IMPERIAL COLLEGE LONDON

BSc and MSci DEGREES – JUNE 2014, 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 17th June 20134, 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.P1 – Thermodynamics

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

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

    i) The chemical potential of an ideal liquid A and its ideal vapour in equilibrium is given by:

$$\mu_A^* = \mu_A^\varnothing + RT \ \ln\left(p_A^* / p_A^\varnothing\right)$$

    In a mixture containing this ideal liquid A the chemical potential of liquid and vapour phases is identical and so

$$\mu_A = \mu_A^{vap} = \mu_A^\varnothing + RT \ln\left(p_A / p_A^\varnothing\right)$$

    Define all of the terms in these two equations and combine them to derive the expression shown below for chemical potential of component A in the mixture in terms of the pure and mixed vapour pressures.

$$\mu_A = \mu_A^* + RT \ \ln\left(p_A / p_A^*\right)$$

                                         (2.5 marks)

    ii) Raoult's law states that the partial vapour pressure in an ideal mixture is the product of the mole fraction x_A and the vapour pressure of the pure liquid.

$$p_A = x_A \ p_A^*$$

    Sketch the variation in total pressure and partial pressures of A and B in an ideal mixture of A and B as the mole fraction of A varies from 0 to 1.

                                         (1.5 marks)

    iii) Given the result of i) above, derive the relationship between the chemical potential of A and its mole fraction in an ideal mixture.

                                         (2 marks)

QUESTION CONTINUED OVERLEAF

iv) Consider a solution and a solvent separated by a membrane. The membrane is semi-permeable; i.e. it permits solvent A to pass freely but not the solute B.

At equilibrium, the chemical potentials on either side of the membrane are equal:

$$\mu_A^*(p) = \mu_A\left(x_A, p + \Pi\right)$$

Where Π is the additional pressure, the osmotic pressure. The chemical potential on the solution side is:

$$\mu_A\left(x_A, p + \Pi\right) = \mu_A^*(p + \Pi) + RT \ln x_A$$

We also know that the effect of the osmotic pressure on the chemical potential of A is:

$$\mu_A^*(p + \Pi) = \mu_A^*(p) + \int_p^{p+\Pi} V_m dp$$

Derive the van't Hoff equation (below) by combining the three expressions above for the case of a dilute solution, assuming that the molar volume is not a function of pressure:

$$\Pi V = n_B RT$$

(4 marks)

v)
    a. Calculate the mole fraction of water in a 2.5% solution of sodium chloride. (m_r of NaCl is 58.45 gmol^{-1} and m_r of water is 18.02 gmol^{-1})

(1 mark)

    b. Taking the molar volume of water as 1.8 x10^{-5} m^3/mol, calculate the pressure required to start producing fresh water at 300 K from a container of this salt solution bounded by a membrane permeable only to water.

(1.5 marks)

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

i) Kirchoff's law is:

$$\Delta_r H[T_2] = \Delta_r H[T_1] + \int_{T_1}^{T_2} \Delta_r C_p^\varnothing \, dT$$

Starting from the definition of specific heat capacity at constant pressure, derive Kirchoff's law and define all of the terms used.

(2 marks)

ii) Starting from the relationship between heat flow and entropy change, derive the relationship analogous to Kirchoff's law but for reaction entropy. i.e:

$$\Delta_r S[T_2] = \Delta_r S[T_2] + \int_{T_1}^{T_2} \frac{\Delta_r C_p^{\varnothing}}{T} \, dT$$

Define all the terms used

(2 marks)

iii)
  a. If the reaction concerned in i) and ii) is the equilibrium unfolding of a protein what is the relationship between ΔG, ΔH and ΔS at a given temperature?

(1 mark)

  b. For lysosyme at 25^0C and pH 4.5:
  $\Delta H = 579 \times 10^3$ Jmol^{-1}
  $\Delta S = 1639$ JK^{-1}mol^{-1}
  $\Delta C_p = 7.2 \times 10^3$ JK^{-1}mol^{-1}

  Calculate the Gibbs energy of unfolding and comment on its sign and magnitude.

(1 mark)

iv)

  a. A protein folding between the native (folded) and denatured (unfolded) states can be treated as a two-state system without any phase change. Assuming that ΔC_p is temperature independent, and using the results of i) and ii) above, derive the expression for the Gibbs free energy difference due to temperature-driven folding/unfolding in terms of the entropy and enthalpy at the starting temperature and the heat capacity at constant pressure.

(2.5 marks)

  b. Calculate the Gibbs energy of unfolding for lysosyme at 0^0C and comment on whether lysosyme is more or less stable at 0^0C compared with 25^0C and whether it can be induced to unfold by cold-denaturation.

(2 marks)

v) Sketch a graph of a differential scanning calorimetry trace for the unfolding of a protein which has a melting temperature of 60^0C. Mark on the graph ΔC_p, the melting temperature T_m and the enthalpy of melting ΔH_m.

(2 marks)

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

For liquids, the surface or interfacial tension can be defined as:

$$\gamma = \left(\frac{\partial G}{\partial \sigma}\right)_{p,T,n}$$

i)   Explain whether the Gibbs free energy increases or decreases with increasing surface or interfacial area and the effect that this has on the geometry of a liquid droplet.

