Chem 241

Lecture 6

Announcements

March 10th class will be moved

Need a note taker

Recap

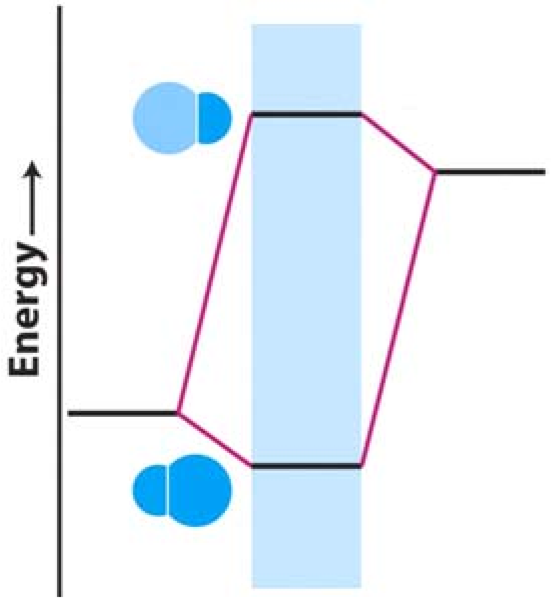
- MO theory for a homo-dimeric molecule

MOT-Heteronuclear Diatomics

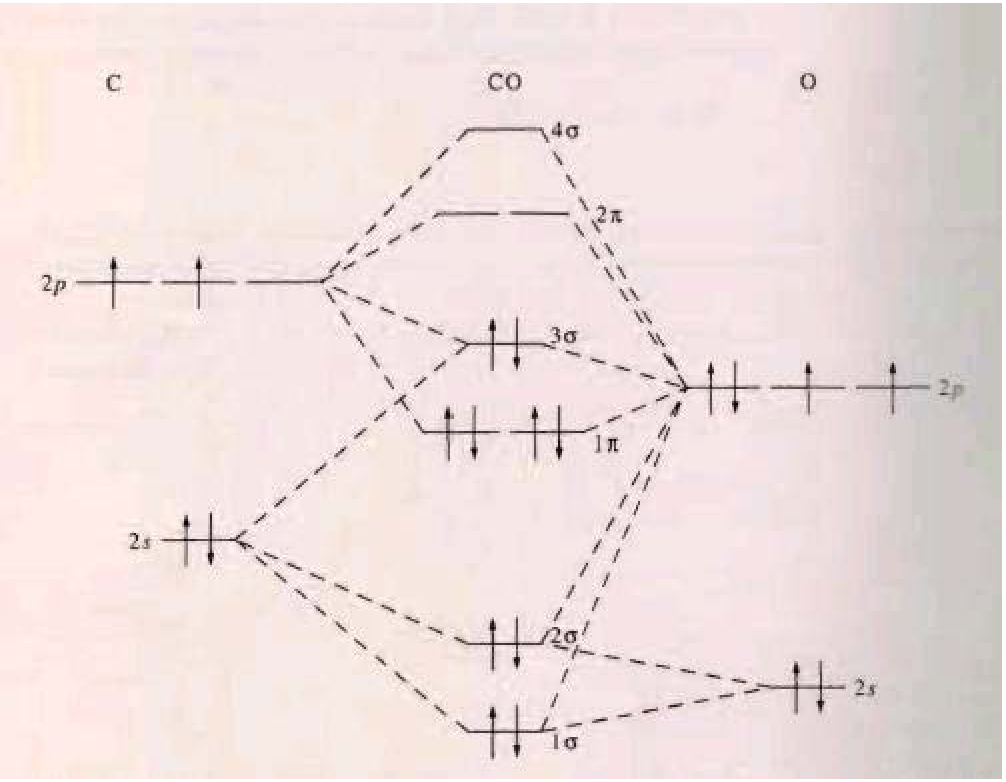
- Differences from Homonuclear case:
  - for $\psi_{bond(1)} = \psi_A + \psi_B$, ψ_A does not = ψ_B
  - Electrons will be drawn to the more electronegative element . Thus bonding orbitals will have more of that element character and antibonding orbitals will have more AO character from the more electropositive element.
  - As a result of having more A character,

