of the principle of belief congruence."

It remains to be seen whether the results of these experiments can be replicated with other kinds of subjects, in other kinds of situations, and in other kinds of cultural and subcultural contexts. And another task for future research is to explore in more detail the personal and social determinants of all the choice patterns we observed.

References and Notes

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10. It is tempting to suggest that these differences are somehow due to the existence of social pressures in the campus community in 1961 and to their disappearance in 1963–64, perhaps as a result of changing social norms concerning civil rights. If this interpretation were valid we would expect to find the campus 1963–64 results under both private and public conditions looking very much like the campus 1961 results found under private conditions. But this does not appear to be the case. A more likely possibility is that the difference between public and private conditions in the campus 1961 study are, because of the small number of cases, unreliable, despite the fact that they turn out to be statistically significant. We are inclined to discount these results because we determined the significance level by first looking at the data and then combining patterns 1–5 (in order to eliminate small frequencies) and, more important, because we have not been able to replicate them.
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Acids and Bases

Hard acids prefer to associate with hard bases, and soft acids prefer to associate with soft bases.

Ralph G. Pearson

The most important of all classes of chemical reactions is the generalized acid-base reaction (*1*):

$$A + :B \rightleftharpoons A:B \qquad (1)$$

A is a Lewis acid, or electron acceptor, and : B is a Lewis base, or electron donor; A : B is the complex formed between them by partial donation of electrons from : B to A. Examples of such complexes include coordination compounds and complex ions in which A is a metal atom or ion, most ordinary inorganic and organic molecules, charge-transfer complexes, hydrogen-bonded complexes, and complexes between free radicals (which act as acids) and various bases. When A is a metal ion, the base B is called a ligand. When the rates of reaction 1 are being discussed, A is called an electrophilic reagent and B is called a nucleophilic reagent.

Indeed one can see that very much of chemistry is included under the heading of acid-base interactions. Any generalizations that can be made about the equilibrium constants for reaction 1, or the stability of the acid-base complex, A : B, will have wide applicability. The special case where A is a metal ion has been extensively studied, and many equilibrium constants for reaction 1 are known (*2*). Actually what is usually known is the equilibrium constants for the competition reaction

$$A{:}B' + A'{:}B \rightleftharpoons A{:}B + A'{:}B' \qquad (2)$$

where A′ and : B′ are the common reference acid and base, H_2O.

Several earlier workers, especially Fajans (*3*) and J. Bjerrum (*4*), had noted that the metal ions fall into two categories according to the kinds of bases they prefer to coordinate with. Schwarzenbach (*5*) divided the metal ions into two classes, A and B. The most typical metal ions of class A were those of the representative elements having no *d*-orbital electrons. The class B metal ions had 8 to 10 outer *d* electrons, occurring near the end of a transition series.

The overall order of stability of class-B metal ions for various bases falls in the approximate sequence

$$S \sim C > I > Br > Cl > N > O > F$$

where the atom shown is the donor atom of the base. For class A metal ions this order is strongly inverted. Hence stable complexes in water solution can only be formed with oxygen donors and F− in many cases. For class A ions the stability of the complexes increases with increasing positive charge: $Al^{3+} > Mg^{2+} > Na^{+}$. For class B ions, the reverse is true, at least for the best donor atoms in the series. $Ag^{+} > Cd^{2+} > Au^{3+} > Sn^{4+}$.

Chatt, Ahrland, and Davies made a very useful advance (*6*) when they classified metal ions according to whether they form their most stable complexes with the first ligand atom of each group, class (a), or with the second or a subsequent member of each group, class (b). The following sequences of complex-ion stability are then found:

(a) $N >> P > As > Sb > Bi$
(b) $N << P > As > Sb > Bi$
(a) $O >> S > Se > Te$
(b) $O << S \sim Se \sim Te$
(a) $F > Cl > Br > I$
(b) $F < Cl < Br < I$

Chatt, Ahrland, and Davies' class (a) metal ions are the same as Schwarzenbach's class A, and their class (b) metal ions are the same as his class B. To avoid confusion with symbols used for Lewis acid and Lewis base, I use (a) and (b) from here on.

