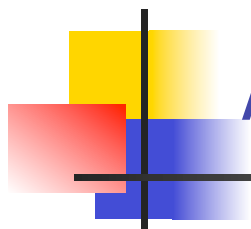


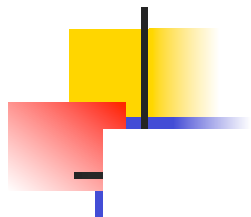
ACIDI E BASI



Acid-Base Concepts

The Acid-Base Concept

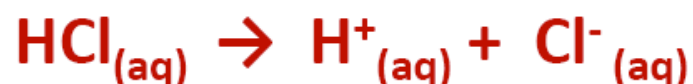
- There are many acid-base definitions, each at times useful
- Acid-Base concepts are not facts or even theories, but are useful generalizations for classification, and organization
- Acid-Base concepts are powerful ways to explain data and predict trends



The Arrhenius Theory

- Svante August Arrhenius (1859 –1927)

- Acid: Substance that produces hydrogen ions in water solution.



- Base: Substance that produces hydroxide ions in water solution.



- An acid neutralizes a base





The Arrhenius Theory

- Acid strength depends on the amount of hydrogen ions produced.

Definition includes acids such as HCl, HBr, HI, HNO_3 , H_2SO_4 , HSO_4^- , $\text{HC}_2\text{H}_3\text{O}_2$, etc.

- Base strength depends on amount of hydroxide ions produced.

Definition includes bases such as NaOH, KOH, Ca(OH)_2 , Mg(OH)_2 , Al(OH)_3 , etc.

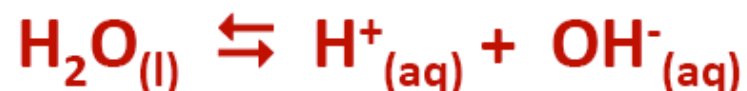


The Arrhenius Theory

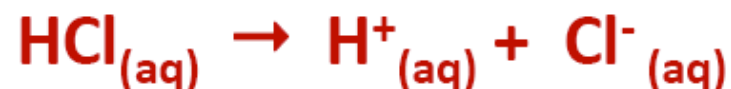
- **Problems with the Arrhenius Theory**
 - The solvent is limited to water, but water is not involved in the acid-base reaction
 - A solution of CO_2 in water is acidic, but H_2CO_3 exists at a concentration less than 1% of the CO_2
 - A solution of NH_3 in water is basic, but NH_4OH does not exist (Note: the formula NH_4OH was invented by Arrhenius to explain the basic nature of NH_3 solutions)
 - The reaction of HCl and NH_3 results in an acidic solution

A Generalized Arrhenius Theory

The solvent (water) can ionize to produce H^+ and OH^- ions

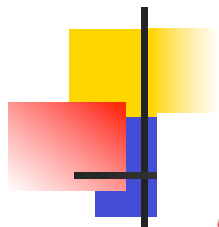


Acid: Substance that increases the concentration of hydrogen ions in solution.



A strong acid is 100% dissociated

A weak acid is only slightly dissociated



A Generalized Arrhenius Theory

Base: Substance that increases the concentration of hydroxide ions in water solution.



A strong base is 100% dissociated

A weak base is only slightly dissociated

Hydrolysis reactions can change H^+ and OH^- concentration in water solution





A Generalized Arrhenius Theory

Solvents other than water can be used:

The solvent can ionize to produce positive and negative ions

Example: liquid ammonia, NH_3

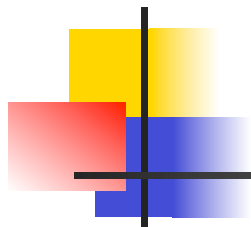


Acid: Substance that increases the concentration of the positive ion in solution.



Base: Substance that increases the concentration of the negative ion in water solution.



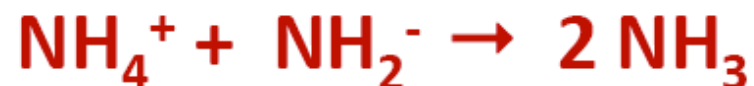


A Generalized Arrhenius Theory

Solvents other than water (continued)

Neutralization produces the solvent:

Example: In liquid ammonia, NH_3





The Brønsted–Lowry Theory

**Johannes Nicolaus Brønsted (1879-1947)
and Thomas Martin Lowry (1874-1936)**

**independently proposed the proton
definition of acids and bases in 1923**

Quoting Brønsted:

**"... acids and bases are substances that are
capable of splitting off or taking up hydrogen
ions, respectively."**

or

**An acid-base reaction consists of the transfer of
a proton (or hydrogen ion) from an acid to a
base**





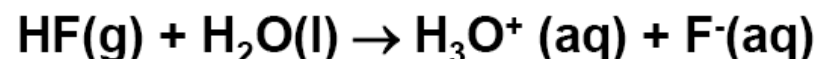
Acidi e Basi

Teoria di Brønsted-Lowry, 1923

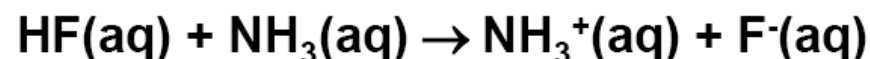
Acido: Sostanza capace di donare un protone ad una che può di accettarlo

Base: Sostanza capace di accettare un protone da una capace di donarlo

Esempi :

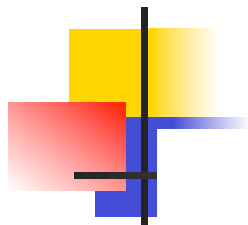


HF dona un protone: acido di Brønsted ; H₂O accetta un protone: base.



HF è un acido di Brønsted ; NH₃, accetta un protone: base.

H₂O può comportarsi sia da acido che da base (è anfotera)



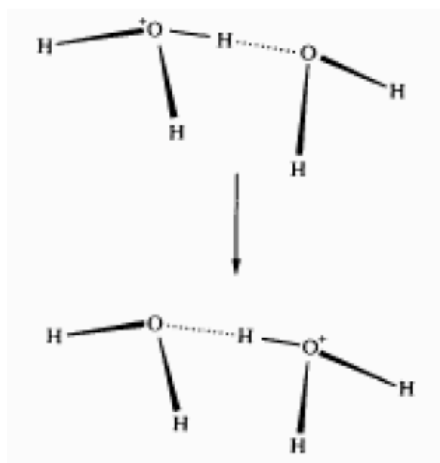
Il protone in acqua e in altri ambienti

In H_2O ed anche in specie solide, non si ha lo ione H^+ libero

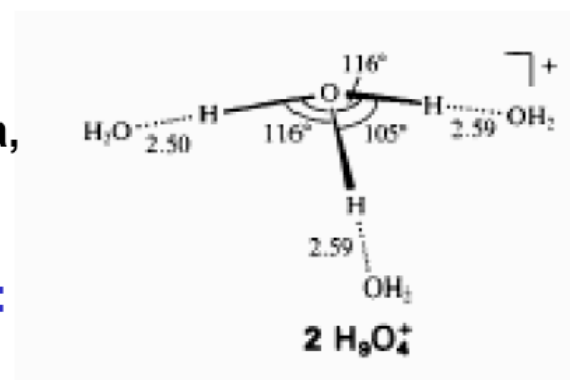
Lo ione **idronio** H_3O^+ è stato individuato **in specie cristalline** come:

$\text{H}_3\text{O}^+\text{ClO}_4^-(s)$ $d(\text{O}-\text{H}) = 1.01 \text{ \AA}$, $\text{H}-\text{O}-\text{H}$ ca. 110°

Studi **in fase gas** (spettroscopia di massa) suggeriscono che H_3O^+ esista in **cluster con altre 20 molecole di H_2O** : $\text{H}^+(\text{H}_2\text{O})_{21}$



In acqua, H_3O^+ dà luogo ad una estesa rete di legami ad idrogeno: misure di conducibilità, e di mobilità ionica, sono in accordo con il **modello di Eigen et al.:** $\text{H}_9\text{O}_4^+(\text{aq})$





Mobilità del protone in acqua: scambio veloce



$k \rightarrow [\text{H}_3\text{O}^+][\text{accettore1}] \quad k \rightarrow \approx 10^{11} \text{ M}^{-1} \text{ s}^{-1}$, controllata dalla diffusione

k (trasferimento inverso) = $k \leftarrow [\text{donatore2}][\text{accettore2}]$

$k \rightarrow \approx 10^{-5} - 10^7 \text{ M}^{-1} \text{ s}^{-1}$ controllata da energia di attivazione reazione inversa

Table 5.1. Rate constants* for aqueous proton transfer reactions at 25°C

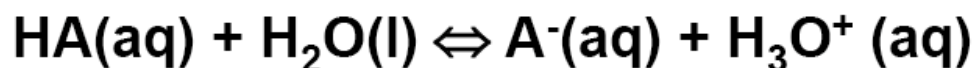
Reaction	$k_{\rightarrow}/(\text{M}^{-1} \text{s}^{-1})$	$k_{\leftarrow}/(\text{M}^{-1} \text{s}^{-1})$
$\text{H}_3\text{O}^+ + \text{OH}^- \rightleftharpoons \text{H}_2\text{O} + \text{H}_2\text{O}$	1.4×10^{11}	2.5×10^{-5}
$\text{H}_3\text{O}^+ + \text{SO}_4^{2-} \rightleftharpoons \text{HSO}_4^- + \text{H}_2\text{O}$	1×10^{11}	7×10^7
$\text{H}_3\text{O}^+ + \text{NH}_3 \rightleftharpoons \text{NH}_4^+ + \text{H}_2\text{O}$	4.3×10^{10}	8.4×10^5
$\text{OH}^- + \text{NH}_4^+ \rightleftharpoons \text{H}_2\text{O} + \text{NH}_3$	3.4×10^{10}	6×10^5

* $k_{\rightarrow}$ is the rate constant for the forward reaction and $k_{\leftarrow}$ is that for the reverse reaction.

Nelle reazioni acido-base in soluzione si raggiunge l'equilibrio molto velocemente



Forza degli acidi



$$K_a = [\text{a}(\text{H}_3\text{O}^+) \text{a}(\text{A}^-)] / [\text{a}(\text{HA}) \text{a}(\text{H}_2\text{O})]$$

dove $a(X)$ è la concentrazione termodinamica effettiva, o attività

Per soluti, all'equilibrio : $a(X) = \gamma[X]$ γ = coefficiente di attività

Per $[X] < 10^{-3} \text{ M}$, $\gamma \approx 1$

L'attività di acqua pura $a(\text{H}_2\text{O})$ a $P = 1 \text{ bar}$ è 1 ;

In soluzioni diluite cambia poco.

$$K_a = [\text{H}_3\text{O}^+][\text{A}^-]/[\text{HA}]$$

In acqua per K_a e K_b della sua base coniugata si ha che:

$$K_a K_b = K_w = 10^{-14} \text{ e quindi } \text{p}K_a + \text{p}K_b = \text{p}K_w = 14$$

Forza di acidi in acqua (espressa come K_A e pK_A)

Table 5.2. Acidity constants for aqueous solution at 25°C

Acid	HA	A ⁻	K_a	pK_a
Hydriodic	HI	I ⁻	10^{11}	-11
Perchloric	HClO ₄	ClO ₄ ⁻	10^{10}	-10
Hydrobromic	HBr	Br ⁻	10^9	-9
Hydrochloric	HCl	Cl ⁻	10^7	-7
Sulfuric	H ₂ SO ₄	HSO ₄ ⁻	10^2	-2
Hydronium ion	H ₃ O ⁺	H ₂ O	1	0.0
Sulfurous	H ₂ SO ₃	HSO ₃ ⁻	1.5×10^{-2}	1.81
Hydrogen sulfate ion	HSO ₄ ⁻	SO ₄ ⁻	1.2×10^{-2}	1.92
Phosphoric	H ₃ PO ₄	H ₂ PO ₄ ⁻	7.5×10^{-3}	2.12
Hydrofluoric	HF	F ⁻	3.5×10^{-4}	3.45
Pyridinium ion	HC ₅ H ₅ N ⁺	C ₅ H ₅ N	5.6×10^{-6}	5.25
Carbonic	H ₂ CO ₃	HCO ₃ ⁻	4.3×10^{-7}	6.37
Hydrogen sulfide	H ₂ S	HS ⁻	9.1×10^{-8}	7.04
Ammonium ion	NH ₄ ⁺	NH ₃	5.6×10^{-10}	9.25
Hydrocyanic	HCN	CN ⁻	4.9×10^{-10}	9.31
Hydrogen carbonate ion	HCO ₃ ⁻	CO ₃ ²⁻	4.8×10^{-11}	10.32
Hydrogen arsenate ion	HAso ₄ ²⁻	AsO ₄ ³⁻	3.0×10^{-12}	11.53
Hydrogen sulfide ion	HS ⁻	S ²⁻	1.1×10^{-12}	11.96
Hydrogen phosphate ion	HPO ₄ ²⁻	PO ₄ ³⁻	2.2×10^{-13}	12.67

I

Effetto livellante solvente: acqua

Ogni acido più forte di H_3O^+ dona un protone ad H_2O e genera H_3O^+

Nessun acido più forte di H_3O^+ può esistere in acqua

HCl ed HBr hanno la stessa forza $\Rightarrow$ danno quantitativamente H_3O^+

Poiché $\text{pK}_a(\text{H}_3\text{O}^+) = 0 \Rightarrow$ qualsiasi acido con $\text{pK}_a < 0$ si comporta allo stesso modo. Analogamente ogni acido con $\text{pK}_a > 14$ si comporta ~ allo stesso modo poiché $\text{pK}_a(\text{H}_2\text{O}) = 14$: è meno acido di H_2O

Lo stesso succede per le basi:

Ogni base più forte di OH^- estrae un protone da H_2O e genera OH^-

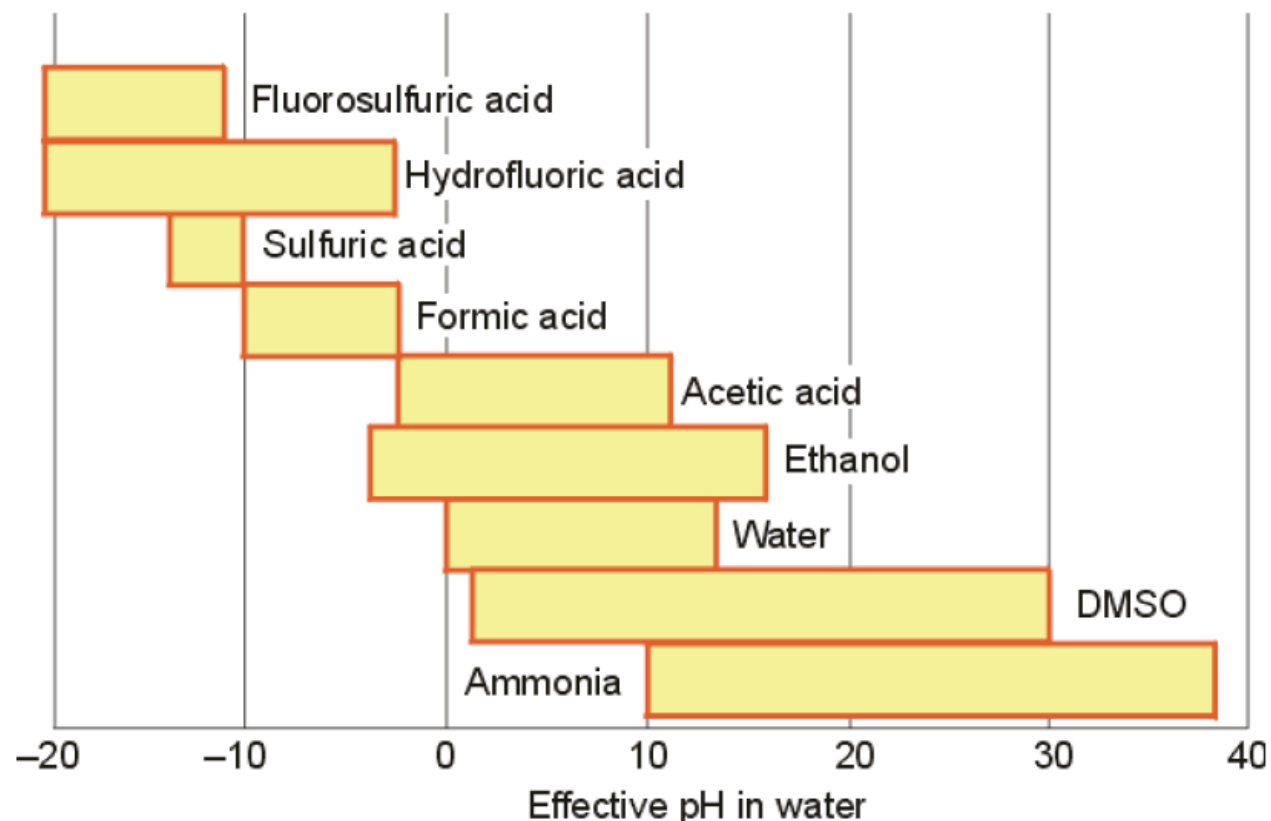
Nessuna base più forte di OH^- può esistere in acqua

NH_2^- e CH_3^- hanno la stessa forza $\Rightarrow$ danno quantitativamente OH^-

Poiché $\text{pK}_b(\text{OH}^-) = 0 \Rightarrow$ qualsiasi base con $\text{pK}_b < 0$ si comporta allo stesso modo. Ogni base con $\text{pK}_b > 14$ si comporta ~ allo stesso modo poiché $\text{pK}_b(\text{H}_2\text{O}) = 14$: è meno basica di H_2O .

La finestra di acidità e basicità studiabili in H_2O è 14 unità $\text{pK} = \text{pK}_w$

Solventi ed effetto livellante



Generalizzando: in un generico solvente SolH, per un acido HX vale la: $K_a = \frac{[H_2Sol^+][X^-]}{[HX]}$.

Tutti gli acidi con $K_a > 1$ si comportano come H_2Sol^+ se disciolti nel solvente HSol. Stesso discorso per le basi: la “finestra utile” per evidenziare la forza di acidi e basi in un dato solvente è = pK_{Sol} . Per NH_3 ho che $pK_{am} = 29$, per CH_3COOH , $pK = 13$ etc.

