

1. Thermodynamic Considerations

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

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

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

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

E. $R = P$

2. Examples of Equilibria and G

G	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

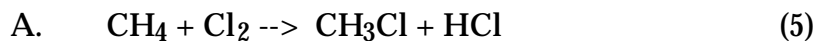
3. Rule of Thumb: $G \sim -5 \text{ kcal/mole}$ is sufficient for "complete" reaction5. Examples of H (Bond Energies)

1. $X-Y \rightarrow X\cdot + Y\cdot$ $G = \text{bond energy}$ (4)

2. $H > 0$ if bond is broken

3. $H < 0$ if bond is made

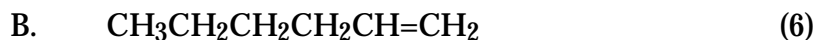
<u>Bond Type</u>	<u>Energy</u>	<u>Bond Type</u>	<u>Energy</u>
C-H	100	C-C	85
N-H	95	C=C	150
O-H	110	C=C	200
O-O	35	C-N	75
C-F	115	C=N	150
C-Cl	80	C=N	215
C=Br	70	C-O	85
C-I	50	C=O	180

6. Examples of S (Entropy Changes)

$S = +3 \text{ e.u. at } 300^\circ\text{K}$ $T \Delta S = 0.9 \text{ kcal/mole}$

Rule of Thumb: Same number of molecules of R and P $\rightarrow \Delta S \sim 0$.

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



$$S = -21 \text{ e.u. at } 300^\circ\text{K} \quad T \quad S = -6.3 \text{ kcal/mole}$$

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.



$$S = -44 \text{ e.u. at } 300^\circ\text{K} \quad T \quad S = -13 \text{ kcal/mole}$$

(8)

$$S = -86 \text{ e.u. at } 300^\circ\text{K} \quad T \quad S = -26 \text{ kcal/mole}$$

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: $G = H - T S$ (9)

$$\Delta G = -2.3 RT \text{ LOG } K_{eq}$$
 (10)

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

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

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

G	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:

G ~25 kcal/mole: reaction "goes" near 300°K