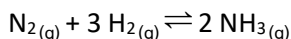


1. Consider the reaction that occurs during the Haber process:



The equilibrium constant is 3.9×10^5 at 300.0 K and 1.2×10^{-1} at 500.0 K. Calculate $\Delta_{\text{rxn}}H^\circ$ and $\Delta_{\text{rxn}}S^\circ$ for this reaction.

$$\ln \frac{K_2}{K_1} = \frac{\Delta_{\text{rxn}}H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

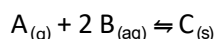
$$\Delta_{\text{rxn}}H^\circ = \frac{R \ln \frac{K_2}{K_1}}{\left(\frac{1}{T_1} - \frac{1}{T_2} \right)} = \frac{(8.314472 \text{ J mol}^{-1} \text{ K}^{-1}) \ln \frac{1.2 \times 10^{-1}}{3.6 \times 10^5}}{\left(\frac{1}{300.0 \text{ K}} - \frac{1}{500.0 \text{ K}} \right)} = -93002.29262 \text{ J mol}^{-1}$$

$$= -9.3 \times 10^4 \text{ J mol}^{-1}$$

$$\Delta_{\text{rxn}}S^\circ = \frac{-RT \ln K - \Delta_{\text{rxn}}H^\circ}{-T} = \frac{-(8.314472 \text{ J mol}^{-1} \text{ K}^{-1})(300.0 \text{ K}) \ln(3.9 \times 10^5) - (-9.3 \times 10^4 \text{ J mol}^{-1})}{-(300.0 \text{ K})}$$

$$= -202.96 \text{ J mol}^{-1} \text{ K}^{-1}$$

2. At 154.3°C the following reaction has a thermodynamic equilibrium constant of 1.4×10^4



What is the **free energy change** when the partial pressure of A is 635.4 mmHg and the concentration of B is 2.357 M?

$$\Delta G^\circ = -RT \ln K = -(8.314472 \text{ J mol}^{-1} \text{ K}^{-1})(427.5 \text{ K}) \ln(1.4 \times 10^4)$$

$$= -3.393 \times 10^4 \text{ J mol}^{-1}$$

$$\Delta G = \Delta G^\circ + RT \ln Q = \Delta G^\circ + RT \ln \frac{1}{\left(\frac{P_A}{P^\circ} \right) \left(\frac{[B]}{c^\circ} \right)^2}$$

$$= -3.393 \times 10^4 \text{ J mol}^{-1} + (8.314472 \text{ J mol}^{-1} \text{ K}^{-1})(427.5 \text{ K}) \ln \frac{1}{\left(\frac{635.4 \text{ mmHg}}{\frac{760 \text{ mmHg}}{1.01325 \text{ bar}}} \right) \left(\frac{2.357 \text{ M}}{1 \text{ M}} \right)^2}$$

$$= -3.6387 \times 10^4 \text{ J mol}^{-1} = -3.6 \times 10^4 \text{ J mol}^{-1}$$

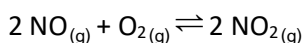
3. Calculate the entropy change when 1.00 mol of water boils at its normal boiling point.

What is the free energy change for this process? Explain or show calculations.

$$\Delta S = \frac{\Delta_{\text{vap}} H}{T} = \frac{40.657 \text{ kJ mol}^{-1}}{373.15 \text{ K}} = 0.10895 \text{ kJ mol}^{-1} \times 1.00 \text{ mol} = 0.109 \text{ kJ}$$

Boiling at the boiling point is an equilibrium process so the free energy change is zero.

4. You have the following reaction at 250 °C.



- a. Determine if the reaction is spontaneous at this temperature.

