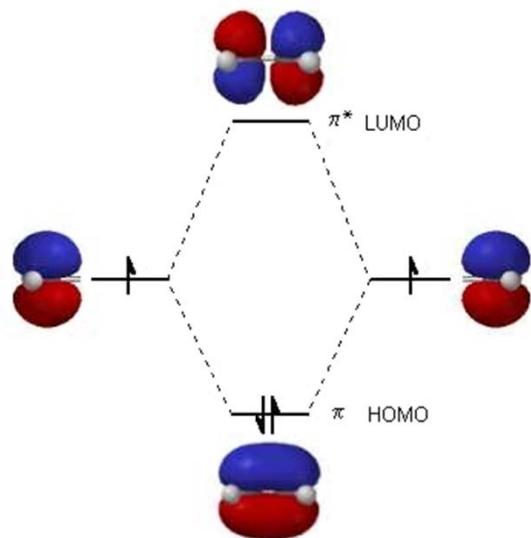
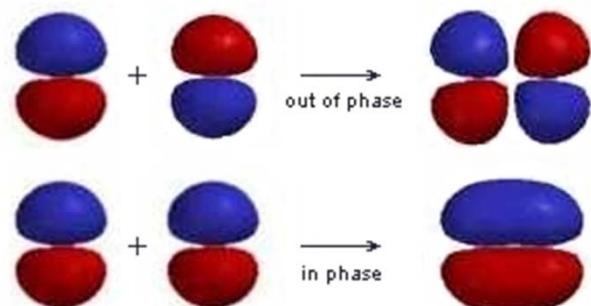


 π Molecular Orbitals of Ethene

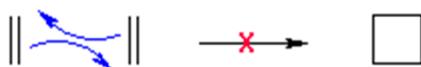
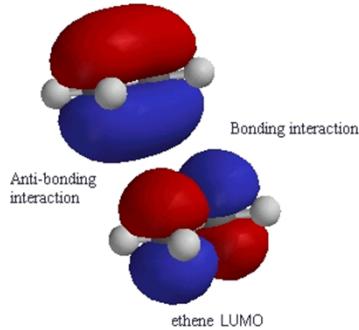


Molecular Orbital Analysis of Ethene Dimerisation

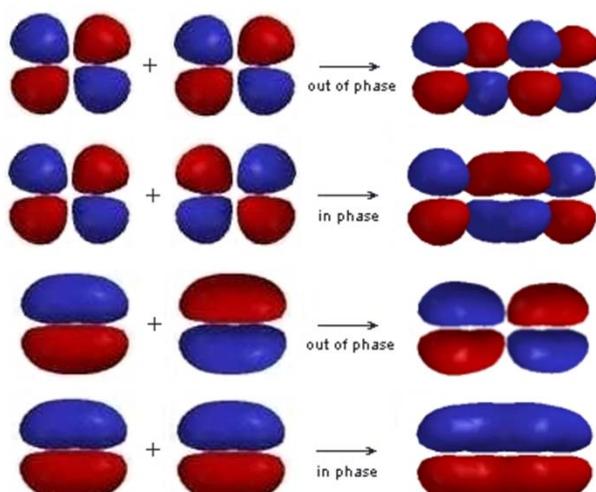


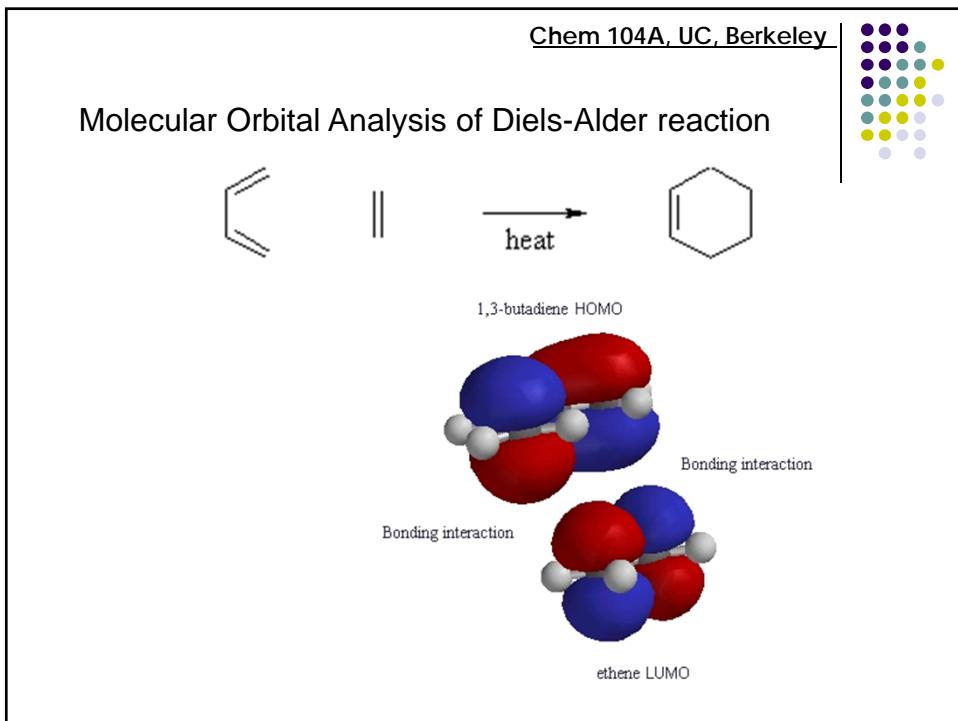
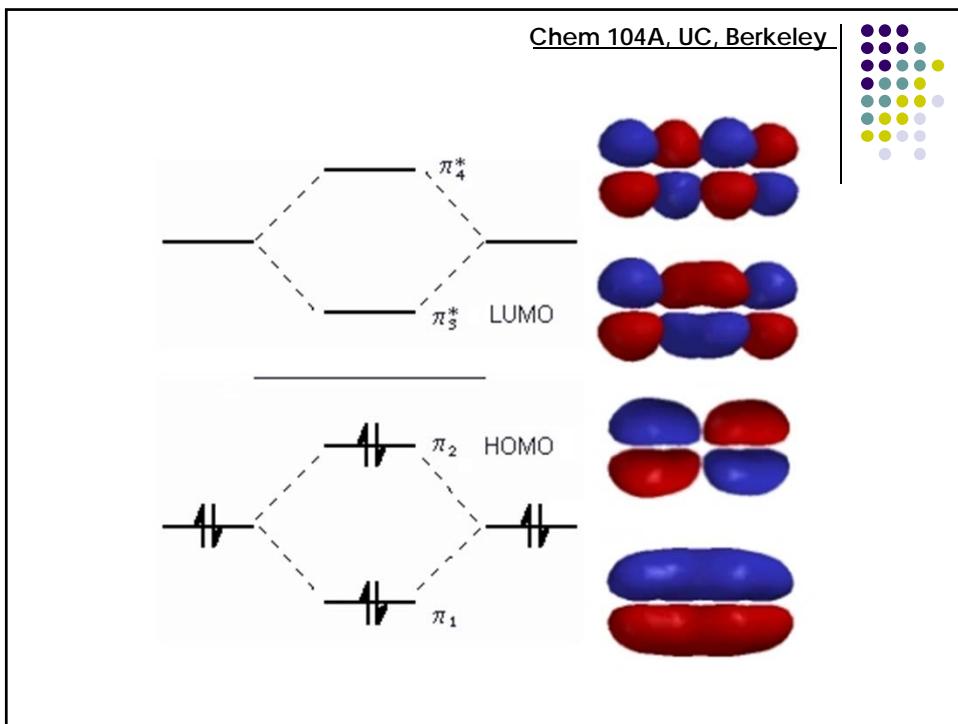
ethene ethene cyclobutane