The rules of Ahrland, Chatt, and Davies can also be used to classify other kinds of generalized Lewis acids (*7*). Where the necessary equilibrium data are not available, other criteria may be used. One is that class (b)

The author is professor of chemistry at Northwestern University, Evanston, Illinois.

acids complex readily with a variety of bases of negligible proton basicity. These include carbon monoxide, olefins, and aromatic hydrocarbons. Rate data may also be used. Table 1 shows a variety of Lewis acids for which the available data allow an assignment of class (a) or class (b) behavior. Some borderline cases are also shown.

Table 1. Classification of Lewis acids.*

Hard [class (a)]	Soft [class (b)]
H^+, Li^+, Na^+, K^+	Cu^+, Ag^+, Au^+, Tl^+, Hg^+, Cs^+
Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Mn^{2+}	Pd^{2+}, Cd^{2+}, Pt^{2+}, Hg^{2+}, CH_3Hg^+
Al^{3+}, Sc^{3+}, Ga^{3+}, In^{3+}, La^{3+}	Tl^{3+}, Au^{3+}, Te^{4+}, Pt^{4+}
Cr^{3+}, Co^{3+}, Fe^{3+}, As^{3+}, Ce^{3+}	$Tl(CH_3)_3$, BH_3, $CO(CN)_5^{2-}$
Si^{4+}, Ti^{4+}, Zr^{4+}, Th^{4+}, Pu^{4+}	RS^+, RSe^+, RTe^+
Ce^{4+}, Ge^{4+}, VO^{2+}	I^+, Br^+, HO^+, RO^+
UO_2^{2+}, $(Ch_3)_2Sn^{2+}$	I_2, Br_2, ICN, etc.
$BeMe_2$, BF_3, BCl_3, $B(OR)_3$	Trinitrobenzene, etc.
$Al(CH_3)_3$, $Ga(CH_3)_3$, $In(CH_3)_3$, AlH_3	Chloranil, quinones, etc.
RPO_2^+, $ROPO_2^+$	Tetracyanoethylene, etc.
ROS_2^+, $ROSO_2^+$, SO_3	O, Cl, Br, I, N
I^{7+}, I^{5+}, Cl^{7+}, Cr^{6+}, Se^{6+}	M° (metal atoms)
RCO^+, CO_2, NC^+	Bulk metals
HX (hydrogen bonding molecules)	

* The following are in a borderline class between (a) and (b): Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Sn^{2+}, Sb^{3+}, Bi^{3+}, Rh^{3+}, Ir^{3+}, $B(CH_3)_3$, SO_2, NO^+, Ru^{2+}, Os^{2+}, R_3C^+.

Hard and Soft Acids and Bases

In order to better characterize the behavior of class (a) and class (b) acids, let us define a soft base as one in which the donor atom is of high polarizability and of low electronegativity and is easily oxidized or is associated with empty, low-lying orbitals (*8*). These terms are not independent, for they describe in different ways a base in which the donor electrons are not held tightly but are easily distorted or removed. They are not exactly equivalent, however. Hard bases have the opposite properties. The donor atom is of low polarizability and high electronegativity, is hard to reduce, and is associated with empty orbitals of high energy and hence inaccessible.

Table 2 lists a variety of bases in order of increasing softness, at least as judged by a criterion of reaction rate with a typical class (b) acid, $Pt(C_5H_5N)_2Cl_2$. Other hard bases are oxygen donors such as acetate, sulfate, and phosphate ions. Other soft bases are carbon monoxide, aromatic hydrocarbons, olefins, alkyl isocyanides, alkide ions, and hydride ions.

We now see that class (a) acids prefer to bind to hard bases (O over S, N over P, F over I) and class (b) acids prefer to bind to the softer, more polarizable bases. The latter acids also form complexes with a variety of soft bases that class (a) acids generally ignore, at least in aqueous solution.

If we examine the properties of class (a) acids, we find that they can be either metals or nonmetals, as can class (b) acids. The distinguishing features of class (a) are small size, high positive oxidation state, and the absence of any outer electrons which are easily excited to higher states. These are all properties which lead to low polarizability, and we may call such acids hard acids. Class (b) acids have one or more of the following properties: low or zero positive charge, large size, and several easily excited outer electrons. For metals these outer electrons are *d*-orbital electrons. All of these properties lead to high polarizability, and class (b) acids may be called soft acids.

