Lecture 9

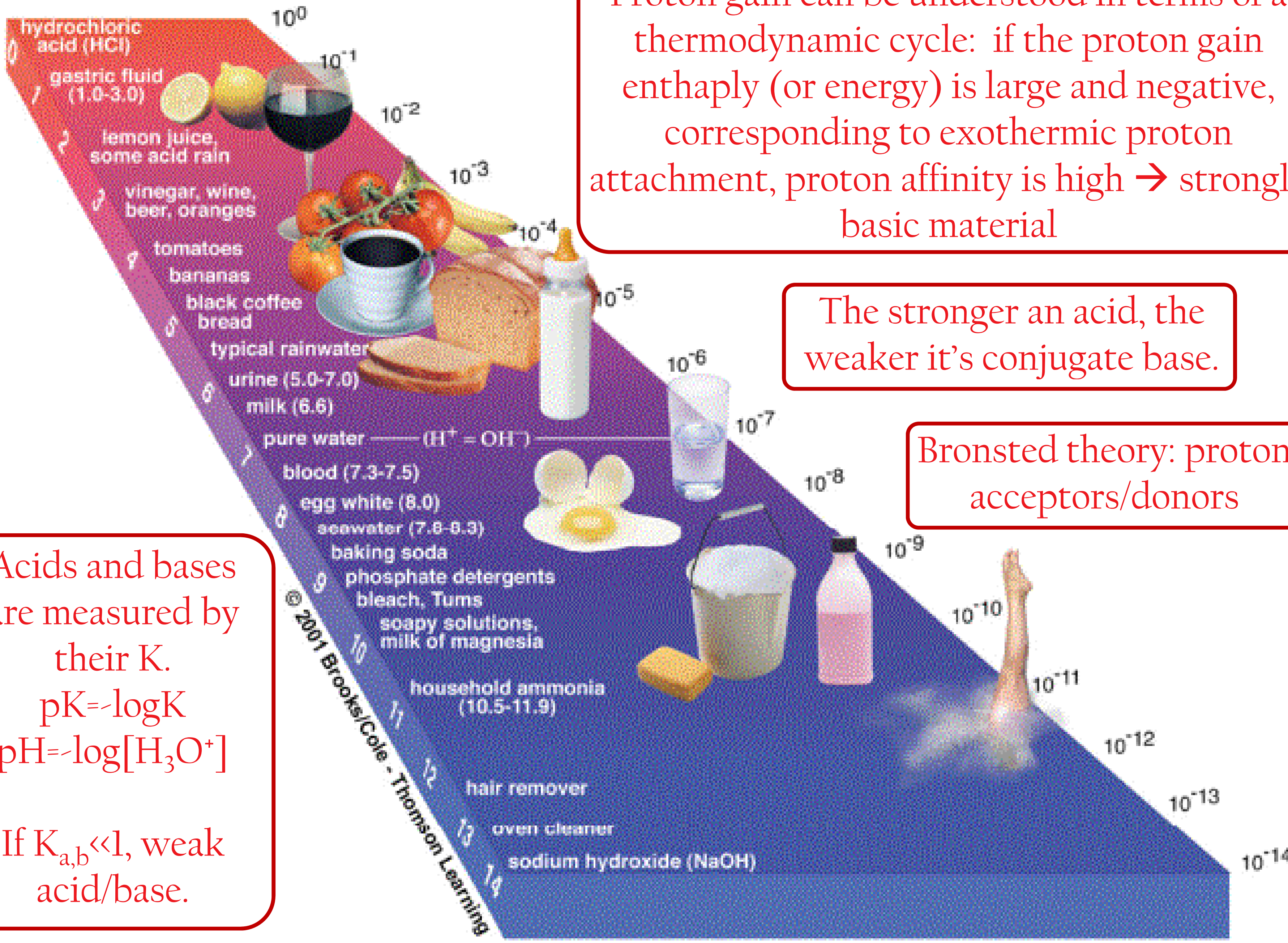
Acids and Bases

Suggested reading: Chapter 4.2-4.11

Proton gain can be understood in terms of a thermodynamic cycle: if the proton gain enthaply (or energy) is large and negative, corresponding to exothermic proton attachment, proton affinity is high → strongly basic material

The stronger an acid, the weaker it's conjugate base.

Bronsted theory: proton acceptors/donors



Acids and bases are measured by their K.

pK=-logK

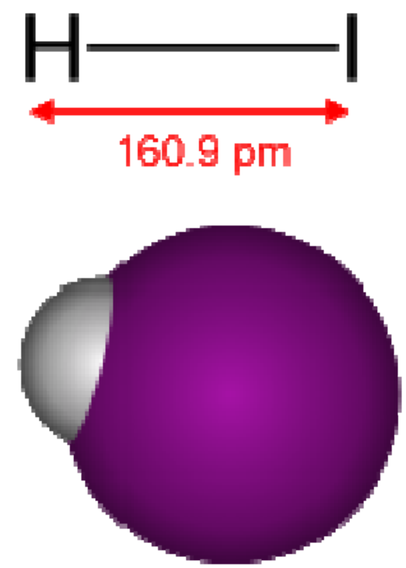
pH=-log[H_3O^+]

If $K_{a,b}$<<1, weak acid/base.

Solvent Levelling

Hydrobromic acid
(K_a=10^9)

Hydroiodic acid
(K_a=10^{10})



Can we distinguish the strengths of these acids in water?

- Both will transfer their protons completely to give H_3O^+
- Water is said to have a leveling effect that brings all the stronger acids down to the acidity of H_3O^+ .

Solvent Levelling

- An acid that is weak in water may appear strong in a solvent that is a more effect proton acceptor.

- In sufficiently basic solvents (i.e., liquid ammonia), almost all acids seem strong.

$$HA(sol) + HSol(l) \rightarrow H_2Sol^+(sol) + A^-(sol)$$

$$K_a = \frac{[H_2Sol^+][A^-]}{[HA]}$$

All acids with $pK_a < 0$ (corresponding to $K_a > 1$) display the acidity of H_2Sol^+ when they are dissolved in solvent HSol.

