IMPERIAL COLLEGE LONDON

BSc and MSci DEGREES – JUNE 2011, for Internal Students of the Imperial College of Science, Technology and Medicine

This paper is also taken for the relevant examination for the Associateship

PHYSICAL CHEMISTRY IIB

Tuesday 21st June 2011, 14:00-15:30

PLEASE NOTE THAT IT IS DEPARTMENTAL POLICY THAT THESE EXAM QUESTIONS MAY REQUIRE UNDERSTANDING OF ANY PRIOR CORE COURSE.

USE A SEPARATE ANSWER BOOK FOR EACH QUESTION. WRITE YOUR CANDIDATE NUMBER ON EACH ANSWER BOOK.

2.P2 – Electrochemistry and Electrochemical Kinetics

Answer part a) and **EITHER** part b) **OR** part c) of this question.

a) Answer **ALL** parts of this question.

The following data are found to apply to two different electrode processes at Pt electrodes at a temperature of 25^{o}C.

Equilibrium Potential/V	Reaction	j_o/Acm^{-2}	α
1.44	$Ce^{4+} + e = Ce^{3+}$	4.0×10^{-5}	0.75
0.77	$Fe^{3+} + e = Fe^{2+}$	2.5×10^{-3}	0.58

i) What are the actual potentials for each electrode when the overpotential is 0.10V?
(2 marks)

ii) Neither of the reactions in the table above has a value of the symmetry factor equal to 0.5. For each reaction, calculate the values of the oxidation and reduction component currents at an overpotential of 0.1V and comment on how the value of α influences the balance between the two component currents at this overpotential.
(7.5 marks)

iii) Briefly discuss how the Tafel plots for the two processes would differ.
(3 marks)

b) Answer **ALL** parts of this question.

i) In discussing the structure of the electrode solution interface, it was stated that the electrode could be treated as if it was a "giant ion". Use this information to describe the structure of the electrode solution interface by drawing parallels between the way in which solvent and ions interact with a charged electrode, and the interactions that occur between ions and solvent in an electrolyte. Note that a discussion of the potential distribution at the electrode solution interface is **NOT** required.
(6 marks)

QUESTION CONTINUED OVERLEAF

ii) The silver-silver chloride electrode is commonly used as a reference electrode. It has a standard potential of 0.222V. Commercially it is available in several versions one of which, where the electrolyte is 3M NaCl, is shown below.

Ag | AgCl | Cl^- (3M NaCl), aq.

Calculate the potential of the electrode shown above at 25^0C, assuming that non-ideal effects can be neglected.

(2 marks)

Why is the calculated potential likely to be different from the measured value?

(2 marks)

Would you expect the calculated potential to be higher or lower than the measured value? Explain your answer.

(2.5 marks)

c) Answer **ALL** parts of this question.

i) The table below shows molar conductivity data at two different concentrations (C_1 and C_2) for two electrolytes, **A** and **B**. One electrolyte is a weak acid, the other is an alkali metal salt. One of the two concentrations corresponds to infinite dilution, the other to a value of 10^{-1} mol dm^{-3}.

Electrolyte	(Λ_m at Conc. C_1)/ S cm^2 mol^{-1}	((Λ_m at Conc. C_2)/ S cm^2 mol^{-1}
A	P	Q
B	X	Y

If X > P > Q >Y, which electrolyte is the weak acid and which concentration corresponds to infinite dilution? Explain the reasons for your choices clearly.

(4 marks)

QUESTION CONTINUED OVERLEAF

ii) The disproportionation of bromine occurs in aqueous solutions according to the following overall reaction.

$$3Br_2(aq) + 3H_2O \rightarrow BrO_3^- + 5Br^- + 6H^+$$

$E^\circ (Br^-/Br_2) = 1.06V$ – Hint - no other species are involved in this half cell reaction.
$E^\circ (Br_2/BrO_3^-) = 1.48V$

Calculate the cell potential for this reaction in a solution of pH 10 and a temperature of 25^{o}C. Assume that all other concentrations are at their standard values, and that non-idealities can be neglected.