The molecular orbital will be closer in

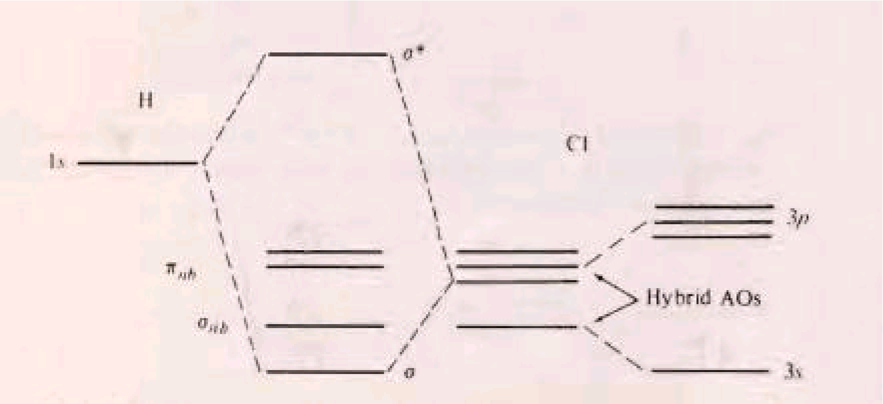
Energy to the AO of A.



Consider CO



Consider HCl



MOT-predicting bond order, bond length and bond strength

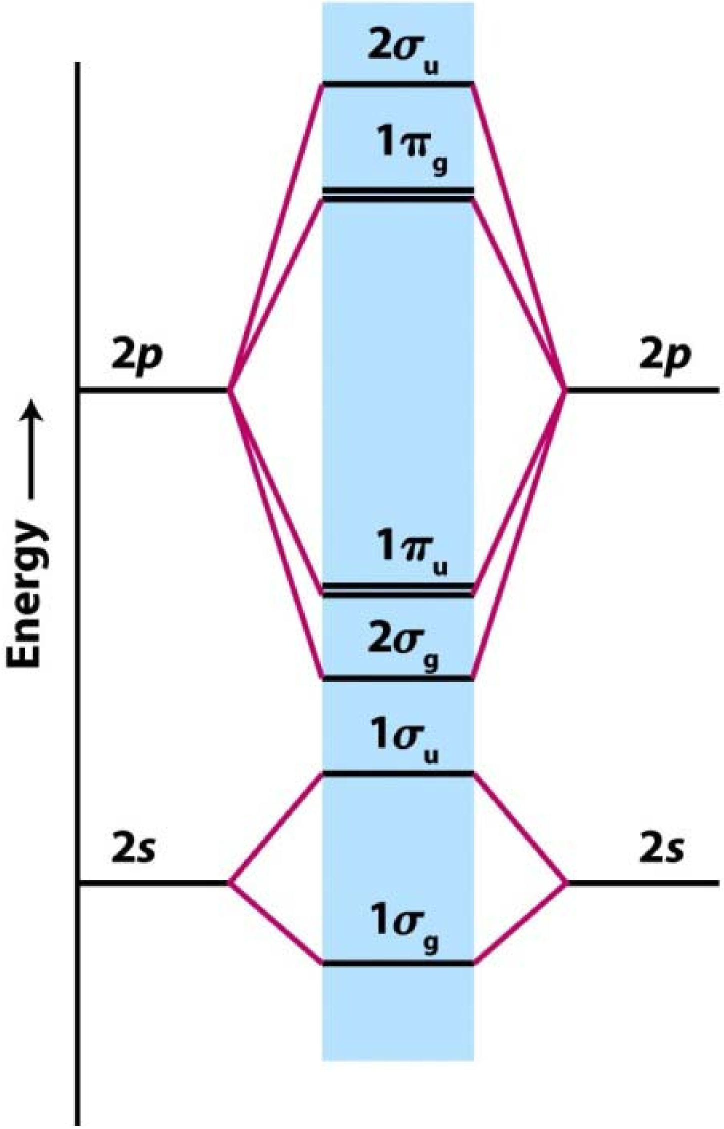
- Consider O_2, O_2^-, O_2^{2-}, O_2^+
- Bond Order b= ½(bond – anti)

$\nu_{o\text{-}o}$ = 1555 cm^{-1}

1108 cm^{-1} (K[O_2^-])

760 cm^{-1} (Na$_2$[O_2^{2-}])

