(19) **Today**

Chap 6 Acid-Base and Donor-Acceptor Chemistry

Next Class (20)

Chap 6 Acid-Base and Donor-Acceptor Chemistry

(21) **Second Class from Today**

Chap 6 Acid-Base and Donor-Acceptor Chemistry

Third Class from Today (22)

Chap 6 Acid-Base and Donor-Acceptor Chemistry

Acidity of Bronstead-Lowry Acids

$$HA \rightleftharpoons H^+ + A^-$$

stabilize the ⊖ charge by

- getting it near a ⊕
- spread it out
  - inductive effect
  - resonance
  - large atoms

the more stable the conjugate base is, the easier it is to form the conjugate base the easier it is to release an H^+

across a period

$pK_a \sim \overset{48}{50}$ $CH_4 \longrightarrow H^{\oplus}\ {}^{\ominus}CH_3$ +6

$pK_a \sim 36$ $NH_3 \longrightarrow H^{\oplus}\ {}^{\ominus}NH_2$ 7

$pK_a = 14.0$ $H_2O \longrightarrow H^{\oplus}\ {}^{\ominus}OH$ 8

$pK_a = 3.18$ $HF \longrightarrow H^{\oplus}\ {}^{\ominus}F$ +9

more ⊕ nucleus
more attraction
for e^-'s
more stable
conj base

LiH
NaH
KH

down a family

Same Column Larger Valence Shell

strong

HI $\rightarrow$ H^+ I^-

charge is much more diffuse... large anions are more stable than smaller anions

HBr $\rightarrow$ H^+ Br^-

HCl $\rightarrow$ H^+ Cl^-

$H{-}OH \rightleftharpoons H^{\oplus}\ {}^{\ominus}OH$

$H{-}SH \rightleftharpoons H^{\oplus} + {}^{\ominus}SH$

HF $\rightleftharpoons$ H^+ F^-

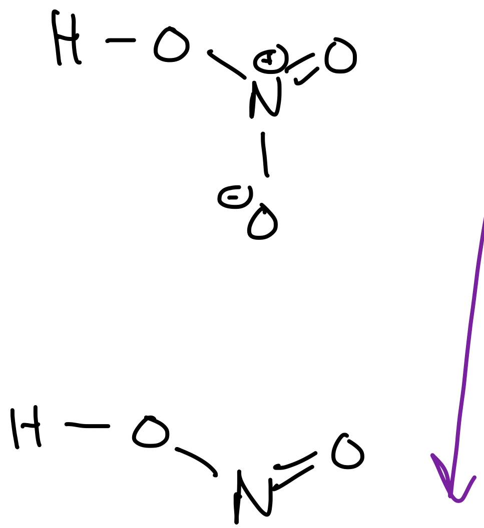
weak

stronger

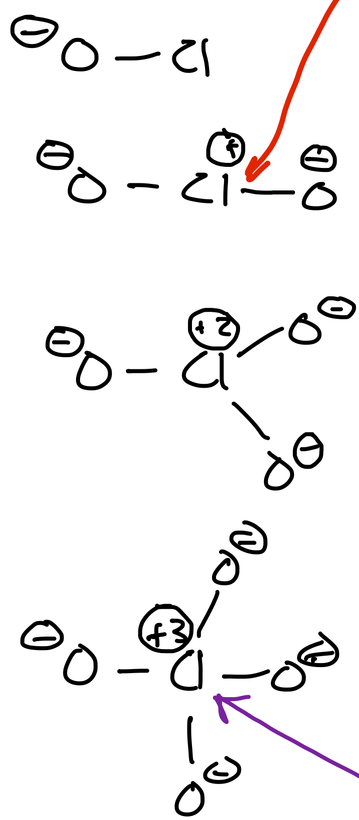
pK_a's HF, 3.18 HCl, -7 HBr, -9 HI, -10 for "oxy-acids"

