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HARD AND SOFT ACIDS AND BASES—THE EVOLUTION OF A CHEMICAL CONCEPT

RALPH G. PEARSON

Department of Chemistry, University of California, Santa Barbara, CA 93106 (U.S.A.)

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A. INTRODUCTION

The term "hard and soft acids and bases" first appeared in the literature in 1963 [1]. Ten years later a book was published which gave a detailed account of the early history of this subject [2] and there is also a shorter review of the topic [3]. Full credit was given to the pioneering contributions of Edwards, Ahrland, Chatt, Davies, Schwarzenbach, Jørgensen, Hudson, Klopman and Saville.

As a result, the present paper will deal mainly with the more recent developments of the concept of chemical hardness. However, a necessary summary of the early work will be given. Also, to expedite matters, it will be stated at once that the symbol η (Greek letter h) will be used to denote hardness. Softness will be denoted by σ, and is simply the reciprocal of hardness, $\sigma = 1/\eta$.

B. SUMMARY OF EARLY WORK

The essential idea was to look at chemistry in terms of the generalized acid–base concept of Lewis:

$$A + :B \rightleftharpoons A:B \tag{1}$$

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Various molecules or complex ions, A : B, were considered to be formed from an electron acceptor A and an electron donor B. The stability of A : B was a result of the acid–base interaction between the two parts.

The coordinate bond energy, $-\Delta H$ for reaction (1), was a function of the properties of A and B. This is a thermodynamic property, obviously, but kinetics could also be included by considering transition states to be A : B complexes as well.

A large number of Lewis acids were put into one of two boxes, eventually labeled hard and soft. The same was done for a number of common bases. The classification was done empirically, but because of a shortage of data, all of one kind, a variety of criteria were used. These included bond energies, equilibrium constants, rates of reaction and even the existence or non-existence of certain compounds.

The properties of the acids and bases in the various boxes were such that it seemed reasonable to label the boxes as hard or soft. In general terms we had the following definitions: (1) soft acid—the acceptor atom is of low positive charge, large size and has polarizable outer electrons; (2) hard acid—the acceptor atom is of high positive charge, small size and has no easily polarized outer electrons; (3) soft base—the donor atom is of low electronegativity, easily oxidized, highly polarizable and with low-lying empty orbitals; (4) hard base—the donor atom is of high electronegativity, hard to oxidize, of low polarizability and with only high energy empty orbitals.

Such qualitative description did not allow for the quantification of hardness or softness. Acids and bases were put into one of two categories, but there was no way to rank order within the boxes. It was still possible to summarize a great deal of diverse chemical information by the principle of hard and soft acids and bases (HSAB): hard acids prefer to coordinate to hard bases and soft acids prefer to coordinate to soft bases.

The HSAB principle is an empirical one, which simply restates the very information which caused each acid or base to be placed in its proper box. It depends on no theory for its validity. Nevertheless, it was very clear that soft–soft combinations depended mainly on covalent bonding and hard–hard combinations mainly on ionic bonding.

The inability to define hardness in an exact way, and to assign numerical values to η, was a very serious drawback and led to much well-deserved criticism. Many empirical scales were proposed, but none were of general utility, or with a sound theoretical base.

A complicating feature was that there is at least one other property of an acid or a base that determines its behavior. For want of a better term, this may be called the intrinsic strength. Thus H_2O and OH^- are both hard bases, but the latter forms stronger bonds to virtually all acids than the former. Also Mg^{2+} and Na^{+} are both hard acids, but Mg^{2+} is the stronger acid.

The strength of the coordinate bond in A : B must depend chiefly on the intrinsic strengths of A and B. The HSAB principle is really stating that there is an extra stabilization in a hard–hard or soft–soft combination. Equally, there can be a destabilization in a hard–soft combination. In spite of these difficulties, the HSAB concept has proved to be useful in a number of different areas of chemistry, to say nothing of more diverse fields such as mineralogy and medicine. The oft-maligned terms, hard and soft, appear to fill a void in our chemical vocabulary. For example, two of the publications on HSAB [1,3] have been identified by *Current Contents* as among the most widely quoted references in the scientific literature.

C. DAWN OF THE NEW ERA

In 1973 I wrote, "As to what the future holds for HSAB, no one can say. It seems inevitable that the entire concept will be replaced by statements that are less ambiguous and more felicitously phrased. Nevertheless these statements will still have to accomplish the same mission of condensing a maximum amount of chemical information into a minimum number of words" [2].

The future began only five years later when Parr et al. [4] published a paper on the application of density functional theory (DFT) to chemical systems. DFT is a quantum mechanical method which focuses on the one-electron density function ρ instead of on wavefunctions [5]. The details of the theory need not concern us [6], but the conclusions that can be drawn are rather simple and easy to apply.

What Parr showed was that for every chemical system there is a quantity μ, called the electronic chemical potential. A chemical system is an atom, molecule, ion or radical, or several such units in a state of interaction. The chemical potential must be constant everywhere in such a system. It also has the important and defining property given by

$$\mu = \left(\frac{\partial E}{\partial N}\right)_v = \left(\frac{\delta E}{\delta \rho}\right)_v \tag{2}$$

where E is the electronic energy, N is the number of electrons and v is the potential due to the nuclei. The symbolism of the second part of eqn. (2) refers to the functional relationship of E to the density ρ.

To understand eqn. (2), Fig. 1 shows a plot of E vs. N for any arbitrary system. The energies are all negative with zero energy high up on top. We only know the energy experimentally for integral values of N from data such as ionization potentials I and electron affinities A. However, it is convenient

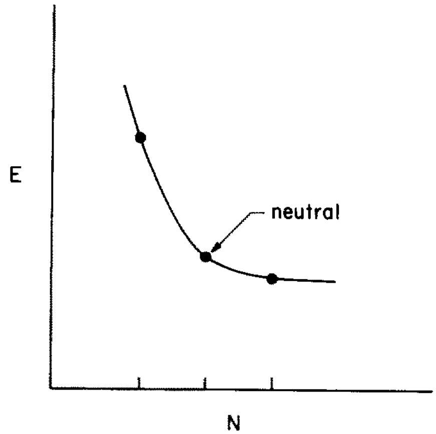


Fig. 1. Plot of electronic energy vs. number of electrons for a fixed set of nuclei.

to think of a smooth curve connecting the known values. In a molecule it is common to think of each atom, for example, having a non-integral number of electrons.