1858 cm^{-1} ([O_2^+]AsF$_6$



MOT of polyatomic molecules

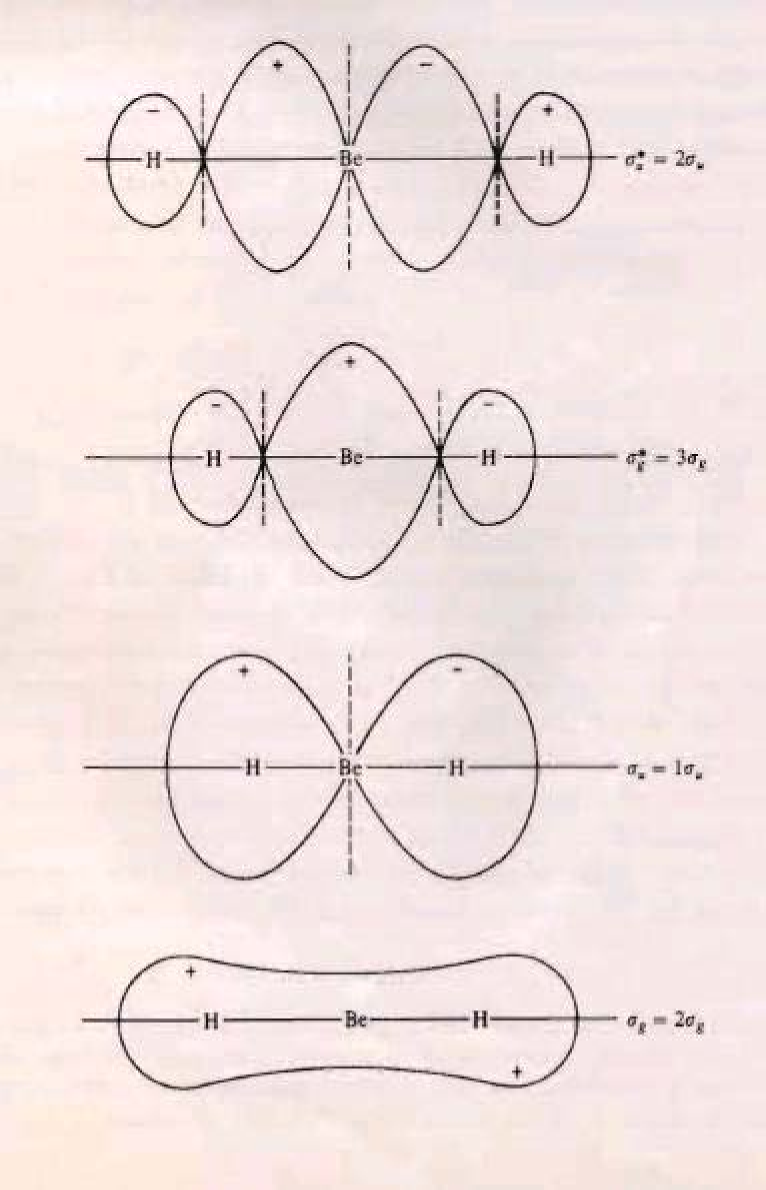
- General rules:
- 1. Molecular orbitals are formed from linear combinations of atomic orbitals with the same symmetry

- 2. The greater the number of nodes in a molecular orbital, the more antibonding and higher in energy it is.

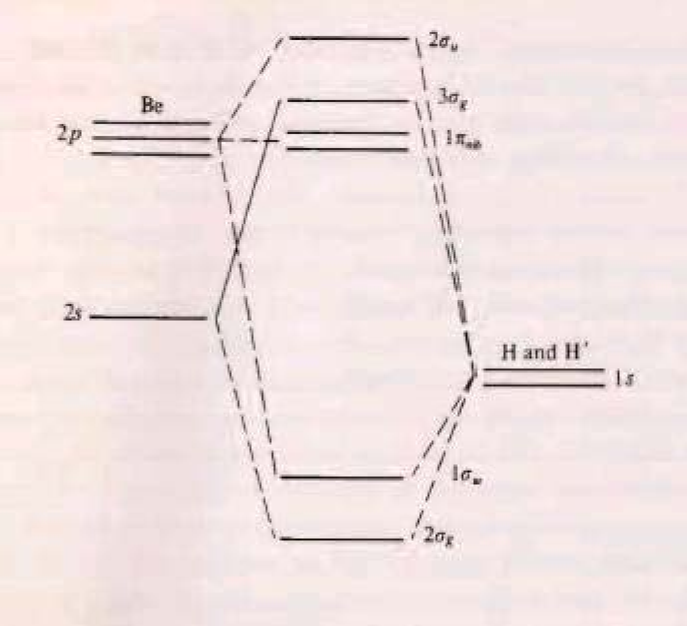
- 3. Interactions between atoms that are not nearest neighbors are weak (bonding or anti-bonding).

