00171

THE OPEN UNIVERSITY OF SRI LANKA
B. Sc. Degree /Continuing Education Programme — Level 4
Final Examination — 2011/2012
CHU 2124/CHE 4124 — Physical Chemistry I

2 hours

20th January 2012	9.30 a.m. — 11.30 a.m.

Please note: You have been allocated **2 h** (NOT 2.5 h) to answer 4 (four) questions in this paper as per instructions given below; accordingly, the time recommended for each question is **30 minutes**

- This question paper consists of six (6) questions, three (3) in **Part A** and three (3) 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; switch off and leave them outside.
- Log tables will be provided.

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

Part A

1. (a) (i) Write down the **Clausius–Clapeyron (CC) equation.**

(ii) The above equation is derived from the **Clapeyron** equation,

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}$$

Name the important assumptions made in deriving the **CC** equation from the Clapeyron equation

(iii) If the vapour pressure of a liquid undergoes a 10-fold increase in pressure when the temperature is raised from 227 ^{O}C to 327 ^{o}C, calculate the mean molar enthalpy of evaporation of this liquid (in units of kJ mol^{-1}).

Assume that the mean molar enthalpy of evaporation is a constant in the above temperature range.

(40 marks)

(b) 10 mol of gaseous nitrogen [$C_{P,,m} = (7R)/2$] at an initial temperature of 900 K and a pressure of 100 atmospheres are cooled through a reversible adiabatic expansion to a final temperature of 600 K. 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.

(30 marks)

(c) Under what conditions and to what type of system are the following expressions applicable in thermodynamic studies.

(i) $\Delta G > 0$ (ii) $\Delta S = \frac{q}{T}$ (iii) $dH = nC_{P,m}dT$

(vi) $TV^{\gamma-1} = \text{Constant}$ (v) $TS = H - G$ (vi) $\Delta T = K_{1000}.m$

(30 marks)

2. (a) Define (i) "Colligative Property"

(ii) Molality

(16 marks)

(b) (i) Write down the relationship between the freezing point depression, cryoscopic constant and molality using the standard symbols

(ii) A solution was prepared by dissolving 1.00 g of Y (a non volatile compound) in 50.00 g of X (relative molar mass = 100) and, the freezing point of this solution was found to be 88.0 ^{o}C. The freezing point of pure X is 89.5 ^{o}C. Calculate the relative molar mass of Y. [Cryscopic constant for X = 6.15×10^{3} K g mol^{-1}]

(28 marks)

(c) In a pressure flask at 27 °C, there are 100 moles of a gas which could be any one of the gases; neon, oxygen, carbon dioxide.

When this gas was expanded adiabatically from 3 to 4 dm^3, the maximum decrease of temperature that could be obtained was 52 °C. Assuming ideal behaviour,

(i) calculate the ratio (γ) of the isochoric ($C_{V,m}$) and isobaric ($C_{P,,m}$) thermal capacities.

(ii) Use the value of γ from (i) to identify which one of the three gases are present.

(iii) Calculate the internal energy change (ΔU) and the Helmholtz free energy change (ΔA) accompanying the process where the maximum decrease in temperature is obtained. (molar entropy of the gas at 27 °C = 100 J mol^{-1} K^{-1})

(56 marks)

3. (a) Given the following standard entropies, calculate the standard entropy of formation of ammonia, in units of J K^{-1} mol^{-1}.

Substance	$N_2(g)$	$H_2(g)$	$NH_3(g)$
$S^0/J\,K^{-1}\,mol^{-1}$	100.0	130.0	190.0

(20 marks)

(b) **Write down** (no proof required) the relationship that exists between

(i) the standard free energy change, ΔG^o, and the thermodynamic equilibrium constant K of a chemical reaction at a thermodynamic temperature T

(ii) the thermodynamic equilibrium constant K_1, at one temperature T_1 and thermodynamic equilibrium constant K_2 at another temperature T_2.

(20 marks)

(c) The **new** thermodynamic properties A, B, C, L, M and N are relevant to a given closed thermodynamic system. The following two thermodynamic expressions are valid for the system.

$$dA = -C\,dN - M dB$$
$$dL = N\,dC - M\,dB$$

(i) Write down the two Maxwell type relationships that are relevant to the two expressions given above.

(ii) Show that $M = N\left(\frac{\partial M}{\partial N}\right)_B - \left(\frac{\partial L}{\partial B}\right)_N$

(24 marks)

(d) (i) Write down the mathematical expressions that **defines** the Joule – Thompson coefficient.

(ii) Considering H = f(P,T) and the corresponding expression for the total differential, dH, derive the expression $-\frac{1}{C_p}\left(\frac{\partial H}{\partial P}\right)_T$, which is an alternate expression for the Joule Thompson Coefficient

(iii) With the aid of the Maxwell relationships derived from the expressions, $dH = VdP + TdS$ and $dG = VdP - SdT$ and, the ideal gas equation $PV = nRT$ **or otherwise**, show that $\frac{1}{C_p}\left(\frac{\partial H}{\partial P}\right)_T$ is zero for an ideal gas

(36 marks)

Part B

4. (a) (i) Write down Beer-Lambert law and identify all the parameters in it.

(ii) In a double beam spectrometer the intensity of the beam incident on the sample is I_0. The intensity of the beam leaving the sample after absorption is I. Write down an expression for the fraction of photon energy in the beam absorbed by the sample in terms of I_0 and I.

