Hard-Soft Acid-Base Theory

Definitions

Arrhenius acids form hydronium ions in water, and bases form hydroxide ions. This definition assumes that water is the solvent.

Brønsted and *Lowry* expanded upon the Arrhenius definitions, and defined acids as proton donors and bases as proton acceptors. They also introduced the concept of *conjugate acid-base pairs*.

Other Solvents

For any solvent that can dissociate into a cation and an anion, the cation is the acid, and the anion is the base. Any solute that causes an increase in the concentration of the cation is an acid, those that increase the concentration of the anion are bases.

Lewis Acids & Bases

The *Lewis* definition further expands the definitions. A base is an electron-pair donor, and an acid is an electron-pair acceptor. The two combine to form an *adduct*.

$$A + :B \rightarrow A\text{-}B$$

Lewis Acids & Bases

This definition includes the “standard” Brønsted-Lowry acid-base reactions:

$$H^+(aq) + :NH_3(aq) \rightarrow NH_4^+(aq)$$

It also includes the reactions of metal ions or atoms with ligands to form coordination compounds:

$$Ag^+(aq) + 2\ :NH_3(aq) \rightarrow Ag(NH_3)_2^+(aq)$$

Slides found at *faculty.uml.edu/ndeluca/84.334/topics/Hard-Soft%20Acid-Base%20Theory.ppt*

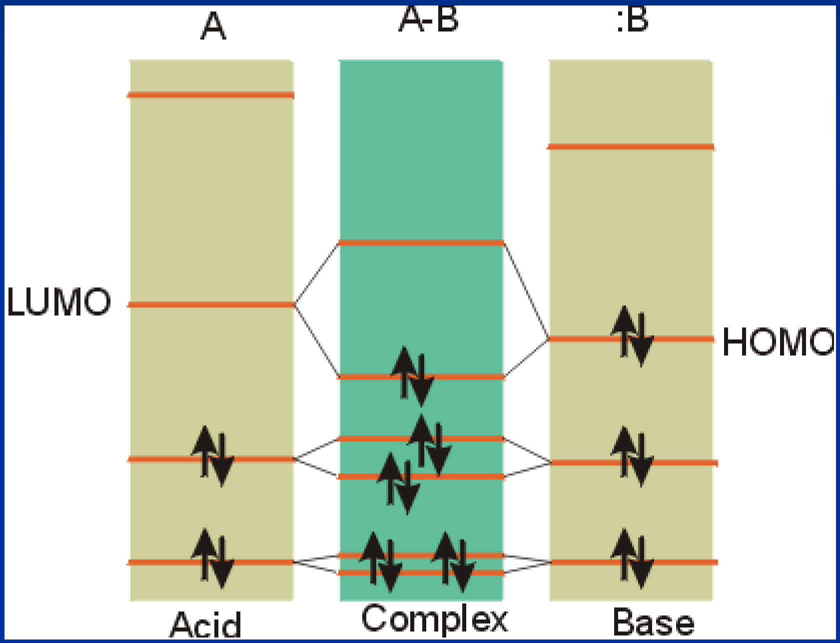
Lewis Acids & Bases

In addition, electron-deficient compounds such as trivalent boron is categorized as a Lewis acid.

$$B(CH_3)_3 + :NH_3 \rightarrow (CH_3)_3B\leftarrow NH_3$$

The HOMO on the Lewis base interacts with the electron pair in the LUMO of the Lewis acid. The MOs of the adduct are lower in energy.