ethene HOMO



the reaction is said to be a "**symmetry forbidden**" – interestingly, this reaction is rare and very slow !

 π Molecular Orbitals of 1,3-Butadiene





Acid-Base Chemistry

Reading : MT 6

The Acid Base Theory of Brønsted and Lowry

In 1923, within several months of each other, Johannes Nicolaus Brønsted (Denmark) and Thomas Martin Lowry (England) published essentially the same theory about how acids and bases behave.

- An acid is a "proton donor."**
- A base is a "proton acceptor."**



HCl - this is an acid, because it has a proton available to be transferred.

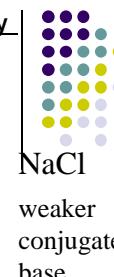
H_2O - this is a base, since it gets the proton that the acid lost.

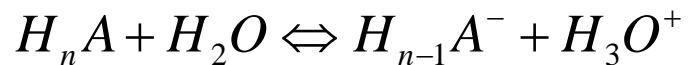
Now, here comes an interesting idea:

H_3O^+ - this is an acid, because it can give a proton.

Cl^- - this is a base, since it has the capacity to receive a proton.

Notice that each pair (HCl and Cl^- as well as H_2O and H_3O^+ differ by one proton (symbol = H^+). These pairs are called **conjugate pairs**.





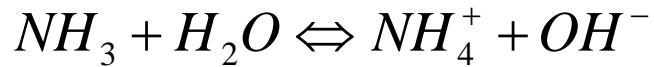
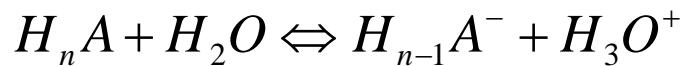
$$pK_{a1} = -\log \frac{[H_{n-1}A^-][H_3O^+]}{[H_nA]}$$

$pK_a < 0 \rightarrow strong$

$pK_a > 0 \rightarrow weak$



Amphoteric Compound

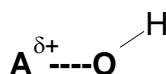




Oxyacids $\text{AO}_p(\text{OH})_q$

$\text{A}=\text{Si, N, P, As, S, Se, Te, Cl, Br, I}$

$p=\# \text{ of nonhydrogenated oxygen atom}$



As atom A is rendered more positive, it becomes easier to break the O-H bond
Because of enhanced bond polarization.

The greater the formal charge on A. the stronger the acid should be.



Oxyacids $\text{AO}_p(\text{OH})_q$

$p=\# \text{ of nonhydrogenated oxygen atom}$

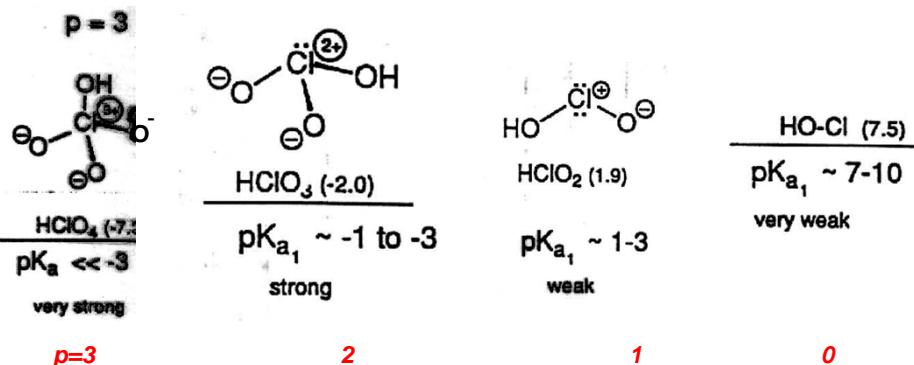
$p=0: \text{PKa } 8-9 \text{ very weak}$

$p=1: \text{PKa } 1-2 \text{ weak}$

$p=2: \text{PKa } -2 \sim -3 \text{ strong}$

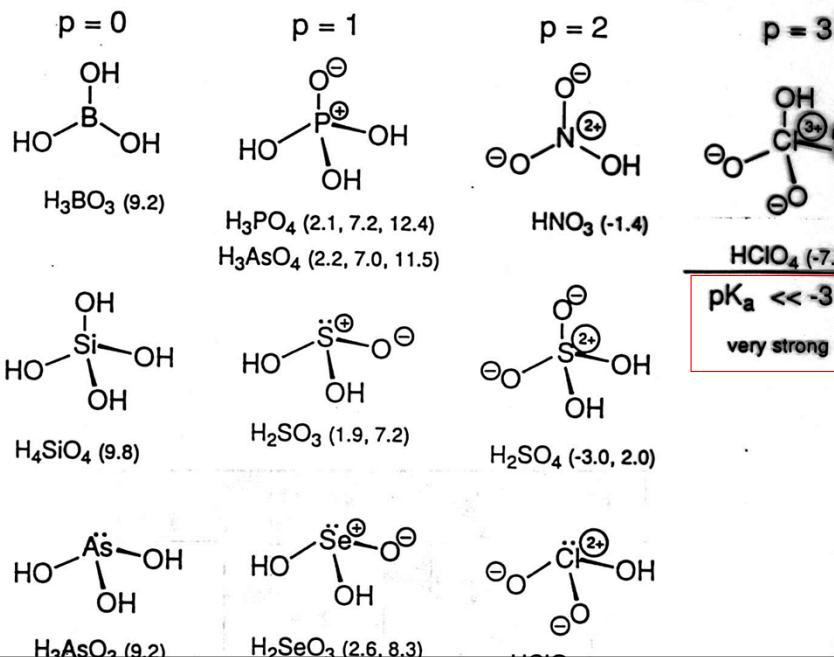
$p=3: \text{PKa } -7 \text{ very strong}$

