THE OPEN UNIVERSITY OF SRI LANKA
B. Sc. Degree /Continuing Education Programme — Level 4
Final Examination — 2006/2007
CHU 2124/CHE 4124 — Physical Chemistry I

$2\frac{1}{2}$ hours

21st November 2006	9.30 a.m. — 12.00 p.m.

- This question paper consists of six (6) questions, three in **Part A** and three in **Part B.**
- Answer **four questions only**, selecting **two (02)** questions from **Part A** and **two (02)** questions from **Part B**.
- If more than four **(4)** questions are answered, **only the first two** from each part, in order of writing, will be marked.
- Use of a non-programmable calculator is permitted.
- Mobile phones are prohibited.
- Log tables will be provided.

Gas constant (R)	=	$8.314\ \mathrm{J\,K^{-1}mol^{-1}}$
Avogadro constant (N_A)	=	$6.023\times10^{23}\ \mathrm{mol^{-1}}$
Faraday constant (F)	=	$96,500\ \mathrm{C\,mol^{-1}}$
Planck constant (h)	=	$6.63\times10^{-34}\ \mathrm{J\,s}$
Velocity of light (c)	=	$3.0\times10^{8}\ \mathrm{m\,s^{-1}}$
Protonic charge (e)	=	$1.602\times10^{-19}\ \mathrm{C}$
Standard atmospheric pressure	=	$10^{5}\ \mathrm{Pa}\left(\mathrm{N\,m^{-2}}\right)$

Part A

1. (a) Under what conditions, if any, and to what type of systems will the following thermodynamic expressions/equations be applicable:

   (i) $\Delta A < 0$

   (ii) $\Delta T = K_{100}.\ m$

   (iii) $q = -w = nRT\ \ln\left(\frac{P_1}{P_2}\right)$

   (iv) $S = n\,C_{P,m}\ln T - nR\ln P + \text{constant}$

   (v) $\ln P + \gamma \ln V = \text{constant}$

   (vi) $\Delta S = nC_{P,m}\ \ln\left(\frac{T_2}{T_1}\right)$

   (vii) $H - U = G - A$

   (viii) $\Delta S = \frac{q_{rev}}{T}$

(32 marks)

(b) The following standard enthalpies (in kJ mol^{-1}) at 300 K are given.

$C_3H_7COOH(l)$ = -500; $CO_2(g)$ = - 400 ;

(i) Given that the standard enthalpy of combustion of $C_3H_7COOH(l)$ at 300 K is 3250 kJ mol^{-1}, calculate the standard enthalpy of dissociation of water according to the equation

$2H_2O(l)$ -----> $2H_2(g)$ + $O_2(g)$

(ii) Assuming that the gaseous reactants and products of the combustion behave ideally, calculate the standard internal energy of combustion of $C_3H_7COOH(l)$. Indicate any other assumptions that you make.

(32 marks)

(c) Assuming that the thermodynamic properties B, L, M, X and Y are relevant to a given closed thermodynamic system and that the thermodynamic equation

$$L = X\,dM - B\,dY$$

applies to this system, write down the corresponding Maxwell type relationship.

(10 marks)

(d) The thermodynamic equation of state can be expressed in the form

$$P = T\left(\frac{\partial P}{dT}\right)_V - \left(\frac{\partial U}{\partial V}\right)_T$$

Show that the internal energy of an ideal gas is independent of volume and depends only on the temperature. Write down the relevant equations for the internal energy change, ΔU and enthalpy change, ΔH, of an ideal gas.

(26 marks)

2. (a) **Write down** (no proof required) the mathematical expressions that can be used to

(i) express the Gibbs free energy change, ΔG, in the chemical process represented by the balanced chemical equation

$$bL + cM \rightleftharpoons aX + eF + fN$$

in terms of the activities of the reactants L and M and the products X, F and N. *a, b, c, e,* and *f* are stoichiometric integers.

