

INTRODUCTION

The HSAB concept is an acronym for 'hard and soft acids and bases'. Also known as the Pearson acid base concept, HSAB is widely used in chemistry for explaining stability of compounds, reaction mechanisms and pathways. It assigns the terms 'hard' or 'soft', and 'acid' or 'base' to chemical species. 'Hard' applies to species which are small, have high charge states (the charge criterion applies mainly to acids, to a lesser extent to bases), and are weakly polarizable. 'Soft' applies to species which are big, have low charge states and are strongly polarizable.

HSAB theory is also useful in predicting the products of metathesis reactions

Theory

The gist of this theory is that *soft* acids react faster and form stronger bonds with *soft* bases, whereas *hard* acids react faster and form stronger bonds with *hard* bases, all other factors being equal.^[6] The classification in the original work was mostly based on equilibrium constants for reaction of two Lewis bases competing for a Lewis acid.

Hard acids and hard bases tend to have:

- small atomic/ionic radius
- high oxidation state
- low polarizability
- high electronegativity
- energy low-lying HOMO (bases) or energy high-lying LUMO (acids).^[6]

Examples of hard acids are: H^+ , alkali ions, Ti^{4+} , Cr^{3+} , Cr^{6+} , BF_3 .

Examples of hard bases are: OH^- , F^- , Cl^- , NH_3 , CH_3COO^- , CO_3^{2-} .

The affinity of hard acids and hard bases for each other is mainly ionic in nature.

Soft acids and soft bases tend to have:

- large atomic/ionic radius
- low or zero oxidation state
- high polarizability
- low electronegativity
- energy high-lying HOMO (bases) and energy-low lying LUMO (acids).^[6]

Examples of soft acids are: CH_3Hg^+ , Pt^{4+} , Pd^{2+} , Ag^+ , Au^+ , Hg^{2+} , Hg_2^{2+} , Cd^{2+} , BH_3 .

Examples of soft bases are: H^- , R_3P , SCN^- , I^- . The affinity of soft acids and bases for each other is mainly covalent in nature.

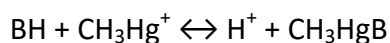
Acids				Bases			
hard		soft		hard		soft	
Hydronium	H ⁺	Mercury	CH ₃ Hg ⁺ , Hg ²⁺ , Hg ₂ ²⁺	Hydroxyl	OH ⁻	Hydride	H ⁻
Alkali metals	Li ⁺ , Na ⁺ , K ⁺	Platinum	Pt ⁴⁺	Alkoxide	RO ⁻	Thiolate	RS ⁻
Titanium	Ti ⁴⁺	Palladium	Pd ²⁺	Halogens	F ⁻ , Cl ⁻	Halogens	I ⁻
Chromium	Cr ³⁺ , Cr ⁶⁺	Silver	Ag ⁺	Ammonia	NH ₃	Phosphine	PR ₃
Boron trifluoride	BF ₃	borane	BH ₃	Carboxylate	CH ₃ COO ⁻	Thiocyanate	SCN ⁻
Carbocation	R ₃ C ⁺	P-chloranil		Carbonate	CO ₃ ²⁻	carbon monoxide	CO
		bulk Metals	M ⁰	Hydrazine	N ₂ H ₄	Benzene	C ₆ H ₆
		Gold	Au ⁺				

Table 1. Hard and soft acids and bases

Borderline cases are also identified: borderline acids are trimethylborane, sulfur dioxide and ferrous Fe²⁺, cobalt Co²⁺ and lead Pb²⁺ cations. Borderline bases are: aniline, pyridine, nitrogen N₂ and the azide, bromine, nitrate and sulfate anions.

The acids and bases, in general, interact and the most stable interactions are hard-hard (ionogenic character) and soft-soft (covalent character).

An attempt to quantify the 'softness' of a base consists in determining the equilibrium constant for the following equilibrium:



Where CH₃Hg⁺ (methylmercury ion) is a very soft acid and H⁺ (proton) is a hard acid, which compete for B (the base to be classified).

