18CYB101J-CHEMISTRY

CONTENTS – Module 4 (S1)

Hard Soft Acid Bases

- **Various Concepts**
- **Theory**
- **Types**
- **Examples**

Hard Acids | Hard Bases

Soft Acids | Soft Bases

The Lewis concept of acids and bases involves covalent interaction to form a covalent (coordination) bond :

An acid = an electron pair acceptor

A base = an electron pair donor

1963 : Ralph Pearson introduced the hard-soft-acid-base (HSAB) principle.

"Hard acids prefer to coordinate the hard bases and soft acids to soft bases".

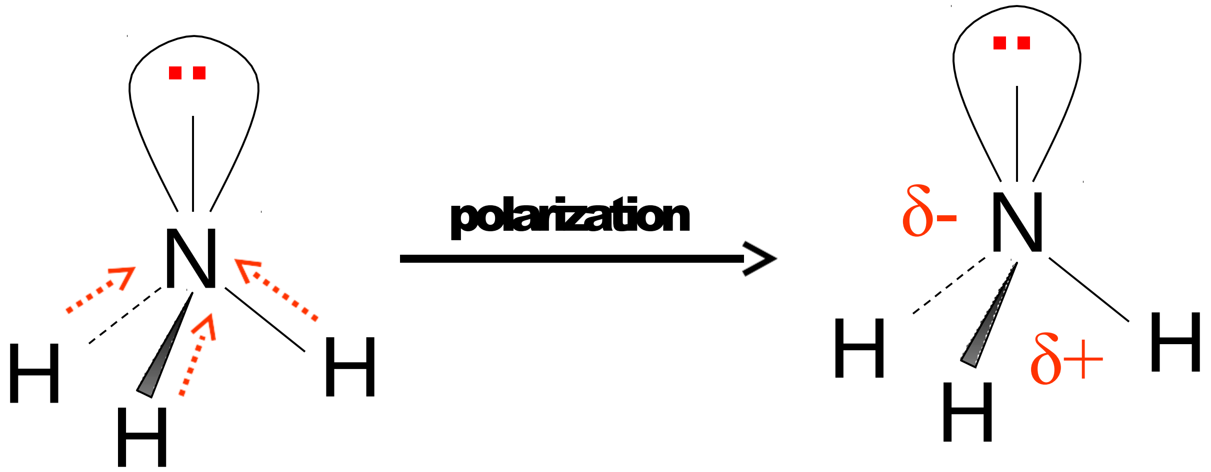
This very simple concept was used to rationalize a variety of chemical information, as an attempt to unify inorganic and organic reactions.

1983 : By Ralph Pearson and Robert Parr, the qualitative definition of HSAB was converted to a quantitative one by using the idea of polarizability.

A less easily polarized atom or ion is "hard" and a more easily polarized atom or ion is "soft"

Polarizability

The capacity of a group of atoms in a molecule and/or an ion to polarize its electron.



Polarizability

CHEMICA L SPECIES

HARD

A less easily polarized species

ELECTROSTATIC (IONIC) INTERCTION

SOFT

A more easily polarized species

ELECTRON SHARING (COVALENT) INTERCTION

Key Characteristics

Hard acids :

- Low polarizability
- High positive charge
- Small size
- Not easily oxidized

Hard bases :

- Low polarizability
- Spread donor orbital
- High electronegativity
- Not easily oxidized

Soft acids :

- High polarizability
- Low positive charge
- Large size
- Easily oxidized

Soft bases :

- High polarizability
- Diffuse donor orbital
- Low electronegativity
- Easily oxidized

The HSAB concept is now widely used to explain :

- **Stability of compounds,**
- **Chemical reactions in term of their mechanisms and pathways**

The theory is used in contexts where a qualitative, rather than quantitative description would help in understanding the predominant factors which drive chemical properties and reactions.

