19.3   Gibbs Free Energy
Gibbs Free Energy and Spontaneity

$$G : H - TS \qquad G = \text{Gibbs Energy}$$
$$\Delta G : \Delta H - T\Delta S$$

Going to do a little equation manipulate to relate ΔS_{UNIV} which must be > 0 for a spontaneous proccess and this new thermodynamic function : ΔG.

For a spontaneous process

$$\Delta S_{UNIV} = \Delta S_{SYS} - \frac{\Delta H_{SYS}}{T} > 0$$
$$T\Delta S_{SYS} - \Delta H_{SYS} > 0$$
$$- T\Delta S_{SYS} + \Delta H_{SYS} < 0 \quad \text{(Multiplied by -1)}$$

$$\underline{\Delta H_{SYS} - T\Delta S_{SYS}} \quad < 0$$
$$\hookrightarrow = \Delta G_{SYS}$$

So for a spontaneous process

$$\Delta G_{SYS} = \Delta H_{SYS} - T\Delta S_{SYS} < 0 \quad \text{(Rem : Sys = Rxn!)}$$

A few notes on ΔG before we move on :

$\Delta G < 0$: Spontaneous process in the forward direction ... product favored reaction.

$\Delta G > 0$: Nonspontaneous process in the forward direction ... reactant favored reaction.

$\Delta G = 0$: At equilibrium

19.3   Gibbs Free Energy
Standard Gibbs Free Energy

2 Methods to determine ΔG°_{RXN}

1. $\Delta G^{\circ}_{RXN} = \sum \Delta G^{\circ}_f (Products) - \sum \Delta G^{\circ}_f (Reactants)$

By far the simplist, with the same rules applying as in ΔH°_{RXN}, if all we wish to know is ΔG°_{RXN}. Just like ΔH°_f, ΔG°_f can be easily looked up.
It lacks however any insights as to what is the primary cause for ΔG°_{RXN} to be > 0 or < 0.

2. $\Delta G^{\circ}_{RXN} = \Delta H^{\circ}_{RXN} - T \Delta S^{\circ}_{RXN}$

A little longer, gives the same result, but it allows us to see what is driving ΔG°_{RXN} to have its value (Enthalpy, Entropy, or both), thereby giving us a handle on whether we can manipulate the reaction (via Temperature) to affect a result that we want. ☺

19.3   Gibbs Free Energy
Free Energy, Standard Free Energy, and the Reaction Quotient

Time to tie in Gibbs Energy to the Equilibrium Constant (K) and thereby Q.

$$aA + bB \rightleftharpoons cC + dD$$

$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

a) $Q < K$:

System not at Equilibrium and the Reaction will continue to make more products until... $Q = K$

b) $Q > K$:

System not at Equilibrium and the Reaction will proceed in the Reverse direction to make more Reactants until... $Q = K$

c) $Q = K$

System is at quilibrium

Now let's look at ΔG, Note the absence of °, if you wish this non standard ΔG is our thermodynamic equivalent of Q.

a) $\Delta G < 0$:

Reaction is spontaneous in the forward direction and thus we will get, Reactants → Products

b) $\Delta G > 0$:

Reaction is spontaneous in the Reverse direction and thus we will get, Products → Reactants

c) $\Delta G = 0$:

Reaction at Equilibrium

With such an obvious correlation in the information gleamed on the Reaction by Q and ΔG, it should come as no surprise that they are Related!
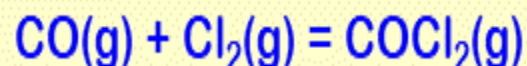
$$\Delta G = \Delta G° + RT \ln Q$$

$$= \Delta G_f° (\text{Products}) - \Delta G_f° (\text{Reactants})$$

19.3   Gibbs Free Energy
Free Energy, Standard Free Energy, and the Reaction Quotient

Consider the reaction $CO(g) + Cl_2(g) = COCl_2(g)$

Calculate ΔG for this reaction at **298.15K** if the pressure of each gas is **35.35 mm Hg**.

ΔG^0_f Values: $CO(g) = -137.2$ kJ.mol^{-1} $COCl_2(g) = -204.6$ kJ.mol^{-1}

$$\Delta G : \Delta G^\circ + RT \ln Q$$

$\Delta G^\circ:$

$$\Delta G^\circ = \Delta G^\circ_f\, COCl_2(g) - \Delta G^\circ_f\, CO(g) - \Delta G^\circ_f\, Cl_2(g) \quad *$$
$$= -204.6 \quad - (-137.2) \quad - \quad (0)$$
$$= -67.4 \text{ kJ.mol}^{-1}$$

* Same as ΔH°_f, the ΔG°_f of an element in its standard state is zero.

$Q:$

$$Q = \frac{P_{COCl_2}}{P_{CO} \; P_{Cl_2}}$$

$$P = \frac{33.35 \text{ mm Hg}}{} \bigg| \frac{1\,atm}{760 \text{ mm Hg}} = 0.04615 \text{ atm}$$

$$Q = \frac{0.04615}{0.04615\,(0.04615)} = 21.51$$

$\Delta G:$

$$\Delta G = \Delta G^\circ + RT \ln Q$$
$$= -67,400 + 8.314\,(298.15) \ln 21.51$$
$$= -67,400 + 7,606$$

$$= -59,794 \text{ J.mol}^{-1}$$
$$OR$$
$$-59.79 \text{ kJ.mol}^{-1}$$

Questions for you: a) Is the reaction at equilibrium?
b) If not at equilibrium in what direction will reaction proceed?

19.3   Gibbs Free Energy
Standard Free Energy and the Equilibrium Constant

$$\Delta G = \Delta G^\circ + RT \ln Q$$

When the system reaches equilibrium, then

$$\Delta G = 0 \quad \text{and} \quad Q = K \quad \text{and}$$
$$\Delta G = \Delta G^\circ + RT \ln Q \quad \text{becomes}$$
$$0 = \Delta G^\circ + RT \ln K$$

$$\boxed{\Delta G^\circ = -RT \ln K}$$

? Does this tie in with everything we have already met ?

a) K > 1 $-(RT \ln K) = -(+) = -$ $\Delta G^\circ < 0$
    Product favored   Product favored.

b) K < 1 $-(RT \ln K) = -(-) = +$ $\Delta G^\circ > 0$
    Reactant favored   Reactant favored.