We can now state a useful, general principle: *Hard acids prefer to associate with hard bases and soft acids prefer to associate with soft bases.*

This rule must not be taken to mean more than it says. For example, it certainly does not say that soft acids do not ever complex with hard bases, or that hard acids do not form stable complexes with any soft bases. Some hard bases such as OH^- form stable complexes in water with most positively charged acids, hard or soft. Since H^+ is the prototype hard acid, any base which binds strongly to the proton will bind to other hard acids as well. In the case of soft bases, these will be negatively charged bases such as H^-, R^-, and S^{2-}.

Perhaps the best way to illustrate what this general principle does tell us is by an example (*9*). Let us compare CH_3Hg^+, a typical soft acid, and H^+, a hard acid. Both form stable complexes with OH^-, a hard base, and with S^{2-}, a soft base. However, the stability constants are such that the competition reaction

$$H^+ + CH_3HgOH \rightleftharpoons H_2O + CH_3Hg^+ \quad (3)$$

has an equilibrium constant of $10^{6.3}$. The competition reaction

$$H^+ + CH_3HgS^- \rightleftharpoons HS^- + CH_3Hg^+ \quad (4)$$

on the other hand, has an equilibrium constant of $10^{-8.4}$. The preferences of the proton for the hard base and of CH_3Hg^+ for the soft base are dramatically demonstrated.

The hardness of an acid is a function of the oxidation state of the acceptor atom, usually increasing as this number becomes more positive. Also the hardness of a given acceptor atom is a function of the other groups attached to it. Thus, BF_3 is a class (a) acid, but BH_3 is a typical class (b) acid, forming complexes such as BH_3CO with the soft base carbon monoxide. The group $Co(NH_3)_5{}^{3+}$ shows class (a) behavior, but $Co(CN)_5{}^{2-}$ shows class (b) behavior. In these cases the boron atom and the cobalt atom have a formal oxidation state of 3+. The rule that is obeyed is that soft bases, when coordinated to an acid, tend to make it softer. The effect is one of reducing the positive charge on the acceptor atom. Thus, the actual positive charge on the boron atom is probably much less in BH_3 than it is in BF_3.

The above rule is the basis for what Jørgensen calls symbiotic behavior (*10*). For a given metal ion, or other acid center, hard ligands will tend to flock together or soft ligands will flock together. For instance, stable $Co(NH_3)_5F^{2+}$ and $Co(CN)_5I^{3-}$, and unstable $Co(NH_3)_5I^{2+}$ and $Co(CN)_5F^{3-}$ illustrate the symbiotic principle. In organic chemistry we find that compounds with several oxygen or fluorine atoms attached to the same saturated carbon atom are unusually stable. Hine has explained this by double bond–no bond resonance (*11*).

$$\mathrm{O{-}C{-}O \leftrightarrow \overset{+}{O}{=}C\ O^{-}} \quad (5)$$

This explanation is a combination of two of the theories of hard and soft behaviors discussed below.

Applications of the Principle

The rule that soft acids prefer soft bases and hard acids prefer hard bases is only qualitative, or, at best, semiquantitative. However, it does permit correlation and better understanding of a very large amount of chemical information.

One application is the explanation of the stabilities of various compounds and complexes. For example, the acylium ion, RCO^+, is listed as a hard acid in Table 1. This means that CH_3COF is more stable than CH_3COI, and that CH_3COOR is more stable than CH_3COSR. But RS^+, the sulfenyl group, is listed as a soft acid. This means that RSI is more stable than RSF, and RSSR is more stable than RSOR.

The case of carbonium ions, R_3C^+, is of special interest. It is put in the borderline category in Table 1. For example, CH_3F is slightly more stable than CH_3I, but CH_3SCH_3 is more stable than CH_3OCH_3 by a factor of 10^3. We may expect that various substituents on tetrahedral carbon will cause changes so that a carbonium ion may be either class (a) or class (b). Hine has recently discussed the subject of carbon basicity in terms of the equilibrium constant for the reaction

$$R_3COH + B^- \rightleftharpoons R_3CB + OH^- \qquad (6)$$

for a number of carbonium and acylium ions (*11*).

Hydrogen-bonded complexes are class (a), so that stronger bonds are formed to N, O, and F donors than to P, S, and I donors. Charge-transfer complexes between acids such as I_2, $(NC)_2C{=}C(CN)_2$, quinones, and various bases show that the acids are in class (b). More stable complexes are formed to thio ethers than to ethers, for example. Aromatic molecules are good bases for these acids.

