The Open University of Sri Lanka
B. Sc. Degree /Continuing Education Programme — Level 4
Final Examination — 2013/2014
CHU 2124/CHE 4124 — Physical Chemistry I

2 hours

3rd July 2014	9.30 a.m. — 11.30 a.m.

- 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.

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

Part A

1. (a) Under what conditions if any, and to what type of systems are the following thermodynamic expressions applicable?

(i) $q = nRT\ln\frac{V_2}{V_1}$ (ii) $\Delta A = \Delta U - T\Delta S$ (iii) $\Delta G = 0$

(iv) $\Delta S = \frac{\Delta H}{T}$ (v) $(\gamma - 1)\ln V + \ln T = constant$

(40 marks)

(b) (i) Starting from the first law of thermodynamics, derive the fundamental equation dH = TdS + VdP for a reversible process in a closed system.

(ii) Write down the Maxwell relationship that can be derived using the above equation.

(30 marks)

(c)1000 moles of a monatomic ideal gas ($C_{v,m}$ = 3R/2) is heated from 27 °C to 327 °C at constant pressure. Calculate ΔH and ΔS for this process.

(30 marks)

2. (a) Write down the equation, that relates

(i) the standard free energy change, ΔG^o, to the equilibrium constant, K, of a chemical reaction.

(ii) the variation of the equilibrium constant, K with temperature, T

(iii) the enthalpy change at one temperature if the enthalpy change at another temperature is known

(30 marks)

(b) The variation of the equilibrium constant K of a reaction at thermodynamic temperature, T, is given by the equation, $\ln K = 9.45 - \frac{490}{T/K}$. Calculate ΔG^o for this reaction at 60 ^{0}C.

(30 marks)

(c) (i) Define "Joule-Thompson Coefficient, μ_{JT}, using a mathematical expression.

(ii) A gas at 25^{0}C undergoes a Joule-Thompson expansion from 20 atm to 10 atm. Calculate the final temperature that will be attained by the gas as a result of this expansion (μ_{JT} for the gas = 1.3 K atm^{-1})

(40 marks)

3. (a) (i) Write down the Clausius Clapeyron equation and identify all the terms in it.
(ii) Under what conditions and to what kind of systems can the Clausius –Clapeyron equation be applied.

(40 marks)

(b) The temperature dependence of the vapour pressure of the solid and liquid form of a given compound "A" are given below;

Solid A: $\log_{10} P/torr = 10 - \frac{2000}{T/K}$

Liquid A: $\log_{10} P/torr = 6 - \frac{1500}{T/K}$

Deduce the temperature corresponding to the triple point of "A". State any assumptions you make.

(30 marks)

(c) Write down the mathematical form of the second law of thermodynamics for spontaneous, equilibrium processes,

(i) based on the entropy change that takes place in an experimental system

(ii) the entropy change in the universe

(iii) based on Gibbs free energy criteria

(30 marks)

Part B

4. (a) (i) Write down the mathematical expressions for the following using the standard symbols; identify, clearly, all the symbols used.

(α) Raoults Law (β) Phase rule

(ii) Consider the following system in equilibrium

$$PCl_{5\,(s)} \rightleftharpoons PCl_{3\,(S)} + Cl_{2\,(g)}$$

Give the number of the phases and components in the above system in accordance with the above rule

(24 marks)

(b) 4.6 g of formic acid is mixed with 50.00 ml of pure ethanol (density = 9.0×10^5 g m^{-3})

Calculate the mole fraction of the solvent. (relative atomic mass: H =1.0; O = 16.0; C= 12.0)

(12 marks)

(c) Define Pressure and **derive** the SI units of Pressure

Liquids **A** and **B** form an ideal mixture, miscible at all compositions. When the mole fraction of **B** in the liquid phase is 0.80, the vapour pressure of the system is 2.4×10^5 Pa. The vapour pressure of pure A is 4.0×10^5 Pa.

(i) Calculate the vapour pressure of pure **B**

(ii) Sketch the Pressure vs Composition phase diagram with appropriate labels for the above system.

(iii) Calculate the mole fraction of **B** in the vapour phase corresponding to the composition given above.

(36 marks)

(d) The normal boiling points of pure liquids, **P** and **Q**, respectively, are 160 °C and 200 °C. An equi-molar mixture of **P** and **Q** forms an azeotrope whose normal boiling point is 150 °C.

(i) What do you understand by the term "azeotrope"?

(ii) Sketch the Temperature vs Composition phase diagram for the above system and label it completely.

(28 marks)

5. (a) List three factors that determine the molar extinction coefficient of a given pure compound in a dilute solution.

(12 marks)

(b) (i) Write down the Beer-Lambert law, for the absorbance of a pure compound in dilute solution, in mathematical form and identify all the parameters in it.

