

Chemistry 2720 Fall 2003 Test 2 Solutions

1. For this reaction,

$$Q = \frac{a_p}{a_A a_{H_2O}}.$$

Note that $a_{H_2O} = X_{H_2O}$. Adding an inert salt to the solution decreases the activity of water, which increases Q . Since

$$\Delta \tilde{G} = \Delta \tilde{G}^\circ + RT \ln Q,$$

increase Q can only make the free energy change more positive, and thus cannot make the reaction spontaneous.

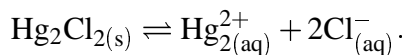
2. The process is $s \rightarrow g$. For ice at 0°C , we have

$$\begin{aligned} T_1 &= 273.15 \text{ K}, \\ \text{and } K_1 &= \frac{a_g}{a_s} = \frac{P_{H_2O}}{P^\circ} = \frac{(0.006025 \text{ atm})(101.325 \text{ kPa/atm})}{100 \text{ kPa}} \\ &= 6.105 \times 10^{-3}. \end{aligned}$$

$T_2 = 261.15 \text{ K}$. We have all the data we need to solve this problem:

$$\begin{aligned} \ln \left(\frac{K_2}{K_1} \right) &= \frac{\Delta \tilde{H}^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right). \\ \therefore \ln \left(\frac{K_2}{6.105 \times 10^{-3}} \right) &= \frac{50920 \text{ J/mol}}{8.314472 \text{ J K}^{-1} \text{ mol}^{-1}} \left(\frac{1}{273.15 \text{ K}} - \frac{1}{261.15 \text{ K}} \right) = -1.03025. \\ \therefore K_2 &= (6.105 \times 10^{-3}) e^{-1.03025} = 2.179 \times 10^{-3}. \\ \therefore P_{H_2O} &= 2.179 \times 10^{-3} \text{ bar}. \end{aligned}$$

3. Everything begins with a balanced reaction:



We can calculate the equilibrium constant for this reaction from

$$K_{sp} = (a_{\text{Hg}_2^{2+}})(a_{\text{Cl}^-})^2.$$

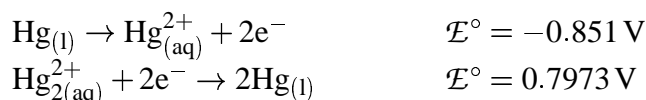
To do this, we need the concentrations (in mol/L) of the two ions. First, convert the solubility to these units:

$$s = \frac{0.0020 \text{ g/L}}{472.09 \text{ g/mol}} = 4.2 \times 10^{-6} \text{ mol/L}.$$

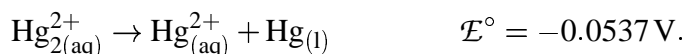
According to our balanced equation, this will be the concentration of mercurous ions, while the concentration of chloride ions will be twice as large. Thus we have

$$\begin{aligned}
 a_{\text{Hg}_2^{2+}} &= 4.2 \times 10^{-6}, \\
 \text{and } a_{\text{Cl}^-} &= 8.5 \times 10^{-6}. \\
 \therefore K_{\text{sp}} &= (4.2 \times 10^{-6})(8.5 \times 10^{-6})^2 = 3.0 \times 10^{-16}. \\
 \therefore \Delta \bar{G}^\circ &= -RT \ln K \\
 &= -(8.314472 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K}) \ln(3.0 \times 10^{-16}) \\
 &= 88.6 \text{ kJ/mol}. \\
 \Delta \bar{G}^\circ &= \Delta \bar{G}_{f(\text{Hg}_2^{2+})}^\circ + 2\Delta \bar{G}_{f(\text{Cl}^-)}^\circ - \Delta \bar{G}_{f(\text{Hg}_2\text{Cl}_2)}^\circ. \\
 \therefore \Delta \bar{G}_{f(\text{Hg}_2^{2+})}^\circ &= \Delta \bar{G}^\circ - 2\Delta \bar{G}_{f(\text{Cl}^-)}^\circ + \Delta \bar{G}_{f(\text{Hg}_2\text{Cl}_2)}^\circ \\
 &= 88.6 - 2(-131.218) + (-210.72) \text{ kJ/mol} = 140.3 \text{ kJ/mol}.
 \end{aligned}$$

4. We aren't given any free energy data for the mercury (II) ion, so we'll have to proceed in a slightly different way. The exam does give a table of standard reduction potentials. From this table, we extract