- 4. Orbitals constructed from lower energy AOs lie lower in energy.

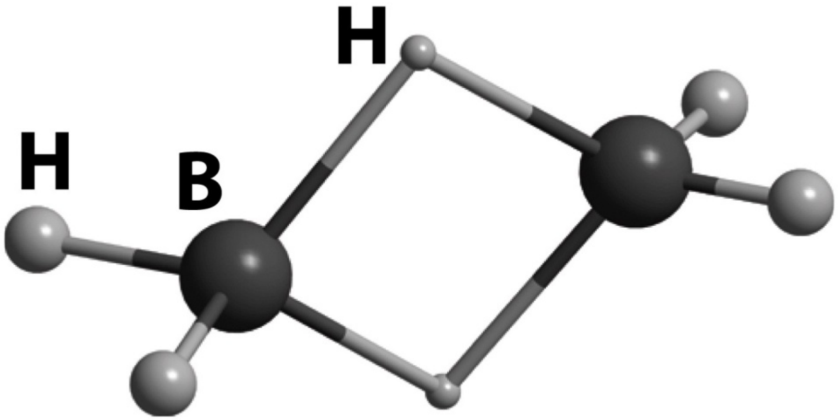
BeH_2


−
+
−
+
H
Be
H
$\sigma_u^* = 2\sigma_u$
−
+
−
H
Be
H
$\sigma_g^* = 3\sigma_g$
+
−
H
Be
H
$\sigma_u = 1\sigma_u$
+
+
H
Be
H
$\sigma_g = 2\sigma_g$

BeH_2



Diborane



27 Diborane, B_2H_6

Structure 2-27
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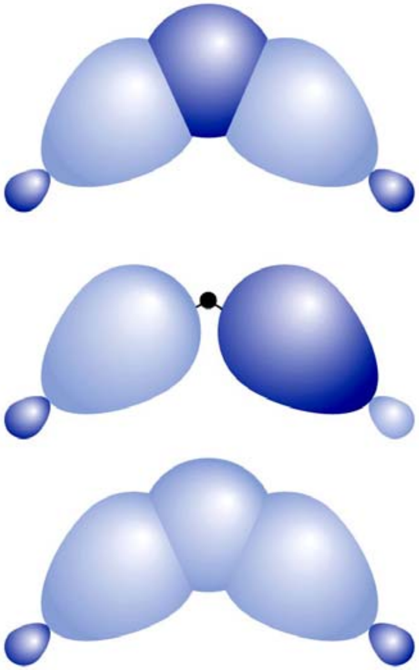

Figure 2-32
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Please look in your book about NH_3, Hypervalence

