

① Lecture 5

FMO Theory: final comments
 HSAB Theory
 Thermodynamics

PS# 2 due today.
 PS# 3 due Tues, 9/22.

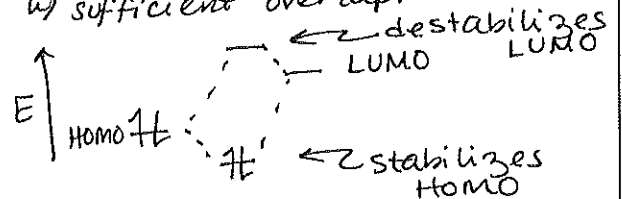
Handouts:
 FMO-Common Orbitals
 JOC Standard Abbreviations
 Benson Tables.

② FMO-final comments

What do orbitals usually look like?

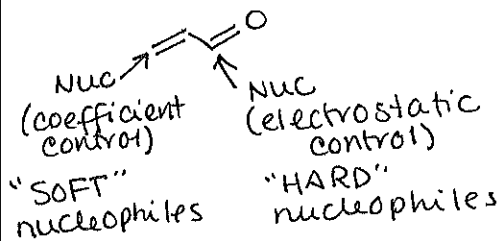
	π	σ	lone pair (lp)	cation
LUMO			N/A	
HOMO			A ⊕ IP	N/A

In making FMO arguments, generally look for FILLED - UNFILLED ORBITALS ~~≠~~ w/ sufficient overlap.



③ HSAB Theory

Recall:



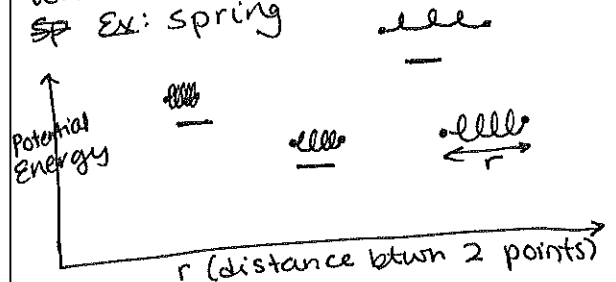
See notes on HSAB (attached).

④ Thermodynamics (A&D, Ch. 2)

- Concerned w/ energies of ground states. → Not how fast!

Useful tool: Rxn Coordinate Diagram
 What is it?

Ex: spring



⑤ We can do the same for a rxn...

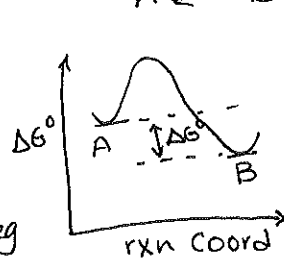
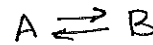
ΔG° = Gibbs free energy
 - closely related to potential energy
 - Determined by equilibrium position btwn 2 chemical states (chemical states = conformations or compounds)

Standard State
 298 K
 1 atm

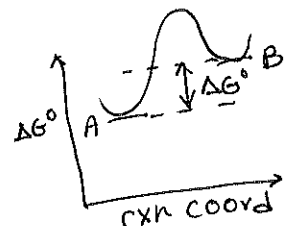
$$\Delta G^\circ = -RT \ln K_{eq} \quad T = K (\text{deg})$$

$R = 1.98 \frac{\text{cal}}{\text{mol} \cdot \text{deg}}$
 unitless

$$K_{eq} = \frac{[\text{Product}]}{[\text{Starting Material}]} = \frac{[B]}{[A]}$$



EXERGONIC
 $\Delta G^\circ \ominus$



ENDERGONIC
 $\Delta G^\circ \oplus$

⑦ Useful Numbers (know these!)

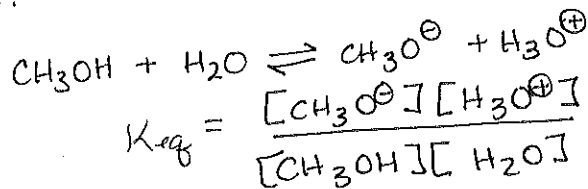
ΔG° of 1.36 kcal/mol \Rightarrow factor of 10 in K_{eq} @ 298K.

ΔG°_{298}	K	% B	% A
0	1	50	50
-1.36	10	90.9	9.1
-2.72	100	99	1
-4.08	1000	99.9	0.1
<hr/>			
298K -1.0	5.44	85	15
195K -1.0	13.2	93	7

298K
195K

⑧ Important Equilibria to Consider:

① Acid/Base; pKa's



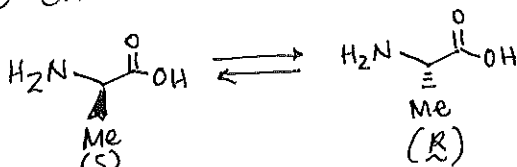
$$[\text{H}_2\text{O}] = 55 \text{ M}$$

$$K_a = K_{eq} [\text{H}_2\text{O}] = \frac{[\text{CH}_3\text{O}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{OH}]}$$

$\text{pK}_a = -\log(K_a)$
Know your pKa's!! Links to pKa tables on course website.