(3 marks)

ii) Values of γ (mN m^{-1}) for pure liquids (X) and for binary water – liquid (X) mixtures are shown below for water, benzene, octane and mercury. Identify which row corresponds to which liquid, explaining your reasoning.

γ (pure liquid (X) – vapour (X))	γ (liquid water - liquid (X))
28.9	35.0
72.8	-
476	375
21.7	51.7

(3 marks)

iii) Explain whether the pressure inside a liquid droplet is larger or smaller than the pressure outside.

(2 marks)

iv) During inhalation the radius of a typical alveolus in the lungs expands from ~50 μm to 100 μm. The surface tension of normal mucosal fluid around alveoli is ~ 0.04 N/m and the pressure difference during respiration is ~130 Pa.

Explain the consequences of the Young-Laplace equation: $p_{in} - p_{out} = \dfrac{2\gamma}{r}$ for the inflation of alveoli in the human lung during breathing and how the biology of the lungs manages to circumvent this problem.

Alveoli can vary in radius by up to a factor of 4. How does the biology make it possible to inflate both small and large alveoli with a single constant pressure?

(4.5 marks)

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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

Consider two electrolytes, NaCl and $CaCl_2$.

Which of the following quantities are the same? Explain your reasoning in each case.

i) λ_m^0 for the chloride ion.
ii) The mobility, u, of the chloride ion at infinite dilution.
iii) The transport number of the chloride ion at infinite dilution.
iv) The mean ionic activity coefficient if we consider solutions of 10^{-3} mol kg^{-1}.
v) The thickness of the ionic atmosphere around the cation at a concentration of 10^{-3} mol kg^{-1}.

(3 marks for each part)

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

A battery system based on potassium and oxygen has recently been suggested as an alternative to lithium battery systems. In this system potassium is oxidised to K^+ while oxygen undergoes a one electron reduction to superoxide.

$$K^+ + e = K \qquad\qquad\qquad E^0 = -2.924V$$
$$O_2 + e = O_2^-$$
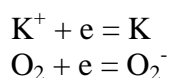
The standard free energy of the cell reaction is -239.4 kJ mol^{-1}.

i) What is the standard half-cell potential for the reduction of oxygen to superoxide in the non-aqueous solvent used for this cell?

(3 marks)

ii) By how much does the cell potential change if oxygen is supplied at a pressure of 6 atm. instead of the standard value of 1 atm.? The temperature may be taken to be 25^0C. You may assume that all other concentrations remain at their standard values and that non-ideal effects may be neglected.

(4 marks)

iii) The reduction of oxygen to superoxide in this battery system might be expected to require a lower overpotential to attain a specific current than the reduction of oxygen to water in an aqueous solution on an electrode material such as Pt. Explain why this might be the case.
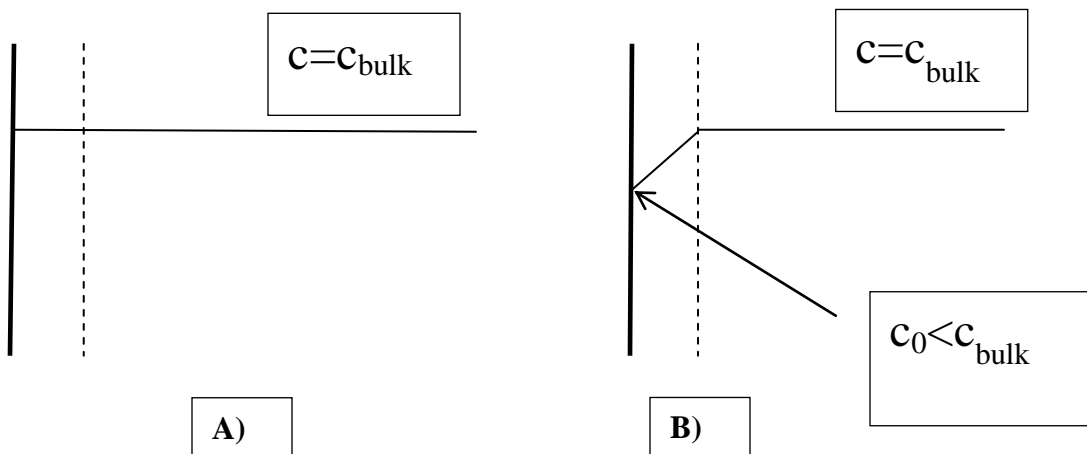
(3 marks)

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

The diagrams A to D represent the variation of concentration with distance for a rotating disc electrode for different experimental conditions. The vertical solid line represents the electrode surface whilst the vertical dotted line represents the outer edge of the Nernst Diffusion Layer.

The electrode is in contact with a solution that contains a redox species which is able to undergo a one-electron oxidation. For diagrams A, B and D the diffusion layer thickness is the same. The diffusion layer thickness is larger for diagram C.

Answer the following questions explaining your reasoning clearly in each case.

i) For each diagram what statements can one make about the potential of the electrode *relative to the equilibrium potential of the electrode*?

(4 marks)

ii) Which of the diagrams corresponds to the highest current that would be observed?

(3 marks)

iii) How are the conditions of experiment C different from those of experiment D?

(3 marks)

$c=c_{bulk}$

A)

$c=c_{bulk}$

$c_0<c_{bulk}$

B)

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C)

D)