Superacids = acids stronger than H_2SO_4

- Hammett Acidity Function = H_0

B = nitroaniline indicator used as the base

$$H_0 = \text{p}K_{\text{BH}^+} - \log \frac{[\text{BH}^+]}{[\text{B}]}$$

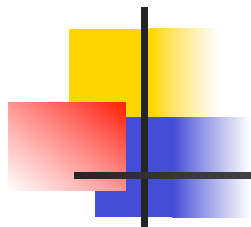
Lewis Superacids are often made by protonating an already strong acid

- This is often done using HF as the acid to be protonated
- It requires a very stable anion to make the reaction proceed
- $2 \text{HF} + 2 \text{SbF}_5 \longrightarrow \text{H}_2\text{F}^+ + \text{Sb}_2\text{F}_{11}^-$ (Fluoroantimonic acid)

Superacids

Acid		H_0
Sulfuric acid	H_2SO_4	-11.9
Hydrofluoric acid	HF	-11.0
Perchloric acid	HClO_4	-13.0
Fluorosulfonic acid	HSO_3F	-15.6
Trifluoromethanesulfonic acid (triflic acid)	HSO_3CF_3	-14.6
Magic Acid*	$\text{HSO}_3\text{F-SbF}_5$	-21.0 to -25 (depending on concentration)
Fluoroantimonic acid	HF-SbF ₅	-21 to -28 (depending on concentration)

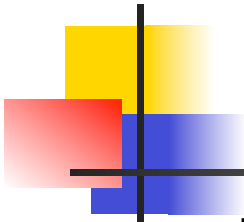
Note: *Magic Acid is a registered trademark of Cationics, Inc., Columbia, SC.



Acids and Bases

Factors that Determine Acid Strength:

- Anything that stabilizes a conjugate base $A:^-$ makes the starting acid $H-A$ more acidic.
- Four factors affect the acidity of $H-A$. These are:
 - ➡ Element effects (trends in periodic table)
 - ➡ Inductive effects (electronegativity)
 - ➡ Resonance effects (multiple resonance structures)
 - ➡ Hybridization effects (sp , sp^2 , sp^3)



Acids and Bases

Factors that Determine Acid Strength:

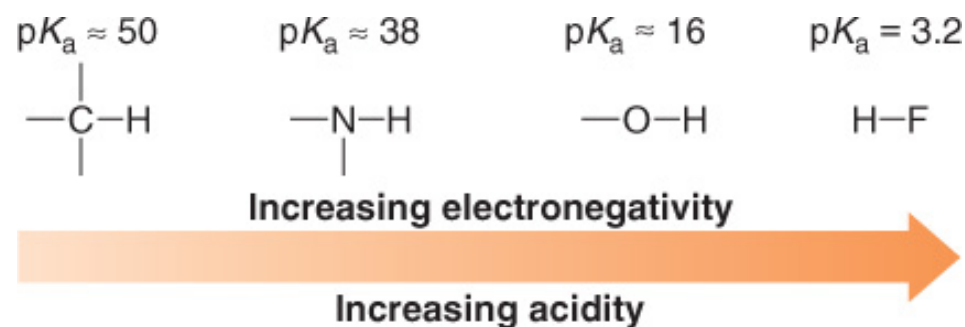
- No matter which of these factors is discussed, to compare the acidity of any two acids:
 - o Always look at the conjugate bases.
 - o Determine which conjugate base is more stable.
 - o The more stable the conjugate base, the more acidic the acid.
- The strengths of a conjugate acid and its conjugate base are inversely related.
 - A strong conjugate base has a weak conjugate acid.
 - A weak conjugate base has a strong conjugate acid.

Acids and Bases

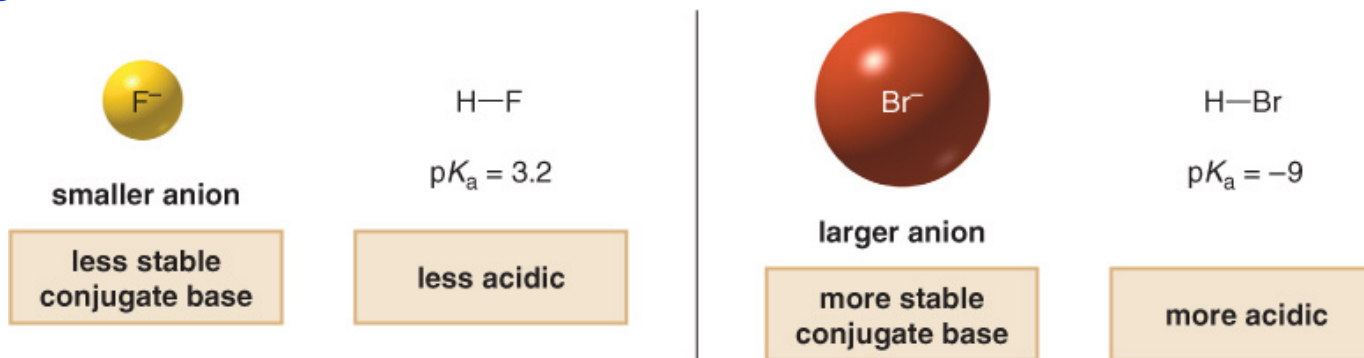
Factors that Determine Acid Strength:

Element Effects—Trends in the Periodic Table.

Across a row of the periodic table, the acidity of H—A increases as the electronegativity of A increases.



Positive or negative charge is stabilized when it is spread over a larger volume.

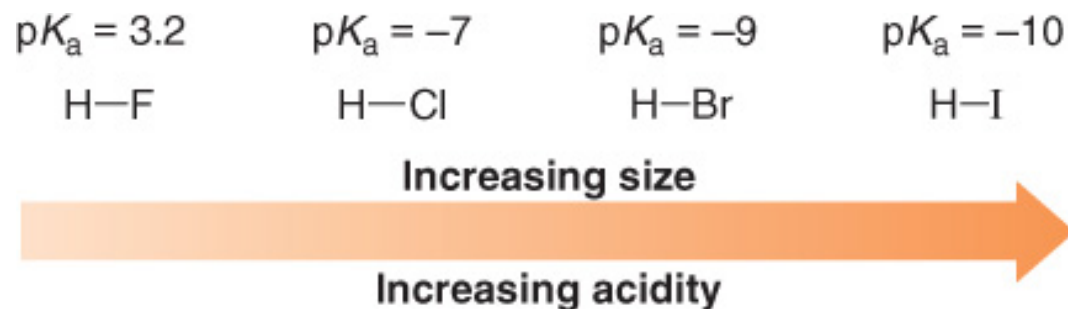


Acids and Bases

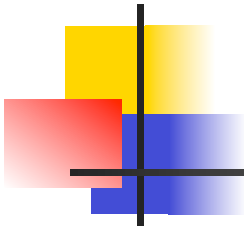
Factors that Determine Acid Strength:

Element Effects—Trends in the Periodic Table.

- Down a column of the periodic table, the acidity of H—A increases as the size of A increases.



- Size, and not electronegativity, determines acidity down a column.
- The acidity of H—A increases both left-to-right across a row and down a column of the periodic table.
- Although four factors determine the overall acidity of a particular hydrogen atom, element effects—the identity of A—is the single most important factor in determining the acidity of the H—A bond.



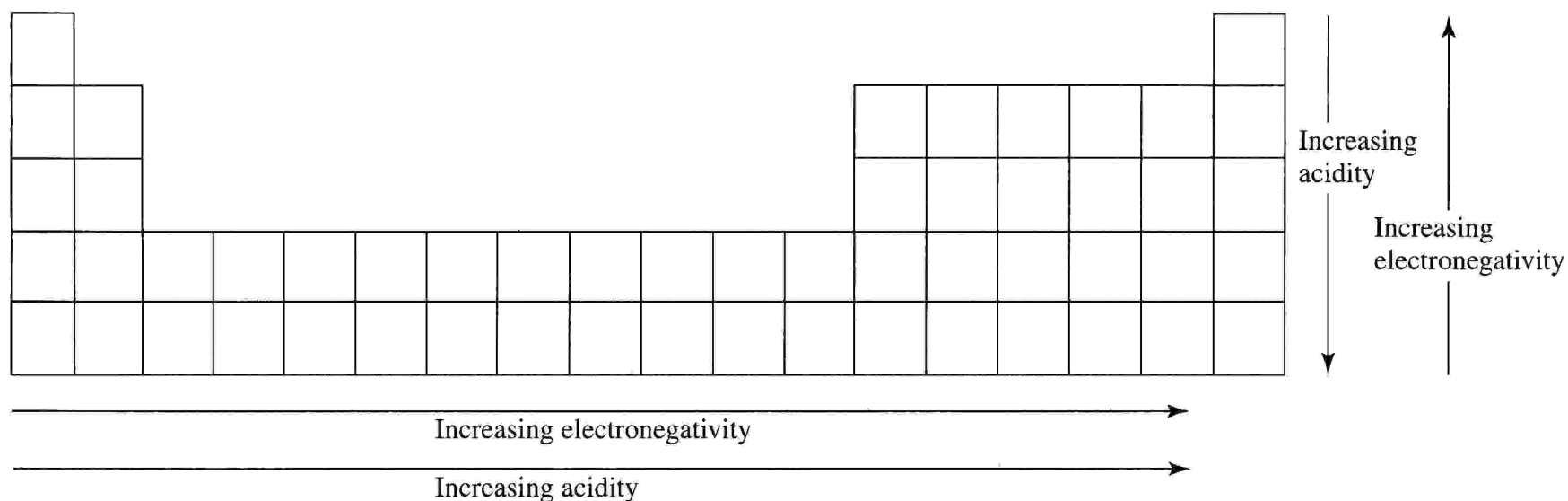
Binary Hydrogen Compounds

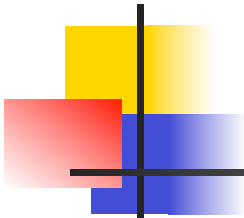
- Acidity increases down a column of the periodic table

- $\text{H}_2\text{Se} > \text{H}_2\text{S} > \text{H}_2\text{O}$
- $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$
- Conjugate bases of larger ions have lower charge density, thus a smaller attraction for H^+

- Acidity increases from left to right of the periodic table

- $\text{NH}_3 < \text{H}_2\text{O} < \text{HF}$
- The more electronegative the conjugate base is, the easier is it for H^+ to dissociate

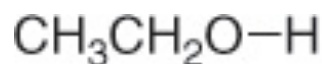




Acids and Bases

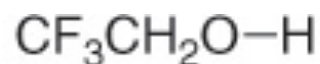
Factors that Determine Acid Strength: Inductive Effects

- An inductive effect is the pull of electron density through σ bonds caused by electronegativity differences between atoms.
- In the example below, when we compare the acidities of ethanol and 2,2,2-trifluoroethanol, we note that the latter is more acidic than the former.



ethanol

$$\text{p}K_{\text{a}} = 16$$



2,2,2-trifluoroethanol

$$\text{p}K_{\text{a}} = 12.4$$

← stronger acid

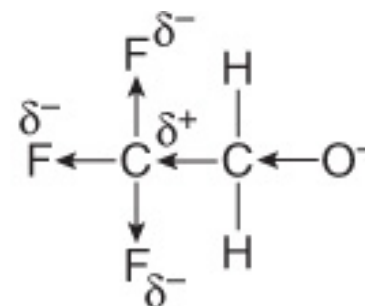
Acids and Bases

Factors that Determine Acid Strength: Inductive Effects

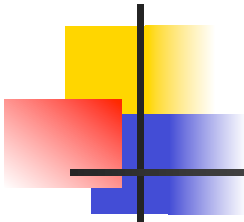
- The reason for the increased acidity of 2,2,2-trifluoroethanol is that the three electronegative fluorine atoms stabilize the negatively charged conjugate base.
- This effect is limited to a three bond distance.



No additional electronegative atoms stabilize the conjugate base.



CF_3 withdraws electron density, stabilizing the conjugate base.



Acids and Bases

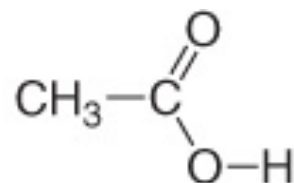
Factors that Determine Acid Strength: **Resonance Effects**

- Resonance is a third factor that influences acidity.
- In the example below, when we compare the acidities of ethanol and acetic acid, we note that the latter is more acidic than the former.



ethanol

$\text{p}K_{\text{a}} = 16$



acetic acid

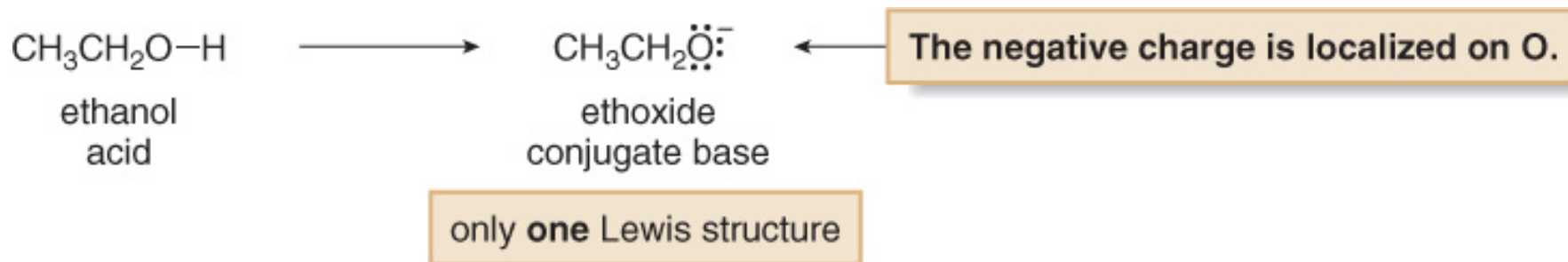
$\text{p}K_{\text{a}} = 4.8$

← **stronger acid**

Acids and Bases

Factors that Determine Acid Strength: **Resonance Effects**

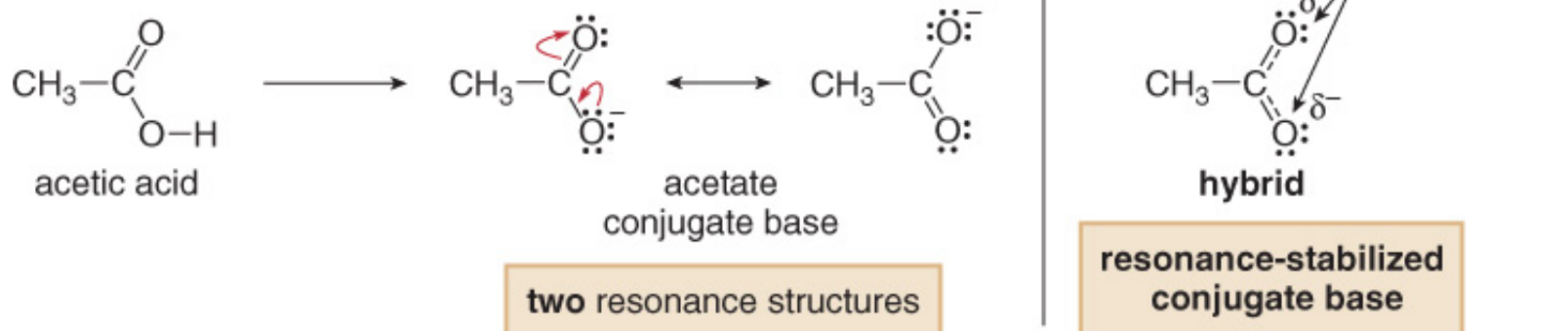
- When the conjugate bases of the two species are compared, it is evident that the conjugate base of acetic acid enjoys resonance stabilization, whereas that of ethanol does not.



Acids and Bases

Factors that Determine Acid Strength: **Resonance Effects**

- Resonance delocalization makes CH_3COO^- more stable than $\text{CH}_3\text{CH}_2\text{O}^-$, so CH_3COOH is a stronger acid than $\text{CH}_3\text{CH}_2\text{OH}$.



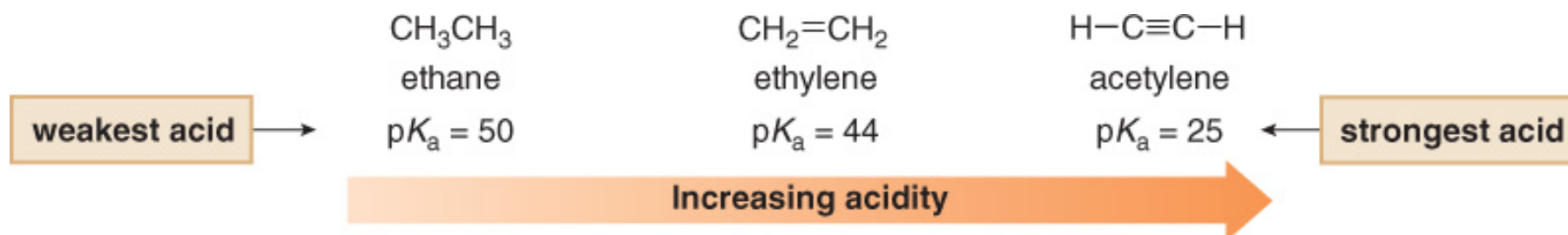
- The acidity of $\text{H}-\text{A}$ increases when the conjugate base A^- is resonance stabilized.

Acids and Bases

Factors that Determine Acid Strength: Hybridization Effects

- The final factor affecting the acidity of H—A is the hybridization.

Let us consider the relative acidities of three different compounds containing C—H bonds.



- The higher the percent of *s*-character of the hybrid orbital, the closer the lone pair is held to the nucleus, and the more stable the conjugate base.

Acids and Bases

Factors that Determine Acid Strength: Hybridization Effects

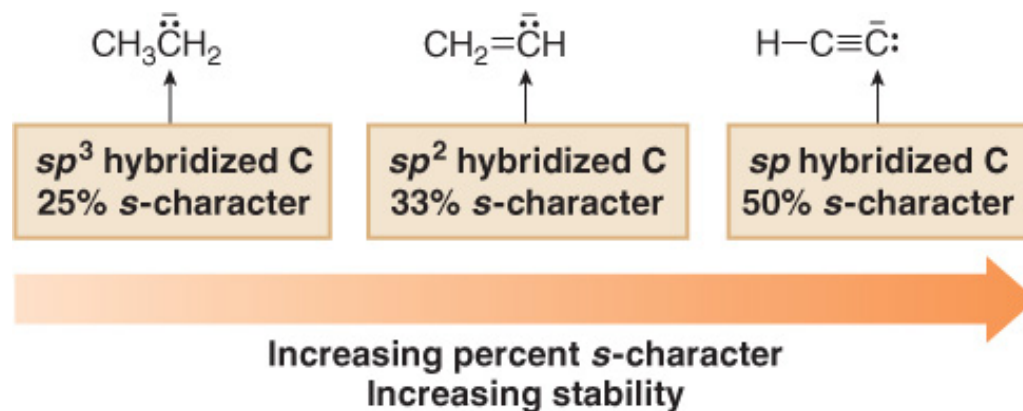
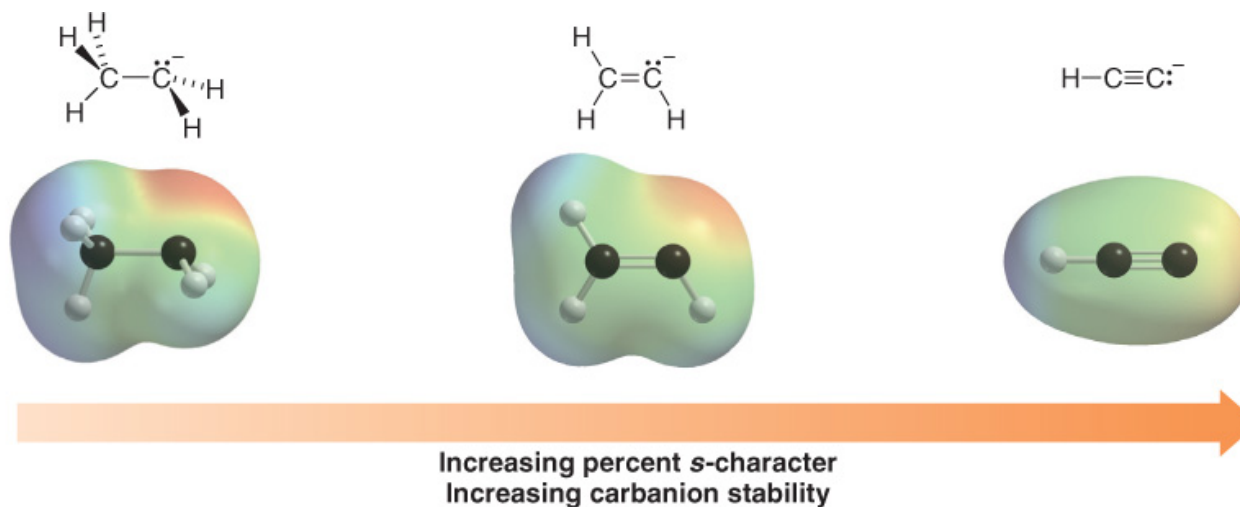


Figure 2.4 Electrostatic Potential plots



- As the lone pair of electrons is pulled closer to the nucleus, the negatively charged carbon appears less intensely red.

Acids and Bases

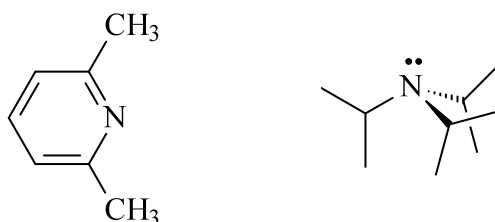
Factors that Determine Acid Strength: Summary of Effects

Figure 2.5 Summary of the factors that determine acidity

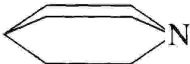
Factor	Example
1. Element effect: The acidity of H–A increases both left-to-right across a row and down a column of the periodic table.	—C—H —N—H —O—H H—F —S—H H—Cl H—Br H—I
2. Inductive effects: The acidity of H–A increases with the presence of electron-withdrawing groups in A.	$\text{CH}_3\text{CH}_2\text{O—H}$ $\text{CF}_3\text{CH}_2\text{O—H}$ more acidic
3. Resonance effects: The acidity of H–A increases when the conjugate base A:^- is resonance stabilized.	$\text{CH}_3\text{CH}_2\text{O—H}$ $\text{CH}_3\text{COO—H}$ more acidic
4. Hybridization effects: The acidity of H–A increases as the percent s-character of A:^- increases.	CH_3CH_3 $\text{CH}_2=\text{CH}_2$ $\text{H—C}\equiv\text{C—H}$

Steric Effects

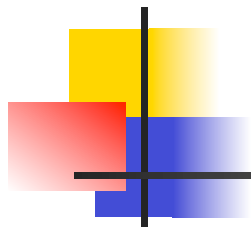
- Steric bulk can repel an acid-base partner, modifying the acid-base strength
 - F = front strain = direct steric interference at the site of interaction
 - B = back strain = bulky groups interfere opposite the interaction site upon binding as the molecule adjusts its VSEPR geometry (BF₃ example)



- The order of basicity can scramble depending on bulk of the acid

Amine	ΔH of hydrogen ion addition (kJ/mol)	pK_b (aqueous)	ΔH of adduct formation		
			BF ₃ (order)	BMe ₃ (kJ/mol)	B(<i>t</i> -Bu) ₃ (order)
NH ₃	-846	4.75	4	-57.53	2
CH ₃ NH ₂	-884	3.38	2	-73.81	1
(CH ₃) ₂ NH	-912	3.23	1	-80.58	3
(CH ₃) ₃ N	-929	4.20	3	-73.72	4
(C ₂ H ₅) ₃ N	-958			~-42	
Quinuclidine	-967			-84	
					
Pyridine	-912			-74.9	

SOURCES: *Hydrogen ion addition*: P. Kebarle, *Ann. Rev. Phys. Chem.*, **1977**, 28, 445. *Aqueous pK values*: N. S. Isaacs, *Physical Organic Chemistry*, Longman/Wiley, New York, 1987, p. 213. *Adduct formation*: H. C. Brown, *J. Chem. Soc.*, **1956**, 1248.



Solvation

- Solvation is interaction with solvent molecules
- Basicity in water: $\text{NHMe}_2 > \text{NH}_2\text{Me} > \text{NMe}_3 > \text{NH}_3$
 - By induction, the more substituted amine should be the most basic
 - This amine has less H's to interact with water



- Acidità di Brønsted e proprietà periodiche

1. Acquo-complessi: il protone acido è legato a molecole d'acqua coordinate ad un metallo (tipicamente) di transizione.

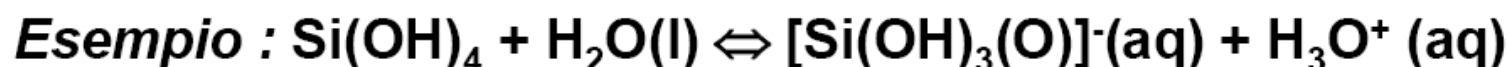


come in :



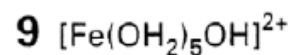
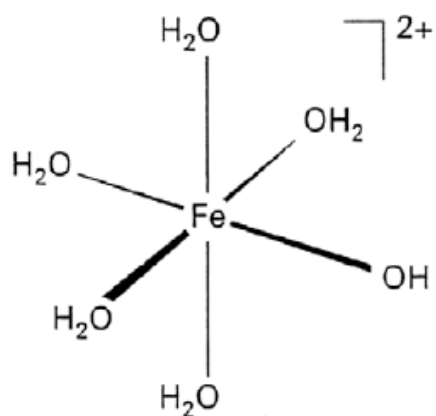
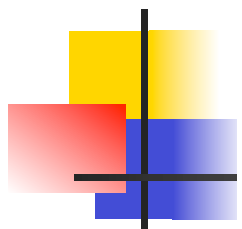
2. Idrossiacidi: il protone acido sta su un gruppo OH

NON *adiacente* a gruppi oxo (E=O)

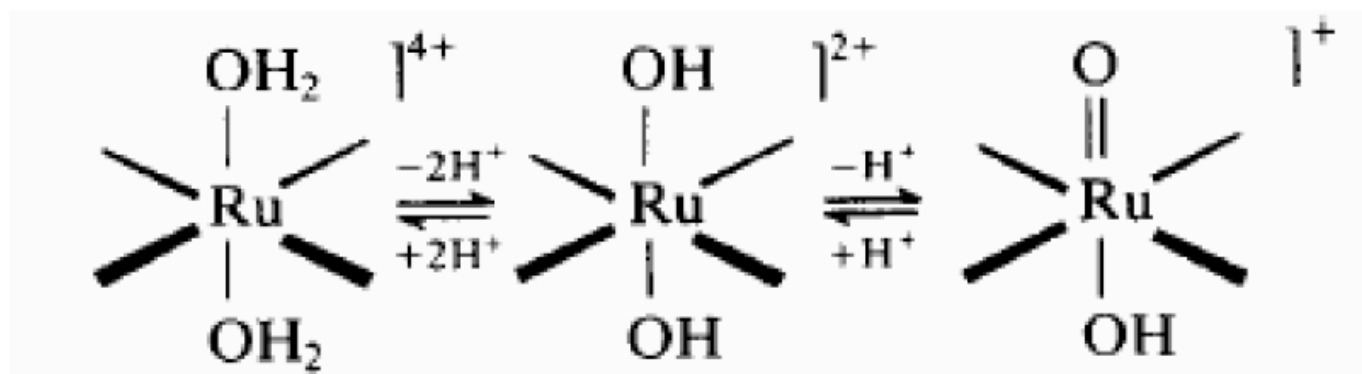


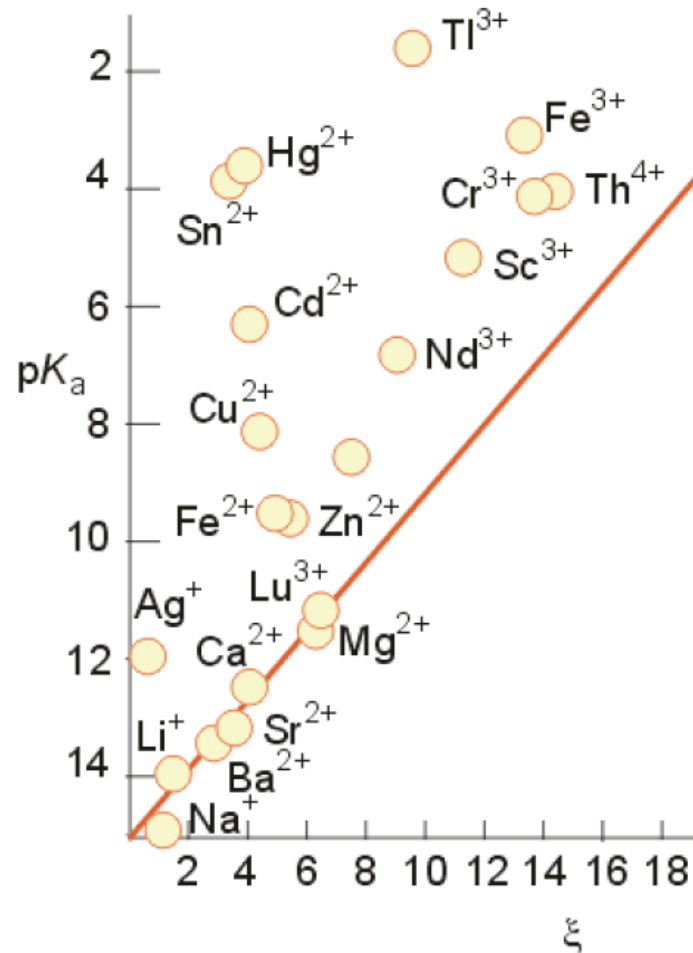
3. Oxoacidi : il protone acido sta su un gruppo OH *adiacente* a gruppi oxo (E =O)





Le tre classi possono essere pensate come stadi successivi di deprotonazione:





ACQUO-COMPLESSI

L'acidità negli acquo-complessi dipende:

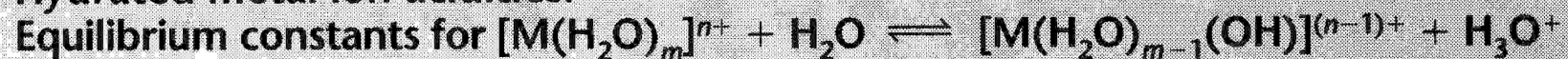
- 1) dalla carica z del metallo centrale
- 2) dal raggio ionico del metallo
- 3) dal grado di covalenza del legame M-OH

Modello elettrostatico

pK_a (in fase gas) di un acquo-complesso dipende dal lavoro L necessario a portare un protone dalla sua posizione nel complesso: $[r_{(M-O)} + d_{(H_2O)}]$ fino a distanza infinita. Nel modello elettrostatico 1) :

$L_{ele} = \Delta G^\circ = -RT \ln K_a = \propto \xi = z^2/(r+d)$
 (z = carica ione, $d_{(H_2O)}$ = diametro H_2O , ξ = parametro elettrostatico, $r = r_+$)

Cationi sulla retta ben descritti dal modello elettrostatico. Quelli sopra la retta sono più acidi: la carica positiva centrale è parzialmente delocalizzata anche sugli atomi di O connessi (modello parzialmente covalente)

Hydrated metal ion acidities:

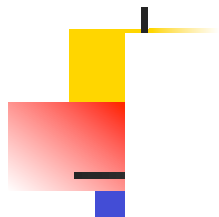
<i>Metal ion</i>	K_a	<i>Metal ion</i>	K_a
Fe^{3+}	6.7×10^{-3}	Fe^{2+}	5×10^{-9}
Cr^{3+}	1.6×10^{-4}	Cu^{2+}	5×10^{-9}
Al^{3+}	1.1×10^{-5}	Ni^{2+}	5×10^{-10}
Sc^{3+}	1.1×10^{-5}	Zn^{2+}	2.5×10^{-10}

4) The stronger acid the cation is, the less soluble the hydroxide complex is. OH^- can't dissociate to dissolve because of strong charge attraction.

We can use this property to estimate the acid strength of the cation

Solubility product constants:

<i>Metal hydroxide</i>	K_{sp}	<i>Metal hydroxide</i>	K_{sp}
$Fe(OH)_3$	6×10^{-38}	$Fe(OH)_2$	8×10^{-16}
$Cr(OH)_3$	7×10^{-31}	$Cu(OH)_2$	2.2×10^{-20}
$Al(OH)_3$	1.4×10^{-34}	$Ni(OH)_2$	2×10^{-15}
$Zn(OH)_2$	7×10^{-18}	$Mg(OH)_2$	1.1×10^{-11}



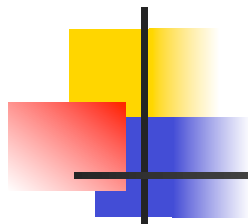
Oxoacidi (ossiacidi):

Regole di Pauling

1. Per un ossiacido di formula : $O_pE(OH)_q$, $pK_a \approx 8 - 5p (\pm 1)$
2. Acidi poliprotici ($q > 1$) hanno pK_a successive che crescono di 5 unità/ protone

The structure and pK_a values of oxoacids

$p = 0$	$p = 1$		$p = 2$	$p = 3$
$HO-Cl$ 7.2	$\begin{array}{c} O \\ \\ HO-C-OH \end{array}$ 3.6		$\begin{array}{c} O \\ \\ O-N-OH \end{array}$ -1.4	
$\begin{array}{c} OH \\ \\ HO-Si-OH \\ \\ OH \end{array}$ 10	$\begin{array}{c} O \\ \\ HO-P-OH \\ \\ OH \end{array}$ 2.1, 7.4, 12.7	$HO-Cl-O$ 2.0	$\begin{array}{c} O \\ \\ O=S-OH \\ \\ OH \end{array}$ -2.0, 1.9	$\begin{array}{c} O \\ \\ O=Cl-OH \\ \\ O \end{array}$ -10
$\begin{array}{c} OH \\ \\ HO-Te-OH \\ \\ OH \end{array}$ 7.8, 11.2	$\begin{array}{c} O \\ \\ HO-I-OH \\ \\ OH \end{array}$ 1.6, 7.0	$\begin{array}{c} O \\ \\ HO-P-H \\ \\ OH \end{array}$ 1.8, 6.6	$\begin{array}{c} O \\ \\ O-Cl-OH \\ \\ O \end{array}$ -1.0	
$\begin{array}{c} OH \\ \\ HO-B-OH \end{array}$ 9.1 [†]	$\begin{array}{c} O \\ \\ HO-As-OH \\ \\ OH \end{array}$ 2.3, 6.9, 11.5	$\begin{array}{c} HO-Se-O \\ \\ OH \end{array}$ 2.6, 8.0		



Oxoacidi (ossiacidi) : Regole di Pauling

1. Per un ossiacido di formula : $O_pE(OH)_q$, $pK_a = 8 - 5p (\pm 1)$

Idrossiacidi neutri hanno $p=0$, $pK_a \approx 8$

Cl-OH pK_a 7.2 ; $Si(OH)_4$ pK_a 10 $Te(OH)_6$ pK_a 7.8 ;

Ossiacidi con $p = 1$, $pK_a \approx 3$

H_2CO_3 pK_a 3.6; H_3PO_4 pK_a 3.1 $HClO_2$ pK_a 2.0

Ossiacidi con $p=2$, $pK_a \approx -2$

H_2SO_4 pK_a -2.0 HNO_3 pK_a -1.4

2. Acidi poliprotici ($q > 1$): pK_a successive maggiori di 5 unità/ protone

H_2SO_4 pK_a -2.0 ; HSO_4^- pK_a +1.9

Per l'acido fosforico, H_3PO_4 $pK_a(1,2,3) = 2.1, 7.4, 12.7$

Per l'acido arsenico, H_3AsO_4 $pK_a(1,2,3) = 2.3, 6.9, 11.5$



Anomalie apparenti rispetto alle regole di Pauling

Per H_2CO_3 , pK_a viene data normalmente 6.4 (Pauling ≈ 3)

H_2CO_3 è veramente meno acido di quanto previsto? In acqua, si ha l'equilibrio: $\text{CO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{OC}(\text{OH})_2(\text{aq})$ $\text{pK} \approx 1.5$

si forma circa l'1% di H_2CO_3 ed il 99% è sotto forma di CO_2 !