Now μ is simply the instantaneous value of the slope of Fig. 1 at any value of N. If we pick the neutral species (or any other) as our starting point, the method of finite differences can be used to estimate the slope

$$-\mu = -\left(\frac{\partial E}{\partial N}\right)_v \approx \frac{(I+A)}{2} = \chi_M \tag{3}$$

$(I+A)/2$ is simply the Mulliken electronegativity χ_M. Because of the fundamental relationship to the chemical potential, χ_M may be called the absolute electronegativity (this identification of the electronegativity with $(\partial E/\partial N)$ was first suggested in ref. 7).

It is important to realize that χ_M, or just χ, is now quite different from Pauling's original meaning of electronegativity, which was a property of an atom in a molecule. Now χ is a property of the entire molecule, atom, ion or radical. This alters the uses of χ dramatically.

For the molecule, χ measures the ability to attract electrons to itself. If two molecules are brought together, electrons will flow from the one of lower χ to that of higher χ. At equilibrium a single value of χ (and of μ) will exist throughout. It can be seen from Fig. 1 that μ and χ change as N changes. This change of slope is the curvature of the non-linear plot. From the method of finite differences, the curvature is equal to $(I-A)$.

Chemical hardness and density functional theory came together in 1983 when Parr spent a sabbatical quarter at the Institute for Theoretical Physics in Santa Barbara. He showed me Fig. 1 and asked if the curvature might have something to do with HSAB. After a few quick calculations, I could answer that it did.

Within a few days we wrote a paper which rigorously defined η and gave an empirical method of evaluating it [8]:

$$\eta = \frac{1}{2}\left(\frac{\partial \mu}{\partial N}\right)_v = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right) - \frac{(I-A)}{2} \tag{4}$$

The factor of one-half was put in to symmetrize with χ. As it turned out, it would have been better not to include it.

For two reactants, A and B, we wrote

$$\mu_A = \mu_A^0 + 2\eta_A \, \Delta N \tag{5}$$

$$\mu_B = \mu_B^0 + 2\eta_B \, \Delta N \tag{6}$$

where ΔN is the number of electrons transferred from the base to the acid. Applying the condition that $\mu_A = \mu_B$, we could write

$$\Delta N = \frac{(\mu_B^0 - \mu_A^0)}{2(\eta_A + \eta_B)} = \frac{(\chi_A^0 - \chi_B^0)}{2(\eta_A + \eta_B)} \tag{7}$$

Clearly the acid must be more electronegative than the base. The difference in absolute electronegativities drives the electron transfer, and the sum of the hardness parameters acts as a drag or resistance.

This was very satisfactory, since the common meaning of hardness is resistance to change or deformation. Also, an explanation of the HSAB principle began to emerge. Two soft molecules would have a large value of ΔN. The transferred electrons are used to form the coordinate covalent bond between A and B. Two hard molecules would have small ΔN, little covalent bonding, and a reliance on ionic bonding instead.

In spite of this, it was by no means clear that eqn. (4) was a valid definition of the hardness implied by the HSAB concept. Only for cations, atoms and a few molecules and radicals could it be shown to give reasonable results. For anions, the approximation $\eta = (I - A)/2$ was clearly not valid. For molecules there were many values of I available, but only a few values of A.

Most common molecules, in fact, have negative electron affinities. Parr and I had decided to use the adiabatic value, $A = 0$, for these cases, since negative values of A did not seem to be reliable. However, eqn. (4) stated clearly that it was the vertical values of A, the negative ones, that were required. Setting A equal to zero did not give good results in most cases.

At this point there were some timely and fortunate developments. The technique of electron transmission spectroscopy had already been invented, to give accurate values of negative electron affinities [9]. In fact, a number of results had been published, although most chemists were unaware of them. Increased activity in the field, leading to many new results, finally came to my attention [10,11]. At the same time new methods were found for rapidly measuring positive electron affinities, and many new values were published [12].

At the same time, Parr and coworkers were making important advances on the theoretical side. Parr and Yang [13] reconciled DFT with the frontier orbital theory of chemical reactivity . Since this theory is very successful, it is important to show that the DFT approach is not inconsistent.

While χ and η are global properties of the system, the electron transfer between two molecules will still involve definite filled orbitals on the donor and definite empty orbitals on the acceptor. The most important donor orbital will usually be the highest occupied molecular orbital (HOMO), and the most important acceptor orbital will usually be the lowest unoccupied molecular orbital (LUMO). The normalized electron densities of these frontier orbitals are called the fukui functions f:

$f = \rho_{\mathrm{HOMO}}$	donor molecule
$f = \rho_{\mathrm{LUMO}}$	acceptor molecule
$f = \frac{1}{2}(\rho_{\mathrm{HOMO}} + \rho_{\mathrm{LUMO}})$	both donor and acceptor

The last equation is for the case where there is electron transfer in both directions, as in $\sigma + \pi$ bonding. This is, in fact, the normal situation, although one direction is usually dominant. Reaction will occur between two molecules in such an orientation as to give maximum overlap between the various HOMOs and LUMOs. The magnitude of the fukui functions at the several sites in each molecule will determine which atom will form the coordinate covalent bonds.

Unlike the chemical potential μ, the hardness η is not constrained to be constant everywhere. Berkowitz et al. [14] defined the local hardness $\tilde{\eta}$:

$$\tilde{\eta} = \frac{1}{2}\left(\frac{\delta \mu}{\delta \rho}\right)_v \tag{8}$$

This measures the change in chemical potential with changing electron density in different parts of the molecule.