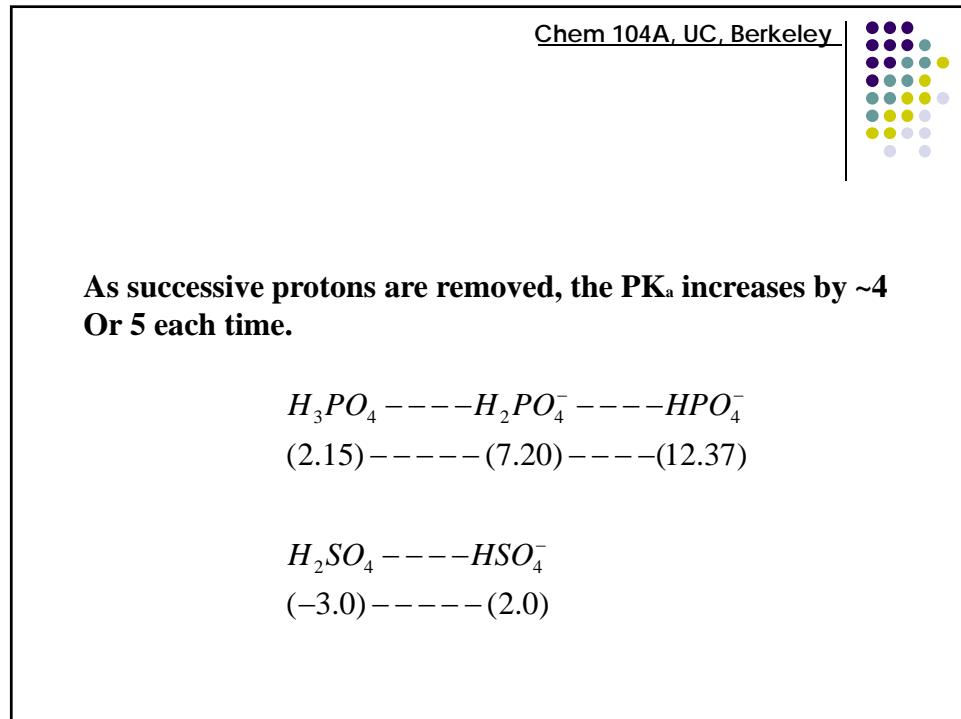
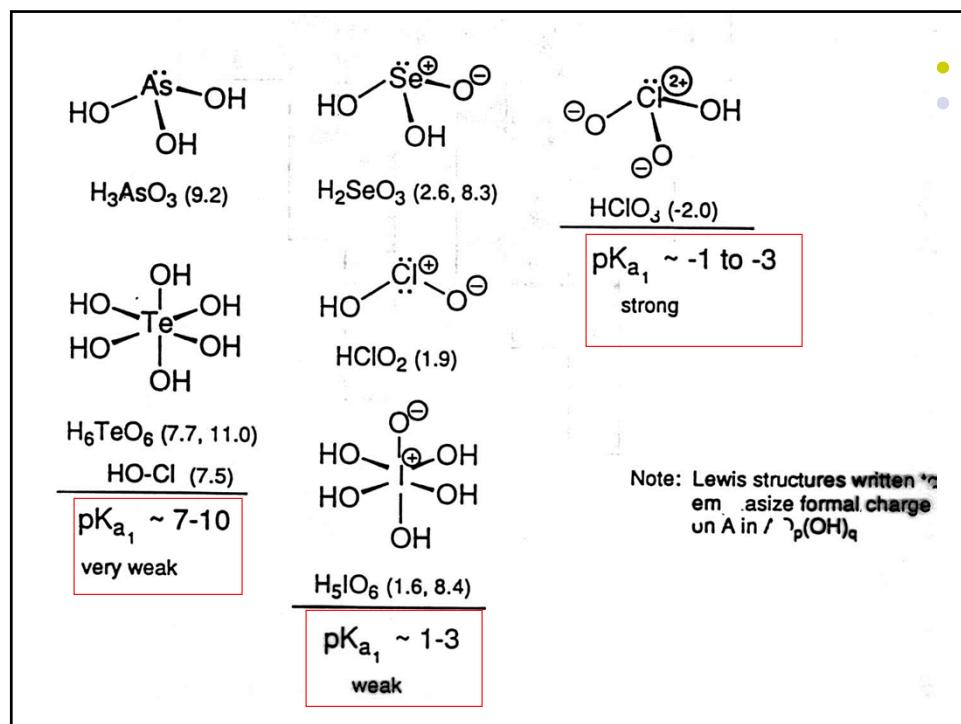
$\text{A}=\text{Si, N, P, As, S, Se, Te, Cl, Br, I}$



Empirical Rule (Pauling)

$$PK_a \approx 8 - 5p$$

Some Common Oxyacids and Their pK_{a_n} Values



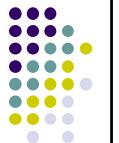
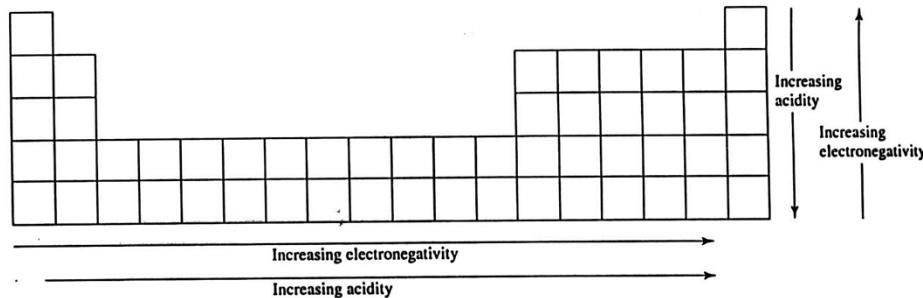
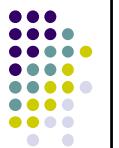
 H_nX 

FIGURE 6-5 Trends in Acidity and Electronegativity.

