Lecture 2

Review of Basic Concepts

Thermochemistry

<u>Enthalpy – H</u>   heat content

 H Changes with all physical and chemical changes

$\Delta H°$ Standard enthalpy (25°C, 1 atm)

(H=O for all elements in their standard forms – by definition)

<u>Exothermic</u> vs   <u>Endothermic</u>

$\Delta H < O$ $\Delta H > O$
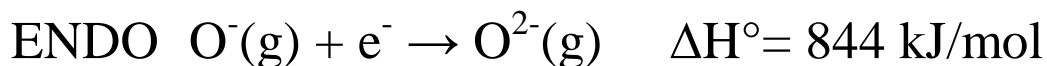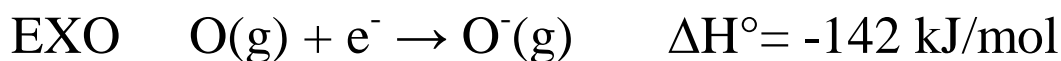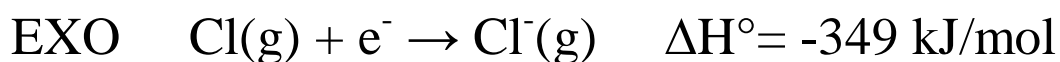
Heat is released   Heat is absorbed

Because $\Delta H = (H \text{ products} - H \text{ reactants})$

Many special Enthalpy changes:

- fusion (melting) (s → l)
- vaporization (l → g)
- sublimation (s → g)
- ionization (loss of an e⁻ or electrons)
- electron affinities (capture of an e⁻ or electrons)

ΔH: look at signs and rationalize

e.g.,

EXO $Cl(g) + e^- \rightarrow Cl^-(g)$ $\Delta H° = -349$ kJ/mol

EXO $O(g) + e^- \rightarrow O^-(g)$ $\Delta H° = -142$ kJ/mol

ENDO $O^-(g) + e^- \rightarrow O^{2-}(g)$ $\Delta H° = 844$ kJ/mol

Bond Energies:

Simple case

$$HF(g) \rightleftharpoons H(g) + F(g)$$

$\Delta H = 566$ kJ/mol   ENDOTHERMIC

The enthalpy of this process is the "H-F" Bond energy – the energy released when the H-F bond is formed.

Not so simple case…

$$H_2\text{-}N\text{-}NH_2 \rightleftharpoons 2N(g) + 4H(g)$$

$\Delta H = 1724$ kJ/mol
                ↑
NOTE: This is not the bond energy for any of the bonds – It is a total enthalpy change.

Need to <u>Estimate</u>

If we know that:

$$NH_3(g) \rightleftharpoons N(g) + 3H(g)$$

$$\Delta H = 1172 \text{ kJ/mol}$$

Then $E_{N\text{-}H} = \dfrac{1172}{3} = 391 \text{ kJ/mol}$

<u>If</u> we assume this number is valid to use for Hydrazine, the formula of which is H_2NNH_2 or N_2H_4

<u>Then</u>

$$E_{N\text{-}N} + 4E_{N\text{-}H} = 1724 \text{ kJ/mol}$$
$$E_{N\text{-}N} = 1724 - 4(391)$$
$$= 160 \text{ kJ/mol}$$

… we have to live with these estimates

Thermochemical data can be tabulated by this method:

Table 1-1   Some Average Thermochemical Bond Energies at 25 °C (in kJ mol⁻¹)

A. Single bond energies

	H	C	Si	Ge	N	P	As	O	S	Se	F	Cl	Br	I
H	436	416	323	289	391	322	247	467	347	276	566	431	366	299
C		356	301	255	285	264	201	336	272	243	485	327	285	213
Si			226	—	335	—	—	368	226	—	582	391	310	234
Ge				188	256	—	—	—	—	—	—	342	276	213
N					160	-200	—	201	—	—	272	193	—	—
P						209	—	-340	—	—	490	319	264	184
As							180	331	—	—	464	317	243	180
O								146	—	—	190	205	—	201
S									226	—	326	255	213	—
Se										172	285	243	—	—
F											158	255	238	—
Cl												242	217	209
Br													193	180
I														151

B. Multiple bond energies

C=C 598	C=N 616	C=O 695	N=N 418
C≡C 813	C≡N 866	C≡O 1073	N≡N 946

Use these values to calculate the energy
that it would take to form a molecule.

