Chapter 2

Classification of Hard and Soft Acid and Bases

Pearson's Generalization:

He focused on nucleophilic displacement reactions.

$$N + S\text{-}X \longrightarrow N\text{-}S + X$$

There are two kinds of substrate acids. One class bind strongly to bases which have a high affinity for protons (Hard base) and second class bind preferentially with highly polarizable bases (Soft base).

The **hardness** of an acid(acceptor) or a base (donor) is characterized:

1. Small atomic radius
2. High effective nuclear charge
3. Low polarizibility

Softness implies as:

1. Large atomic radius
2. Small effective nuclear charge
3. High polarizibility

Hard acids will form complexes whose stability sequences are:

N» P > As > Sb >Bi

O» S > Se > Te

F» Cl > Br > I

Soft acids with bases decreases as the base varies:

N« P> As > Sb > Bi

O « S< Se ~Te

F « Cl < Br < I

TABLE 1: classification of Hard and Soft Acids

Hard acids:

H^+ ,Li^+, Na^+, K^+, (Rb^+ , Cs^+)

Be^{2+}, $Be(CH_3)_2$, Mg^{2+} , Ca^{2+} ,Sr^{2+} (Ba^{2+})

Ti^{4+},Zr^{4+},Hf^{4+},Vo^{2+},Cr^{3+},Cr^{6+},MoO^{3+},WO^{4+},Mn^{2+},Mn^{7+},Fe^{3+},Co^{3+}

BF_3,BCl_3,$B(OR)_3$,Al^{3+} ,$AL(ch_3)_3$,$AlCl_3$,ALH_3,Ga^{3+} ,In^{3+}

CO_2,RCO^+,NC^+,Si^{4+} ,Sn^{4+} ,CH_3Sn^{3+} ,$(CH_3)_2Sn^{2+}$

N^{3+} ,RPO_2^+,$ROPO_2^+$,As^{3+}
SO_3,RSO_2^+,$ROSO_2^+$
Cl^{3+} ,Cl^{7+} ,I^{3+} ,I^{7+}
HX (hydrogen bonding molecules)

Borderline acids:
Fe^{2+} ,Co^{2+} ,Ni^{2+} ,Cu^{2+} ,Zn^{2+}
Rh^{3+} ,Ir^{3+} ,Ru^{3+} ,Os^{2+}
$B(CH_3)_3$,GAH_3
R_3C^4,$C_6H_5^+$,Sn^{2+} ,Pb^{2+}
NO^+,Sb^{3+} ,Bi^{3+}
SO_2

Soft acids:
$Co(CN)_5^3$,Pd^{2+} ,Pt^{2+} ,Pt^{4+}
Cu^+,Ag^+,Au^+,Cd^{2+},Hg^+,Hg^{2+},CH_3Hg^+
BH_3,$Ca(CH_3)_3$,$GaCl_3$,$GaBr_3$,GaI_3,Tl^+,$Tl(CH_3)_3$
CH_2,carbenes

π acceptors: trinitrobenzene, chloroanil, quinones, tetracyanoethylene,etc.
HO^+, RO^+, RS^+, RSe^+, Te^{4+}, RTe^+
Br_2, Br^+, I_2, I^+, ICN, etc.
O, Cl, Br, I, N, RO, RO_2
M^0(metal atoms) and bulk metals

The softness of a base is defined by the equilibrium

$$MeHg^+ (aq) \quad BH^+ (aq) \rightleftarrows MeHgB^+ (aq) + H^+ (aq)$$

If K>>1the base B is soft; If K near unity or less than unity, the base is hard.

TABLE 2 Classification of Hard and Soft Bases

Hard bases:
NH_3, RNH_2,N_2H_4
H_2O,OH^-,O^{2-},ROH,RO^-,R_2O

$CH_3COO^-, CO_3^{2-}, NO_3^-, PO_4^{3-}, SO_4^{2-}, ClO_4^-$

F-,(Cl-)

Borderline bases:

$C_6H_4NH_2, C_5H_5N, N_3^-, N_2$

NO_2^-, SO_3^{2-}

Br^-

:Soft bases

H^-

$R^-, C_2H_4, C_6H_6, CN^-, RNC, CO$

$SCN^-, R_3P, (RO)_3P, R_3As$

$R_2S, RSH, RS^-, S_2O_3^{2-}$

I^-

Hard acids prefer to bind to hard bases and soft acids prefer to bind to soft bases. This statement, known as the Hard and Soft Acids and Bases Principle.