The calculation of the local hardness is difficult. A related function $\tilde{\sigma}$, the local softness, is easier to work with [15]:

$$\tilde{\sigma} = \left(\frac{\delta \rho}{\delta \mu}\right)_v = \sigma f \tag{9}$$

If the global softness σ and the frontier orbitals are known, we can calculate $\tilde{\sigma}$ at each atom. In a chemical reaction the most efficient interaction will be between the softest parts of each molecule. This allows the maximum transfer of electrons for a given difference in chemical potentials.

Although $\tilde{\sigma}$ and $\tilde{\eta}$ are related, one is not simply the reciprocal of the other [16]. Fortunately there is another way of estimating local hardness at a given atom in a polyatomic system. This is based on the distribution of electron density at each atom, leading to a net charge on the atom. The assumption is then made that the local hardness increases with the net positive charge.

Equation (7) must not be used as a way to calculate the net charges on molecules A and B. It only measures the initial effects of bringing A and B into interaction with each other. As the distance between the reactants decreases, there will be further charge shift and large energy effects due to covalent and ionic bonding. Using semiempirical molecular orbital (MO) theory, an equation for ΔN can be calculated similar to eqn. (7), but including ionic bonding and covalency [17]. For two neutral atoms, each with one valence electron

$$\Delta N = \frac{\left(\chi_A^0 - \chi_B^0\right)}{2(\eta_A + \eta_B) - (1/R) - \left[2\beta/(N_A N_B)^{1/2}\right]} \tag{10}$$

Here β is the one-electron exchange integral, which has a negative value, R is the internuclear distance and N_A and N_B are the final numbers of electrons of A and B.

DFT may also be used to investigate the further interaction of A and B as R decreases [18]. The results show that there will be changes in ρ which correspond to ionic bonding and covalency. The final equations are not easy to use, but they do confirm that there will be strong directional preferences for the chemical interaction of two systems.

In spite of its shortcomings, eqn. (7) is still useful. It has the great virtue of trying to predict as much chemistry as possible from two properties of an isolated system, the ionization potential and the electron affinity.

Theory suggests that it is the sum and difference of these two properties that are significant. For an electron acceptor, it is clear that A is an important parameter, but why should I be considered. Similarly for a base, I must be important, but why should A be considered? One reason can be seen rather easily. If we have two molecules C and D, which is the acid and which is the base? To answer this question, we can look at the difference in energy

$$(I_C - A_D) - (I_D - A_C) = 2\left(\chi_C^0 - \chi_D^0\right) \tag{11}$$

A positive value for the difference means that it costs less energy to transfer an electron from D to C than the reverse. Hence C is the Lewis acid.

Suppose we transfer electrons equally in both directions, as in $\sigma + \pi$ bonding. Now the total energy must be considered:

$$(I_C - A_D) + (I_D - A_C) = 2(\eta_C + \eta_D) \tag{12}$$

Hard molecules, where η_C and η_D are both large, will resist such dual transfer of electrons. Soft molecules will favor such a cooperative effect.

Further insight into the fundamental meaning of η comes from consideration of an atom where N valence electrons all have the same values for n and l. The energy of the valence electrons is known to be given by the quadratic equation

$$E = aN + bN^2 \tag{13}$$

We can use eqns. (3) and (4) to calculate

$$\chi^0 = -a - 2bN = \frac{(I + A)}{2} \tag{14}$$

$$\eta = b = \frac{(I - A)}{2} \tag{15}$$

The constant a is a combination of a core integral and a valence shell electron–electron repulsion integral; b is exactly one-half the average valence shell electron–electron repulsion integral [19].

Such electron–electron repulsions are a function of size and charge. Large atoms that are neutral, or negative, have a small value of b and η. Small atoms with a positive charge have large b and η.

It is interesting to note that as early as 1965 Huheey [20] used eqn. (14) and Sanderson's postulate of equalization of electronegativity to derive an analog of eqn. (7) for atoms and univalent radicals. Instead of identifying b with hardness, Huheey called it the inverse charge capacitance. The capacitance of a spherical condenser is equal to $4\pi\epsilon_0 R$ in SI units. Komorowski [21] has suggested that $\eta = (4\pi\epsilon_0 R)^{-1}$ for atoms.

However, if some of the valence shell electrons, or orbitals, have different values of n and l, then eqn. (13) is not valid. There will be discontinuities at certain values of N, and these discontinuities will contribute to χ and η. To see their effect, it is necessary to use an orbital description of the atom or molecule.

D. CORRELATION WITH MOLECULAR ORBITAL THEORY

According to Koopmans' theorem, the frontier orbital energies are given by

$$\begin{aligned} -E_{\mathrm{HOMO}} &= I \\ -E_{\mathrm{LUMO}} &= A \end{aligned} \tag{16}$$

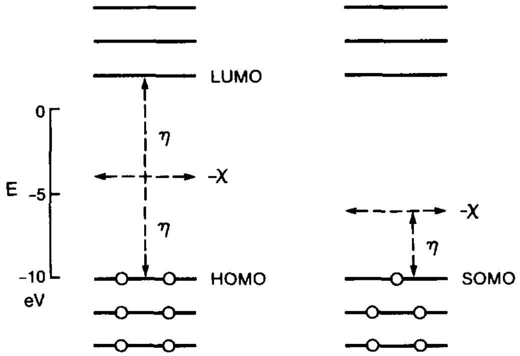


Fig. 2. Orbital energy diagram showing χ and η for a filled shell molecule (left) and an atom or radical (right).

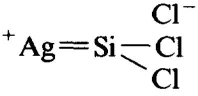
Figure 2 shows the usual orbital energy diagram for a filled shell molecule where $I = 10.0$ eV and $A = -2.0$ eV. Then $\chi^0 = 4.0$ eV and $\eta = 6.0$ eV. The former is shown as a broken horizontal line on the diagram. It is just the average of the HOMO–LUMO energies, with change in sign. The broken line also locates the electronic chemical potential, $\mu = -4.0$ eV.

The hardness is shown as a broken vertical line. The HOMO–LUMO gap is equal to twice the value of η. This gives a new insight into the meaning of hardness. A hard molecule is characterized by a large HOMO–LUMO gap. A soft molecule has a small gap.

