IMPERIAL COLLEGE LONDON

BSc and MSci DEGREES – JUNE 2015, for Internal Students of the Imperial College of Science, Technology and Medicine

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

ADVANCED CHEMISTRY THEORY IIB

Physical Chemistry

Thursday 18th June 2015, 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 part a) and **EITHER** part b) **OR** part c) of this question.

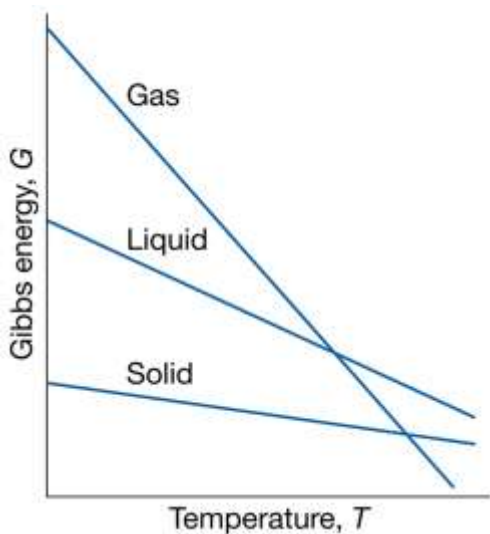a) Answer **ALL** parts of this question.

    i) $G = H - TS$; $\Delta G = \Delta H - T\Delta S$; $dG = dH - TdS$

       Explain the difference in meaning of the three expressions above. Remember to define all of the symbols used.

                                                                                         (3 marks)

    ii) Starting from the mathematical definition of Gibbs Free Energy derive the temperature dependence of Gibbs Free Energy at constant pressure. Define all of the symbols which you use.

                                                                                                 (4 marks)

    iii) The relative relationships between G and T for the solid, liquid and gaseous forms of a substance at constant pressure generally look as follows:

       Given the results of ii) above, explain this graph in terms of the relative properties of solids, liquids and gasses.

                                                                                       (3 marks)

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

Two liquids A and B, with A having the higher vapour pressure, are mixed together to form an ideal solution.

    i)   Sketch a graph which shows the vapour pressure of A, the vapour pressure of B and the total vapour pressure as a function of the mole fraction of A. Define any symbols that you use

                                        (2 marks)

    ii)   Combine Raoult's Law with Dalton's Law to derive the relationship between total pressure and the liquid mole fraction of A in terms of the partial pressures of pure A and pure B.

                                          (2 marks)

    iii)   Similarly derive the total pressure in terms of the molar fraction of A in the gas phase Y_A.

                                          (3 marks)

    iv)   Sketch a graph showing the liquid and vapour phase boundaries for this two-component system. Label clearly the regions corresponding to the various phases.

                                          (2 marks)

    v)   For this two component system at a particular pressure P_1 the mole fraction z_A at the liquid phase boundary is 0.5. The mole fraction z_A at the vapour phase boundary is 0.9. Use the lever rule to calculate the mole fraction in the middle of the coexistence region and the proportions of each component A and B in the gas and vapour phases at this point such that the total composition adds up to 1.

                                          (6 marks)

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

    i)   Sketch a graph of the relationship between chemical potential and temperature for a pure substance. Include the liquid-vapour and liquid-solid phase boundaries in your graph and explain the reasoning behind your sketch

                                          (3 marks)

    ii)   At the boundary between the liquid and vapour phases for a pure substance the two phases are in equilibrium. Use this fact and the Fundamental Equation, to derive the Clapeyron Equation which relates the gradient of the pressure-temperature graph to the molar enthalpy and molar volume change of vaporisation.

          Remember to define all the symbols that you use.

                                          (3 marks)

    iii)   Starting with the Clapeyron Equation make appropriate approximations to derive the Clausius-Clapeyron Equation.

                                          (5 marks)

    iv)   Water boils at 373 K, and the enthalpy of vaporization is 40.7 kJ mol^{-1}. Estimate the vapour pressure at temperatures of 363 and 383 K. Use units of Atmospheres for convenience.

2.P2 – Electrochemistry and Electrochemical Kinetics

Answer **BOTH** parts of this question.

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

   i)   Describe clearly what you understand by any **TWO** of the following.

        A. The hydrodynamic radius of an ion.
        B. The cathodic overpotential.
        C. The exchange current density.
        D. The Nernst diffusion layer.

<div align="right">(3 marks each)</div>

   ii) In a solution of 0.01M lanthanum chloride ($LaCl_3$), the cation has a transport number of 0.4625. If the mobility of the chloride ion is 7.91×10^{-8} m^2 s^{-1} V^{-1}, what is the mobility of the La^{3+} ion? Assume complete dissociation of the salt.

<div align="right">(4 marks)</div>

   iii) The molar conductivities at infinite dilution of the ferricyanide and ferrocyanide ions are shown below. The molar ionic conductivity of the ferrocyanide ion is significantly larger. What is the reason for this increased molar ionic conductivity for the ferrocyanide ion?

Anion	$10^4\ \lambda_-^{\circ}/$ S m^2mol^{-1}
$[Fe(CN)_6]^{3-}$	302.7
$[Fe(CN)_6]^{4-}$	442.0

<div align="right">(3 marks)</div>

b) Answer parts i) and ii) and **EITHER** part iii) **OR** part iv) of this question.

   The following cell is prepared:
   Pt | H_2 (g) | NaOH (aq), NaCl (aq) | AgCl| Ag
   The concentrations of NaOH and NaCl are both equal to c mol kg^{-1}. The pressure of hydrogen gas is 1 atmosphere.

   i)   What is the purpose of the Pt electrode in this cell?

<div align="right">(2 marks)</div>

   ii) What are the two half-cell reactions that take place in this cell?

<div align="right">(3 marks)</div>

iii) It is found that if the value of c is changed so that the concentrations of NaOH and NaCl both now equal c_1, the measured cell potential does <u>not</u> change.

By considering the Nernst equation for the two half cells, explain this observation.

(7 marks)

iv) Suppose that the cell is operated as a galvanic cell and is required to pass a specific current. Explain how a Tafel plot would provide information that would help you calculate the cell output voltage when a specific current is being passed. What other information would be required in order to calculate the cell output voltage? Explain clearly how the information would be used in order to calculate the cell output voltage

(7 marks)