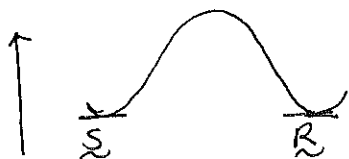
⑨

② Enantiomers:



$\Delta G^\circ = ?$

$\Delta G^\circ = \phi$



⑩

What about rxns w/ more than 2 ground states to consider?
Rxn coordinate becomes more complicated...

PS 1, #5. \rightarrow See answer key.

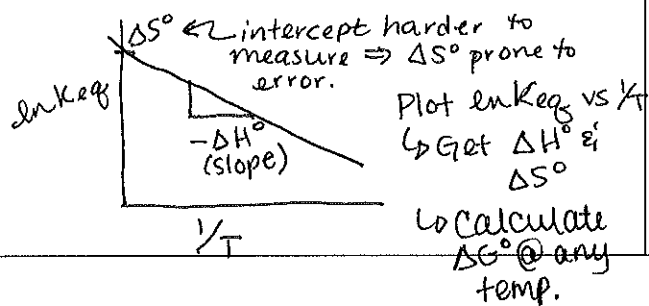
⑪ Back to ΔG° :

Components of ΔG°

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$$

$$-RT \ln K_{eq} = \Delta H^\circ - T \Delta S^\circ$$

$$R \ln K_{eq} = \frac{-\Delta H^\circ}{T} + \Delta S^\circ$$



⑫ ΔH° : ENTHALPY

- : kcal/mol
- : reflects strength or energy of bonds.
- : heat of reaction

Exothermic: $\ominus \Delta H^\circ$
Rxn gives off heat/energy.

Endothermic: $\oplus \Delta H^\circ$
Rxn requires heat/energy.

Often, rxn coordinate diagrams plot ENTHALPY on y-axis (not ΔG°).

Why?

⑬ ENTROPY \equiv measure of disorder of a system.

Increased temp \Rightarrow more disorder
Hard to think about intuitively...

Degrees of Freedom

- # of ways molecules can move.
- Translational (through space)
 - Rotational (tumbling)
 - Vibrational (internal motion)
↳ More complex.

Often ΔS° will be small if structures are similar \Rightarrow BUT NOT ALWAYS!!

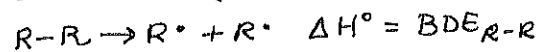
⑭ How do we estimate ΔG° ?

\rightarrow Estimate ΔH°

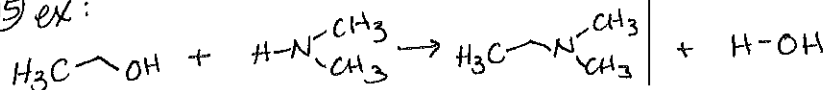
Method #1: Bond Dissociation Energies (BDE's)

$$\Delta H_{rxn}^\circ = \text{BDE (bonds formed)} - \text{BDE (bonds broken)}$$

BDE \equiv homolytic bond cleavage energy.



⑮ ex:



BDE's: kcal/mol	92.3 (CH ₃ -OH)	107.4 (NH ₂ -H)	84.9 (CH ₃ -NH ₂)	119 (H-OH)
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$$\Delta H^\circ = (84.9 + 119) - (92.3 + 107.4) = +4.2$$

\Rightarrow Endothermic, so not favorable enthalpically.

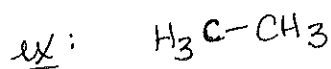
Limitation: We don't consider what each atom is connected to.

⑯ Estimation method #2:

Benson Increment Tables.
(see Handout \S A & D)

- more accurate if you can find the group you're looking for.

- How does it work?



⑰ Corrections for steric effects, ring strain, etc.

13 Nucleophilic Attack on π -systems

(See notes at end of Lecture 3.)

