Statistical Molecular Thermodynamics

Christopher J. Cramer

Video 12.5

Reaction Quotient Redux
Utility of the Reaction Quotient

Cf. video 12.2:

In general: \[ \Delta_r G = \Delta_r G^\circ(T) + RT \ln Q_P \]

\[ Q_P = \left( \frac{P_Y^v P_Z^v}{P_A^v P_B^v} \right) \]

At equilibrium: \[ \Delta_r G^\circ(T) = -RT \ln K_P \]

\[ K_P = \left( \frac{P_Y^v}{P_A^v} \right) \left( \frac{P_Z^v}{P_B^v} \right)_{eq} \]

substitute: \[ \Delta_r G = -RT \ln K_P + RT \ln Q_P \]

\[ \Delta_r G = RT \ln \frac{Q_P}{K_P} \]
**Reaction Quotient Dictates Direction**

\[ \nu_A A(g) + \nu_B B(g) \rightleftharpoons \nu_Y Y(g) + \nu_Z Z(g) \]

\[ \Delta_r G = RT \ln \frac{Q_P}{K_P} \quad Q_P = \left( \frac{P_Y^{\nu_Y} P_Z^{\nu_Z}}{P_A^{\nu_A} P_B^{\nu_B}} \right) \quad K_P = \left( \frac{P_Y^{\nu_Y} P_Z^{\nu_Z}}{P_A^{\nu_A} P_B^{\nu_B}} \right)_{eq}^* \]

- At equilibrium, \( \Delta_r G = 0 \) and \( Q_P = K_P \).

- If \( Q_P < K_P \) then \( Q_P \) must *increase* to proceed toward equilibrium. This means the pressure of the products will *increase* and the pressure of the reactants will *decrease*, and the reaction will go to the *right*.

- If \( Q_P > K_P \) then \( Q_P \) must *decrease* to proceed toward equilibrium. This means the pressure of the products will *decrease* and the pressure of the reactants will *increase* and the reaction will go to the *left*.
Self-assessment

Consider the reaction below, for which $K_p = 10$ at 960 K:

$$2 \text{SO}_2 (g) + \text{O}_2 (g) \rightleftharpoons 2 \text{SO}_3 (g)$$

Given 960 K starting partial pressures of $1.0 \times 10^{-3}$, 0.20, and $1.0 \times 10^{-4}$ bar for SO$_2$, O$_2$, and SO$_3$, respectively, predict the direction in which the reaction will spontaneously proceed and the overall $\Delta r G$. 
Self-assessment Explained

\[ 2 \text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2 \text{SO}_3(g) \quad K_P = 10 \text{ at } 960 \text{ K} \]

Given 960 K starting partial pressures of \(1.0 \times 10^{-3}\), 0.20, and \(1.0 \times 10^{-4}\) bar for \(\text{SO}_2\), \(\text{O}_2\), and \(\text{SO}_3\), respectively, predict the direction in which the reaction will spontaneously proceed and the overall \(\Delta_r G\)

To begin, \[ Q_P = \frac{P_{\text{SO}_3}^2}{P_{\text{O}_2} P_{\text{SO}_2}^2} = \frac{(0.0001)^2}{(0.001)^2(0.2)} = 0.05 \]

as \(Q_P < K_P\), the reaction will proceed to the right

And, \[ \Delta_r G = RT \ln \frac{Q_P}{K_P} \]

\[ = (8.314 \text{ J K}^{-1} \text{ mol}^{-1})(960 \text{ K}) \ln \left(\frac{0.05}{10}\right) \]

\[ = -42.3 \text{ kJ mol}^{-1} \]
\[ dU = \delta q + \delta w \]

Next: Temperature Dependence of K