Example: HBr and HI have indistinguishable strengths in Water, even though HI is a stronger proton donor.

Solvent Levelling

- An acid that is weak in water may appear strong in a solvent that is a more effect proton acceptor.

- In sufficiently basic solvents (i.e., liquid ammonia), almost all acids seem strong.

$$B(sol) + HSol(l) \rightarrow BH^{+}(sol) + Sol^{-}(sol)$$

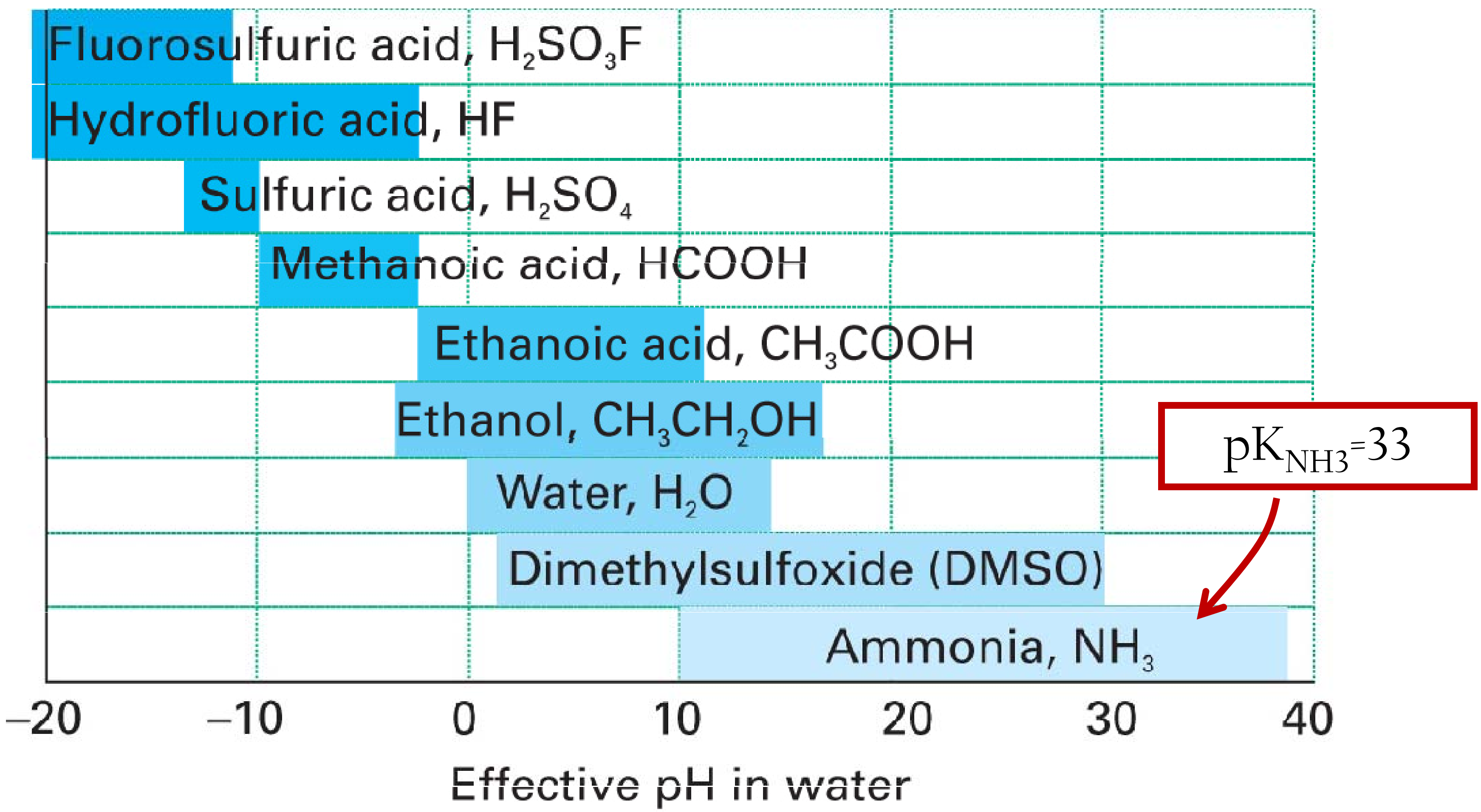
$$K_b = \frac{[BH^+][Sol^-]}{[B]}$$

All bases with $pK_b < 0$ (corresponding to $K_b > 1$) display the basicity of Sol^- when they are dissolved in solvent HSol.

Example: Alkali metal amides (NH_2^-) or methides (CH_3^-) cannot be distinguised in water, since both anions generate OH- and become fully protenated.

Solvent Levelling

Which solvents could be used to differentiate the acidities of HCl (pK_a=-6) and HBr (pK_a=-9)?



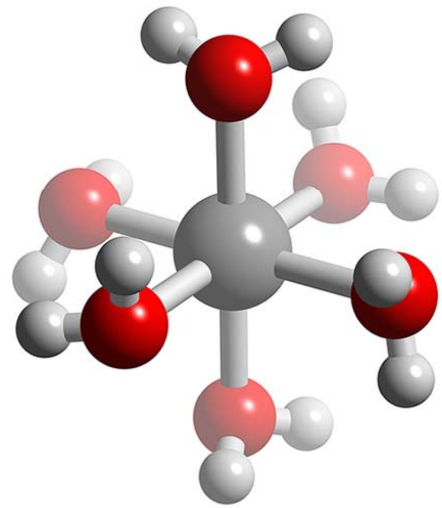
Acid-base discrimination window for a variety of solvents. The width is proportional to the autoprotolysis constant of the solvent.

