IMPERIAL COLLEGE LONDON

BSc and MSci DEGREES – JUNE 2013, 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

Monday 17th June 2013, 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 any **TWO** of the three parts a), b) and c) of this question.

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

i) For an aqueous solution of LiCl, there are two concentrations (or ranges of concentration) where the mean ion activity coefficient ($\gamma_{\pm}$) will be equal to unity. Identify (approximately) these two concentrations or concentration ranges. In each case explain why the mean ionic activity coefficient is unity.

(5 marks)

ii) Indium Sulphate ($In_2(SO_4)_3$) has a mean ion activity coefficient ($\gamma_{\pm}$) of 0.014 when the concentration of the salt is 0.50 mol kg^{-1}.
What is the equilibrium potential of an Indium electrode immersed in such a solution?

E^0 (In^{3+}/In) = -0.338V.

(5 marks)

iii) The hypochlorite ion (OCl^-) is a bleaching agent and is formed by the following overall reaction.

$$Cl_2 + 2OH^- = Cl^- + OCl^- + H_2O$$

If one half-cell reaction for the overall process involves only chlorine and chloride, write a balanced reaction for the other half cell reaction.

(2.5 marks)

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

i) Given the two half-cell reactions below, calculate the formation constant (stability constant) for the diamminesilver (I) complex $[Ag(NH_3)_2]^+$ in aqueous solution.

$$Ag^+ + e = Ag$$
$$Ag(NH_3)_2^+ + e = Ag + 2NH_3$$

$E^0(Ag^+/Ag) = 0.799V$
$E^0(Ag(NH_3)_2^+ /Ag) = 0.37V$

(5.5 marks)

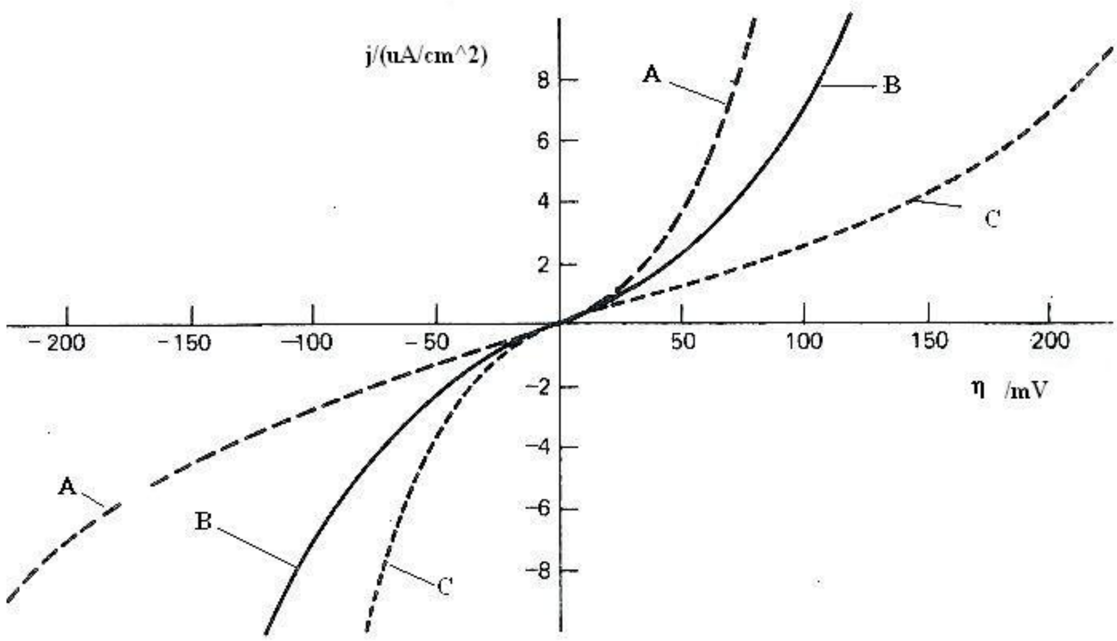
QUESTION CONTINUED OVERLEAF

ii) The development of new electrode materials which will improve the kinetics of reactions and allow higher currents to be obtained at lower overpotentials is an area of intense research activity. An electrode process involving a one electron oxidation is found to have an exchange current density of 0.35 μA cm^{-2}. Suppose a new electrode material has been developed which increases the exchange current density by 15%. By how much does this new material decrease the over-potential required to obtain an oxidation current of 20 μA cm^{-2}? Assume that the value of the symmetry factor is 0.5 and the temperature is 25 ^{0}C. You may also assume that both required overpotentials are greater than 0.1V.

(7 marks)

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

i) The diagram below shows current (j/(μA/cm^2) vs. overpotential (η/mV) curves, labelled A, B and C for three electrode processes all of which involve a one electron transfer. All curves were recorded at the same temperature (25 ^{o}C). Which characteristic of the electrode reactions is different? Explain your answer briefly.



(4 marks)

QUESTION CONTINUED OVERLEAF

ii) Suppose you had to consider preparing a battery by choosing the anodic component of one of the electrode processes shown in the Figure in part i) above and the cathodic component of another (making the assumption that the equilibrium potentials for your chosen couples are sufficiently different that a suitable equilibrium voltage would be generated when the two half-cell reactions were combined). Which combination would you choose to prepare a battery in order to minimise voltage losses when current is drawn? Explain your answer.

(3.5 marks)

iii) In a solution of 1mM $CuSO_4$ in which potassium sulphate is also present, the transport number of the cupric ion was found to be equal to 0.001. What is the concentration of the potassium sulphate in the solution?