We can also consider the stabilization of a given element in a certain oxidation state. If we wish to have a low, or zero, oxidation state for a metal, it is necessary to surround it with soft bases, or soft ligands. This follows because the metal would be a soft acid if zero-valent. Suitable ligands would be carbon monoxide, phosphines, isocyanides, and the like. An element in a high oxidation state, Fe(V) or Cr(VI), would be stabilized best by hard ligands such as F^- or O^{2-}.

In a similar way, we may wish to prepare organic compounds of a metal which ordinarily does not form stable alkyl derivatives, such as one of the transition metals. The reasoning would be that R^- is a soft base; therefore, the metal should be in a low valence state, or soft condition. This would require stabilizing it with a number of other soft ligands. Therefore, we expect $CH_3Mn(CO)_5$, but not $CH_3Mn(H_2O)_5$, to be stable.

The formation of compounds containing metal-metal bonds is of great current interest (*12*). Some help in understanding what systems will be stable comes from the new principle. A metal atom can be a Lewis acid, as already indicated. It can also be a Lewis base, since a metal is defined chemically as an electron donor. Hence, we may regard a metal-metal bond formally as an example of an acid-base complex,

$$L{-}M + :M'{-}L \rightarrow L{-}M:M'{-}L \qquad (7)$$

where L stands for other ligands attached to the metal atom.

Since a metal atom must be in a low oxidation state to be a good electron donor, we see that M′ should be a soft metal atom. From our rule, M must also be a soft metal atom, to act as a soft acid. Accordingly, M and M′ should be of zero or low valence, and the groups L should be soft bases to stabilize the metals in this condition. Most of the known metal-metal bonds satisfy these conditions (*13*):

$$Mn_2(CO)_{10},\ Fe_2(CO)_8{}^{2-},\ [MoC_5H_5(CO)_3]_2$$
$$Pt(NH_3)_4PtCl_4,\ Ph_3PAuCo(CO)_4,\ Pt(SnCl_3)_5{}^{3-}$$

A few examples are known of a hard metal forming a metal-metal bond (*14*). In these cases the second metal, which acts as the base, is also relatively hard.

The idea that a metal atom in the zero oxidation state is both a soft acid and a soft base can be used to explain surface reactions of bulk metals. Soft bases such as carbon monoxide and olefins are strongly adsorbed on surfaces of the transition metals. Bases containing P, As, Sb, Se, and Te in low oxidation states are the typical poisons in heterogeneous catalysis by metals. These soft bases are strongly adsorbed, blocking off the active sites. Strong bases containing oxygen and nitrogen are not poisons. Also metal ions of class (b) are poisons, whereas metal ions of class (a) are not. This shows the soft-base character of the free metal. Heterogeneous catalysis on metals is generally viewed today as the formation of unstable organometallic compounds and hydrides on the metal surface (*15*).

There is much evidence that free radicals and atoms behave as Lewis acids in that they form complexes with bases prior to reaction 7. The most stable complexes are formed with molecules of high polarizability, or soft bases. The reactivity of chlorine atoms, for example, shows that aromatic solvents stabilize them so they are less reactive, but oxygen and nitrogen donors do not. This is the expected behavior if chlorine is a soft acid. A recent study (*16*) shows that nitrogen atoms attack sulfur atoms in the molecules S_2Cl_2, H_2S, CS_2, COS, S_8 and SCl_2, and do not react with SO_2, $SOCl_2$, and SO_3. Thus the nitrogen atom acts as a soft Lewis acid, attacking only soft basic atoms.

Solubility may often be discussed in terms of acid-base interactions between solvent and solute molecules. Each solvent can be classified as hard or soft, though a separate classification for its acid function and its basic function may be necessary. A useful rule is that hard solutes dissolve well in hard solvents and soft solutes dissolve well in soft solvents (*17*). This is a rephrasing of the old adage *similia similibus dissoluntur.*

Water is a hard solvent in both its acid and its basic functions. It will solvate strongly such bases as OH^-, F^-, and other oxygen anions. Dipolar, aprotic solvents such as dimethyl sulfoxide, sulfolane, demethylformamide, nitroparaffins, and acetone will be much softer. Hard solvents will level basicity while soft solvents will not. For example, CH_3O^- is some 10^9 times more reactive in dimethylsulfoxide than in methanol as a basic catalyst for a proton removal reaction (*18*). Class (a) characteristics will always be partly destroyed, and class (b) characteristics enhanced, by hard solvents, in comparison with soft solvents, and by any solvent, in comparison with the gas phase (*7*).