It has been recognized for a long time that a strong acid forms a strong bond with a strong base, i.e., the equilibrium constant of the reaction is determined by the strength factor *S.*

$$\mathrm{A} + \mathrm{:B} \rightleftharpoons \mathrm{A:B}$$

However, such a simple correlation is not always adequate and a four-parameter equation appears to be the minimum requirement.

Pearson proposed that the equilibrium be expressed

$$\mathrm{Log}\ K = S_A S_B + \delta_A \delta_B$$

S is Strength factor, and $\boldsymbol{\delta_{A,}\delta_B}$ are Softness factors. The equation is similar to that of Edwards.

$$\mathrm{Log}\ (K/K_0) = \alpha E_n + \beta H$$

The α and β values for many common metal ions have been determined. For *Lewis acids* with a *high positive charge* and *small size*, *β is large*, whereas Lewis acids with low charge and large size have small β values. **It follows that β corresponds to Pearson's S_A; therefore:**

$$\beta H = S_A S_B \text{ and } \alpha E_n = \delta_A \delta_B$$

The **softness parameters** are correlated with the **oxidation potential** and, hence, **polarizability of the acids and bases**.

SOFTNESS SCALES

Pearson and Mawby calculated the **coordinate bond energy** (CBE) for **metal halides** and defined a parameter $CBE(F^-)-CBE(I^-)/CBE(F^-)$ which provides a measure of the softness of the acceptor (acid) within a charge group (e.g, M^+,M^{2+} ,M^{3+} etc.)

Klopman’s theoretical treatment of HSAB leads to the conclusion that ***the hardness of an acceptor is associated with the low energy of its empty frontier orbital relative to desolvation energy of the acceptor.*** *He also was able to estimate the energy difference ,with reference to water.* **Very hard acceptors have large negative values and very soft ones have large positive values.**

Ahrland reasoned that the more completely the energy for positive ion formation in the gas phase is regained by introduction of the ion in a hard solvent (e.g. H_2O) the harder the ion is. *He then proposed a softness parameter based on the dehydration energy and the ionization potential for the formation of* M^{n+} *(gas).* **A large difference between the two quantities indicates a soft ion.**

Yingst and McDaniel used the α/β ratio from Edwards equation as a criterion for assessing the softness of metal ions. *Hard acids generally have a low α (polarizability) and a high β (basicity) value, therefore α/β permits simultaneous consideration of both factors.*

Despite a certain degree of success achieved from these and other attempts, exceptions have always been noted. Pearson himself has questioned the overall **usefulness of quantification** of the HSAB concept.

Apart from the inherent limitations of each approach, it is difficult to imagine that prescribed values are flexible enough to give a meaningful picture when dealing with external influences such as **ligand effects** and **ambident behavior.**

Although an exact softness scale is neither available nor advisable, **empirical systematization** of various acids and bases is **essential for correlating experimental observations.** The best compromise would be to establish guidelines for the rough estimation of softness in a comparative sense.

Softness parameters for donors (bases) have been similarly calculated.

Hardness increases (or Softness decreases) with increasing positive oxidation state.

Examples:

Ni(0) is soft, Ni(II) is borderline, Ni(IV) is hard

RS^+ is soft, RSO^+ is borderline, RSO_2^+ is hard

$S^{2-}$is softer than SO_3^{2-}

Exceptions:

Tl(III), Sn(IV), Pd(IV) are softer than Tl(I), Sn(II), Pb(II)

These lower valent ions have $d^{10}s^{2}$ electron in their outermost shells, the shielding of the d electrons decreases the softness of the lower valent species.

One factual demonstration of this reverse hardness/valence relationship is that inorganic thallium compounds are generally more stable in the +1 valence state, while covalent organothallium derivatives are stable only in the +3 state.

It may be that hardness correlates with fractional charge on the central atom rather than its oxidation number. This rationalization receives support from observations of ligand effects. Despite a formal B^{3+} core possessed by both BF_3 and BH_3, the former compound is a hard Lewis acid, and the latter is a soft one.

This occurs because hydride ions effectively reduce the charge of the boron atom in borane. This phenomenon is particularly evident with soft donor ligands from which the negative charge is easily transferred.

For a series of bases with congeneric central atoms, the **heavier or more electropositive member is usually softer:**

$R_3P>R_3N$ $R_2Se>R_2S>R_2O$ $I^->Br^->Cl^->F^-$

The isoelectronic anions from the **lower family on the same row (period) of elements are the softer:**

$CH_3^->NH_2^->OH^->F^-$

Softness and strength are two independent properties, a base can be both soft and strongly binding toward proton . Carbanions are cases in point.

The softness is related to the hybridization of the carbon. **Higher *p* character increases the softness and configurational instability of the carbanion**

($sp^3 > sp^2 > sp$)

Reactions involving carbanions formally derived from alkanes often lead to racemization, whereas configuration is retained at the alkenic carbanion center.

