Lecture 7: Thermodynamics

Today:
- Definitions and equations of Thermodynamics
- Conformational analysis (the beginning)

Announcements:
- Problem Set 2 due Thurs, 9/22, at beginning of lecture.
- Seminar: Prof. John Arnold (UC, Berkeley), Wed, 4pm, 219 BRL
  "Catalytic and Stoichiometric Reactivity with Early Transition Metals"
- OJC on Thursday, 12:30, 219 BRL

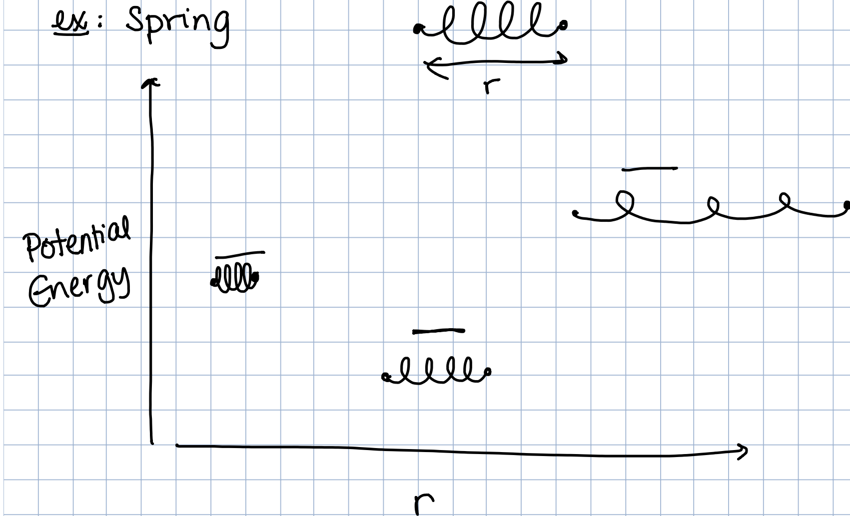
Thermodynamics

Energies of ground states

↳ Not transition states, rates, kinetics

Reaction Coordinate Diagrams (useful tool)

ex: Spring



~Same for a rxn...

ΔG° = Gibbs free energy (° ← standard conditions/state: 298 K, 1 atm)

↳ ≈ potential energy

↳ determined by equilibrium (→ Keq) position between 2 chemical states

↳ conformations or intermediates or compounds

$$\Delta G^\circ = -RT \ln K_{eq}$$

ΔG°: kcal/mol; $\ln K_{eq}$: unitless

R = 1.98 cal/mol·deg (← not kcal)

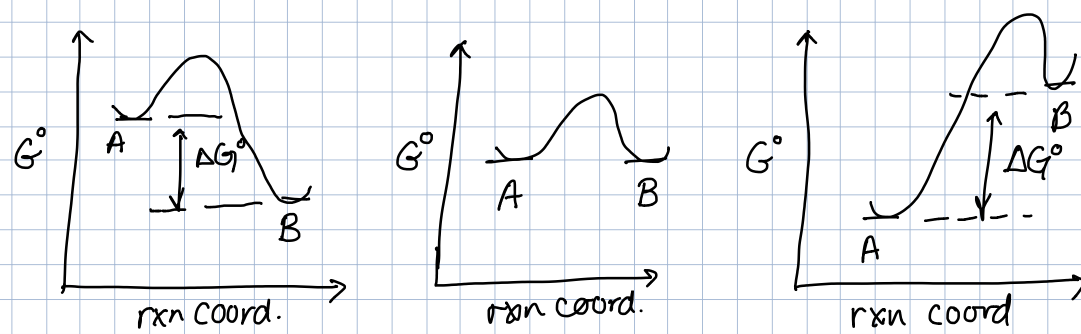
T in K (deg)

$K_{eq} =$

$A \rightleftharpoons B$

$$K_{eq} = \frac{[B]}{[A]} = \frac{[\text{products}]}{[\text{starting materials}]}$$