0.1 M HCl, H₂S, H₂O, H₃PO₄, H₂PO₄⁻, HPO₄²⁻, PO₄³⁻

Acidity



→ Conjugated bases SeH⁻, SH⁻, OH⁻ of larger molecules

→ lower charge density

→ weaker attraction for H⁺



Acidity

$\text{NH}_3 < \text{H}_2\text{O} < \text{HF}$

→ Conjugated bases NH_2^- , OH^- , F^-

$\text{NH}_2^- \rightarrow -1/2$ on each lone pair

$\text{HO}^- \rightarrow -1/3$ on each lone pair

$\text{F}^- \rightarrow -1/4$ on each lone pair

Strongest attraction for proton

Strongest conjugated base

Weakest acid NH_3



Lewis Concept

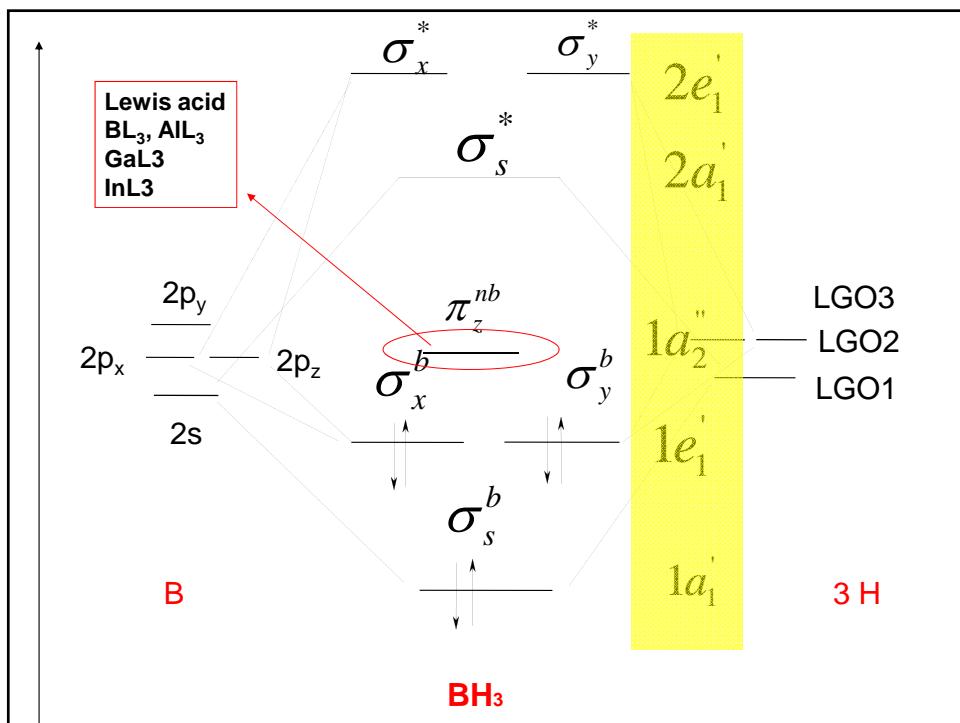
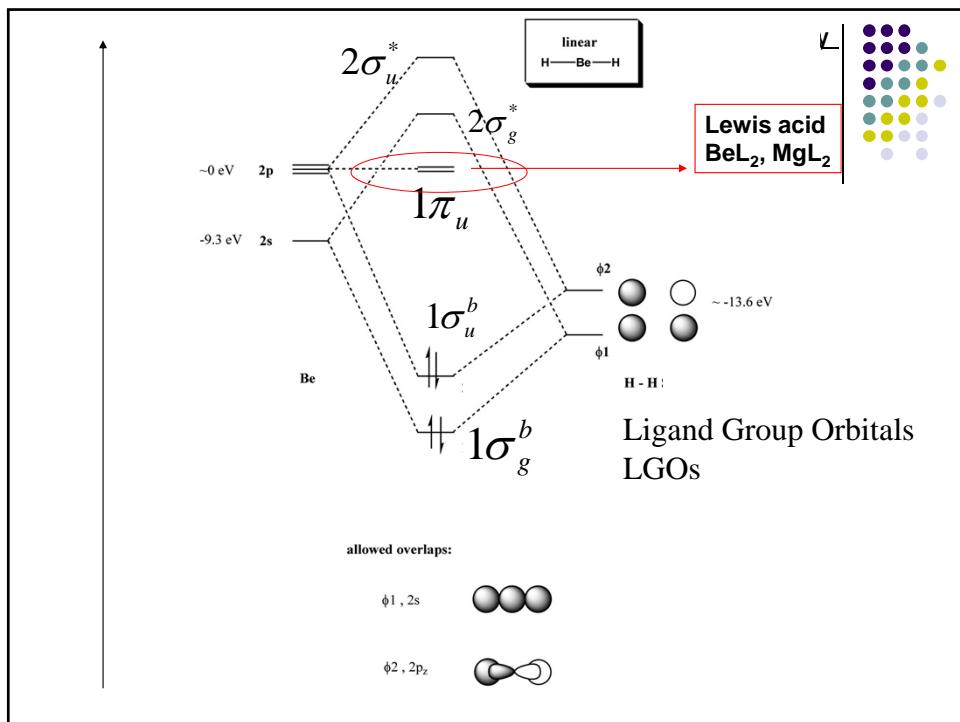
A base: an electron-pair donor

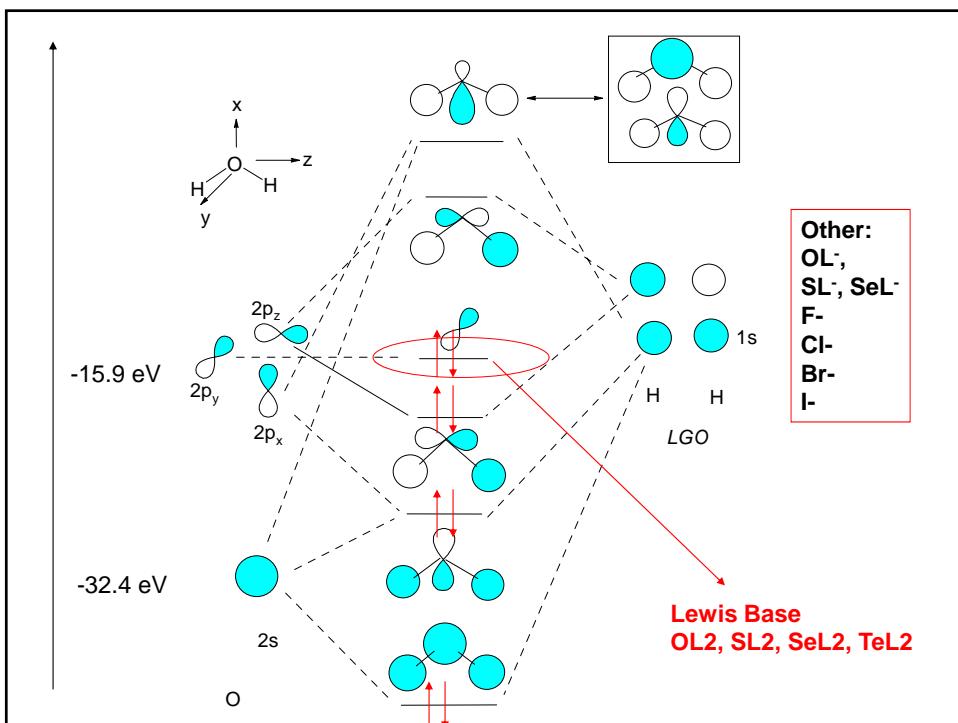
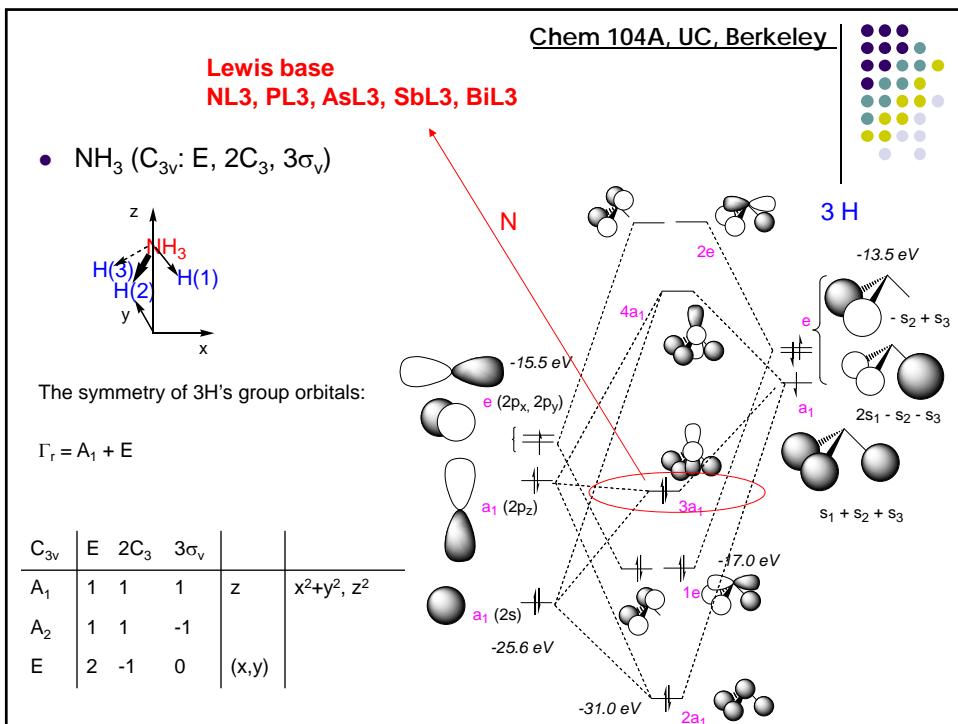
Species with lone pair type orbitals

