Thermodynamics & Organic Reactions

UCI Chem 51A
Dr. Link

Goals

- After this lesson you should be able to
  - Differentiate between enthalpy, entropy, and Gibbs free energy
  - Explain the relationship between these three thermodynamic properties
  - Calculate the enthalpy for a reaction
  - Calculate the free energy change for a reaction
  - Identify the sign of entropy change for a reaction
  - Draw and interpret reaction coordinate diagrams.

Thermodynamics Review

- In general chemistry:
  - ΔH (enthalpy change)
  - ΔS (entropy change)
  - ΔG (Gibb's free energy change)
  - Reaction coordinate diagrams

Thermodynamics

- Energy comparisons
  - Relative energy of reactants versus products
  - Distribution of reactants and products in equilibrium
  - (NOT rates of reaction)

ΔH: Enthalpy

- Enthalpy
  - Heat energy
  - State function (how we get there doesn't matter)
  - Mainly bond enthalpies for us
  - Note: Point of view of system

Breaking and Making Bonds

- Breaking bonds costs energy (ALWAYS)
- Making bonds releases energy (ALWAYS)

Bond Dissociation Energies

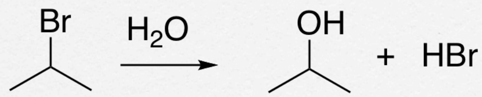
- Energy required to break a bond (homolytically)

Where do we find BDEs?

*Tables! (don't memorize!)

Calculating Enthalpy of Reaction

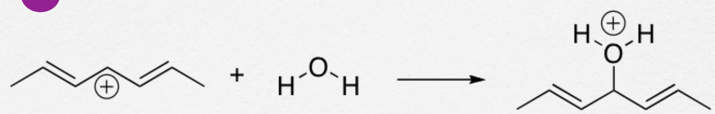
- Previously ΔH°_f for reactants and products
  - Not always available!
- Calculate energy gained/lost by bonds formed/broken

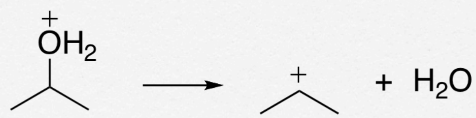


Broken (kcal/mol)	Formed (kcal/mol)

What About ΔS (Entropy)?

Organization costs the system entropy!

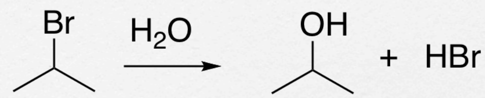




Intramolecular vs. Intramolecular

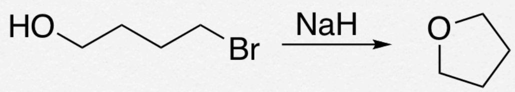
<u>Intermolecular:</u> Two (or more) particles come together

Costs entropy! ΔS –



<u>Intramolecular:</u> Rxn occurs within molecule

Costs entropy! ΔS –, but less – than intermolecular



Relating ΔG, ΔH, & ΔS

For most organic reactions ΔS is small, so

When does ΔS matter for us?

Comparing 2 rxns where ΔH are equal

ΔG & Equilibrium

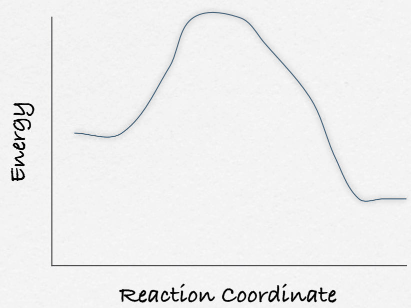
How does ΔG relate to equilibrium?

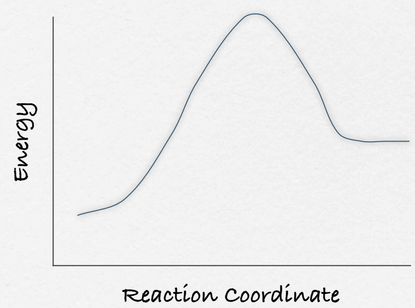
$$\Delta G = -RT \ln K_{eq} = -2.303RT \log K_{eq}$$

K_{eq}	$\log K_{eq}$	ΔG
<1		
>1		

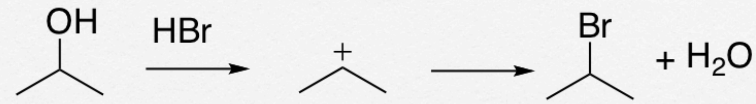
Reaction Coordinate Diagrams

Diagrams of energy changes
as reaction progresses





Reactions with Multiple Steps



Each step has its own values!

Wrapping Up

- Practice calculating ΔH from BDE values
- Practice determining sign of ΔG based on ΔH, ΔS, and T
- Practice determining whether a process is endothermic or exothermic
- Practice predicting the sign of ΔS for a process
- Practice drawing and interpreting reaction coordinate diagrams