For atoms or radicals where the HOMO is only singly occupied (SOMO) the situation is different, since the electron affinity usually refers to adding an electron to the SOMO. Figure 2 shows an example where $I = 10.0$ eV and $A = +2.0$ eV. Both $\chi^0 = 6.0$ eV and $\eta = 4.0$ eV are shown on the figure. The (unknown) energy of the LUMO plays no part. The quantity $(I - A) = 2\eta$ is just the mean repulsion energy of the two electrons in the SOMO [22].

Figure 2 for the filled shell case is very satisfying. For example, optical polarizability in quantum theory results from mixing suitable excited state wavefunctions with the ground state wavefunction. The mixing coefficient is inversely proportional to the excitation energy from the ground to the excited state. A small HOMO–LUMO gap means small excitation energies to the manifold of excited states. Therefore soft molecules are more polarizable than hard molecules, and we regain the classical definition of softness.

There are also chemical consequences of high polarizability. A soft acid and a soft base can stabilize their union by mutual polarization. This is more than just van der Waals' bonding, since real bonds can be formed. An example is given by soft Ag^+ combining with soft CN^- and $SiCl_3^-$:


$^{+}Ag{=}Si(Cl^{-})(Cl)Cl$

$^{+}Ag{=}C{=}N^{-}$

Such conjugation, or hyperconjucation, requires the *d* orbital electrons of Ag^+. Hard Na^+ cannot enter into such bonding. Clearly we have another reason for the HSAB principle.

There are further chemical deductions to be drawn from Fig. 2. Soft molecules should be more reactive than hard molecules in unimolecular processes such as dissociation or isomerization. The basis for this statement is the quantum mechanical treatment of chemical reactions, based on second-order perturbation theory. Various formulations may be used [23], but for present purposes the method based on the second-order Jahn–Teller effect is most appropriate [24].

We start with a collection of nuclei and electrons at some point Q_0 representing an initial nuclear configuration. The wave equation is assumed to be solved, giving rise to a number of eigenvalues $E_0, E_1, \ldots, E_k$, and the corresponding electronic eigenstates $\psi_0, \psi_1, \ldots, \psi_k$. We now move the nuclei a small distance Q along the reaction coordinate. The new ground state energy is now calculated by second-order perturbation theory.

After distortion the Hamiltonian may be written as a Taylor–Maclaurin series

$$H = H_0 + \left(\frac{\partial U}{\partial Q}\right) Q + \frac{1}{2}\left(\frac{\partial^2 U}{\partial Q^2}\right) Q^2 \ldots \tag{17}$$

where H_0 is the original Hamiltonian, U is the nuclear–nuclear and nuclear–electronic potential energy and Q is the small displacement along the reaction coordinate. We truncate the series at Q^2.

The energy becomes

$$E_0 + \left\langle \psi_0 \left| \frac{\partial U}{\partial Q} \right| \psi_0 \right\rangle Q + \left\langle \psi_0 \left| \frac{\partial^2 U}{\partial Q^2} \right| \psi_0 \right\rangle \frac{Q^2}{2} + \sum_k \frac{\left[\left\langle \psi_0 \left| \frac{\partial U}{\partial Q} \right| \psi_k \right\rangle Q\right]^2}{(E_0 - E_k)} \tag{18}$$

E_0 is the original energy at point Q_0, the next two terms are the first-order perturbation energy, and the last term is the second-order perturbation energy. The angular brackets indicate integration over the electronic coordinates only.

At the same time the wavefunction changes from ψ_0 by mixing in the excited state wavefunctions:

$$\psi = \psi_0 + \sum_k \frac{\left\langle \psi_0 \left| \frac{\partial U}{\partial Q} \right| \psi_k \right\rangle Q}{(E_0 - E_k)} \psi_k \tag{19}$$

Only the excited states of the same multiplicity can be mixed. Also, ψ_k and E_k must be those for the ground state nuclear positions.

The first order perturbation energy simply averages the effect of changing the nuclear positions over the original electronic distribution. The second-order perturbation energy is an effect due to a change in the electron distribution. This change is called the transition density. Clearly this lowers the energy, as can be seen in eqn. (18). The quantity $(E_0 - E_k)$ always has a negative value. Both E_0 and E_k are negative, for bound states, with E_0 having the greater magnitude.

There are important symmetry restrictions contained in eqns. (17)–(19), but these are not important at this time. What is important is that a chemical reaction (changing nuclear positions) cannot occur unless the last term in eqn. (18) has an appreciable value. This will be more likely as the transition energies $(E_0 - E_k)$ have smaller values. Large values of $(E_0 - E_k)$ will mean a large energy barrier to all changes.

In eqns. (18) and (19), there is a sum over all excited states. However, only a few will be useful in driving the reaction. In MO terms, the most important states will be those in which an electron is promoted from a filled MO to an empty MO, both in the valence shell. The MOs are selected to correspond to the old bonds that are to be broken and the new bonds that are to be made during the reaction. For bimolecular reactions, the important states are those in which electrons are promoted from filled MOs in one reactant to empty MOs in the other.

In simple MO theory the HOMO and the LUMO (the frontier orbitals) define the lowest energy transition. They are also the orbitals that drive the chemical reaction in the usual case [25]. Actually neither of these statements need be true. However, as a general rule, it is expected that the excited states that drive these reaction will be close to the first excited state. Thus we will have

$$h\nu_{\max} = E_1 - E_0 \approx E_k - E_0 \tag{20}$$

where E_k identifies the chemically significant state (or states).

In eqn. (20), $\nu_{\max}$ is the frequency at maximum intensity of the first excited state of the same multiplicity as the ground state. At first glance, one might be tempted to identify this with the energy gap 2η of Fig. 2. However, it is quickly found that $h\nu_{\max}$ is not equal to $(I - A)$. In H_2S, for example, it is equal to 6.4 eV [41], whereas $(I - A) = 12.6$ eV.

