20.4 Free Energy, Equilibrium, and Reaction Direction

➤ The direction of reaction can be predicted from the sign of ΔG or by comparing Q and K

  ➤ If $Q < K \rightarrow Q/K < 1 \rightarrow \ln Q/K < 0$ and $\Delta G < 0$, the forward reaction proceeds

  ➤ If $Q > K \rightarrow Q/K > 1 \rightarrow \ln Q/K > 0$ and $\Delta G > 0$, the reverse reaction proceeds

  ➤ If $Q = K \rightarrow Q/K = 1 \rightarrow \ln Q/K = 0$ and $\Delta G = 0$, the reaction is at equilibrium

$\Rightarrow \Delta G$ and $\ln Q/K$ have the same signs and are related:

$$\Delta G_r^T = RT \ln \frac{Q}{K} = RT \ln Q - RT \ln K$$

$\Rightarrow \Delta G_r$ is concentration dependent (depends on Q)

$\Rightarrow \Delta G_r$ can be viewed as a difference between the free energy of the system at the current concentrations of reactants and products, Q, and that at equilibrium, K

➤ At standard-state conditions, all concentrations and pressures are equal to **1**, so $Q = 1$ and $\Delta G_r = \Delta G_r^o$

$\Rightarrow \Delta G_r^{o,T} = RT \ln 1 - RT \ln K = 0 - RT \ln K$

$$\boxed{\Delta G_r^{o,T} = -RT \ln K}$$

→ The equation is used to calculate ΔG^o from K and vice versa

  ➤ If $K > 1 \rightarrow \Delta G^o < 0 \rightarrow$ products are favored at equilibr.
  ➤ If $K < 1 \rightarrow \Delta G^o > 0 \rightarrow$ reactants are favored at equilibr.
  ➤ If $K = 1 \rightarrow \Delta G^o = 0$

Example: Calculate K_p at 298 K for the reaction

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$
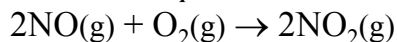
→ Calculate $\Delta G_r^{o,298}$

→ $T = 298$ K $\Rightarrow \Delta G_f^{o,298}$ values from Appendix B can be used

$\Delta G_r^{o,298} = 2 \times \Delta G_f^{o,298}(NO_2(g)) -$

$\qquad - [2 \times \Delta G_f^{o,298}(NO(g)) + 1 \times \Delta G_f^{o,298}(O_2(g))] =$

$= 2(+51.3) - [2(+86.6) + 1(0)] =$ **-70.6 kJ/mol**

$\Delta G_r^{o,T} = -RT \ln K \Rightarrow \ln K = -\Delta G_r^{o,T}/RT$

$$K = e^{\frac{-\Delta G_r^{o,T}}{RT}} = e^{\frac{-(-70.6\,\text{kJ/mol})}{8.314 \times 10^{-3}\,\text{kJ/mol·K} \times 298K}} = \boxed{2.4 \times 10^{12} = K_p}$$

$K_p \gg 1 \Rightarrow$ the products are highly favored

➤ Combining $\Delta G_r^T = RT \ln Q - RT \ln K$
with $\Delta G_r^{o,T} = - RT \ln K$ leads to:

$$\boxed{\Delta G_r^T = \Delta G_r^{o,T} + RT \ln Q}$$

→ The equation is used to calculate ΔG_r^T for any nonstandard state from $\Delta G_r^{o,T}$ for the respective standard state both at temperature, T, and the reaction quotient of the nonstandard state, Q

→ $\Delta G_r^{o,T}$ is calculated as $\Delta G_r^{o,T} = \Delta H_r^o - T\Delta S_r^o$

→ $R = 8.314 \times 10^{-3}$ kJ/mol·K

→ T is the same for all quantities in the equation

$\Rightarrow \Delta G_r^T$ is associated with a certain composition (Q) and a certain temperature (T)

Example: Calculate the free energy change for the reaction $H_2(g) + I_2(g) \rightarrow 2HI(g)$ at **500 K** if the partial pressures of H_2, I_2, and HI are **1.5**, **0.88** and **0.065 atm**, respectively.

