Question 1 For this question, consider the following half-cell reaction, which is used in lead-acid car batteries.

$$PbO_2\,(s) + HSO_4^-\,(aq) + 3\,H^+\,(aq) + 2\,e^-\,(aq) \leftrightarrows PbSO_4\,(s) + 2\,H_2O\,(l)$$

Under standard conditions (pH = 0), the half-cell potential is $E° = 1.70$ V.

(a) The solvent is H_2SO_4, which means that diluting the solvent with water will lower the pH and change the voltage (as well as increasing the risk of generating H_2 gas). Calculate the cell voltage at pH 6.

Using the cell-voltage/pH formula,
$E = E° - {}^{\nu}/_{n}(0.0592)(\mathrm{pH}) = 1.70 - {}^{3}/_{2}(0.0592)(6) = 1.17$ V 2 points

(b) Calculate the cell voltage (at pH = 0) 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.

$\Delta G° = -RT\ln K = -\mathrm{n}FE°$
therefore, $E° = RT\ln K/\mathrm{n}F$

Using thus, the ratio of $E°_1/E°_2 = T_1/T_2$ (because we assume $K_1 = K_2$, and everthing else is a constant!)
or, $E°_1 = (T_1/T_2)E°_2 = (243\text{ K}/298\text{ K})(1.70\text{ V}) = 1.39$ V 2 points

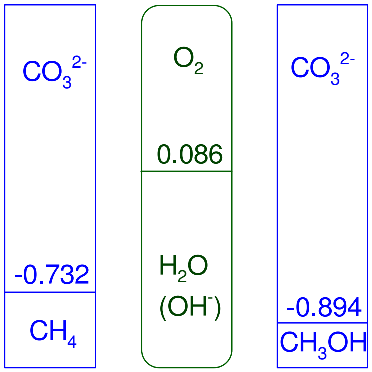
Question 2 An emission-free fuel cell can theoretically be made if basic conditions are used, because CO_3^{2-} is generated instead of CO_2.

(a) Calculate the overall voltage of the half-reaction generated if methane was used as the fuel. Do the same for methanol.

using the multi-step voltage equation, the reduction potential would be,
$E°(CO_3^{2-}$ to $CH_4) = [2(-0.245)+2(-0.591)+2(-1.160)+2(-0.930)]/8 = -0.732$ V
Or, for the oxidation reaction CH_4 to CO_3^{2-}, $E° = 0.732$ V

for methanol, $E°(CO_3^{2-}$ to $CH_3OH) = [2(-0.591)+2(-1.160)+2(-0.930)]/6 = -0.894$ V
Or, for the oxidation, $E° = 0.894$ V 3 points

(b) Using the cell voltages in your text (for basic conditions!), create Pourbaix diagrams for carbon (CH_4 to CO_3^{2-}) and oxygen (O_2 to OH^-) and determine the products of the reaction between methanol and O_2 (*i.e.*, will the methanol be fully oxidized to CO_3^{2-}?). HINT: there are many metastable species for C, so you might want to make a simplified diagram just containing your reactants and the product.



Because H_2O (or OH^- - they have the same oxidation state, so for the purposes of this question we can treat them as the same) overlaps with CO_3^{2-} in both redox diagrams, the O_2 is capable of fully oxidizing the fuel to carbonate.

2 points

<u>Question 3</u> Carbon (often as coal) is used to reduce ruthenium from it's mined forms to the neutral metal. If the ruthenium is predominantly Ru^{3+}, calculate how much carbon is required to prepare 1.00 kg of Ru (*s*).

Ru^{3+} is capable of fully oxidizing C to CO_2 under these acidic conditions (the Pourbaix diagrams show overlap between Ru and CO_2). Therefore,

$$Ru^{3+} + 3\,e^- \rightarrow Ru \quad (\times 4)$$

$$\underline{C + 2\,H_2O \rightarrow CO_2 + 4\,H^+ + 4\,e^-} \quad (\times 3)$$

$$4\,Ru^{3+} + 3\,C + 6\,H_2O \rightarrow 4\,Ru + 3\,CO_2 + 12\,H^+ \qquad (\textit{i.e.}\text{ a 4:3 molar ratio})$$

stiochiometry part: 1000 g Ru (1 mol Ru/101.07 g)(3 mol C/4 mol Ru)(12.01 g/1 mol C) = 89.1 g C

3 points