The fact that cyclopropyl carbanions maintain their original stereochemistry concurs with the above notion, as the *s* character of cyclopropane exocyclic orbital is > 25%.

Carbon acids are relatively Soft. The *hardness sequence* of several carbenium ions is :

$Ph^{+} > t\text{-}Bu^{+} > i\text{-}Pr^{+} > Et^{+} > Me^{+}$

The increasing stability of isomeric butanols are

n< iso < sec < tert

Which is parallel of hardness of carbenium ions **R^{+}**

This is an explanation for isomerization such as

$$i\text{-}BuOH\ (g) \longrightarrow t\text{-}BuOH\ (g)$$

Since H^{-} is one of the softest bases, CH_3^{+} is soft carbon acid that bearing a positive charge. Replacement of H atom in CH_3^{+} by electronegative groups increase the hardness of cations.

The only way to improve on its softness is remove a proton and create a carbene **$:CH_2$**. A carbon free radical that is soft, acts as an acceptor and as a donor.

Olefins act as soft bases by using the π-electron system.

THEORTICAL DESCRIPTION OF HSAB

Ionic bonding is favored by small size and large charge of species.

Good covalent bonding requires similar size and electronegativity.

Chatt has proposed a π-bonding theory for metal ions. *Soft metal ions have loosely held outer d–orbital electrons which can form* π *bonds by back-donation to suitable ligands.*

Mulliken considered the extra stability of the bonds between large atoms as being derived from *d - p* hybridization, whereby some *d* characterize instilled into both π and π* molecular orbitals.

This has the effect of increasing bonding orbital overlap, but decreasing the overlap of antibonding orbitals.

Klopman applied the quantum mechanical perturbation method to analyze the interaction of two systems R and S.

Total energy generated by a combination of:

1) Neighboring effects which accounts for interactions due to ion-pair formation without electron transfer.

2) Partial charge transfer during covalent bonding.

The most important feature of this approach is the inclusion of solvation phenomena.

When the perturbation under consideration is small, the total perturbation energy can be expressed as:

$$\underset{\text{Є}}{\Delta E_{total}} = -q_R q_s \frac{\Gamma}{\epsilon} + \Delta solv(I) + \sum_{m\ occ} \sum_{n\ unocc} \frac{[2(C_R^m)^2(C_s^n)^2\beta^2]}{E^*_m - E^*_n}$$

q_R and q_s = total initial charge of atoms R and S

Γ = coulomb repulsion term between R and S

Є = local dielectric constant of the solvent

E^*_m = highest occupied orbital of the donor

E^*_n = lowest unoccupied orbital of the acceptor

When $| E^*_m - E^*_n |$» $4\ \beta^2$ very little charge transfer occurs.

Thus ΔE_{total} becomes:

$$\Delta E_{total} = -q_R q_s \frac{\Gamma}{\epsilon} + \Delta solv(I) + 2\sum_{m\ occ} (C_R^m)^2 \sum_{n\ unocc} (C_s^n)^2\, \gamma$$

Where $\gamma = \beta^2 /(E^*_m - E^*_n)_{av}$

The total charges on the two reactants are the dominant factors of the reaction (charge-controlled reaction). This type of reaction occurs when:

1. Donor is difficult to ionize or polarize (E^*_m very low) and the acceptor has a slight tendency to accept electrons (E^*_n very high)

2. Both are strongly solvated. The charge controlled reaction is therefore synonymous with a hard-hard interaction.

Where $| E^*_m - E^*_n | \approx 0$ interaction of the frontier orbitals becomes important, and a strong electron transfer take place (frontier-controlled reaction).

The reactivity is determined by the frontier electron density (C_R^m, C_s^n), when uncharged or weakly charged species interact. Polarizability of the reactants and low solvation energies occur in the reaction, therefore such an interaction is identified with soft – soft interactions.

$$\Delta E_{total} = 2C_R^m C_s^n \beta^2$$

Type and Rate of Interaction Between Hard and Soft Reagents

Donor E^*_m	Acceptor E^*_n	$E^*_m - E^*_{nv}$	$\underline{\Gamma}$	β	Reactivity
High(Soft) Large orbital	High(Hard) Small orbital	Medium	Small	Very Small	Undefined Low
High(Soft) Large orbital	Low(Soft) Large orbital	Small	Very Small	Large	Frontier controlled High
Low(Hard) Small orbital	High(Hard) Small orbital	Large	Large	Small	Charge Controlled High
Low(Hard) Small orbital	Low(Soft) Large orbital	Medium	Small	Very Small	Undefined Low