Br, I

weak



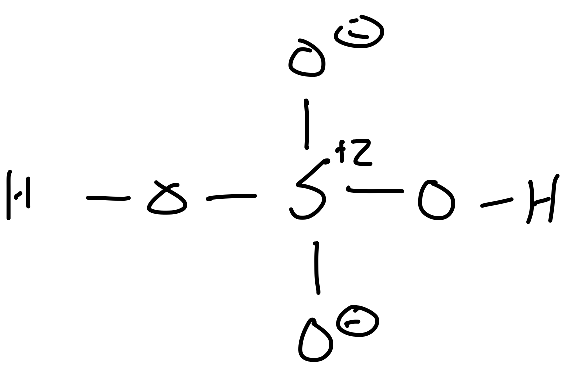
H^+

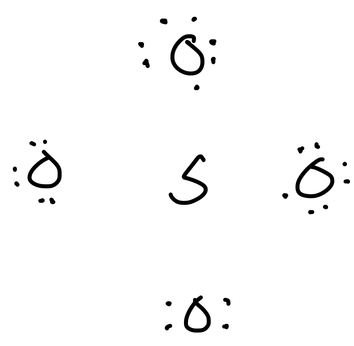


strong

strong

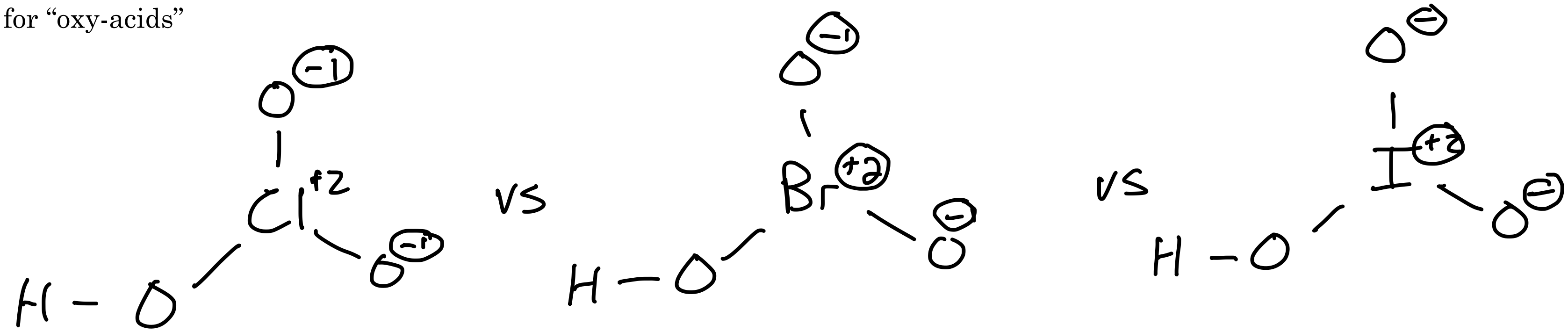
more + more ⊕ atom to attract e^-





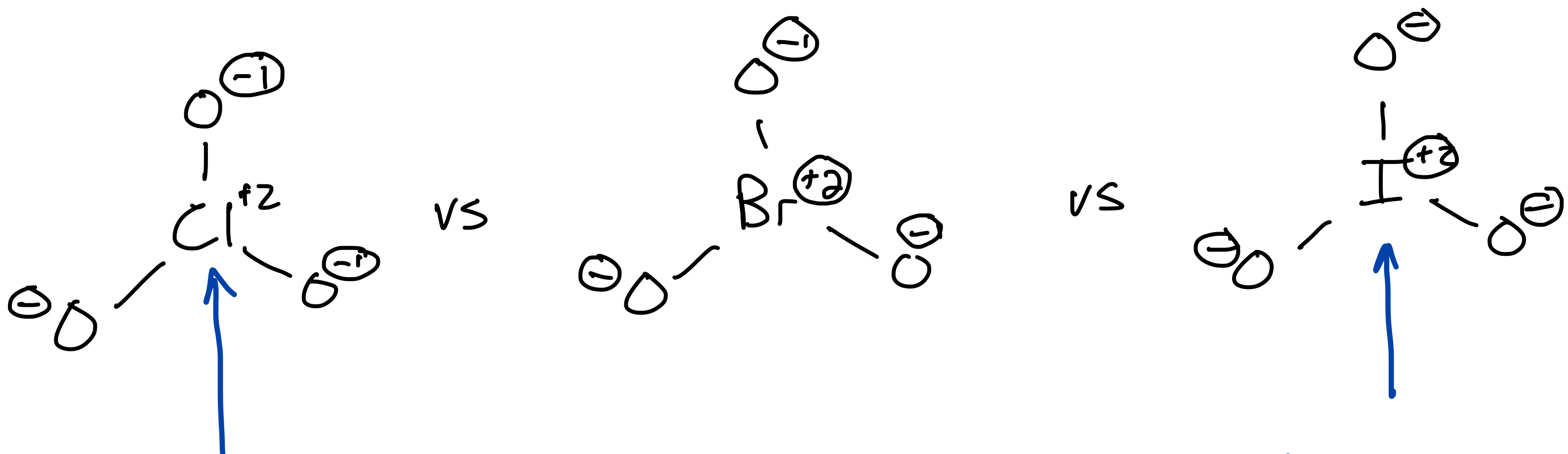
SO_4^{2-}

for "oxy-acids"