Characteristics of Bronsted Acids

The largest class of acids in water are species that donate protons from an "OH" group.
Three classes of –OH (hydroxy group) acids:

1. **Aqua acids:** the acid proton is on a water molecule coordinated to a central metal ion

$$[Fe(OH_2)_6]^{3+}(aq) + H_2O(l) \rightarrow [Fe(OH_2)_5OH]^{2+}(aq) + H_3O^+(aq)$$

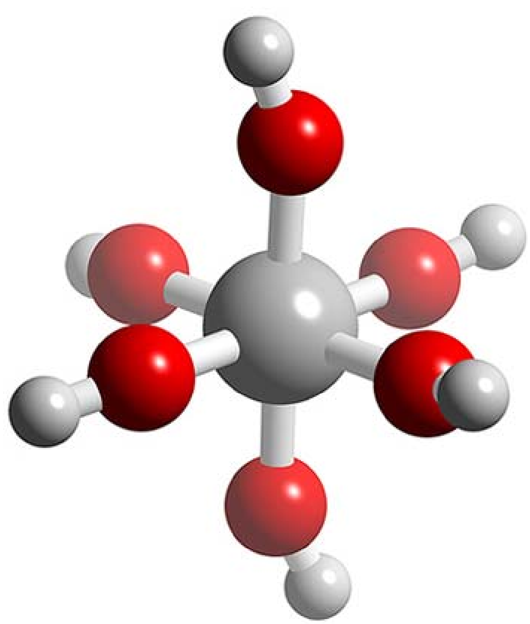


Hexaaquairon (III) ion

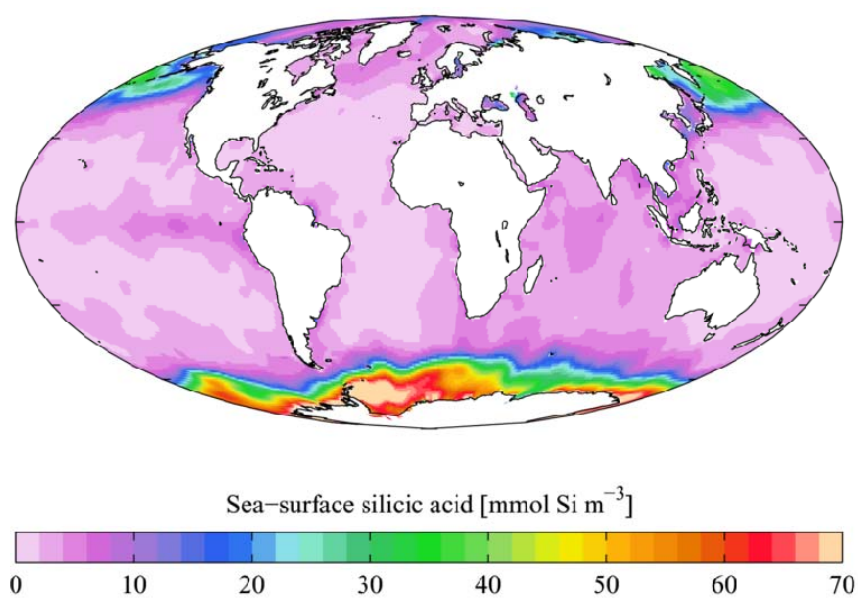
Characteristics of Bronsted Acids

The largest class of acids in water are species that donate protons from an "OH" group.
Three classes of –OH (hydroxy group) acids:

2. Hydroxoacids: the acid proton is on a hydroxyl group without a neighboring oxo group (=O). For example, Si $(OH)_4$ and $Te(OH)_4$.



$Te(OH)_6$

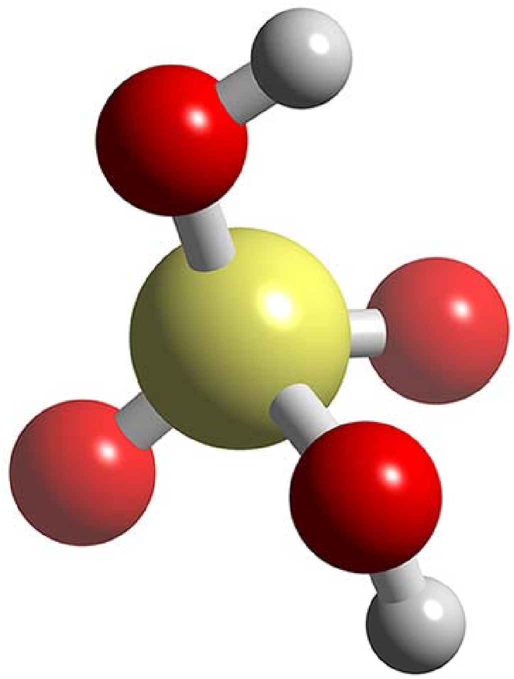


In the ocean, silicon exists primarily as orthosolicic acid. Algae polymerize this acid to form their cell walls.

Characteristics of Bronsted Acids

The largest class of acids in water are species that donate protons from an "OH" group.
Three classes of –OH (hydroxy group) acids:

3. **Oxoacids:** the acid proton is on a hydroxyl group with an oxo group (=O)attached to the same atom. For example, H_2SO_4.



Sulfuric acid

Characteristics of Bronsted Acids

The largest class of acids in water are species that donate protons from an "OH" group.

Three classes of –OH (hydroxy group) acids –

1) aqua acid, 2) hydroxoacid, 3)oxoacid.

