

Absolute Electronegativity and Absolute Hardness of Lewis Acids and Bases

Ralph G. Pearson

Contribution from the Chemistry Department, University of California, Santa Barbara, California 93106. Received April 15, 1985

Abstract: The relationship of χ° , the absolute electronegativity, and η , the absolute hardness, to chemical bonding in Lewis acid-base complexes is examined. This is done by using semiempirical MO theory in which the same experimental parameters appear. The a priori electronegativity of a Lewis acid or base is shown to be $(I + A)/2$. For any two atoms, ions, or molecules, the direction of net electron flow is determined by the difference in χ° values. For a specific pair of reactants, the effective value of χ° can range from A_A for a pure electron acceptor to I_B for a pure electron donor. The most common situation will have electron transfer in both directions (σ plus π bonding). Then χ° will be a weighted mean of I and A for both acid and base. The absolute hardness, $\eta = (I - A)/2$, determines the magnitude of the total electron transfer, both σ and π . Small values of η_A and η_B lead to the greatest amount of covalent bonding. For neutral molecules and cations, values of I and A for the species are used. For anions it is both necessary and theoretically logical to use values of I and A for the corresponding neutral atoms or radicals.

Recent work based on density functional theory has developed the concepts of absolute electronegativity, χ ,¹ and absolute hardness, η .² The definitions are

$$\chi = -\left.\frac{\partial E}{\partial N}\right|_Z = -\mu; \eta = \frac{1}{2}\left.\frac{\partial^2 E}{\partial N^2}\right|_Z \quad (1)$$

Where E is the electronic energy of a molecule, atom, or ion, N is the number of electrons, and Z is a fixed set of nuclear charges. The absolute electronegativity is also equal to the electronic chemical potential, μ , with change in sign. The operational (and approximate) definitions are

$$\chi = \frac{1}{2}(I + A); \eta = \frac{1}{2}(I - A) \quad (2)$$

where I is the ionization potential, and A is the electron affinity. The absolute electronegativity is the same as the Mulliken value.

We assume that for small changes in N , we can write

$$\mu = \mu^\circ + 2\eta\Delta N \quad (3)$$

If we have two chemical species, A and B, which are allowed to react, there will be a shift of electrons from the less electronegative molecule, B, to the more electronegative molecule, A. The condition of equilibrium is that the chemical potentials, μ_A and μ_B , become equal.³ This leads to a shift in charge, ΔN , from B to A.

$$\Delta N = \frac{(\chi^\circ_A - \chi^\circ_B)}{2(\eta_A + \eta_B)} \quad (4)$$

Electron transfer leads to an energy lowering, given by²

$$\Delta E = -\frac{(\chi^\circ_A - \chi^\circ_B)^2}{4(\eta_A + \eta_B)} \quad (5)$$

Note in (4) and (5) that electronegativity difference drive the electron transfer, and the sum of hardness parameters inhibit it. The hardness is the resistance of the chemical potential to change in the number of electrons. That is, $2\eta = (\partial\mu/\partial N)_Z$.

The chemical potential and the absolute electronegativity are molecular properties and not orbital properties. However, in considering the transfer of electrons from B to A, it becomes

necessary to consider the electrons as coming from definite occupied orbitals in B and going into definite empty orbitals in A. This defines the relative orientations of A and B, to give the greatest possible overlap between these frontier orbitals.⁴ Also η and χ are state functions, and while ground states are most often considered, sometimes it is useful to consider valence states or excited states, particularly for the reactions of atoms.

Equations 4 and 5 are obviously incomplete. The chemical potential is also a function of changing external fields, so that if A (or B) is charged, this will affect μ_B (or μ_A) as a function of the distance between A and B.⁵ Also there is no indication of the delocalization of electron density corresponding to covalent bonding.

In spite of these shortcomings, eq 4 and 5 are very appealing. They have the great virtue (and weakness) of trying to predict chemical behavior with a minimum number of parameters. Values of I are becoming available for more and more molecules.⁶ Values of A are still few in number. In fact for most molecules, the electron affinity cannot be detected. In such cases A is set equal to zero, meaning that E is a minimum when the electron is at infinity. Clearly this is inconsistent with the idea of electrons transferring to definite orbitals. It suggests instead negative values of A , related to, but not equal to, the energy of appropriate empty orbitals.⁷

The use of eq 4 and 5 actually predates the development of density functional theory.⁸ Attempts have also been made to include the effects of Coulombic interactions (ionic bonding) and of covalent bonding.⁹ However, this earlier work considered only atoms and radicals with one valence electron to contribute to a bond. Also the interest was in estimating the percent of ionic character in the bond, and the results are not convenient for bond energies.

In this paper we will consider the interaction of a Lewis acid and a base:



(4) Parr, R. G.; Yang, W. *J. Am. Chem. Soc.* **1984**, *106*, 4049.

(5) Nalewajski, R. F. *J. Am. Chem. Soc.* **1984**, *106*, 944.

(6) Rosenstock, H. M. et al. *J. Phys. Chem. Ref. Data* **1977**, *6*, suppl. no. 1.

(7) Lowe (Lowe, J. P. *J. Am. Chem. Soc.* **1977**, *99*, 5557) gives a useful discussion of the electron affinities of small molecules.

(8) Hinze, J.; Whitehead, M. A.; Jaffe, H. H. *J. Am. Chem. Soc.* **1963**, *85*, 148.

(9) Iczkowski, R. P. *J. Am. Chem. Soc.* **1964**, *86*, 2329. Evans, R. S.; Huheey, J. E. *J. Inorg. Nucl. Chem.* **1970**, *32*, 373. Reed, J. L. *J. Phys. Chem.* **1981**, *85*, 148.