Tenendo conto di questo equilibrio, $\text{pK}_a (\text{H}_2\text{CO}_3) = 3.6$

Per l'acido solforoso, H_2SO_3 , pK_{a1} viene data 1.8 (Pauling ≈ 3)

H_2SO_3 è veramente più acido di quanto previsto ?

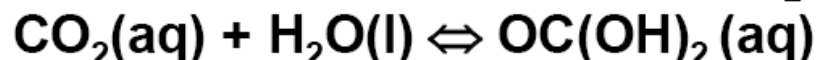
In acqua, si ha l'equilibrio :

$\text{SO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_2\text{SO}_3(\text{aq})$ $\text{pK} \approx 9$

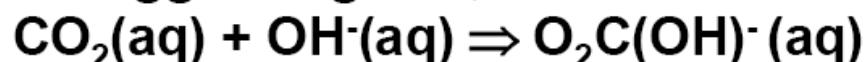
+ vari altri equilibri, che formano $\text{S}_2\text{O}_5^{2-}$ e composti con legami S-H

Ossidi anidri

Ossidi acidi: reagiscono con $\text{H}_2\text{O}(\text{l})$ a dare H_3O^+ o con OH^- a dare H_2O :



a maggior ragione, sono anche in grado di reagire con basi acquose :



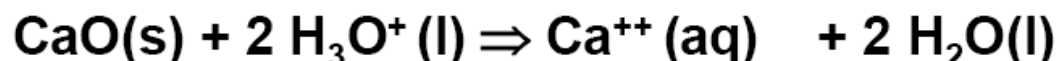
Sono covalenti quelli formati con elementi del blocco **p** o del blocco **d** in alti stati di ossidazione.

Alcuni ossidi, specialmente quelli più covalenti (e.g. : CO , SiO_2 , OsO_4), non reagiscono con $\text{H}_2\text{O}(\text{l})$: $\text{CO} + \text{H}_2\text{O}$ non dà HCOOH
(acido formico)

Ossidi basici: reagiscono tanto con $\text{H}_2\text{O}(\text{l})$ a dare OH^- che con H_3O^+ a dare H_2O :

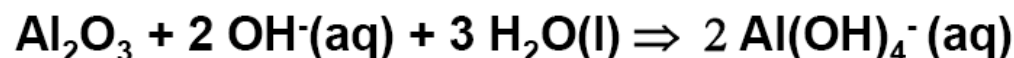
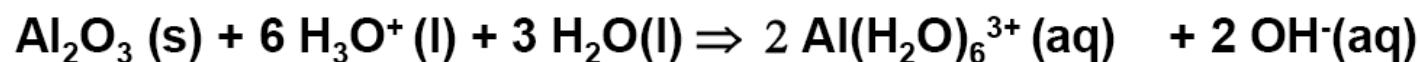


ovviamente anche con con acidi a dare $\text{H}_2\text{O}(\text{l})$



sono **essenzialmente ionici** formati con elementi del **blocco s** oppure **d** in bassi stati di ox

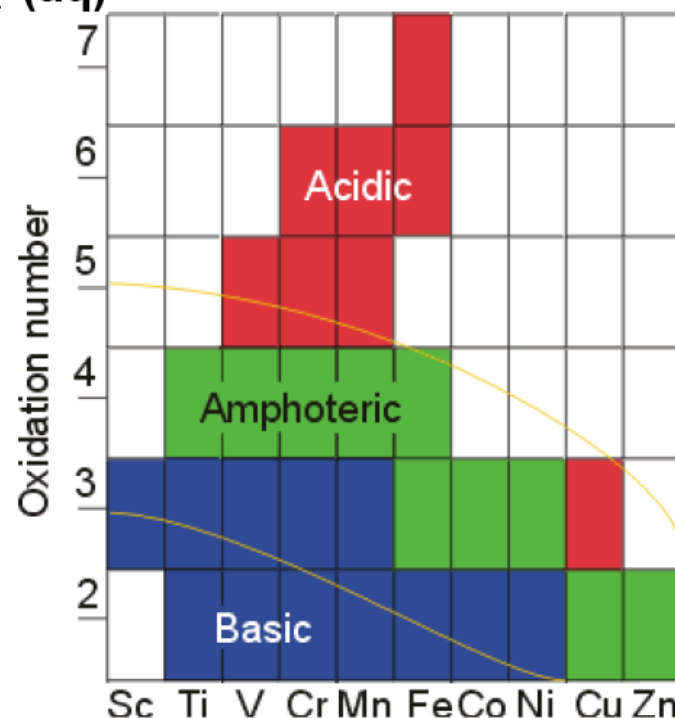
Ossidi anfoteri: reagiscono tanto con H_3O^+ che con OH^-



Acidic region

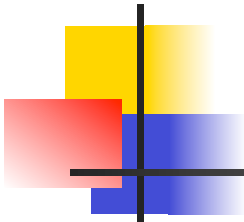
1	2	13	14	15	16	17
	Be					
		Al				
		Ga	Ge	As		
		In	Sn	Sb		
			Pb	Bi		

Basic region



Nella tavola periodica, gli elementi che danno **ossidi anfoteri** sono:

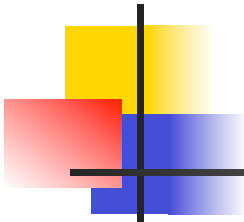
1. elementi nella zona di confine tra metalli e non metalli. (verdi: anfoteri anche in stato di ox. più alto; grigio: anfoteri in stati ox. bassi, acidi con nr. ox. + elevati)
2. molti metalli di transizione con numeri di ossidazione “intermedi”



Acids and Bases

Lewis Acids and Bases:

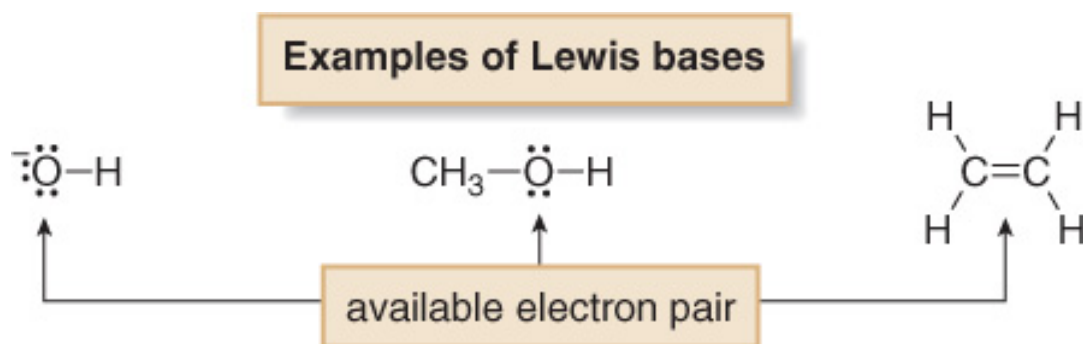
- The Lewis definition of acids and bases is more general than the Brønsted-Lowry definition.
 - A Lewis acid is an electron pair acceptor.
 - A Lewis base is an electron pair donor.
- Lewis bases are structurally the same as Brønsted-Lowry bases. Both have an available electron pair—a lone pair or an electron pair in a π bond.
- All Brønsted-Lowry acids are also Lewis acids, but the reverse is not necessarily true.

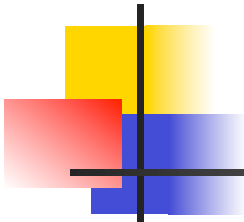


Acids and Bases

Lewis Bases:

- A Brønsted-Lowry base always donates this electron pair to a proton, but a Lewis base donates this electron pair to anything that is electron deficient.
- Common examples of Lewis bases (which are also Brønsted-Lowry bases)

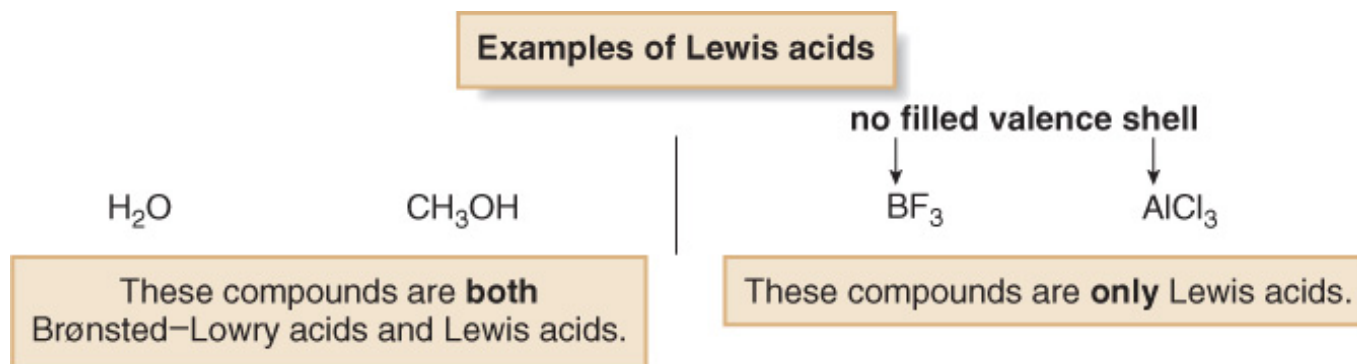




Acids and Bases

Lewis Acids:

- A Lewis acid must be able to accept an electron pair and can be any species that is electron deficient and capable of accepting an electron pair.
- Common examples of Lewis acids (which are not Brønsted-Lowry acids) include BF_3 and AlCl_3 .

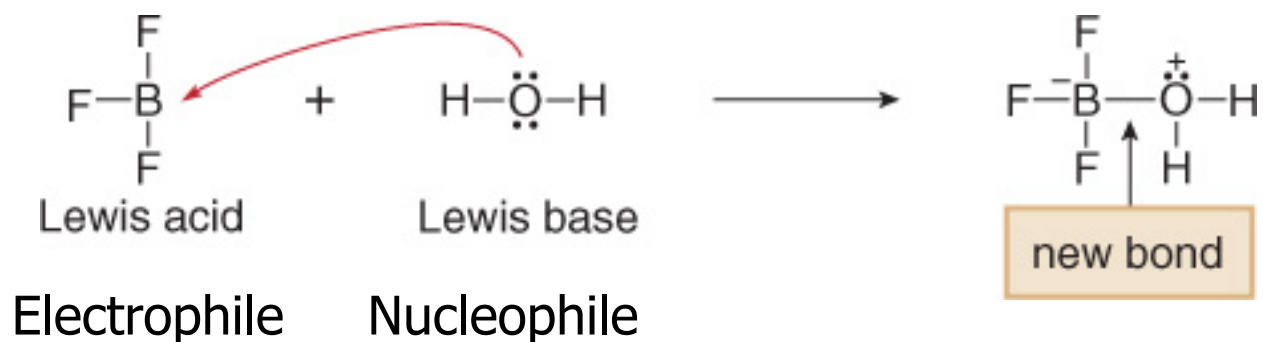


Acids and Bases

Electrophiles and Nucleophiles:

- A Lewis acid is also called an **electrophile**.
- When a Lewis base reacts with an electrophile other than a proton, the Lewis base is also called a **nucleophile**. In this example, BF_3 is the electrophile and H_2O is the nucleophile.

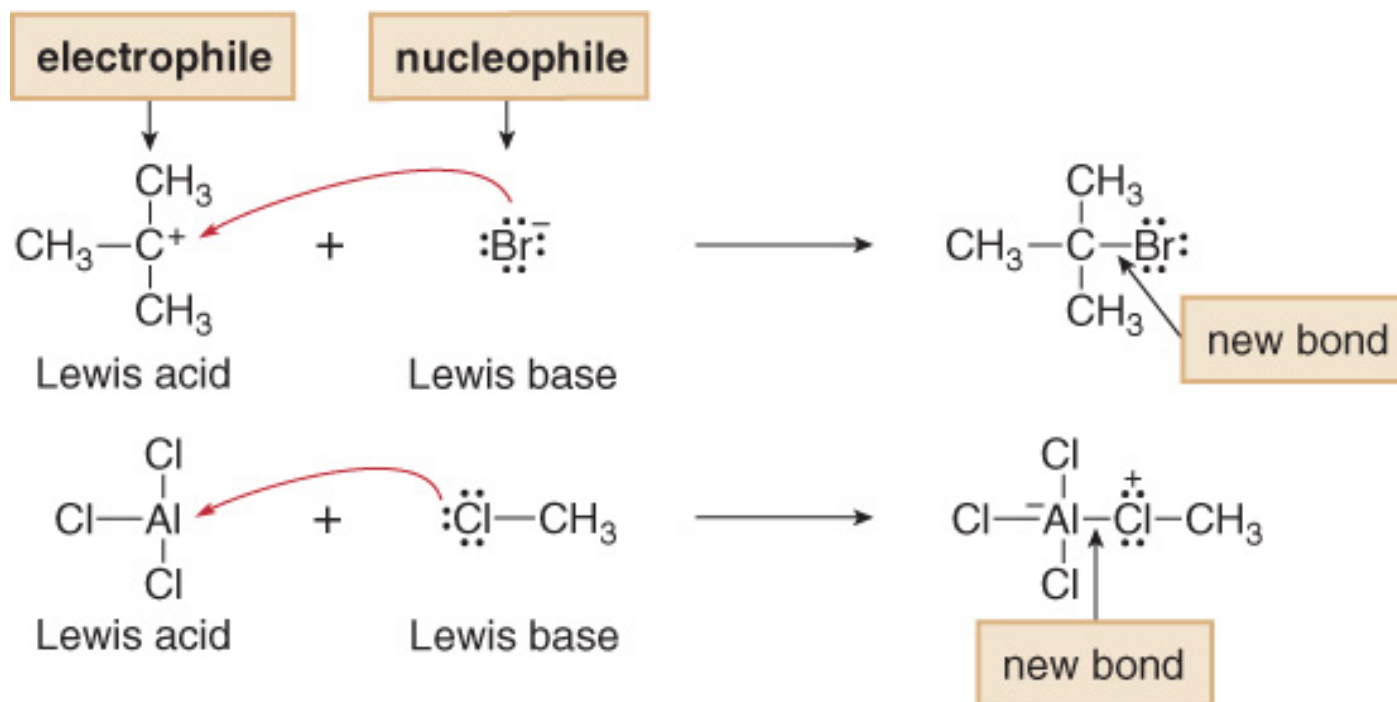
A Lewis Acid-Base Reaction:

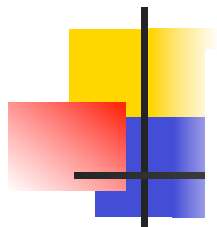


Acids and Bases

Lewis Acid-Base Reactions:

- Two other examples are shown below. Note that in each reaction, the electron pair is not removed from the Lewis base. Instead, it is donated to an atom of the Lewis acid and a new covalent bond is formed.





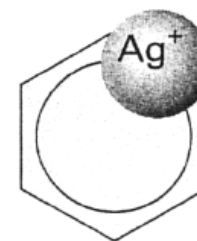
ACIDI E BASI di Lewis (1923-1930)

Acido: sostanza capace di accettare una coppia di elettroni (A)

Base: sostanza capace di donare una coppia di elettroni (:B)

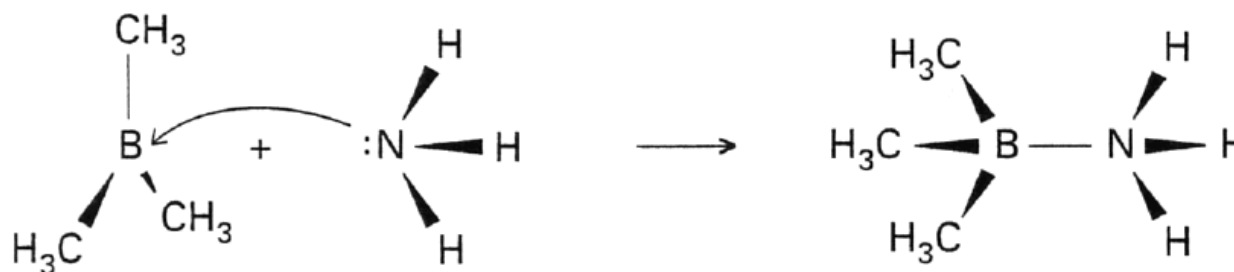
In una reazione acido-base di Lewis si forma il complesso A-B

1) Catione + :B

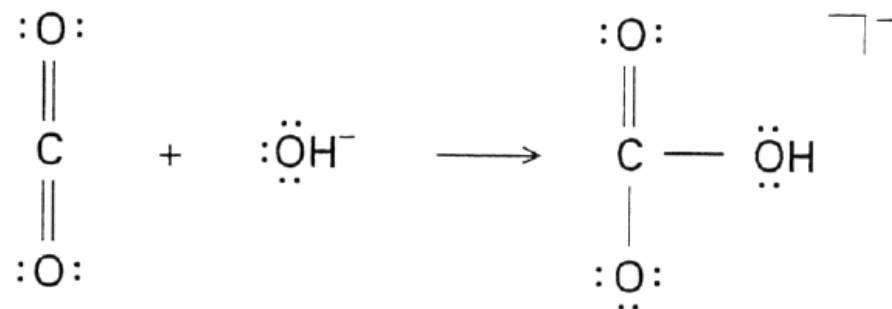


19 $[\text{C}_6\text{H}_6\text{Ag}]^+$

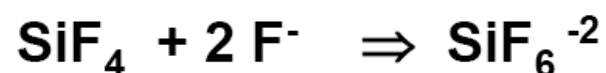
2) Specie ad ottetto incompleto $\text{A} + \text{:B} \Rightarrow \text{A:B}$



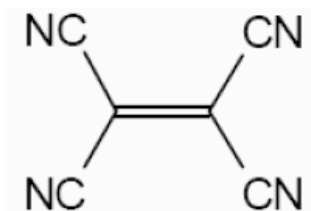
3) Specie con ottetto completo A (che si riarrangia) $A + :B \Rightarrow A:B$



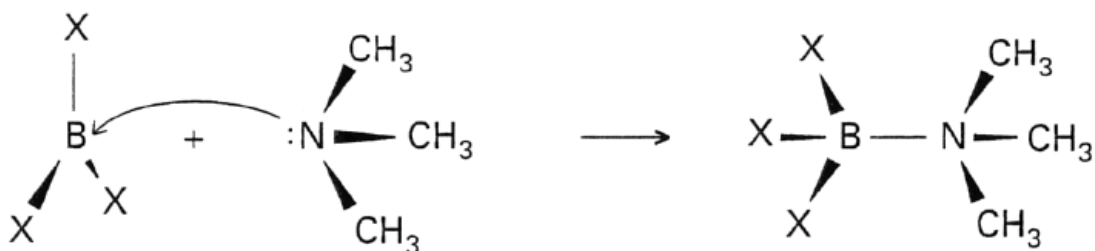
4) Specie A con ottetto completo che si espande) $A + :B \Rightarrow A:B$



5) Molecole ad ottetto completo e orbitali di non legame (o antilegame) vuoti a bassa energia (complessi Charge-Transfer = a trasferimento di carica): ad es.