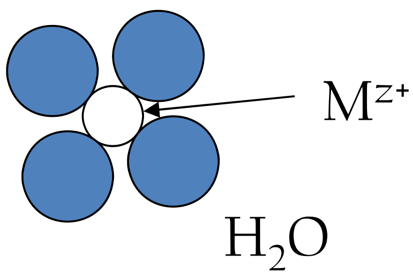
The 3 classes can be regarded as successive stages in the deprotenation of an aqua acid:

$$H_2O - E - OH_2 \xleftrightarrow{-2H^+} HO - E - OH^{2-} \xleftrightarrow{-H^+} HO - E = O^{3-}$$

Periodic Trends in Aqua Acid Strength

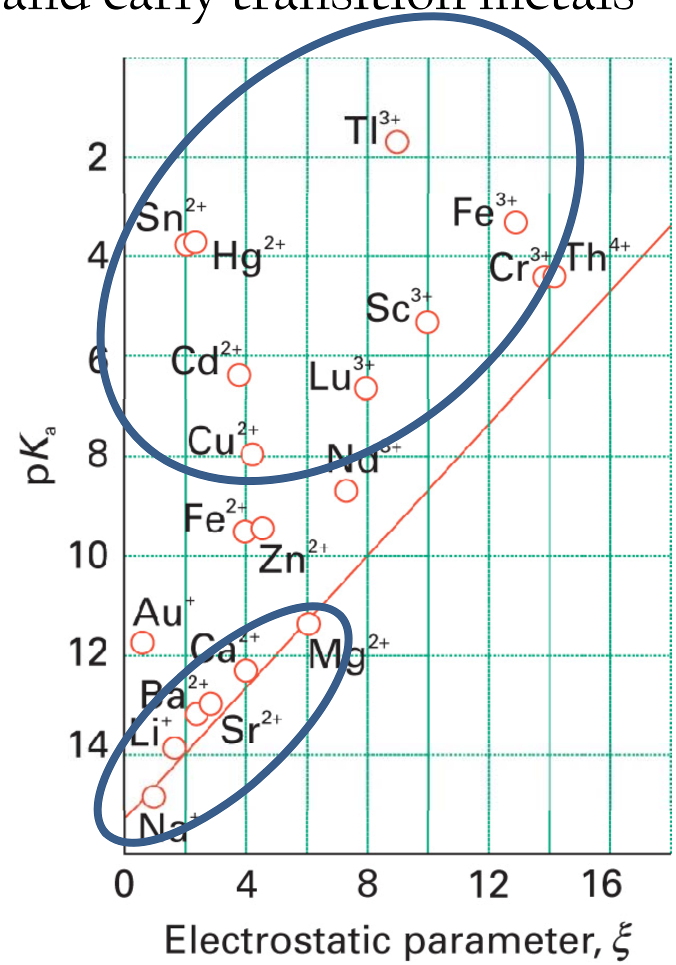
The strengths of aqua acids increase with increasing positive charge of the central metal ion and with decreasing ionic radius.

Ionic model: for s-block and early transition metals



$$\xi = \frac{z^2}{(r+d)}$$

r, radius of ion
d, diameter of water



Periodic Trends in Aqua Acid Strength

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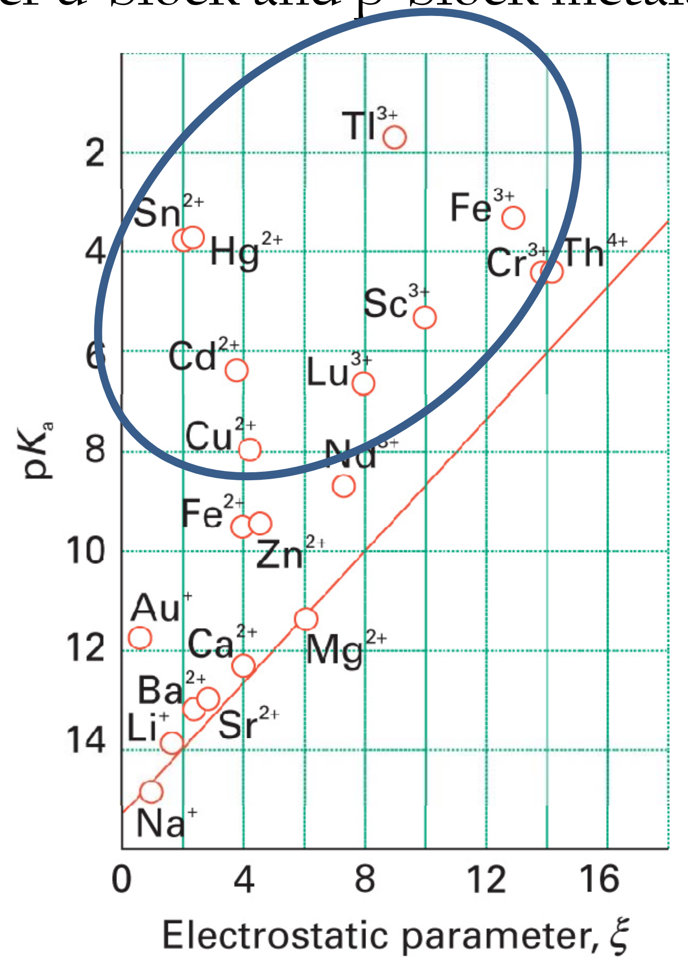
Covalent model: for the later d-block and p-block metals

These metals repel the departing proton more strongly than is predicted from the ionic model → delocalized charge and covalent bonds between element and oxygen.



Periodic Trends in Aqua Acid Strength

The strengths of aqua acids increase with increasing positive charge of the central metal ion and with decreasing ionic radius.

Example: acidity sequence

$$Fe(OH_2)_6^{2+} < Fe(OH_2)_6^{3+} < Al(OH_2)_6^{3+}$$

Large ionic radius and low charge

Smaller ionic radius and higher charge

Oxo Acids

Mononuclear acids: contain one atom of the parent element.

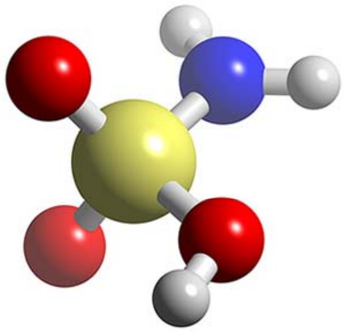
H_2CO_3, HNO_3, H_3PO_4, H_2SO_4.

Substituted oxoacids:
One of the hydroxyl groups can be replaced by another group.
If replaced by a more electronegative group, acidity is increase.

Examples: Fluorosulfuric acid $O_2SF(OH)$

→ F is very electronegative and draws electrons away from S...makes S seem more positive, therefore a stronger acid than $O_2S(OH)_2$.