In precipitating salts, chemists have long known that a large cation is precipitated best by a large anion, while a small cation needs a small anion. This is, of course, a lattice energy effect, but it also is an example of the softness-hardness principle. Consider the solid-state reaction

$$LiI + CsF \rightarrow LiF + CsI \qquad (8)$$

which is exothermic to the extent of 33 kcal/mole. Thus, the hard Li^+ prefers the hard F^- and the much softer Cs^+ is left with the soft I^-.

The standard method for increasing solubility in hydrocarbon solvents, or lipid solubility, is to add long alkyl chains to the molecule. It is also possibe to decrease water solubility and increase solubility in soft solvents by replacing oxygen atoms in the solute molecule with softer sulfur or selenium atoms (*19*).

Application to Kinetic Behavior

Instead of equilibrium data for acid-base reactions, we may look at rate data. These will usually be in the form of second-order rate constants for the nucleophilic displacement reaction

$$A{:}B' + B \xrightarrow{k} A{:}B + B' \qquad (9)$$

though a certain amount of information on the electrophilic displacement reaction is also available.

$$A{:}B + A' \xrightarrow{k} A'{:}B + A \qquad (10)$$

If the vast amount of data on reaction 9 is analyzed (*20*), it is found that for some substrates, A : B′, the rates are sensitive chiefly to the ordinary proton basicity of the nucleophile B. Other substrates are sensitive chiefly to the polarizability of B. The properties of the acid site (or electrophilic center) of A : B′ determine which type of behavior is found. If the properties of the acid center are those that make it a hard acid, then basicity is the dominant factor. If the acid site is a soft center, then polarizability is the important factor in the rates.

Accordingly, we may call the P(V) atom of a phosphate ester a hard electrophilic center. Displacements on P(V) will be fast for OH^- and F^- and other good bases toward the proton. A Pt(II) complex will have a soft electrophilic center. Fast substitution reactions will occur with phosphines, olefins, and iodide ion (see Table 2). Hard reagents will be ineffective.

Experimentally it turns out to be true that polarizability is always more important for rates than for equilibria. Any central atom which is known from rate data to be a hard electrophile will certainly be a hard acid by equilibrium standards. A borderline hard acid, such as the methyl carbonium ion, will become a rather soft electrophilic center. Thus, for nucleophilic displacements on tetrahedral carbon, polarizability and basicity of the nucleophile will both be important, with polarizability the dominant factor.

Table 2. Softness parameter of some bases.*

Base	Constant†
H_2O	0
OH^-, OCH_3^-, F^-	<1
Cl^-	1.65
NH_3	1.67
C_5H_5N	1.74
NO_2^-	1.83
N_3^-	2.19
NH_2OH	2.46
$H_2N{-}NH_2$	2.47
C_6H_5SH	2.75
Br^-	2.79
I^-	4.03
SCN^-	4.26
SO_3^{2-}	4.40
$(C_6H_5)_3Sb$	5.26‡
$(C_6H_5)_3As$	5.36‡
$SeCN^-$	5.71
$C_6H_5S^-$	5.78
$S{=}C(NH_2)_2$	5.78
$S_2O_3^{2-}$	5.95
$(C_6H_5)_3P$	7.51‡

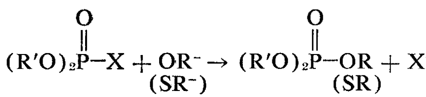
* For another scale, see *29*. † From log *k* for rates of reaction with *trans*-Pt $(C_5H_5N)_2Cl_2$ (see *30*). ‡ See *31*.