(iii) Calculate the fraction of energy absorbed by a chemical compound X when a $0.015 \text{ mol dm}^{-3}$ aqueous solution of it is placed in a beam of radiation in a cell of path length 1.5 cm. The molar extinction coefficient of X in this aqueous solution is $10.0 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ at the frequency of the radiation used in the experiment.

(28 marks)

(b) Giving reasons identify the molecules that can give a microwave spectrum out of the following.

(i) CO (ii) ICl (iii) H_2 (iv) F_2 (v) HI

(12 marks)

(c) (i) Write down an expression for the separation between adjacent lines in the microwave spectrum of a diatomic molecule in terms of the rotational constant, B.

(ii) Write down the relationship between the bond length of a diatomic molecule which behaves as a rigid rotor and B and identify all the parameters in it.

(iii) Two consecutive lines in the microwave spectrum of a gaseous molecule XY appears at 75.624 cm^{-1} and 100.832 cm^{-1}. Calculate the bond length, X–Y, if XY behaves as a rigid rotor.? [Relative atomic masses: X = 27.00, Y = 1.00]

(60 marks)

5. (a) Derive the expression $P_T = x_A [P^o_A - P^o_B] + P^o_B$ where the symbols used have their usual meanings .[Marks will be awarded for writing down all relevant mathematical expressions]

(18 marks)

(b) Two liquids, 60.0 g of A (of relative molar mass = 90) and 80.00 cm^3 of B (of relative molar mass = 136 and density = 0.85 g cm^3), were mixed together at a given temperature. The vapour pressures of pure A and pure B at this temperature are reported as 60 torr and 40 torr respectively. [Assume that A and B form an ideal solution at all compositions and that, the composition of the liquid phase remains unchanged].

(i) Calculate the total vapour pressure of the mixture

(ii) Calculate, the vapour composition corresponding to the given mixture

(28 marks)

(c) At standard atmospheric pressure, a liquid X [relative atomic mass 60 and boiling point 75 °C] and a liquid Y [relative atomic mass 80 and boiling point 110 °C] form a constant boiling mixture (boiling point 140 °C) of composition 60 % by mass of X. This is a fully miscible system at all compositions.

(i) Calculate the mole fraction of Y corresponding to the constant boiling composition.

(ii) Sketch and label fully the boiling point / composition diagram (composition in terms of mole fraction of Y) for this system.

(30 marks)

(d) (i) Define the term "Upper critical temperature" for a pair of partially miscible liquids A and B, and, identify this point on a sketch of a fully labeled solubility curve for such a pair of liquids.

(ii) When 25.0 g each of A and B are mixed, two layers, labeled as p and q, are formed. The layer p contains 25 % of A by weight while the layer q contains 70 % of A by weight. Calculate the weight of A in the layer p.

(24 marks)

6 (a) 45.0 g of acetic acid is mixed with 10.10 ml of pure ethanol (density = 9.1×10^5 g m^{-3})

(i) Making use of relevant calculations, identify the solvent and the solute in the above system and, give the reason for your choice.

(ii) Calculate the mole fraction of the solvent. (R.A.M: H =1.0; O = 16.0; C= 12.0)

(15 marks)

(b) It is found that metal A (Melting Point = 650 °C) and metal B (Melting Point = 1200 °C) form two compounds with composition given by X_B = 0.4 and X_B = 0.6 whose congruent melting points are 450 °C and 950 °C respectively. It was found that three of the cooling curves corresponding to the compositions given by X_B = 0.25 and X_B = 0.5 and X_B = 0.7, did not show any "breaks"; the respective **halt** temperatures reported for each of these compositions were 250 °C, 350 °C, and 700 °C. (X_B = mole fraction of B)

(i) What is the term used to define the compositions corresponding to the halt temperatures mentioned above?

(ii) Sketch **any one** of the cooling curves mentioned above.

(iii) Based on the above information, sketch a fully labeled phase diagram (identify all relevant regions, points etc)

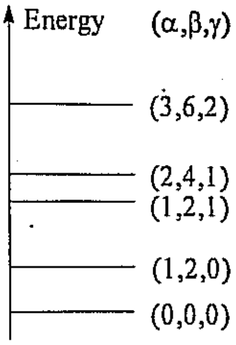
(35 marks)

(c) (i) Write down the relationship between the energy of a photon and its frequency and identify all the parameters in it.

(ii) A search light flashes every second giving a burst of 1 mol of photons of frequency 3×10^{15} Hz. Assuming that all the energy supplied is converted into energy of photons, calculate the amount of energy supplied to the search light every second.

(20 marks)

(d)(i) Imagine a molecule having only 5 energy levels. Each energy level is identified by 3 quantum numbers, (α,β,γ). The selection rules in absorption spectroscopy for the molecule are $\Delta\alpha = +1$ and $\Delta\beta = +2$ and $\Delta\gamma = +1$. The five energy levels along with their quantum numbers are schematically represented in the figure to the right.



With the aid of a sketch of the given figure, indicate, giving reasons, the maximum number of transitions/lines that may be observed in the absorption spectrum of a pure sample of these molecules.

(ii) Supposing a student observed only two lines in the spectrum of a sample of these molecules. Give two possible reasons for the difference between the expected number of lines, as indicated in your answer to part (i) above, and the actual observation.

(30 marks)