The difference arises from the extra electron–electron repulsion that results from adding an electron. This is missing from the electronic transition giving $h\nu_{\max}$. The equation relating the two energy differences is given by

$$(I - A) = h\nu_{\max} + J_{\mathrm{if}} - 2K_{\mathrm{if}} \tag{21}$$

J_{if} and K_{if} are the Coulomb and exchange integrals between the initially occupied MO and that occupied in its place in the excited state.

There are two final conclusions that can be drawn. One is that soft molecules are more reactive than hard molecules in all reactions where electron transfer or rearrangement is necessary. Hard molecules resist change, not only in their number of electrons, but also in their distribution about the nuclei [26].

The other is that chemical reactivity can be correlated with electronic spectra [27]. Low-lying absorption bands are a clue to high reactivity or instability. Indeed there are many interesting correlations that can be found between spectra and reactivity [27]. However, care must be taken to identify the nature of the first excited state to see what kind of chemical reaction is favored.

MO theory is related to HSAB in one other way, as already mentioned. The local softness $\tilde{\sigma}$ depends on the one-electron density function of the frontier orbitals, as shown in eqn. (9). This concept is of great importance in determining which part of a polyatomic system is reactive towards various reagents.

As an example we can take the thiocyanate ion, NCS^-, which can react as a nucleophile or base at either nitrogen or sulfur. The HOMO of the ion is given by [28]

$$\Phi = 0.855\psi_S + 0.139\psi_C - 0.444\psi_N \tag{22}$$

The ψ parameters are suitable valence shell atomic orbitals. Squaring Φ to obtain ρ, we see that the coefficient at sulfur is four times as great as that at nitrogen. Adding up all the changes of occupied MOs, it is found that nitrogen has the larger net charge, -0.68 vs. -0.25. Therefore soft electrophiles or acids will react at sulfur and hard ones will react at nitrogen.

The conclusions that are drawn from this type of analysis are exactly the same as those of frontier orbital theory [29]. However, the reasons are somewhat different. Instead of stressing that the best overlap is obtained, to give good covalent bonding, DFT stresses that electron density can be changed most readily at certain sites.

E. SOME APPLICATIONS OF THE CONCEPTS

Searching the literature for values of I and A, it has been possible to assign values of χ^0 and η to some 200 atoms, molecules, radicals and monatomic cations [30,31]. Anions and polyatomic cations require special treatment, as will be discussed shortly, but it is still possible to rank order them in terms of increasing hardness [32]. In addition, for anions and cations, the values of I and A respectively give good rank orderings of absolute electronegativity.

In all but a few cases the values of η, or the rank orders, agree very well with the expectations based on the older work on HSAB. The exceptions all seem to have simple and reasonable explanations. An example would be the lanthanide ions, which have low values of η because of ionizable $4f$ electrons, but which behave as hard Lewis acids. The explanation is that $4f$ electrons are chemically inert.

Using the available experimental values, a number of applications have been made, both in inorganic [30] and organic [31] chemistry. In this section some of these applications will be illustrated. We start with a number of χ^0 and η values for molecules in Table 1.

The molecules are arranged in order of decreasing χ, so that Lewis acids start the list and Lewis bases are at the bottom. Generally, the ordering is very reasonable, although there are some surprises, with SF_6, CO, N_2 and H_2 shown as Lewis acids of high electronegativity. However, the order shown must not be taken as an order of acid strength, but of inherent tendency to give up or take up electrons. The acid strength depends strongly on two other characteristics: the charge or the dipole moment of the acid and the nature of the orbital that accepts the electron density. The same properties of each base must also be considered.

For example, SF_6 is essentially inert. Being neutral and non-polar, it must accept electrons to interact with a base. However, the accepting orbital is an antibonding orbital, which is physically inaccessible. If filled, it would form unstable products such as $BF^+SF_5^-$, where B is the base. Both CO and N_2 are non-polar and have accepting π-type orbitals. Bonding to σ donors, such as NH_3, would be weak. Only π bases of low electronegativity will bind well. It should be noted that H_2 and N_2 are both very hard, which helps to account for their low reactivity. Acids such as Cl_2 and I_2 are much softer.

Among the bases, the most significant feature is that molecules where the donor atom is F, O or N are all very hard. This results from large negative values of the electron affinity. For similar molecules where the donor atom is Cl, S or P, there is always a large drop in η. A further, smaller drop occurs for Br, I, Se and As. The second feature to note in Table 1 is the softening effect of unsaturation (compare C_6H_6 and C_2H_4 with CH_4, $C_6H_5NH_2$ with NH_3 and CH_3COCH_3 with $(CH_3)_2O$). This effect is consistent with the increased polarizability due to unsaturation.

Let us use eqn. (7) to see what can be predicted for the reaction of two neutral species. The assumption is that a large value of ΔN is favorable for reaction. However, caution is needed since it is quite possible to have strong bonding between two systems of equal electronegativity, where $\Delta N = 0$.

Cases where eqn. (7) should relate to bond energies would be those where ΔN is not large and where electron transfer in one direction is more important than the other. If ΔN is too large, we will get ionic bonding where

