THE CONCEPT OF HSAB

HARD AND SOFT ACIDS AND BASES

The Goldschmidt (1935) :
Geochemical Ore Classification

Nickel (Ni), zinc (Zn), and copper (Cu) ores are exclusively found as sulfides, whilst aluminum (Al) and calcium (Ca) are usually found as oxide and carbonate, respectively.

Why?

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".

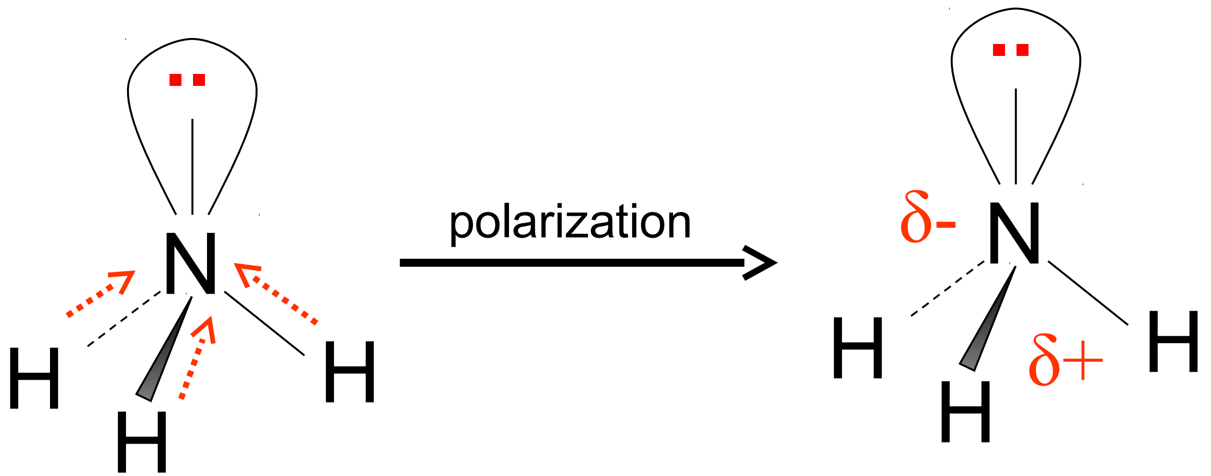
This very simple concept was used to rationalize a variety of chemical information, as an attempt to unify inorganic and organic reactions.