(1) Parr, R. G.; Donnelly, R. A.; Levy, M.; Palke, W. E. *J. Chem. Phys.* **1978**, *68*, 3801. See also: Iczkowski, R. P.; Margrave, J. L. *J. Am. Chem. Soc.* **1961**, *83*, 3547.

(2) Parr, R. G.; Pearson, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 7512. See also: Huheey, J. E. *J. Phys. Chem.* **1965**, *85*, 148.

(3) This condition was first given by Sanderson as the postulate of electronegativity equalization. Sanderson, R. T. *Science (Washington, D.C.)* **1951**, *114*, 670. It is provable in density functional theory (ref 1).

Table I. Parameters for Some Atoms and Molecules^a

	χ° , eV	η , eV		χ° , eV	η , eV
BF ₃	8.3	7.3	H ₂ O	6.3	6.3
N ₂	7.0	8.6	I ₂	6.0	3.4
Cl ₂	7.0	4.6	Pt	5.6	3.5
CO ₂	6.9	6.9	H ₂ S	5.3	5.3
SO ₂	6.7	5.6	CH ₃	5.3	4.7
H ₂	6.7	8.7	(C ₂ H ₅) ₂ O	4.8	4.8
HCl	6.35	6.35	NO	4.6	4.6
O ₂	6.3	5.9	C ₆ H ₆	4.1	5.2
PF ₃	6.3	5.3	(CH ₃) ₃ P	4.0	4.0
CO	6.1	7.9	(C ₂ H ₅) ₃ N	3.8	3.8
			V	3.6	3.1

^aData from the following: Rosenstock, H. M. et al. *J. Phys. Chem. Ref. Data*, 1977, 6, suppl. no. 1; also ref 7. When unknown, A has been set equal to zero, so that $\chi = \eta$. For NO, $A = 0.02$ eV.

The emphasis will be on D_e , the bond dissociation energy of (6). To what extent can D_e be predicted from the isolated properties of A and B? The reactants can be atoms, ions, or molecules. Only gas-phase species and reactions will be considered at this time, though for neutral A and B the results in inert solvents will not differ greatly.

We wish to use the concepts of absolute hardness and absolute electronegativity. In the previous work² it was found that it was possible to get agreement between η , as defined in eq 2, and the chemical hardness or softness of various acids and bases, as embodied in the HSAB principle.¹⁰ A large value of η corresponded to a hard acid or base and a low value of η to a soft acid or base. However, this was only possible if experimental I and A values were used for A and B⁺, not A⁻ and B⁺ or A and B. This asymmetry is disturbing.

Since density functional theory is not familiar to most chemists¹¹ and since its extension to chemical bond formation is not trivial, a semiempirical molecular orbital approach will be used. This has the advantage of using quantities such as I and A as parameters, so that correspondences to (4) and (5) can be looked for.

There have been many previous MO treatments of Lewis acid-base reactions. The most relevant is that of Mulliken in his treatment of donor-acceptor interactions in charge-transfer complexes.¹² As is well-known, this successful theory uses only A_A for the electron acceptor, and only I_B for the electron donor. The quantity $(I_B - A_A)$ is an energy cost of transfer, per electron, from donor to acceptor.

To decide which of two molecules, A and B, is the electron donor and which the acceptor, it is clear that we must look at the difference

$$(I_A - A_B) - (I_B - A_A) = 2(\chi^\circ_A - \chi^\circ_B) \quad (7)$$

A positive value for the difference means that it costs less energy to transfer an electron from B to A. Thus the *direction* of electron transfer is determined by the absolute electronegativities, and the magnitude of $(\chi^\circ_A - \chi^\circ_B)$ is an a priori driving force for electron transfer.

Table I contains values of χ° and η for a number of neutral atoms and molecules. Any molecule high in the list is an electron acceptor for a molecule lower in the list. As far as the evidence goes, this rule is obeyed. At least it would be very unexpected to find that the net electron flow is in the opposite direction to that predicted. However, as shall be shown later, there can be cases of no electron transfer, in spite of a positive value for $(\chi^\circ_A - \chi^\circ_B)$.

The above remarks apply to *net* electron transfer from B to A. But in many, if not most, cases, there will be some electron transfer in both directions. If the transfer in both directions is the same, then the total energy cost is given by the sum

$$(I_A - A_B) + (I_B - A_A) = 2(\eta_A + \eta_B) \quad (8)$$

Thus hard molecules (large η) resist the transfer of electrons in both directions and soft molecules (small η) favor such a cooperative effect.

The factors which determine the value of η are easily discernible. Consider first the atomic case where N valence shell electrons all have the same value of n and l . The energy is given quite well by a quadratic equation

$$E = aN + bN^2 + E_{\text{core}} \quad (9)$$

So that we can use eq 1 to calculate

$$\chi = -a - 2bN = (I + A)/2 \quad (10)$$

$$\eta = b = (I - A)/2$$

The constant a is a combination of a core integral and a valence shell electron-electron repulsion integral. But b is exactly one-half the average valence shell electron-electron repulsion integral, as shown by Klopman.¹³

If some of the valence shell electrons have different values of n and l , then E cannot be a continuous function of N . There will be discontinuities at certain values of N and the average values, $(I + A)/2$ and $(I - A)/2$, will include these discontinuities. That is, there will be substantial changes in I or A when n or l changes for the next electron. These effects will be very large if we leave the valence shell in adding or removing an electron.