TABLE 1

Experimental parameters (eV) for molecules

Molecule	I [a]	A [a]	χ	η
SF_6	15.4	0.5	8.0	7.4
O_3	12.8	2.1	7.5	5.4
SO_3	12.7	1.7	7.2	5.5
Cl_2	11.6	2.4	7.0	4.6
H_2	15.4	−2.0	6.7	8.7
SO_2	12.3	1.1	6.7	5.6
N_2	15.58	−2.2	6.70	8.9
O_2	12.2	0.4	6.3	5.9
BF_3	15.8	−3.5	6.2	9.7
CO	14.0	−1.8	6.1	7.9
I_2	9.4	2.6	6.0	3.4
HNO_3	11.03	0.57	5.80	5.23
CH_3NO_2	11.13	0.45	5.79	5.34
PF_3	12.3	−1.0	5.7	6.7
HCN	13.6	−2.3	5.7	8.0
PBr_3	9.9	1.6	5.6	4.2
CS_2	10.08	0.62	5.35	5.56
HI	10.5	0.0	5.3	5.3
CO_2	13.8	−3.8	5.0	8.8
HF	16.0	−6.0	5.0	11.0
CH_2O	10.9	−0.9	5.0	5.9
CH_3I	9.5	0.2	4.9	4.7
SiH_4	10.6	≈ −1.0	4.8	5.8
HCl	12.7	−3.3	4.7	8.0
CH_3CN	12.2	−2.8	4.7	7.5
CH_3CHO	10.2	−1.2	4.5	5.7
C_2H_4	10.5	−1.8	4.4	6.2
C_5H_5N	9.3	−0.6	4.4	5.0
H_2S	10.5	−2.1	4.2	6.2
C_2H_2	11.4	−2.6	4.4	7.0
$HCONH_2$	10.2	−2.0	4.1	6.1
C_6H_6	9.3	−1.2	4.1	5.3
CH_3Cl	11.2	−3.7	3.8	7.5
H_2O	12.6	−6.4	3.1	9.5
$(CH_3)_3As$	8.7	−2.7	3.0	5.7
$(CH_3)_3P$	8.6	−3.1	2.8	5.9
$(CH_3)_2S$	8.7	−3.3	2.7	6.0
NH_3	10.7	−5.6	2.6	8.2
CH_4	12.7	−7.8	2.5	10.3
$(CH_3)_2O$	10.0	−6.0	2.0	8.0
CH_3NH_2	9.0	−5.3	1.9	7.2

[a] For sources see ref. 31.

TABLE 2

Transition metal atoms reacting with carbon monoxide

Metal	χ^0 (eV) [a]	η (eV) [a]	ΔN [b]	$\Delta H^{\ddagger}$ (kcal) [c]
V	2.24	1.24	0.211	$V(CO)_6$ stable [d]
Cr	2.47	1.58	0.196	40
Mn	3.10	2.19	0.149	37
Fe	2.55	1.55	0.188	42
Co	4.12	3.04	0.091	22
Ni	3.50	2.30	0.128	22
Cu	5.84	4.61	0.010	Very unstable [e]
Mo	3.18	1.98	0.148	40
Ru	3.54	2.34	0.125	28
Pd	4.45	3.89	0.070	Unstable [f]
Ag	6.87	5.57	−0.029	Very unstable [e]
Pt	5.30	2.90	0.037	Unstable [f]
Au	6.70	4.40	−0.026	Very unstable [e]

[a] For low spin valence state. [b] For reaction (23). [c] For dissociation of first CO from stable carbonyls such as $Cr(CO)_6$. [d] Reacts by S_N2 mechanism [33]. [e] Stable at 10 K. [f] Stable at 200 K.

size factors dominate the bond energy. However, even in such cases eqn. (7) may be useful, since it measures the initial driving force for reaction. A large value of ΔN could lower the energy barrier to reaction and affect the rate [30,31].

As an example of a relation to bond energies, we can take the reaction of carbon monoxide with transition metal atoms. Table 2 gives the values of χ^0 and η for a number of such atoms. They are calculated, not for the high spin ground state, but for the low spin valence state [32]. Table 2 also contains the values of ΔN calculated for the reaction

$$M(vs) + CO = M\text{–}CO \qquad (23)$$

Finally, the table lists the activation enthalpies for the dissociation of the first CO ligand from the stable carbonyls of each metal, such as $Ni(CO)_4$. Some remarks on unstable carbonyls are also included.

The agreement between the values of ΔN and the apparent bond energies is really quite remarkable. CO is the Lewis acid in all cases where stable metal carbonyls are known. Thus π bonding is more important than σ bonding, in agreement with the most recent theoretical studies of metal carbonyls [34].

The success of eqn. (7) in this example depends very much on the comparison of a single reactant, CO, with a series of reactants which use very similar orbitals for bonding. If we were to calculate ΔN for a series of ligands from Table 1, reacting with a constant metal atom, the results would be much more scattered. We would now be dealing with a series where the acceptor orbitals vary quite markedly in size, orientation and energy.

Even N_2, compared with the very similar CO, would present problems. For the reaction with a nickel atom, ΔN for N_2 is calculated to be 0.143, compared with 0.128 for nickel and CO. This contradicts the known bond energies, much less for N_2 than for CO. Accurate calculations, using DFT, show that both σ and π bonding are weaker for N_2 than for CO [34]. The π bonding is weaker because the electron-accepting π^* orbital of CO is concentrated on carbon, giving good overlap with the metal d orbital. Loss of π bonding naturally diminishes σ bonding, which is difficult for N_2 in any case because of the high value of I.

There is a second way in which bond energies are related to chemical hardness. This is in the HSAB principle itself. While bond energies still cannot be calculated, the principle can be used to rank order acids and bases. Let us consider the exchange reaction

$$\mathrm{A:B'(g) + A':B(g) = A:B(g) + A':B'(g)} \qquad (24)$$

If other bond-determining factors are constant, the reaction will be exothermic if A′ is softer than A and B′ is softer than B. This may be restated as

$$\mathrm{hs + sh = hh + ss} \qquad 0 > \Delta H \qquad (25)$$

where h and s are read as the harder of the two acids (bases) and the softer of the two bases (acids).

There are obviously many other bond-determining factors such as the electronegativities of A and B, their charges and sizes, the matching of orbital overlaps and steric repulsions. It is impossible to keep all of these factors constant, but one should only compare acids, or bases, or the same charge. Also, a series of acids, or a series of bases, should only be compared when their mean bond strengths to the reference acids, or bases, are about the same.

The HSAB principle refers to heterolytic bond energies, e.g.

$$\mathrm{AgBr(g) = Ag^+(g) + Br^-(g)} \qquad (26)$$

Because only differences are needed, it is possible to use the more familiar standard homolytic bond dissociation energies, $D^\ominus = \Delta H^\ominus_{298}$:

$$\mathrm{AgBr(g) = Ag(g) + Br(g)}\ (D^\ominus) \qquad (27)$$

Since η values are now known for some Lewis acids, particularly monatomic cations, and since many more values of $D^\ominus$ are known, it is possible to use eqn. (25) much more effectively than in 1963. To rank order cations in terms of hardness, we only need bond energy data for two different bases such as F^- and I^-. The bases must differ markedly in hardness. In this way a large number of relative η values for polyatomic cations have been calculated [35]. Bond energies will be more sensitive to local hardness $\tilde{\eta}$ at the reaction sites than to global hardness η.