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

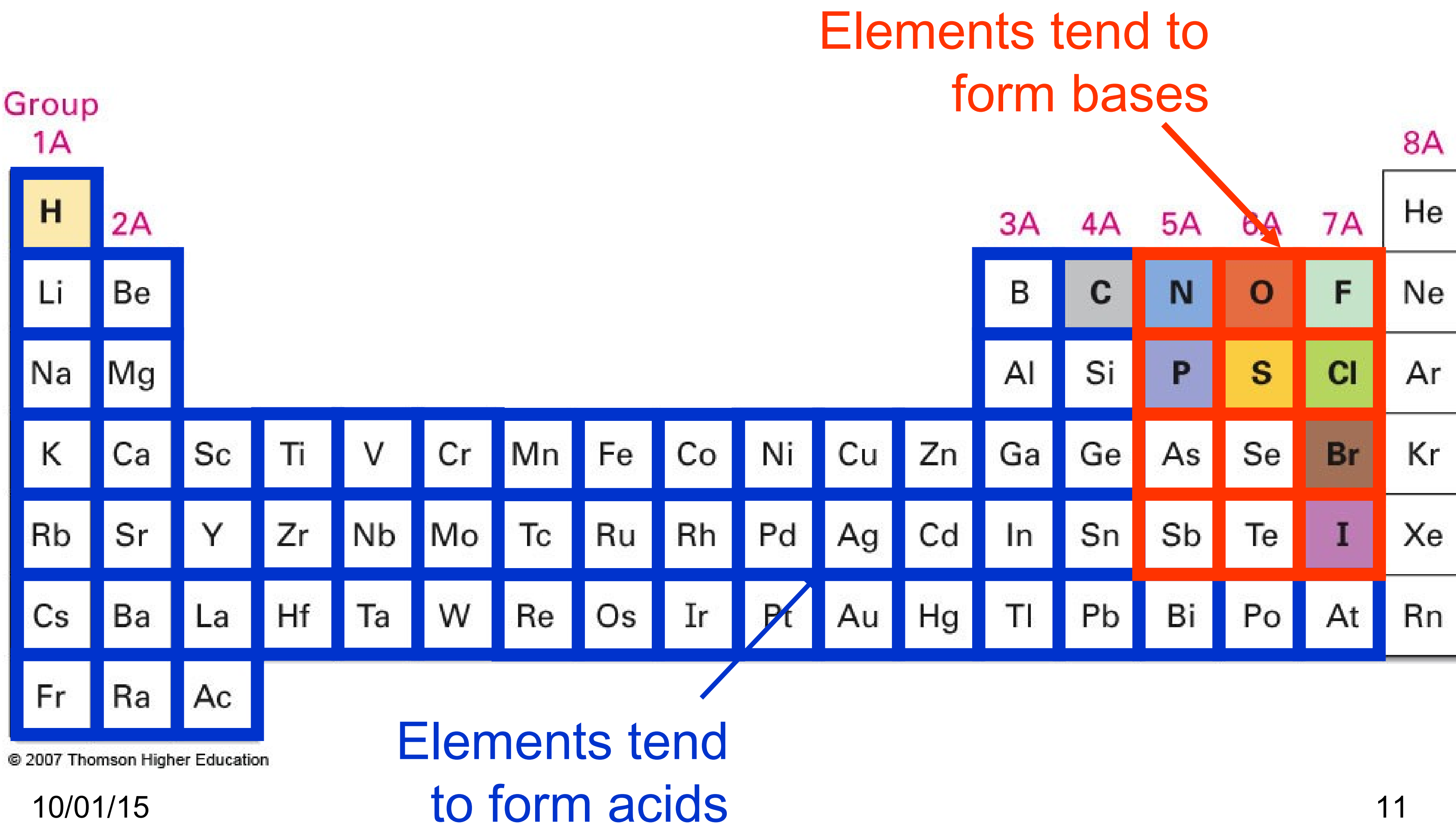
The theory is used in contexts where a qualitative, rather than quantitative description would help in understanding the predominant factors which drive chemical properties and reactions.