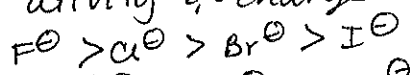
14 Hard/Soft Acid/Base Theory

ϵ' Polarizability

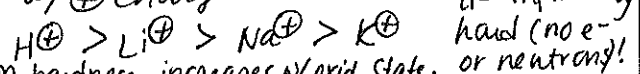
- qualitative arguments to explain reactivity
- Relatively large atom or ion w/ a small effective nuclear charge is relatively easily distorted (polarized) by external charge \equiv SOFT
- Compact e^- distribution from higher net nuclear charge & less effective screening \equiv HARD

15
 Ref: Pearson et al. J Am Chem Soc 1967, 89, 1827.
 " J. Org. Chem. 1989, 54, 1423.
 " Acc Chem Res. 1993, 26, 250.

Anion Hardness increases w/ electronegativity & \ominus charge

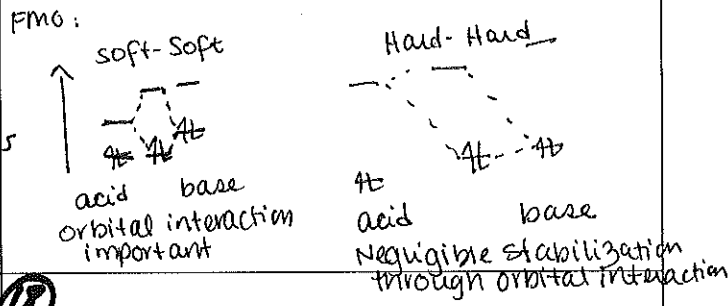
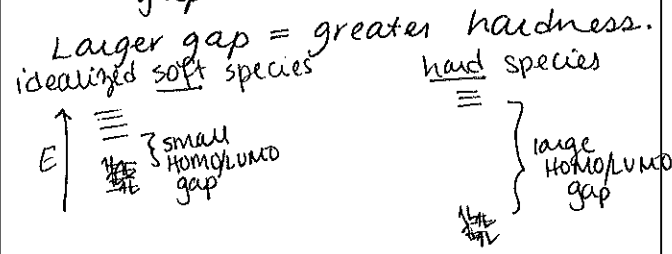


Cation Hardness decreases w/ size & increases w/ \oplus charge



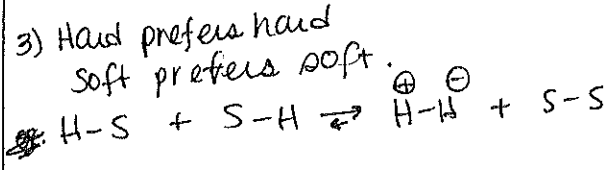
Metal ion hardness increases w/ oxid. state. e^- cloud shrinks.

16 Polyatomic molecules hardness & softness related to HOMO/LUMO gap.

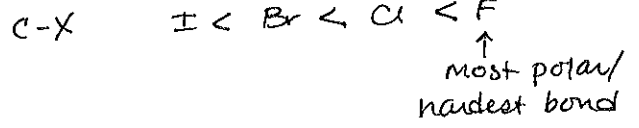


17 Generalities:

- 1) Hard-Hard interactions dominated by electrostatics
- 2) Softer compds usually more reactive & more nucleophilic (wants to donate e^- to El^+)
 Nucleophilicity: $CH_3^\ominus > NH_2^\ominus > OH^\ominus > H^\ominus > F^\ominus$



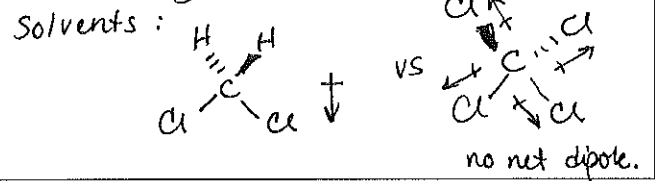
18 Hard-soft & Polarizability



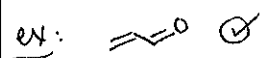
Polarizability & Hybridization

$sp^3 > sp^2 > sp$ ← lower ϵ , closer to nucleus.
 more polarizable $\left\{ \begin{array}{l} \text{less polarizable.} \end{array} \right.$

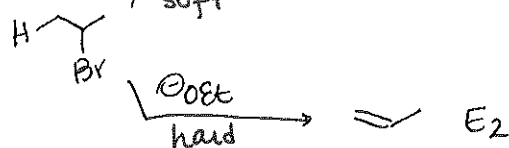
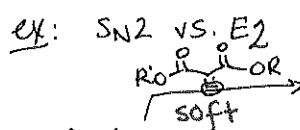
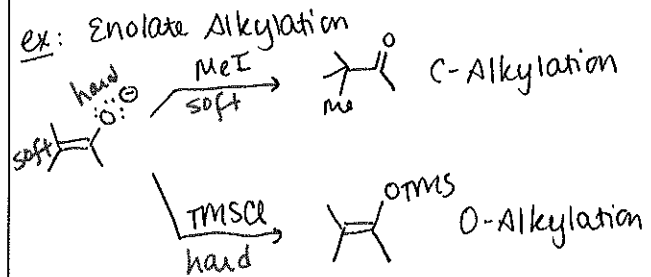
Note: Polarization is directional.



Application of HSAB to Chemoselectivity:



ex: Enolate Alkylation



~~SN1~~