Hard and Soft Acids and Bases

1965- Ralph Pearson introduced the hard-soft-acid-base (HSAB) principle.

“Hard acids prefer to coordinate the hard bases and soft acids to soft bases”

This very simple concept was used by Pearson to rationalize a variety of chemical information.

1983 – the qualitative definition of HSAB was converted to a quantitative one by using the idea of polarizability.

A less polarizable atom or ion is “hard” and a more easily polarized atom or ion is “soft”

The Quantitative Definition of hardness:

$\boxed{N = (\text{I.P.} - \text{E.A.})/2}$ The average of ionization potential and electron affinity

Actually, the electronegativity, X, of a neutral species is the same $\boxed{X = (\text{I.P.} - \text{E.A.})/2}$

One can relate n (hardness) to the gap between the HOMO and LUMO:

$\boxed{2n = (E_{LUMO} - E_{HOMO})}$

E (energy)

HOMO and LUMO orbitals (molecules) or simply highest occupied and lowest unoccupied orbitals in atoms participate in the bonding more than any other levels.

(The lower the energy of the HOMO and the higher the energy of the LUMO, the more stable the species is thermodynamically)

The greater the *n* value - the more hard the species is.

Basically, HSAB theory endeavors to help one decide if

$$AB + CD \rightleftharpoons AC + BD$$

goes to the left or the right

(also helps you to know if AB + CD
forms AC + BD or AD + BC)

<u>Hard and Soft Acids and Bases</u>

Hard acid: High positive charge
Small size
Not easily polarizable

Hard base: Low polarizability
High electronegativity
Not easily oxidized

Soft acid: Low positive charge
Large size; easily oxidized
Highly polarizable

Soft base: High polarizability
Diffuse donor orbital
Low electronegativity
Easily oxidized

Hard acids prefer to bind to hard bases and soft acids prefer to bind to soft bases.

This statement is neither an explanation or a theory. It is simply a guideline that helps one to qualitatively predict the relative stability of acid-base adducts.

Lewis acids: A^+
Lewis bases: B: or $B:^-$

A^{+n} the smaller and more highly charged, the harder it will be

B: or $B:^{-n}$ the larger the atom (or ion) the softer it will be

<u>Classification of hard and soft acids</u>

Listings of hard and soft acids and bases are the result of observing the preferences for reactions to go to the right or left.

Example: a given base, B, may be classified as hard or soft based on the equilibrium:

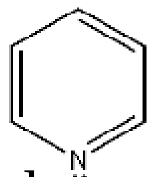
$$\underset{\text{Hard Acid}}{BH^+} + \underset{\text{Soft Acid}}{CH_3Hg^+} \rightleftharpoons CH_3HgB^+ + H^+$$

There is a competition here between the acid H^+ and CH_3Hg^+.
If B is soft then → to the right
If B is hard then ← to the left

Important to remember that the listings in the tables do not have a sharp dividing line between them. These terms, "hard" & "soft", are relative

Some are borderline and even though within the same category are not all of the same degree of "hardness" and "softness" e.g. although all alkali metals in ionic form M^+ are "hard", the larger, more polarizable, Cs^+ ion is much softer than Li^+

- also N: compounds are not all equal

  H_3N: versus 

  pyridine is much more polarizable

more examples:

common soft species } PR_3, SR_2, are "soft bases
Hg^{2+}, Pd^{2+}, Pt^{2+} are soft acids

common hard species } NH_3, ROH, H_2O are "hard" bases
Ti^{4+}, Si^{4+}, Co^{3+} are "hard acids

RS^- versus RO^-

$$Hg\text{–}SR + H^+ \rightleftharpoons Hg^{2+} + HSR$$

does this reaction proceed to the left or right?

$$Hg\text{–}OR + H^+ \rightleftharpoons Hg^{2+} + HOR$$

left or right?

Table 7.6 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})
Sc^{+3}, La^{+3}, Ce^{+4}, Gd^{+3}, Lu^{+3}, Th^{+4}, U^{+4}, UO_2^{+2}, Pu^{+4}
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^{+5}, 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^+, $C_6H_5^+$, 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, $Ga(CH_3)_3$, $GaCl_3$, $GaBr_3$, GaI_3, Tl^+, $Tl(CH_3)_3$
CH_2, carbenes
Pi-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, $RO\cdot$, $RO_2\cdot$
M° (metal atoms) and bulk metals

Table 7.7 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

$C_6H_5NH_2$, 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^-

$$Ti^{4+}\text{-}SR^- + H^+ \rightleftharpoons Ti^{4+} + HSR$$

left or right?

Remember it is all relative

$$Ti^{4+}\text{-}OR^- + H^+SR^- \rightleftharpoons Ti^{4+} + SR^- + H^+OR^-$$

Predict which way the following reactions will go.

$HI + NaF \rightleftharpoons HF + NaI$		R
$AlI_3 + 3NaF \rightleftharpoons AlF_3 + 3NaI$		R
$CaS + H_2O \rightleftharpoons CaO + H_2S$		R
$TiF_4 + 2TiI_2 \rightleftharpoons TiI_4 + 2TiF_2$		L
$CoF_2 + HgBr_2 \rightleftharpoons CoBr_2 + HgF_2$		L
$H_gO + H_2S \rightleftharpoons H_gS + H_2O$		R

How about the following?

1) $SiS_2 + 2H_2O \longrightarrow SiO_2 + 2H_2S$

2) $SiO_2 + 2H_2S \longrightarrow SiS_2 + 2H_2O$

3) $Cu_2S + H_2O \longrightarrow Cu_2O + H_2S$

4) $Cu_2O + H_2S \longrightarrow Cu_2S + H_2O$

Which ones will proceed as written?

R (1) Si^{4+} (hard) S^{2-} (soft) O^{2-} (hard) H^{+} (hard)

L (2) Si^{4+} (hard) O^{2-} (hard)

L (3) Cu^{+} (soft) S^{2-} (soft) O^{2-} (hard)

R (4) Cu^{+} (soft) S^{2-} (soft) O^{2-} (hard)

(1) and (4) will proceed as written