Adding these two reactions, we get

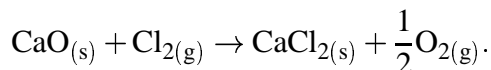


Note that $\bar{n} = 2$. The standard free energy for this reaction is therefore

$$\begin{aligned}
 \Delta \bar{G}^\circ &= -\bar{n} \mathcal{F} \mathcal{E}^\circ \\
 &= -2(96485.342 \text{ C/mol})(-0.0537 \text{ V}) = 10.4 \text{ kJ/mol}. \\
 \therefore K &= e^{-\Delta \bar{G}^\circ / (RT)} \\
 &= \exp\left(\frac{-10.4 \times 10^3 \text{ J/mol}}{(8.314472 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}\right) = 0.0153.
 \end{aligned}$$

This value of K implies that the reaction is reactant favored, i.e. that there will be more Hg_2^{2+} than Hg^{2+} at equilibrium.

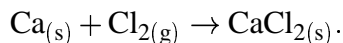
5.



We want to know if $\Delta \bar{G}$ is positive or negative under the stated conditions. To do this, we need $\Delta \bar{G}^\circ$ at 85°C. We start by calculating $\Delta \bar{G}^\circ$ at 85°C:

$$\Delta \bar{G}_{25}^\circ = \Delta \bar{G}_{f(\text{CaCl}_2)}^\circ - \Delta \bar{G}_{f(\text{CaO})}^\circ.$$

In the tables, we have $\Delta\bar{G}_{f(\text{CaO})}^\circ$, but not $\Delta\bar{G}_{f(\text{CaCl}_2)}^\circ$. However, we have the enthalpy of formation of calcium chloride, along with some relevant entropy data. The formation reaction is



Thus,

$$\begin{aligned}\Delta\bar{S}_{f(\text{CaCl}_2)}^\circ &= \bar{S}_{\text{CaCl}_2}^\circ - (\bar{S}_{\text{Ca}}^\circ + \bar{S}_{\text{Cl}_2}^\circ) \\ &= 104.62 - (41.6 + 223.081) \text{ J K}^{-1}\text{mol}^{-1} = -160.1 \text{ J K}^{-1}\text{mol}^{-1}. \\ \therefore \Delta\bar{G}_{f(\text{CaCl}_2)}^\circ &= \Delta\bar{H}_{f(\text{CaCl}_2)}^\circ - T\Delta\bar{S}_{f(\text{CaCl}_2)}^\circ \\ &= -795.80 \text{ kJ/mol} - (298.15 \text{ K})(-0.1601 \text{ kJ K}^{-1}\text{mol}^{-1}) \\ &= -748.08 \text{ kJ/mol}. \\ \therefore \Delta\bar{G}_{25}^\circ &= -748.08 - (-603.30) \text{ kJ/mol} = -144.78 \text{ kJ/mol}.\end{aligned}$$

To adjust the free energy to 85°C, we need the standard enthalpy and entropy changes for the reaction:

$$\begin{aligned}\Delta\bar{H}^\circ &= \Delta\bar{H}_{f(\text{CaCl}_2)}^\circ - \Delta\bar{H}_{f(\text{CaO})}^\circ \\ &= -795.80 - (-634.92) \text{ kJ/mol} = -160.88 \text{ kJ/mol}. \\ \Delta\bar{S}^\circ &= \frac{\Delta\bar{H}^\circ - \Delta\bar{G}^\circ}{T} \\ &= \frac{-160.88 - (-144.78) \text{ kJ/mol}}{298.15 \text{ K}} = -0.05401 \text{ kJ K}^{-1}\text{mol}^{-1}. \\ \therefore \Delta\bar{G}_{85}^\circ &= \Delta\bar{H}^\circ - T\Delta\bar{S}^\circ \\ &= -160.88 - (358.15 \text{ K})(-0.05401 \text{ kJ K}^{-1}\text{mol}^{-1}) = -141.54 \text{ kJ/mol}.\end{aligned}$$

We will now use the formula

$$\Delta\bar{G} = \Delta\bar{G}^\circ + RT \ln Q$$

to determine whether the reaction is spontaneous or not.

$$\begin{aligned}\Delta\bar{G} &= -141.54 \text{ kJ/mol} + (8.314472 \times 10^{-3} \text{ kJ K}^{-1}\text{mol}^{-1})(358.15 \text{ K}) \ln \left(\frac{(0.2)^{1/2}}{0.8} \right) \\ &= -143.27 \text{ kJ/mol}.\end{aligned}$$

Since $\Delta\bar{G}$ is negative, the reaction will be spontaneous.