Entropy and Free Energy

Two factors in chemical reactions:

1. Enthalpy, H, (kJ/mol)
   Energy (heat) dissipated

2. Entropy, S, ($kJ/Tmol$)
   State of organization
   "order versus disorder"
   which is a statistical probability

   When ΔH is more negative (exothermic)
   and ΔS is more positive (more disordered)
   a reaction is more favored.

   ΔG Free energy which is in kJ/mol
   Involves the relationship between $\Delta H, \Delta S$
   $\Delta G = \Delta H - T\Delta S$ (T in degrees K)

<u>Example:</u>

CH_2Cl_2 <u>Heat of formation ofDicholoromethane</u>

C-H   H= 416 kJ/mol

C-Cl   H= 327 kJ/mol

$2 \times 416 + 2 \times 327 = H_{formation} (CH_2Cl_2)$
$= 1308$ kJ/mol

<u>Using $\Delta G°$ as a Predictive Tool</u>

$\Delta G° = \sum \Delta G_f° \text{ (products)} - \Delta G_f° \text{ (reactants)}$

Of course

$\Delta G° = \Delta H° - (298.15) \Delta S°$
$\uparrow$
(standard temperature)   T= 25°C or 298.15 K

The entropy change for a reaction is the difference between the absolute entropies of reactants and products.

$$\Delta S° = \sum S° \text{ (products)} - S° \text{ (reactants)}$$

Q When is S = 0?

A At absolute zero for a perfectly crystalline solid

Now, what is the relationship between ΔG and the Equilibrium Constant K?

...recall $K = \dfrac{[C]^c[D]^d}{[A]^a[B]^b}$ $aA + bB \rightleftharpoons cC + dD$

$\Delta G = -RT \ln K$

$\uparrow$

gas constant $R = 8.314$ J/Kmol

at 25°C we have:

$\Delta G° = -5.69 \log K_{298.15}$

Q for $\Delta G° = 0$ what is K?

A 1

Note:
The more negative is $\Delta G°$, the more the reaction proceeds as written *i.e.* K is large so -5.69 log K is getting larger and more negative. Conversely, the more positive is $\Delta G°$, the more the reaction will tend to the left $\leftarrow$ rather then to the right$\rightarrow$ as written.

<u>Q</u> How does a reaction become overall thermodynamically favored?

<u>A</u> 3 Ways.

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

1. $\Delta H°$ and $\Delta S°$ favor the reaction that is, $\Delta H° < O$, $\Delta S° > O$

2. $\Delta H°$ favors the reaction, but $\Delta S°$ does not that is, $\Delta H° < O$, $\Delta S° < O$ but $\Delta H°$ is still more negative than $T\Delta S°$ is positive

3. $\Delta H°$ disfavors the reaction, but $\Delta S°$ favors it $\Delta H° > O$, $\Delta S° > O$ but $T\Delta S°$ is larger

Examples of all three types of situations:

1. formation of CO; SO_2 common case

$\frac{1}{2} O_2(g) + C(s) \rightleftharpoons CO(g)$
$\Delta G° = -137.2$ kJ/mol
$\Delta H° = -110.5$ kJ/mol
$T\Delta S° = 26.7$ kJ/mol   In both cases:
                                                                Enthalpy favors rxn

$S(s) + O_2(g) \rightleftharpoons SO_2(g)$ *Entropy favors rxn*
$\Delta G° = -300.4$ kJ/mol
$\Delta H° = -292.9$ kJ/mol
$T\Delta S° = 7.5$ kJ/mol

2. synthesis of ammonia (NH_3)
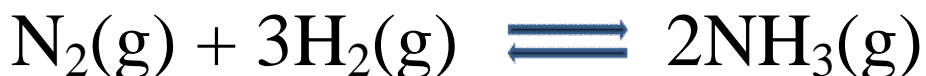
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
$\Delta G° = -16.7$ kJ/mol
$\Delta H° = -46.2$ kJ/mol   *Enthalpy favors rxn*
$T\Delta S° = -29.5$ kJ/mol   *Entropy disfavors rxn*

3.rare

$$NaCl(s) \rightleftharpoons Na^+(ag) + Cl^-(ag)$$

$\Delta G° = -2.7$

$\Delta H° = +1.9$ (endothermic) *Enthalpy disfavors rxn*

$T\Delta S° = +4.6$ *Entropy favors rxn*

(less ordered in the dissolved form)

<u>Q</u> Does $\Delta G°$ value (sign) tell you whether a reaction will occur or not?

