Chemistry 2850 Test 2 Solutions

1. The standard hydrogen electrode consists of a platinum electrode over which hydrogen gas at a pressure of $1\,\text{bar}$ is bubbled, and bathing in a $1\,\text{mol/kg}$ aqueous solution of H^+.

2. "Salting in" refers to the increase in solubility of ionic compounds when foreign ions are used to increase the ionic strength. The Debye-Hückel limiting law predicts salting in since γ_i (or $\gamma_\pm$) decreases with increasing ionic strength according to this theory.

3. The activity of the solvent is its mole fraction. Except for very concentrated solutions, the mole fraction of the solvent is usually very close to unity.

4. Plot $\ln K$ vs $1/T$. The slope of the graph is $-\Delta H^\circ/R$.

5. Either of the following two answers would be acceptable.

   - If one of the ions is an acid or base, it can react with water, decreasing its concentration in solution and thus increasing the solubility according to Le Chatelier's principle.

   - High-valent ions often speciate in water, i.e. they combine with other ions in solution to form complex ions. This decreases the concentration of the high-valent ion and thus increases the solubility, in accord with Le Chatelier's principle.

6.

$$
\begin{aligned}
S_{\text{ice},0^\circ\text{C}} &= S_{\text{water},25^\circ\text{C}} + \Delta S_{25\to0^\circ\text{C}} + \Delta S_{\text{freezing}}. \\
\Delta S_{25\to0^\circ\text{C}} &= \int_{T_1}^{T_2} \frac{C_P dT}{T} = C_P \int_{298.15}^{273.15\,\text{K}} \frac{dT}{T} \\
&= (75.40\,\text{J K}^{-1}\text{mol}^{-1})\ln\left(\frac{273.15\,\text{K}}{298.15\,\text{K}}\right) = -6.603\,\text{J K}^{-1}\text{mol}^{-1}. \\
\Delta S_{\text{freezing}} &= \frac{\Delta H_{\text{freezing}}}{T} = \frac{-6007\,\text{J/mol}}{273.15\,\text{K}} = -21.99\,\text{J K}^{-1}\text{mol}^{-1}. \\
\therefore S_{\text{ice},0^\circ\text{C}} &= 69.65 + (-6.603) + (-21.99)\,\text{J K}^{-1}\text{mol}^{-1} = 41.36\,\text{J K}^{-1}\text{mol}^{-1}.
\end{aligned}
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7. (a)

$$CaO_{(s)} + CO_{2(g)} \rightarrow CaCO_{3(s)}$$
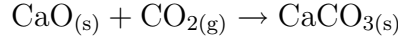
$$
\begin{aligned}
\Delta G^\circ_{25} &= \Delta_f G^\circ_{CaCO_3} - \left(\Delta_f G^\circ_{CaO} + \Delta_f G^\circ_{CO_2}\right) \\
&= -1128.8 - [-603.30 + (-394.37)] \text{ kJ/mol} = -131.1 \text{ kJ/mol}. \\
\Delta H^\circ &= \Delta_f H^\circ_{CaCO_3} - \left(\Delta_f H^\circ_{CaO} + \Delta_f H^\circ_{CO_2}\right) \\
&= -1206.9 - [-634.92 + (-393.51)] \text{ kJ/mol} = -178.5 \text{ kJ/mol}. \\
\Delta S^\circ &= \frac{\Delta H^\circ - \Delta G^\circ}{T} \\
&= \frac{-178.5 - (-131.1) \text{ kJ/mol}}{298.15 \text{ K}} = -0.159 \text{ kJ K}^{-1}\text{mol}^{-1}. \\
\therefore \Delta G^\circ_5 &= \Delta H^\circ - T\Delta S^\circ \\
&= -178.5 \text{ kJ/mol} - (278.15 \text{ K})(-0.159 \text{ kJ K}^{-1}\text{mol}^{-1}) = -134.3 \text{ kJ/mol}.
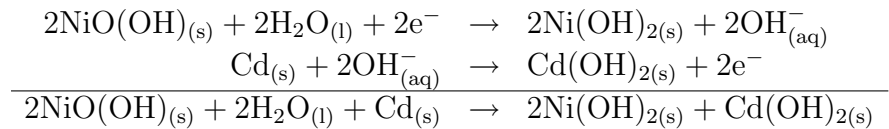\end{aligned}
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(b)

$$
\begin{aligned}
\Delta G &= \Delta G^\circ + RT \ln Q \\
&= \Delta G^\circ + RT \ln \left(\frac{1}{a_{CO_2}}\right) \\
&= -134.3 \text{ kJ/mol} + (8.314\,472 \times 10^{-3} \text{ kJ K}^{-1}\text{mol}^{-1})(278.15 \text{ K}) \ln \left(\frac{1}{4 \times 10^{-4}}\right) \\
&= -116.2 \text{ kJ/mol}.
\end{aligned}
$$

Since $\Delta G < 0$, we conclude that this conversion is spontaneous in air.

8. (a)

$$
\begin{aligned}
\mathcal{E}^\circ &= \mathcal{E}^\circ_{red,NiO(OH)} - \mathcal{E}^\circ_{red,Cd(OH)_2}. \\
\therefore \mathcal{E}^\circ_{red,NiO(OH)} &= \mathcal{E}^\circ + \mathcal{E}^\circ_{red,Cd(OH)_2} \\
&= 1.4 + (-0.809) \text{ V} = 0.6 \text{ V}.
\end{aligned}
$$

(b) The overall reaction is obtained as follows:

$$
\begin{array}{rcl}
2NiO(OH)_{(s)} + 2H_2O_{(l)} + 2e^- &\rightarrow& 2Ni(OH)_{2(s)} + 2OH^-_{(aq)} \\
Cd_{(s)} + 2OH^-_{(aq)} &\rightarrow& Cd(OH)_{2(s)} + 2e^- \\
\hline
2NiO(OH)_{(s)} + 2H_2O_{(l)} + Cd_{(s)} &\rightarrow& 2Ni(OH)_{2(s)} + Cd(OH)_{2(s)}
\end{array}
$$

Thus we have $z = 2$, and we have also been given $\mathcal{E}^\circ = 1.4 \text{ V}$. The standard free energy change for the reaction is therefore

$$
\begin{aligned}
\Delta_r G^\circ &= -zF\mathcal{E}^\circ = -2(96\,485.3383 \text{ C/mol})(1.4 \text{ V}) = -270 \text{ kJ/mol}. \\
\text{But } \Delta_r G^\circ &= 2\Delta_f G^\circ_{Ni(OH)_2} + \Delta_f G^\circ_{Cd(OH)_2} - \left(2\Delta_f G^\circ_{NiO(OH)} + 2\Delta_f G^\circ_{H_2O} + \Delta_f G^\circ_{Cd}\right). \\
\therefore \Delta_f G^\circ_{NiO(OH)} &= \frac{1}{2}\left[2\Delta_f G^\circ_{Ni(OH)_2} + \Delta_f G^\circ_{Cd(OH)_2} - \left(2\Delta_f G^\circ_{H_2O} + \Delta_f G^\circ_{Cd}\right) - \Delta_r G^\circ\right] \\
&= \frac{1}{2}\left[2(-444) + (-469.8) - (2(-237.140) + 0) - (-270) \text{ kJ/mol}\right] \\
&= -307 \text{ kJ/mol}.
\end{aligned}
$$