TDC Part III
Paper VI
Inorganic Chemistry

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TOPIC:-
HARD SOFT ACID BASE PRINCIPLE(HSAB)
TOPIC 1,2 and 3

HARD AND SOFT ACID AND BASE (HSAB)

CONTENTS:

OBJECTIVES

- After going through this unit, you will be able to:
- To know the relationship between acid strength and the value of p*K*a.
- To understand the relationship between polarizability and the hardness or softness of an acid or base.
- To predict the stability of a chemical bond using the hard-soft acid base theory.
- To predict the relative acid or base strength of two organic compounds.
- To understand how the presence of a particular functional group affects the acid or base strength of another functional group.

INTRODUCTION

Lewis acid and base theory (also known as e- donor-acceptor theory) is a broad, widely applicable approach to the classification of chemical substances and the analysis of chemical reactions. According to this theory, a base is an electron pair donor, and an acid is an electron pair acceptor. Donation of an electron pair from base to acid results in the combining of the acid and base with a covalent bond. The bonded acid-base species is called an adduct, a coordination compound, or a complex compound.

Since the strength of Lewis acids and bases is found to depend on the type of reaction, it is not possible to arrange them in any order of their relative strength. Thus, from the above criteria, an acid base reaction should be a rapid reaction. The HSAB concept is a shortening for "hard and soft (Lewis) 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. Soft Lewis base are those in which the donor atoms are easily polarized and have low electronegativity. While Hard Lewis base are those in which the donor atoms have low polarisabilities and high electronegativities. A hard Lewis acid, like hard base, is difficult to polarize, small size, high positive charge, having small size and a noble gas electronic configuration. While soft acid, like soft base, are readily polarized these have large size, low positive or zero charge and do not have a noble gas configuration.

Hard soft Acid Base Concept (HSAB Concept):

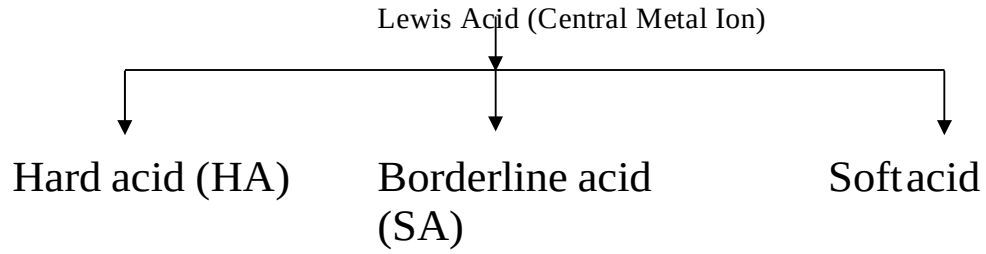
Experimentally, it was observed that certain ligands having a tendency to form the stable complexes with the lighter metal ion like Na+, Li+, Mg+2, Sc+3, Ti+4 etc. and certain other ligands having the tendency to form the stable complexes with the heavier metal ions like Ag+, Cu+2, Hg+2, Cu+2 etc.

On the basis of this preferential bonding nature of ligand (Lewis base and Lewis acid), Pearson had categorised both the acid and bases into three different categories each, which are given in the next section.

CLASSIFICATION OF ACIDS AND BASES AS HARD AND SOFT

Classification of the Lewis's acid:

According to the Pearson, Lewis's acids can be of the three different types, which are given below:-



Hard acid:- All the Lewis acids having the following characteristic properties are known as hard acid:

- Should exhibit the smaller size.
- Should have high + ve oxidation state.

- Polaris ability should be very low (on the basis of this property they are known as hard).
- Should have vacant d- orbital or approximate vacant d-orbital configuration (in the case of d – block elements)

Soft acid: All the Lewis acids having the following characteristic properties are known as soft acids:
Should exhibit larger size.