For the displacement reactions

$$CH_3I + RO^- \rightarrow CH_3OR + I^- \qquad (11)$$

$$CH_3I + RS^- \rightarrow CH_3SR + I^- \qquad (12)$$

the rate constant for reaction 12 will exceed that of reaction 11 by a factor of 100. For displacement reactions on $(R'O)_2POX$, OR^- will be a better nucleophile than SR^- by a factor of about 30 (*21*).



$$(R'O)_2\overset{\overset{\displaystyle O}{\|}}{P}{-}X + \underset{(SR^-)}{OR^-} \rightarrow (R'O)_2\overset{\overset{\displaystyle O}{\|}}{P}{-}\underset{(SR)}{OR} + X^- \qquad (13)$$

The rates of proton transfer reaction usually follow the Brønsted law (*22*).

$$HA + B \xrightarrow{k} A^- + BH^+ \qquad (14)$$

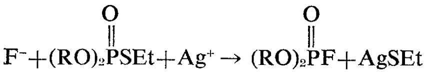
The rates increase with increasing (ordinary) acid strength of HA and increasing base strength of B. Linear relationships are found between log *k* and pK_a or pK_b. However, if either B or A^- is a soft base, then lower rate constants are found than are predicted from the Brønsted relation (*23*). Proton transfers to and from soft bases are abnormally slow (provided the equilibrium constant of reaction 14 is not overwhelmingly large). An extreme example is the slow protonation of carbanions.

$$R_3C^- + HA \rightarrow R_3CH + A^- \qquad (15)$$

Saville (*24*) has used the softness-hardness principle as a guide to selecting electrophilic catalysts for nucleophilic displacement reactions.

$$B{:} + A{:}B' + A' \rightarrow B{:}A + A'{:}B' \qquad (16)$$

The rules are simply that if B′ is a hard base, then a hard acid A′ is used as a catalyst; if B′ is a soft base, then A′ should be a soft acid. The nucleophile B should also match the characteristic of the electrophilic center A. For example,



$$F^- + (RO)_2\overset{\overset{\displaystyle O}{\|}}{P}SEt + Ag^+ \rightarrow (RO)_2\overset{\overset{\displaystyle O}{\|}}{P}F + AgSEt \qquad (17)$$

$$I^- + H_2O_2 + H^+ \rightarrow IOH + H_2O \qquad (18)$$

The best possibilities for catalysis occur when the substrate, A : B′, has a mismatch of a hard acid with a soft base, or vice versa. In reaction 17 the hard base F^- is used to attack the hard phosphorus atom. Catalysis is provided by the soft Ag^+, which helps pull off the soft SEt^- group. In reaction 18 we have a nucleophilic attack by the soft I^- on the soft electrophilic oxygen atom of OH^+. Catalysis is brought about by coordinating the hard hydrogen ion to the hard nucleophilic oxygen of OH^-. Note that the same atom, in this case the oxygen of H_2O_2, can simultaneously be a soft acid and a hard base center. Electron donation puts greater stress on polarizability than does electron acceptance.

The position of attack by an ambident nucleophile can usually be predicted by the use of the softness-hardness principle (*21*). An ambident ion has two possible donor atoms, such as nitrogen or oxygen in NO_2^-. Usually one donor atom is softer than the other—for example, sulfur in NCS^- or in $(RO)_2POS$, and nitrogen in NO_2^-. In these cases the hardness or softness of the electrophile determines the point of attack. A hard center like Fe(III) in $Fe(H_2O)_6^{3+}$ is attacked by nitrogen to form $Fe(H_2O)_5NCS^{2+}$, whereas the softer center Co(III) in $Co(CN)_5H_2O^{2-}$ forms $Co(CN)_5SCN^{3-}$.

Theory Underlying Hard and Soft Behavior

What are the reasons for the preferential hard-hard and soft-soft acid-base interactions? Actually, no one factor seems universally responsible, and several different theories have been proposed by investigators looking at different aspects of acid-base behavior. It should be emphasized that the answer must lie in interactions occurring in the acid-base complex itself. Solvation effects, while important for ionic acids and bases, will not cause a separation into class (a) and class (b), each with its characteristic behavior.

The oldest and most obvious explanation may be called the ionic-covalent theory. It goes back to the ideas of Grimm and Sommerfeld for explaining the differences in properties of AgI and NaCl. Hard acids are assumed to bind bases primarily by ionic forces. High positive charge and small size would favor such ionic bonding. Bases of large negative charge and small size would be held most tightly—for example, OH^- and F^-. Soft acids bind bases primarily by covalent bonds. For good covalent bonding, the two bonded atoms should be of similar size and similar electronegativity. For many soft acids ionic bonding would be weak or nonexistent because of the low charge or the absence of charge. It should be pointed out that a very hard center, such as I(VII) in periodate or Mn (VII) in MnO_4^-, will certainly have much covalent character in its bonds, so that the actual charge is reduced much below +7. Nevertheless, there will be a strong residual polarity.