For molecules the situation is more complicated.^{13b} However, η will consist of two parts: an averaged interelectronic repulsion term and discontinuities due to going from bonding, or nonbonding, to antibonding molecular orbitals.

Molecular Orbital Calculations. We will consider first a two-atom, two-electron system in which there is only σ bonding between A and B. However, the method can easily be extended to the reactions of molecules. The wave function is written as

$$\psi = (\phi_B + \lambda\phi_A)/(1 + \lambda^2)^{1/2} \quad (11)$$

where ϕ_A and ϕ_B are atomic, or molecular, orbitals. Overlap is ignored and λ is a mixing coefficient so that $\lambda^2/(1 + \lambda^2)$ is the fraction of time an electron spends on atom A.

If we define q_A and q_B as one-center, one-electron coulomb integrals, and β as the two-center, one-electron exchange integral, then for constant values of q_A , q_B , and β , the energy derived from (11) is

$$E = (q_A + q_B) - ((q_A - q_B)^2 + 4\beta^2)^{1/2} \quad (12)$$

Equation 12 is not very useful because the coulomb integrals are not constant but are functions of λ . Notice, however, the appearance of the term $(q_A - q_B)^2$, which is Pauling's "ionic resonance energy", and suggests that $(q_A - q_B)$ and $(\chi_A - \chi_B)$ are related.¹⁵

Let N_A equal the average number of electrons on A and N_B the corresponding number for B. Then (11) leads to¹⁶

$$E = N_A q_A + N_B q_B + 2(N_A N_B)^{1/2} \beta$$

$$N_A + N_B = 2 \quad (13)$$

Each value of q consists of an intraatomic part and an interatomic part. For the intraatomic part, it is assumed that

$$q_A' = -I_A + (I_A - A_A)N_A/4$$

$$q_B' = -I_B + (I_B - A_B)N_B/4 \quad (14)$$

If $N_A = 0$ then $q_A' = -I_A$, and if $N_A = 2$ then $q_A' = -(I_A + A_A)/2$, which are correct at this level of approximation. The values of I and A are those of the neutral atoms, A and B, each with one valence electron. If $N_A = 1$, then $q_A' = -3/4 I_A - A_A/4$, which agrees with the statistical fact that 25% of the time both electrons

(13) (a) Klopman, G. *J. Am. Chem. Soc.* 1964, 86, 1463. (b) Klopman, G. *Ibid.* 1984, 86, 4550.

(14) Perdew, J. P.; Parr, R. S.; Levy, M.; Balduz, J. L. *Phys. Rev. Lett.* 1982, 49, 1691.

(15) Pearson, R. G. *J. Chem. Phys.* 1949, 17, 969.

(16) Pearson, R. G.; Gray, H. B. *Inorg. Chem.* 1963, 2, 358.

(10) Pearson, R. G. *J. Am. Chem. Soc.* 1963, 85, 3533.

(11) For example, see: Robles, J.; Bartolotti, L. J. *J. Am. Chem. Soc.* 1984, 106, 3723.

(12) Mulliken, R. S.; Person, W. B. *Annu. Rev. Phys. Chem.* 1962, 13, 107.

are on A, 50% of the time only one electron is on A, and 25% of the time both are on B.

The interatomic part of q depends on the final charges on A and B. There will be an ionic energy of interaction given by

$$U_c = (-1 + N_A N_B / 2) e^2 / R \quad (15)$$

where R is the internuclear separation. When $N_A = 0$ and $N_B = 2$, this ionic term is $-e^2/R$, corresponding to A^+ , B^- . If $N_A = N_B = 1$, the ionic term is equal to $-e^2/2R$. This corresponds to the reduced interelectronic repulsion when two electrons are delocalized over two atoms. Equation 15 comes from a point charge approximation. Equation 13 may now be written as

$$E = N_A I_A + \frac{(I_A - A_A) N_A^2}{4} - N_B I_B + \frac{(I_B - A_B) N_B^2}{4} - \frac{1}{R} + \frac{N_A N_B}{2R} + 2\beta (N_A N_B)^{1/2} \quad (16)$$

(using electronic units of charge, $e^2 = 1$). This could be solved for μ_A (or μ_B) by holding N_B (or N_A) fixed. It is more useful to hold $(N_A + N_B)$ fixed at two. Then setting $(\partial E / \partial N_A) = 0$, we find

$$N_A = \frac{I_A - A_B - 1/R - 2\beta / (N_A(2 - N_A))^{1/2}}{(I_A - A_A)/2 + (I_B - A_B)/2 - 1/R - 2\beta / (N_A(2 - N_A))^{1/2}} \quad (17)$$

There is a corresponding equation for N_B . If the parameters are known, (17) may be solved for N_A by successive approximation, and (16) may be solved for the energy.

An interesting result is found for the difference $(N_B - N_A)$, which determines the polarity of the bond.

$$(N_B - N_A) = \frac{2(\chi^\circ_B - \chi^\circ_A)}{(\eta_A + \eta_B) - 1/R - 2\beta / (N_A N_B)^{1/2}} \quad (18)$$

The standard definitions are used for χ° and for η , eq 2. The I and A values refer to neutral A and B, or to $N_A = N_B = 1$.

Equation 18 is related to the "ionic resonance energy". The energy in eq 16 for $N_A = N_B = 1$ is clearly higher than for the optimum values. The difference is given by

$$\Delta E = - \frac{(\chi^\circ_A - \chi^\circ_B)^2}{4[(\eta_A + \eta_B) - 1/R + 2\beta]} \quad (19)$$

if the polarity is not too large. This equation is closely related to eq 5.

