

Hard-Soft Acid Base (HSAB) Theory

Introduction

- Hard and Soft Acids and Bases (HSAB) theory is a qualitative concept introduced by **Ralph Pearson** to explain the stability of metal complexes and 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.**
- Arrhenius acids form hydronium ions in water, and bases form hydroxide ions. This definition assumes that water is the solvent.
- Brønsted and Lowry expanded upon the Arrhenius definitions, and defined acids as proton donors and bases as proton acceptors.
- They also introduced the concept of **conjugate acid-base pairs.**
- For any solvent that can dissociate into a cation and an anion, the cation is the acid, and the anion is the base.
- Any solute that causes an increase in the concentration of the cation is an acid, those increase the concentration of the anion are bases.

Lewis Acids and Bases

- The Lewis definition further expands the definitions. **A base is an electron-pair donor, and an acid is an electron-pair acceptor.** The two combine to form an adduct.



- This definition includes the “standard” Brønsted-Lowry acid-base reactions:



- It also includes the reactions of metal ions or atoms with ligands to form coordination compounds:

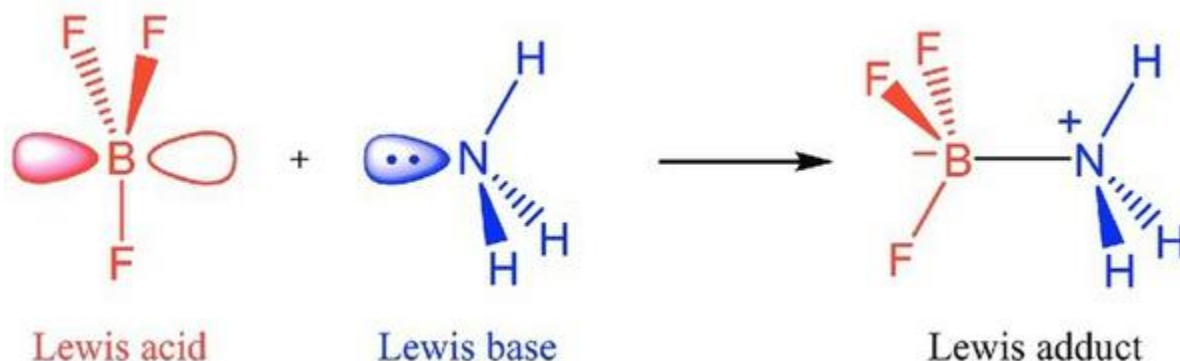


Lewis Acid-Base Adduct

- In addition, electron-deficient compounds such as trivalent boron is categorized as a Lewis acid.



- The HOMO on the Lewis base interacts with the electron pair in the LUMO of the Lewis acid. The MOs of the adduct are lower in energy.
- A Lewis base has an electron pair in its highest occupied molecular orbital (HOMO) of suitable symmetry to interact with the LUMO of the Lewis acid. The closer the two orbitals are in energy, the stronger the bond in the adduct.



Hard and Soft Acids and Bases

- The polarizability of an acid or base plays a role in its reactivity.
- Hard acids and bases are small, compact, and relatively nonpolarizable donor atoms (such as N, O, and F).
- Soft acids and bases are larger, with a more diffuse distribution of electrons, relatively polarizable donor atoms (such as P, S, and Cl, Br, I).
- HSAB theory is a useful tool to predict thermodynamic stability or kinetic lability of Metal-Ligand complexes.
- But, other important factors like the chelate effect or ligand field stabilization energy (LFSE) must also be considered and may outweigh the effects of HSAB.
- *Hard acids preferentially bind with hard bases, and soft acids bind preferentially with soft bases.*

Hard Acids

- Small ionic radii
- High positive charge (high charge density)
- Strongly solvated
- Empty orbitals in the valence shell
- High 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+}

Soft Acids

- Large ionic radii
- Low positive charge (lower charge density)
- Completely filled atomic orbitals
- Low energy LUMOs

- Cu^+ , Ag^+ , Au^+ , Hg^+ , Cs^+ , Tl^+
- Hg^{2+} , Pd^{2+} , Cd^{2+} , Pt^{2+}

Hard Bases	Soft Bases
<ul style="list-style-type: none"> • Small ionic radii • Highly electronegative • Weakly polarizable • Strongly solvated • High energy LUMOs 	<ul style="list-style-type: none"> • 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^- , $\text{S}_2\text{O}_3^{2-}$, R_3P , R_3As , $(\text{RO})_3\text{P}$, RNC , CO , C_2H_4 , C_6H_6 , R^- , H^-

The Border line Lewis acids and bases have intermediate properties.

