

1. Consider the following reaction: $4\text{NO}(g) \rightarrow 2\text{N}_2\text{O}(g) + \text{O}_2(g)$

a. Calculate ΔH° , ΔS° , and ΔG° for this reaction at 25 °C (Find ΔH_f° , S° and ΔG_f° values in the appendix.) (6 pts)

$$\Delta H^\circ = [(2)\Delta H_f^\circ(\text{N}_2\text{O}) + (1)\Delta H_f^\circ(\text{O}_2)] - (4)\Delta H_f^\circ(\text{NO})$$

$$= [(2)(81.56 \frac{\text{kJ}}{\text{mol}}) + (1)(0 \frac{\text{kJ}}{\text{mol}})] - (4)(90.4 \frac{\text{kJ}}{\text{mol}}) = -198 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta S^\circ = [(2)S^\circ(\text{N}_2\text{O}) + (1)S^\circ(\text{O}_2)] - (4)S^\circ(\text{NO})$$

$$= [(2)(219.99 \frac{\text{J}}{\text{K} \cdot \text{mol}}) + (1)(205.0 \frac{\text{J}}{\text{K} \cdot \text{mol}})] - (4)(210.6 \frac{\text{J}}{\text{K} \cdot \text{mol}}) = -197.4 \frac{\text{J}}{\text{K} \cdot \text{mol}}$$

$$\Delta G^\circ = [(2)\Delta G_f^\circ(\text{N}_2\text{O}) + (1)\Delta G_f^\circ(\text{O}_2)] - (4)\Delta G_f^\circ(\text{NO})$$

$$= [(2)(103.6 \frac{\text{kJ}}{\text{mol}}) + (1)(0 \frac{\text{kJ}}{\text{mol}})] - (4)(86.7 \frac{\text{kJ}}{\text{mol}}) = -139.6 \frac{\text{kJ}}{\text{mol}} \Rightarrow -140. \frac{\text{kJ}}{\text{mol}}$$

$$(\text{or from } \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -198 \frac{\text{kJ}}{\text{mol}} - (298 \text{ K})(-0.1974 \frac{\text{kJ}}{\text{K} \cdot \text{mol}}) = -139 \frac{\text{kJ}}{\text{mol}})$$

b. Calculate the value of the equilibrium constant, K_p , at 25 °C. (2 pts)

$$K = e^{\frac{-\Delta G^\circ}{RT}}$$

$$K = e^{\frac{-(-140 \frac{\text{kJ}}{\text{mol}})}{(8.314 \frac{\text{J}}{\text{K} \cdot \text{mol}})(1000 \text{ J})(298 \text{ K})}} = e^{56.5}$$

$$K = 3.47 \times 10^{24}$$

$$(\text{or from } \Delta G^\circ = -139 \frac{\text{kJ}}{\text{mol}}; K = e^{56.1} = 2.32 \times 10^{24})$$

c. Calculate ΔG at 25 °C when the initial pressures of the reaction mixture are $P_{\text{NO}} = 2.05 \text{ atm}$, $P_{\text{N}_2\text{O}} = 1.25 \text{ atm}$, and $P_{\text{O}_2} = 0.715 \text{ atm}$. (4 pts)

$$\Delta G = \Delta G^\circ + RT \ln Q \quad Q = \frac{P_{\text{N}_2\text{O}}^2 P_{\text{O}_2}}{P_{\text{NO}}^4}$$