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

Harder Base

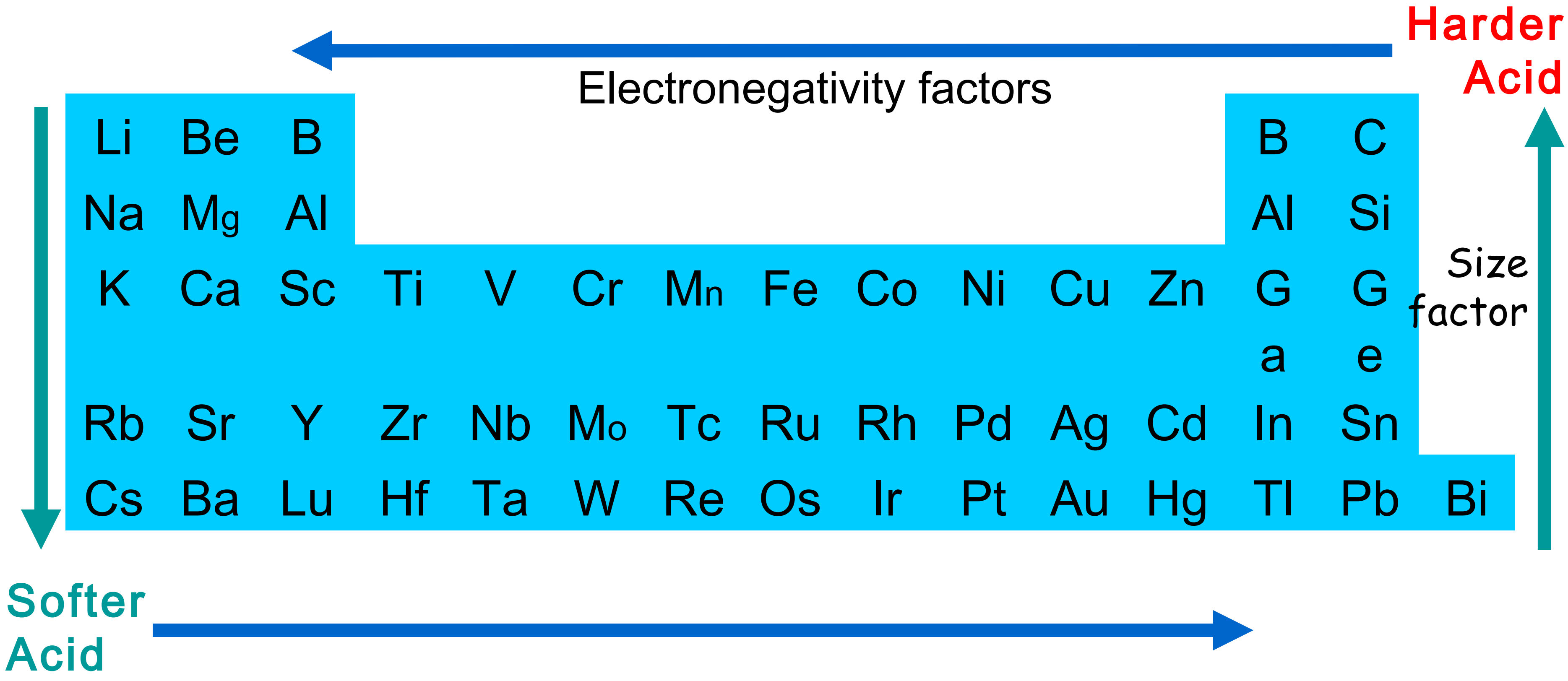
Electronegativity factors

N	O	F
P	S	Cl
As	Se	Br
Sb	Te	I

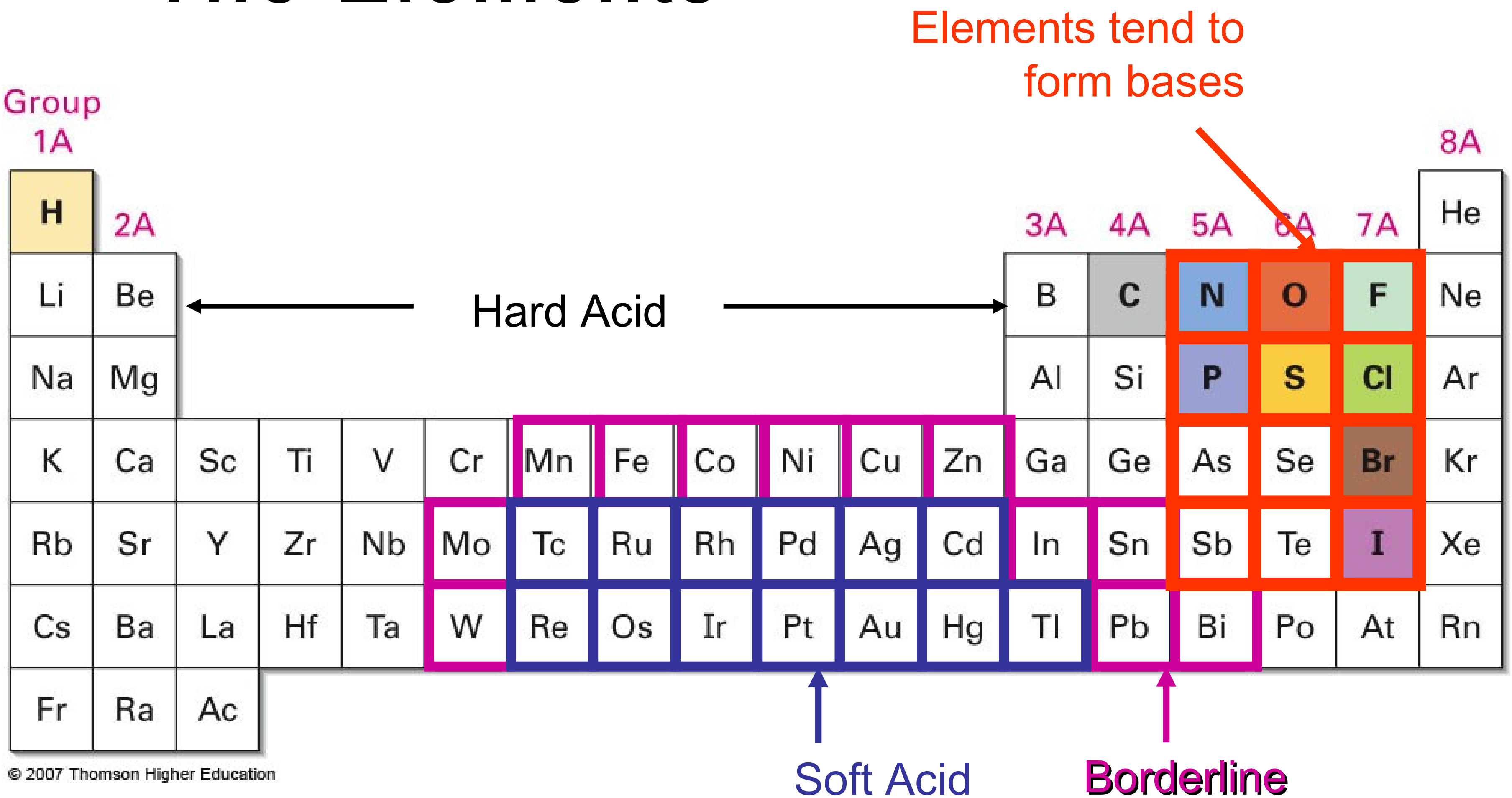
Size factor

Softer Base

Elements tend to form acids



The Elements



Pearson's classification of metal ions :

Pearson, R.G., Journal of American Chemical Society, **1963**, 85, 3533–3539.

class (a) metal ions :

- 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 :

N >> P > As > Sb

O >> S > Se > Te

F > Cl > Br > I

Tendency to complex with class (b) metal ions

N << P < As < Sb

O << S < Se < Te

F < Cl < Br < I

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+}.

class (b) metal ions

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

Tendency to complex with class (a) metal ions :