Some examples illustrating the effectiveness of the theory:

- Bulk metals are soft acids and are poisoned by soft bases such as phosphines and sulfides.
- Hard solvents such as hydrogen fluoride, water and the protic solvents tend to solvate strong solute bases such as the fluoride anion and the oxygen anions. On the other hand dipolar aprotic solvents such as dimethyl sulfoxide and acetone are soft solvents with a preference for solvating large anions and soft bases.
- In coordination chemistry soft-soft and hard-hard interactions exist between ligands and metal centers.

Pearson's HSAB Classification System:

Classification of Lewis Acids

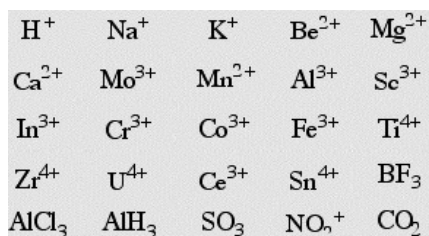
Class (a)/Hard	Class (b)/Soft
H^+ , Li^+ , Na^+ , K^+ Be^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} , Sn^{2+} Al^{3+} , Se^{3+} , Ga^{3+} , In^{3+} , La^{3+} Cr^{3+} , Co^{3+} , Fe^{3+} , As^{3+} , Ir^{3+} Si^{4+} , Ti^{4+} , Zr^{4+} , Th^{4+} , Pu^{4+} , VO^{2+} UO_2^{2+} , $(CH_3)_2Sn^{2+}$ $BeMe_2$, BF_3 , BCl_3 , $B(OR)_3$ $Al(CH_3)_3$, $Ga(CH_3)_3$, $In(CH_3)_3$ RPO_2^+ , $ROPO_2^+$ RSO_2^+ , $ROSO_2^+$, SO_3 I^{7+} , I^{5+} , Cl^{7+} R_3C^+ , RCO^+ , CO_2 , NC^+	Cu^+ , Ag^+ , Au^+ , Tl^+ , Hg^+ , Cs^+ Pd^{2+} , Cd^{2+} , Pt^{2+} , Hg^{2+} CH_3Hg^+ Tl^{3+} , $Tl(CH_3)_3$, RH_3 RS^+ , RSe^+ , RTe^+ I^+ , Br^+ , HO^+ , RO^+ I_2 , Br_2 , INC , etc. Trinitrobenzene, etc. Chloranil, quinones, etc. Tetracyanoethylene, etc. O , Cl , Br , I , R_3C M^0 (metal atoms) Bulk metals

HX (hydrogen-bonding molecules)

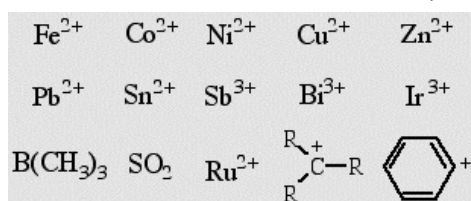
Borderline

Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Pb^{2+}
 $B(CH_3)_3$, SO_2 , NO^+

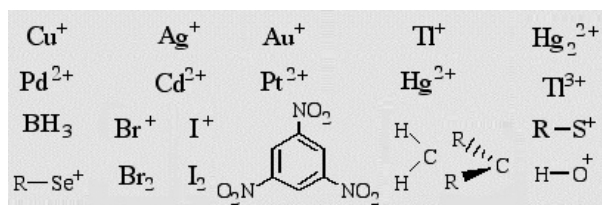
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- Pearson's *Hard* Lewis Acids (from the Chemical Thesaurus), here:



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- Pearson's *Borderline* Lewis Acids, here:



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- Pearson's *Soft* Lewis Acids, here:



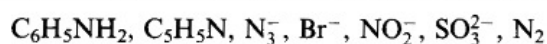
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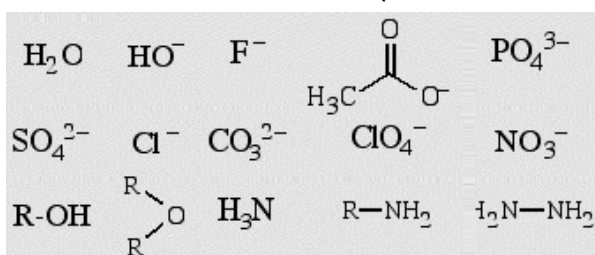
Classification of Bases