(6 marks)

Is the disproportionation spontaneous under standard conditions? Is it spontaneous at pH 10? Explain your answer.

(2.5 marks)

2.P1 – Interfacial Thermodynamics

Answer any **TWO** of the three parts a), b) and c) of this question.

a) Answer **ALL** parts of this question.

The fundamental equation states: $dG = Vdp - SdT$

i) Sketch how the molar Gibbs free energy G_m of pure water varies with temperature upon crossing its normal boiling point, T_b, labelling any important features.

(2 marks)

ii) If an additional pressure of Δp = 100 bar is applied only to the liquid water and not the water vapour, calculate by how much G_m (liq) will change, assuming the water to be incompressible.

(3 marks)

iii) Hence show from your sketch whether T_b will increase or decrease when the additional pressure is applied.

(1 mark)

iv) Estimate the change in T_b, using your sketch to guide your calculation.

(4 marks)

v) Calculate the radius of a spherical droplet of liquid water that would have the same shift in the boiling point.

(2.5 marks)

1 bar = 10^5 Pa;

V_m (liq) = 18 cm^3 mol^{-1};

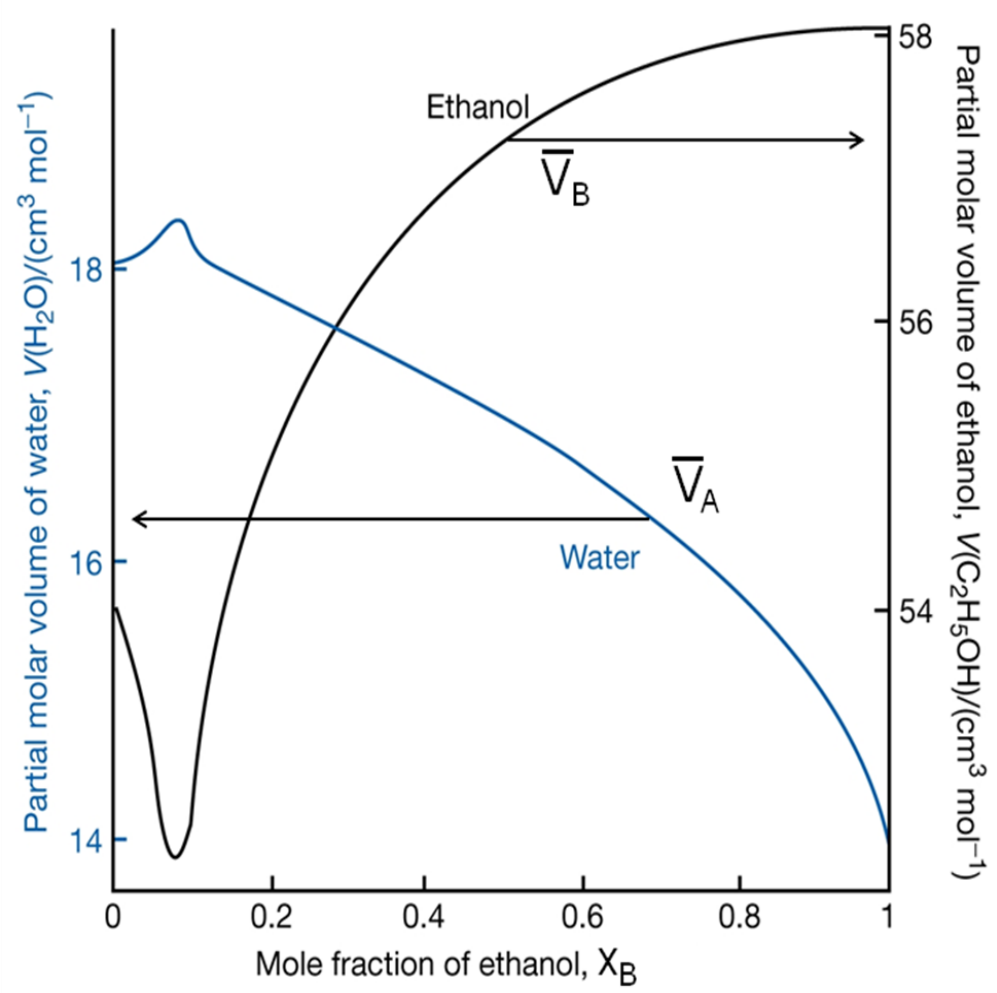
ΔS_{vap} = 109.1 J K^{-1} mol^{-1};

