Condensed Matter 2

Coursework 6, 7 and 8

Deadlines: Thursday March 29 at 1600 hours

These questions are being set in a different manner to that in previous years. Previously questions of the type given below had been released on a weekly basis as individual questions. The problem with that is the questions did not seem to link to each other, and hence gave little indication of what Section B question would be like in the exam. Additionally, the study of equilibrium electrochemistry makes more sense when seen as a whole.

The three questions below are actual Section B questions. As you study this final part of the course there will be some parts that you will be able to answer early on and others that you will need information from week 11 to answer. Therefore, you should attempt the parts you can as we go along –with the final deadline being the second-last day of term.

Question Set 6 (a complete Section B Question)

- (a) Show that when 2.73 g of $Ca(NO_3)_2$ is added to a 0.150 mol kg⁻¹ aqueous solution of KNO₃ containing 500 g of solvent the ionic strength increases to 0.250. The molar mass of $Ca(NO_3)_2 = 164 \text{ g mol}^{-1}$. [6 marks]
- (b) With an explanation of your method, estimate the mean ionic activity coefficient and activity of a solution that is 0.010 mol kg⁻¹ CaCl₂ (aq) and 0.030 mol kg⁻¹ NaF (aq).

[7 marks]

- (c) The mean activity coefficient of HBr in three dilute aqueous solutions at 298 K are 0.930 (at $5.0 \times 10^{-3} \text{ mol kg}^{-1}$), 0.907 (at $10.0 \times 10^{-3} \text{ mol kg}^{-1}$), and 0.879 (at $20.0 \times 10^{-3} \text{ mol kg}^{-1}$).
 - (i) Estimate the value for B in the Extended Debye-Huckel law. Explain your reasoning.
 - (ii) Comment on how well HBr obeys the Extended Debye-Huckel law [2 marks] [2 marks]

TURN OVER

Question Set 7 (a complete Section B Question)

a) Devise an electrochemical cell to investigate the following reaction:

$$\operatorname{AgCl}(s) + \operatorname{FeCl}_2(aq) \rightleftharpoons \operatorname{FeCl}_3(aq) + \operatorname{Ag}(s).$$

[3 marks]

(b) Given that the standard electrode potential at 298 K of the Ag/AgBr/Br⁻ half-cell is +0.071 V, calculate the potential at 298 K of the cell:

$$Pt(s) | H_2(g) (1 atm) | HBr(aq) (a = 0.02) | AgBr(s) | Ag(s).$$

[6 marks]

(c) The standard potential of the cell

 $\operatorname{Zn}(s) | \operatorname{Zn}(\operatorname{NO}_3)_2(aq) || \operatorname{AgNO}_3(aq) | \operatorname{Ag}(s)$

is +1.561 V at 298 K and +1.550 V at 308 K. Write down the cell reaction and determine $\Delta_r G^{\Theta}$, $\Delta_r S^{\Theta}$ and $\Delta_r H^{\Theta}$ for the reaction at 298 K. [10 marks]

(d) Calculate, using the Debye-Huckel limiting law, the activity of magnesium ions in a $0.300 \text{ mol kg}^{-1}$ aqueous solution of MgCl₂ at 298 K. (Debye-Huckel constant for water is, A = 0.509 at 298 K). [6 marks]

TURN OVER

Question B4

(a) Consider the cell:

$$Zn(s) | ZnCl_2 (0.0050 \text{ mol kg}^{-1}) | Hg_2Cl_2 (s) Hg (l),$$

for which the cell reaction is:

$$\text{Hg}_2\text{Cl}_2(s) + \text{Zn}(s) \rightarrow 2 \text{Hg}(l) + 2\text{Cl}^-(aq) + \text{Zn}^{2+}(aq).$$

Given that E^{Θ} (Zn²⁺, Zn) = -0.7628 V, E^{Θ} (Hg₂Cl₂, Hg) = +0.2676 V, and that the EMF is 1.2272 V:

(i) Write the Nernst Equation for the cell in terms of molalities and activity coefficients.

[6 marks]

[3 marks]

- (ii) Determine the standard EMF.
- (iii) Determine $\Delta_{\rm r}G$, $\Delta_{\rm r}G^{\Theta}$, and the equilibrium constant *K* for the cell reaction. [6 marks]
- (b) Fuel cells provide power for spacecraft and also show potential for use in electric cars. A fuel cell develops an electric potential from the chemical reaction of reagents supplied by an outside source. By explicit consideration of the half-reactions and thereby the number of electrons transferred, calculate the EMF of a cell fuelled by the combustion of butane at 1.00 atm and 298.15 K.

$$C_4H_{10}(g) + {}^{13/2}O_2(g) \rightarrow 4 CO_2(g) + 5 H_2O(l)$$

You may find the following helpful: $\Delta_{\rm r} G ({\rm CO}_2) = -394.36 \text{ kJ mol}^{-1}$ $\Delta_{\rm r} G ({\rm H}_2 {\rm O}) = -237.13 \text{ kJ mol}^{-1}$ $\Delta_{\rm r} G ({\rm C}_4 {\rm H}_{10}) = -17.03 \text{ kJ mol}^{-1}$

[10 marks]