Intensive Organic Chemistry for Freshmen **C3045x** **Fall 1996**

1. Thermodynamic Considerations

   A. $\Delta G = \Delta H - T\Delta S$ (1)

   B. $\Delta G = -2.3\ RT \log K_{eq}$ (2)

   C. At 300°K, $-2.3\ RT \sim -1.4$ kcal / mole

   D. $\Delta G = -1.4 \log K_{eq}$ (in kcal / mole) (3)

   E. R P

2. Examples of Equilibria and ΔG

ΔG	**R**	**P**	**K_{eq}**
0	50	50	1.0
-1	15	85	5
-2	4	96	25
-3	0.5	99.5	150
-5	0.1	99.9	4000
-10	~0	~100	2×10^7

3. Rule of Thumb: ΔG ~ -5 kcal / mole is sufficient for "complete" reaction

5. Examples of ΔH (Bond Energies)

   1. X-Y --> X· + Y· ΔG bond energy (4)
   2. ΔH > 0 if bond is broken
   3. ΔH < 0 if bond is made

Bond Type	**Energy**	**Bond Type**	**Energy**
C-H	100	C-C	85
N-H	95	C=C	150
O-H	110	C=C	200
O-O	35	C-N	75
C-F	115	C=N	150
C-Cl	80	C=N	215
C=Br	70	C-O	85
C-I	50	C=O	180

6. Examples of ΔS (Entropy Changes)

   A. $CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$ (5)

   ΔS = +3 e.u. at 300°K $T\Delta S = 0.9$ kcal / mole

   Rule of Thumb: Same number of molecules of R and P --> ΔS ~ 0.

If $|\Delta H| > 20$, enthalpy will determine K_{eq} at ordinary temperatures. Qualifications: R and P must be similar structurally (comparable reorganizational energy)

B. $CH_3CH_2CH_2CH_2CH=CH_2$ (6)

ΔS = -21 e.u. at 300°K $T\Delta S$ = -6.3 kcal / mole

Rule of Thumb: The greater the freedom of movement of the atoms of a molecule, the more positive the entropy of the molecule. Reduction of degrees of freedom (i.e., chain into a ring) results in a decrease of entropy.

C. $2CH_2=CH_2$ ---> (7)

ΔS = -44 e.u. at 300°K $T\Delta S$ = -13 kcal / mole

(8)

ΔS = -86 e.u. at 300°K $T\Delta S$ = -26 kcal / mole

Rule of Thumb: If $|\Delta H| > 20$ kcal / mole, enthalpy will dominate K_{eq} unless there are two or three more molecules on one side of an equilibrium.

D. Kinetic Considerations

By Analogy: $\Delta G = \Delta H - T\Delta S$ (9)

$DG = -2.3\ RT\ LOG\ KEQ$ (10)

$$Rate = \frac{dR}{dt} = \frac{dP}{dt} = k\ K_{eq}\ [R[$$ (11)

$$Rate = k[R]\ 10^{\frac{-\Delta G}{1.4}}$$ at 300°K (12)

E. Examples of Rates and ΔG ($k = 10^{13}\ sec^{-1}$; R = 1M; T = 300°K

ΔG	**Rate (sec^{-1})**	**$t_{1/2}$ (sec)**
0	10^{13}	10^{-13}
1	10^{12}	10^{-12}
5	10^{10}	10
10	10^{6}	10^{-6}
14	10^{3}	10^{-3}
20	10^{-1}	10

25	10^{-5}	1700 min.
30	10^{-8}	50,000 (hours)

Rule of Thumb: ΔG ~25 kcal / mole: reaction "goes" near 300°K