Assignment 1 Solutions

Q1 (a) At pH 0, cerium can be used to reduce fully oxidised manganese (MnO_4^-) to its metallic state (assuming a limitless supply of Ce). Write a balanced equation and predict the standard potential ($\Delta E°$) of the reaction.

$7\ Ce + 3\ MnO_4^- + 24\ H^+ \rightarrow 7\ Ce^{3+} + 3\ Mn + 12\ H_2O$ $\Delta E° = 3.08$ V

note that $E°$ for MnO4- $\rightarrow$ Mn is: $E° = [3(1.70)+2(1.23)+2(-1.18)]/7 = 0.743$ V
(this can vary slightly depending on where you got your $E°$ values)

2 points

Q1 (b) If only 1.00 g of Ce is available, what would be the final product(s) if reduction is carried out on 1.00 g of $KMnO_4$? Assume stepwise reduction occurs (*e.g.*, all MnO_4^- will convert to MnO_4^{2-}, before any becomes MnO_2, etc.).

1.00 g Ce = 1.00 g/140.12 g/mol = 7.14 mmol
because each Ce releases 3 electrons, there are 7.14*3 = 21.4 mmol of electrons available

1.00 g $KMnO_4$ = 1.00 g/158.03 g/mol = 6.33 mmol of MnO_4^-

Therefore, reduction to MnO_2 (Mn^{7+} to Mn^{4+}) will use 3*6.33 = 19.0 mmol e^-
Now not enough electrons to fully reduce MnO_2 to Mn^{3+} (only 21.4-19.0 = 2.4 mmol e^-)
So there will be leftover MnO_2, and some Mn^{3+} (which disproportionates under these conditions to $MnO_2 + Mn^{2+}$)

Therefore the products are MnO_2 and Mn^{2+} (I also accepted MnO_2 and Mn^{3+})

2 points

Q2: Generate a Pourbaix diagram for Co under conditions of pH 5. Include all metastable species. Are there any species that change from unstable (thermodynamically) to stable on moving from pH 0 to pH 5? You may assume all other conditions are standard.

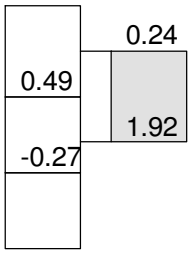
All the reactions that don't contain H+ will have no pH dependence (*i.e.* the Co^{2+}/Co and the Co^{3+}/Co^{2+} couples). For the others,

$CoO_2 + 4\,H^+ + e^- \rightarrow Co^{3+} + 2\,H_2O$ $\quad E = 1.42 - (0.0592)(4/1)(5) = 0.236$ V

$CoO_2 + 4\,H^+ + 2\,e^- \rightarrow Co^{2+} + 2\,H_2O$ $\quad E = 1.67 - (0.0592)(4/2)(5) = 0.486$ V

The Co^{3+} disproportionation reaction is still spontaneous ($\Delta E = 0.486\text{-}0.236 = +^{ve}$), therefore it is still unstable (and all the other oxidation states are still stable).

Therefore, the Pourbaix diagram is:



3 points

Q3: The redox reaction taking place in a lead-acid battery (a typical car battery) is:

$$Pb\,(s) + PbO_2\,(s) + 4\,H^+\,(aq) + 2\,SO_4^{2-}\,(aq) \leftrightharpoons 2\,PbSO_4\,(s) + 2\,H_2O\,(l)$$

Calculate the cell voltage as the temperature drops to -30ºC, a typical overnight temperature in Thunder Bay in January. You may assume that the equilibrium constant for the reaction is the same at both temperatures.

In the back of the Shriver and Atkins book, the two reduction potentials (at 298 K) are given as

$PbSO_4 \leftrightharpoons Pb$ $\quad E° = -0.356$

$PbO_2 \leftrightharpoons PbSO_4$ $\quad E° = 1.70$

Therefore, at 298 K the $\Delta E° = 2.06$ V

If $E° = -(RT/nF)\ln K$ and $K_{298} = K_{243}$,

$\ln K = -E°(nF/RT)$

$E_{243} = -(RT/nF)[-E°(nF/RT)] = (243/298)*2.06 = 1.68$ V

2 points