stronger

weaker



More eneg atom

draws e⁻'s from O towards Cl, stabilizing them

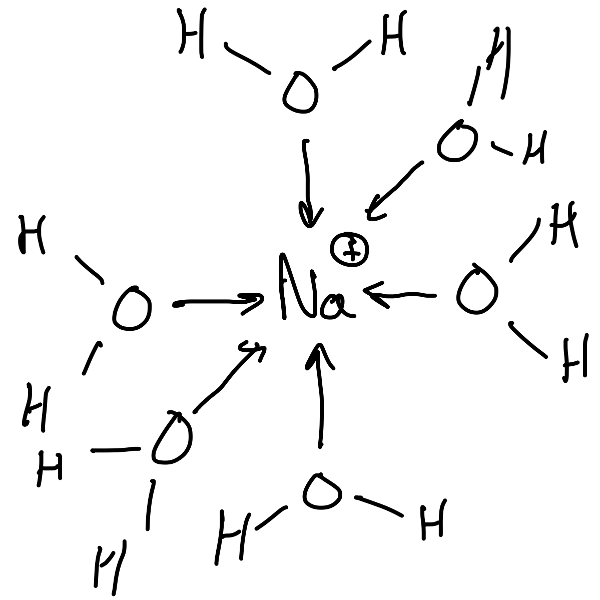
least eneg

Trends in Acid Strength

Section 6.3.8

For Lewis acids

Na^+ vs H_2O

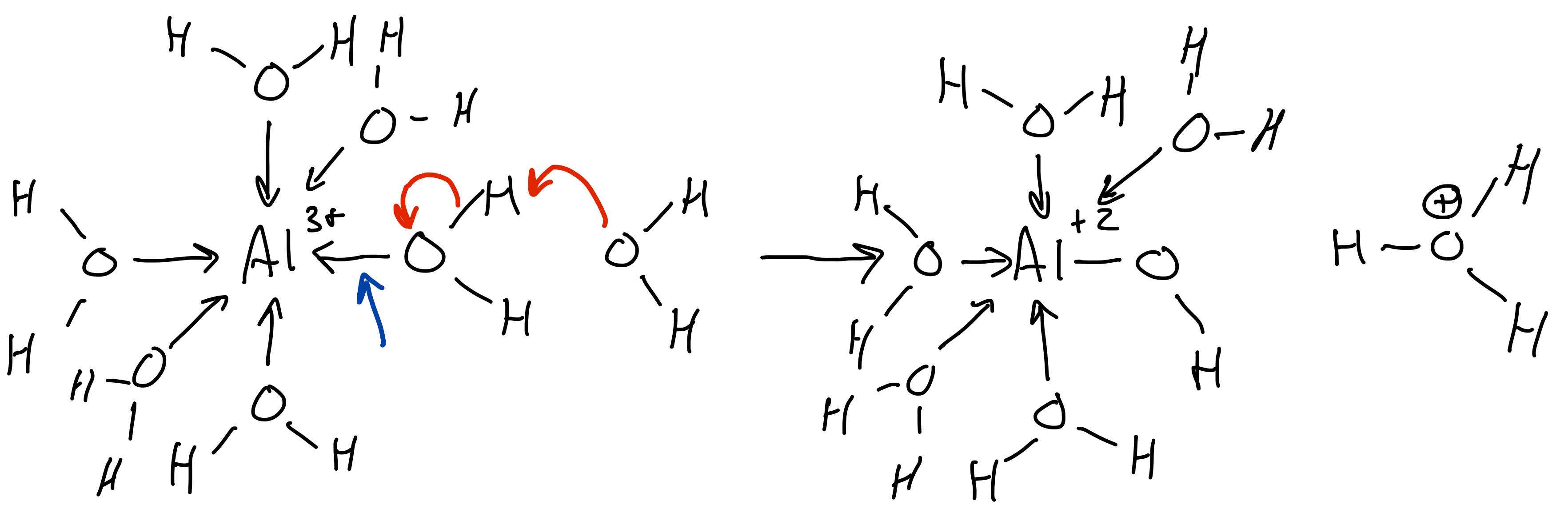


Increasing the charge on similarly sized ions increases Lewis acidity

Mg^{2+} vs Hg^{2+}

In similarly charged ions larger ions are more acidic

$$AlCl_3 + 3H_2O \longrightarrow Al(OH)_3 + 3HCl_{(g)}$$



Gas phase basicity

$$NMe_3 < NHEt_2 < NHBu_2 < NEt_3 < NBu_3$$

Increasing base strength in water

$$NH_3 < Me_3N < MeNH_2 < Me_2NH$$

$$NH_3 < EtNH_2 < Et_3N < Et_2NH$$

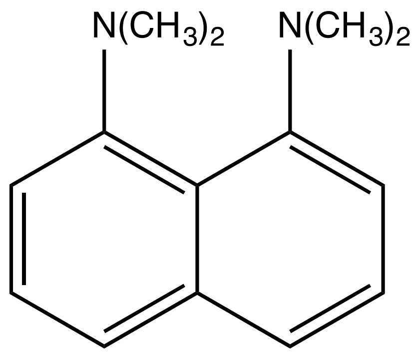
Super acids

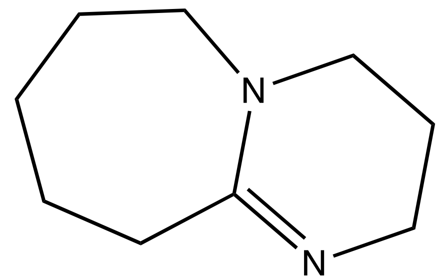
Section 6.1, 6.2, 6.3, 6.4

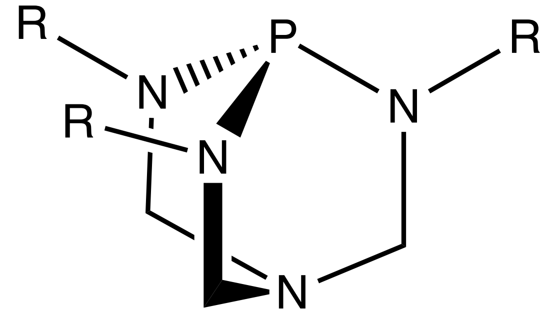
$$H_0 = pK_{BH^+} - \log([BH^+]/[B])$$

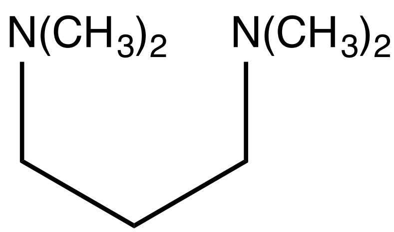
H_2SO_4	-11.9
$HClO_4$	-13.0
HSO_3CF_3	-14.6
HSO_3F	-15.6
$HSO_3F–SbF_5$	-21– -25
$HF + SbF_5 \Leftrightarrow H^+ + SbF_6^-$	-21 – - 28

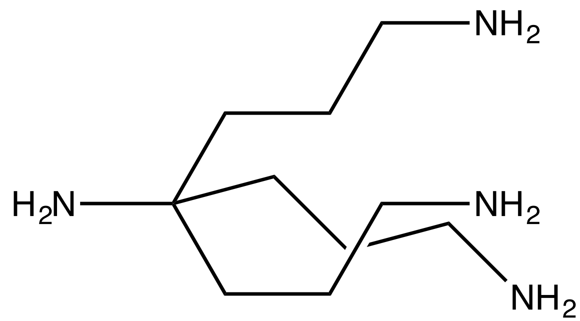
$CH_3CH_2CH_2CH_2Li$



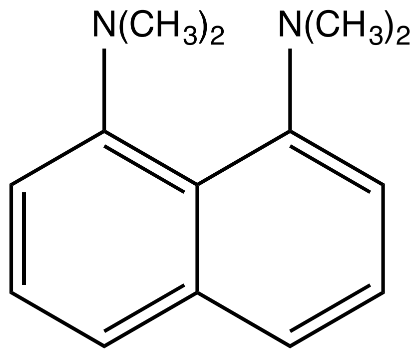


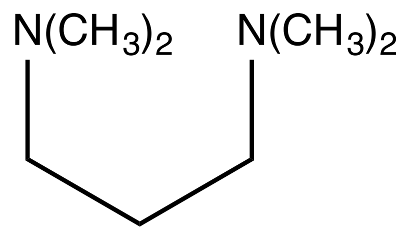


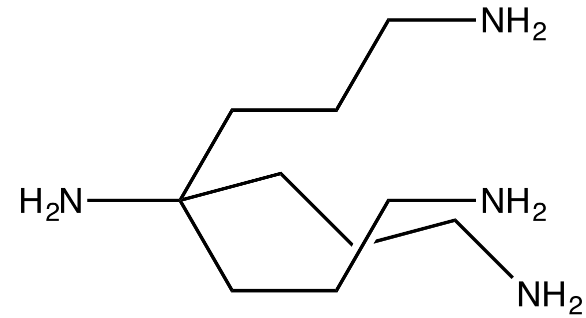


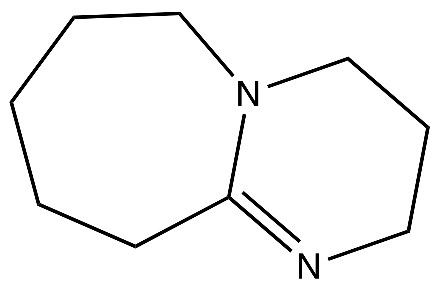


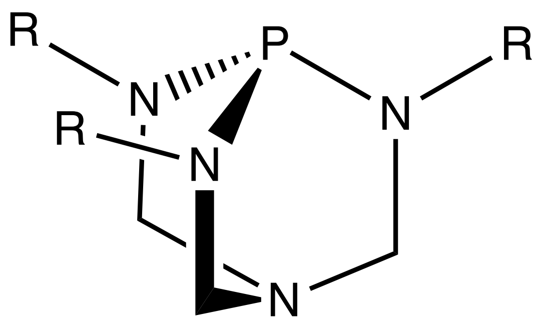
$CH_3CH_2CH_2CH_2Li$


N(CH3)2
N(CH3)2


N(CH3)2
N(CH3)2


NH2
H2N
NH2
NH2


N
N


R
P
R
N
N
R
N
N

(24) **Today**

Chap 6 Acid-Base and Donor-Acceptor Chemistry

Next Class (25)

