is possible that the assumed values of β in eq. 14 are far too small, and that all the molecules are much less ionic than indicated by the results. Some calculations are shown in Table IV which rule out this possibility, at least within the framework of the model used. It can be seen that changing β over a substantial range does not affect the degree of ionic character severely. Also, since the experimental bond energy and the calculated ones depart from each other more and more as β increases, it is unlikely that a higher value of β is correct.

TABLE IV

EFFECT OF VARYING β FOR $BeCl_2$

-2β, e.v.	x	E_{calcd}, e.v.
2.50	0.86	14.42
3.00	.82	14.70
3.60	.80	15.10
4.00	.76	15.30
4.50	.73	15.63

$E_{exp} = 14.64$ e.v.

Overlap integrals have been omitted in the calculations. This is a common procedure and experience shows that the energies are little affected by this procedure, even in the case of inorganic molecules.[21] The inclusion of the overlap integrals in the present work greatly complicates the calculations. In addition to the usual uncertainties of the proper representation of atomic orbitals to use, a choice must be made of some reasonable hybrid of atomic orbitals on both the metal atom and the chlorine to form the localized MO's.

As a check on the values of β used from eq. 14, the exchange integral also was calculated from Mulliken's "magic formula" in a few cases.[22] Overlap integrals for several assumed hybrids were calculated from formulas in the literature. Slater-type atomic orbitals appropriate to the neutral atoms, not the ions, were used. Converting to the meaning of β implied in the present work, Mulliken's formula becomes

$$-2\beta = \frac{ASI}{1 + S} \tag{17}$$

A may be taken as unity,[22] S is the overlap integral, and I is a mean ionization potential of the metal and chlorine atoms. The few calculations made indicated that β values calculated from eq. 14 and 17 are similar. For example, for $BeCl_2$ β from (14) is 3.60 e.v.; from (17) β is 3.09 e.v. for (2s, 3p) overlap and 4.0 e.v. for (2sp, 3p) overlap. The value of I used is given by eq. 18.

$$I = \frac{(IP_1 + IP_2 - VSPE)/2 + IP_a}{2} \tag{18}$$

These results indicate that the variation of β with the ionicity parameter x is contained chiefly in the overlap integral, the mean ionization potential being nearly independent of x.

The Criterion for Degree of Ionic Character.—The values of x shown in Table II seem very reasonable. The only experimental data of any value in checking such theoretical quantities are bond dipole moments and quadrupole coupling constants. These data unfortunately are very incomplete for the compounds listed. An examination of the dipole data[23] shows that the required relationship

$$x > \mu/eR \tag{19}$$

always is obeyed. The basis of eq. 19 is that polarization, overlap, and hybridization effects always will make the observed bond moment, μ, less than the simple value, exR.[24] The quadrupole coupling data agree reasonably well with Table II in that rather high degrees of ionic character are shown for the metal halides in general.[25] Again the compounds listed in Table II

---

[18] Unfortunately it has been shown that the polarized ion model is not useful in calculating properties more sensitive than the energies, for example, the infrared bending frequencies (see ref. 3e). However it gives reasonable results for stretching frequencies; see R. G. Pearson, *J. Chem. Phys.*, **30**, 1537 (1959).

[19] For a general review see C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., New York, N. Y., 1962, Chapter 7; and C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford, 1962.

[20] See A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961.

[21] (a) G. W. Wheland, *J. Am. Chem. Soc.*, **63**, 2025 (1941); (b) R. G. Pearson, *J. Chem. Phys.*, **17**, 969 (1949).

[22] R. S. Mulliken, *J. Phys. Chem.*, **56**, 295 (1952).

[23] See B. Lakatos and J. Bohus, *Acta Chim. Acad. Sci. Hung.*, **20**, 115 (1959); and B. Lakatos, J. Bohus, and G. Medgyesi, *ibid.*, **20**, 1 (1959), for a compilation of data.

[24] (a) J. C. Slater, *Phys. Rev.*, **91**, 528 (1953); (b) R. S. Mulliken, *J. Chem. Phys.*, **3**, 573 (1935); (c) B. P. Dailey and C. H. Townes, *ibid.*, **23**, 118 (1955).