<u>A</u> NO. It tells you what is thermodynamically possible to attain at 25°C but does not tell you whether it will happen to an appreciable extent at 25°C simply upon mixing reactants.

<u>Q</u> What else needs to be considered?

<u>A</u> Kinetics or rate of the reaction. Activation energies for reactants to go to products can be very high, and the reaction will require a catalyst to occur.   e.g. $NH_3(g)$ synthesis
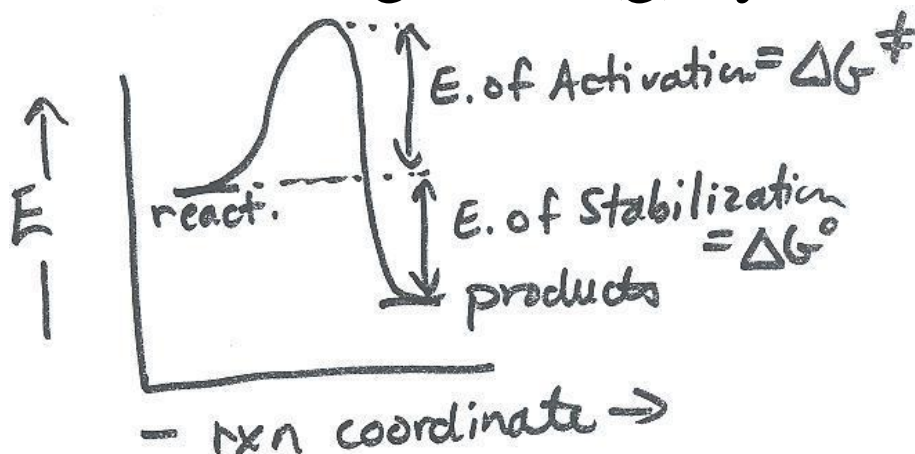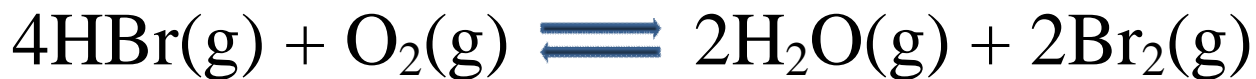

To occur, a reaction needs a $-\Delta G°$ <u>and</u> for the rate to be appreciable.

The study of <u>Kinetics</u> is the way we know the mechanism of a reaction **à** how it occurs.

<u>Reaction conditions affect rate</u>
  • Temperature, concentration, solvent, pressure, presence of a catalyst

One can write a rate law for any reaction

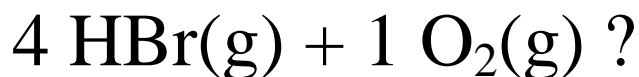$$4HBr(g) + O_2(g) \rightleftharpoons 2H_2O(g) + 2Br_2(g)$$

rate constant, k
$\downarrow$

$$\frac{d[O_2]}{dt} = -k \, [HBr] \, [O_2]$$

rate of disappearance of O_2 is related to the product of the concentration of the two reactants.

Q Did I make a mistake here?

Why isn't the [HBr] concentration reflecting the molar ratio of the reaction?

$$4 \, HBr(g) + 1 \, O_2(g) \, ?$$

<u>A</u> No mistake. The rate law that best describes the speed of the reaction is the one based on a rate-limiting step. Obviously, in this reaction the rate limiting step is the reaction of one mole of O_2 with one mole of HBr.

$1 + 1 = 2$

2nd order reaction (sum of exponents on conc.)

<u>Q</u> What is a first order reaction?

<u>A</u> One in which the rate law depends on the concentration of only one reactant.
(easy to envision in decomposition reactions)

$2N_2O_5(g) \rightleftharpoons 4\ NO_2(g) + O_2\ (g)$

$$\frac{d[N_2O_5]}{dt} = -k[N_2O_5]$$

Effect of temperature on Rates
Dependence of the rate constant, k, on Temp.,
T, in degrees Kelvin follows the Arrhenius Law

$$K = A e^{-Ea/RT}$$

E_a is the activation energy
A is called the "frequency factor"

- The higher the activation energy, the slower
the reaction

- A plot of log K versus T allows for E_a to be
determined