The π-bonding theory of Chatt (*25*) seems particularly appropriate for metal ions, but it can be applied to many of the other entries in Table 1 as well. According to Chatt the important feature of class (b) acids is considered to be the presence of loosely held outer *d*-orbital electrons which can form π-bonds by donation to suitable ligands. Such ligands would be those in which empty *d* orbitals are available on the basic atom, such as phosphorus, arsenic, sulfur, or iodine. Also, unsaturated ligands such as carbon monoxide and isonitriles would be able to accept metal electrons by means of empty, but not too unstable, molecular orbitals. Class (a) acids would have tightly held outer electrons, but also there would be empty orbitals available, not too high in energy, on the metal ion. Basic atoms such as oxygen and fluorine in particular could form π-bonds in the opposite sense, by donating electrons from the ligand to the empty orbitals of the metal. With class (b) acids, there would be a repulsive interaction between the two sets of filled orbitals on metal and oxygen and fluorine ligands. Figure 1 shows schematically a *p* orbital on the ligand and a *d* orbital on the metal which are suitable for forming π-bonds.

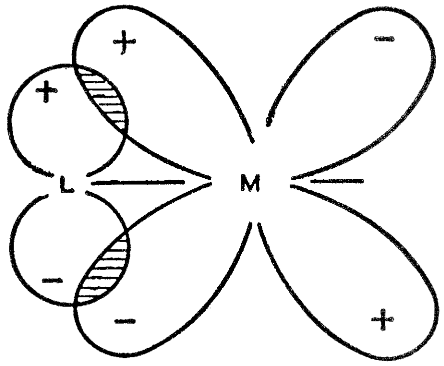


Fig. 1. A *p* atomic orbital on a ligand atom and a *d* orbital on a metal atom suitable for π-bonding. The *d* orbital is filled and the *p* orbital is empty for a soft acid–soft base combination. The *d* orbital is empty and the *p* orbital is filled for a hard acid–hard base combination. The plus and minus signs refer to the mathematical sign of the orbital.

The importance of the *d* electrons in metals for determining class (a) or class (b) behavior is very marked. In fact no class (b) metal ion containing less than five *d* electrons is known. A neutral metal atom, such as potassium or calcium, while soft in some respects, will still not show many of the typical reactions of class (b) metals, such as formation of normal carbonyl or olefin complexes. A decrease in the shielding of the *d* shell by removal of outer electrons will sometimes enhance (b) character (*26*). Thus, Tl(III) is softer than Tl(I) in spite of its greater positive charge. Also Sn(IV) and As(V) seem to show more (b) behavior than Sn(II) or As(III).

Occasionally metal ions show soft behavior even when they are of high positive charge—for example, Pt(IV) in Table 1. This behavior seems paradoxical. However, an explanation may be offered for these cases in terms of the actual charge on the metal ion rather than the formal charge (*10*). Thus, there is evidence that platinum in PtI_6^{2-} has a charge near zero, and certainly not plus four. It is characteristic of cases where a high oxidation state leads to soft behavior that all the ligands are soft. Covalent bonding will then cause a large transfer of charge from ligands to metal and extensive charge neutralization on the metal ion. Thus, we have the complexes $Mo(NCS)_6^{3-}$, with Mo(III) acting as a hard acid, and $Mo(SCN)_6^-$, with Mo(V) acting as a soft acid. In the first case we have metal-nitrogen bonding and in the second case, metal-sulfur bonding.

Pitzer has suggested (*27*) that London, or van der Waals, disperson forces between atoms or groups in the same molecule may lead to an appreciable stabilization of the molecule. Such London forces depend on the product of the polarizabilities of the interacting groups and vary inversely with the sixth power of the distance between them. These forces are large when both groups are highly polarizable. It seems plausible to generalize and state that additional stability due to London forces will always exist in a complex formed between a polarizable acid and a polarizable base. In this way the affinity of soft acids for soft bases can be partly accounted for.