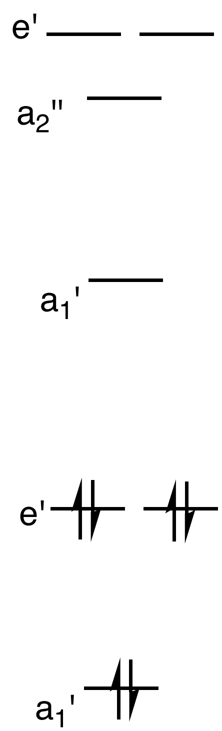
Chap 6 Acid-Base and Donor-Acceptor Chemistry

(26) **Second Class from Today**

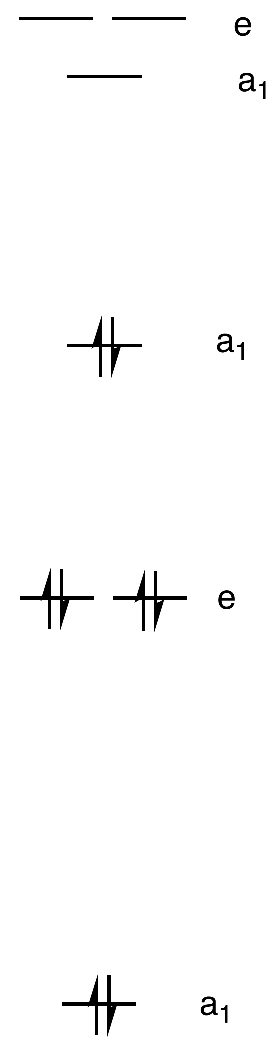
Chap 9.1 Introduction to Coordination Chemistry

Third Class from Today (27)

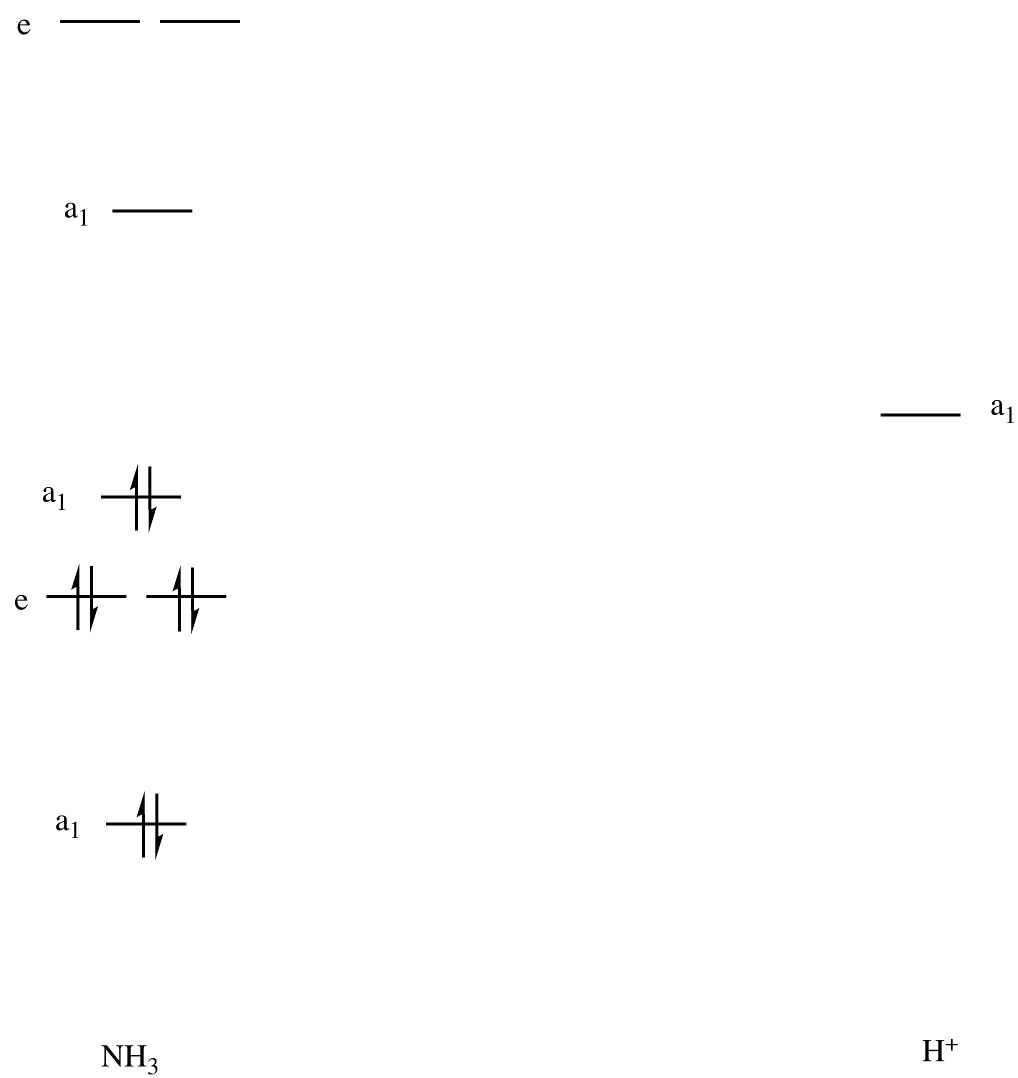
Chap 9.1 Introduction to Coordination Chemistry