Hard	Soft
H ₂ O, OH ⁻ , F ⁻	R ₂ S, RSH, RS ⁻
CH ₃ CO ₂ ⁻ , PO ₄ ³⁻ , SO ₄ ²⁻	I ⁻ , SCN ⁻ , S ₂ O ₃ ²⁻
Cl ⁻ , CO ₃ ²⁻ , ClO ₄ ⁻ , NO ₃ ⁻	R ₃ P, R ₃ As, (RO) ₃ P
ROH, RO ⁻ , R ₂ O	CN ⁻ , RNC, CO
NH ₃ , RNH ₂ , N ₂ H ₄	C ₂ H ₄ , C ₆ H ₆
	H ⁻ , R ⁻

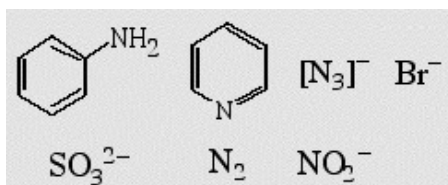
Borderline



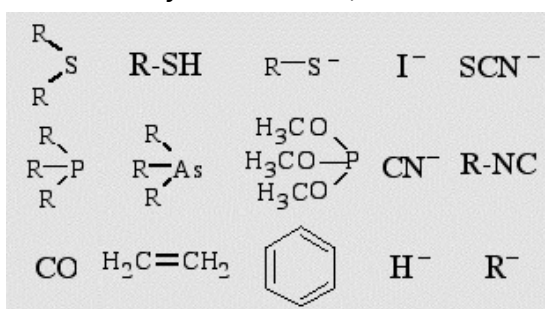
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- Pearson's *Hard* Lewis Bases (from The Chemical Thesaurus), here:



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- Pearson's *Borderline* Lewis Bases, here:



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- Pearson's *Soft* Lewis Bases, here:



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- Combining Pearson's and Klopman's Ideas

- **Hard Lewis acids:**

- Atomic centres of small ionic radius
- High positive charge
- Species do not contain electron pairs in their valence shells
- Low electron affinity
- Likely to be strongly solvated
- High energy LUMO

- **Soft Lewis acids:**

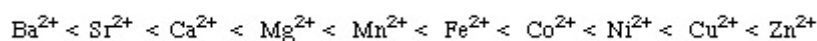
- Large radius

- Low or partial (δ^+) positive charge
- Electron pairs in their valence shells
- Easy to polarise and oxidise
- Low energy LUMOs, but large magnitude LUMO coefficients
- **Hard Lewis bases:**
 - Small, highly solvated, electronegative atomic centres: 3.0-4.0
 - Species are weakly polarisable
 - Difficult to oxidise
 - High energy HOMO
- **Soft Lewis bases:**
 - Large atoms of intermediate electronegativity: 2.5-3.0
 - Easy to polarise and oxidise
 - Low energy HOMOs but large magnitude HOMO coefficients.
- **Borderline** species have intermediate properties.
- There is a qualifier in Klopman's paper saying that it is not necessary for species to possess all properties.

The Hard Soft [Lewis] Acid Base Principle

Ralph Pearson introduced the Hard Soft [Lewis] Acid Base (HSAB) principle in the early nineteen sixties, and in doing so attempted to unify inorganic and organic reaction chemistry. The impact of the new idea was immediate, however over time the HSAB principle has rather fallen by the wayside while other approaches developed at the same time, such as frontier molecular orbital (FMO) theory and molecular mechanics, have flourished.

The Irving-Williams stability series (1953) pointed out that *for a given ligand* the stability of dipositive metal ion complexes increases:



It was also known that certain ligands formed their most stable complexes with metal ions like Al^{3+} , Ti^{4+} and Co^{3+} while others formed stable complexes with Ag^+ , Hg^{2+} and Pt^{2+} .

In 1958 Ahrland *et al.* Classified metal cations as Type A and Type B, where:

Type A metal cations included:

- Alkali metal cations: Li^+ to Cs^+
- Alkaline earth metal cations: Be^{2+} to Ba^{2+}
- Lighter transition metal cations in higher oxidation states: Ti^{4+} , Cr^{3+} , Fe^{3+} , Co^{3+}
- The proton, H^+

Type B metal cations include:

- Heavier transition metal cations in lower oxidation states: Cu^+ , Ag^+ , Cd^{2+} , Hg^+ , Ni^{2+} , Pd^{2+} , Pt^{2+} .