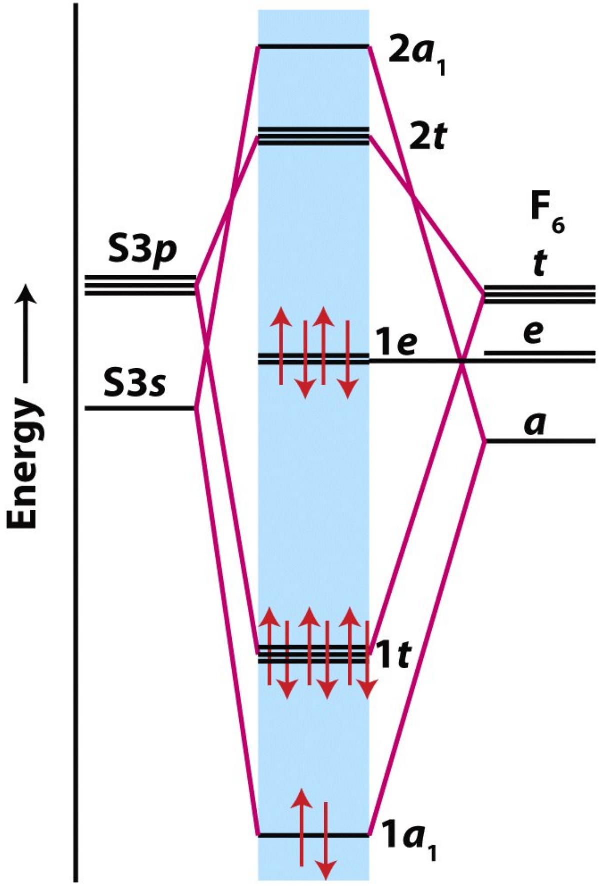

Figure 2-31
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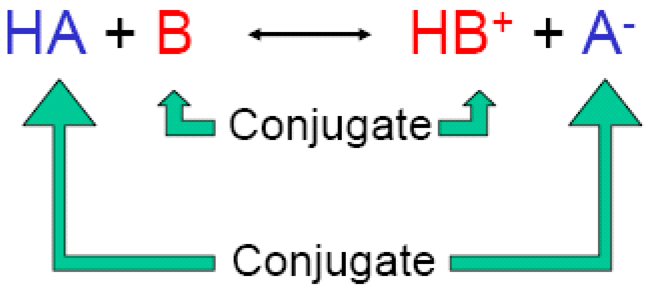
$K_A h = \frac{[H_2Sol^+][A^-]}{[HA]}$

Acids and Bases

- Bronsted Acids are proton donors. (HCl, $HOOCCH_3$)
- Bronsted Bases are proton acceptors (OH^-, R-COO^-, $NH_3 \rightarrow NH_4^+$)

$$HA(\mathit{sol}) + HSol(\mathit{l}) \leftrightharpoons A^-(\mathit{sol}) + H_2Sol^+(\mathit{sol})$$

$$B(\mathit{sol}) + HSol(\mathit{l}) \leftrightharpoons HB^+(\mathit{sol}) + Sol^-(\mathit{sol})$$



$$HA + B \longleftrightarrow HB^+ + A^-$$

$$K_A = \frac{[H_2Sol^+][A^-]}{[HA]} \qquad K_B = \frac{[Sol^-][HB^+]}{[B]}$$

Major Classes of Bronsted Acid

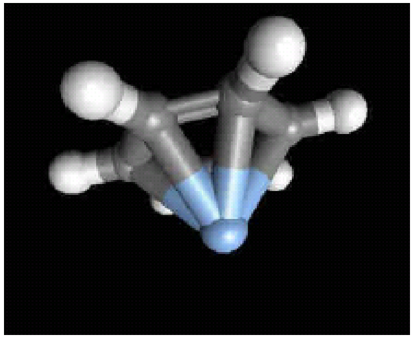
- Aqua acid
- Hydroxo acid
- Oxo acid

$$\begin{tikzcd}
H_2O\text{-}E\text{-}OH_2 \arrow[d, "- 2\ H^+"] \\
{[HO\text{-}E\text{-}OH]^{2-}} \arrow[d, "- H^+"] \\
{[HO\text{-}E{=}O]^{3-}}
\end{tikzcd}$$

Lewis Acids and Bases

- Lewis acids are electron pair acceptors (electron deficient; BH_3)
- Lewis bases are electron pair donors.