Table 3 contains relative $\tilde{\eta}$ values for a large number of common anions. These have been ordered according to relative bond energies towards H^+ and CH_3^+ [35]. We define the bond energy difference

$$\Delta = D^{\ominus}_{HB} - D^{\ominus}_{CH_3B} \tag{28}$$

The methyl cation is softer than H^+ so that a larger Δ value indicates a harder base.

The results are usually very consistent with prior expectations. For simple anions we find the orders $F^- > Cl^- > Br^- > I^-$; $OH^- > SH^- > SeH^-$; $NH_2^- > PH_2^- \approx AsH_2^-$; $CH_3^- > SiH_3^- > GeH_3^-$; $F^- \approx OH^- > NH_2^- > CH_3^-$; $Cl^- > HS^- > PH_2^- > SiH_3^-$; $Br^- > HSe^- > AsH_2^- > GeH_3^-$. These are certainly as expected on the basis of polarizability. They are also in the same order as the corresponding radicals. This is not accidental since it has been shown to be expected for spherical, uniformly charged ions [30]. However, there is no such relationship between radicals and their corresponding cations, since the latter are not uniformly charged.

A noteworthy exception is the hydride ion, which is the softest base listed in Table 3, even though η for the hydrogen atom is large. The softness of H^- resides in its ability to donate charge to an acid for σ bonding. It is not capable of π bonding or π antibonding. This means that acids with electronic structures suitable for π bonding may bind less strongly to H^- than expected.

For ambident bases we find the expected results. For CN^-, Δ is much less for the C-bonded isomers than for the harder N-bonded ones. For NO_2^-, Δ is less for the N-bonded than for the O-bonded isomers.

Relative η values can be used in many different ways. Equation (25) can be used to set limits on unknown bond energies. If we consider the exchange reaction

$$CH_3NCS(g) + HSCN(g) = CH_3SCN(g) + HNCS(g) \tag{29}$$

we predict that $\Delta H^{\ominus}$ for this reaction will be negative. Therefore the unknown H–SCN bond energy must be considerably less than 89 kcal mol^{-1}.

Equation (25) must not be considered as infallible, however. Specific interactions between a given Lewis acid and base can cause the relationship to fail.

TABLE 3

Empirical hardness parameters for anionic bases

Base	$D^{\ominus}_{\mathrm{HB}}$ (kcal)	$D^{\ominus}_{\mathrm{CH_3B}}$ (kcal)	Δ (kcal)
F^-	136	109	27
Cl^-	103	85	19
Br^-	88	70	18
I^-	71	56	15
OH^-	119	92	27
SH^-	91	74	17
SeH^-	79	67	12
NH_2^-	107	85	22
PH_2^-	87	76	11
AsH_2^-	75	63	12
$CH_3CO_2^-$	106	83	23
$C_6H_5O^-$	87	64	23
NO_3^-	102	80	22
CH_3O^-	104	83	21
HO_2^-	88	69	19
ONO^-	78 [a]	60 [a]	18
NO_2^-	< 78 [b]	61 [b]	<17
NCS^-	96 [b]	77 [b]	19
$C_6H_5NH^-$	88	71	17
n-$C_3H_7S^-$	87	72	15
$C_6H_5S^-$	83	69	14
CH_3^-	105	90	17
SiH_3^-	91	89	2
GeH_3^-	87	83	4
$C_6H_5CH_2^-$	88	72	16
$NCCH_2^-$	93	81	12
$CH_3COCH_2^-$	98	86	12
$C_3H_5^-$	86	74	12
$C_6H_5^-$	111	100	11
$C_2H_3^-$	115	105	10
HC_2^-	130	122	8
CH_3CO^-	96	91	5
CF_3^-	106	101	5
CN^-	124 [c]	122 [c]	2
NC^-	110 [d]	98 [d]	12
H^-	104	105	−1

Data from ref. 35. [a] O-bonded isomer. [b] N-bonded isomer. [c] C-bonded isomer. [d] N-bonded isomer.

(i) Solution effects

Equation (25) refers to the gas phase and most coordination chemists are interested in complex ions in water solution. There is a large amount of data, not only on equilibrium constants, but also on heats of reaction of metal ions with various ligands. Unfortunately, solvation energies make it very difficult to apply eqn. (25) in a quantitative way.

A typical example in solution might be

$$Ni(H_2O)_5F^+(aq) + I^-(aq) = Ni(H_2O)_5I^+ + (aq) + F^-(aq) \qquad (30)$$

The difference between the heats of hydration of F^- and I^- is known to be 53 kcal mol^{-1}. Therefore F^- is strongly deactivated in solution, and I^- can compete effectively for the metal ion. However, we do not know the heats of hydration of the two complex ions, and it is not safe to assume that they will be equal. Overall, the ΔH values of reactions such as eqn. (30) will be small.

Nevertheless, some useful generalizations may be made. Let us consider the typical reaction for the formation of a complex in water (charges are omitted for simplicity):

$$ML_n(H_2O)(aq) + Y(aq) = ML_nY(aq) + H_2O(l) \qquad (31)$$

There are four interactions in eqn. (31) which are acid–base in character. One is the interaction of ML_n with H_2O, the second is the ML_n interaction with Y, the third is the interaction of Y with the solvent, and the fourth is the interaction of water with itself, a constant factor. The solvation energies of the large complex ions, $ML_n(H_2O)$ and ML_nY, are primarily governed by the Born equation.

If ML_n is hard and Y is soft, or vice versa, we can expect $\Delta H^{\ominus}$ to be positive, or only a small negative number. Therefore complexation will not be favorable. If we suppose that ML_n is hard and Y is hard, then their interaction will be favorable. H_2O is a hard molecule, both as an acid and a base. Therefore Y(aq) and $ML_n(H_2O)$ are also stabilized. Overall, only a small negative value for $\Delta H^{\ominus}$ can be hoped for, and moderately stable complexes.