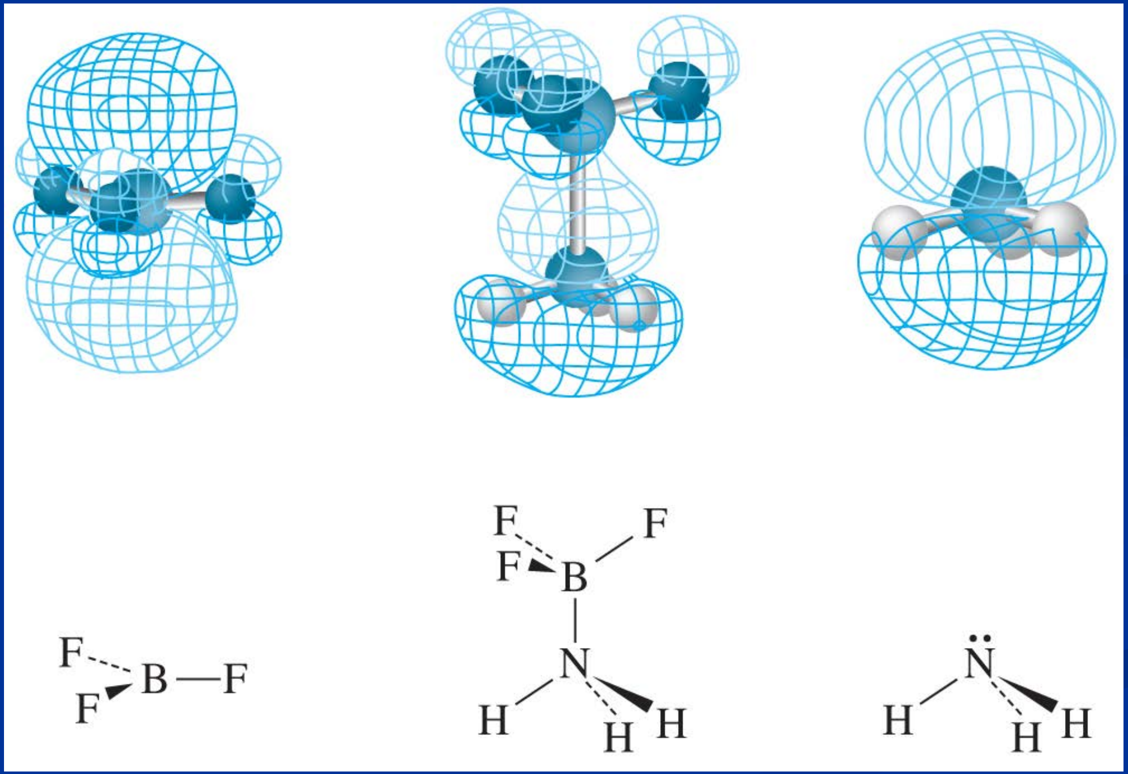
Lewis Acids & Bases



The LUMO and HOMO are called *frontier orbitals*. If there is a net lowering of energy, the adduct is stable.

$BF_3 + NH_3$

The LUMO of the acid, the HOMO of the base and the adduct are shown below:



Lewis Acids & Bases

There is the possibility of competing reaction pathways depending upon which reactants are present, and the relative energies of possible products. As a result, a compound such as water may serve as an acid, a base, an oxidizing agent (with Group IA and IIA metals) or a reducing agent (with F_2).

Lewis Acids & Bases

A Lewis base has an electron pair in its highest occupied molecular orbital (HOMO) of suitable symmetry to interact with the LUMO of the Lewis acid. The closer the two orbitals are in energy, the stronger the bond in the adduct.

Hard and Soft Acids and Bases

The polarizability of an acid or base plays a role in its reactivity. *Hard* acids and bases are small, compact, and non-polarizable.

Soft acids and bases are larger, with a more diffuse distribution of electrons.

Hard and Soft Acids and Bases

In addition to their intrinsic strength,

Hard acids react preferentially with hard bases, and soft acids react preferentially with soft bases.

Examples: Aqueous Solubility
Silver Halides

Compound	solubility product
AgF	205
AgCl	1.8×10^{-10}
AgBr	5.2×10^{-13}
AgI	8.3×10^{-17}

$$AgX(s) + H_2O(l) \leftrightarrow Ag^+(aq) + X^-(aq)$$

Solubility of Lithium Halides

LiBr> LiCl> LiI> LiF

LiF should have a higher Δ_{solv} than the other salts, yet it is the least soluble in water. This is due to the strong hard acid (Li^+)/hard base (F^-) interaction.