Aminosulfuric acid $O_2S(NH_2)OH$.



Pauling's Rules

The strengths of a series of oxoacids containing a specific central atom with a variable number of oxo and hydroxyl groups are given by Pauling's rules:

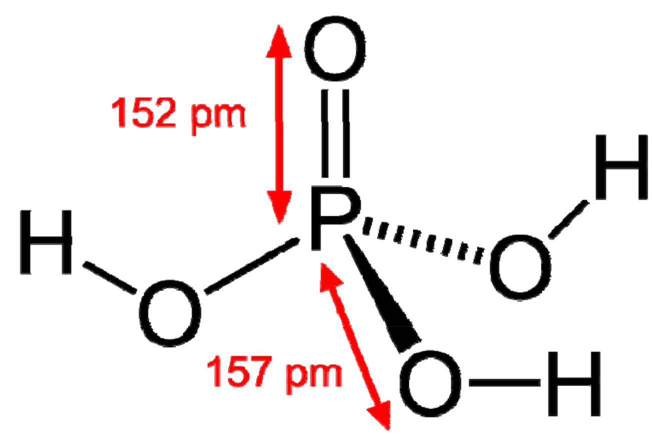
p=# oxo groups **q=#hydroxyl groups**

1. For the oxoacid $O_pE(OH)_q$, pK_a=8-5p

2. For the successive pK_a of polyprotic acids (q>1), increase by 5 units for each successive proton transfer.

Example: identify the structures consistent with the following pK_a's

H_3PO_4, : pKa=2.1



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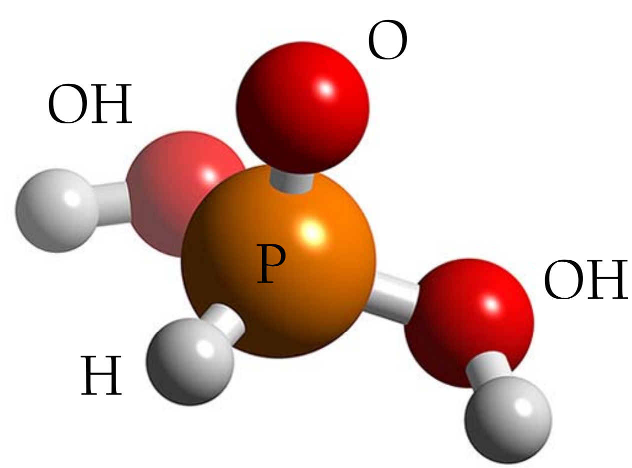
Example: identify the structures consistent with the following pK_a's

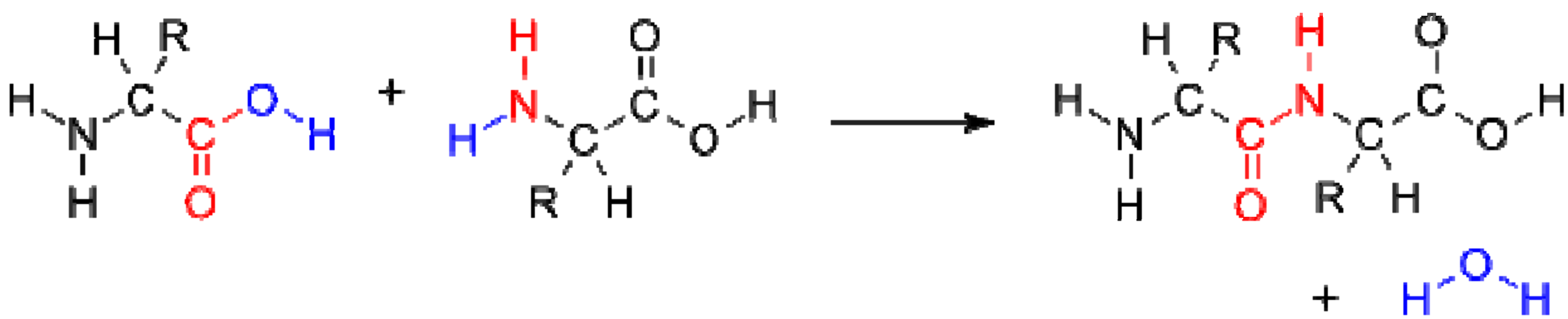
H_3PO_3, : pKa=1.8



Polyoxo compound formation

Acids containing OH condense to form polyoxoanions

First class of Important Chemical reactions:
Condensation reactions

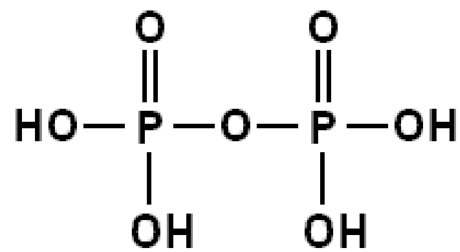


Two amino acids condensing to form a peptide bond (in red)

Note: precipitation usually occurs as the pH is increased

Orthophosphate condensation

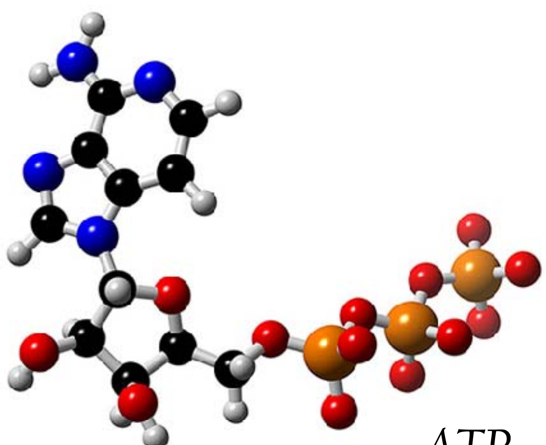
$2PO_4^{-}$ + $6H^{+}$ $\longrightarrow$