3 Possibilities:



Exergonic	THERMONEUTRAL	Endergonic
$\Delta G° < \emptyset$	$\Delta G° = \emptyset$	$\Delta G° > \emptyset$

$$\Delta G° = -RT \ln K_{eq}$$

$$\Delta G° = -(1.98\ \text{cal/mol}\cdot\text{K})(298\ \text{K})\left(\frac{\text{kcal}}{1000\ \text{cal}}\right) \ln K_{eq}$$

$$\Delta G° = (-0.59\ \text{kcal/mol}\cdot\text{K}) \ln K_{eq}$$

ΔG° (kcal/mol)	Keq	%B	% A
0	1	50	50
−1.36 (≈ −1.4)	10	90.9	9.1
−2.72 (~ −2.8)	100	99	1
−4.08 (~ −4.2)	1000	99.9	0.1

@ 298 K, every 1.4 kcal/mol difference in ΔG°

⇓

Factor of 10 in Keq

Note: Temperature Matters!

T	ΔG°	K_{eq}	% B	% A
298 K	− 1.0	5.44	85	15
195 K	−1.0	13.2	93	7

Important Equilibrium: Acid / Base ⇒ pKa's

$$CH_3OH + H_2O \rightleftharpoons CH_3O^\ominus + H_3O^\oplus$$

$$K_{eq} = \frac{[CH_3O^\ominus][H_3O^\oplus]}{[CH_3OH][H_2O]}$$

$[H_2O]$ = 55 M in pure water

$$K_a = K_{eq}[H_2O] = \frac{[CH_3O^\ominus][H_3O^\oplus]}{[CH_3OH]}$$

$$pKa = -\log K_a$$

Components of $\Delta G°$:

$$\Delta G° = \Delta H° - T\Delta S°$$

$\Delta H°$ = enthalpy

- → kcal/mol
- → reflects strength/energy of bond (or interactions)
- → heat of rxn.

$\Delta H° < \varnothing$ → exothermic $\Delta H° > \varnothing$ endothermic

$\Delta S°$ = entropy

- → eu = cal/mol·K
- → measure of disorder of a system
- → related to temperature
  - ↑ temp → ↑ disorder

Degrees of Freedom → # of ways molecules can move

- translational (through space)
- rotational (tumbling)
- vibrational (internal motion)
  - ↳ complex

Often ΔS is small if structures are similar.

Experimental Determination of ΔG, ΔH, ΔS:

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

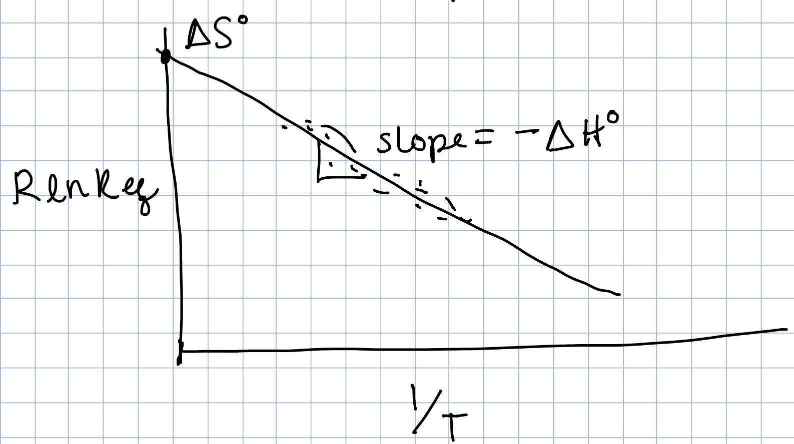
$$\frac{-R\cancel{T}\ln K_{eq}}{\cancel{T}} = \frac{\Delta H^\circ}{T} - \frac{\cancel{T}\Delta S^\circ}{\cancel{T}}$$

$$y = mx + b$$

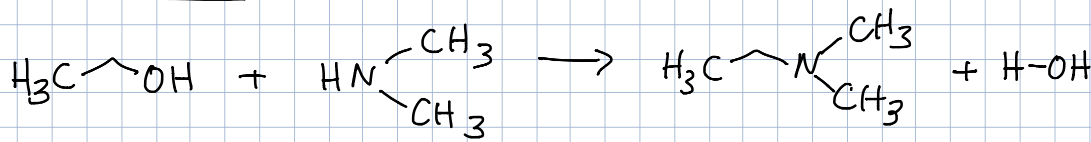
$$+R\ln K_{eq} = -\frac{\Delta H^\circ}{T} + \Delta S^\circ$$

$$\underbrace{R\ln K_{eq}}_{y} = -\Delta H^\circ\left(\frac{1}{T}\right) + \Delta S^\circ$$

