Relationship Between ΔG and the Equilibrium Constant

I have mentioned earlier that the equilibrium constant is a thermodynamic quantity and varies only as a function of temperature.
It is possible to relate the equilibrium constant to other thermodynamic values.

When we are <u>not</u> at equilibrium,

$$\Delta G_{rxn} = \Delta G^\circ_{rxn} + 2.303\ RT \log Q$$

where Q is reaction quotient

But <u>at</u> equilibrium, $\Delta G_{rxn} = 0$ and $Q = K$ (ΔG°_{rxn} is constant obtained from Tables - see below !! only at 25°C !!)

$$\therefore 0 = \Delta G^\circ_{rxn} + 2.303\ RT \log K$$

<u>or</u>

$$\boxed{\Delta G^\circ_{rxn} = -2.303\ RT \log K}$$

where K is the THERMODYNAMIC equilibrium constant

Consider $A_{(g)} \rightleftarrows B_{(g)}$

Case (1) if $\Delta G^\circ < 0$ for this reaction as written - the reaction is spontaneou
then $\log K > 1$ and $K = \frac{(P_B)}{(P_A)}$ is very large

the equilibrium is shifted far to the right (products)

Case (2) if $\Delta G^\circ > 0$ for this reaction as written - the reaction is nonspontane
then $\log K < 0$ and K is very small number
the equilibrium is shifted far to the left (reactants)
and very little products have formed.

Note : $\Delta G^\circ_{rxn} = \Sigma n \Delta G^\circ_f$ products $- \Sigma n \Delta G^\circ_f$ reactants

Example: Consider the following reaction at 25°C.

$$N_2O_4\ (g) \rightleftharpoons 2\ NO_2\ (g)$$

(a) Calculate K_p for this gas reaction at 25°C from thermodynamic data

Solution is (1) determine ΔG° for this reaction either by

(i) using ΔG_f°

(ii) using ΔS°_{rxn} and ΔH°_{rxn}

$$\Delta G^\circ_{rxn} = \Delta H^\circ_{rxn} - T\Delta S^\circ_{rxn}$$

(2) determine K (= K_p for reactions containing only gases)

since $\Delta G^\circ_{rxn} = -2.303\ RT \log K$

$$\Delta G^\circ_{rxn} = \Sigma n\ \Delta G_f^\circ \text{ products} - \Sigma n\ \Delta G_f^\circ \text{ reactants}$$

$$= 2\ \Delta G_f^\circ\ NO_2(g) - \Delta G_f^\circ\ N_2O_4(g)$$

$$= 2\left(51.30 \tfrac{kJ}{mol}\right) - 97.82 \tfrac{kJ}{mol}$$

$$= +4.78\ kJ$$

the forward reaction is nonspontaneous (the reverse reaction is spontaneous)

∴ the reaction will proceed in reverse until equilibrium is reached. At that point we will have more reactants present than products.

∴ K (= K_p in this case) will be a small number for this reaction (< 1)

$$\Delta G^\circ_{rxn} = -2.303\ RT \log K_p$$

Note: in this equation we do NOT worry about the units of K (If ΔG° is in kJ, then R must be in kJ/mol K)

$$+4.78\ kJ = -2.303\ (8.314 \times 10^{-3}\ \tfrac{kJ}{K})(298\ K) \log K_p$$

$$-0.838 = \log K_p$$

$$K_p = 0.145 \quad \text{atm} = \frac{(P_{NO_2})^2}{(P_{N_2O_4})}$$

units

(b) Calculate K_c: $K_p = K_c (RT)^{\Delta n_{gas}}$ $\quad R = 0.0821 \tfrac{L\,atm}{mol\,K}$

$$0.145\ atm = K_c\ (0.0821 \times 298)^{(2-1)}$$

$$K_c = 5.93 \times 10^{-3}\ M$$

$$= \frac{[NO_2]^2}{[N_2O_4]}$$

Dependence of Equilibrium Constants on Temperature (Review)

As I have stated before, the equilibrium constant is a thermodynamic quantity and as such varies only with temperature (K).

This relationship is given by the van't Hoff Equation

$$\log \frac{K_2}{K_1} = \frac{\Delta H^\circ}{2.303\,R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

So, if you know K at a certain temperature and have access to thermodynamic tables, you can calculate the thermodynamic equilibrium constant at any temperature.