The condition for minimizing the energy is to set $(\partial E / \partial N_A) = 0$ and similarly for N_B . This does not mean, however, that μ_A and μ_B are zero. The constraint that $(N_A + N_B) = 2$ has been used. To get μ_A we must vary N_A , holding N_B constant in eq 16, and similarly for μ_B . When this is done, we find $\mu_A = \mu_B$ and

$$\mu_A = -I_A + \frac{(I_A - A_A) N_A}{2} - 1/R + N_B/2R + \beta (N_B/N_A)^{1/2} \quad (20)$$

also that each is equal to μ_{AB} , the chemical potential of the molecule. These are the required conditions from density functional theory. The details are given in the Appendix.

A more useful result is found by taking the case where A and B are still some distance apart so that the interaction terms are negligible. Then we find

$$\begin{aligned} \mu_A &= -I_A + \frac{(I_A - A_A) N_A}{2} \\ \mu_B &= -I_B + \frac{(I_B - A_B) N_B}{2} \end{aligned} \quad (21)$$

For $N_A = 0$, we find $\chi^\circ_A = I_A$, and for $N_B = 2$, we find $\chi^\circ_B = A_B$. These are the appropriate values for the reaction of A with B before any electron transfer occurs. Then N_A in eq 17 is the number of electrons transferred from B to A. This number is

indeed proportional to $(\chi^\circ_A - \chi^\circ_B)$, but there are corrections due to the ionic and covalent terms. The difference between eq 3 and 21 is due to the choice of $N_A = 0$ and $N_B = 2$ for χ° .

These results are fortunate, because only parameters which are generally available are needed. For example, it would be impossible to know the electron affinity of Br^- , to form Br^{2-} . However, if we consider next the acid-base reaction of two neutral molecules, the reverse is true. If we carry out the same MO treatment as above for the reaction of iodine with benzene, we would need the electron affinity of I_2^- and the ionization potential of $C_6H_6^+$.

In this case, a reasonable compromise is to change the problem to a one-electron one. This was done by Flurry in his treatment of charge transfer complexes by MO methods.¹⁷

This treatment, translated into the same form as used above, gives

$$\Delta N = \frac{(A_A - I_B) + 1/R - \beta / (\Delta N(1 - \Delta N))^{1/2}}{-2\beta / (\Delta N(1 - \Delta N))^{1/2}} \quad (22)$$

$$E = (\Delta N - 1)I_B - \Delta N A_A + 2\beta (\Delta N(1 - \Delta N))^{1/2} - \Delta N/R \quad (23)$$

Now A and B stand for I_2 and C_6H_6 , as is customary, and ΔN is the fraction of an electron transferred from B to A. Since ΔN is small, the chance of a second electron being transferred is negligible. As a result (22) is much simpler than (17), to which it is otherwise related. The hardness parameters do not appear. The value of χ°_A is A_A and that of χ°_B is I_B .

If reasonable values of β and R are selected, eq 16 to 23 give good values for D_e . The repulsive potential can be absorbed in the value of β . In spite of a considerable difference in symbolism, eq 16 is essentially the same as an equation given earlier by Klopman.^{13b} A modification was introduced in the terms in $1/R$, in order to correct for penetration effects. This correction is important for bonds to hydrogen. Klopman obtained very good values for bond energies in some 40 examples. The method can also be extended to polyatomic molecules.³⁰

As long as only one-way electron transfer is occurring (σ -bonding only), we do not find $\chi^\circ = (I + A)/2$ for either the acid or the base. But there is a situation whereby two-way electron transfer can occur. This is the case of π -back-bonding, which will often be important in the reactions of neutral molecules.

In the reaction of I_2 with C_6H_6 , σ -bonding involves electron transfer from the filled π -orbitals of benzene to the empty σ^* orbital of iodine. But the geometry of the complex is such¹⁸ that there is also interaction between the filled π^* -orbitals of I_2 and empty π^* -orbitals of C_6H_6 . Even in the reaction of I_2 with NH_3 , there will be empty MO's on the ammonia of e' symmetry. These will have a positive overlap with the π^* orbitals of I_2 . While ordinarily there is little reason to believe in any significant use of these orbitals in NH_3 , the situation becomes different if we go to PH_3 and similar molecules.¹⁹ Furthermore, in all cases the charges developed on A and B by σ -transfer will favor π -back-bonding.

With some simplification, it is possible to make a molecular orbital calculation of simultaneous σ - and π -bonding, in the spirit of eq 13 to 18. We have

$$\begin{aligned} N_\pi \\ A \rightleftharpoons B \\ N_\sigma \end{aligned} \quad (24)$$

where N_π is the number of electrons transferred from a filled π -orbital on A to an empty π -orbital on B and similarly for N_σ . We assume that N_σ is larger than N_π , though the reverse might

(17) Flurry, R. L. *J. Phys. Chem.* **1965**, *69*, 1927; **1969**, *73*, 2111.

(18) Hassel, O.; Stromme, K. O. *Acta Chem. Scand.* **1958**, *12*, 1146; **1959**, *13*, 1781.

(19) For an excellent discussion of the π -accepting orbitals of phosphines see: Xiao, S. X.; Troglor, W. C.; Ellis, D. E.; Berkovitch-Yellin, B. *J. Am. Chem. Soc.* **1983**, *105*, 7033.

be true. Then $\Delta N = (N_\sigma - N_\pi)$ determines the net charges developed on A and B.