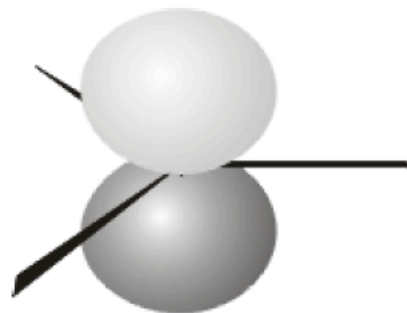
Acidi dei gruppi del Boro e del Carbonio



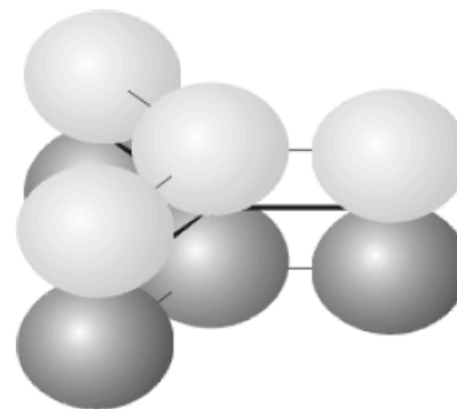
Alogenuri di Boro

L'ordine di stabilità termodinamica per complessi $\text{Me}_3\text{N}:\text{BX}_3$ è $\text{F} < \text{Cl} < \text{Br}$, e cioè inverso rispetto all'elettronegatività:

la spiegazione corrente è che la molecola BX_3 può formare legami π utilizzando l'orbitale vuoto $\text{B}(2p_z)$. Questo tipo d'interazione è max tra elementi del 2° periodo - quindi tra B e F. Viene quindi stabilizzato il BF_3 (reagenti), rispetto all'addotto (prodotti).



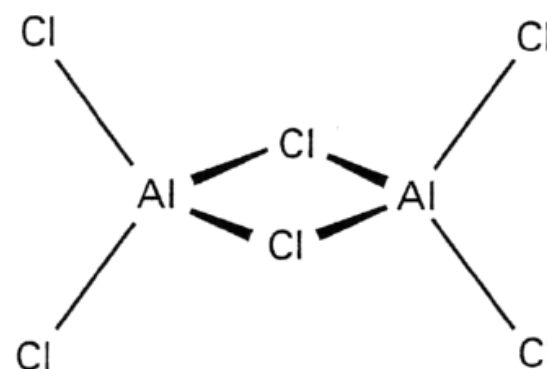
21 AlX_3 and BX_3



22

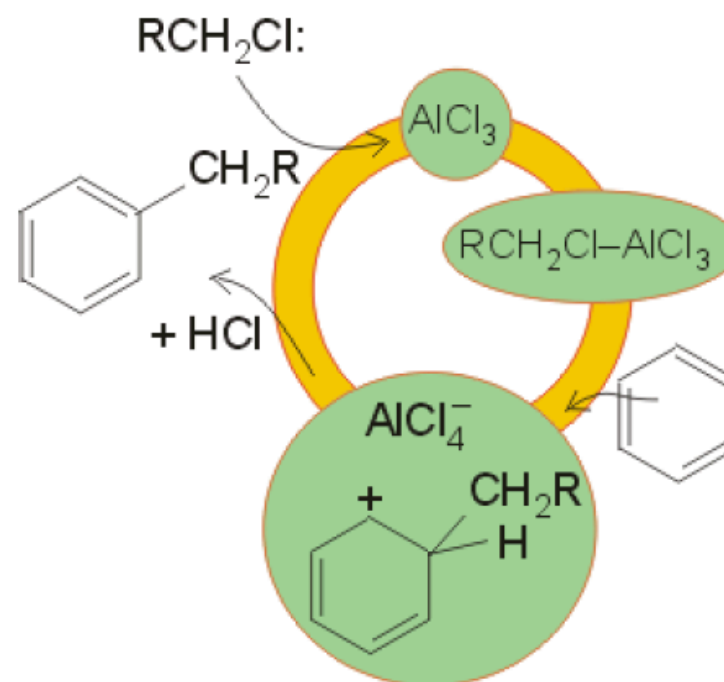
Alogenuri di Al

In fase gas si ha dimerizzazione con -Cl: che agisce da base rispetto ad AlCl_3 .

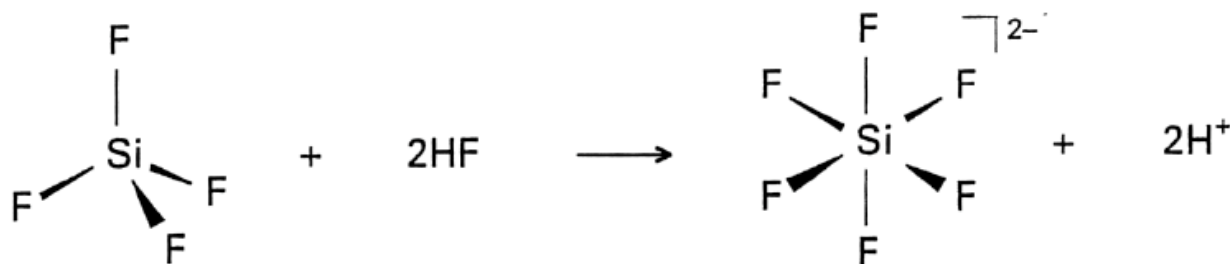


23 Al_2Cl_6

AlCl_3 . È usato come catalizzatore acido in molte reazioni organiche e.g. nelle alchilazioni e nelle acilazioni di Friedel-Crafts



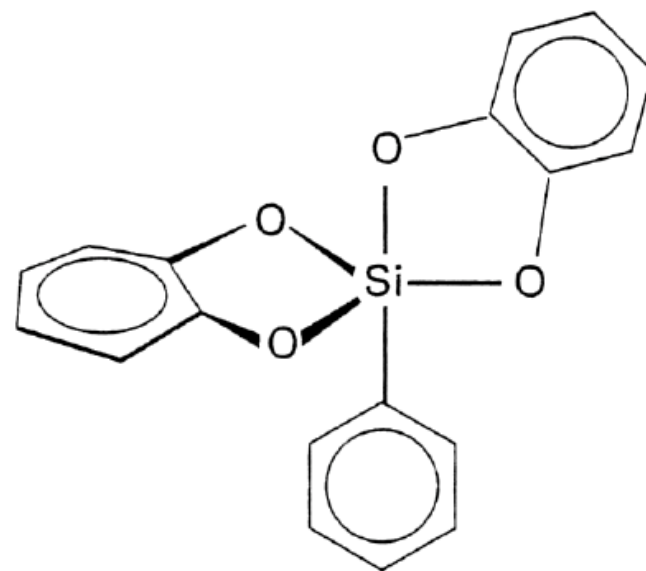
Complessi di Silicio e Stagno



Alogenuri di Silicio

Per l'ordine di acidità di specie SiX_4 si ha $\text{F} > \text{Cl} > \text{Br} > \text{I}$ che correla quindi direttamente con l'elettronegatività di X. Questo è ragionevole per la più bassa tendenza di Si rispetto a B a formare legami π .

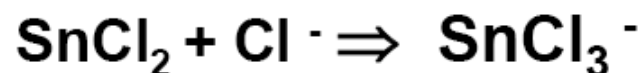
Il silicio può assumere, oltre al 4 e al 6, anche nr. di coordinazione 5 (e.g. 24)



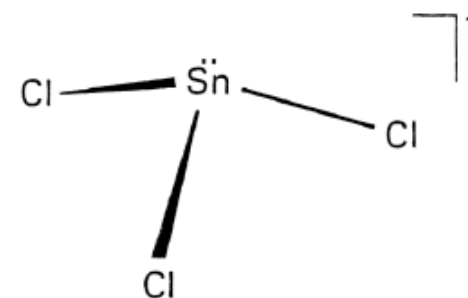
24 $[\text{Si}(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_4\text{O}_2)_2]^-$

I cloruri di Sn(II) : possono essere tanto acidi che basi di Lewis ha $F > Cl > Br$

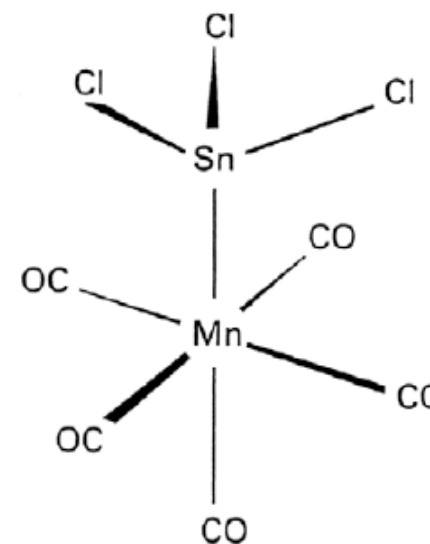
Ad esempio SnCl_2 può agire da acido:



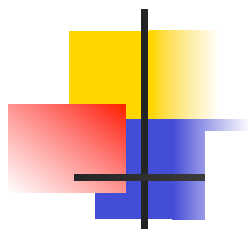
La specie SnCl_3^- è basica e può formare legami metallo-metallo



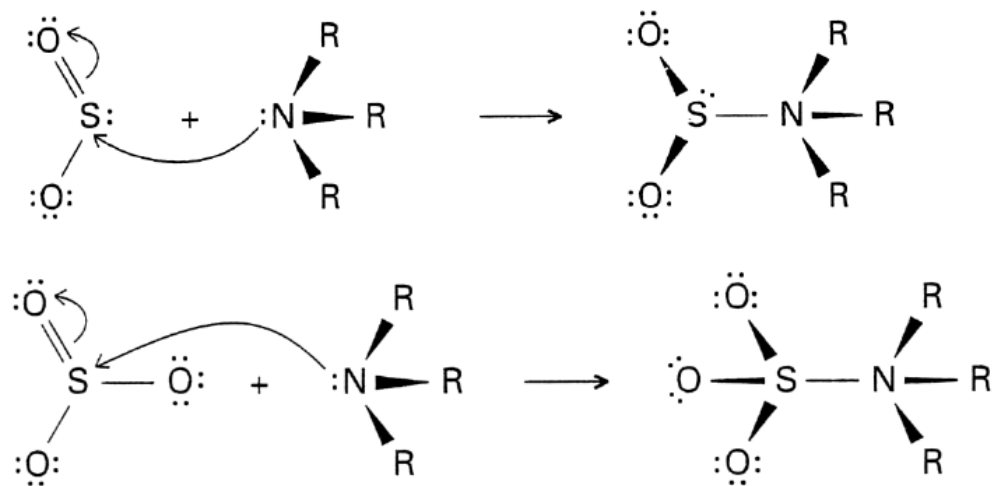
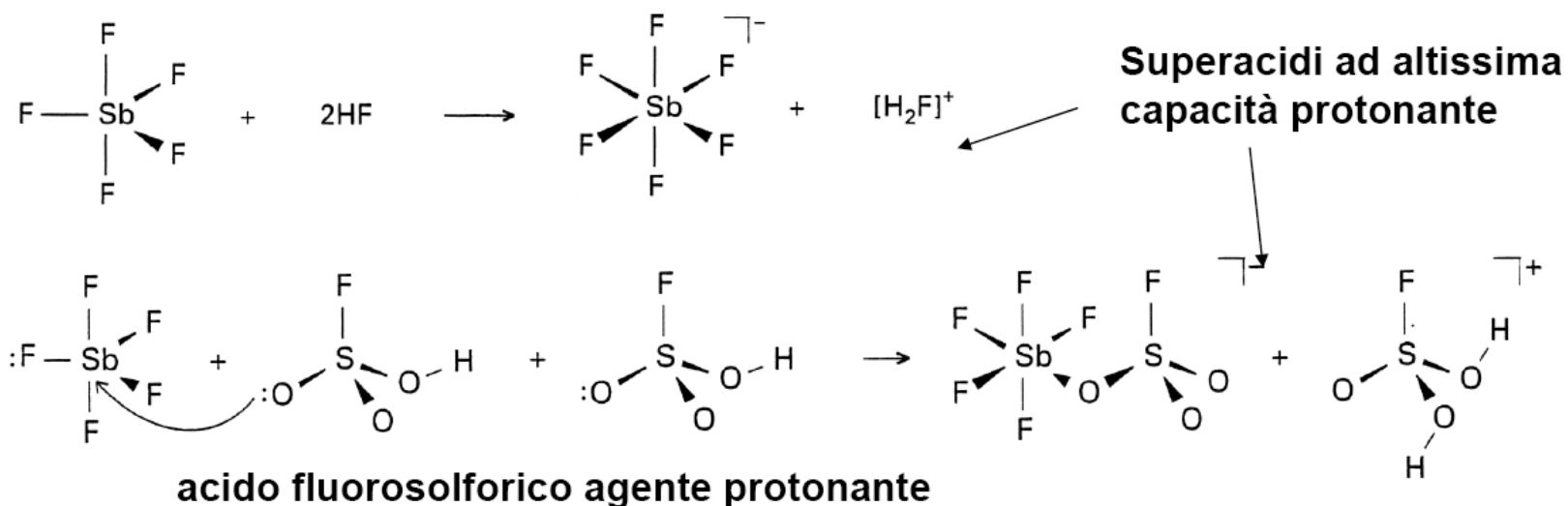
25 $[\text{SnCl}_3]^-$



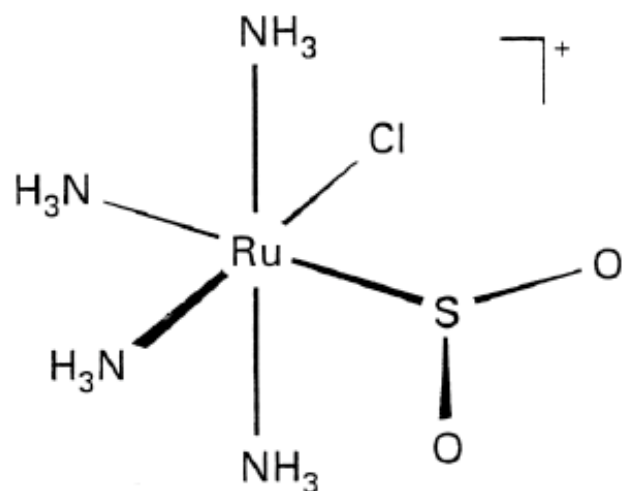
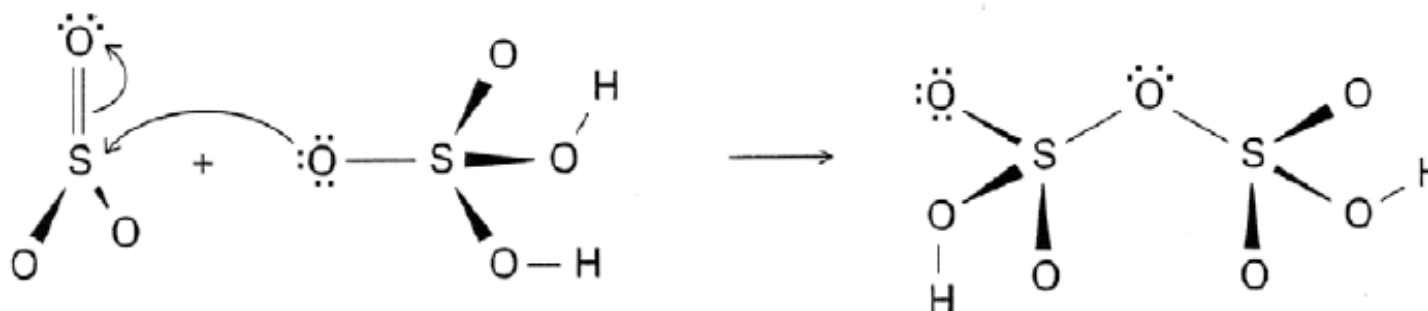
26 $(\text{CO})_5\text{MnSnCl}_3$



Acidi del gruppo dell' Azoto e dell'Ossigeno

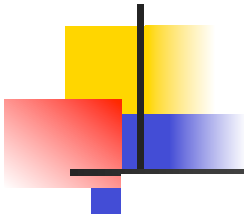


Acidi del gruppo dell' Azoto e dell'Ossigeno



28 $[\text{RuCl}(\text{NH}_3)_4(\text{SO}_2)]^+$

La specie SO_2 può anche agire come base nella formazione di complessi con metalli