\+ H_2O

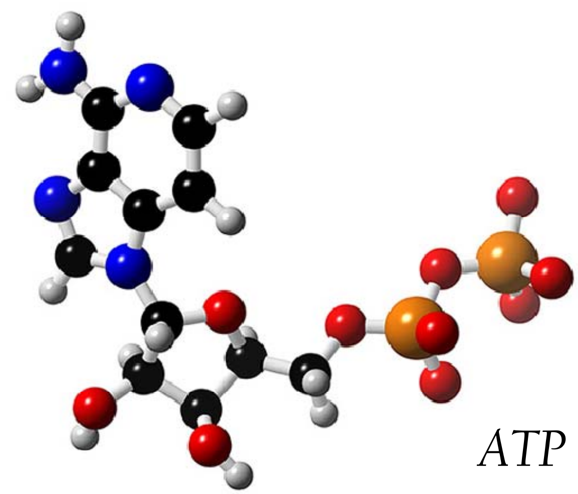
At pH=7.4, the P-O-P bond is unstable with respect to hydrolysis.

In the presence of water, it will dissociate, releasing energy in the process



ATP

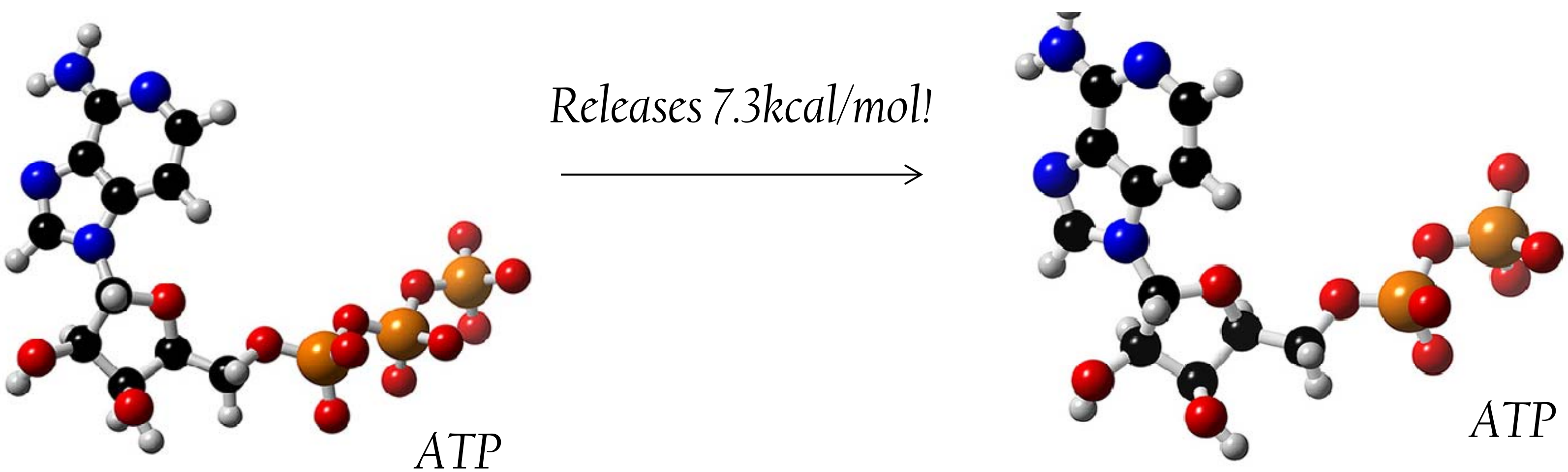
Releases 7.3kcal/mol! $\longrightarrow$



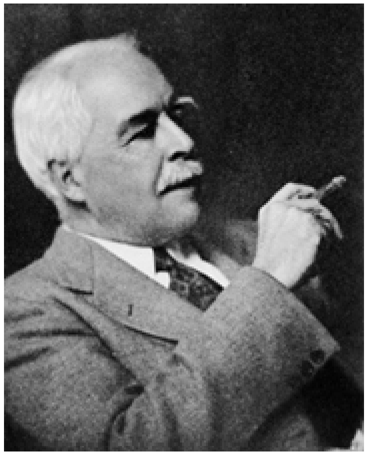
ATP

Orthophosphate condensation: Metabolism

ATP is in itself an unstable molecule which hydrolyzes to ADP and phosphate. This happens because the strength of the bonds between the phosphate residues in ATP is less than the strength of the bonds between its products, that is, ADP and phosphate with water. Normal cells maintain a certain ratio of ATP to ADP at a point ten orders of magnitude from equilibrium, with ATP concentrations more than a thousand times compared to ADP. Thus, displacement from equilibrium means that the hydrolysis of ATP in the cell releases a large amount of energy, which is in fact one of the most important functions of mitochondrial DNA.



Lewis Acid/Base Theory (1930's)



A Lewis acid acts as an electron pair acceptor.
A Lewis base acts as an electron pair donnor.

$$A \quad + \quad :B \longrightarrow A\text{-}B$$

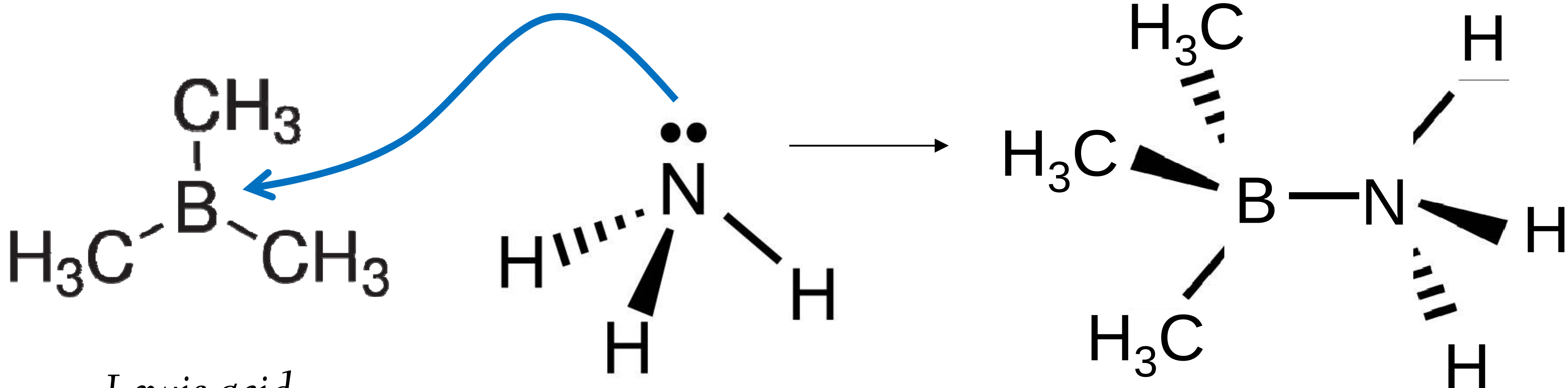
All the Bronsted acids are Lewis acids.
All the Bronsted bases are Lewis bases.