Example: Thiocyanate Bonding

SCN^- displays *linkage isomerism* as the ligand coordinates to metals via the sulfur or the nitrogen. Mercury (II) ion bonds to the sulfur (a soft-soft interaction) whereas zinc ion bonds to the nitrogen atom.

Example: K for ligand exchange reactions

Compare:

$[MeHg(H_2O)]^+ + HCl \longleftrightarrow MeHgCl + H_3O^+$

$K = 1.8 \times 10^{12}$

$[MeHg(H_2O)]^+ + HF \longleftrightarrow MeHgF + H_3O^+$

$K = 4.5 \times 10^{-2}$

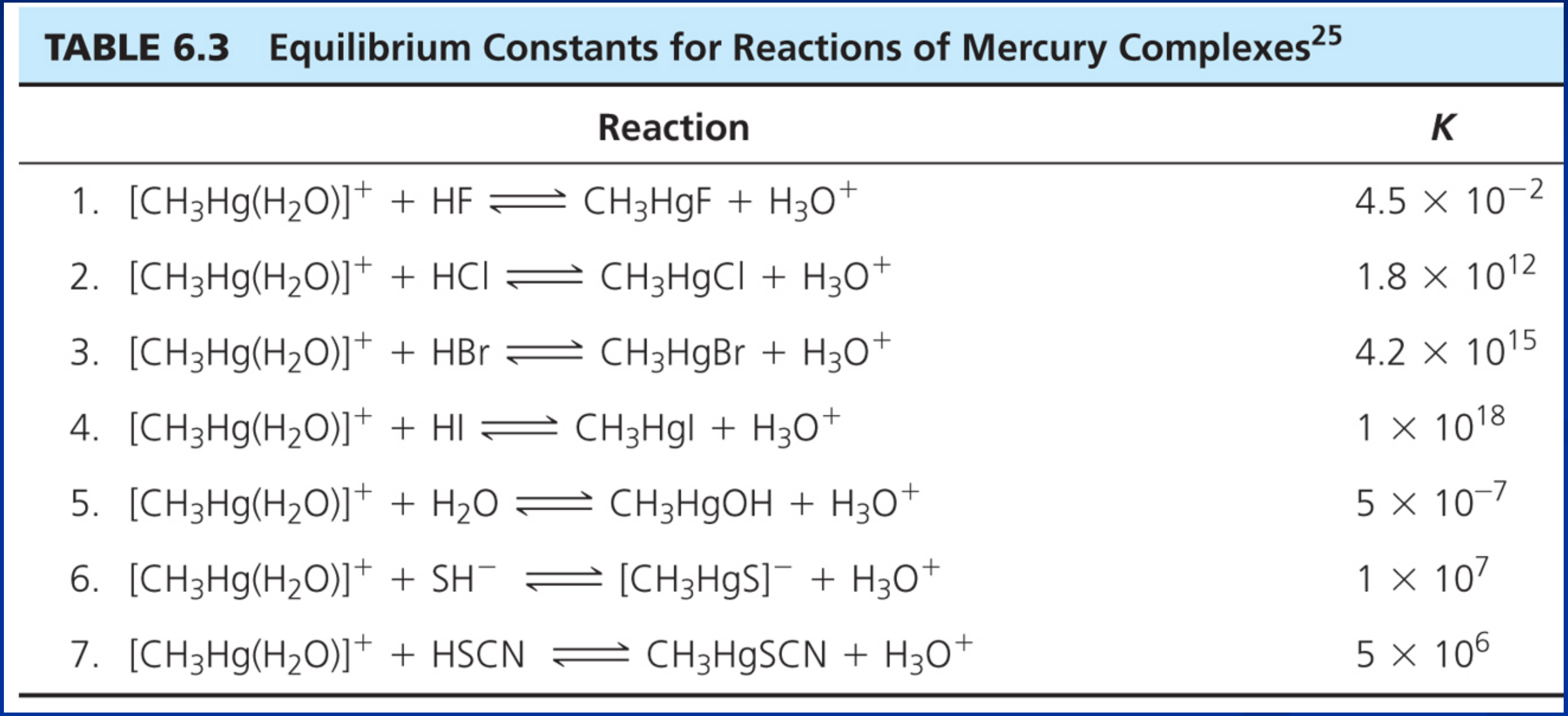


TABLE 6.3 Equilibrium Constants for Reactions of Mercury Complexes[25]

