IMPERIAL COLLEGE LONDON

BSc and MSci DEGREES – JUNE 2012, 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

Thursday 21st June 2012, 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 **THREE** of the four parts a), b), c) and d) of this question.

8 marks for each part attempted plus 1 bonus mark = 25. The bonus mark will be awarded if full marks are obtained for **ANY** of the three parts answered.

The constants below MAY be of use for this question.

$F = 9.648 \times 10^4$ C mol^{-1}: RT/F at 25°C= 25.693 mV

Debye Huckel Constant for water at 25^{o}C: A = 0.509 – this constant does not have units.

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

i) The slope of the linear portion of a plot of log $\gamma_\pm$ versus $(I/m^o)^{1/2}$ for a salt $M^{p+} X_y^{q-}$ (y is an integer that is equal to or greater than one) is found to be -2.036. What information about the salt or its constituent ions may be obtained from this statement?

(2 marks)

ii) The ionic strength of a solution of the compound referred to in part i) is found to be 10 times the molality. Use this fact and your answer to i) to find the values of q, p and y.

(3 marks)

iii) The limiting molar ionic conductivity of LiCl is 115 S cm^{2}mol^{-1} whereas that for $[N(C_2H_5)_4]Cl$ is 108.9 S cm^{2}mol^{-1}. Comment on the fact that these two values are quite similar.

(3 marks)

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

i) Many metals produce ions which can exist in several different oxidation states, one example being tin. Disproportionation reactions are thus possible, for example as shown below.

$2Sn^{2+} \leftrightarrow Sn^{4+} + Sn$

The equilibrium constant for this process is 2.07×10^{-10}.
Is the disproportionation process spontaneous? Explain your answer.

(2 marks)

QUESTION CONTINUED OVERLEAF

ii) Calculate the standard cell potential for the overall reaction shown above.

(2 marks)

iii) If the potential of a Sn electrode immersed in a solution of 1mM Sn^{2+} is -0.2251V, calculate the standard electrode potential of the Sn^{4+}/Sn^{2+} couple.

(4 marks)

c) This question has only one part.

In lectures it was stated that the Butler-Volmer equation may be simplified when the overpotential is greater than 0.1V (if we are considering oxidation processes). Some textbooks offer different views. Bard and Faulkner[1] suggest that the equation should be simplified when the overpotential reaches a value where the opposite component current (i.e. reduction for a net oxidation process or vice versa) contributes 1% of the total current.

On this basis, what is the value of overpotential above which we may simplify the Butler-Volmer equation? You may assume a temperature of 25^0C. Note that no other information is needed to answer this question.

(8 marks)

[1]***Bard and Faulkner: Electrochemical Processes Fundamentals and Applications.***

QUESTION CONTINUED OVERLEAF

d) Answer **ALL** parts of this question

i) The solubility of a poorly soluble salt is enhanced if a second more soluble salt is added. This is known as “salting in”, a well-known phenomenon in studies of the behaviour of electrolytes.

At 25^{o} C, the potential of a silver/silver chloride electrode in contact with a solution of saturated silver chloride in water (half cell shown below) has a value of 0.5124V.

Ag|AgCl (s)|AgCl (aq, satd.)

If the solution in the half cell above is replaced with a saturated silver chloride solution prepared in 0.01 $molkg^{-1}$ KNO_3, the potential of the silver/silver chloride electrode becomes 0.5076V.

By how much does the concentration of dissolved silver chloride change when the solution is prepared in 0.01 $molkg^{-1}$ KNO_3?

(5 marks)

ii) What assumptions have had to be made in this calculation and are any of them likely to be invalid? Why?

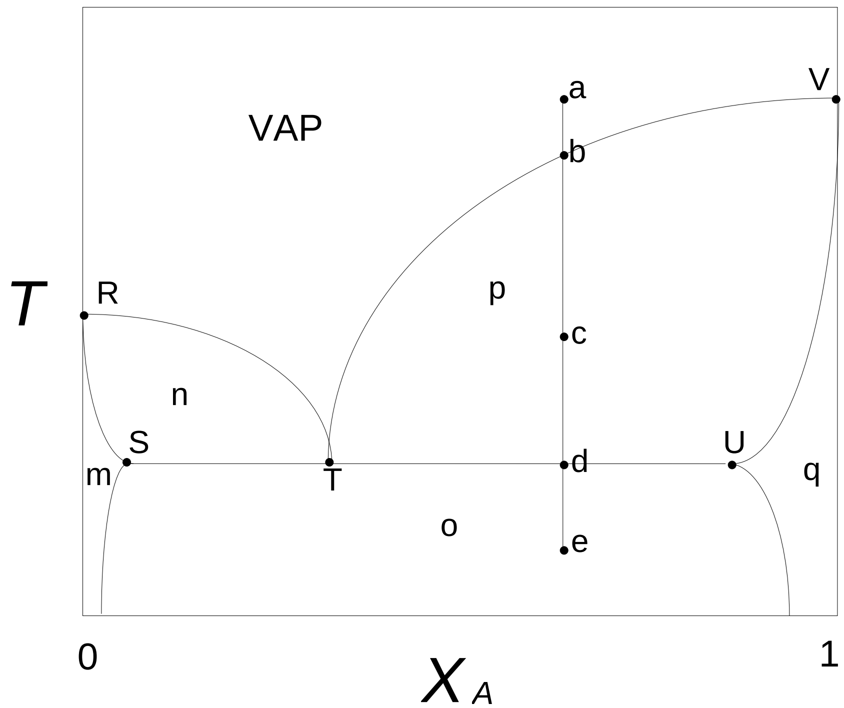
(3 marks)

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



i) Explain whether the two liquids A and B are fully miscible.