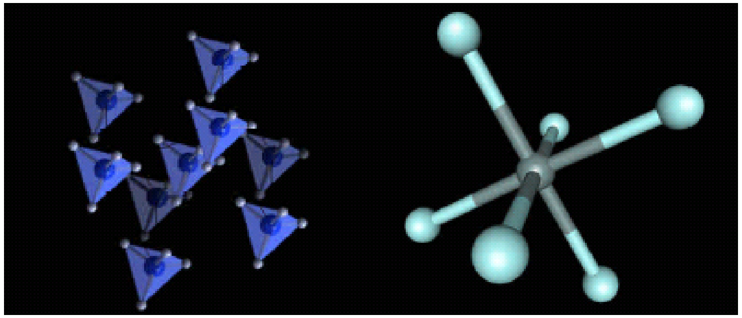
$[Ag\text{-}C_6H_6]^+$



$H_3B\text{-}NMe_3$

HCO_3^- $[O=C=O + OH^-]$

SiF_6^{2-} $[SiF_4 + 2\ :F^-]$



Group 13

- $B(CH_3)_3$ + $:NH_3$ → $CH_3B:NH_3$

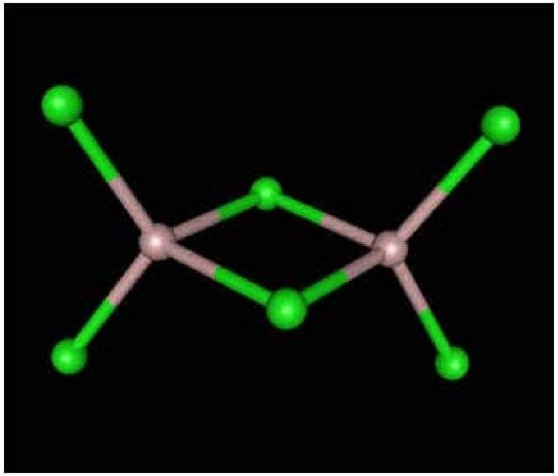
  Trend for acidity of BX_3 is: X = F < Cl < Br

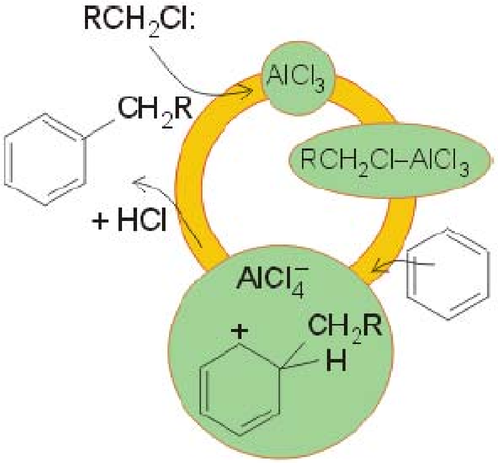
  BF_3 has better B-F π-bonding

- $AlCl_3$ is a dimer.

  $AlCl_3$ is used as a Lewis acid catalyst

  (e.g., Freidel-Crafts alkylation)

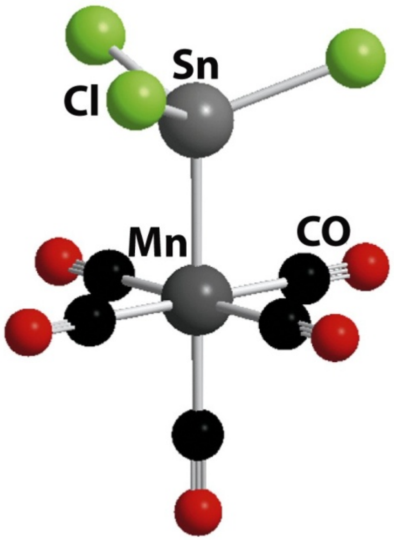




Group 14

- Elements that can expand their octet are good Lewis acids. (e.g., group 14)
  - SiF_4 + $2F^-$ → SiF_6^{2-}
  - Sn(II) is both a Lewis acid and a Lewis base

    $SnCl_2$ + Cl^- → $SnCl_3^-$



21 $[Mn(SnCl_3)(CO)_5]$

Structure 4-21
Shriver & Atkins Inorganic Chemistry, Fourth Edition
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Sn(IV) is a good Lewis acid

$SnCl_4$ + 2 Cl^- → $SnCl_6^{2-}$
Acidity of SnXor SiX_4: F > Cl > Br > I

Group 15 & 16

- Group 15 Lewis acids include “super acids” which use the Lewis acidity of SbF_5 to form SbF_6^- and a “solvated proton” that is acidic enough to protonate hydrocarbons.