An acid: an electron-pair acceptor

Species with empty non-bonding type orbitals



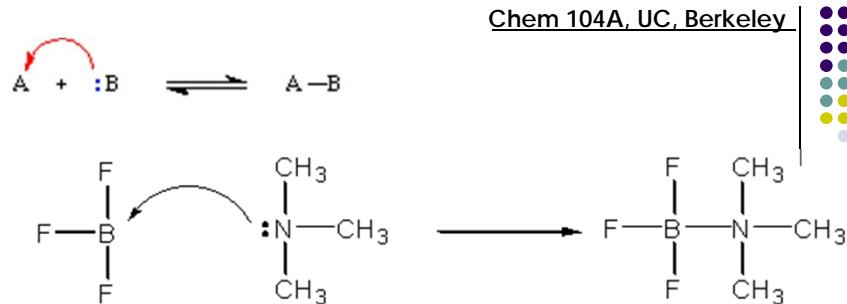




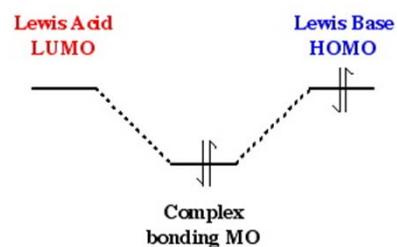


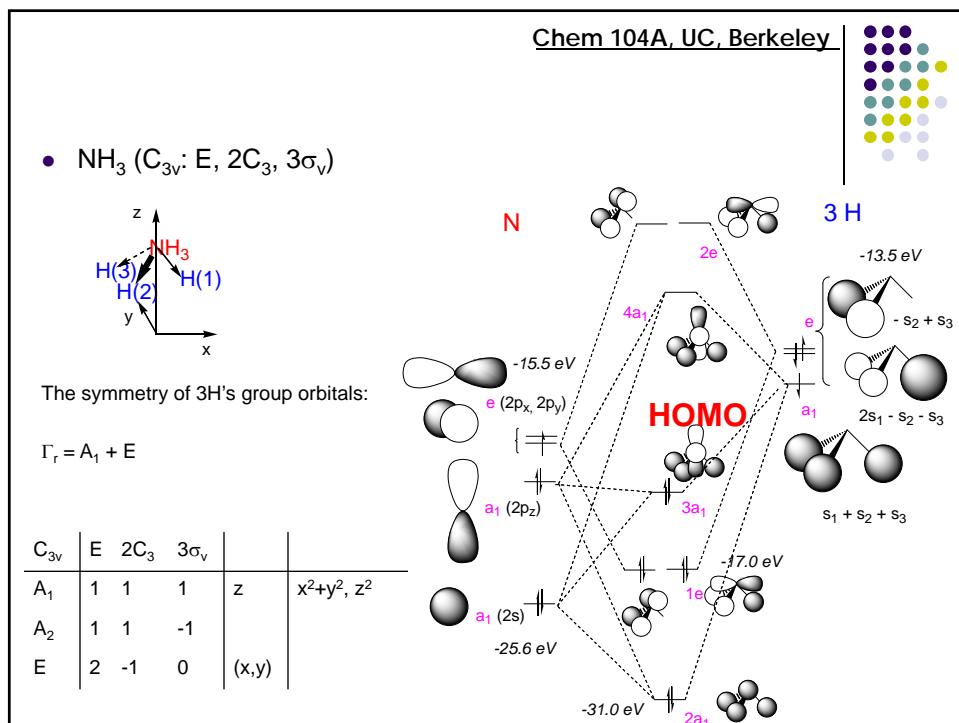
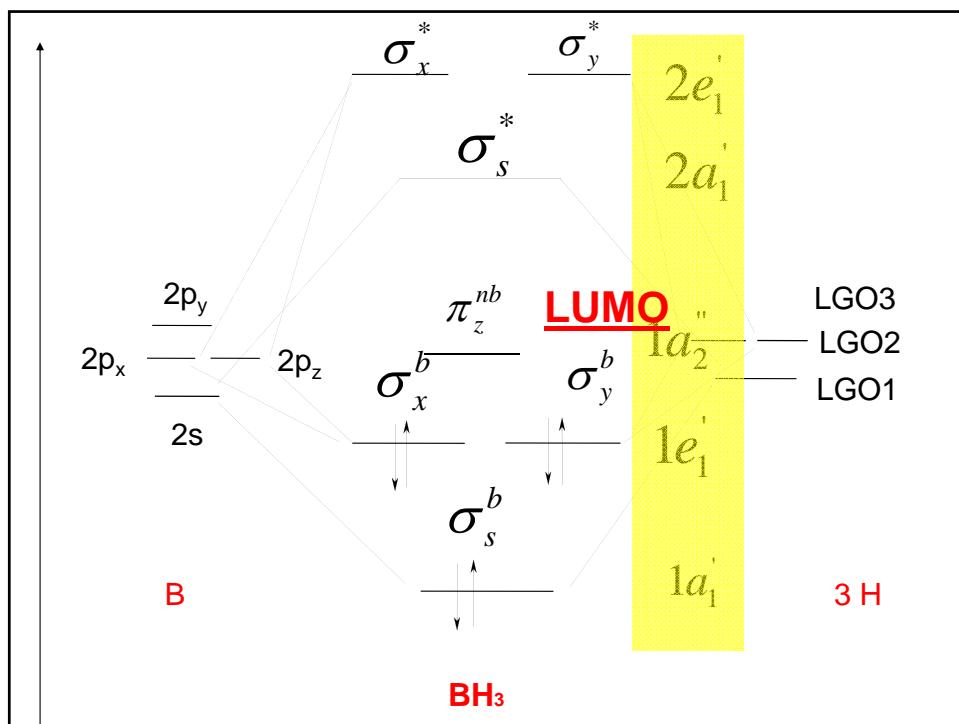
Type of non-protic acid-base reactions:

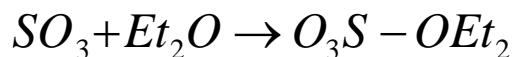
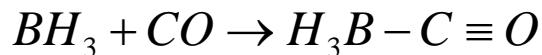
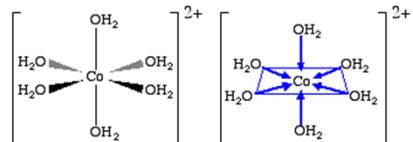
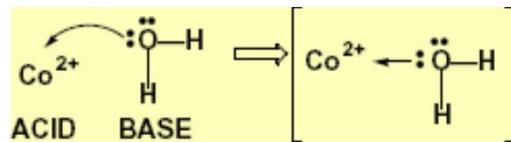
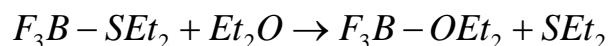
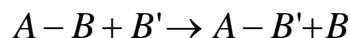
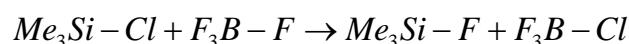
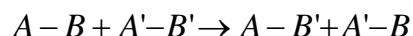
- 1. Adduct formation:** acid-base react to form a bond and produce a single molecule.
- 2. Displacement:** one base (or acid) displace another
- 3. Double displacement (Metathesis):** interchange of acids and bases



Lewis Acid/Base FMO Interaction Diagram





**Adduct formation****Displacement:** one base (or acid) displace another**Double displacement (Metathesis):**
interchange of acids and bases



Relative strength of acid/base

Reference acid	Base strength
H^+, Mg^{2+}, Sc^{3+}	$F^- > Cl^- > Br^- > I^-$
Hg^{2+}	$F^- < Cl^- < Br^- < I^-$



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



Acids

Have vacant orbitals held in tight

H^+ , Li^+ , Na^+ , $\text{K}^+(\text{Rb}^+, \text{Cs}^+)$
 Be^{2+} , $\text{Be}(\text{CH}_3)_2$, Mg^{2+} , Ca^{2+} , $\text{Sr}^{2+}(\text{Ba}^{2+})$
 Sc^{3+} , La^{3+} , Ce^{4+} , Gd^{3+} , Lu^{3+} , Th^{4+} , U^{4+} , UO_2^{2+} , Pu^{4+}
 Ti^{4+} , Zr^{4+} , Hf^{4+} , VO^{2+} , Cr^{3+} , Cr^{4+} , MoO_4^{2-} , WO_4^{2-} , Mn^{2+} , In^{3+} , Fe^{3+} ,
 Co^{3+} ,
 BF_3 , BCl_3 , $\text{B}(\text{OR})_3$, Al^{3+} , $\text{Al}(\text{CH}_3)_3$, AlCl_3 , AlH_3 , Ga^{3+} , In^{3+}
 CO_2 , RCO^- , NC^- , Si^{4-} , Sn^{4-} , $\text{CH}_3\text{Sn}^{4-}$, $(\text{CH}_3)_2\text{Sn}^{4-}$
 N^{3-} , RPO_4^{3-} , ROPO_4^{3-} , As^{3-}
 SO_4^{2-} , RSO_3^- , ROSO_3^-
 Cl^{2-} , Cl^{3-} , I^{3-} , I^{4-}
 HX (hydrogen bonding molecules)

Borderline acids

Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+}
 Rh^{3+} , Ir^{3+} , Ru^{3+} , Os^{3+}
 $\text{B}(\text{CH}_3)_3$, GaH_3 ,
 R_3C^+ , C_6H_5 , Sn^{2+} , Pb^{2+}
 NO_3^- , Sb^{3-} , Bi^{3-}
 SO_3^{2-}

Soft acids

Have vacant orbitals, but larger radius

$\text{Cu}(\text{CN})_4^{3-}$, Pd^{2+} , Pt^{2+} , Pt^{4+}
 Cu^+ , Ag^+ , Au^+ , Cd^{2+} , Hg_2^{2+} , Hg^{2+} , CH_3Hg^+
 BH_4^- , $\text{Ga}(\text{CH}_3)_3$, GaCl_3 , GaBr_3 , GaI_3 , Ti^{4+} , $\text{Ti}(\text{CH}_3)_3$
 CH_3 , carbenes,
π-acceptors: trinitrobenzene, chloroanil, quinones, tetracyanoethylene, etc.
 HO^- , RO^- , RS^- , RSe^- , Te^{2+} , RTe^-
 Br_2 , Br^- , I_2 , I^- , ICN , etc.
 O^- , Cl^- , Br^- , I^- , N^- , RO^- , RO_3^-
 M^0 (metal atoms) and bulk metals

Bases

Br_2 , Br^- , I_2 , I^- , ICN , etc.
 O^- , Cl^- , Br^- , I^- , N^- , RO^- , RO_3^-
 M^0 (metal atoms) and bulk metals

Bases

Have lone pairs in tightly held orbitals

NH_3 , RNH_2 , N_2H_4
 H_2O , OH^- , O^{2-} , ROH , RO^- , R_2O
 CH_3COO^- , CO_3^{2-} , NO_3^- , PO_4^{3-} , SO_4^{2-} , ClO_4^-
 $\text{F}^-(\text{Cl}^-)$

Borderline bases

$\text{C}_8\text{H}_5\text{NH}_2$, $\text{C}_6\text{H}_5\text{N}$, N_3^- , N_2
 NO_2^- , SO_3^{2-}
 Br^-

Have lone pairs in larger orbitals

H^-
 R^- , C_2H_5^- , C_6H_5^- , CN^- , RNC , CO
 SCN^- , $\text{R}_2\text{P}(\text{RO})_3\text{P}^-$, R_3As^-
 R_2S , RSH , RS^- , $\text{S}_2\text{O}_3^{2-}$
 I^-