Mulliken has given a different explanation for the extra stability of the bonds between large atoms—for example, two iodine atoms (*28*). It is assumed that *d*- *p*-orbital hybridization occurs, so that both the π-bonding molecular orbitals and the π*-antibonding orbitals contain some admixed *d*-character. This has the twofold effect of strengthening the bonding orbital by increasing overlap and weakening the antibonding orbital by decreasing overlap.

Mulliken's theory is the same as Chatt's π-bonding theory as far as the π-bonding orbital is concerned. The new feature is the stabilization due to the antibonding molecular orbital. As Mulliken points out, this effect can be more important than the more usual π-bonding. The reason is that the antibonding orbital is more antibonding than the bonding orbital is bonding, if overlap is included. For soft-soft systems, where there is considerable mutual penetration of charge clouds, this amelioration of repulsion due to the Pauli principle would be great.

One final point in connection with theory is illustrated by reaction 8. Clearly it is the strong binding in LiF, compared to all other factors, which drives the equilibrium to the right. Since most acid-base reactions are actually double exchanges, or competitions (see reaction 2), it is the strongest bonding, A : B, which dominates. The weakest bonding, A′ : B′, may simply be dragged along as a necessary consequence. The strongest bonding will usually be between the hard acid and the hard base.

Biological Applications of the Principle

One wonders, naturally, what the applications of the concept of hard and soft acids and bases may be in biochemistry and biology. To the extent that biochemistry can be considered to involve simple chemical reactions, many of the applications discussed above can be taken over directly. Unfortunately, most reactions of biological systems are characterized not only by complexity but also by specificity. This means that it is unlikely that general rules will be of much value.

Nevertheless, a few generalizations can be drawn. If the lists of hard and soft acids and bases of Tables 1 and 2 are examined, it is seen that hard acids and bases are usually the normal, abundant components of biological systems. Thus, an organism will tolerate most hard acids or bases, unless some specific reaction occurs. One may say, *"La vie est dure."*

Contrariwise, most soft acids and bases are poisons to living organisms. While specific effects are no doubt common, the general effect must be poisoning by the formation of complexes with the soft bases and acids that are present, in small amounts, in the organism—the heavier metals and sulfide groups, for example. It is of interest to find that the same substances that are poisons in heterogeneous catalysis are poisons for living things.

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NEWS AND COMMENT

Daddario Study Says NSF Should Be in Forefront of Policymaking

The National Science Foundation is perhaps the favorite administrative creation of the leadership of American basic science. It is prudent and usually elitist in fulfilling its mandate to support basic research and science education; it is so apolitical that in its 15-year existence its officers have served from administration to administration without idealogical strain, and, by design, NSF is generally passive: it waits for proposals, summons panels of scientists to select the most promising, and then parcels out whatever funds are available.

In the prevailing view of the leaders of science, the Foundation could use a great deal more money, and it would be pleasant if it were free of the bit of congressional tinkering it has encountered. But outside of differences that usually are matters of emphasis rather than substance, the leaders generally approve NSF's administrative style, and particularly its traditional aloofness from political currents and interagency combat. It is safe to say that they would like to see NSF do nothing but expand in its present role of judicious banker of American basic science.

This week, a jarring contrast with this vision was put forth in a study made by Representative Emilio Q. Daddario's subcommittee on Science, Research, and Development, whose parent committee, Science and Astronautics, has jurisdiction over NSF's legislative charter. Titled, "The National Science Foundation, Its Present and Future,"* the Daddario study says, in effect, that it is time for NSF to abandon wallflower tactics, that the Foundation should become a leader in national science policy, and that, while holding to its role in basic research, the Foundation should also focus its efforts on the employment of basic research for the solution of environmental and social problems. In sum, the Daddario committee is telling this carefully conceived, nontruculent creation of basic science that science is too powerful and the Foundation is too important for either to cling to a sheltered position in the governmental structure. The report states:

> There should be, and is, a scientific and technological stature about the Foundation sufficient to warrant an extraordinary voice in the science policy of the administration. NSF is the only Federal agency with an

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* 118 pages, available without charge from the Committee on Science and Astronautics, U.S. House of Representatives, Washington, D.C. Related documents are: "The National Science Foundation," a report of the Science Policy Division, Library of Congress; and "Government and Science: A Review of the National Science Foundation"; hearings, vols. 1 and 2, also available from the committee.