Lewis Concept

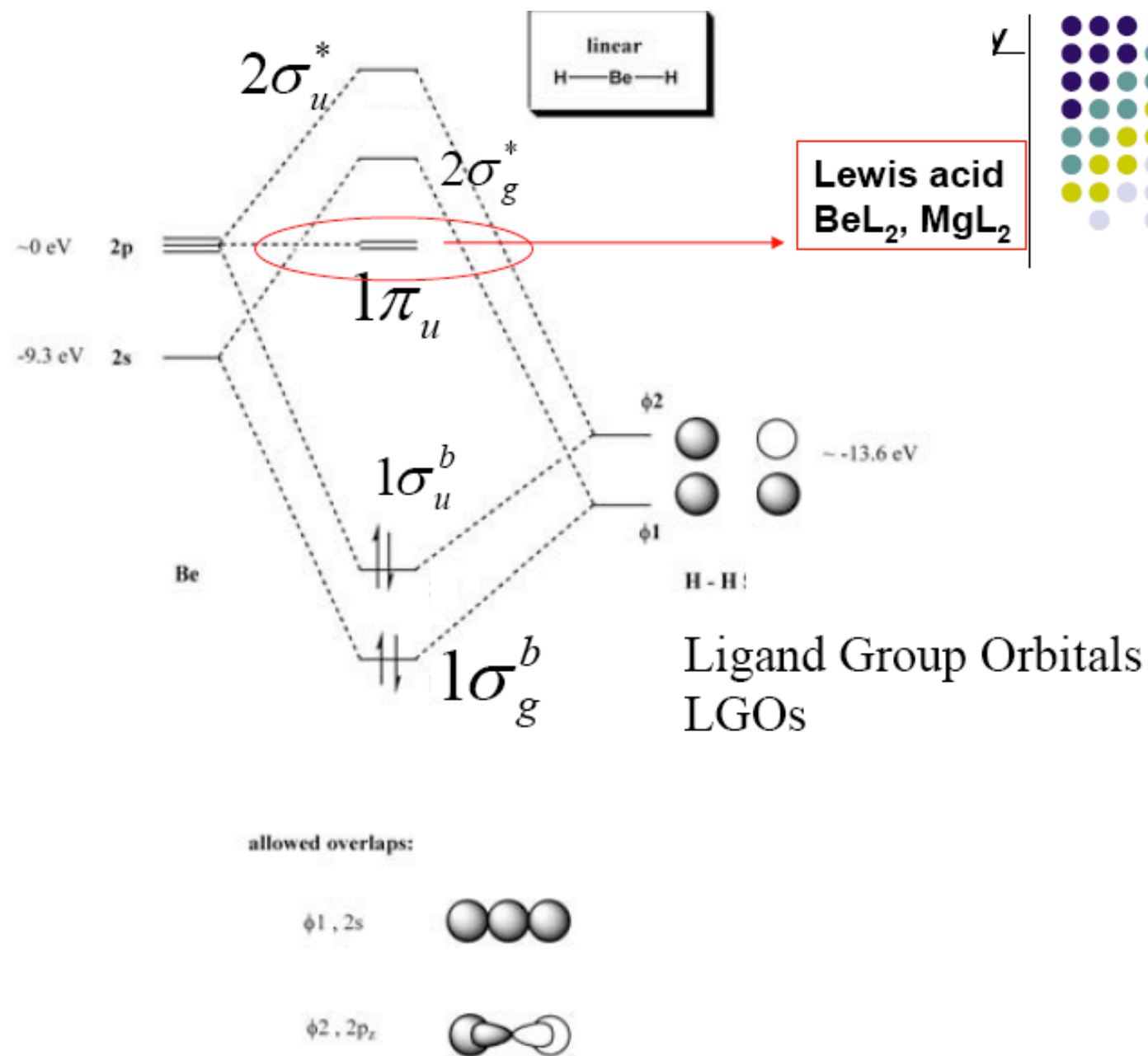
A base: an electron-pair donor

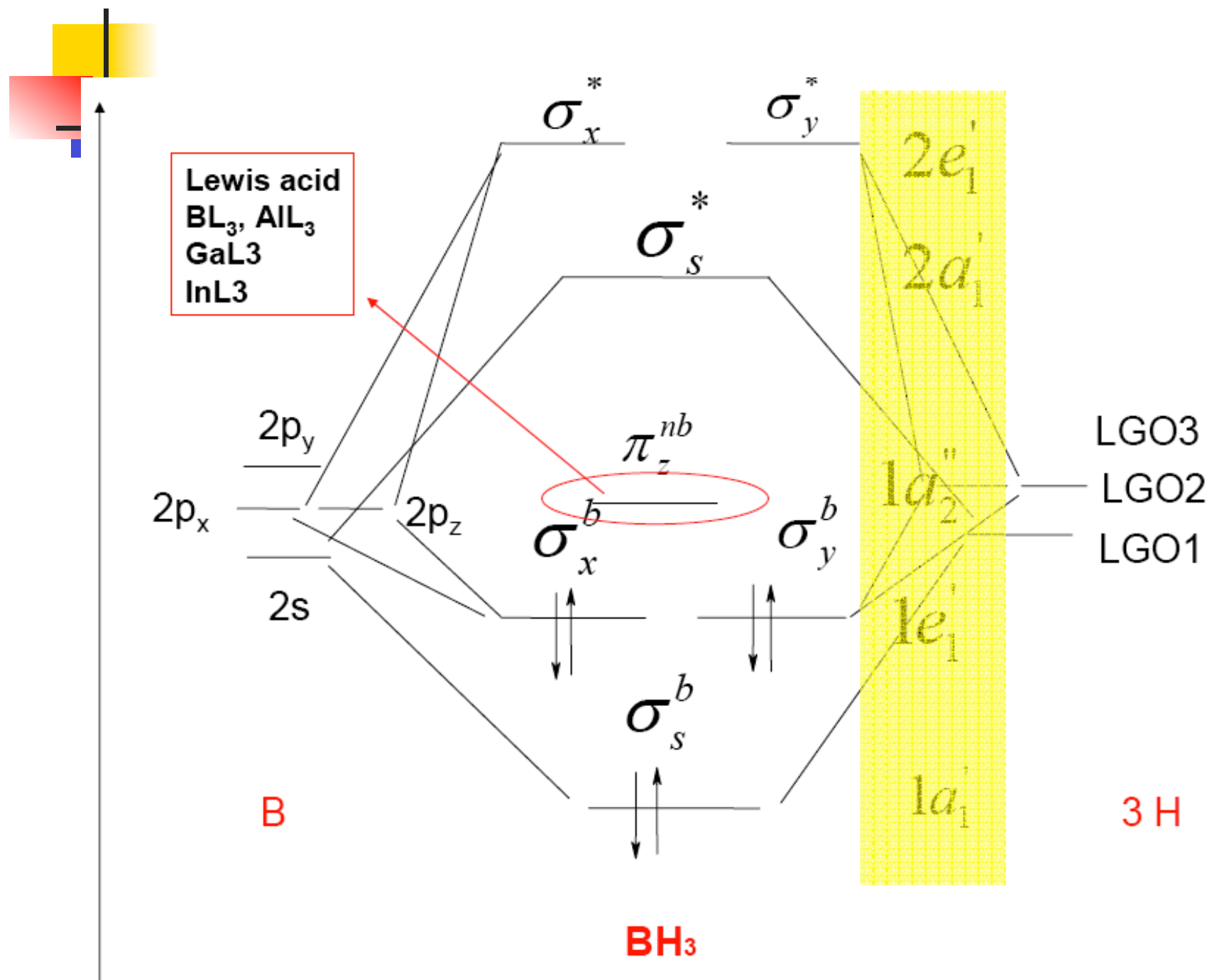
Species with lone pair type orbitals

An acid: an electron-pair acceptor

Species with empty non-bonding type orbitals



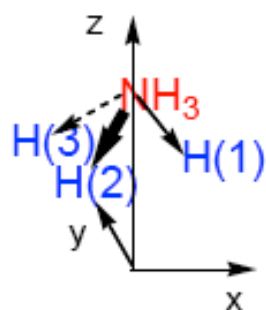




Lewis base
NL3, PL3, AsL3, SbL3, BiL3



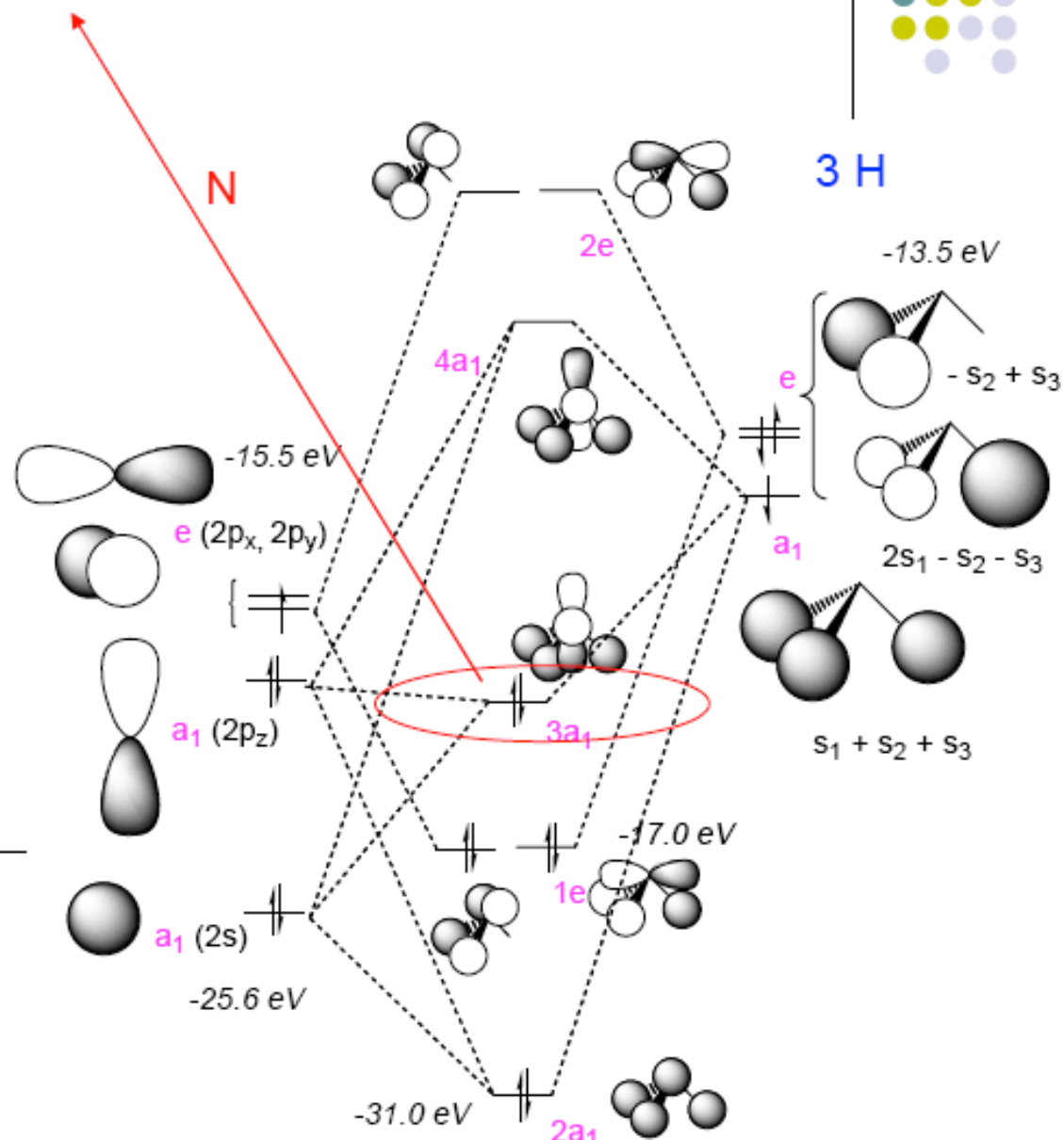
- NH_3 (C_{3v} : E, $2C_3$, $3\sigma_v$)

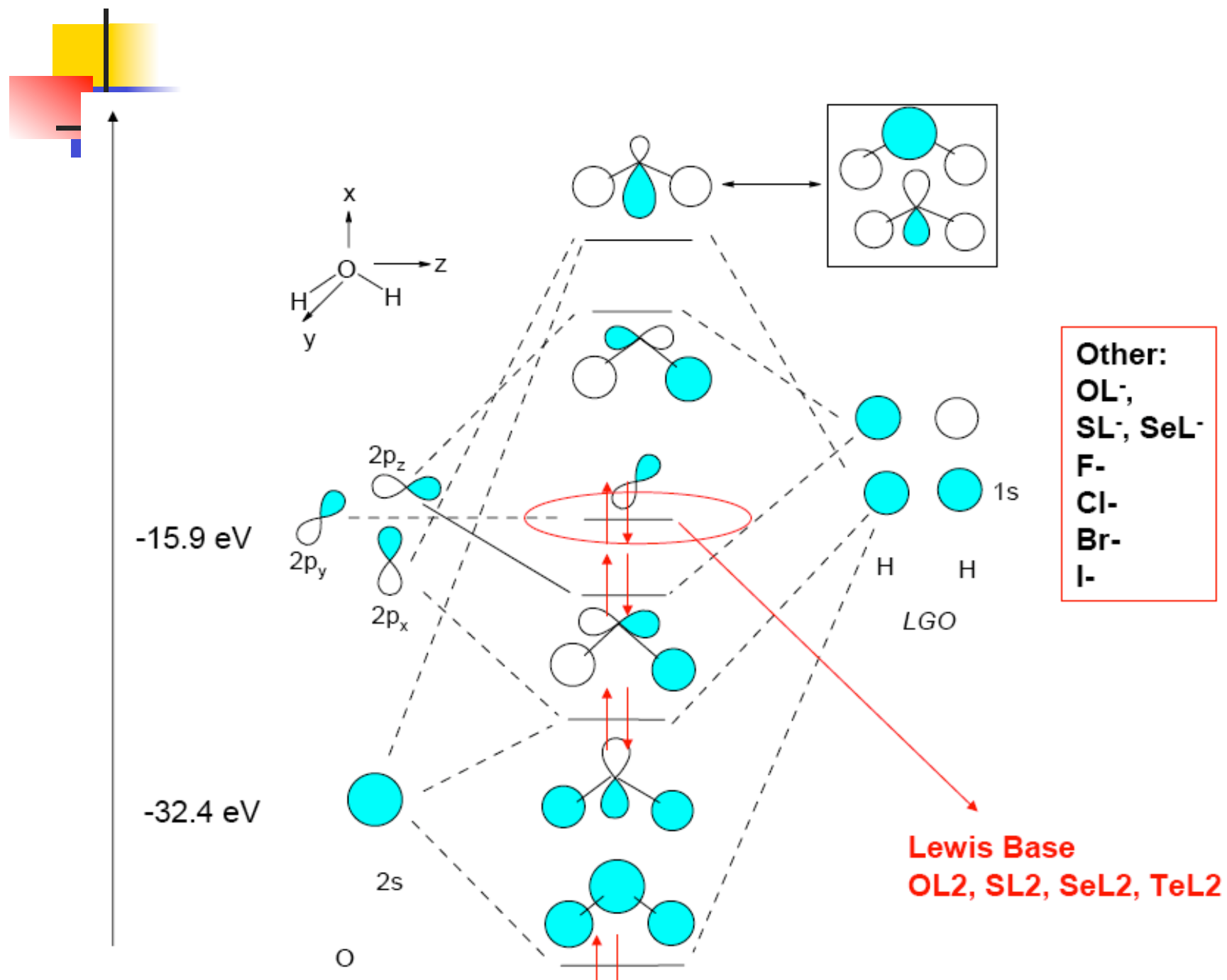


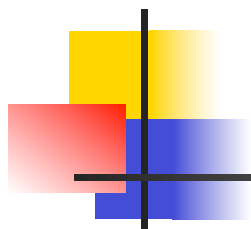
The symmetry of 3H's group orbitals:

$$\Gamma_r = A_1 + E$$

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	-1		
E	2	-1	0	(x,y)	







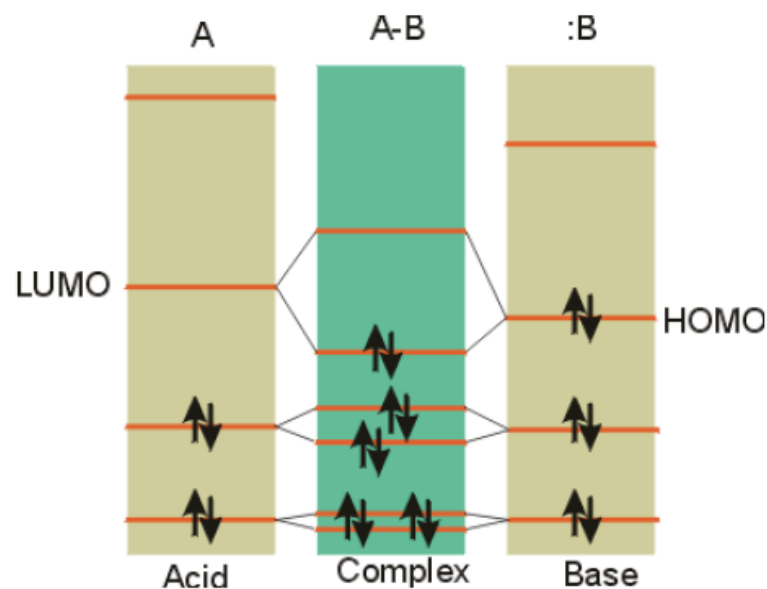
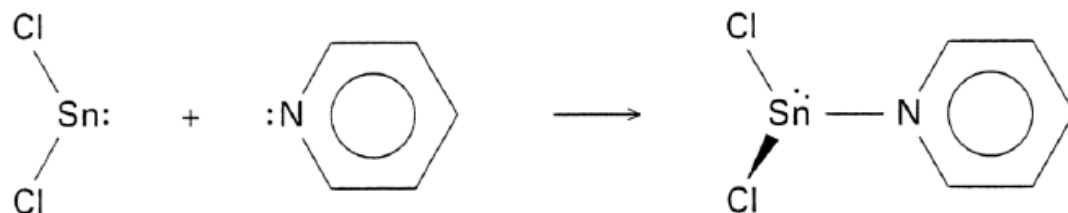
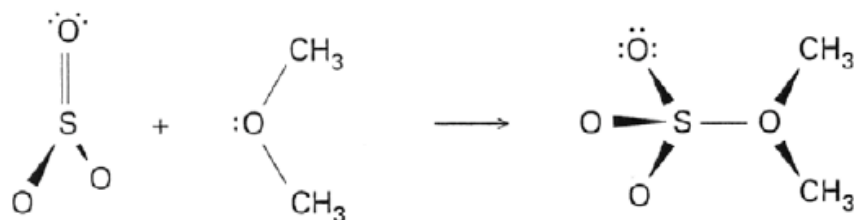
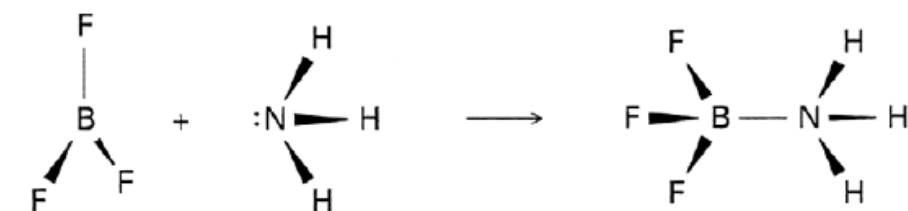
Type of non-protic acid-base reactions:

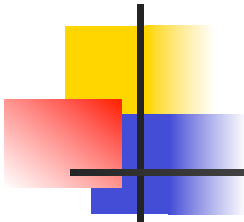
- 1. Adduct formation:** acid-base react to form a bond and produce a single molecule.
- 2. Displacement:** one base (or acid) displace another
- 3. Double displacement (Metathesis):**
interchange of acids and bases



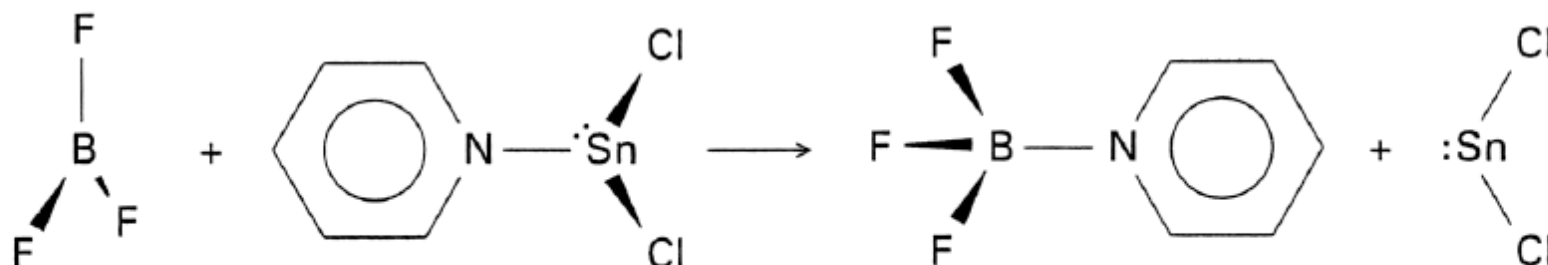
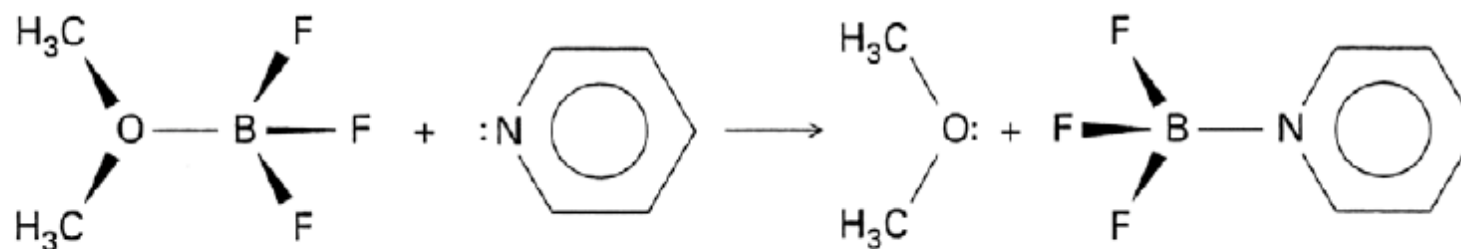
Tipi fondamentali di reazione acido-base di Lewis

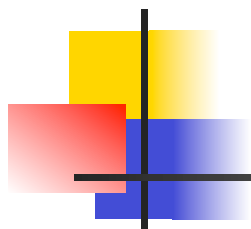
1. Formazione del complesso (o addotto) : $A + :B \rightarrow A-B$



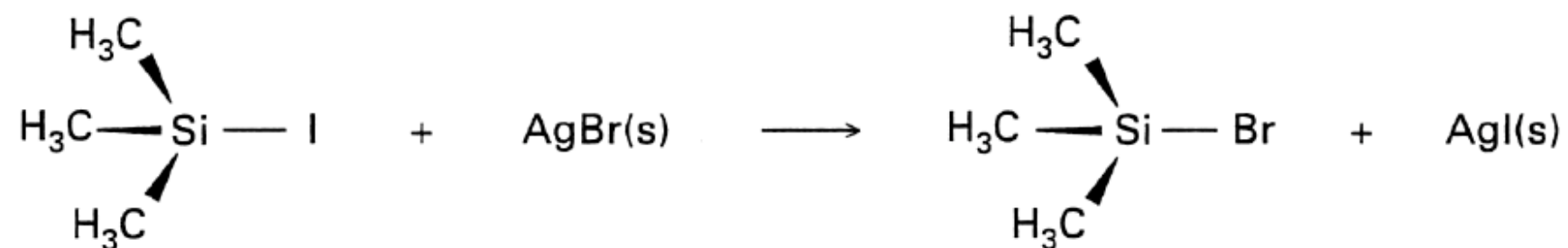
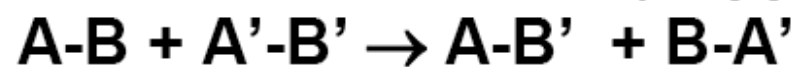


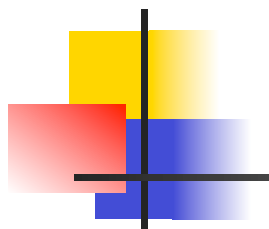
2. Reazioni di spostamento: $A-B + :B' \rightarrow A-B' + B$:



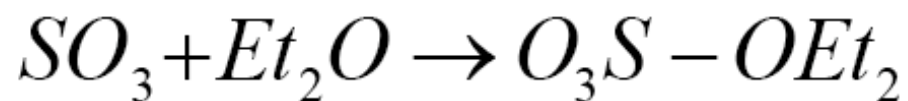
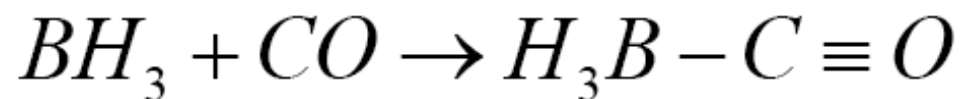
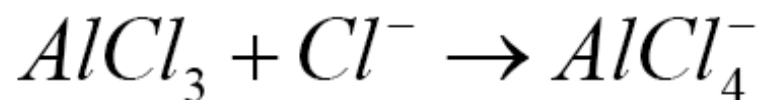
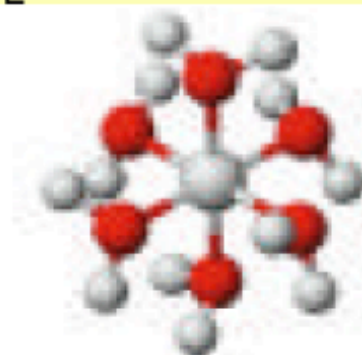
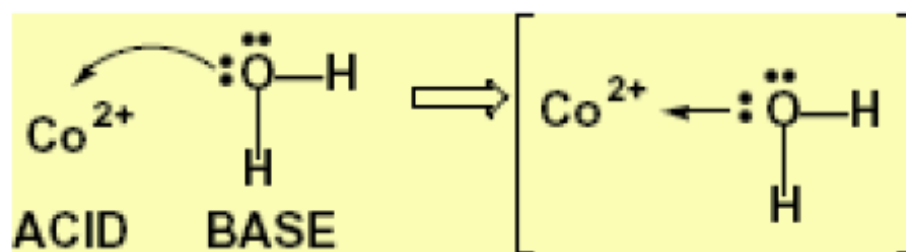


3. Reazioni di metatesi (doppio spostamento):

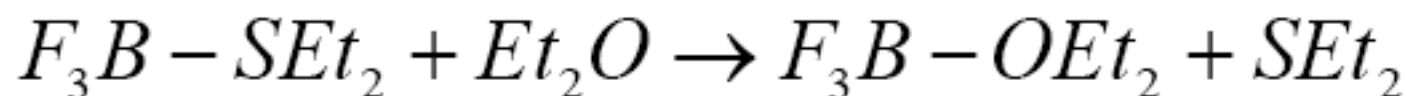
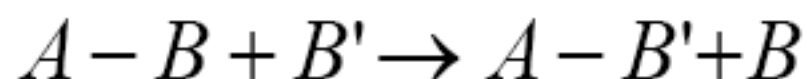




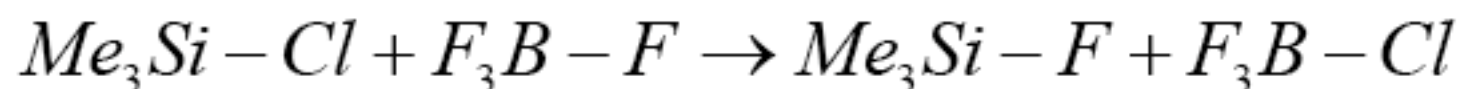
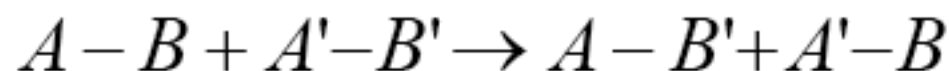
Adduct formation



Displacement: one base (or acid) displace another



Double displacement (Metathesis):
interchange of acids and bases



Predicting which LAB Adducts are Favoured

Why hasn't LAB Theory displaced other acid/base models?

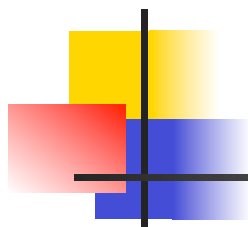
- **Qualitative vs. Quantitative**
- The Bronsted-Lowry model for protic acids has relatively simple methods to quantitatively determine the strength of an acid (pH, pKa)
- Depends primarily on electrostatics

Because the chemical breadth of Lewis acids and bases is so much greater, different trends exist

- Some acids (BF_3 , AlMe_3) act very much like “ H^+ ”
- Others (Hg^{2+}) have predominantly covalent bonding, and the same quantification cannot be used!

If we cannot readily quantify, how can we predict products?

Simple, extremely useful, categorization of LAs and LBs called the **Pearson Hard-Soft Acid Base Theory (HSAB)**



Hard and Soft Acids and Bases (HSAB)

Hard (class a):

having contracted (tightly held) frontier orbitals
Not readily polarized

Soft (Class b):

Having diffuse frontier orbitals
Readily polarized



Pearson HSAB Theory

Pearson examined the thermodynamic strength of various Lewis Acid adducts of the halogens:

“Class A” Acids: **Hard**

- **H⁺, Al³⁺, B³⁺ many others**
- Bind well with **F > Cl > Br > I**

“Class B” Acids: **Soft**

- **Hg²⁺, Pd²⁺, Ag⁺ many others**
- Bind well with **I > Br > Cl > F**

Not only did Pearson note these qualitative trends for the halogens, but for many other bases as well!

- **Hard acids** bind: [N >> P > As > Sb], [O >> S > Se > Te], etc.
- **Soft acids** bind: [N << P > As > Sb], [O << S < Se ≈ Te], etc.

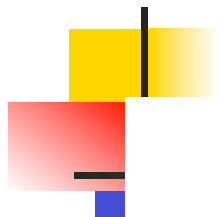


Hard species, both acids and bases, tend to be small and minimally polarizable

Soft species, both acids and bases, tend to be larger and more polarizable

Hard acids prefer to bind hard bases and soft acids prefer to bind to soft bases

- Note (1) **This is not theory or even an explanation**, simply a rule of thumb which enables the user to predict qualitatively the relative stability of acid-base adducts!
- Note (2) **This principle is qualitative and relative!** We will use it to compare two outcomes, and will talk about Lewis acids and bases in terms of their relative hardness and softness.



Basis of Classification

Pearson's classification of hard and soft bases derives from electronegativity:



Hard acid-base interactions are predominantly electrostatic

Soft acid-base interactions are predominantly covalent

Both hard and soft acids and bases derive from the *polarizability* of an atom or molecule

- **Polarizability**: a measure of the degree to which it may be distorted, especially by an electric field of an adjacent atom or ion; increases with atomic size and lower electronegativity

Classification

H

He

Li

Be

Na

Mg

K

Ca

Sc

Ti

V

Cr

Mn

Fe³⁺
Fe²⁺

Co³⁺
Co²⁺

Ni

Cu²⁺
Cu⁺

Zn

Ga

Ge

Rb

Sr

Y

Zr

Nb

Mo

Tc

Ru

Rh³⁺
Rh⁺

Pd

Ag

Cd

In³⁺
In⁺

Sn⁴⁺
Sn²⁺

Sb

Te

I

Cs

Ba

La^{*}

Hf

Ta

W

Re

Os

Ir³⁺
Ir⁺

Pt

Au

Hg

Tl

Pb

Bi

Po

At

Rn

hard Lewis acids

borderline Lewis acids

soft Lewis acids

hard Lewis bases

borderline Lewis bases

soft Lewis bases

B

C

N

O

F

Ne

Al

Si

P

S

Cl

Ar

As

Se

Br

Kr

Sb

Te

I

Xe

Property	Hard Acids	Hard Bases	Soft Acids	Soft Bases
%P	0.7 – 1.6	3.4 – 4.0	1.9 – 2.5	2.1 – 3.0
Ionic Radius	small	small	large	large
Ionic Charge	high	-	low	-

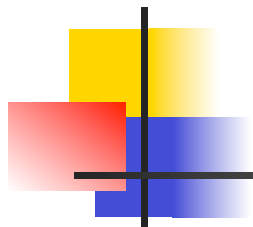
Borderliners

There is no sharp dividing line between “hard” and “soft”, as illustrated by the “borderline” category

Even within “hard acids”, there are trends...

– Alkali metals, chalcogens

H																	He
Li	Be	hard Lewis acids borderline Lewis acids soft Lewis acids hard Lewis bases borderline Lewis bases soft Lewis bases										B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe ³⁺ / Fe ²⁺	Co ³⁺ / Co ²⁺	Ni	Cu ²⁺ / Cu ⁺	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh ³⁺ / Rh ⁺	Pd	Ag	Cd	In ³⁺ / In ⁺	Sn ⁴⁺ / Sn ²⁺	Sb	Te	I	Xe
Cs	Ba	La*	Hf	Ta	W	Re	Os	Ir ³⁺ / Ir ⁺	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn



Conceptual to Tabular :: ACIDS

- Pearson, J. Am. Chem. Soc., 1963.

Classification of Lewis Acids

Class (a)/Hard	Class (b)/Soft
H^+ , Li^+ , Na^+ , K^+ Be^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} , Sn^{2+} Al^{3+} , Se^{3+} , Ga^{3+} , In^{3+} , La^{3+} Cr^{3+} , Co^{3+} , Fe^{3+} , As^{3+} , Ir^{3+} Si^{4+} , Ti^{4+} , Zr^{4+} , Th^{4+} , Pu^{4+} , VO^{2+} UO_2^{2+} , $(CH_3)_2Sn^{2+}$ $BeMe_2$, BF_3 , BCl_3 , $B(OR)_3$ $Al(CH_3)_3$, $Ga(CH_3)_3$, $In(CH_3)_3$ RPO_2^+ , $ROPO_2^+$ RSO_2^+ , $ROSO_2^+$, SO_3 I^{7+} , I^{5+} , Cl^{7+} R_3C^+ , RCO^+ , CO_2 , NC^+	Cu^+ , Ag^+ , Au^+ , Tl^+ , Hg^+ , Cs^+ Pd^{2+} , Cd^{2+} , Pt^{2+} , Hg^{2+} CH_3Hg^+ Tl^{3+} , $Tl(CH_3)_3$, RH_3 RS^+ , RSe^+ , RTe^+ I^+ , Br^+ , HO^+ , RO^+ I_2 , Br_2 , INC , etc. Trinitrobenzene, etc. Chloranil, quinones, etc. Tetracyanoethylene, etc. O , Cl , Br , I , R_3C M^0 (metal atoms) Bulk metals
<i>HX (hydrogen-bonding molecules)</i> <i>Borderline</i> Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Pb^{2+} $B(CH_3)_3$, SO_2 , NO^+	

Conceptual to Tabular :: BASES

Pearson, J. Am. Chem. Soc., 1963.