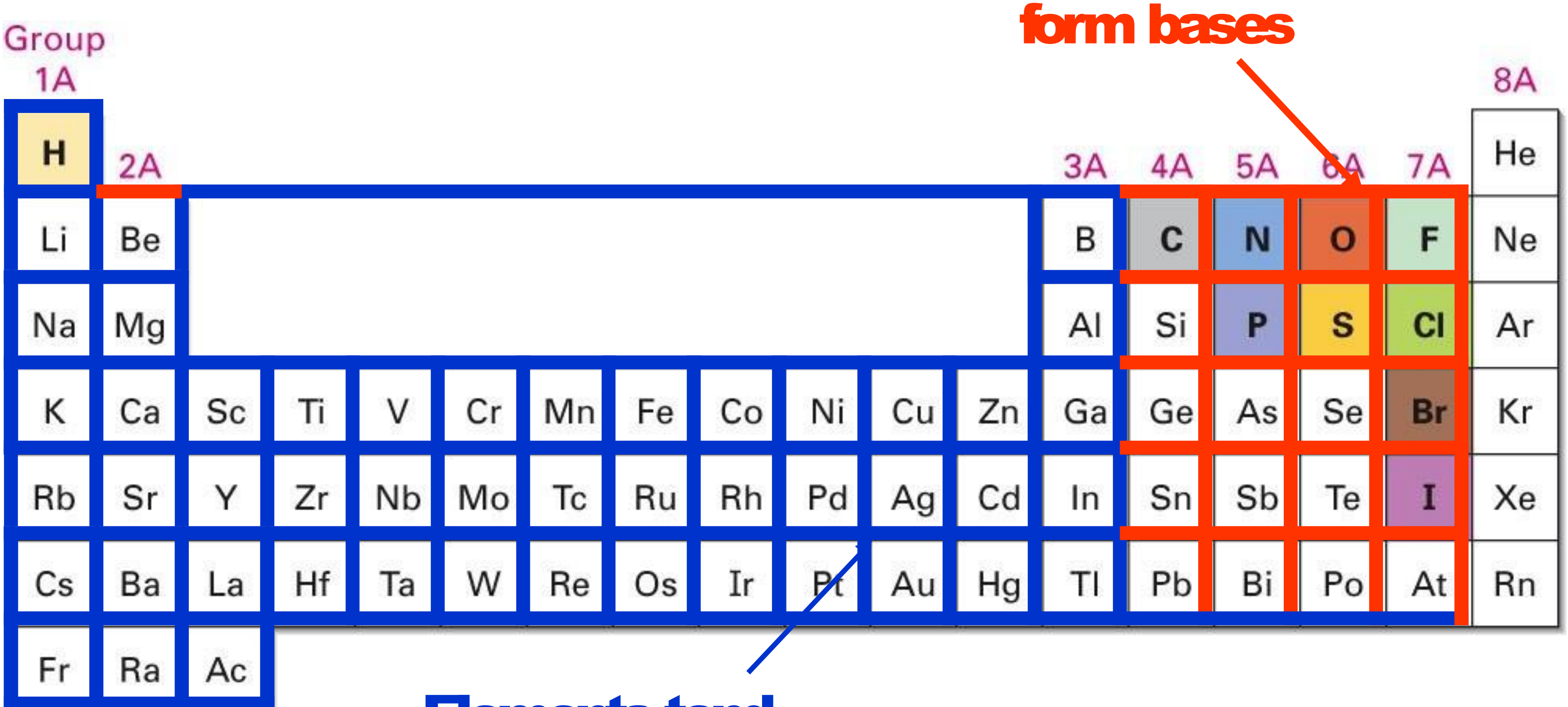
The HSAB Theory

Providing all other factors being equal, *soft* acids react faster and form stronger bonds with *soft* bases, whereas *hard* acids react faster and form stronger bonds with *hard* bases.

The classification in the original work was mostly based on equilibrium constants for reaction of two Lewis bases competing for a Lewis acid.

