CHEMISTRY 114
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Worksheet 4

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

$$2\,NO_2\,(g) \rightleftarrows N_2O_4\,(g)$$

a) What is the reaction quotient for the reaction? If $P_{N_2O_4}$ is 1 atm at 25°C, what is P_{NO_2}?

$Q = \frac{P_{N_2O_4}}{(P_{NO_2})^2}$ $K = \frac{P_{N_2O_4}}{P_{NO_2}^2}$ $P_{NO_2}^2 = \frac{P_{N_2O_4}}{K}$ $P_{NO_2} = \sqrt{\frac{1}{6.8}} \approx$ **0.383 atm**

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

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

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

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

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

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

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

$\Delta G = \Delta H - T\Delta S$ $T\Delta S = \Delta H - \Delta G$ $\Delta S = \frac{\Delta H - \Delta G}{T} =$ **$-178 \frac{J}{mol\,K}$**

2. The enthalpy of vaporization of ethanol (CH_3CH_2OH) is 38.7 kJ/mol at 78.0°C, its normal boiling point. Calculate q, w, ΔH, ΔE, ΔS_{sys} and ΔG.

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

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

$w = -p\Delta V = -\Delta(pV) = -\Delta(nRT) = -(\Delta n)RT = -(1)(8.314)(351) =$ **−2.92 kJ**

$\Delta E = q + w = 35.8\,kJ$

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

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

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

3. The preparation of $NO_2(g)$ from $N_2(g)$ and $O_2(g)$ is an endothermic reaction. The enthalpy change for the balanced equation *with lowest whole number coefficients* is $\Delta H = 67.7$ kJ. If 300.0 mL of $N_2(g)$ at 100.0 °C and 2.50 atm and 500.0 mL of $O_2(g)$ at 100.0 °C and 2.50 atm are mixed, what amount of heat is necessary to synthesize $NO_2(g)$?

$N_{2(g)} + 2O_{2(g)} \longrightarrow 2NO_{2(g)}$ $\quad n_{N_2} = \frac{PV}{RT} = \frac{(2.5\,atm)(0.3L)}{(0.0821\frac{atm\,L}{mol\,K})(373.15)} = 0.024494\ mol\ N_2$

(LR) $n_{NO_2} = \frac{0.040823\ mol\ O_2}{1} \times \frac{2\ mol\ NO_2}{2\ mol\ O_2} = 0.040823\ mol\ NO_2$

$\frac{0.024494\ mol\ N_2}{1} \times \frac{2\ mol\ NO_2}{1\ mol\ N_2} = 0.048988\ mol\ NO_2$

$\frac{0.040823\ mol\ NO_2}{1} \times \frac{67.7\ KJ}{2\ mol\ NO_2} = 1.38KJ$

4. The K^+ concentration in blood plasma is ~ 5.0×10^{-3} 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?

$\Delta G = \Delta G^\circ + RT\ln Q = \Delta G_f^\circ(K^+, cell) - \Delta G_f^\circ(K^+, plasm) + RT\ln$

$(8.314\frac{J}{mol\,K})(273 + 37^\circ C)\ln\left(\frac{0.15\ M}{5.0\times10^{-3}\ M}\right) =$ $8.77\frac{KJ}{mol}$

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:

$$H_3PO_4\,(aq) \rightleftarrows H^+\,(aq) + H_2PO_4^-\,(aq)$$

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

$\Delta G = \Delta G^\circ + RT\ln Q$ $\quad \Delta G^\circ = (-1130.28\times10^3\frac{J}{mol}) + 0 - (-1142.54\times10^3\frac{J}{mol}) =$

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

$$0 = \Delta G^\circ + RT\ln K \Rightarrow \ln K = \frac{-\Delta G^\circ}{RT} = \frac{-12.26\times10^3\frac{J}{mol}}{(8.314\frac{J}{mol\,K})(298K)} = -4.9456 \quad K_a = e^{-4.9456} = 7.1\times10^{-3}$$

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

weak,
equilibrium lies to the left since $K<<1$

c) If ΔG° = 15.65 kJ/mol at 75°C for this reaction, what is the \entropy change for the ionization?

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

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