Classification of Bases	
Hard	Soft
H ₂ O, OH ⁻ , F ⁻ CH ₃ CO ₂ ⁻ , PO ₄ ³⁻ , SO ₄ ²⁻ Cl ⁻ , CO ₃ ²⁻ , ClO ₄ ⁻ , NO ₃ ⁻ ROH, RO ⁻ , R ₂ O NH ₃ , RNH ₂ , N ₂ H ₄	R ₂ S, RSH, RS ⁻ I ⁻ , SCN ⁻ , S ₂ O ₃ ²⁻ R ₃ P, R ₃ As, (RO) ₃ P CN ⁻ , RNC, CO C ₂ H ₄ , C ₆ H ₆ H ⁻ , R ⁻
Borderline	
C ₆ H ₅ NH ₂ , C ₅ H ₅ N, N ₃ ⁻ , Br ⁻ , NO ₂ ⁻ , SO ₃ ²⁻ , N ₂	

- Notice the difference between our “conceptual” periodic table and Pearson’s data.
- **Chlorine is HARD, not borderline. Bromine is BORDERLINE, not soft.**
 - Now we have a better understanding and a greater breadth of results, so go with the periodic table...
- **Although H⁺ is a HARD ACID, H⁻ is a SOFT BASE!**



Pearson has attempted to quantify his HSAB theory:

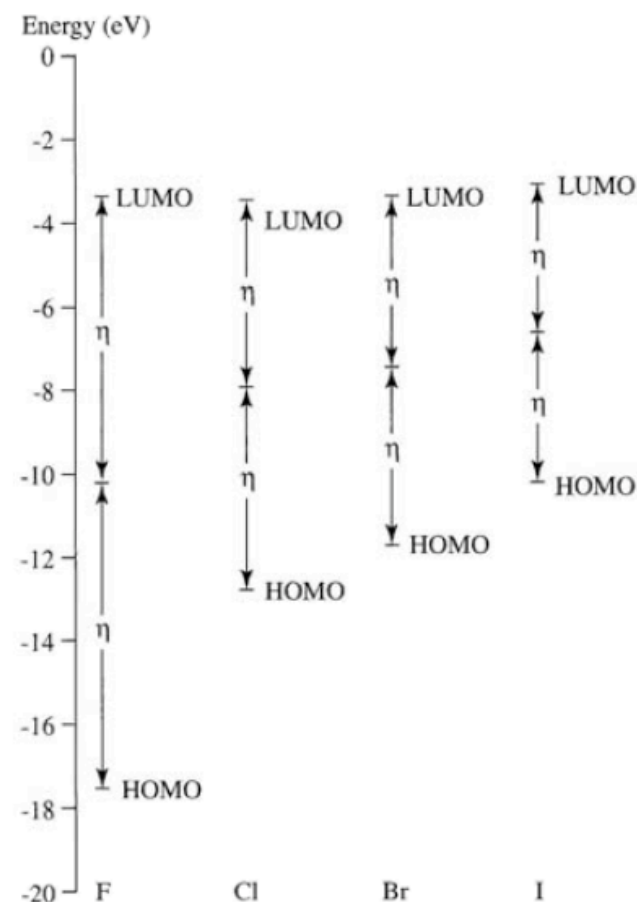
$$\eta = \frac{I - A}{2} \quad \sigma = \frac{1}{\eta}$$

Absolute hardness **Absolute softness**

...where **I** and **A** are inversely related to the energies of the HOMO and LUMO respectively

Therefore “**absolute hardness**” is proportional to a large HOMO / LUMO gap... And “**absolute softness**” is inversely proportional

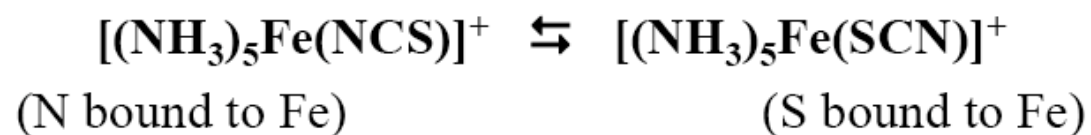
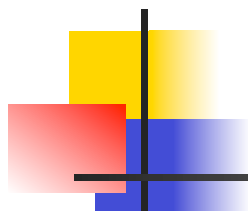
Other quantification routes (i.e. the Drago-Wayland approach) offer benefits, but require extensive tabulation of empirical parameters limiting the breadth of application





Which side of the equilibrium is favoured?

H																	He						
Li	Be	hard Lewis acids borderline Lewis acids soft Lewis acids						hard Lewis bases borderline Lewis bases soft Lewis bases						B	C	N	O	F	Ne				
Na	Mg																	Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe ³⁺ / Fe ²⁺	Co ³⁺ / Co ²⁺	Ni	Cu ²⁺ / Cu ⁺	Zn	Ga	Ge	As	Se	Br	Kr						
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh ³⁺ / Rh ⁺	Pd	Ag	Cd	In ³⁺ / In ⁺	Sn ⁴⁺ / Sn ²⁺	Sb	Te	I	Xe						
Cs	Ba	La [*]	Hf	Ta	W	Re	Os	Ir ³⁺ / Ir ⁺	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn						



Which side of the equilibrium is favoured?

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe ³⁺ / Fe ²⁺	Co ³⁺ / Co ²⁺	Ni	Cu ²⁺ / Cu ⁺	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh ³⁺ / Rh ⁺	Pd	Ag	Cd	In ³⁺ / In ⁺	Sn ⁴⁺ / Sn ²⁺	Sb	Te	I	Xe
Cs	Ba	La*	Hf	Ta	W	Re	Os	Ir ³⁺ / Ir ⁺	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn

hard Lewis acids

borderline Lewis acids

soft Lewis acids

hard Lewis bases

borderline Lewis bases

soft Lewis bases

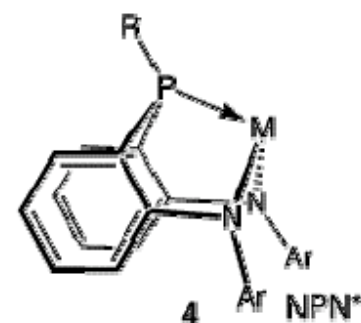
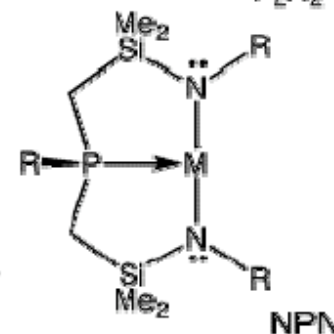
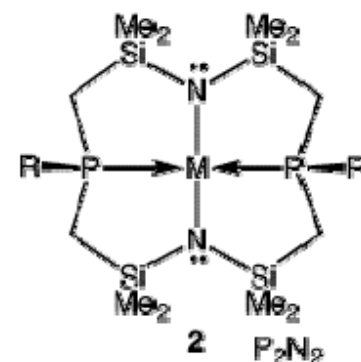
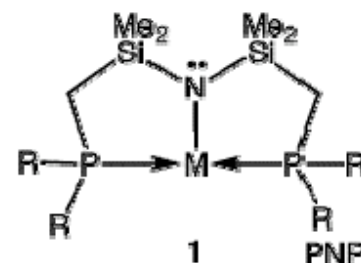
Last But Not Least...

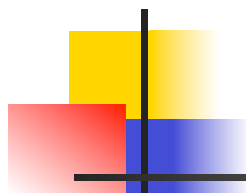
As chemists, can we force the situation?

- Can we make a **SOFT Lewis Base** bond to a **HARD Lewis Acid**?
- Can we make a **HARD Lewis Base** bond to a **SOFT Lewis Acid**?

Remember that HSAB Theory is only **one** of the factors determining complex stability

- Exploit the chelate effect!





Hard Bases
(nucleophiles)

Donor atoms have *high electronegativity (low HOMO)* and *low polarizability* and are hard to oxidize. They hold their valence electrons tightly.

Soft Bases
(nucleophiles)

Donor atoms have *low electronegativity (high HOMO)* and *high polarizability* and are easy to oxidize. They hold their valence electrons loosely.

Hard Acids
(electrophiles)

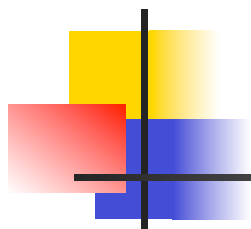
Possess small acceptor atoms, have high positive charge and do not contain unshared electron pairs in their valence shells. They have *low polarizability* and *high electronegativity (high LUMO)*.

Soft Acids
(electrophiles)

Possess large acceptor atoms, have low positive charge and contain unshared pairs of electrons (p or d) in their valence shells. They have *high polarizability* and *low electronegativity (low LUMO)*

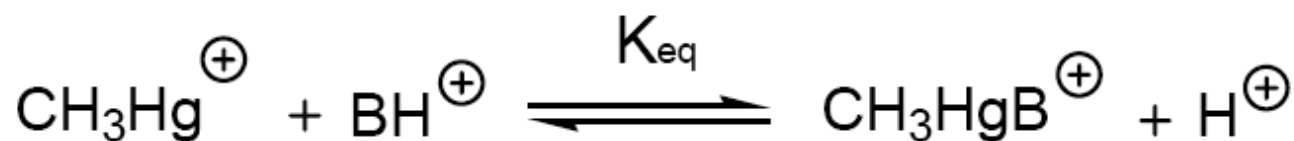
n.b “*The HSAB principle is not a theory but a statement of experimental facts.*”

Pearson, R.G, Songstad, *J.Amer.Chem.Soc.*, 1967, **89**, 1827



Pearson's Principle:

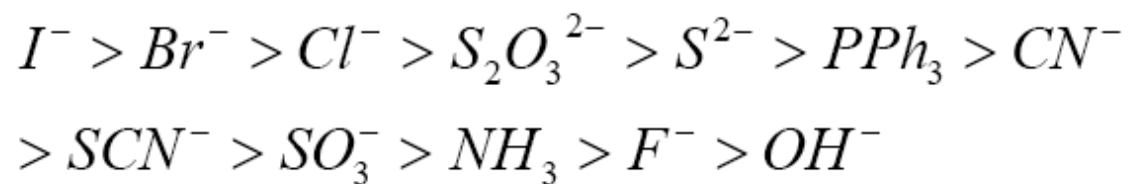
**Hard acids prefer to bind to hard bases
And soft acids prefer to bind to soft bases.**

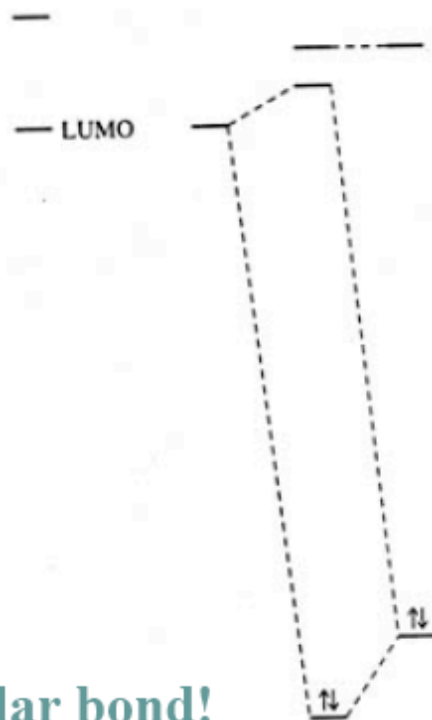


The simplest hard acid is the proton and methyl mercury cation is the simplest soft acid.

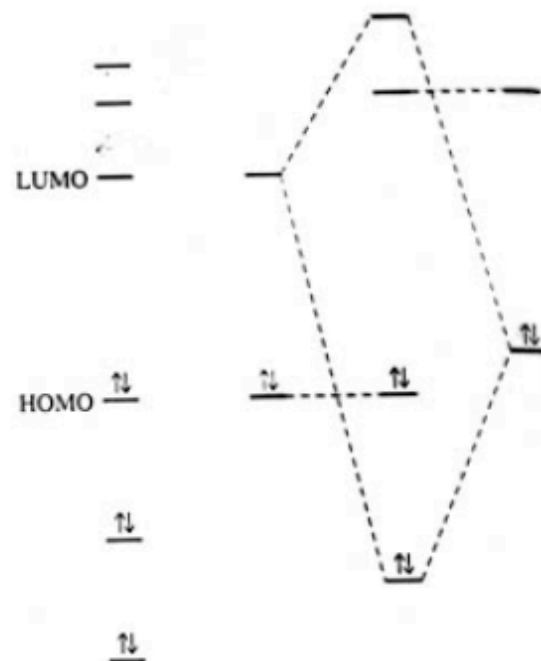
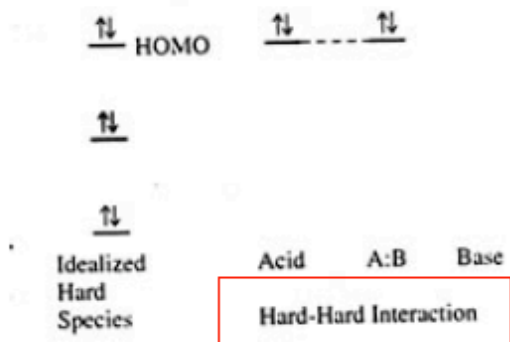
K_{eq} small $\rightarrow$ B hard base

K_{eq} large $\rightarrow$ B soft base

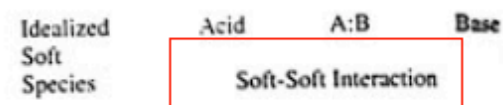




Strong polar bond!



Strong covalent bond!



Classificazione hard e soft di acidi e basi (1)

Abbiamo visto che la hardness (durezza) $= \eta = c[E.I.(E) - A.E.(E)]/2$

Poichè $E.I. \gg A.E.$ (quasi sempre!), $2\eta \approx c E.I.(E) \Rightarrow \eta \propto E.I.(E)$

In generale si ha la corrispondenza:

hard (η grande) $\rightarrow$ poco polarizzabile (α piccolo), r piccolo, $(E_{LUMO} - E_{HOMO})$ grande

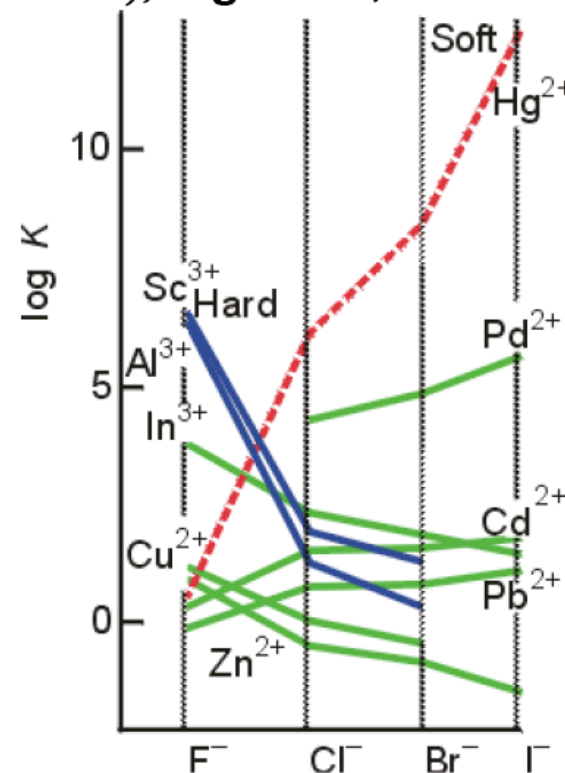
soft (η piccola) $\rightarrow$ molto polarizzabile (α grande), r grande, $(E_{LUMO} - E_{HOMO})$ piccola

L'interazione tra specie hard è quindi di tipo elettrostatico (cariche, dipoli), quella tra specie soft ha parziale carattere covalente, CT etc.

Reazioni di formazione di complessi tra ioni hanno K (costanti di stabilità) per acidi (cationi):

hard, crescenti nella serie $I^- < Br^- < Cl^- < F^-$

soft, crescenti nella serie $F^- < Cl^- < Br^- < I^-$



Classificazione hard e soft di acidi e basi (2)

Reazioni di formazione di complessi tra molecole neutre hanno K (costanti di stabilità) per acidi :

hard, crescenti nella serie $R_3P \ll R_3N, R_2S \ll R_2O$

soft, crescenti nella serie $R_2O \ll R_3N, R_2S < R_3P$

Table 5.3 The classification of Lewis acids and bases*

Hard	Borderline	Soft
Acids H^+, Li^+, Na^+, K^+ $Be^{2+}, Mg^{2+}, Ca^{2+}$ $Cr^{2+}, Cr^{3+}, Al^{3+}$ 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 $CO_3^{2-}, NO_3^-, O^{2-}$ $SO_4^{2-}, PO_4^{3-}, ClO_4^-$	<u>NO_2^-</u> , <u>SO_3^{2-}</u> , Br^- N_3^-, N_2 C_6H_5N, SCN^-	$H^-, R^-, \underline{CN}^-, \underline{CO}, I^-$ <u>SCN^-</u> , R_3P, C_6H_6 R_2S

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

Dalle definizioni date (operative e modellistiche) e dai dati si ha che:
acidi hard si legano meglio a basi hard, acidi soft a basi soft

Classificazione hard e soft di acidi e basi (3)

- Interazioni hard prevalentemente elettrostatiche e ioniche
- Interazioni soft prevalentemente di polarizzabilità e “covalenti

Nella formazione di addotti e complessi vanno però considerati anche altri fattori:

- 1) riarrangiamento dei sostituenti
- 2) effetti sterici repulsivi (dimensioni sostituenti)
- 3) competizione con il solvente

La classificazione hard-soft permette di comprendere:

- qualitativamente la reattività chimica:

Ad es.: la reazione $(\text{Me})_3\text{Si-I} + \text{AgBr(s)} \rightarrow (\text{Me})_3\text{Si-Br} + \text{AgI(s)}$

anione bidentato SCN^- che si lega con N (hard) a Si (hard) e con S soft a Pt (soft)

- la classificazione di Goldschmidt in elementi litofili e calcofili:

litofili, nella litosfera (crosta terrestre) che tendono a formare ossidi :
ioni Li^+ , Mg^{2+} , Ca^{2+} , Al^{3+} , Cr^{3+} , Ti^{4+} , Si^{4+} (hard) con O^{2-} (hard)

calciofili, tendono a formare solfuri : Cd^{2+} , Pb^{2+} , Ag^+ , Hg^{2+} , Sb , Bi ,
(Zn^{2+} , Fe^{2+}) con S^{2-} , Se^{2-} , Te^{2-}

Parametri termodinamici di acidità

Un modo alternativo di considerare la reattività acido-base e prevedere esiti di reazioni di spostamento e metatesi esamina

$$\Delta H^\circ (\text{A-B}) =$$



L'equazione di Drago-Wayland:

$$\Delta H^\circ (\text{A-B}) / \text{kJmol}^{-1} = E_A E_B + C_A C_B$$

riesce a prevedere questi $\Delta H^\circ (\text{A-B})$ con un errore di $\pm 3 \text{ kJmol}^{-1}$ per reazioni in fase gas o solventi non-coordinanti (quindi non va per ioni!)

E e **C** originalmente introdotti come contributi **elettrostatici** e **covalenti**.

In realtà non sembra così semplice: tengono conto di “tutto” (salvo solvatazione)

Table 5.4 Drago-Wayland parameters for some acids and bases*

	<i>E</i>	<i>C</i>
<i>Acids</i>		
Antimony pentachloride	15.1	10.5
Boron trifluoride	20.2	3.31
Iodine	2.05	2.05
Iodine monochloride	10.4	1.70
Phenol	8.86	0.90
Sulfur dioxide	1.88	1.65
Trichloromethane	6.18	0.32
Trimethylboron	12.6	3.48
<i>Bases</i>		
Acetone	2.02	4.67
Ammonia	2.78	7.08
Benzene	0.57	1.21
Dimethyl sulfide	0.70	15.26
Dimethylsulfoxide	2.76	5.83
Methylamine	2.66	12.00
<i>p</i> -Dioxane	2.23	4.87
Pyridine	2.39	13.10
Trimethylphosphine	17.2	13.40

**E* and *C* parameters are often reported to give ΔH in kcal mol^{-1} ; we have multiplied both by $\sqrt{(4.184)}$ to obtain ΔH in kJ mol^{-1}