We generate both a σ -MO and a π -MO, similar to (11). The energy change after the dual electron transfer is

$$\Delta E = -(A_A - I_B)N_\sigma - (A_B - I_A)N_\pi + (\eta_A' + \eta_B')(\Delta N)^2 - (\Delta N)^2/R + 2\beta_\sigma(N_\sigma(2 - N_\sigma))^{1/2} + 2\beta_\pi(N_\pi(2 - N_\pi))^{1/2} \quad (25)$$

The ionic energy term is simplified to be the interaction of the net charges on A and B. The parameters $(\eta_A' + \eta_B')$ include all factors which hinder the building up of charges. Setting the derivatives of ΔE with respect to N_σ and N_π equal to zero, we find

$$N_\sigma = N_\pi + \frac{(A_A - I_B) + 2\beta_\sigma(1 - N_\pi)/(N_\sigma(2 - N_\sigma))^{1/2}}{2(\eta_A' + \eta_B') - 2/R + 2\beta_\sigma/(N_\sigma(2 - N_\sigma))^{1/2}} \quad (26)$$

$$N_\pi = N_\sigma + \frac{(A_B - I_A) + 2\beta_\pi(1 - N_\sigma)/(N_\pi(2 - N_\pi))^{1/2}}{2(\eta_A' + \eta_B') - 2/R + 2\beta_\pi/(N_\pi(2 - N_\pi))^{1/2}} \quad (27)$$

Equations 26 and 27 are awkward to solve further, and the calculated energies would not be very meaningful. But several key features can be extracted. If we assume that both σ - and π -bonding are comparable, so that

$$2\beta_\pi/(N_\pi(2 - N_\pi))^{1/2} \approx 2\beta_\sigma/(N_\sigma(2 - N_\sigma))^{1/2} = 2\beta^* \quad (28)$$

we find

$$(N_\sigma + N_\pi) = 2 - \frac{(I_A - A_A + I_B - A_B)}{2\beta^*} = 2 - \frac{(\eta_A + \eta_B)}{\beta^*} \quad (29)$$

$$(N_\sigma - N_\pi) = \Delta N = \frac{(I_A + A_A - I_B - A_B)}{4(\eta_A' + \eta_B') - 4/R + 2\beta^*} = \frac{(\chi^\circ_A - \chi^\circ_B)}{2(\eta_A' + \eta_B') - 2/R + \beta^*} \quad (30)$$

The important conclusions are that the total amount of charge transferred and the net charge depend on the hardness factors and electronegativities of the neutral species, A and B. The bond energy is related to ΔN to some degree. If the energy is calculated from eq 25 to $N_\sigma = N_\pi$, then an "ionic resonance energy" exists for the optimum values of N_σ and N_π .

It is eq 29, however, which is much more closely related to bond energies. In most cases where neutral (and nonpolar) molecules form acid-base adducts, the ionic part of the bonding is small, and covalent bonding dominates. The best possible covalent bonding would have $N_\sigma = N_\pi = 1$ (compare the covalent terms in (25)). If ΔN is small, the best value has $(N_\sigma + N_\pi) = 2$. In eq 29 we see that $(\eta_A + \eta_B)$ should be small, and β^* should be large, to maximize covalent bonding.

Furthermore, both η_A and η_B should be small. If one is large, normally η_A , then it means that I_A is large and A_A is small, or negative. This clearly favors one-way electron transfer only, from B to A. In this case, eq 28 to 30 may not be valid.

The values of χ° are found from eq 25. Only the intraatomic part is used, as before. We find

$$\mu_A = -A_A f - I_A(1 - f) \quad \mu_B = -I_B f - A_B(1 - f) \quad (31)$$

where f is the fraction of the change in N_A due to σ -bonding. We have two possibilities: if there is no bias, then $f = (1 - f) = 1/2$. This leads to $\chi^\circ = (I + A)/2$ for both A and B. This value would be relevant for a given molecule before a particular reaction partner was selected.

For a particular pair of reactants we would have

$$\chi^\circ_A = \frac{I_A N_\pi}{N_\pi + N_\sigma} + \frac{A_A N_\sigma}{N_\pi + N_\sigma}$$

$$\chi^\circ_B = \frac{I_B N_\sigma}{N_\pi + N_\sigma} + \frac{A_B N_\pi}{N_\pi + N_\sigma} \quad (32)$$

If $N_\sigma \gg N_\pi$, or the reverse, we would revert to the conditions of eq 21.

Table II. Parameters for Some Cationic Acids^a

acid	χ° , eV	η , eV	acid	χ° , eV	η , eV
Na ⁺	26.2	21.1	Zn ²⁺	28.8	10.8
Ag ⁺	14.6	6.9	Pd ²⁺	26.2	6.8
I ⁺	14.8	4.3	Hg ²⁺	26.5	7.7
Mn ⁺	24.4	9.3	Al ³⁺	74.2	45.8
Ca ²⁺	31.6	19.7	Sc ³⁺	49.3	24.6
Fe ²⁺	23.4	7.3	Tl ³⁺	40.3	10.5

^aData from the following: Moore, C. E. "Atomic Energy Levels" Natl. Bur. Stand. Cir. (U.S.) Vol. I, 1949; Vol. II, 1952; Vol. III, 1958.

To summarize, if there is only one-way electron transfer in the reaction of an acid and a base, we have $\chi^\circ_A = A_A$ and $\chi^\circ_B = I_B$. If there is two-way electron transfer of equal magnitude in both directions, we have $\chi^\circ_A = (I_A + A_A)/2$ and $\chi^\circ_B = (I_B + A_B)/2$. These results are in complete agreement with those of density functional theory.¹⁴ For one-way electron transfer the values of η_A and η_B are those of the neutral atoms, even if A⁺ and B⁻ are the reactants. For neutral molecules as reactants, the values of η_A and η_B are also for the neutral species, assuming that there is appreciable π -back-bonding. The possibility of such π -bonding in ions will be discussed below.