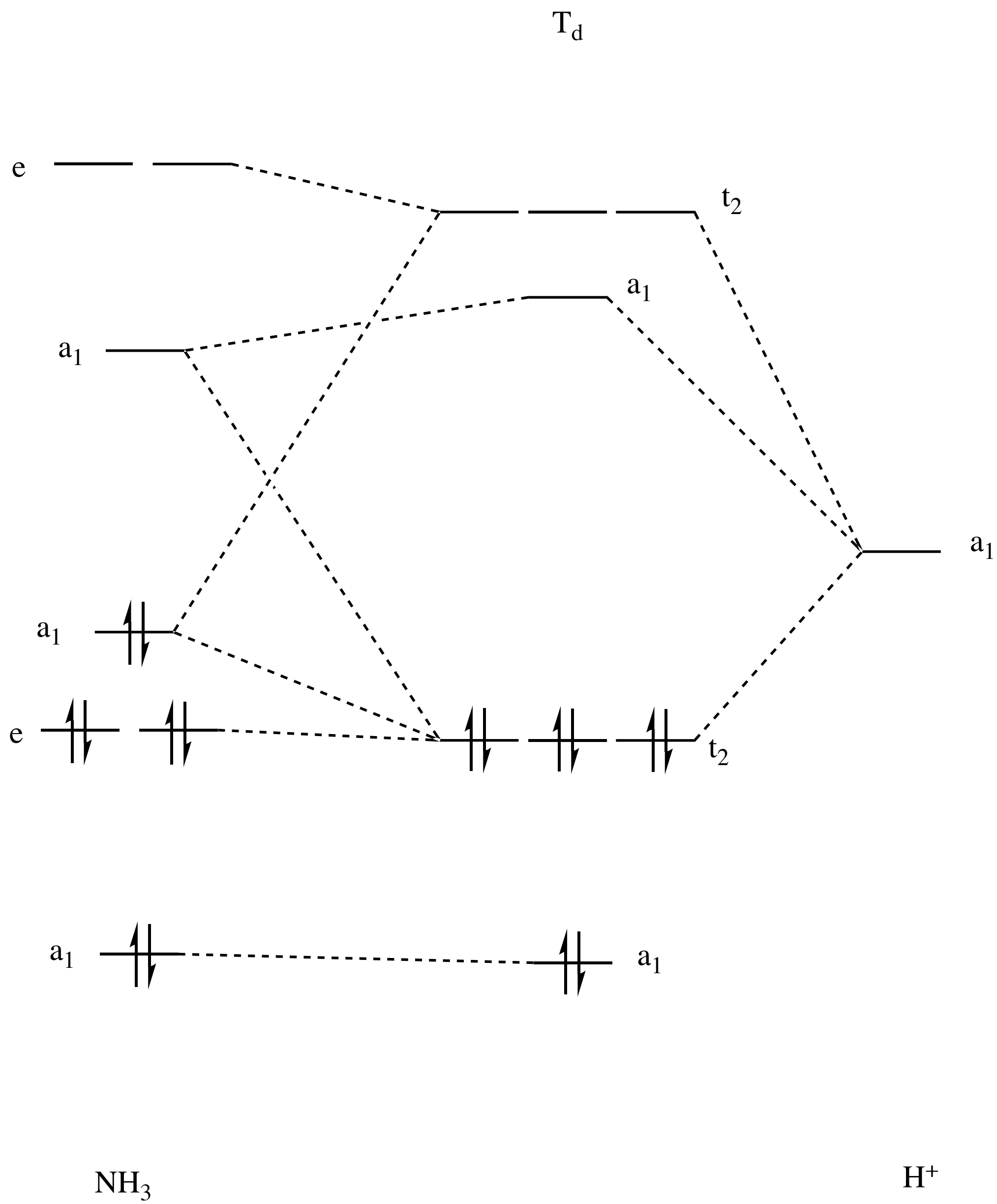


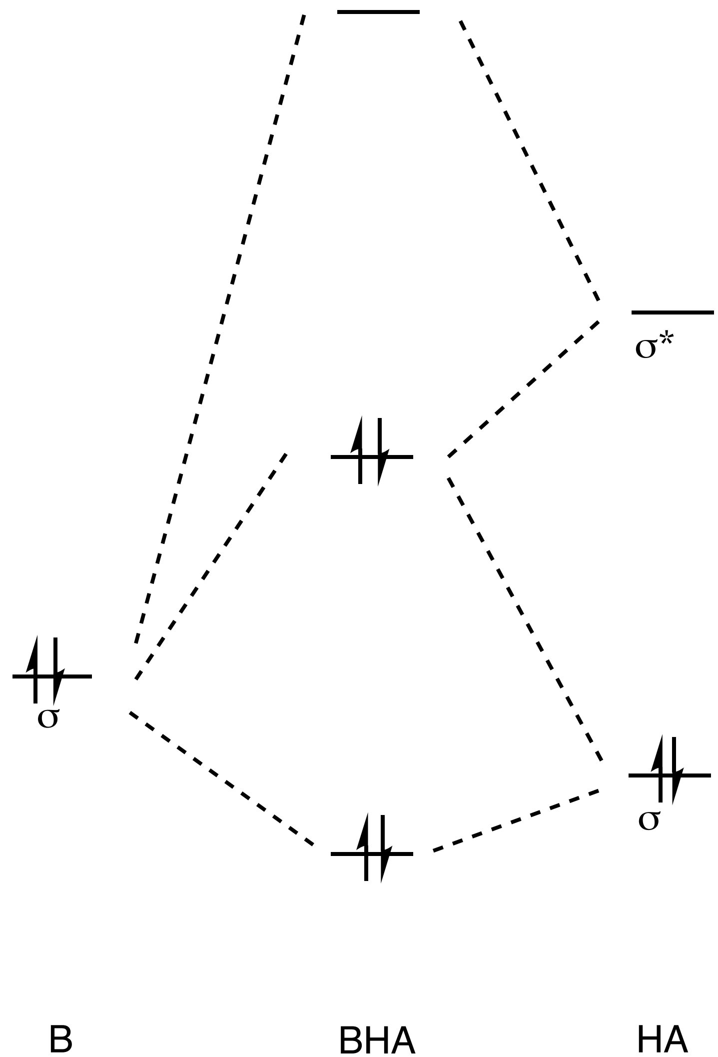
BH_3

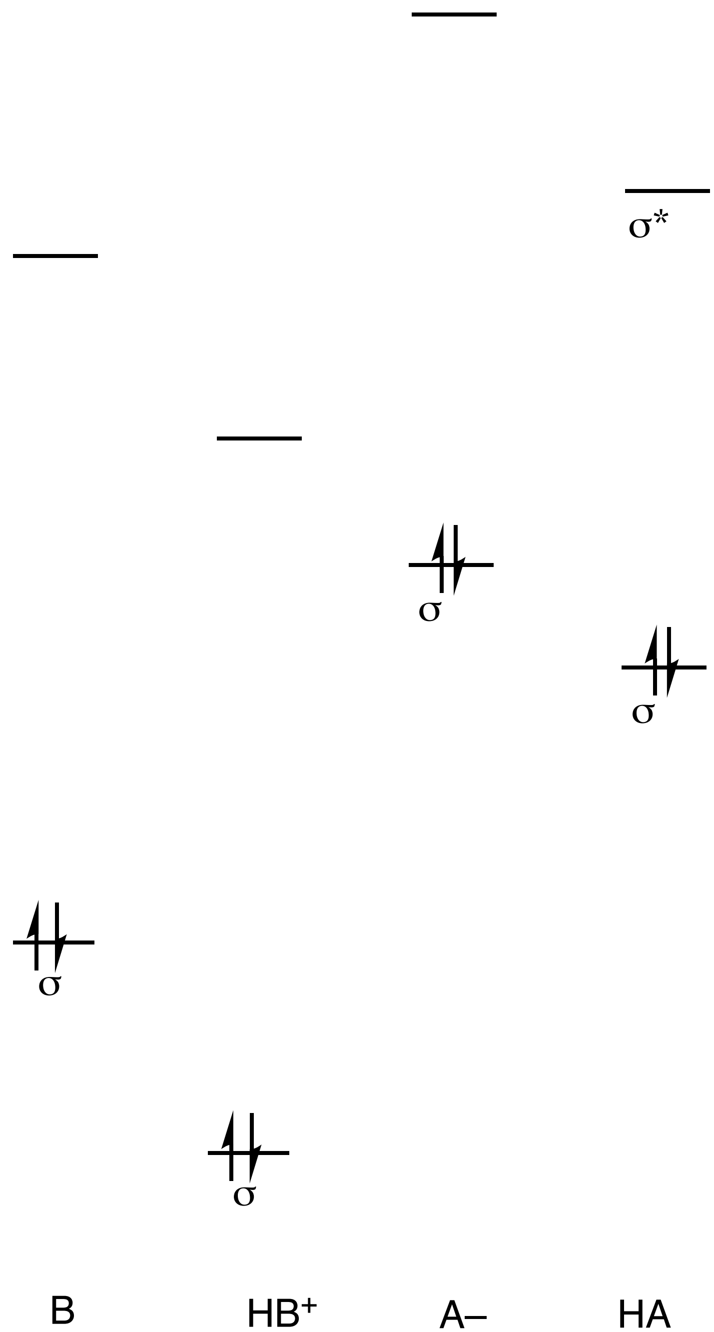


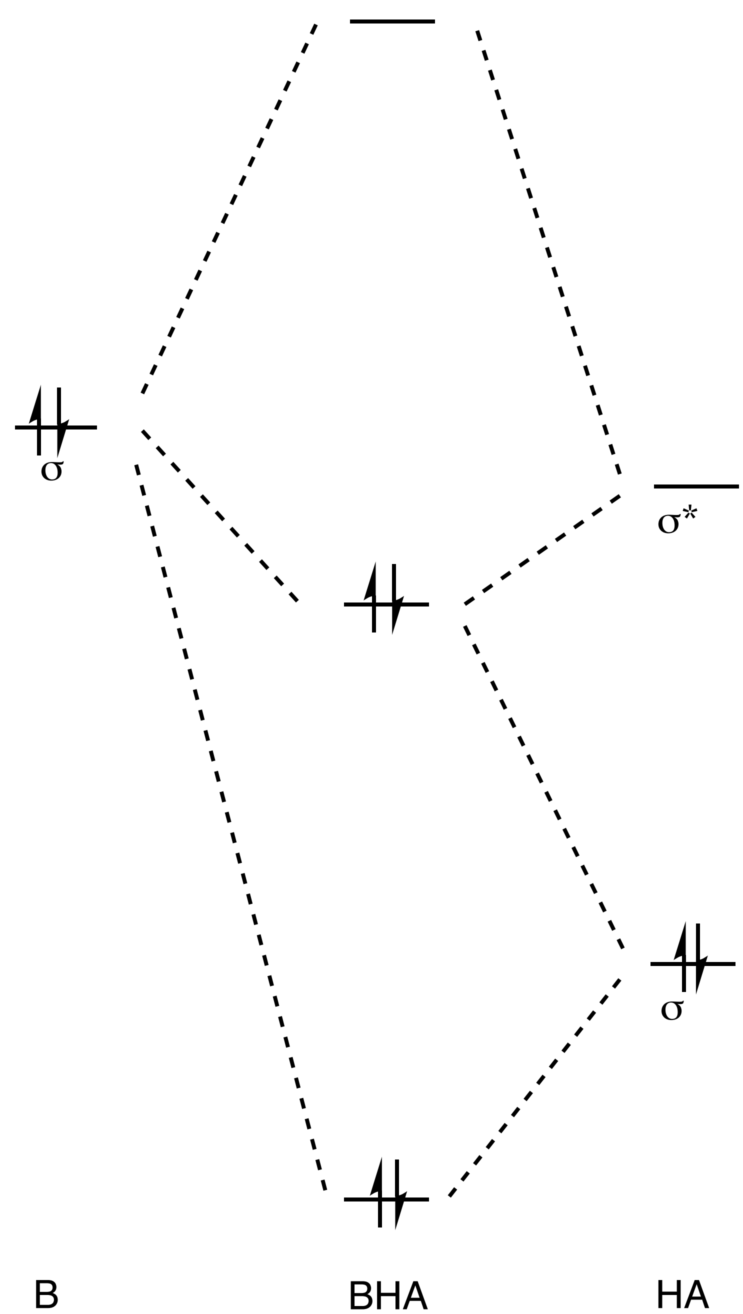
NH_3

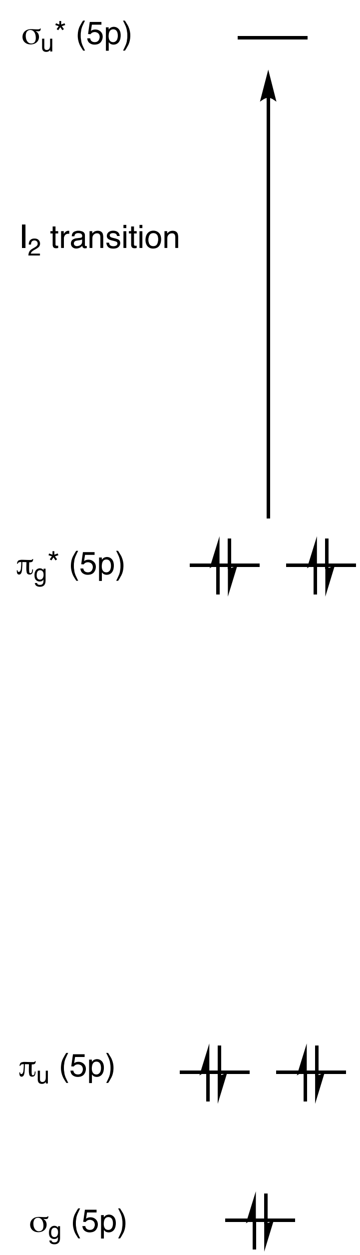

e
a1
a1
e
a1
NH3
a1
H+

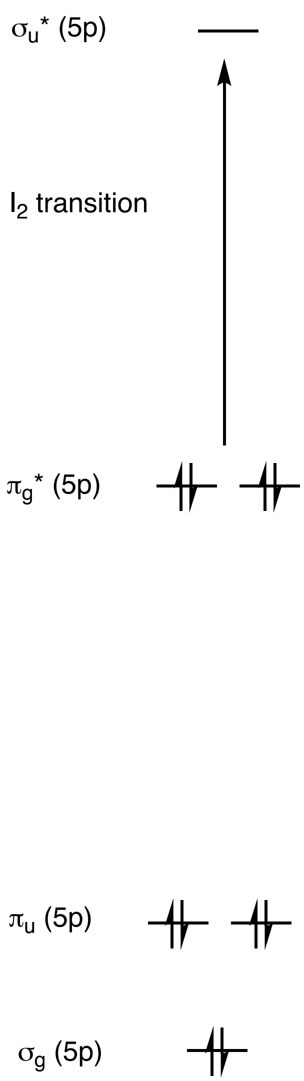

T_d