However, if ML_n is soft and Y is soft, then everything works in favor of a large negative value for $\Delta H^{\ominus}$ and very stable complexes. Ahrland [36] has made a detailed study of the available data and has found remarkable agreement with the above predictions. Hard acids rarely form complexes with soft bases, and hard bases do not form very stable complexes with soft acids, except for strong bases such as OH^-. Hard acids form only moderately stable complexes, even with hard bases, and $\Delta H^{\ominus}$ is close to zero. Soft acids and soft bases usually form very stable complexes in aqueous solution, and $\Delta H^{\ominus}$ is a large negative number.

There is another important effect of solvation to consider. The I and A values, which are used to calculate η, are gas phase values. Perhaps in solution we should use the corresponding values, I' and A':

$$M(aq) = M^+(aq) + e^-(g) \qquad I' \qquad (32)$$

$$M(aq) + e^-(g) = M^-(aq) \qquad A' \qquad (33)$$

These numbers are in fact, the one-electron oxidation and reduction potentials of the molecule M on the absolute scale. They cannot be measured directly, but they can be calculated in several independent ways [37]. These all depend on the absolute potential of the hydrogen electrode:

$$H^+(aq) + e^-(g) = \tfrac{1}{2}H_2(g) \qquad E^\ominus = 4.50\ \mathrm{V} \tag{34}$$

Fortunately, there is now agreement that this value is very close to 4.50 V. Using this value, a number of I' and A' values have been calculated for various neutral radicals and molecules.

To do this we first need to calculate the hydration energies of the corresponding cations and anions. This is possible, and the resulting values should be useful in a number of ways [37,38]. Typically, I' is 2–4 eV less than I and A' is 2–4 eV larger than A. This leaves the sum $(I' + A')/2$ little changed from the gas phase value, but $(I' - A')/2$ is dramatically reduced.

This seems to imply that neutral species are much softer in water than in the gas phase. In a sense this is true, since it is much easier to add or remove electrons in solution because the solvent stabilizes the resultant charges.

However, in the wider sense, the solution values do not have the same meaning as the gas phase values. The interaction between an acid and a base involves only the partial transfer of electrons, and the polarization of other valence shell electrons. Free A^- and B^+ are not formed, and their solvation energies are not relevant.

In addition, the spectroscopic energy gap of Fig. 2 is little affected by solvation. The important energy difference between the ground state and the excited states remains about the same. Clearly the gas phase values of I and A still determine the softness of a molecule, even in solution.

F. CONCERNING THE FUTURE

I am much more confident in 1988 about the future of hard and soft acids and bases than I was in 1973. The biggest change, obviously, has been the rigorous definition of what is meant by hardness, and an operational definition for assigning values. However, there are several other positive developments. Firstly, there was already a large amount of information and perception about hardness. A critical test was to see if this prehistory was compatible with the new developments. It appears that this is the case.

Secondly, it was necessary to show that a quantitative treatment of hardness led to values which could be tested by calculations pertaining to chemical reactivity. It seems that this can be done, although it is still a long way from calculating bond energies or activation energies for reactions.

In addition, it was important to have a firm theoretical basis for the concept. Both DFT and quantum mechanical perturbation theory provide such a basis. The correlation with molecular orbital theory is particularly important. Molecular orital theory and the closely related frontier orbital theory are almost universally used to explain structure, bonding, spectra and mechanisms of chemical reactions.

Tying in chemical hardness with absolute electronegativity is, I believe, a very positive feature for both concepts. Certainly electronegativity has proved its value over the years. However, a new electronegativity has been created. It no longer applies just to atoms in a molecule, but to the entire molecule, radical or ion. Perhaps the word electronegativity should not have been employed and the term electronic chemical potential should have been used instead.

In any case, the two quantities $(I+A)$ and $(I-A)/2$ seem to be the two properties of a chemical system that give the greatest amount of a priori information about it. They are neatly summarized in the broken lines of Fig. 2.

The two quantities, χ^0 and η, refer to any system, not just to Lewis acids and bases. However, they are particularly appropriate for the latter, since the value of χ determines whether we have an acid or a base. Partial donation of electrons from the base to the acid is the key reaction of Lewis acids and bases.

The energy gap between the HOMO and the LUMO is certainly an important property of any molecule. It has the feature of measuring the energy difference between the ground state and the manifold of excited states. It is also a useful property of solids.

Some idea of the importance of the gap may be gained by relating it to stability in another way. We have already seen that it determines chemical reactivity due to electron density changes. However, it also seems to determine the structure of molecules, including bond angles and distances [39]: that is, a given collection of nuclei and electrons will take up the structure which maximizes the difference in energy between the HOMO and the LUMO, or the energy required to reach the first excited state.

Parr and I have called this gap the hardness, but perhaps in time another name will prove to be more popular. However, hardness does seem very appropriate, for the reasons already given. Perhaps one more connection with the common meaning of hardness will be useful. Suppose it is argued that the word refers to resistance to mechanical forces rather than chemical? It can be shown that the same energy gap determines the mechanical hardness.

Mechanical hardness is equal to the reciprocal of the compressibility β multiplied by a number density factor [40]. However, β^{-1} can be related to the force constant for lattice vibrations in a solid [41]. Referring back to eqn. (18), the force constant is simply the sum of the coefficients of the two terms multiplying Q^2. Thus a solid, or a molecule, that is soft because of a small energy gap, will have a large value of β and a small value of mechanical hardness!

This analysis suggests that there may be applications of HSAB which go well beyond the limits of chemistry. However, we should exercise caution in claiming too much power for χ and η. Jorgensen has already informed me that he refuses to believe that Charlotte Moore's Tables contain the genetic code for Beilstein (Moore's Tables are the energy levels of atoms and monatomic ions). However, since all molecules are made of atoms, Moore's Tables must contain important parts of the genetic code, if not all of it.

Finally, it should be mentioned that, in addition to the literature cited, there is a rapidly growing list of papers dealing with χ and η. A few of these are of particular interest because they give independent tables of numerical values for these quantities [42].

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