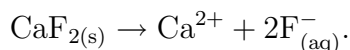


Chemistry 2720 Fall 2005 Test 2 Solutions

1. The information given suggests that the imine condensation is thermodynamically unfavorable on its own, i.e. $\Delta\bar{G}^\circ$ is large and positive. By coupling this reaction with the hydrolysis of trimethylorthoformate, a reaction which is presumably strongly favored, i.e. one which has a large negative $\Delta\bar{G}^\circ$, we get a reaction with an overall negative $\Delta\bar{G}^\circ$. The coupling in this case is achieved by the removal of water by reaction with the solvent trimethylorthoformate.
2. The reaction is

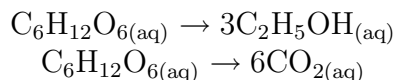


$$\begin{aligned} c &= \frac{0.017 \text{ g/L}}{78.07 \text{ g/mol}} = 2.2 \times 10^{-4} \text{ mol/L.} \\ \therefore [\text{Ca}^{2+}] &= c = 2.2 \times 10^{-4} \text{ mol/L,} \\ \text{and } [\text{F}^-] &= 2c = 4.4 \times 10^{-4} \text{ mol/L.} \\ \therefore K_{\text{sp}} &= (a_{\text{Ca}^{2+}})(a_{\text{F}^-})^2 = (2.2 \times 10^{-4})(4.4 \times 10^{-4})^2 = 4.1 \times 10^{-11}. \end{aligned}$$

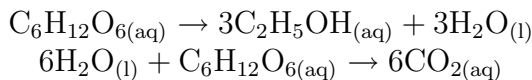
So far, we haven't made any approximations, except insofar as we are ignoring non-ideal effects. The solubility is given at 26°C. Because this is so close to 25°C, and because there is no way to adjust the data to this temperature with the data we have available, I'm going to treat our K_{sp} as if it had been measured at 25°C.

$$\begin{aligned} \Delta\bar{G}^\circ &= -RT \ln K_{\text{sp}} = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K}) \ln (4.1 \times 10^{-11}) \\ &= 59.3 \text{ kJ/mol} \\ &= \Delta\bar{G}_{f(\text{Ca}^{2+})}^\circ + 2\Delta\bar{G}_{f(\text{F}^-)}^\circ - \Delta\bar{G}_{f(\text{CaF}_2)}^\circ. \\ \therefore \Delta\bar{G}_{f(\text{CaF}_2)}^\circ &= \Delta\bar{G}_{f(\text{Ca}^{2+})}^\circ + 2\Delta\bar{G}_{f(\text{F}^-)}^\circ - \Delta\bar{G}^\circ \\ &= -552.8 + 2(-281.52) - 59.3 \text{ kJ/mol} = -1175 \text{ kJ/mol.} \end{aligned}$$

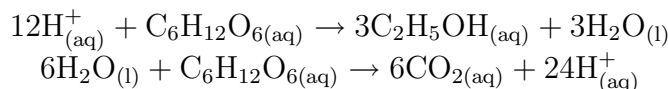
3. (a) Half-reactions:



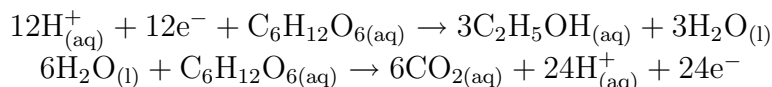
Balance for O:



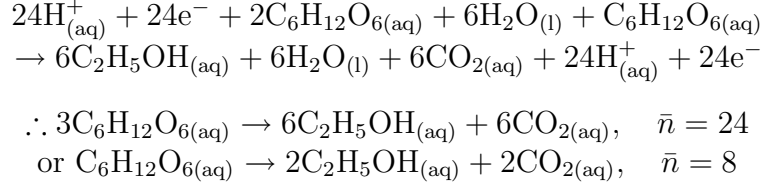
Balance for H:



Balance for charge:



Multiply the first reaction by 2 and add:



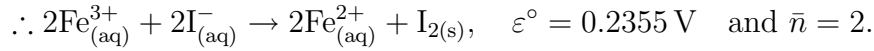
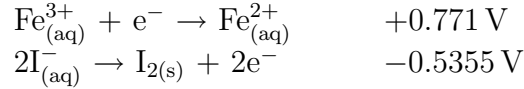
(b)

$$\begin{aligned}
\Delta\bar{G} &= \Delta\bar{G}^\circ + RT \ln Q \\
&= \Delta\bar{G}^\circ + RT \ln \left(\frac{(a_{\text{C}_2\text{H}_5\text{OH}})^2 (a_{\text{CO}_2})^2}{a_{\text{C}_6\text{H}_{12}\text{O}_6}} \right). \\
\Delta\bar{G}^\circ &= 2\Delta\bar{G}_{f(\text{C}_2\text{H}_5\text{OH})}^\circ + 2\Delta\bar{G}_{f(\text{CO}_2)}^\circ - \Delta\bar{G}_{f(\text{C}_6\text{H}_{12}\text{O}_6)}^\circ \\
&= 2(-181.64) + 2(-386.05) - (-910.23) \text{ kJ/mol} = -225.15 \text{ kJ/mol}. \\
\therefore \Delta\bar{G} &= -225.15 \text{ kJ/mol} \\
&\quad + (8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K}) \ln \left(\frac{(1.3)^2 (0.03)^2}{0.7} \right) \\
&= -240.35 \text{ kJ/mol}.
\end{aligned}$$

The maximum non- PV work is therefore 240.35 kJ/mol glucose.

$$(c) \quad \varepsilon = \frac{-\Delta\bar{G}}{\bar{n}\mathcal{F}} = \frac{240.35 \times 10^3 \text{ J/mol}}{8(96485.342 \text{ C/mol})} = 0.311 \text{ V}.$$

4. From the table of standard reduction potentials, we have



$$\begin{aligned}
\therefore \Delta\bar{G}^\circ &= -\bar{n}\mathcal{F}\varepsilon^\circ \\
&= -2(96485.342 \text{ C/mol})(0.2355 \text{ V}) = -4.544 \times 10^4 \text{ J/mol}. \\
\therefore K &= e^{-\Delta\bar{G}^\circ/(RT)} = \exp \left(\frac{4.544 \times 10^4 \text{ J/mol}}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})} \right) \\
&= 9.153 \times 10^7.
\end{aligned}$$

5. According to Raoult's law, $P_{\text{H}_2\text{O}} = X_{\text{H}_2\text{O}}P_{\text{H}_2\text{O}}^\bullet$, where $P_{\text{H}_2\text{O}}^\bullet$ is the vapor pressure of pure water.

$$X_{\text{H}_2\text{O}} = \frac{54.56 \text{ mol/L}}{54.56 + 3(0.4) \text{ mol/L}} = 0.978.$$

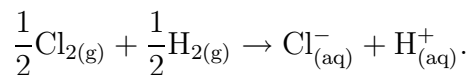
The factor of 3 in the calculation above comes from the fact that sodium sulfate dissociates into three ions in solution.

$$\therefore P_{\text{H}_2\text{O}} = (0.978)(149.38 \text{ Torr}) = 146 \text{ Torr}.$$

6. (a) For our reaction, $\Delta\bar{G} = \Delta\bar{G}^\circ + RT \ln(a_{\text{H}^+})^\nu$, since all other reactants and products are at unit activity. Since $\Delta\bar{G}^{\circ'} = \Delta\bar{G}$ at pH 7, we have

$$\begin{aligned}\Delta\bar{G}^{\circ'} &= \Delta\bar{G}^\circ + \nu RT \ln(10^{-7}) \\ &= \Delta\bar{G}^\circ - 7\nu RT \ln 10.\end{aligned}$$

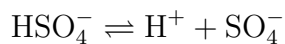
- (b) The formation reaction for a chloride ion would be



Thus $\nu = 1$, so that

$$\begin{aligned}\Delta\bar{G}^{\circ'} &= -131.218 \text{ kJ/mol} - 7(1)(8.314 472 \times 10^{-3} \text{ kJ K}^{-1}\text{mol}^{-1})(298.15 \text{ K}) \ln 10 \\ &= -171.174 \text{ kJ/mol}.\end{aligned}$$

Bonus: HSO_4^- is a relatively strong acid. Its dissociation



would perturb the $\text{HSO}_4^-/\text{SO}_3$ equilibrium.