e
t_2
a_1
a_1
a_1
a_1
e
t_2
a_1
a_1
NH_3
H^+

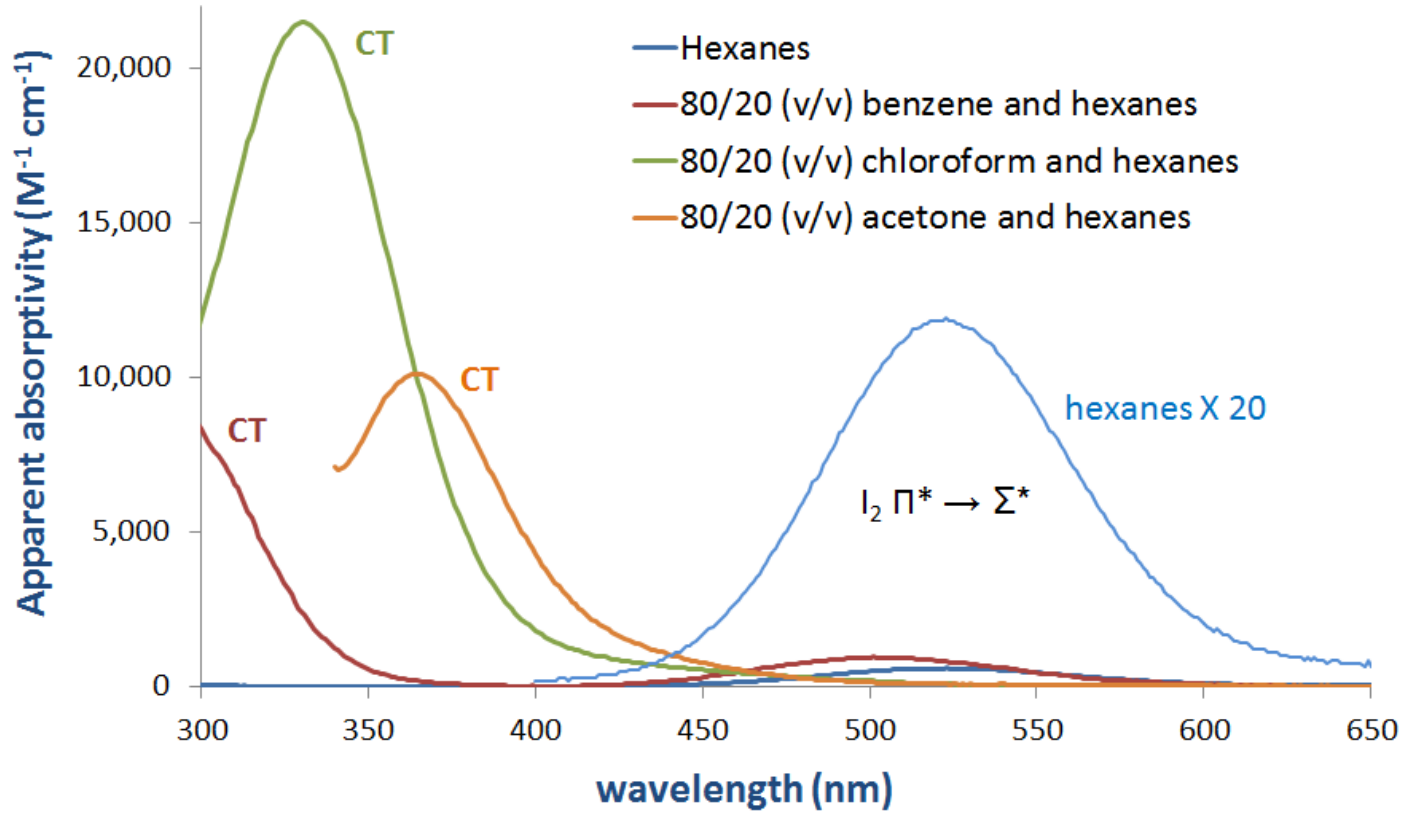

σ*
σ
σ
B
BHA
HA


σ*
σ
σ
σ
σ
B
HB+
A–
HA


σ
σ*
σ
B
BHA
HA


σ_u* (5p)
I_2 transition
π_g* (5p)
π_u (5p)
σ_g (5p)





https://chem.libretexts.org/Bookshelves/Inorganic_Chemistry/Map%3A_Inorganic_Chemistry_(Miessler_Fischer_Tarr)/06%3A_Acid-Base_and_Donor-Acceptor_Chemistry/6.04%3A_Lewis_Concept_and_Frontier_Orbitals/6.4.03%3A_The_electronic_spectra_of_charge_transfer_complexes_illustrate_the_impact_of_frontier_orbital_interactions_on_the_electronic_structure_of_Lewis-Acid_base_adducts.