(1 mark)

ii) What are points R and V?

(1 mark)

iii) Explain which pure liquid is more volatile, A or B.

(1 mark)

iv) In regions m, n, o, p, and q, state which are single-phase regions, and which exhibit two-phase coexistence.

(2.5 marks)

QUESTION CONTINUED OVERLEAF

v) Name point T and explain its significance.

(2 marks)

vi) Describe what would be observed upon cooling from point a, through points b, c, and d, ending at point e.

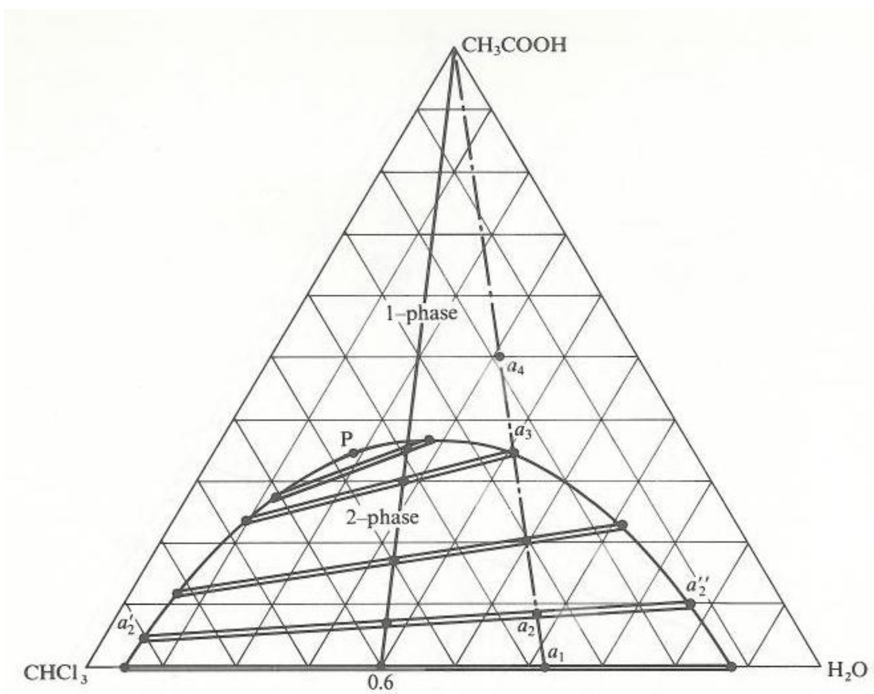
(2.5 marks)

vii) If a tie-line were drawn through point c, explain what information it would yield.

(2.5 marks)

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

The ternary (three-component) phase diagram for chloroform, water and acetic acid at 25 °C and p = 1 bar is shown below.



The Gibbs Phase rule states: F = C – P + 2

i) Define F, C and P, and explain their significance.

(2 marks)

ii) What is the maximum number of phases that can coexist, at a chosen temperature and pressure, for a ternary mixture?

(1 mark)

QUESTION CONTINUED OVERLEAF

iii) Estimate the maximum solubility of chloroform in water from the ternary phase diagram above.

(1 mark)

iv) Similarly, estimate the maximum solubility of water in chloroform.

(1 mark)

v) Estimate the binary composition of point a_1.

(1 mark)

vi) At overall composition a_2, explain the significance of points a_2' and a_2''.

(2.5 marks)

vii) Estimate the ternary composition at point a_3.

(1.5 marks)

viii) Name point P, and describe its significance.

(2.5 marks)

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

The Young-Laplace equation states: $\Delta p = 2\gamma / r$.

i) Define all the terms in this equation.

(1.5 marks)

ii) Estimate the pressure at 20 °C inside a 5 nm diameter nanodroplet of water, and inside a 10 nm diameter nanodroplet of mercury.

(2 marks)

iii) Define the contact angle θ_C for a liquid on a solid surface.

(1 mark)

iv) Derive an expression for the height h by which a liquid will rise (or fall) inside a glass tube of internal radius r. (The downward pressure due to gravity is $p = \rho g h$, where g = 9.8 m s^{-2}; also, it is necessary to multiply the right hand side of the Young-Laplace equation above by cos θ_C to allow for the possibility of a non-zero contact angle).

(3 marks)

QUESTION CONTINUED OVERLEAF

v) Using the data below, hence calculate the height h, for water and for mercury within glass capillaries of internal diameter 0.1 mm, dipped vertically into the two liquids.

(3 marks)

vi) For water, explain whether increasing temperature will increase h, or decrease it.

(2 marks)

	Water	**Mercury**
γ **/ mN m^{-1}**	72.8 (20 °C); 62.7 (80 °C)	476
θ_C **/ °**	0	140
ρ **/ g cm^{-3}**	0.998 (20 °C) ; 0.972 (80 °C)	13.6