N >> P > As > Sb

O >> S > Se > Te

F > Cl > Br > I

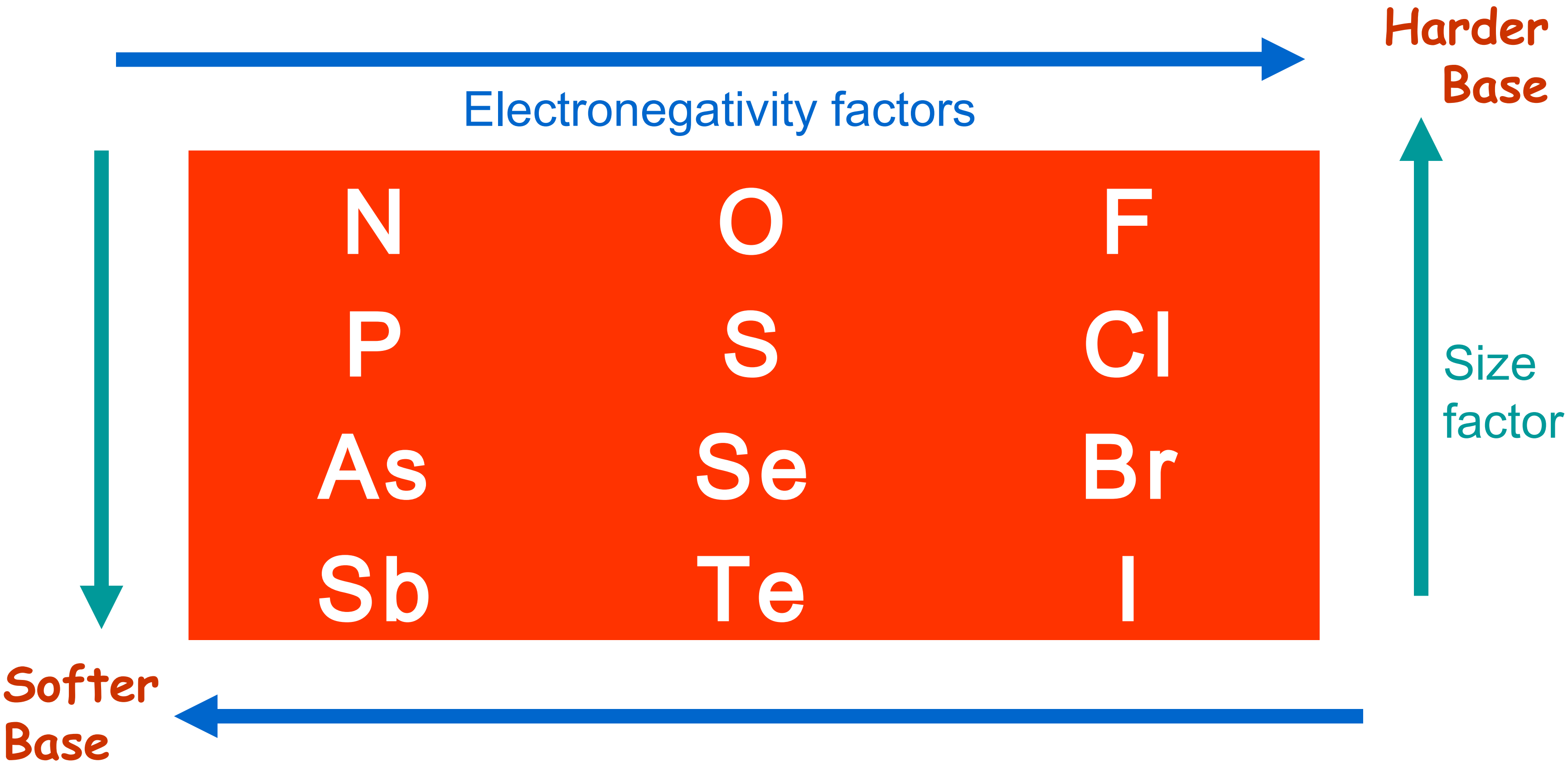
Tendency to complex with class (b) metal ions

N << P < As < Sb

O << S < Se < Te

F < Cl < Br < I

Elements tend to form bases



N P As Sb

O S Se Te

HARDER ← → SOFTE

F Cl Br R I

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

Tendency to complex with class (a) metal ions :

N >> P > As > Sb

O >> S > Se > Te

F > Cl > Br > I

Tendency to complex with class (b) metal ions

N << P < As < Sb

O << S < Se < Te

F < Cl < Br < I

Hard Acids

Hard Bases

Soft Acids

Soft Bases

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 :

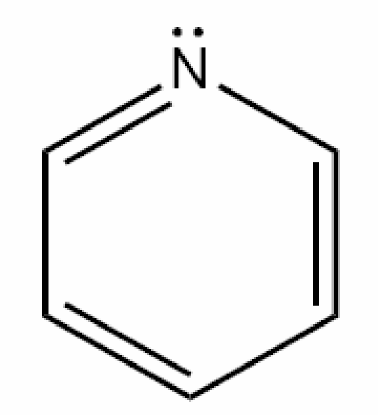
- The listings in the tables do not have a sharp dividing line between them.
- These terms, “hard” & “soft”, are relative in nature
- Some are borderline and even though within the same category are not all of the same degree of “hardness” and “softness”

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