$u(Cu^{2+}) = 5.56 \times 10^{-8}\ m^2s^{-1}V^{-1}$
$u(K^+) = 7.62 \times 10^{-8}\ m^2s^{-1}V^{-1}$
$u(SO_4^{2-}) = 8.29 \times 10^{-8}\ m^2s^{-1}V^{-1}$

(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.

One form of the Fundamental equation, for a single-component system, reads:

$$d\mu = V_m dp - S_m dT$$

i) Define each term in this equation.

(2.5 marks)

ii) Hence deduce thermodynamic relations for the pressure-dependence and the temperature-dependence of the chemical potential.

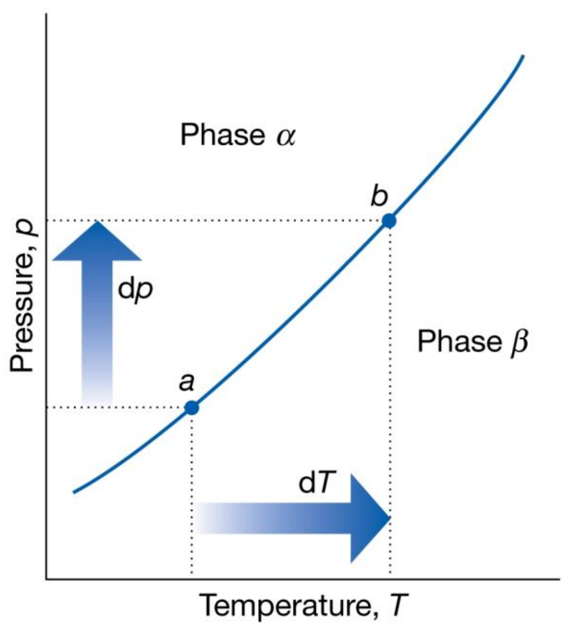
(3 marks)

iii) In the pressure-temperature phase diagram, part of a two-phase coexistence curve (where $\mu(\alpha) = \mu(\beta)$) is shown in the Figure below. By equating $d\mu(\alpha)$ and $d\mu(\beta)$, derive an expression for dp/dT (the Clapeyron equation).

(3 marks)

iv) At one point on the coexistence curve, at a temperature of 372.78 K, it is found that dp/dT = +3,600 Pa K^{-1}, and the volume change of the α-β transition at that point is ΔV_m = +0.0303 m^3 mol^{-1}. Hence estimate the enthalpy of the transition. (The data refer to the boiling point of water at 10^5 Pa = 10^5 N m^{-2}).

(4 marks)



QUESTION CONTINUED OVERLEAF

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

A binary mixture of liquid A (benzene) and liquid B (toluene) at 298 K is found to obey Raoult's Law:

$$p_A = x_A\, p_A^* \qquad p_B = x_B\, p_B^*$$

i) Define all the terms in these equations.

(3 marks)

ii) Sketch how the total vapour pressure p of the solution varies with x_A. The vapour pressures of the pure liquids are 12.7 kPa (benzene) and 3.8 kPa (toluene).

(2 marks)

iii) Use the fact that the chemical potential of liquid A is given by:

$$\mu_A = \mu_A^* + RT \ln x_A$$

and that the free energy of a binary liquid mixture is:

$$\Delta G_{mix} = n_A \mu_A + n_B \mu_B - n_A\, \mu_A^* - n_B\, \mu_B^*$$

to derive an expression for $\Delta G_{mix} / nRT$ involving only x_A and x_B as variables.

(4 marks)

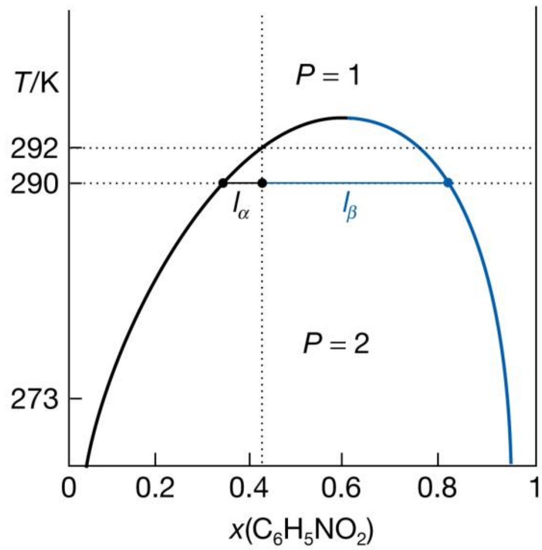
iv) Explain whether the mixing of the liquids is driven by enthalpy or by entropy.

(3.5 marks)

QUESTION CONTINUED OVERLEAF

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

The figure shows part of the temperature-composition phase diagram of a binary liquid mixture of hexane (C_6H_{14}) and nitrobenzene ($C_6H_5NO_2$).



A sample with composition $x_{C6H5NO2} = 0.42$ is placed in a glass test tube.

i) How many liquid phases are present at 300 K for this sample?

(1 mark)

ii) As the sample is progressively cooled to 292 K, then 290 K, and then to 273 K, describe as fully as you can what occurs, estimating compositions where appropriate from the phase diagram.

(4.5 marks)

iii) Describe fully what information can be deduced from the two lengths l_α and l_β at 290 K.

(3 marks)

iv) Estimate the location of the UCST in the temperature-composition phase diagram, explain its significance, and discuss what happens when the sample is heated through the UCST.

(4 marks)