**Table 1** Hard and Soft Acids and Bases

Hard Bases			Soft Bases			Borderline Bases	
H ₂ O	OH ⁻	F ⁻	R ₂ S	RSH	RS ⁻	ArNH ₂	C ₅ H ₅ N
AcO ⁻	SO ₄ ²⁻	Cl ⁻	I ⁻	R ₃ P	(RO) ₃ P	N ₃ ⁻	Br ⁻
CO ₃ ²⁻	NO ₃ ⁻	ROH	CN ⁻	RCN	CO	NO ₂ ⁻	
RO ⁻	R ₂ O	NH ₃	C ₂ H ₄	C ₆ H ₆			
RNH ₂			H ⁻	R ⁻			
Hard Acids			Soft Acids			Borderline Acids	
H ⁺	Li ⁺	Na ⁺		Cu ⁺	Ag ⁺	Pd ²⁺	Fe ²⁺ Co ²⁺ Cu ²⁺
K ⁺	Mg ²⁺	Ca ²⁺		Pt ²⁺	Hg ²⁺	BH ₃	Zn ²⁺ Sn ²⁺ Sb ³⁺
Al ³⁺	Cr ²⁺	Fe ³⁺		GaCl ₃	I ₂	Br ₂	Bi ³⁺ BMe ₃ SO ₂
BF ₃	B(OR) ₃	AlMe ₃		CH ₂	carbenes		R ₃ C ⁺ NO ⁺ GaH ₃
AlCl ₃	AlH ₃	SO ₃					C ₆ H ₅ ⁺
RCO ⁺	CO ₂						
HX (hydrogen-bonding molecules)							



- 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)*

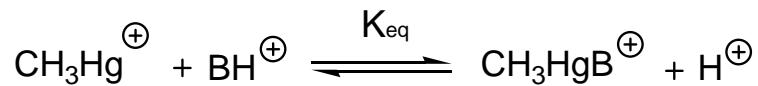
n.b “The HSAB principle is not a theory but a statement of experimental facts.”

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



Pearson's Principle:

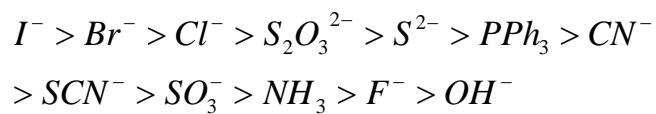
**Hard acids prefer to bind to hard bases
And soft acids prefer to bind to soft bases.**

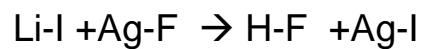


The simplest hard acid is the proton and methyl mercury cation is the simplest soft acid.

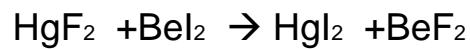
K_{eq} small \rightarrow B hard base

K_{eq} large \rightarrow B soft base





$$\Delta H = -17 \text{ kcal/mol}$$



$$\Delta H = -95 \text{ kcal/mol}$$

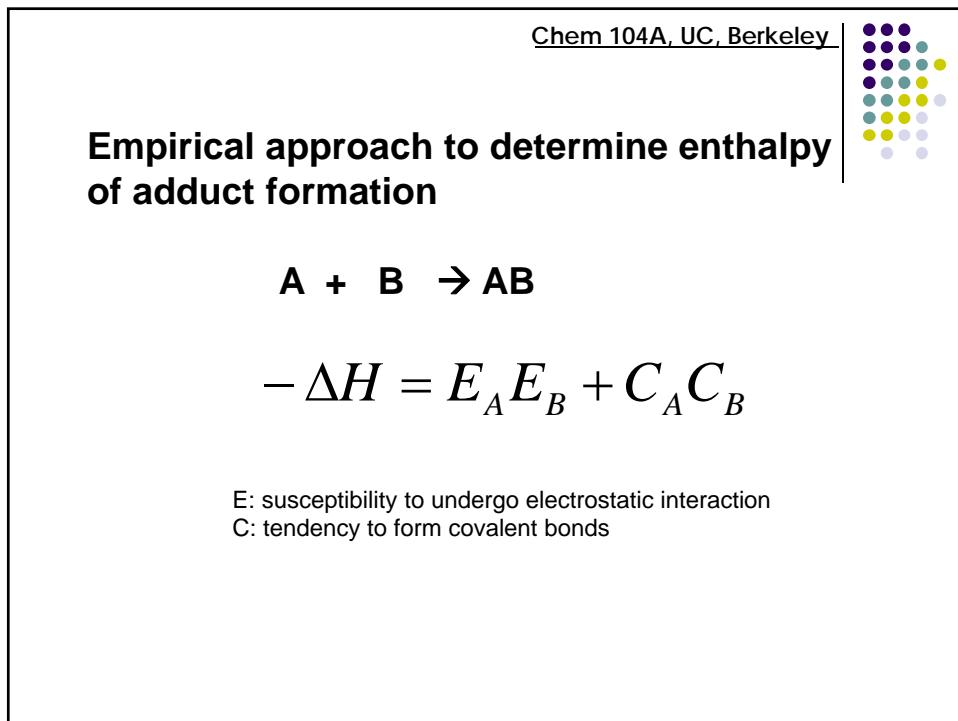
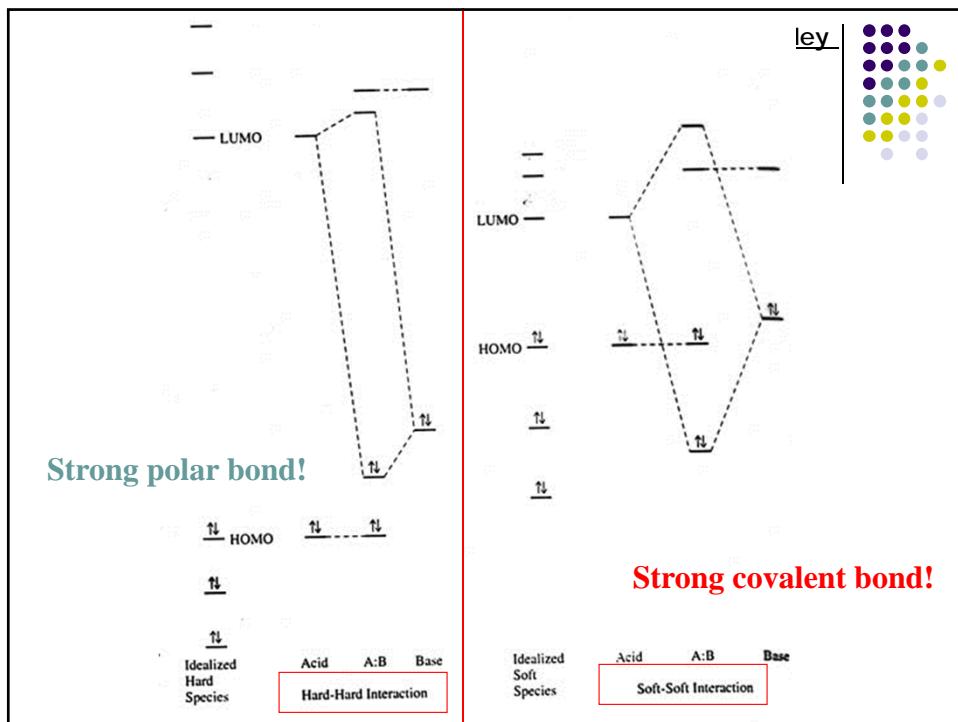