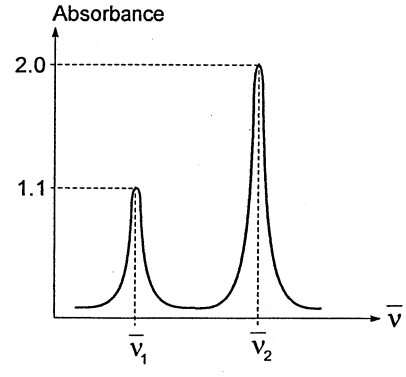
(ii) Consider a sample of a solution of a pure compound X, in a cell of path length 1.50 cm, placed in a single beam spectrometer for the measurement of the absorbance using electromagnetic radiation of frequency, 4.5×10^{2} Hz at 25^{0}C. The concentration of X in the solution is 0.010 mol dm^{-3} and the molar extinction coefficient of X in the solution for radiation of frequency 4.5×10^{2} Hz at 25^{0}C is 66.0 dm^{3} mol^{-1} cm^{-1}.

(α) Calculate the absorbance of the solution in the sample cell for radiation of frequency, 4.5×10^{2} Hz at 25^{0}C. State assumption/s, if any, you make in this calculation.

(β) Calculate the intensity of the emergent beam of radiation if the intensity of the incident beam is 4.0×10^{-5} W m^{-2}. State assumption/s, if any, you make in this calculation.

(53 marks)

(c) A hypothetical molecule has only 3 energy levels with energy E_1, E_2 and E_3. The absorption spectrum at low temperature has only two lines as shown in the following figure.



Here, $\bar{\nu}_1 = 1800\ cm^{-1}$ and $\bar{\nu}_2 = 2000\ cm^{-1}$. Calculate E_2 and E_3 if $E_1 = 1.00 \times 10^{-20}\ J$. State assumption/s, if any, you make in this calculation.

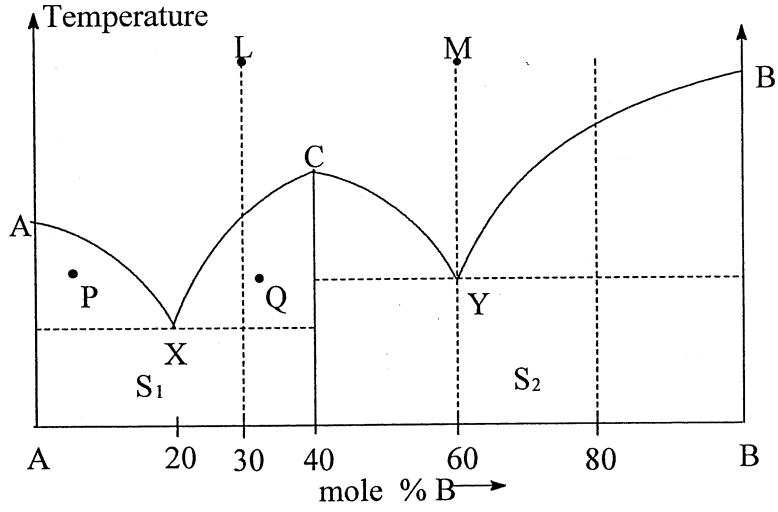
(35 marks)

6. (a) What is meant by "eutectic composition" with respect to a binary system.?

(10 marks)

(b) Metal A (Melting Point = 700 °C) and Metal B (Melting Point = 1250 °C) form a compound with a congruent Melting Point of 900 °C Two eutectics are formed, with the following Melting Points: 400 °C, and 500 °C.

Copy the phase diagram given below and clearly indicate the temperature values given above on this diagram.



(i) Write down the formula of the compound formed between A and B.

(ii) What are the compositions of the two eutectics formed between A and B in terms of the mole fraction of A?

(iii) Identify, clearly, the regions, labeled as P, Q, S_1 and S_2

(iv) Sketch cooling curves corresponding to a melt represented by the point L and M respectively. Identify the points "break" and "halt" in your sketch and explain the reason for their appearance in the cooling curve

(40 marks)

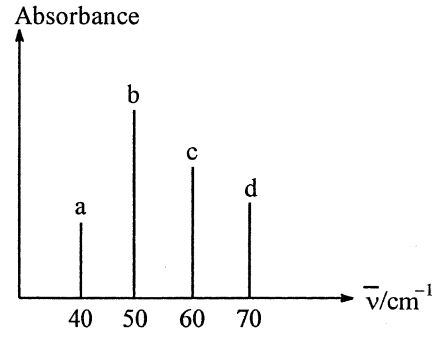
(b) Rotational energy of a molecule of $H^{35}Cl$ is given by $\bar{E}_J = B\left(cm^{-1}\right)J(J+1)$.

(i) Identify all the parameters in the above expression for rotational energy.

(ii) What is the specific selection rule in the microwave spectroscopy of $H^{35}Cl$?

(iii) Starting with the expression for rotational energy levels, derive an equation for the positions of lines in the microwave spectrum of $H^{35}Cl$.

(iv) Four consecutive lines in the microwave spectrum of $H^{35}Cl$ are sketched in the following figure.



(α) Calculate the rotational constant of $H^{35}Cl$.

(β) Identify the rotational transitions that produce the four lines in the above diagram

(50 marks)