$$\Delta_{\text{rxn}} H = \left[\left(\frac{2 \text{ mol NO}_2}{1 \text{ mol rxn}} \right) \left(\frac{33.18 \text{ kJ}}{\text{mol NO}_2} \right) \right] - \left[\left(\frac{2 \text{ mol NO}}{1 \text{ mol rxn}} \right) \left(\frac{90.25 \text{ kJ}}{\text{mol NO}} \right) + \left(\frac{1 \text{ mol O}_2}{1 \text{ mol rxn}} \right) \left(\frac{0.00 \text{ kJ}}{\text{mol O}_2} \right) \right]$$

$$= -114.14 \text{ kJ mol}^{-1}$$

$$\Delta_{\text{rxn}} S = \left[\left(\frac{2 \text{ mol NO}_2}{1 \text{ mol rxn}} \right) \left(\frac{240.06 \text{ J}}{\text{mol NO}_2 \text{ K}} \right) \right] - \left[\left(\frac{2 \text{ mol NO}}{1 \text{ mol rxn}} \right) \left(\frac{210.761 \text{ J}}{\text{mol NO K}} \right) + \left(\frac{1 \text{ mol O}_2}{1 \text{ mol rxn}} \right) \left(\frac{205.138 \text{ J}}{\text{mol O}_2 \text{ K}} \right) \right]$$

$$= -146.54 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta G = \Delta H - T\Delta S = (-114.14 \times 10^3 \text{ J mol}^{-1}) - (523.15 \text{ K})(-146.54 \text{ J mol}^{-1} \text{ K}^{-1})$$

$$= -37\,477 \text{ J mol}^{-1}$$

The reaction is spontaneous at this temperature.

- b. If the reaction is not spontaneous at this temperature, calculate the temperature at which it becomes spontaneous.

See A.

- c. Calculate the equilibrium constant for this reaction at 250 °C.

$$K = e^{-\Delta G/RT} = e^{\frac{-(-37477 \text{ J mol}^{-1})}{(8.314472 \text{ J mol}^{-1} \text{ K}^{-1})(523.15 \text{ K})}} = 5.52 \times 10^3$$

5. An ideal solution forms between hexane and octane. Calculate the mole fraction of hexane in the vapor above the solution when 100.0 g of hexane and 154.3 g of octane are mixed. The vapor pressure of pure hexane is 17.60 kPa and the vapor pressure of pure octane is 1.47 kPa.

$$n_{hex} = 100.0 \text{ g C}_6\text{H}_{14} \times \frac{1 \text{ mol C}_6\text{H}_{14}}{86.1754 \text{ g C}_6\text{H}_{14}} = 1.1604 \text{ mol C}_6\text{H}_{14}$$

$$n_{oct} = 154.3 \text{ g C}_8\text{H}_{18} \times \frac{1 \text{ mol C}_8\text{H}_{18}}{114.2285 \text{ g C}_8\text{H}_{18}} = 1.3508 \text{ mol C}_8\text{H}_{18}$$

$$x_{hex} = \frac{n_{hex}}{n_{tot}} = \frac{1.1604 \text{ mol}}{2.5112 \text{ mol}} = 0.46209$$

$$x_{oct} = 1 - x_{hex} = 0.53791$$

$$P_{sol'n} = x_{hex} P_{hex}^* + x_{oct} P_{oct}^* = (0.46209)(17.60 \text{ kPa}) + (0.53791)(1.47 \text{ kPa}) = 8.92 \text{ kPa}$$

$$x_{hex,vapor} = \frac{P_{hex}}{P_{sol'n}} = \frac{x_{hex} P_{hex}^*}{P_{sol'n}} = \frac{(0.46209)(17.60 \text{ kPa})}{8.92 \text{ kPa}} = 0.911$$

6. 6.5973 g of myoglobin is dissolved into enough water to make 100.00 mL of solution. The osmotic pressure of the solution is determined to be 9.696 kPa at 26.5 °C. What is the molar mass of myoglobin?

$$\Pi = MRT$$

$$M = \frac{\Pi}{RT} = \frac{9.696 \text{ kPa}}{(8.314472 \text{ L kPa mol}^{-1} \text{ K}^{-1})(299.7 \text{ K})} = 4.140 \times 10^{-5} \text{ M}$$

$$n_{myo} = 100.00 \text{ mL} \times \frac{10^{-3} \text{ L}}{1 \text{ mL}} \times \frac{4.140 \times 10^{-5} \text{ mol myo}}{\text{L}} = 4.140 \times 10^{-6} \text{ mol}$$

$$\text{molar mass} = \frac{6.5973 \text{ g}}{4.140 \times 10^{-6} \text{ mol}} = 1.594 \times 10^4 \text{ g mol}^{-1}$$