[25] Some pertinent references are 3c; W. Gordy, *Discussions Faraday Soc.*, **19**, 14 (1955); T. Chiba, *J. Phys. Chem. Japan*, **13**, 860 (1958); R. P. Hamlen and W. S. Koski, *J. Chem. Phys.*, **25**, 360 (1956); R. G. Barnes and S. L. Segel, *ibid.*, **25**, 180, 578 (1956); A. H. Reddock, *ibid.*, **35**, 1085 (1961); D. Nakamura, Y. Kurita, K. Ito, and M. Kubo, *J. Am. Chem. Soc.*, **82**, 5783 (1960).

have not all been studied, nor have clean assignments of per cent ionic character been made for many of them. An exception is the family of alkali chlorides, for which nearly 100% ionic character is estimated from quadrupole coupling data.

The same group of compounds is the most ionic of any listed in Table II, but only about 90% ionic character is calculated. In fact from the equations of Table III, it can be seen that no compound will even be predicted to be 100% ionic, unless the exchange integral is identically zero. This result is a consequence of the model, but it does seem to be physically reasonable. However the interesting question is raised as to what other theoretical criteria for assessing the degree of ionic character of chemical bonds might be used.

A number of such criteria have been given in the literature. The most popular one has been based on the concept of electronegativity. The essence of this method is to assume that if two atoms of different electronegativities combine with each other, a transfer of charge will occur from the least electronegative to the most electronegative. Equilibrium then will correspond to the equalization of electronegativities. Hence the bond polarity is determined by the amount of charge necessary to raise the one element, and lower the other, on the electronegativity scale, until they meet. This proposal has appeared in several equivalent forms which differ only in the way in which electronegativity is defined.[26] Sanderson defines electronegativity in terms of the electron density of an atom or ion compared to a hypothetical inert gas (the stability ratio); Lakatos, *et al.*, define it as the average force acting on an electron at the bonding radius of the atom (this is the same as one of the definitions of Allred and Rochow[27]); and Margrave and Iczkowski define it in terms of the differential change in the ionization potential or electron affinity of an atom or ion as the charge on it varies.

In spite of the intuitive attractiveness of the equalization of electronegativities as a criterion of charge transfer, there is no theoretical justification for such an assumption. The statement of Lakatos, *et al.*, that the virial theorem implies a minimum value of the net force on an electron is not correct. The only property that is minimized is the total energy. The picture of two atoms exchanging charge until their affinity for electrons is equalized ignores two important aspects of the total energy. One is the mutual electrostatic energy of the ions produced by charge transfer and the other is the favorable effect on the kinetic energy because the electrons have a greater region of low potential energy space available to them (delocalization effect). The model of ionic–covalent binding seems to include these two effects as well as that of changing electronegativities.

Another criterion of bond polarity which has been widely quoted is that of "The Postulate of Essential Electroneutrality" due to Pauling.[28] This postulate states that atoms in a state of chemical combination are as near to being electrically neutral as possible. There seems to be no theoretical reason for such a statement, and the principle is in direct disagreement with the large amount of experimental evidence which indicates strong polarities in molecules and complex ions. Indeed the only evidence cited by Pauling for the postulate of electroneutrality is that of several cases in which an electron-rich area is brought near an electron-poor area. The resulting electron transfer, or polarization, is quite expected. The statement that electroneutrality is the point of equilibrium is purely an assumption which seems unreasonable in view of the foregoing discussion.

Acknowledgments.—This work was supported by the U. S. Atomic Energy Commission under Contract AT-(11-1)-1087. The authors are grateful to Professor S. Yamada of Osaka University, who checked and extended the calculations.

---

(26) References 2d and 23; R. T. Sanderson, *J. Chem. Educ.*, **36**, 507 (1959); R. P. Iczkowski and J. L. Margrave, *J. Am. Chem. Soc.*, **83**, 3547 (1961).

(27) A. L. Allred and E. G. Rochow, *J. Inorg. Nucl. Chem.*, **5**, 264, 269 (1958).

(28) L. Pauling, *J. Chem. Soc.*, 1461 (1948).