- $SbF_5 + 2HF \rightarrow SbF_6^- + H_2F^+$
  $SbF_5 + 2HSO_3F \rightarrow SbF_5SO_3F^- + H_2SO_3F^+$

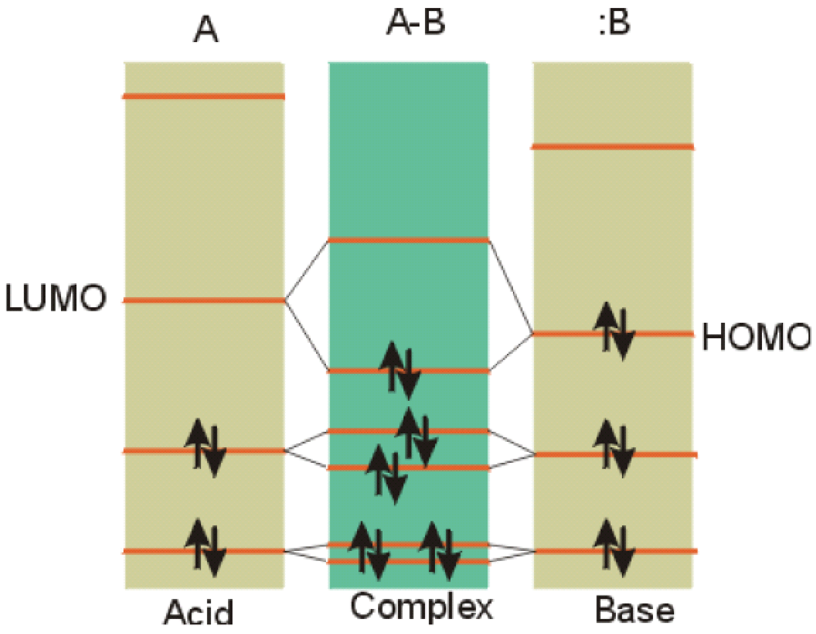
Sulfur oxides can be Lewis acids or bases:

$SO_2 + NR_3 \rightarrow O_2S\text{-}NR_3$

Can coordinate to metals via S or O

Lewis Acids and Bases

- A + :B → A-B
- A Lewis acid has a low-lying LUMO;
- A Lewis base has a high-lying HOMO



HSABT

Hard acids tend to bind best to hard bases and *vice versa*.