- Should have very low +ve oxidation state or zero oxidation state.
- Polaris ability should be very high (on the basis by this property they are known as soft).
- Should have filled d-orbital or approximate filed d-orbital configuration (in the case of d-black dements)

Borderline acids:- All the Lewis acids which exhibit the properties intermediate in between the hard & soft acids are known as borderline acids. Some of the samples of hard acid, soft acid & borderline acids are given in Table 1.1

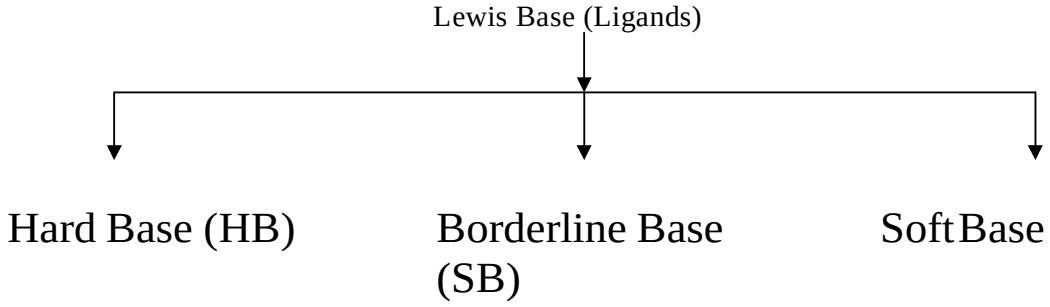
Hard acids	Soft acids	Borderline acids
Li^{+}	Cu^{+}	Fe^{+2}
Na^{+}	Ag^{+}	Co^{+2}
K^{+}	Au^{+}	Ni^{+2}
Mg^{+2}	Hg^{+}	Cu^{+2}
Ca^{+2}	Pt^{+2}	Zn^{+2}
Al^{+3}	Hg^{+2}	Pb^{+2}
Ba^{+2}	Pd^{+2}	Sn^{+2}
Ga^{+3}	Ed^{+2}	SO_2

La^{+3}	BH_3	Bi^{+3}
Cr^{+3}	I^{+}	Sb^{+3}
Cr^{+6}	Br^{+}	NO^{+}
Co^{+3}	Metal atoms at zero oxidation states	GaH_3
Fe^{+3}		$B(CH_3)_3$
Si^{+4}		
Ti^{+4}		
Ce^{+3}		
Sn^{+4}		
SO_3		
BF_3, BCl_3, $B(OR)_3$, $Al(CH_3)_3$		
I^{+7}		
I^{+5}		
CO_2		

Table 1.1: *Examples of hard acid, soft acid & borderline acids*

Classification of the Lewis base

According to the Pearson concept, Lewis basis can be divided into 3 different types which are given below:-



Hard base: All the Lewis bases having the following characteristic properties are known as hard base:

- Donor atom of the base should be highly electronegative like F, O, N & O.
- Polarisability of the donor atom should be very high low.

Soft base: All the Lewis bases which have the following characteristic properties are known as soft bases:

- Donor atom of the base should be less electronegative.
- Polaris ability of the donor atom should be very high.

Borderline base: All the Lewis bases which have the properties intermediate the soft & hard bases are known as borderline bases.

Some of the examples of hard bases, soft bases and borderline bases can be given as:-

Hard base: H_2O, OH^-, CH_3COO^-, PO_4^{-3}, SO_4^{-2}, CO_3^{-2}, ClO_4^- NO^-, ROH, R-O^-, R_2O (Doner O), NH_3, R-NH_2, N_2H_4 (doner N), F^-, Cl^-

Soft base: R_2S, R-SH, R-S^-, I^-, SON^- , S_2O_3, R_3P, $(RO)_3P$, CN^-, RNC, CO, C_2H_4, C_6H_6 , H^-, R^-, S^{-2}

Borderline base: C_6H_5-NH_2, C_5H_5N, Br^-, SO_3^{-2}, NO_2^-