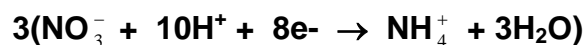
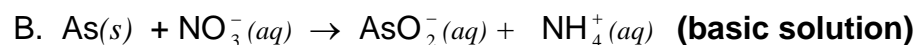
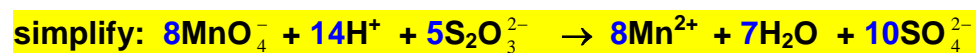
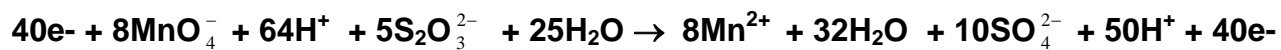
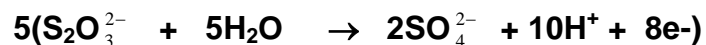
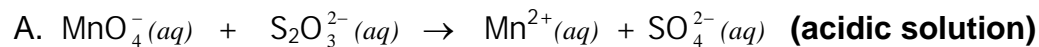
$$\Delta G = -140. \frac{\text{kJ}}{\text{mol}} + (8.314 \times 10^{-3} \frac{\text{kJ}}{\text{Kmol}})(298 \text{ K}) \left(\ln \frac{(1.25)^2 (0.715)}{(2.05)^4} \right)$$

$$\Delta G = -140. \frac{\text{kJ}}{\text{mol}} + 2.478 \frac{\text{kJ}}{\text{mol}} (\ln 6.326 \times 10^{-2})$$

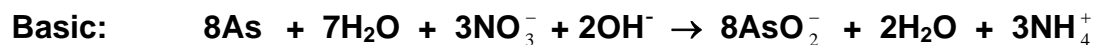
$$\Delta G = -140. \frac{\text{kJ}}{\text{mol}} + -6.84 \frac{\text{kJ}}{\text{mol}} = -146.8 \frac{\text{kJ}}{\text{mol}} \Rightarrow -147 \frac{\text{kJ}}{\text{mol}}$$

$$(\text{or from } \Delta G^\circ = -139 \frac{\text{kJ}}{\text{mol}}, \Delta G = -146 \frac{\text{kJ}}{\text{mol}})$$

2. Balance the following redox reactions (9 pts):



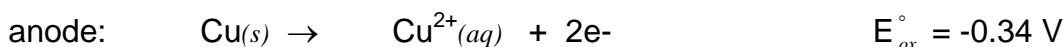
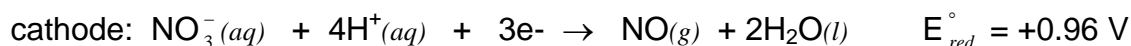
Make Basic: add 2 OH⁻ both sides



3. A certain voltaic cell is constructed based on the following half reactions and operates at 298 K:



a) Write and label the anode and cathode half reactions for the cell. (Make sure that you write the anode and cathode reactions in the appropriate direction!) Also, write an overall balanced reaction for this voltaic cell. (3 pts)



b) What is the emf of this cell, E° , under standard conditions? (2 pts)

$$E_{cell}^\circ = E_{red}^\circ + E_{ox}^\circ = +0.96 \text{ V} + -0.34 \text{ V} = 0.62 \text{ V}$$

c) Calculate the free energy change, ΔG° , for the overall reaction. (2 pts)

$$\Delta G^\circ = -nFE^\circ$$

$$\Delta G^\circ = -(6) \left(\frac{96500 \text{ J}}{\text{V} \cdot \text{mol} e^-} \right) (0.62 \text{ V}) = -3.6 \times 10^5 \frac{\text{J}}{\text{mol}} \quad (\text{or } -3.6 \times 10^2 \frac{\text{kJ}}{\text{mol}})$$

d) Calculate the equilibrium constant, K , for the overall reaction. (2 pts)

$$E^\circ = \frac{0.0592}{n} \log K \quad \log K = \frac{(0.62)(6)}{0.0592} = 62.84$$

$$K = 10^{62.84} = 6.9 \times 10^{62}$$

$$\text{or can use } K = e^{\frac{-\Delta G^\circ}{RT}}; K = e^{\frac{-(-360 \frac{\text{kJ}}{\text{mol}})}{\left(8.314 \frac{\text{J}}{\text{K} \cdot \text{mol}}\right) \left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right) (298 \text{ K})}} = e^{145.3} = 1.3 \times 10^{63}$$

K comes out a little different with the 2 methods because Faraday's constant is actually 96485 C/mol, and 0.0592 is 0.059161 w/ more significant figures.