Ligands were classified as Type A or Type B depending upon whether they formed more stable complexes with Type A or Type B metals:

Tendency to complex with Type A metals	Tendency to complex with Type B metals
N >> P > As > Sb	N << P > As > Sb
O >> S > Se > Te	O << S < Se ~ Te
F > Cl > Br > I	F < Cl < Br < I

From this analysis, a principle can be derived: Type A metals prefer to bind to Type A ligands and Type B metals prefer to bind to Type B ligands

These empirical (experimentally derived) rules tell us that Type A metals are more likely to form oxides, carbonates, nitrides and fluorides, while Type B metals are more likely to form phosphides, sulfides and selenides.

This type of analysis is of great economic importance because some metals are found in nature as sulfide ores: PbS, CdS, NiS, etc., while others are found as carbonates: MgCO₃ and CaCO₃ and others as oxides: Fe₂O₃ and TiO₂.

This approach has been very successfully developed in recent years by Bruce Railsback with his *excellent* and highly recommended "*Earth Scientist's Periodic Table*", here.

The Railsback analysis uses contours of behaviour superimposed upon the Mendeleev periodic table. (As Bruce told me in a personal communication: "*Earth scientists love contours...*").

See the paper: *A Synthesis of Systematic Mineralogy* by Bruce Railsback that develops this analysis.

Pearson's Hard Soft [Lewis] Acid Base Principle

In the nineteen sixties, Ralph Pearson developed the Type A and Type B logic by explaining the differential complexation behaviour of cations and ligands in terms of electron pair donating Lewis bases and electron pair accepting Lewis acids:

Lewis acid + Lewis base \longrightarrow Lewis acid/base complex

Pearson classified Lewis acids and Lewis bases as *hard*, *borderline* or *soft*.

According to Pearson's *hard soft* [Lewis] acid base (HSAB) principle:

Hard [Lewis] acids prefer to bind to *hard* [Lewis] bases and

Soft [Lewis] acids prefer to bind to *soft* [Lewis] bases

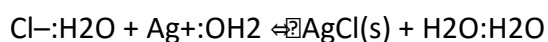
At first sight, HSAB analysis seems rather similar to the Type A and Type B system. However, Pearson classified a very wide range of atoms, ions, molecules and molecular ions as *hard*, *borderline* or *soft* Lewis acids or Lewis bases, moving the analysis from traditional metal/ligand inorganic chemistry into the realm of organic chemistry.

Applications of HSAB:

1. Solubility of Halides and Chalcogenides

Remember solubility rules developed earlier. Almost all of the anions discussed were oxo-anions- typically hard bases. What about the solubilities of salts with soft base anions? Previously these were problematic because, Cl⁻ is nonbasic and silver(I) is weakly acidic and the resultant cross-combination should technically be soluble but it is, in fact, insoluble. However, using HSAB principle we see that Cl⁻ is a borderline base (i.e., between hard and soft)

Recall from previous section that



Cl⁻ is BB, H hard SA:BB

SA:HB HB:HA

K⁺:OH₂ HA:HB doesn't change

Using a similar reasoning we predict that the chlorides, bromides and iodides of all of the soft acids are insoluble.

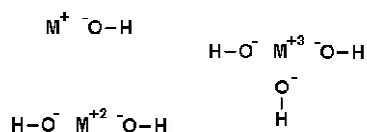
Examples: CuCl(not CuCl₂), AgCl, AuCl(not AuCl₃), TlCl, Hg₂Cl₂(not HgCl₂),

OsCl₂, IrCl₂, PdCl₂, PtCl₂(not PtCl₄), PbCl₂

Bromide and iodide lists are similar but slightly larger

Oxides, Hydroxides, Hydrides, and the Strength of Acids and Bases

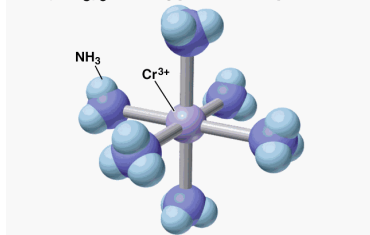
Consider Metal Hydroxides (soluble)