Reaction	K
1. $[CH_3Hg(H_2O)]^+ + HF \rightleftharpoons CH_3HgF + H_3O^+$	4.5×10^{-2}
2. $[CH_3Hg(H_2O)]^+ + HCl \rightleftharpoons CH_3HgCl + H_3O^+$	1.8×10^{12}
3. $[CH_3Hg(H_2O)]^+ + HBr \rightleftharpoons CH_3HgBr + H_3O^+$	4.2×10^{15}
4. $[CH_3Hg(H_2O)]^+ + HI \rightleftharpoons CH_3HgI + H_3O^+$	1×10^{18}
5. $[CH_3Hg(H_2O)]^+ + H_2O \rightleftharpoons CH_3HgOH + H_3O^+$	5×10^{-7}
6. $[CH_3Hg(H_2O)]^+ + SH^- \rightleftharpoons [CH_3HgS]^- + H_3O^+$	1×10^{7}
7. $[CH_3Hg(H_2O)]^+ + HSCN \rightleftharpoons CH_3HgSCN + H_3O^+$	5×10^{6}

Hard and Soft Acids & Bases

There have been many attempts to categorize various metal ions and anions to predict reactivity, solubility, etc.

R.G. Pearson (1963) categorized acids and bases as either *hard* or *soft* (using K_f values).

Hard acids bond in the order: $F^- > Cl^- > Br^- > I^-$

Soft acids bond in the order: $I^- > Br^- > Cl^- > F^-$

Hard and Soft Acids & Bases

Hard acids or bases are compact, with the electrons held fairly tightly by the nucleus. They are not very polarizable. F^- is a hard base, and metal ions such as Li^+, a hard acid.

Hard and Soft Acids & Bases

Large, highly polarizable ions are categorized as "soft." Iodide is a soft base, and transition metals with low charge density, such as Ag^+, are considered to be soft acids.

Hard and Soft Acids & Bases

Hard acids tend to bind to hard bases.

Soft acids tend to bind to soft bases.

Problem

- Predict the solubility (high or low) of silver fluoride, silver iodide, lithium fluoride and lithium iodide using the hard-soft acid/base approach. Identify each Lewis acid and Lewis base, and categorize each as hard or soft.

Charge Density – Hard Acids

Hard acids typically have a high charge density. They are often metal ions with a (higher) positive charge and small ionic size. Their *d* orbitals are often unavailable to engage in π bonding.

Charge Density – Soft Acids

Soft acids typically have lower charge density (lower ionic charge and greater ionic size). Their *d* orbitals are available for π bonding. Soft acids are often 2nd and 3rd row transition metals with a +1 or +2 charge, and filled or nearly filled *d* orbitals.

Acids

Hard Acids	Borderline	Soft Acids
H^+, Li^+, Na^+, K^+		
Be^{2+}, Mg^{2+}, Ca^{2+}		
BF_3, BCl_3, $B(OR)_3$	BBr_3,$B(CH_3)_3$	BH_3,Tl^+, $Tl(CH_3)_3$
Al^{3+},$Al(CH_3)_3$,$AlCl_3$,AlH_3		
Cr^{3+},Mn^{2+}, Fe^{3+}, Co^{3+}	Fe^{2+},Co^{2+},Ni^{2+}	Cu^+,Ag^+, Au^+,
	Cu^{2+},Zn^{2+},Rh^{3+}	Cd^{2+},$Hg_2{}^{2+}$,
	Ir^{3+}, Ru^{3+}, Os^{2+}	Hg^{2+}, Pd^{2+},Pt^{2+},
SO_3	SO_2	Pt^{4+}

Acids – Effect of Oxid'n

Hard Acids	Borderline	Soft Acids
H^+, Li^+, Na^+, K^+		
Be^{2+}, Mg^{2+}, Ca^{2+}		
BF_3, BCl_3, $B(OR)_3$	BBr_3,$B(CH_3)_3$	BH_3,Tl^+, $Tl(CH_3)_3$
Al^{3+},$Al(CH_3)_3$,$AlCl_3$,AlH_3		
Cr^{3+},Mn^{2+}, $\boxed{Fe^{3+}}$, $\boxed{Co^{3+}}$	$\boxed{Fe^{2+}}$,$\boxed{Co^{2+}}$,Ni^{2+}	$\boxed{Cu^+}$,Ag^+, Au^+,
	$\boxed{Cu^{2+}}$,Zn^{2+},Rh^{3+}	Cd^{2+},Hg_2^{2+},
	Ir^{3+}, Ru^{3+}, Os^{2+}	Hg^{2+}, Pd^{2+},Pt^{2+},
$\boxed{SO_3}$	$\boxed{SO_2}$	Pt^{4+}

Bases

Hard Bases	Borderline	Soft Bases
F^-, Cl^-	Br^-	H^-, I^-
H_2O, OH^-, O^{2-}		H_2S, HS^-, S^{2-}
ROH, RO^-, R_2O, $CH_3CO_2^-$		RSH, RS^-, R_2S
NO_3^-, ClO_4^-	$\underline{N}O_2^-$, N_3^-, N_2	$\underline{S}CN^-$, $\underline{C}N^-$, RNC, CO
CO_3^{2-}, SO_4^{2-}, PO_4^{3-}	SO_3^{2-}	$S_2O_3^{2-}$
NH_3, RNH_2	$C_6H_5NH_2$, pyr	R_3P, C_6H_6

Bases – effect of Oxid’n

Hard Bases	Borderline	Soft Bases
F^-, Cl^-	Br^-	H^-, I^-
H_2O, OH^-,O^{2-}		H_2S, HS^-, S^{2-}
ROH, RO^-, R_2O, $CH_3CO_2^-$		RSH, RS^-, R_2S
NO_3^-, ClO_4^-	$\underline{N}O_2^-$, N_3^- , N_2	$\underline{S}CN^-$, $\underline{C}N^-$,RNC, CO
CO_3^{2-}, $\boxed{SO_4^{2-}}$, PO_4^{3-}	$\boxed{SO_3^{2-}}$	$S_2O_3^{2-}$
NH_3, RNH_2	$C_6H_5NH_2$, pyr	R_3P, C_6H_6

Effect of Linkage Site

$\mathrm{SC\underline{N}^-}$ vs. $\mathrm{NC\underline{S}^-}$

The nitrogen tends to coordinate with harder acids such as Si, whereas the sulfur tends to coordinate with softer acids such as Pt^{2+}.

Effect of Oxidation Number

Cu^{2+}/Cu^{+} on acid hardness

SO_3/SO_2 on acid hardness

NO_3^-/NO_2^- on base hardness

SO_4^{2-}/SO_3^{2-} on base hardness

Acid or Base Strength

It is important to realize that hard/soft considerations have nothing to do with acid or base strength. An acid or a base may be hard or soft and also be either weak or strong.

In a competition reaction between two bases for the same acid, you must consider both the relative strength of the bases, and the hard/soft nature of each base and the acid.

Acid or Base Strength

Consider the reaction between ZnO and LiC_4H_9.

$$ZnO + 2\ LiC_4H_9 \leftrightarrow Zn(C_4H_9)_2 + Li_2O$$

Zinc ion is a strong Lewis acid, and oxide ion is a strong Lewis base.

Acid or Base Strength

Consider the reaction between ZnO and LiC_4H_9.

$$ZnO + 2\ LiC_4H_9 \leftrightarrow Zn(C_4H_9)_2 + Li_2O$$

soft -hard   hard -soft   soft -soft   hard -hard

Zinc ion is a strong Lewis acid, and oxide ion is a strong Lewis base. However, the reaction proceeds to the right (K>1), because hard/soft considerations override acid-base strength considerations.

The Nature of the Adduct

Hard acid/hard base adducts tend to have more ionic character in their bonding. These are generally more favored energetically.

Soft acid/soft base adducts are more covalent in nature.

Other Considerations

- As the adduct forms, there is usually a change in geometry around the Lewis acid site.

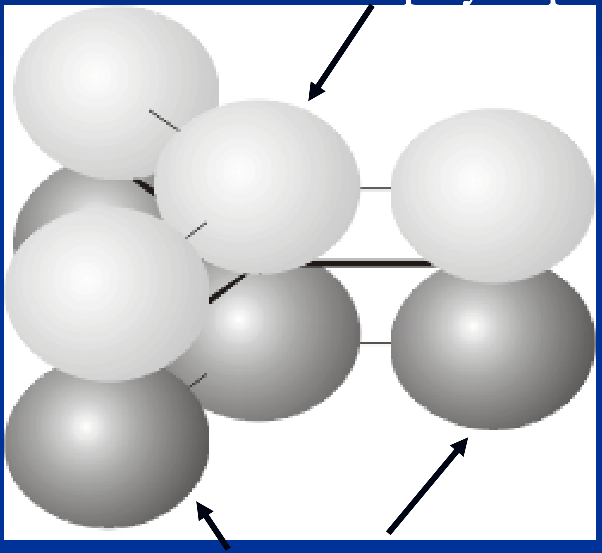
  $BX_3 + N(CH_3)_3 \rightarrow X_3B\text{-}NMe_3$

  The stability of the adduct is:

  $BBr_3 > BCl_3 > BF_3$

  This order seems opposite of what would be expected based on halogen size or electronegativity.

Other Considerations



empty 2p orbital

filled orbitals

The reactivity pattern suggests some degree of π bonding in BF_3.

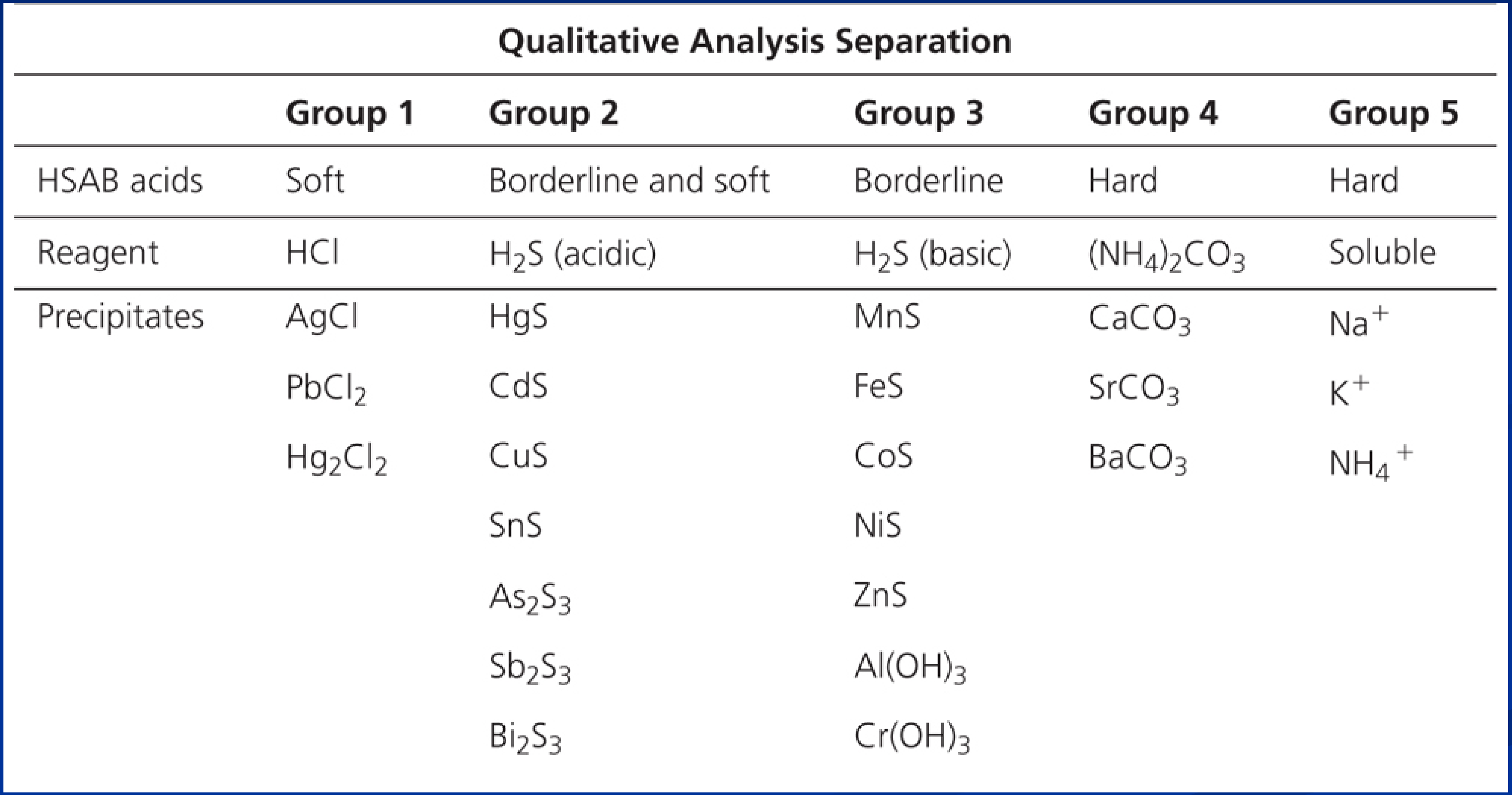
Other Considerations

- Steric factors can play a role. An example is the unfavorable reaction between $:N(C_6H_5)_3$ and BCl_3. The large phenyl groups interact with the chlorine atoms on boron to destabilize the product.

Applications of Hard/Soft Theory

The *Qual Scheme*, a series of chemical reactions used to separate and identify the presence of dozens of metal ions, is based largely on the hard and soft properties of the metal ions.

The softer metals are precipitated out as chlorides or sulfides, with the harder ions formed as carbonates.



Qualitative Analysis Separation

	Group 1	Group 2	Group 3	Group 4	Group 5
HSAB acids	Soft	Borderline and soft	Borderline	Hard	Hard
Reagent	HCl	H_2S (acidic)	H_2S (basic)	$(NH_4)_2CO_3$	Soluble
Precipitates	AgCl	HgS	MnS	$CaCO_3$	Na^+
	$PbCl_2$	CdS	FeS	$SrCO_3$	K^+
	Hg_2Cl_2	CuS	CoS	$BaCO_3$	NH_4^+
		SnS	NiS		
		As_2S_3	ZnS		
		Sb_2S_3	$Al(OH)_3$		
		Bi_2S_3	$Cr(OH)_3$		

Evidence in Nature

In geochemistry, the elements in the earth's crust are classified as *lithophiles or chalcophiles.*

The lithophile elements are typically found as silicates (bonded via the O atom): Li^+, Mg^{2+}, Ti^{3+}, Al^{3+} and $Cr^{2+,3+}$. These are hard Lewis acids.

Evidence in Nature

The chalcophile elements are typically found as sulfides or bonded to Se^{2-} or Te^{2-}. They include: Cd^{2+}, Pb^{2+}, Sb^{3+}, and Bi^{3+}. These are soft Lewis acids. Zinc ion, which is borderline, is typically found as a sulfide.