Hard and Soft Acids and Bases (HSAB) Theory

Hard and Soft Acids and Bases (HSAB) Theory is a qualitative concept introduced by Ralph Pearson to explain the stability of metal complexes and the mechanisms of their reactions.

However it is possible to quantify this concept based on Klopman's FMO analysis using interactions between HOMO and LUMO.

According to this theory, the Lewis acid and bases can be further divided into hard or soft or border line types.

Hard Acids	Soft Acids
Small ionic radii, High positive charge, Strongly solvated, Empty orbitals in the valence shell High energy LUMOs.	Large ionic radii, Low positive charge, Completely filled atomic orbitals Low energy LUMOs.
H^+, Li^+, Na^+, K^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Sn^{2+} **Al^{3+}, Ga^{3+}, In^{3+}, Cr^{3+}, Co^{3+}, Fe^{3+}, La^{3+}, Si^{4+}, Ti^{4+}, Zr^{4+}, Th^{4+},**	**Cu^+, Ag^+, Au^+, Hg^+ , Cs^+ , Tl^+ , Hg^{2+} Pd^{2+}, Cd^{2+} , Pt^{2+}**

Hard Bases	Soft Bases
Small ionic radii, Highly electronegative, Weakly polarizable, Strongly solvated, High energy LUMOs.	Large ionic radii, Intermediate electronegativity, highly polarizable Low energy LUMOs.
H_2O, OH^-, F^-, Cl^-, CH_3CO_2-, PO_4^{3-}, SO_4^{2-}, CO_3^{2-}, NO_3^-, ClO_4^-, ROH, RO^-, R_2O, NH_3,	**RSH, RS^-, R_2S, I^-, CN^-, SCN^-, $S_2O_3^-$, R_3P, R_3As $(RO)_3P$, RNC, CO, C_2H_4, C_6H_6, R^-, H^-**

The **Border line** Lewis acids and bases have intermediate properties.

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HSAB Principle: According to HSAB concept,

- **Hard acids prefer binding to the hard bases to give ionic complexes, whereas**
- **Soft acids prefer binding to soft bases to give covalent complexes.**

* The large electronegativity differences between hard acids and hard bases give rise to strong ionic interactions.

* The electronegativities of soft acids and soft bases are almost same and hence have less ionic interactions. i.e., the interactions between them are more covalent.

* The interactions between hard acid - soft base or soft acid - hard base are mostly polar covalent and tend to be more reactive or less stable. The polar covalent compounds readily form either more ionic or more covalent compounds if they are allowed to react.

APPLICATIONS OF HSAB PRINCIPLE

1. Recovery of Au

The softest metal ion Au+(*aq*) is recovered in mining operations by suspending it in a dilute solution of CN-, which dissolves the Au.

$$4\ Au(s) + 8\ CN^-(aq) + O2(g) + 2\ H2O \Rightarrow 4\ [Au(CN)2]\text{-}(aq) + 4\ OH^-$$

2. Why is AgI(s) water-insoluble, but LiI water-soluble?

AgI is a soft acid-soft base combination, while LiI is hard-soft.

The interaction between Li^+ and I^- ions is not strong.

AgI(s) + H2O(l) ➔ essentially no reaction

LiI(s) + H2O(l) ➔ Li^+ (aq) + I^- (aq)

3. In Hydrogen Bonding:

The strong hydrogen bond is possible in cases of H_2O, NH_3 and HF, since the donor atoms **(F, O & N)** are **HARD BASES** and their interactions with partially positively charged **H**, which is a **HARD ACID**, are stronger.

4. Precipitation reactions:

The softer acids like Ag^+, Hg^+, Hg^{2+} etc., and border line acids like Fe^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+} etc., can be precipitated as sulfides from their aqueous solutions since S^{2-} ion is a softer base.

CuS, HgS, NiS, FeS, ZnS, PbS etc.

But Ca^{2+} and Mg^{2+} hard acids appear as carbonates CaCO3, MgCO3

5. Other Reactions formation of stable compounds :

1 LiI + CsF ----------- > LiF + CsI

Hard-hard soft-soft

2. AgI^{2-} is stable but AgF^{2-} is uinstable.

$$\underset{\text{Soft acid}}{Ag^+} + \underset{\text{Soft base}}{2I^-} \longrightarrow \underset{\text{Stable}}{AgI_2^-}$$

$$\underset{\text{Soft acid}}{Ag^+} + \underset{\text{Soft base}}{2F^-} \longrightarrow \underset{\text{Unstable}}{AgF_2^-}$$

3. $[CoF6]^{2-}$ is stable but $[CoI6]^{2-}$ is not so stable because Co^{+3} and F^- both are hard and hard.

4. Precipitates formed in the Qualitative Analysis

Qualitative Analysis Separation

	Group 1	Group 2	Group 3	Group 4	Group 5
HSAB acids	Soft	Borderline and soft	Borderline	Hard	Hard
Reagent	HCl	H_2S (acidic)	H_2S (basic)	$(NH_4)_2CO_3$	Soluble
Precipitates	AgCl	HgS	MnS	$CaCO_3$	Na^+
	$PbCl_2$	CdS	FeS	$SrCO_3$	K^+
	Hg_2Cl_2	CuS	CoS	$BaCO_3$	NH_4^+
		SnS	NiS		
		As_2S_3	ZnS		
		Sb_2S_3	$Al(OH)_3$		
		Bi_2S_3	$Cr(OH)_3$		