Standard Gibbs free energy for this process = ΔG^o

(ii) predict the variation of the standard enthalpy change, ΔH^o, of a reaction with temperature at constant pressure.

(iii) predict the variation of the melting point of an univariant system with pressure.

(iv) predict the variation of the equilibrium constant, K_P, with temperature.

(v) predict the spontaneity of a given process that takes place in the universe.

(25 marks)

(b) 2000 mol of gaseous nitrogen [$C_{P,,m} = (7R)/2$] at an initial temperature of 727 °C and a pressure of 100 atmospheres are cooled through a reversible adiabatic expansion to a final temperature of 227 °C. Calculate

(i) the change in enthalpy, ΔH, accompanying the expansion.

(ii) the change in entropy, ΔS, accompanying the expansion.

(iii) the final pressure attained by the system.

Will the change in Gibbs free energy, ΔG, for this process be equal to zero? Briefly give reasons in support of your answer.

(40 marks)

(c) The variation of the equilibrium constant K of a reaction at thermodynamic temperature T is given by the equation

$$\ln K = 10.52 - \frac{320}{T}$$

Calculate ΔG^o, ΔH^o, and ΔS^o for this reaction at 27 °C. **(35 marks)**

3. (a) Using an appropriate **mathematical** equation, define

(i) "isobaric thermal capacity, C_p" of a substance, indicating to what type of system the concept can be applied.

(ii) the "Joule Thompson coefficient, $\mu_{J,T}$" and explain why an isoenthalpic expansion of hydrogen gas at 300 K results in a heating of the gas while that of most other gases will result in a cooling.

(iii) "chemical potential of the i^{th} component, μ_i, in a mixture of several components and show that μ_i is an **intensive** thermodynamic property.

(40 marks)

(b) State the third law of thermodynamics.

(10 marks)

(c) The vapor pressure P of a substance as a function of temperature is given below.

T /°C	57	100	133	157
P/torr	1	10	40	100

(i) With the aid of a graphical plot, calculate the molar enthalpy of vaporization of the substance indicating any assumptions that you make.
(ii) Deduce the standard boiling point of the substance.

(50 marks)

Part B

(Relative atomic mass : H = 1.0; N = 14.0 C = 12.0; O = 16.0)

4 (a) Vapour pressures of pure methanol and pure ethanol are, respectively, 8.0×10^4 N m^{-2} and 4.5×10^4 N m^{-2} at 60 °C. Methanol and Ethanol are miscible at all compositions and form an ideal solution.
(i) Sketch a fully labeled vapour pressure vs composition diagram for the above system.
(ii) Calculate, the vapour composition corresponding to a mixture formed by mixing 64 g of methanol with 46 g of ethanol at the above temperature. Write down the relevant equation/s required for your calculation and identify, clearly, all the symbols used.

(35 marks)

(b) At standard atmospheric pressure, nitric acid (boiling point 87 °C) and water form a constant boiling mixture (boiling point 122 °C) of composition 65 % by mass of nitric acid. This is a fully miscible system at all compositions.
(i) Calculate the mole fraction of nitric acid corresponding to the constant boiling composition.
(ii) What is meant by "constant boiling mixture"?
(iii) Sketch and label fully the boiling point / composition diagram (composition in terms of **mole fraction of nitric acid**) for this system.
(iv) State Raoults Law.
(v) What is meant by the statement "Nitric acid /water mixture shows a negative deviation from the above law"?

(50 marks)

(c) Two liquids, composed of 40.0 g of a compound A (rel. molar mass = 80) and 80.0 g of a compound B (rel. molar mass = 160), were mixed together at room temperature. The vapour pressures of pure A and pure B at this temperature are 60 torr and 40 torr respectively. Calculate the total vapour pressure of this mixture assuming ideal behaviour.