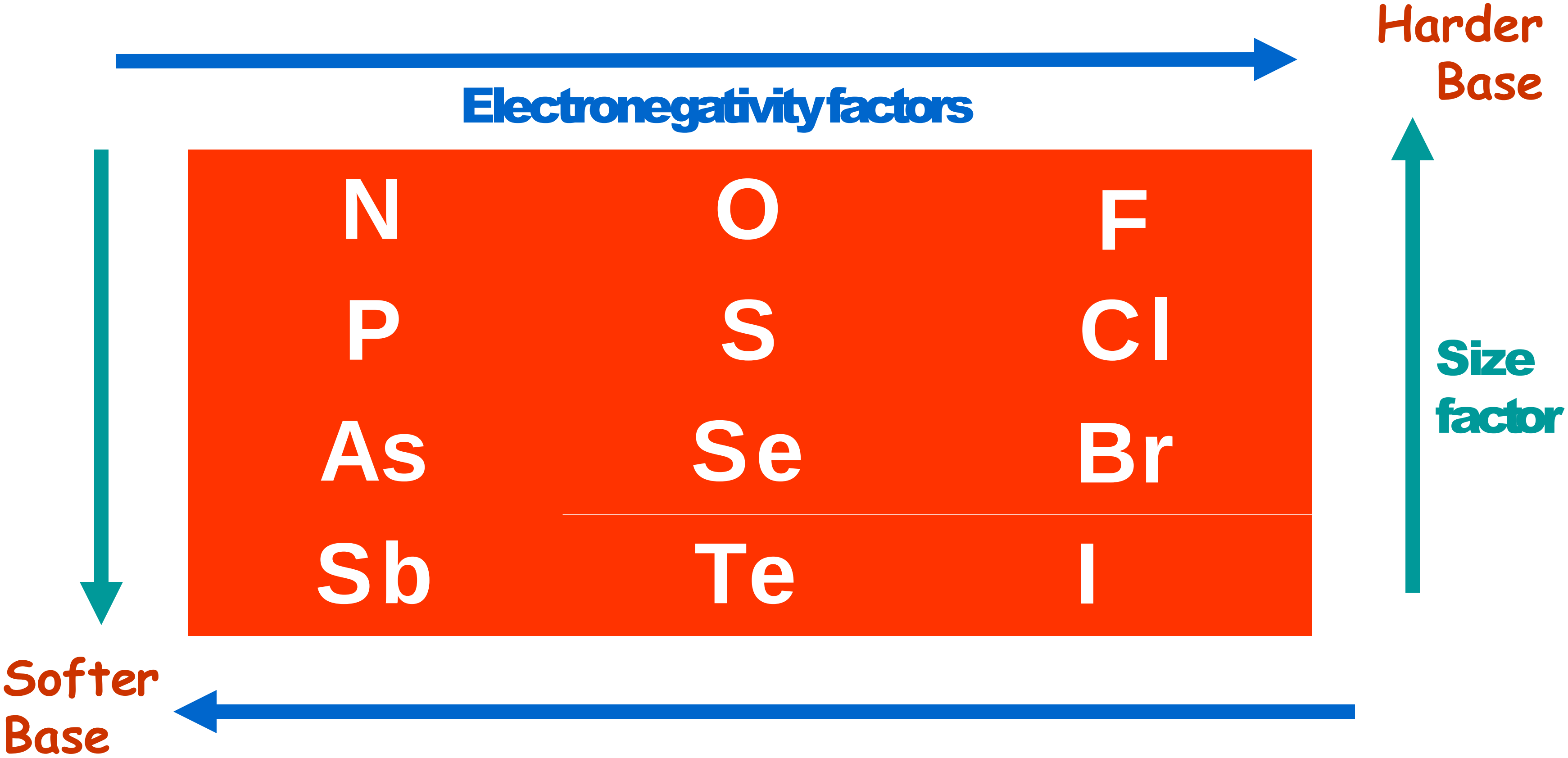
The Elements

Elements tend to form bases

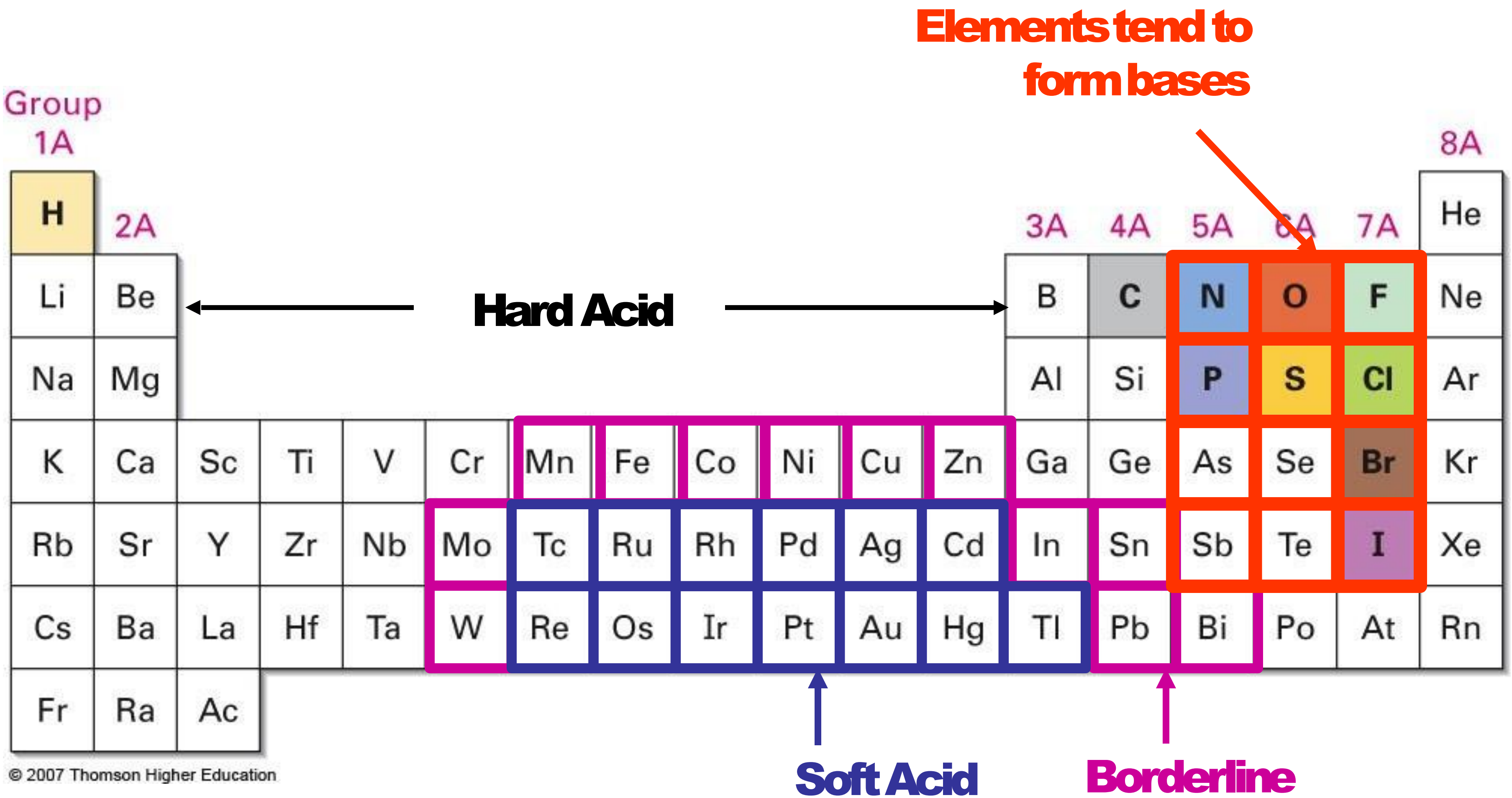


Elements tend to form acids

Elements tend to form bases



The Elements



Pearson's classification of metal

Class (a) metalions :

- Alkali : H^+, Li^+, Na^+, K^+, Rb^+, and Cs^+,
- alkaline earth: Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+},
- Lighter transition metals of higher oxidation states: Ti^{4+}, Cr^{3+}, Fe^{3+}, and Co^{2+}.