($\frac{1}{T}$ ← x, ΔS° ← b)

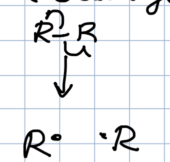


Estimate ΔG°?

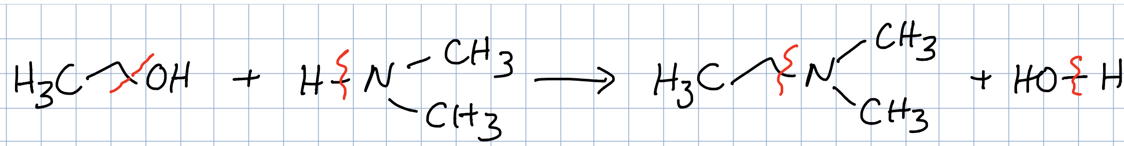


Bond dissociation energies (BDE's) ← Homolytic Bond Cleavage

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



See Table 2.2 in A & D.



BDE's kcal/mol	92.3 (H_3C-OH)	107.4 (H_2N-H)	84.9 (H_3C-NH_2)	119

$$-\Delta H^\circ = (84.9 + 119) - (92.3 + 107.4)$$

$$-\Delta H^\circ = +4.2 \text{ kcal/mol}$$

$$\Delta H^\circ = -4.2 \text{ kcal/mol}$$ exothermic ☺

↑ 1000:1

Conformational Analysis

- analysis of 3D conformation of molecule
- You should be able to visualize 3D structures in your head.

PRACTICE THIS

↳ Model kit.

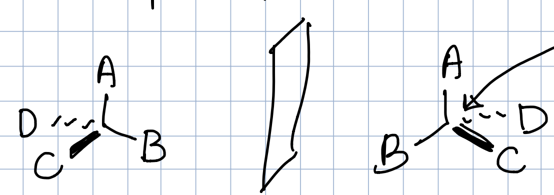
Stereochemistry

chirality = "handedness"

Types of Stereoisomers ← same connectivity, different conformation/configuration

(1) Enantiomers

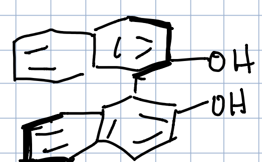
- non-superimposable mirror images

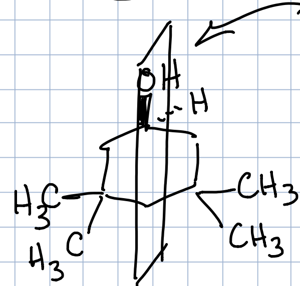


stereogenic center

stereo → stereochem/chirality

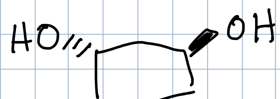
genic → gives birth to



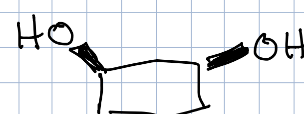


← σ plane of symmetry

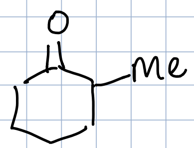
achiral



chiral



achiral
meso



chiral
racemic

2 Ways to Report Unequal Mixtures

(1) % ee = % enantiomeric excess
related to optical rotation (α)

$$\frac{\alpha_{obs}}{\alpha_{max}} = ee = \frac{(\text{major enant} - \text{minor enant})}{(\text{major} + \text{minor})}$$

↑ of enantiopure material

(2) er = enantiomeric ratio

major	minor	% ee	er
1	1	Ø	50:50
3	1	50	75:25
10	1	82	91:9
100	1	98	99:1