→ Nonstandard state at 500 K ($\Delta G_r^{500} = ?$)

→ Calculate $\Delta G_r^{o,500}$ as $\Delta G_r^{o,T} = \Delta H_r^o - T\Delta S_r^o$

→ $\Delta H_r^o = 2 \times \Delta H_f^o(HI(g)) -$
$$- [1 \times \Delta H_f^o(H_2(g)) + 1 \times \Delta H_f^o(I_2(g))] =$$
$= 2(+25.9) - [1(0) + 1(+62.4)] =$ **-10.6 kJ**

→ $\Delta S_r^o = 2 \times S^o(HI(g)) - [1 \times S^o(H_2(g)) + 1 \times S^o(I_2(g))] =$
$= 2(206) - [1(131) + 1(261)] = +$**20 J/K**

→ $\Delta G_r^{o,500} = $ -10.6 kJ – 500 K×(0.020 kJ/K) = **-20.6 kJ**

$$Q_p = \frac{P_{HI}^2}{P_{H_2} P_{I_2}} = \frac{(0.065)^2}{1.5 \times 0.88} = 3.2 \times 10^{-3}$$

$$\Delta G_r^{500} = \Delta G_r^{o,500} + R \times 500\ \text{K} \times \ln Q$$

$$= -20.6\frac{\text{kJ}}{\text{mol}} + 8.314 \times 10^{-3}\frac{\text{kJ}}{\text{mol}\cdot\text{K}} \times 500\text{K} \times \ln(3.2 \times 10^{-3})$$

$$= -20.6\frac{\text{kJ}}{\text{mol}} - 23.9\frac{\text{kJ}}{\text{mol}}$$

$$\Rightarrow \boxed{\Delta G_r^{500} = -44.5\frac{\text{kJ}}{\text{mol}}}$$

$$\Rightarrow \Delta G_r^{500} < 0$$

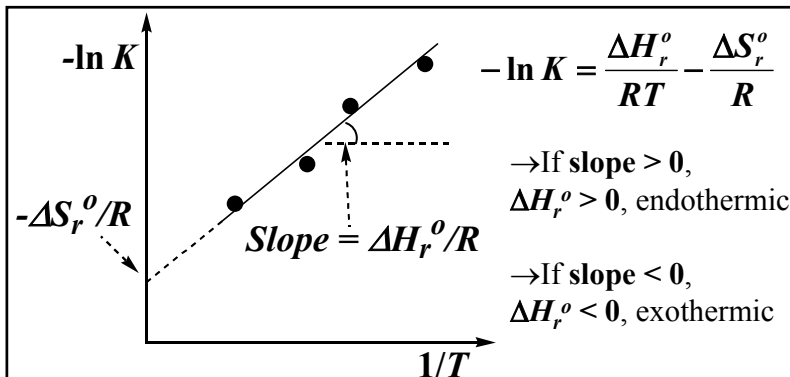$\Rightarrow$ The reaction **is spontaneous** at this nonstandard state and 500 K

Deriving the van't Hoff Equation

➢ The van't Hoff equation gives the temperature dependence of the equilibrium constant

$$\Delta G_r^{o,T} = -RT \ln K \quad \Big| \quad -RT \ln K = \Delta H_r^o - T\Delta S_r^o$$

$$\Delta G_r^{o,T} = \Delta H_r^o - T\Delta S_r^o \Big|$$

$$\boxed{-\ln K = \frac{\Delta H_r^o}{RT} - \frac{\Delta S_r^o}{R}}$$

➢ If the equation is applied for two different Ts, and ΔH_r^o and ΔS_r^o are assumed independent of T

$$\rightarrow \quad \ln\frac{K_2}{K_1} = -\frac{\Delta H_r^o}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$-\ln K = \frac{\Delta H_r^o}{RT} - \frac{\Delta S_r^o}{R}$$

→ If **slope > 0**, $\Delta H_r^o > 0$, endothermic

→ If **slope < 0**, $\Delta H_r^o < 0$, exothermic

➢ A plot of $-\ln K$ versus $1/T$ gives a straight line with a **Slope** $= \Delta H_r^o/R$ and **Intercept** $= -\Delta S_r^o/R$

➢ Allows the experimental determination of ΔH_r^o and ΔS_r^o from measurements of K at different Ts