Thermodynamics II: The Equilibrium Constant as a Function of Temperature

1. The Ostwald process is used to make sulfuric acid from sulfur trioxide, which is itself made from the combustion of sulfur. The first product in the combustion of sulfur is sulfur dioxide which then reacts with excess oxygen to form sulfur trioxide.

$$SO_2(g) + \tfrac{1}{2}O_2(g) \rightleftarrows SO_3(g) \qquad K_p = 2.7 \times 10^{12} \ (25°C)$$

The sulfur trioxide produced is then passed through a fine mist of water. The sulfur trioxide reacts with the water to produce sulfuric acid.

$$SO_3(g) + H_2O(l) \rightleftarrows H_2SO_4(l) \qquad K = 2.2 \times 10^{14} \ (25°C)$$

Calculate the $\Delta H°$ for the reaction of sulfur trioxide with water.

$$\Delta H° = -813.989 \times 10^3 \ {}^{\text{J}}\!/_{\text{mol}} - \left(-395.72 \times 10^3 \ {}^{\text{J}}\!/_{\text{mol}} + \left(-285.830 \times 10^3 \ {}^{\text{J}}\!/_{\text{mol}}\right)\right)$$

$$\Delta H° = -1.324 \times 10^3 \ {}^{\text{J}}\!/_{\text{mol}} = -1.324 \ {}^{\text{kJ}}\!/_{\text{mol}}$$

Calculate the equilibrium constant for the reaction at the boiling point of sulfuric acid (340°C).

$\Delta H°$ was calculated above so now we need $\Delta S°$

$$\Delta S° = 156.904 \ {}^{\text{J}}\!/_{\text{mol·K}} - \left(256.76 \ {}^{\text{J}}\!/_{\text{mol·K}} + 69.91 \ {}^{\text{J}}\!/_{\text{mol·K}}\right) = -169.77 \ {}^{\text{J}}\!/_{\text{mol·K}}$$

Estimate $\Delta G°$ at 340°C

$$\Delta G° = -1.324 \times 10^3 \ {}^{\text{J}}\!/_{\text{mol}} - (613.2 \text{ K})(169.77 \ {}^{\text{J}}\!/_{\text{mol·K}}) = -28{,}340 \ {}^{\text{J}}\!/_{\text{mol}}$$

Calculate K

$$\Delta G° = -RT \ln K$$

$$\ln K = -\frac{-28{,}340 \ {}^{\text{J}}\!/_{\text{mol}}}{\left(8.314 \frac{\text{J}}{\text{mol·K}}\right)\left(613.2 \text{ K}\right)} = 5.56 \qquad K = e^{5.56} = 259$$