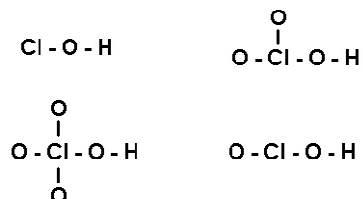
Clearly, these are electrolytes that produce stoichiometric quantities of OH⁻ so they are all strong bases

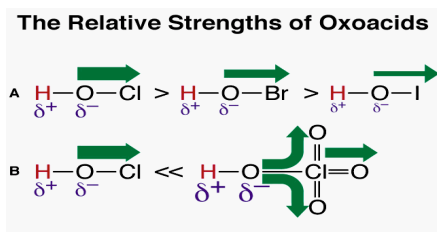
Danger!! Sometimes metal ions form covalent 'coordination' complexes with OH⁻ or H₂O, making their solubility/acidity highly 'irregular' Such Coordination Complexes will be studied in later courses, NOT here.

Cr(NH₃)₆³⁺, a Typical Complex Ion



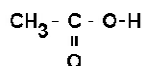
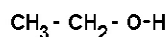
Consider Non-Metal Hydroxides



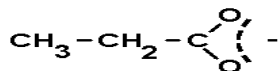


These species are Acids because the weak bond is the $\text{O}^- - \text{H}^+$ bond releasing H^+ upon dissolution

Consider "organic" hydroxides



Don't forget 'Resonance' and the Carboxylic Acid



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K_a Values for Some Monoprotic Acids

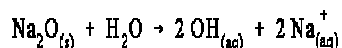
Table 18.2 K_a Values for Some Monoprotic Acids at 25°C

Name (Formula)	Lewis Structure*	K_a
Iodic acid (HIO_3)		1.6×10^{-1}
Chlorous acid (HClO_2)		1.12×10^{-2}
Nitrous acid (HNO_2)		7.1×10^{-4}
Hydrofluoric acid (HF)		6.8×10^{-4}
Formic acid (HCOOH)		1.8×10^{-4}
Benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$)		6.3×10^{-5}
Acetic acid (CH_3COOH)		1.8×10^{-5}
Propanoic acid ($\text{CH}_3\text{CH}_2\text{COOH}$)		1.3×10^{-5}
Hypochlorous acid (HClO)		2.9×10^{-8}
Hypobromous acid (HBrO)		2.3×10^{-9}
Hydrocyanic acid (HCN)		6.2×10^{-10}
Phenol ($\text{C}_6\text{H}_5\text{OH}$)		1.0×10^{-10}
Hypoiodous acid (HIO)		2.3×10^{-11}

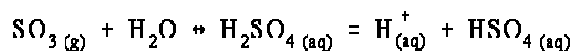
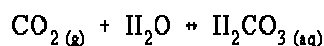
*Red type indicates the ionizable proton; structures have zero formal charge.

(p. 762)

Metal Oxides are STRONG Bases because they hydrate to form metal hydroxides



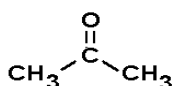
Non-metal Oxides may hydrate to form acids



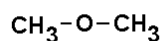
Organic Oxides are not good acids or bases

Examples:

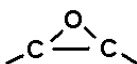
Ketones



Ethers



Epoxides



The Periodic Properties of the Elements, in Acid / Base terms, are not as powerful as one might think. This is because the origin of the acidity (or basicity) of a molecule is more related to the overall structure of the molecule than any single bond or atom, as we discussed above. However, some features may be commented on.

The Effect of Atomic and Molecular Properties on Nonmetal Hydride Acidity

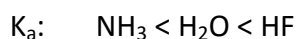
Electronegativity increases, acidity increases →

	6A(16)	7A(17)
	H ₂ O	HF
	H ₂ S	HCl
	H ₂ Se	HBr
	H ₂ Te	HI

↓ Bond strength decreases, acidity increases

Fig. 18.11

Across a row (period) of the periodic table, increasing electronegativity make the H-X bond more polar, or ionic, and thus more like H⁺ - X⁻. Therefore acidity should increase.



Down a column (group) of the Periodic Table, the size increase of the element makes the H-X bond strength decreases. Thus the acidity will increase down the group:

