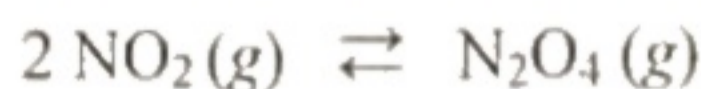


Worksheet 4

1. For the following reaction the equilibrium constant is 6.8 at 25°C and 1.21×10^{-3} at 200°C.



- a) What is the reaction quotient for the reaction? If $P_{\text{N}_2\text{O}_4}$ is 1 atm at 25°C, what is P_{NO_2} ?

$$Q = \frac{P_{\text{N}_2\text{O}_4}}{(P_{\text{NO}_2})^2} \quad K = \frac{P_{\text{N}_2\text{O}_4}}{P_{\text{NO}_2}^2} \quad P_{\text{NO}_2}^2 = \frac{P_{\text{N}_2\text{O}_4}}{K} \quad P_{\text{NO}_2} = \sqrt{\frac{1}{6.8}} \approx \boxed{0.383 \text{ atm}}$$

- b) What is ΔG° at 25°C for this reaction?

$$\Delta G = \Delta G^\circ + RT \ln Q \quad \text{At equil, } \Delta G = 0 \quad K = Q$$

$$0 = \Delta G^\circ + RT \ln K \quad \Delta G^\circ = -RT \ln K = -4.751 \frac{\text{kJ}}{\text{mol}}$$

- c) Determine ΔH° at 25°C assuming it to be independent of temperature.

$$\ln \frac{K_1}{K_2} = -\frac{\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) + \frac{\Delta S}{R}$$

$$\frac{R \ln \frac{K_1}{K_2}}{\left(\frac{1}{T_1} - \frac{1}{T_2} \right)} = -\Delta H = \frac{R \ln \frac{K_1}{K_2} (T_1 T_2)}{(T_2 - T_1)} = \boxed{57.869 \frac{\text{kJ}}{\text{mol}}}$$

- d) Determine ΔS° assuming it to be independent of temperature.

$$\Delta G = \Delta H - T\Delta S \quad T\Delta S = \frac{\Delta H - \Delta G}{1} \quad \Delta S = \frac{\Delta H - \Delta G}{T} = \boxed{-178 \frac{\text{J}}{\text{mol K}}}$$

2. The enthalpy of vaporization of ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) is 38.7 kJ/mol at 78.0°C, its normal boiling point. Calculate q , w , ΔH , ΔE , ΔS_{sys} and ΔG .

$$\Delta H = 38.7 \frac{\text{kJ}}{\text{mol}}$$

$$q = 38.7 \frac{\text{kJ}}{\text{mol}}$$

$$w = -p\Delta V = -\Delta pV = -\Delta(nRT) = -(\Delta n)RT = -(1)(8.314)(351) = \boxed{-2.92 \text{ kJ}}$$

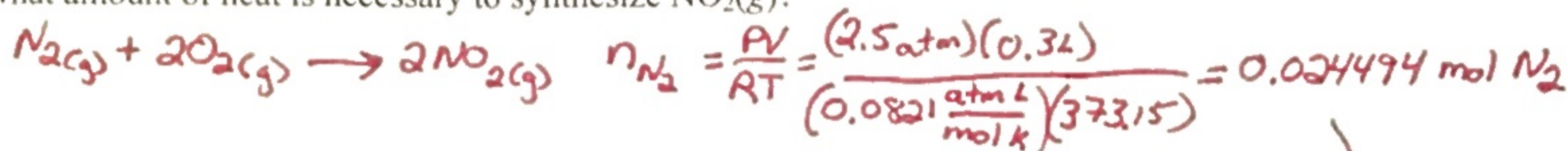
$$\Delta E = q + w = 35.8 \text{ kJ}$$

$$\Delta S = \frac{\Delta H_{\text{vap}}}{T} = \frac{38700 \frac{\text{J}}{\text{mol}}}{351 \text{ K}} = 110.2 \frac{\text{J}}{\text{mol K}}$$

$$\Delta G = \Delta H - T\Delta S = 38700 - (351 \text{ K})(110.2 \frac{\text{J}}{\text{mol K}}) = 0$$

no usable energy from a phase change so $\Delta G = 0$, all enthalpy goes to disorder.

3. The preparation of $\text{NO}_2(\text{g})$ from $\text{N}_2(\text{g})$ and $\text{O}_2(\text{g})$ is an endothermic reaction. The enthalpy change for the balanced equation with lowest whole number coefficients is $\Delta H = 67.7 \text{ kJ}$. If 300.0 mL of $\text{N}_2(\text{g})$ at 100.0 °C and 2.50 atm and 500.0 mL of $\text{O}_2(\text{g})$ at 100.0 °C and 2.50 atm are mixed, what amount of heat is necessary to synthesize $\text{NO}_2(\text{g})$?



$$\text{(LR)} \quad n_{\text{NO}_2} = \frac{0.040823 \text{ mol O}_2}{1} \times \frac{2 \text{ mol NO}_2}{2 \text{ mol O}_2} = 0.040823 \text{ mol NO}_2$$

$$\rightarrow \frac{0.024494 \text{ mol N}_2}{1} \times \frac{2 \text{ mol NO}_2}{1 \text{ mol N}_2} = 0.048988 \text{ mol NO}_2$$

$$\frac{0.040823 \text{ mol NO}_2}{1} \times \frac{67.7 \text{ kJ}}{2 \text{ mol NO}_2} = 1.38 \text{ kJ}$$

4. The K^+ concentration in blood plasma is $\sim 5.0 \times 10^{-3} \text{ M}$ while the concentration in muscle-cell fluid is 0.15 M. The plasma and intracellular fluid are separated by the cell membrane taken to be permeable only to K^+ .

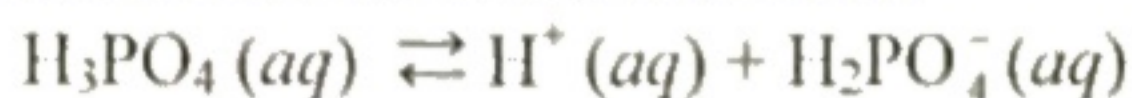
a) What is the ΔG of transfer of 1 mol of K^+ from blood plasma to the cellular fluid at body temperature, 37°C?

$$\Delta G = \Delta G^\circ + RT \ln Q = \Delta G^\circ_f(\text{K}^+, \text{cell}) - \Delta G^\circ_f(\text{K}^+, \text{plasm}) + RT \ln \left(\frac{0.15 \text{ M}}{5.0 \times 10^{-3} \text{ M}} \right) = 8.77 \frac{\text{kJ}}{\text{mol}}$$

b) What is the minimum amount of work that must be done on the system to transfer this K^+ ?

Same as a)

5. K_{a1} for H_3PO_4 is the equilibrium constant for the ionization:



a) Given that ΔG_f° of $H_3PO_4(aq)$ is -1142.54 kJ/mol , ΔG_f° of H^+ is 0 and ΔG_f° of $H_2PO_4^-(aq)$ is -1130.28 kJ/mol determine K_{a1} for H_3PO_4 at 25°C .

$$\Delta G = \Delta G^\circ + RT \ln Q \quad \Delta G^\circ = (-1130.28 \times 10^3 \frac{\text{J}}{\text{mol}}) + 0 - (-1142.54 \times 10^3 \frac{\text{J}}{\text{mol}}) =$$

at equilibrium, $\Delta G = 0$, $Q = K$

$$0 = \Delta G^\circ + RT \ln K \Rightarrow \ln K = \frac{-\Delta G^\circ}{RT} = \frac{-12.26 \times 10^3 \frac{\text{J}}{\text{mol}}}{(8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}})(298\text{K})} = -4.9456 \quad K_a = e^{-4.9456} = \boxed{7.1 \times 10^{-3}}$$

b) Is H_3PO_4 a weak or a strong acid? Justify your answer.

Weak,
equilibrium lies to the left since $K \ll 1$

c) If $\Delta G^\circ = 15.65 \text{ kJ/mol}$ at 75°C for this reaction, what is the entropy change for the ionization?

$$\Delta G^\circ(T_1) = \Delta H^\circ - T_1 \Delta S^\circ$$

$$- \Delta G^\circ(T_2) = \Delta H^\circ - T_2 \Delta S^\circ$$

$$\Delta G^\circ(T_1) - \Delta G^\circ(T_2) = (T_2 - T_1) \Delta S^\circ$$

$$\Delta S^\circ = \frac{\Delta G^\circ(T_1) - \Delta G^\circ(T_2)}{(T_2 - T_1)} = \frac{(12.26 \frac{\text{kJ}}{\text{mol}} - 15.56 \frac{\text{kJ}}{\text{mol}})(1000 \frac{\text{J}}{\text{kJ}})}{(75^\circ\text{C} - 25^\circ\text{C})} = \boxed{-67.8 \frac{\text{J}}{\text{K}}}$$