Class (b) metal ions

- Heavier transition metals of lower oxidation states : Cu^+, Ag^+, Hg^+, Hg^{2+}, Pd^{2+}, and Pt^{2+}.

Pearson’s classification of bases (ligands) :

Tendency to complex with class (a) metal ions :

$\mathrm{N} \gg \mathrm{P} > \mathrm{As} > \mathrm{Sb} \quad \mathrm{O}$

$\gg \mathrm{S} > \mathrm{Se} > \mathrm{Te} \quad \mathrm{F} >$

$\mathrm{Cl} > \mathrm{Br} > \mathrm{I}$

Tendency to complex with class (b) metal ions

$\mathrm{N} \ll \mathrm{P} < \mathrm{As} < \mathrm{Sb} \quad \mathrm{O}$

$\ll \mathrm{S} < \mathrm{Se} < \mathrm{Te} \quad \mathrm{F} <$

$\mathrm{Cl} < \mathrm{Br} < \mathrm{I}$

Hard Acids	Soft Acids

Class (a) metal ions :

- H^+, Li^+, Na^+, K^+, Rb^+, Cs^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+},
- Ti^{4+}, Cr^{3+}, Fe^{3+}, and Co^{2+}.

- Tendency to complex with class (a) metal ions :

N. >> P > As > Sb

O. >> S > Se > Te

F > Cl > Br > I

Class (b) metal ions

Cu^+, Ag^+, Hg^+, Hg^{2+}, Pd^{2+}, and Pt^{2+}.

Tendency to complex with class (b) metal ions

N. << P < As < Sb

O.<< S < Se < Te

F < Cl < Br < I

The HSAB Concept :

Hard Acids prefer to form complex with Hard Bases

&

Soft Acids prefer to form complex with Soft Bases

HSAB Classification of Acids and Bases

	Hard	Borderline	Soft
ACIDS	H^+, Li^+, Na^+, K^+, Rb^+, Cs^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Ba^{2+}, Cr^{3+}, SO_3, BF_3.	Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, SO_2, BBr_3.	Cu^+, Ag^+, Au^+, Tl^+, Hg^+, Pd^{2+}, Cd^{2+}, Pt^{2+}, Hg^{2+}, BH_3.
BASES	F^-, OH^-, H_2O, NH_3, CO_3^{2-}, NO_3^-, O^{2-}, SO_4^{2-}, PO_4^{3-}, ClO_4^-.	NO_2^-, SO_3^{2-}, N_3^-, Cl^-, C_6H_5N, SCN^-	H^-, R^-, CN^-, CO, I^-, R_3P, C_6H_6, R_2S

It is important to remember that :

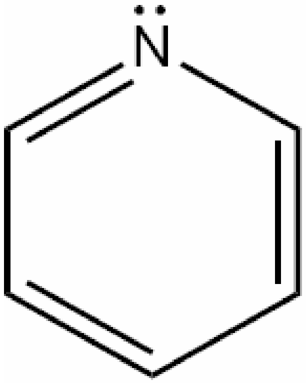
- The listings in the tables do not have a sharp dividing line between them.
- These terms, "hard" & "soft", are relative in nature
- Some are borderline and even though within the same category are not all of the same degree of "hardness" and "softness"

Examples

- Although all alkali metals in ionic form M^+ are “hard”, the larger, more polarizable, Cs^+ ion is much softer than Li^+

- Also N compounds are not all equal (H_3N versus pyridine): pyridine is much more polarizable

H_3N:



Examples

Common hard species :

NH_3, ROH, H_2O are hard bases

Ti^{4+}, Si^{4+}, Co^{3+} are hard acids

Common soft species :

PR_3, SR_2, are soft bases

Hg^{2+}, Pd^{2+}, Pt^{2+} are soft acids

Thank You