γ = 72 mN m^{-1}

QUESTION CONTINUED OVERLEAF

b) Answer **ALL** parts of this question.

The plot below shows the partial molar volumes of the two components in a liquid mixture of ethanol (B) and water (A).



$$dV = \overline{V}_A dn_A + \overline{V}_B dn_B$$

$$V = \overline{V}_A n_A + \overline{V}_B n_B$$

i) Sketch what the two curves would look like if ethanol and water exhibited ideal mixing.

(1 mark)

QUESTION CONTINUED OVERLEAF

ii) If this were the case, what would be the total volume V of a mixture of 1 mole of ethanol plus 9 moles of water?

(1.5 marks)

iii) Use the plot above to estimate the actual total volume V of such a 1:9 mixture.

(3 marks)

iv) Prove that $d\overline{V}_A = \left(\frac{x_A - 1}{x_A}\right) d\overline{V}_B$

Hint: use the chain rule to differentiate the expression above for V, and compare with the expression above for dV.

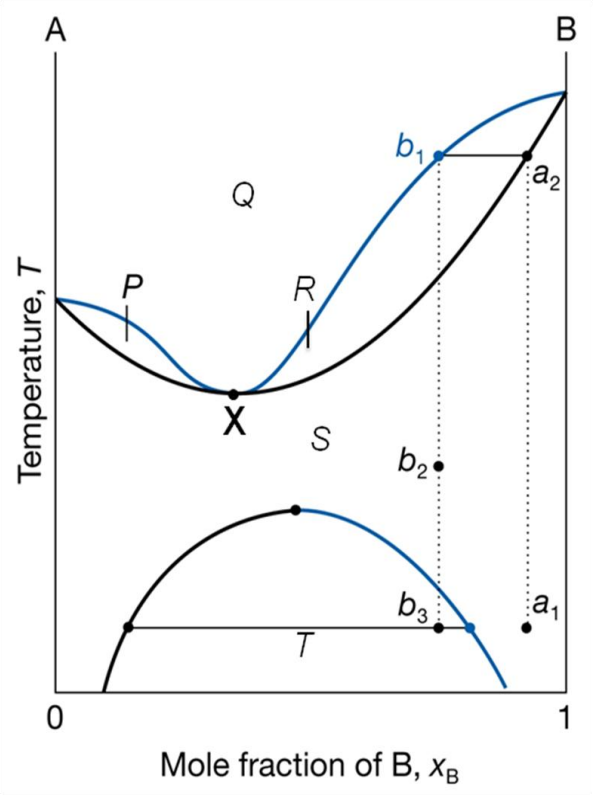
(4 marks)

v) Explain why the changes in $\overline{V}_B$ are mirrored in corresponding changes in $\overline{V}_A$.

(3 marks)

c) Answer **ALL** parts of this question.

The figure shows the temperature-composition phase diagram for a mixture of two liquids, A and B.



QUESTION CONTINUED OVERLEAF

i) Explain which liquid is more volatile.

(1 mark)

ii) Do the two liquids exhibit ideal mixing? Explain your answer fully.

(3 marks)

iii) Identify the phases in the five regions labelled P, Q, R, S, T.

(2.5 marks)

iv) Name point X and explain what is special about it.

(2 marks)

v) Describe what is observed on heating a sample from point a_1 to point a_2.

(1.5 marks)

vi) Describe what is observed upon cooling a sample from b_1 to b_2 to b_3.

(2.5 marks)