(15 marks)

5. (a) Define the following : (i) Phase rule
(ii) Eutectic composition

(10 marks)

(b) Metal A (M.Pt = 600 °C) and Metal B (M.Pt = 1200 °C) form two compounds, at elevated temperatures, of formula A_2B_3 and A_2B with congruent M.Pt's 1000 °C and 800 °C respectively. Three eutectics of compositions 0.10, 0.50 and 0.80 (given in terms of the mole fraction of A) are formed, with the following M.Pt's: 300 °C, 500 °C and 200 °C, respectively.

(i) Sketch a fully labeled phase diagram for the above system.

(ii) Sketch cooling curves corresponding to a melt of composition 30 mole % of A. and 40 mol % of A. Comment on the shapes of the two cooling curves.

(40 mark)

(c) (i) Write down the relationship between the number of photons crossing a unit area in unit time and the intensity of a monochromatic beam of electromagnetic radiation and, identify all the terms in it.

(ii) The intensity of a beam of light of wavelength 10 nm is $2.5x10^{-5}$ W m^{-2}. Calculate the number of photons crossing an area (perpendicular to the beam) of1.0 cm^2 in 2 seconds

(25 marks)

(d)(i) Write down an equation to express Beer-Lambert law and identify all the terms in it.

(ii) A 0.03 mol dm^{-3} aqueous solution of a compound X shows an absorbance of 2.0 at 25 °C when the path length of radiation (of wavelength 700 μm) is 1.0 cm. Calculate the molar absorption coefficient of X at 25 °C in an aqueous solution.

(25 marks)

6 (a) Write down two effects that determine the peak widths in an absorption spectrum

(06 marks)

(b) Write down the relationship between the rotational constant and the moment of inertia of a diatomic molecule and identify all the terms in it.

(12 marks)

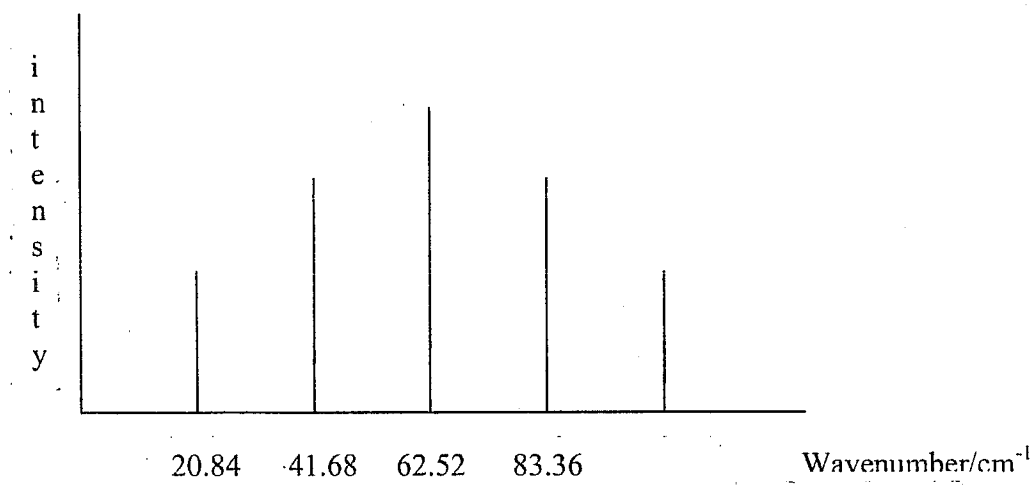
(c) Write down the relationship between the moment of inertia and the atomic masses of a diatomic molecule and identify all the terms in it.

(12 marks)

(d) Write down the relationship between the wavenumbers of lines in the microwave spectrum and the rotational constant of a diatomic molecule and identify all the terms in it.

(12 marks)

(e) The first few lines of the microwave spectrum of a diatomic molecule $H^{35}A$ is shown below



Calculate the wavenumber of the first two lines of the microwave spectrum of $H^{45}A$. State any assumption/s you make

(Rel. Atomic Mass: $^{1}H = 1.0$, $^{35}A = 35.0$, $^{45}A = 45.0$)

(58 marks)