Hard and Soft Acids and Bases. For neutral acids and bases, the foregoing is a reasonable theoretical justification for the principle of hard and soft acids and bases,²⁰ at least as it refers to soft acids and bases. If η_A and η_B are both small, we can have stabilization of A:B by double bonding. It is interesting to note that this is essentially the π -bonding theory of Chatt,²¹ for explaining various metal ion-ligand preferences.

Hard acids and bases normally will have little two-way electron transfer. Equation 17 also shows that there will be little one-way transfer from B to A if η_A and η_B are large. The main source of bonding will come from ionic bonding or ion-dipole bonding. This is the accepted explanation for hard acid-hard base interaction.²²

Neutral molecules are the most likely to have two-way electron transfer. The unbiased values of $(\chi^\circ_A - \chi^\circ_B)$ determine the direction of net electron transfer. The total amount of electron transfer is governed by $(\eta_A + \eta_B)$, small values being favorable for maximum covalent bonding.

For cationic acids the likelihood of double bonding is greatly reduced. Still the values of χ° and η given by eq 2 contain information. Table II gives values of χ°_A and η_A for a number of monatomic cations. Large values of χ°_A are characteristic of hard Lewis acids, such as Na⁺, Mg²⁺, and Al³⁺. In these cases we can safely assume that only σ bonding will occur. Equations 16 to 19 are the relevant ones for energies. The effective value of χ°_A becomes I_A , and the effective value of the hardness parameter becomes η_A for the neutral atom. Numbers such as the second ionization potential of the sodium atom play no further role. This is, of course, just what we would expect.

For soft cations, such as Mn⁺, Cu⁺, and Ag⁺, the possibility of π -bonding must still be considered. We want η_A to be small, but χ°_A should not be too large. For example, consider the reactions of Mn⁺ and Cu⁺ with carbon monoxide.

$$\text{Mn}^+(\chi^\circ_A - \chi^\circ_B) = 5.4 \quad (\eta_A + \eta_B) = 12.0$$

$$\text{Cu}^+(\chi^\circ_A - \chi^\circ_B) = 7.9 \quad (\eta_A + \eta_B) = 14.2$$

These numbers are consistent with the stability of Mn(CO)₆⁺ and the instability of Cu(CO)₄⁺. The net direction of electron flow is from CO to the metal ion, by way of σ -bonding. But π -back-bonding must be substantial for Mn⁺ and less for Cu⁺.

The possibility of π -back-bonding for ions such as Hg²⁺ and Tl³⁺ will depend very much on the other ligands normally attached to them. Soft ligands lower χ° and η very substantially, while hard ligands have a smaller effect.²

(20) Hard acids prefer to coordinate to hard bases and soft acids to soft bases.

(21) Ahrlund, S.; Chatt, J.; Davies, N. R. *Q. Rev. Chem. Soc.* **1958**, *12*, 265. Chatt, J. *J. Inorg. Nucl. Chem.* **1958**, *8*, 515. Ahrlund, S. *Struct. Bonding (Berlin)* **1966**, *1*, 207.

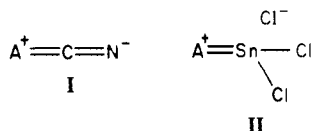
(22) Klopman, G. *J. Am. Chem. Soc.* **1968**, *90*, 223.

Table III. Parameters for Some Atoms and Radicals Whose Anions Are Bases^a

	χ° , eV	η , eV		χ° , eV	η , eV
F	3.40	7.0	Br	3.36	4.2
OH	1.83	5.7	I	3.06	3.7
NH ₂	0.74	5.3	H	0.74	6.8
CH ₃	0.08	4.9	CH ₃ S	1.9	3.1
Cl	3.62	4.7	<i>t</i> -C ₄ H ₉	-0.3	3.6
SH	2.30	4.1	C ₆ H ₅	1.1	4.1
PH ₂	1.25	4.3	NO ₂	3.1	3.3

^a Data from the following: Rosenstock, H. M. et al. as in Table I; also: DePuy, C. H.; Bierbaum, V. M. and Damrauer, R. *J. Am. Chem. Soc.* **1984**, *106*, 4051. χ° is assumed to be equal to A .

For anionic bases the probability of π -bonding, in which the base accepts the electron, must become quite small. Exceptions can exist if the anion is unsaturated, such as CN⁻, since plausible resonance structures can be written (I). Also for anions such as SnCl₃⁻, the possibility of π -bonding exists. Structure II, in this case, corresponds to hyperconjugation.



This structure derives from putting electrons from filled π -orbitals of the acid into empty orbitals of the base of the right symmetry. These empty orbitals are antibonding MO's. Similar hyperconjugation could exist even for CH₃⁻. But it must be easier to use these orbitals for the weaker bonds of tin than for the stronger bonds of carbon. Also an atom such as chlorine can bear the negative charge more readily than the less electronegative hydrogen.

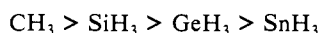
Most anions will act as σ -donors only, and χ°_B will equal A_B , the electron affinity of neutral B. The relevant value of η is also that for neutral B, since eq 16-19 give the bond energy. Table III gives values of A_B and of $(I_B - A_B)/2$ for a number of atoms and radicals, from which the common anions are derived.