Lewis acidity is much broader than Bronsted acidity.

Examples of Lewis Acids

1) A metal cation can bond to an electron pair supplied by the base to form a coordination compound. $[Co(OH_2)_6]^{2+}$
→Will revisit in our discussion of complexes ☺

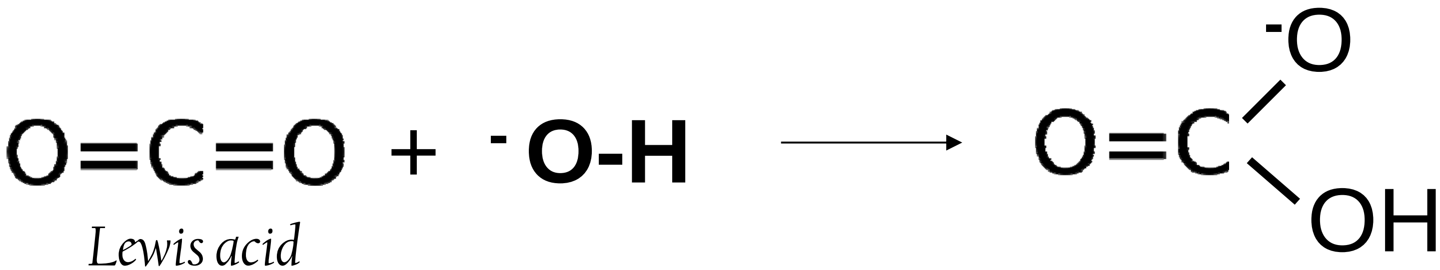
2) A molecule with an incomplete octet can complete its octet by accepting an electron pair.



Lewis acid

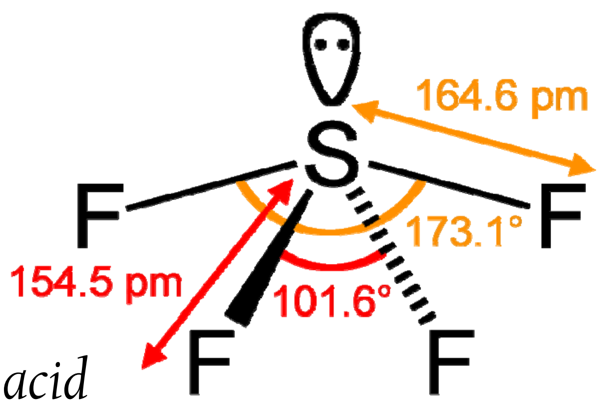
Examples of Lewis Acids

3) A molecule or ion with a complete octet may be able to arrange its valence electrons and accept an additional electron pair. CO_2 and OH^-

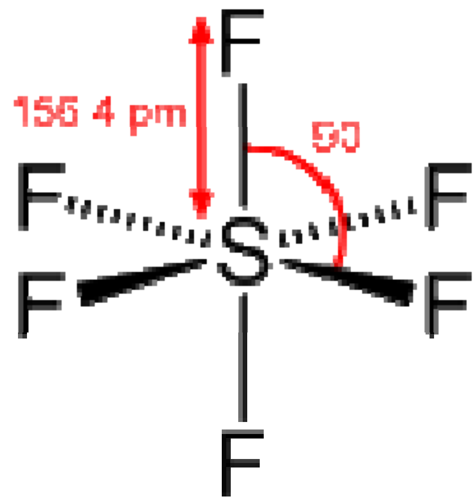


Lewis acid

4) A molecule or ion may be able to expand its valence shell (or simply be large enough) to accept another electron pair).
Example: SF_4 to SF_6^{2-}



Lewis acid



Classifications of Lewis Acids and Bases

Soft and hard acids and bases are identified empirically by the strengths to form complexes with halide ion bases (measured by equilibrium constant of formation)

Hard acids bond in the order:

$$I^- < Br^- < Cl^- < F^-$$

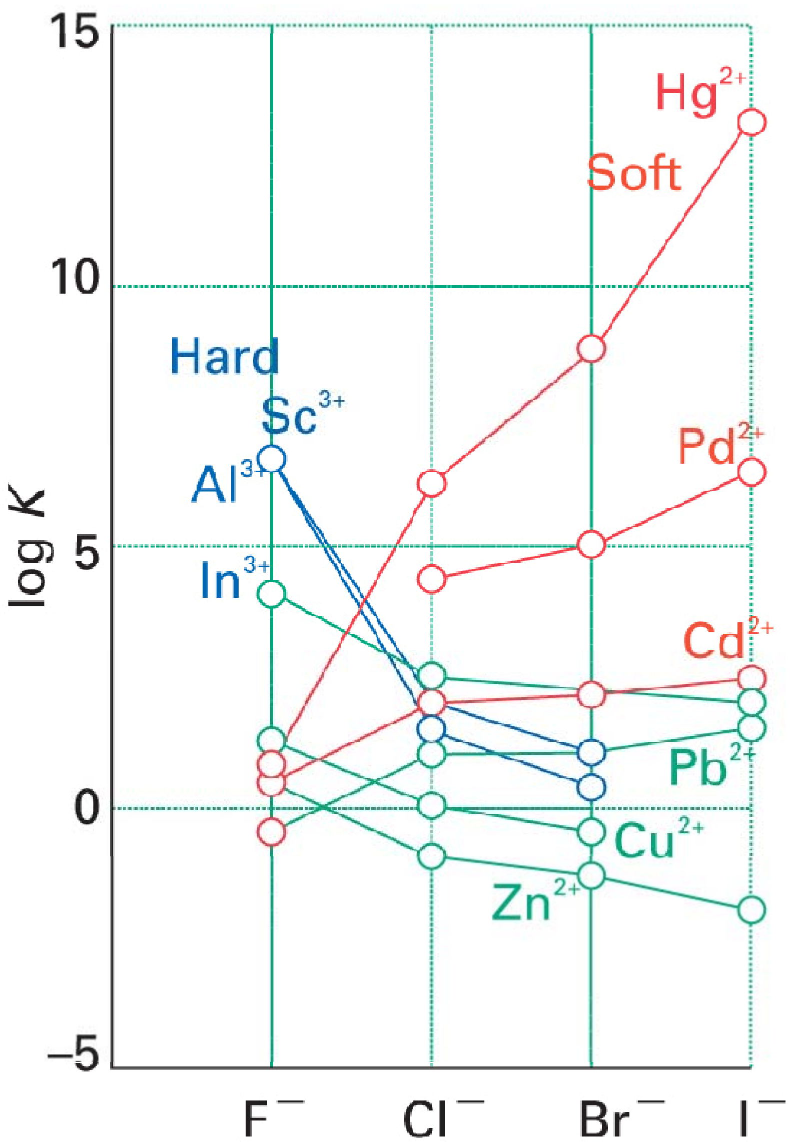
$$R_3P < R_3N,$$

$$\text{or } R_2S < R_2O.$$

Hard acid and base: electrostatic interaction

Soft acid and base: large polarizability, covalent bonding.

Trends in stability constants



Rule of thumb:

-Small cations are hard and form complexes with small anions

-Large cations (such as Hg) are more polarizable and are soft.

Elements & Solvents

Hard: Water, Alcohol, Ethers, Amines, DMSO: $(CH_3)_2SO$, DMF: $(CH_3)_2NCHO$, Acetonitrile: CH_3CN, THF: Tetrahydrofuran

Soft: Thiol, Benzene

Table 4.5 The classification of Lewis acids and bases*

Hard	Borderline	Soft
Acids		
H^+, Li^+, Na^+, K^+	Fe^{2+}, Co^{2+}, Ni^{2+}	Cu^+, Au^+, Ag^+, Tl^+, Hg_2^{2+}
Be^{2+}, Mg^{2+}, Ca^{2+}	Cu^{2+}, Zn^{2+}, Pb^{2+}	Pd^{2+}, Cd^{2+}, Pt^{2+}, Hg^{2+}
Cr^{2+}, Cr^{3+}, Al^{3+}	SO_2, BBr_3	BH_3
SO_3, BF_3		
Bases		
F^-, OH^-, H_2O, NH_3	NO_2^-, SO_3^{2-}, Br^-	H^-, R^-, $\underline{C}N^-$, CO, I^-
CO_3^{2-}, NO_3^-, O^{2-}	N_3^-, N_2	$\underline{S}CN^-$, R_3P, C_6H_5
SO_4^{2-}, PO_4^{3-}, ClO_4^-	C_6H_5N, $SC\underline{N}^-$	R_2S

* The underlined element is the site of attachment to which the classification refers.

Important rules:

- Hard acids tend to bind to hard bases
- Soft acids tend to bind to soft bases.

Consequences of Softness/Hardness

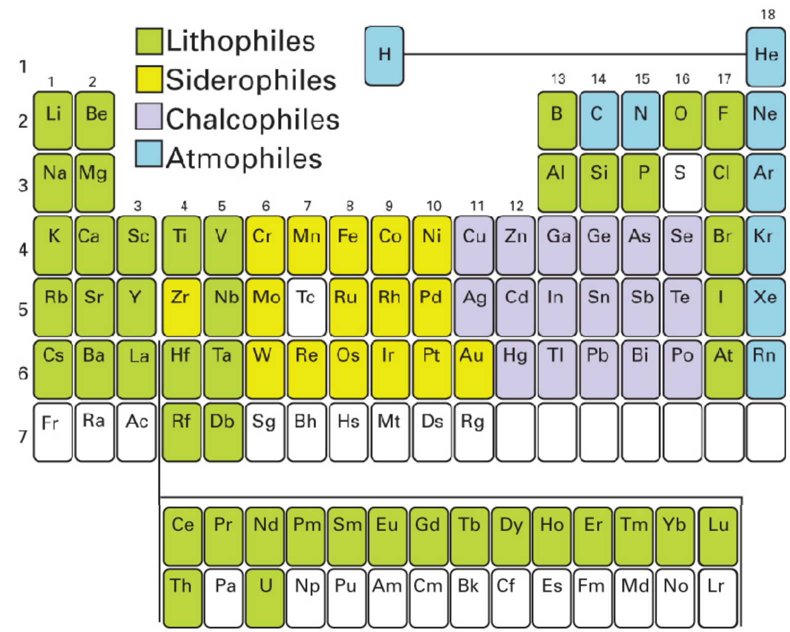
Cation Exchange in Nanoparticles

- The monovalent Ag^{+} cation is softer than the divalent Cd^{2+} cation. Therefore, MeOH, a hard base, preferentially binds Cd^{2+} cations. Similarly, the soft base, TBP, binds strongly to Ag^{+} cations.

Geochemistry: Mineral abundance

Goldschmidt classification:

- Li, Mg, Ti, Al Cr exist in oxide form, (Lithophile elements)
- Cd, Pb, Sb, Bi exist in chalcogenide form, (chalcophile elements).



Basic Reaction Chemistry