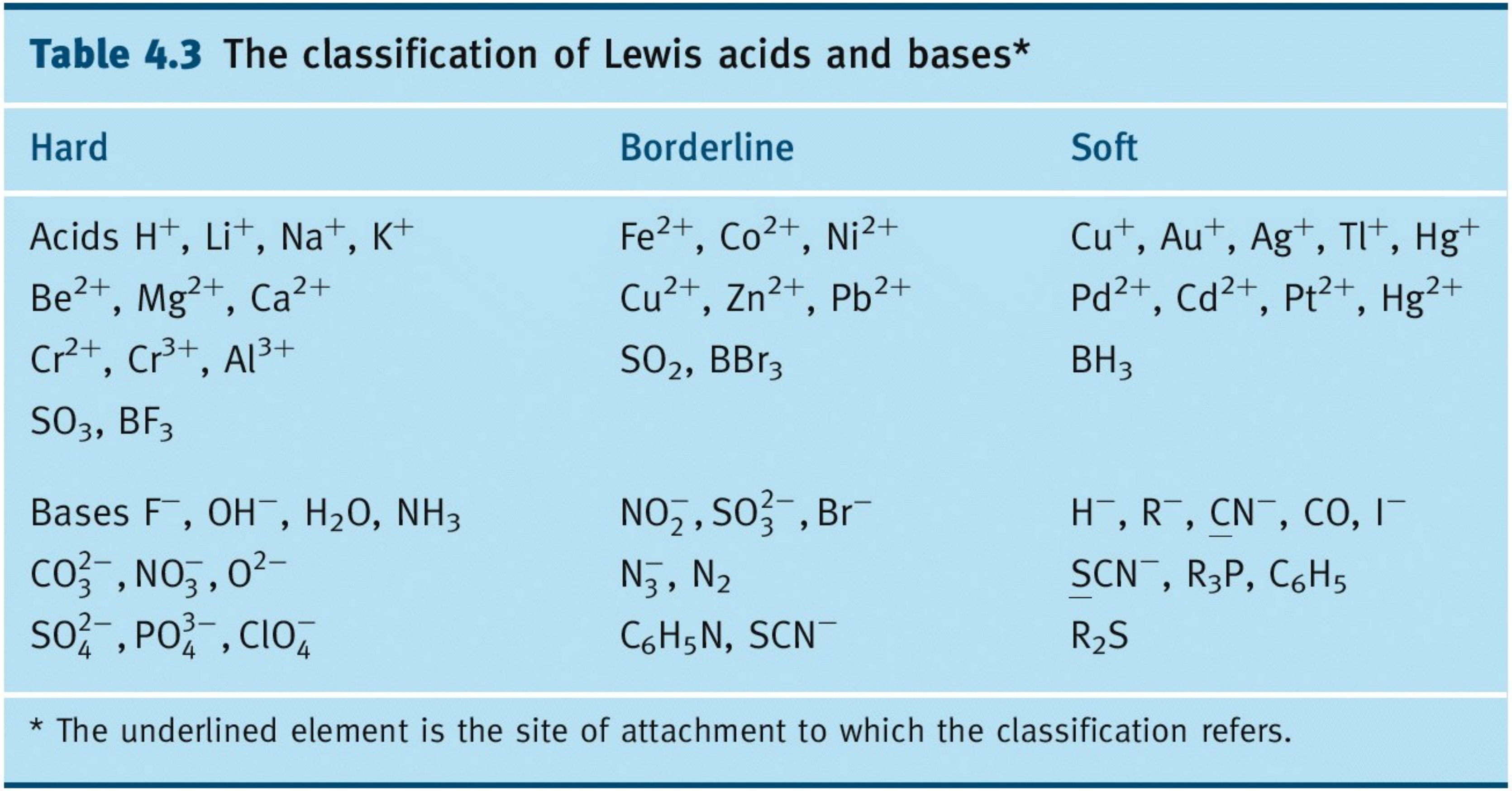


Table 4.3 The classification of Lewis acids and bases*

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^+, Au^+, Ag^+, 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-}, Br^- N_3^-, N_2 C_6H_5N, SCN^-	H^-, R^-, $\underline{C}N^-$, CO, I^- $\underline{S}CN^-$, R_3P, C_6H_5 R_2S

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

Hard-hard interactions max. ionic character; soft-soft max. covalency.

HSABT

- E and C parameters predict bond enthalpies
- $-\Delta H^0(\text{A-B}) = E_A E_B + C_A C_B$
- Strong bonds can be highly ionic, highly covalent, or have contributions from both.

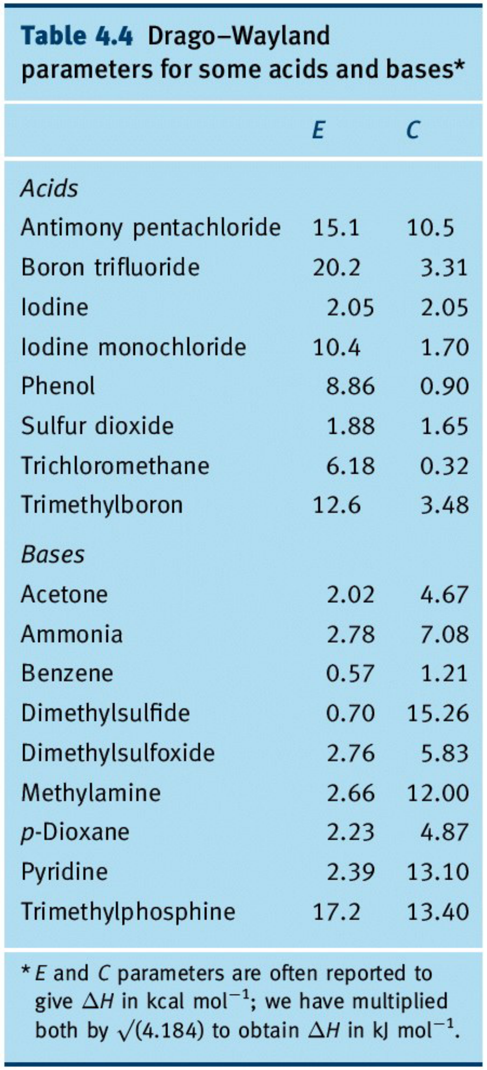


Table 4.4 Drago–Wayland parameters for some acids and bases*

	E	*C*
Acids		
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
Bases		
Acetone	2.02	4.67
Ammonia	2.78	7.08
Benzene	0.57	1.21
Dimethylsulfide	0.70	15.26
Dimethylsulfoxide	2.76	5.83
Methylamine	2.66	12.00
p-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}.