Absolute Hardness

$$\eta = \frac{IE - EA}{2} \propto (E_{LUMO} - E_{HOMO})$$

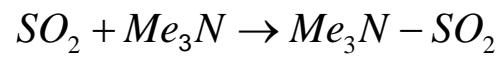
Hard: large HOMO-LUMO gap

Soft: small HOMO-LUMO gap,
ease of mixing ground/excited states, electron
Density redistributed (polarized).



Acid	E_A	C_A	R_A	Acid	E_A	C_A	R_A
I^-	0.50	2.60	—	H^+	45.00	13.03	130.21
H_2O	1.54	0.13	0.20	CH_3^+	19.70	12.61	55.09
SO_4^{2-}	0.56	1.52	0.85	Li^+	11.72	1.45	24.21
HF^b	2.03	0.30	0.47	K^{+b}	3.78	0.10 ^b	20.79
HCN^b	1.77	0.50	0.54	NO^{-b}	0.1 ^b	6.86	45.99
CH_3OH	1.25	0.75	0.39	NH_4^+	4.31	4.31	18.52
H_2S^b	0.77	1.46	0.56	$(\text{CH}_3)_2\text{NH}^{+b}$	3.21	0.70	20.72
HCl^b	3.69	0.74	0.55	$(\text{CH}_3)_3\text{N}^{+b}$	1.96	2.36	8.33
$\text{C}_6\text{H}_5\text{OH}$	2.27	1.07	0.39	$\text{C}_5\text{H}_5\text{NH}^{+b}$	1.81	1.33	21.72
$(\text{CH}_3)_3\text{COH}$	1.36	0.51	0.48	$(\text{C}_2\text{H}_5)_3\text{NH}^{+b}$	2.43	2.05	11.81
HCCl_3	1.49	0.46	0.45	$(\text{CH}_3)_3\text{NH}^{+b}$	2.60	1.33	15.95
$\text{CH}_3\text{CO}_2\text{H}^b$	1.72	0.86	0.63	H_2O^-	13.27	7.89	20.01
$\text{CF}_3\text{CH}_2\text{OH}$	2.07	1.06	0.38	$(\text{H}_2\text{O})_2\text{H}^+$	11.39	6.03	7.36
$\text{C}_2\text{H}_5\text{OH}$	1.34	0.69	0.41	$(\text{H}_2\text{O})_3\text{H}^{+b}$	11.21	4.66	2.34
$i\text{-C}_3\text{H}_7\text{OH}$	1.14	0.90	0.46	$(\text{H}_2\text{O})_3\text{Sn}^+$	10.68	4.11	3.25
PF_3^b	0.61	0.36	0.87	$(\text{CH}_3)_3\text{Ni}^+$	7.05	3.15	26.93
$\text{B}(\text{OCH}_3)_3^b$	0.54	1.22	0.84	$(\text{C}_6\text{H}_5)_3\text{NH}^{+b}$	11.88	3.49	32.64
AsF_3^b	1.48	1.14	0.78	$(\text{CH}_3)_3\text{NH}^{+b}$	2.18	2.38	20.68
$\text{Fe}(\text{CO})_5^b$	0.10	0.27	1.00				
CHF_3^b	1.32	0.91	0.27				
$\text{B}(\text{C}_2\text{H}_5)_3^b$	1.70	2.71	0.61				
Base ^c	E_B	C_B	T_B	Base ^c	E_B	C_B	T_B
NH_3	2.31	2.04	0.56	$\text{C}_6\text{H}_5\text{NO}$	2.29	2.33	0.67
CH_3NH_2	2.16	3.12	0.59	$(\text{CH}_3)_3\text{P}$	1.46	3.44	0.90

CHF_3^b	1.32	0.91	0.27
$\text{B}(\text{C}_2\text{H}_5)_3^b$	1.70	2.71	0.61
Base ^c	E_B	C_B	T_B
NH_3	2.31	2.04	0.56
CH_3NH_2	2.16	3.12	0.59
$(\text{CH}_3)_2\text{NH}$	1.80	4.21	0.64
$(\text{CH}_3)_3\text{N}$	1.21	5.61	0.75
$\text{C}_2\text{H}_5\text{NH}_2$	2.35	3.30	0.54
$(\text{C}_2\text{H}_5)_2\text{N}$	1.32	5.73	0.76
$\text{HCl}(\text{C}_2\text{H}_5)_3\text{N}$	0.80	6.72	0.83 ^d
$\text{C}_2\text{H}_5\text{N}$	1.78	3.54	0.73
$4\text{-CH}_3\text{C}_6\text{H}_4\text{N}$	1.74	3.93	0.73 ^d
$3\text{-CH}_3\text{C}_6\text{H}_4\text{N}$	1.76	3.72	0.74 ^d
$3\text{-ClC}_6\text{H}_4\text{N}$	1.78	2.81	0.75 ^d
CH_3CN	1.64	0.71	0.83
$\text{CH}_3\text{C}(\text{O})\text{CH}_3$	1.74	1.26	0.80
$\text{CH}_3\text{C}(\text{O})\text{OCH}_3$	1.63	0.95	0.86
$\text{CH}_3\text{C}(\text{O})\text{OC}_2\text{H}_5$	1.62	0.98	0.89
$\text{HC}(\text{O})\text{N}(\text{CH}_3)_2$	2.19	1.31	0.74 ^d
$(\text{C}_2\text{H}_5)_2\text{O}$	1.80	1.63	0.76
$\text{O}(\text{CH}_2\text{CH}_2)_2\text{O}$	1.86	1.29	0.71
$(\text{CH}_3)_2\text{O}$	1.64	2.18	0.75
$(\text{CH}_3)_3\text{O}$	1.70	2.02	0.74 ^d
$(\text{C}_2\text{H}_5)_2\text{S}$	0.24	3.92	1.10 ^d
$(\text{CH}_3)_2\text{SO}$	2.40	1.47	0.65



$$\Delta H = -(0.56 \cdot 1.21 + 1.52 \cdot 5.61) = -9.2 \text{ kcal/mol}$$

Experimental value: -9.6 kcal/mol