❖ Hard and Soft Acids and Bases

Most of the Lewis acids can be distributed into two categories; class *a* and class be acids. Generally speaking, class *a* acids prefer to bind with Lewis bases with donor atom from second row non-metal (i.e. F, O or N); whereas class *b* acids prefer to bind with Lewis bases with donor atom coming from third or below row (i.e. Br, I, S or P). An American chemist Ralph Pearson then developed a model where Lewis acids and bases can be characterized by strength and softness. To understand the concept, consider a typic acid-base reaction i.e.

$$A + \ddot{B} \rightleftharpoons A{:}B \qquad (21)$$

Where A is the acid, $\ddot{B}$ is the base and $A{:}B$ represents the complex. The equilibrium constant for the reaction (21) can be written as

$$\log K = S_A S_B + \sigma_A \sigma_B \qquad (22)$$

Where S_A and S_B represent the strength of acid *A* and base *B*, respectively. The symbol σ_A and σ_B represent the softness of acid *A* and base *B*, respectively. The experimental data showed that class *a* metals form stable complexes with ligands having N, O, or F as the donor site; whereas class *b* metals form stable complexes with ligands having P, S, or Cl like donor atoms. Therefore, Ralph Pearson articulated his observation as given below.

This trend is explainable by the hard-soft acid-base principle which states that hard acid prefers a hard base while soft acid prefers a soft base for binding to yield stable systems.

The typical classification of different species based on hardness or softness is quite useful in the understanding of the chemical reactivity of organic reactions.

➢ *Hard and Soft Acids*

Metals such as Li^{1+}, Ba^{2+}, Mg^{2+}, and Al^{3+}, which have large negative reduction potential have a lesser tendency to attract electrons, and hence, form stable complexes with highly electronegative groups like N, F, or O so that they become unable to draw the unwanted electron density due to polarization. However, Metals like Pd^{2+} or Pt^{2+} which have large positive reduction potential have a greater tendency to accept electrons and hence form stable complexes with less electronegative groups like P so that they can easily grab the electron density by polarizing the surrounding.

A typical hard acid has a small size, high polarizing power, less distortable outer cloud, and high positive oxidation sometimes. On the other hand, a typical soft acid has a large size, low polarizing power, a highly distortable outer cloud, and zero or low positive oxidation sometimes.

Borderline cases are also identified: borderline acids are trimethylborane, sulfur dioxide and ferrous Fe^{2+}, cobalt Co^{2+} cesium Cs^{+} and lead Pb^{2+} cations. It is also very important to mention that the borderline list may vary from book to book it is also medium-dependent.

Table 1. The class *a*, class *b,* and borderline metals.

Hard acid	Soft acid	Borderline acids
H^+, Li^+, Na^+, K^+	Cu^+, Ag^+, Au^+, Tl^+	
Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}	Hg^{2+}, Pd^{2+}, Pt^{2+}	Mn^{2+}, Fe^{2+}, Co^{2+}, Sr^{2+} Ni^{2+}, Cu^{2+}, Zn^{2+}
Al^{3+}, Ga^{3+}, In^{3+} Cr^{3+}, Mn^{3+}, Fe^{3+}, Co^{3+}, La^{3+}, Ce^{3+}, Gd^{3+}	Tl^{3+}	
In^{4+}, Zr^{4+}, Hf^{4+}, Th^{4+}, U^{4+}, Pu^{4+}	Pt^{4+}	

➢ ***Hard and Soft Bases***

The base becomes more and more soft as the donor atom is selected from the lower part of a particular group in the periodic table. For instance, *F*⁻ is the hardest, and *I*⁻ is the softest base in its group.

A typical soft base has the donor atom of low polarizability, high electronegativity, high negative charge density, and tightly held electron cloud. On the other hand, a typical soft base the donor atom of high polarizability, low electronegativity, less negative charge density, and loosely held electron cloud.

Borderline cases are also identified: borderline bases are aniline, pyridine, nitrogen N_2, and the azide, chloride, bromide, nitrate, and sulfate anions. It is also very important to mention that the borderline list may vary from book to book it is also medium-dependent.

Table 2. The hard, soft, and borderline bases.

Hard bases	Soft bases	Borderline bases
F^-, OH^-, F^-, CH_3COO^-, H_2O, SO_4^{2-}	RSH, R_2S, R_3P	$C_6H_5NH_2$
NO_3^-, Cl^-, ROH, R_2O, RO^-	RS^-, I^-, SCN^-, H^-, $(RO)_3P$, CN^-, Alkenes, R^-	N_3^-, Br^-, NO_2^-, N_2
N_2H_4, NH_3, RLi, RMgX		SO_2^{2-}
RCOOR, RNH_2		

It is also worthy to mention that hard nucleophiles or hard bases have the highest occupied molecular orbitals (HOMO) of higher energy whereas soft nucleophiles or soft bases have HOMOs of lower energy.

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A TEXTBOOK OF ORGANIC CHEMISTRY

Volume I

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