It is easy to see why hard cations will prefer to bond to hard anions, since ionic bonding will be greatest for small, highly charged ions. But there also is an increased stabilization for a molecule like AgI, not found in KI or in AgF. That is, eq 16-19 cannot explain the bonding in AgI completely.

There are theories which predict additional stabilization when certain acid-base complexes are formed.²³ These are cases where both the donor and acceptor have filled π orbitals so that the normal π -back-bonding cannot occur. This is the situation in AgI. There will be a repulsion between the two filled π -orbitals, but this can be lessened by a mutual polarization. More specifically, the filled d or p orbitals on each atom are hybridized with empty p or d orbitals on the same atom.

The resultant energy lowering depends inversely on the excitation energy from the filled to the empty orbitals.²⁴ For atoms and monatomic ions it is found that the necessary promotion energies correlate with the values of η in Tables II and III. It is easier to promote Ag⁺ from the (3d)¹⁰ configuration to the (3d)⁹(4p) than to promote K⁺ from (3p)⁶ to (3p)⁵(3d). Similarly, it is easier to promote I than F. We may assume that the same is true for I⁻ and F⁻. There is evidence for this in the optical polarizabilities, which also vary inversely with promotion energies. However, they depend heavily on promotion to the continuum. Optical polarizabilities are not quite the same as the chemical polarizabilities under discussion.²⁵

For CH₃⁻ and SiH₃⁻ the necessary promotion would become indistinguishable from hyperconjugation. While data are scarce, it seems reasonable that the series



(23) Pitzer, K. S. *J. Chem. Phys.* **1955**, *23*, 1735. Mulliken, R. S. *J. Am. Chem. Soc.* **1955**, *77*, 884.

(24) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533.

(25) Jorgensen, C. K. *Struct. Bonding (Berlin)* **1967**, *3*, 106.

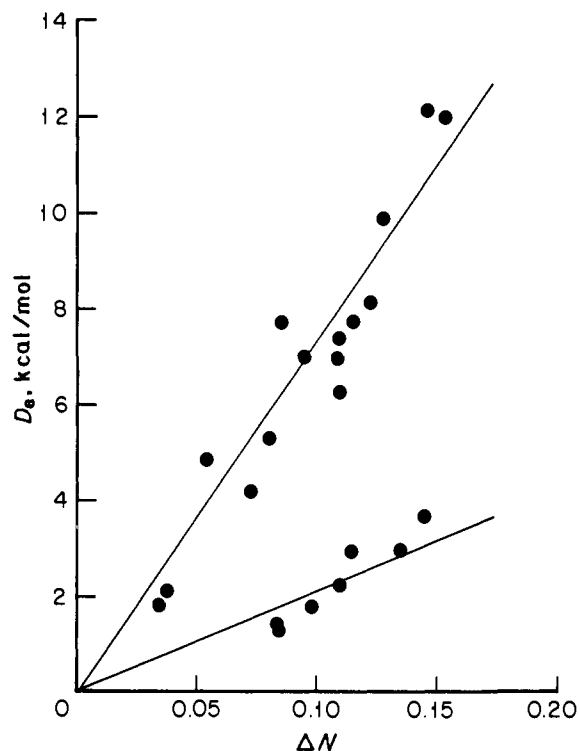


Figure 1. Upper curve is for O-, N-, and S-donors; lower curve is for benzene and methylbenzenes. Ordinate is dissociation energy of a complex at 25 °C and in inert solvents.

is the order of decreasing values of η , as well as increasing hyperconjugation. For ions such as NH₂⁻ and OH⁻, there will be some mixture of hyperconjugation and intraatomic excitation on the donor atom. In either case the series, F > OH > NH₂ > CH₃, should represent not only decreasing values of η but also increasing stabilization by way of π -interactions.

The conclusion is that the η_B values of Table III for neutral atoms and radicals can be used in place of the unavailable values for the corresponding anions. This agrees with the results found in ref 2. Though different mechanisms may operate, there will be additional stabilization between acids and bases with low values of η in Table I, II, and III.

Generally the values of η_B in Table III agree with expectation based on chemical behavior. There are exceptions, such as H⁻, which has a high value of η_B but is considered a soft base. The high value of η_B shows that H⁻ does not have π -stabilization, a reasonable result. The explanation for its chemistry lies in the small electron affinity of the hydrogen atom. This makes it possible for H⁻ to donate charge to very weak electron acceptors, such as transition-metal atoms and other soft Lewis acids.

A different kind of exception occurs in the case of CO, usually considered a soft base. It has a high value of η but also a high electronegativity. This means that it is the Lewis acid in its reactions with transition-metal atoms. The neutral metal carbonyls are an unusual case of π -bonding exceeding σ -bonding.²⁶

Concluding Remarks. Only limited theoretical justification can be given for eq 4 and 5, at least on the basis of molecular orbital theory. Still they seem to have some validity. Recently it has been shown that there is a good correlation between D_e , the mean bond energy in metal carbonyls, and $\Delta N/n$, the amount of electron density transferred from metal atom to CO per bond.²⁶ A variation of eq 4 was used to calculate $\Delta N/n$

$$\frac{\Delta N}{n} = \frac{(\chi^\circ_{\text{CO}} - \chi^\circ_{\text{M}})}{2(\eta_{\text{CO}} + n\eta_{\text{M}})} \quad (33)$$

In retrospect, the good results are probably due to the appearance of η_{M} in the denominator. A small value means a large

(26) Pearson, R. G. *Inorg. Chem.* **1984**, *23*, 4675.

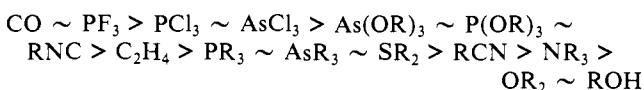
value of $\Delta N/n$. But it also means good covalent bonding, both σ and π , according to eq 29. A correlation between $(I - A)$ for Ni, Pd, and Pt with D_e was pointed out by DeKock some time ago.²⁷

Equation 4 may be useful in other cases, at least for neutral molecules. Figure 1 shows a plot of D_e vs. ΔN , from eq 4, for two series of bases reacting with I_2 in inert solvents. The lower curve is for several alkylbenzenes, and the upper curve is for a number of O, N-, and S-donor molecules. The different slopes presumably depend on values of β_σ and β_π , which would be smaller for the aromatic bases because of greater distances. It is of interest that D_e becomes too small to measure for H_2O acting as a base with I_2 . This is just when $\chi^\circ_A = \chi^\circ_B$ and $\Delta N = 0$, according to Table I.

There appears to be no obvious exception to the predicted direction of electron flow using (4). But there can be examples where $\Delta N = 0$, in contradiction to (4). The molecule SF_6 has $\chi^\circ = 9.9$ eV, much larger than for most molecules, but it is unreactive toward almost all. The accepting orbital in SF_6 is S-F antibonding, and breaking the strong SF bond requires more energy than forming a new bond which the base will create.

The main driving force for electron transfer in acid-base reactions must be the formation of a new covalent bond. The molecule BF_3 has $\chi^\circ = 8.3$ but shows no interaction with C_6H_6 , $\chi^\circ = 4.1$. In this case there is an empty nonbonding orbital available in BF_3 . But because of size and distance factors, there is poor overlap between this orbital and the filled π -orbitals of benzene. Thus β is too small to allow covalent bond formation to overcome the difference between A_A of BF_3 (about 1 eV) and I_B of benzene (9.3 eV). The value of η_A is too large for π -bonding to be a factor. Larger and softer acids, like $AlCl_3$, will form complexes with C_6H_6 .

For most molecules the electron affinity is not known. The convention is to set $A = 0$, in such cases. But this must lead to some error. Consider the series



The ordering is that of decreasing π -bonding with transition metals.²⁸ The order cannot be explained by considering ionization potentials alone, since these are high at either end of the series. While the value of β_π must vary and could explain some of the ordering, it must also be true that the effective value of A must become a larger negative number as we go from CO and PF_3 to amines and ethers.³¹

As mentioned earlier, the effective electron affinity must be related to the energy of the empty orbital which accepts the electrons. This may differ from an experimental value in some cases. For example, any polar molecule with a dipole moment greater than 1.63 D must have a finite, though small, electron affinity.²⁹ The electron in such cases is in a very diffuse Rydberg-like orbital. Such orbitals cannot be used to form bonds to electron donors and have little chemical significance.

Appendix

Equation 20 and the corresponding equation for μ_B are simplified by inserting the equilibrium values of N_A and N_B , written as $N_A = (1 - \Delta N/2)$ and $N_B = (1 + \Delta N/2)$, and by expanding the square root term in powers of ΔN . For ΔN less than one, the results are given reasonably well by the first term only.

$$\mu_A = -\frac{(I_A + A_A)}{2} - 1/2R + \beta + \frac{\Delta N}{2} \left(\beta + 1/2R - \frac{(I_A - A_A)}{2} \right) \quad (34)$$

$$\mu_B = -\frac{(I_B + A_B)}{2} - 1/2R + \beta - \frac{\Delta N}{2} \left(\beta + 1/2R - \frac{(I_B - A_B)}{2} \right) \quad (35)$$

If ΔN is given its value from eq 18, it is found that $\mu_A = \mu_B$, again expanding the square root and keeping only the linear term.

The chemical potential of the molecule, μ_{AB} , is found by writing $N_A = (N - \Delta N)/2$ and $N_B = (N + \Delta N)/2$ in eq 16. Here N is the total number of electrons in the orbital.

$$\mu_{AB} = \left(\frac{\partial E}{\partial N} \right) = -\frac{(I_A + I_B)}{2} + \frac{(\eta_A + \eta_B)}{2} - 1/2R + \beta - \frac{\Delta N}{4}(\eta_A - \eta_B) \quad (36)$$

After some manipulation, this result gives

$$\mu_{AB} = (\mu_A + \mu_B)/2 = -\frac{(I_A + A_A + I_B + A_B)}{4} - 1/2R + \beta - \frac{\Delta N}{4}(\eta_A - \eta_B) \quad (37)$$

It is interesting to note that μ_{AB} is less than the mean value, $(\mu^\circ_A + \mu^\circ_B)/2$, before reaction. This is true whether the reaction occurs between A and B with zero and two electrons, respectively, or A and B each with one valence electron.

Acknowledgment. This work was supported by a grant from the Department of Energy, Contract DE-AS03-76SF00034.

(27) DeKock, R. L. *Inorg. Chim. Acta* **1976**, *19*, L27.

(28) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry," 3rd ed.; Wiley-Interscience: New York, 1972; p 720.

(29) Crawford, O. H. *Mol. Phys.* **1971**, *20*, 585; **1973**, *26*, 139.

(30) Klopman, G. *J. Am. Chem. Soc.* **1965**, *87*, 3300.

(31) For recent results on negative electron affinities see: Tossell, J. A.; Moore, J. H.; Giordan, J. C. *Inorg. Chem.* **1985**, *24*, 1100.