AgF $K_{sp} = 205$
AgCl $K_{sp} = 1.8 \times 10^{-10}$
AgBr $K_{sp} = 5.2 \times 10^{-13}$
AgI $K_{sp} = 8.3 \times 10^{-17}$

$[Hg(SCN)_4]^{2-}$ vs $[Zn(NCS)_4]^{2-}$

$[CH_3Hg(H_2O)]^+ + HCl$ $CH_3HgCl + H_3O^+$ $K = 1.8 \times 10^{12}$

$[CH_3Hg(H_2O)]^+ + HF$ $CH_3HgF + H_3O^+$ $K = 4.5 \times 10^{-2}$

$[Hg(SCN)_4]^{2-}$ vs $[Zn(NCS)_4]^{2-}$

												B	C				
						Mn	Fe	Co	Ni	Cu							
					Mo	Tc	Ru	Rh	Pd	Ag	Cd				Te		
					W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po		

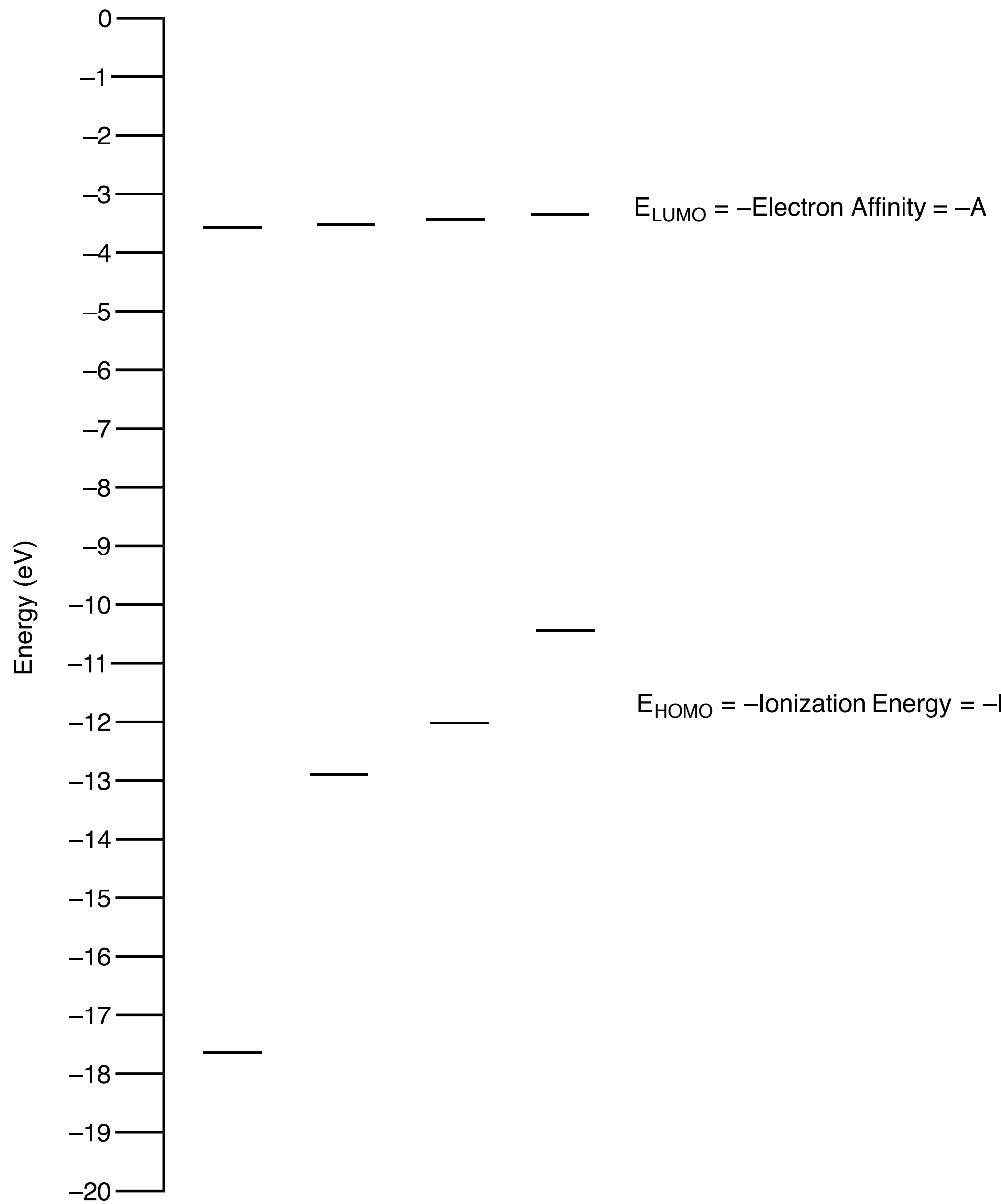
Hard Bases	Borderline Bases	Soft Bases
		H^-
F^-, Cl^-	Br^-	I^-
H_2O, OH^-, O^{2-}		H_2S, SH^-, S^{2-}
ROH, RO^-, R_2O, CH_3COO^-		RSH, RS^-, R_2S
NO_3^-, ClO_4^-	NO_2^-, N_3^-	SCN^-, CN^-, RNC, CO
CO_3^{2-}, SO_4^{2-}, PO_4^{3-}	SO_3^{2-}	$S_2O_3^{2-}$
NH_3, RNH_2, N_2H_4	$C_6H_5NH_2$, C_5H_5N, N_2	PR_3, $P(OR)_3$, AsR_3, C_2H_4, C_6H_6

AgF	$K_{sp} = 205$
$AgCl$	$K_{sp} = 1.8 \times 10^{-10}$
$AgBr$	$K_{sp} = 5.2 \times 10^{-13}$
AgI	$K_{sp} = 8.3 \times 10^{-17}$

$[CH_3Hg(H_2O)]^+ + HCl$ $CH_3HgCl + H_3O^+$ $K = 1.8 \times 10^{12}$

$[CH_3Hg(H_2O)]^+ + HF$ $CH_3HgF + H_3O^+$ $K = 4.5 \times 10^{-2}$

$$\eta = \frac{I - A}{2}$$



Energy (eV)
0
–1
–2
–3
–4
–5
–6
–7
–8
–9
–10
–11
–12
–13
–14
–15
–16
–17
–18
–19
–20
E_LUMO = –Electron Affinity = –A
E_HOMO = –Ionization Energy = –I