

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 not at equilibrium,

$$\Delta G_{\text{rxn}} = \Delta G_{\text{rxn}}^{\circ} + 2.303 RT \log Q$$

where Q is reaction quotient

But at equilibrium, $\Delta G_{\text{rxn}} = 0$ and $Q = K$ ($\Delta G_{\text{rxn}}^{\circ}$ is constant obtained from Tables - see below
!! only at 25°C !!)

$$\therefore 0 = \Delta G_{\text{rxn}}^{\circ} + 2.303 RT \log K$$

or

$$\Delta G_{\text{rxn}}^{\circ} = -2.303 RT \log K$$

where K is the
THERMODYNAMIC
equilibrium constant

Consider $A(g) \rightleftharpoons B(g)$

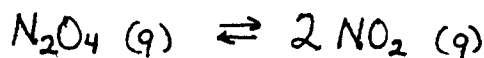
Case (1) if $\Delta G^{\circ} < 0$ for this reaction as written - the reaction is spontaneous
then $\log K > 0$ and $K = \frac{(P_B)}{(P_A)}$ is very large

the equilibrium is shifted far to the right (products)

Case (2) if $\Delta G^{\circ} > 0$ for this reaction as written - the reaction is nonspontaneous
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 : $\Delta G_{\text{rxn}}^{\circ} = \sum n \Delta G_f^{\circ} \text{ products} - \sum n \Delta G_f^{\circ} \text{ reactants}$

Example: Consider the following reaction at 25°C.



(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 $\Delta S_{\text{rxn}}^\circ$ and $\Delta H_{\text{rxn}}^\circ$

$$\Delta G_{\text{rxn}}^\circ = \Delta H_{\text{rxn}}^\circ - T \Delta S_{\text{rxn}}^\circ$$

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

$$\text{since } \Delta G_{\text{rxn}}^\circ = -2.303 RT \log K$$

$$\Delta G_{\text{rxn}}^\circ = \sum n \Delta G_f^\circ \text{ products} - \sum n \Delta G_f^\circ \text{ reactants}$$

$$= 2 \Delta G_f^\circ \text{NO}_2(\text{g}) - \Delta G_f^\circ \text{N}_2\text{O}_4(\text{g})$$

$$= 2 (51.30 \frac{\text{kJ}}{\text{mol}}) - 97.82 \frac{\text{kJ}}{\text{mol}}$$

$$= +4.78 \text{ kJ}$$

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

$\therefore$ the reaction will proceed in reverse until equilibrium is reached.

At that point we will have more reactants present than products.

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

$$\Delta G_{\text{rxn}}^\circ = -2.303 RT \log K_p$$

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)

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

$$-0.838 = \log K_p$$

$$K_p = 0.145 \frac{\text{atm}}{\text{units}} = \frac{(P_{\text{NO}_2})^2}{(P_{\text{N}_2\text{O}_4})}$$

(b) Calculate K_c :

$$K_p = K_c (RT)^{\Delta n_{\text{gas}}} \quad R = 0.0821 \frac{\text{L atm}}{\text{mol K}}$$

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

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

$$= \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$$

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.