- Acids: Fe^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Pb^{2+} , NO^+ etc.
- Bases: NH_3 , Cl^- , RCl , Br^- , NO_2^- , SO_3^{2-} , aniline, pyridine etc.

HSAB Principle: the HSAB concept

- ❖ Hard acids prefer binding to the hard bases to give ionic complexes
 - ❖ Soft acids prefer binding to soft bases to give covalent compounds.
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- 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 the HSAB Principle

Recovery of Au

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



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

- AgI is a combination of soft acid-soft base, while LiI is a combination of hard acid-soft base.
- The interaction between Li^+ and I^- ions is not so strong.
 - $\text{AgI(s)} + \text{H}_2\text{O(l)} \longrightarrow$ essentially no reaction (insoluble)
 - $\text{LiI(s)} + \text{H}_2\text{O(l)} \longrightarrow \text{Li}^+ (\text{aq}) + \text{I}^- (\text{aq})$

- Solubility of Lithium Halides in non-polar solvents:



Applications of the HSAB Principle

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.

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.

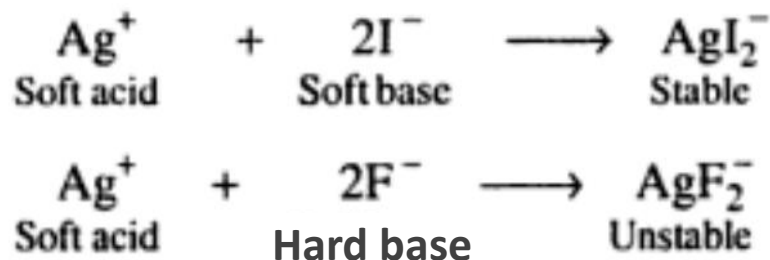
- But Ca^{2+} and Mg^{2+} hard acids appear as carbonates CaCO_3 , MgCO_3 .

Applications of the HSAB Principle

- Other Reactions, formation of stable compounds:



➤ AgI_2^- is stable but AgF_2^- is unstable!



➤ $[\text{CoF}_6]^{3-}$ is stable, but $[\text{CoI}_6]^{3-}$ is not so stable, because Co^{+3} and F^- both are hard and hard.

Applications of the HSAB Principle

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 ₂ S (acidic)	H ₂ S (basic)	(NH ₄) ₂ CO ₃	Soluble
Precipitates	AgCl	HgS	MnS	CaCO ₃	Na ⁺
	PbCl ₂	CdS	FeS	SrCO ₃	K ⁺
	Hg ₂ Cl ₂	CuS	CoS	BaCO ₃	NH ₄ ⁺
		SnS	NiS		
		As ₂ S ₃	ZnS		
		Sb ₂ S ₃	Al(OH) ₃		
		Bi ₂ S ₃	Cr(OH) ₃		

Ambidentate Ligands

SCN⁻ vs. **N**CS⁻

- Thiocyanate (**S**CN⁻) and Isothiocyanate (**N**CS⁻)
- This shows linkage isomerism in coordination compounds, depending on its donor atom.
- **S-atom is soft base and N-atom is hard base.**
- The nitrogen donor atom tends to coordinate with harder acids such as Co³⁺, Fe³⁺, Si⁴⁺, etc.
- Whereas, the soft sulfur donor atom tends to coordinate with softer acids such as Pt²⁺, Hg²⁺, Cu⁺, Ag⁺, Au⁺, etc.
- Similarly, **carbon atom of cyanide (CN⁻) is a soft base.**
- **Note (do not confuse!): Cyanide is a strong field ligand, in spectrochemical series.**

Thank You