THE OPEN UNIVERSITY OF SRI LANKA

B.SC. DEGREE/CONTINUING EDUCATION

PROGRAMME – LEVEL 4

FINAL EXAMINATION – 2008/2009

CHU 2124/CHE 4124 - PHYSICAL CHEMISTRY I

DURATION : 2 ½ HOURS.

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Date : 16th January 2008 Time 9.30 a.m. – 12.00 noon

- This question paper consists of six (6) questions, three in **Part A** and three in **Part B.**
- Answer **four questions only**, by 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 non-programmable calculator is permitted.
- Mobile phones are prohibited.
- Log tables will be provided, if requested.

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

PART – A

01. (a) Under what conditions and/or to what type of systems can the following thermodynamically deducible equations apply.

(i) $q = -w = nRT ln\left(\frac{V_2}{V_1}\right)$

(ii) $\Delta S < 0$

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

(iv) $\Delta T = K . m$

(v) $lnT + (\gamma - 1)\ lnV =$ constant

(vi) $\Delta S = \int \frac{Dq_{rev}}{T}$

(vii) $\Delta G = \Delta H - T\Delta S$

(viii) $S = n\ C_{v,m} lnT + nRlnV +$ constant

(40 marks)

(b) (i) State the third law of thermodynamics

(ii) State what thermodynamic property remains unchanged during
(α) a Joule-Thompson Compression?
(β) a reversible expansion?

(iii) Write down a mathematical expression to define the "Joule-Thompson Coefficient (μ_{JT})"

(iv) <u>Define</u> "Thermal Capacity" of a system by writing down a mathematical expression. Clearly indicate the type of system to which this concept applies.

(23 marks)

(c) Complete the Gibbs-Helmholtz equation written in the form.

$$\left[\frac{\partial\left(\Delta G^0 / T\right)}{\partial T}\right]_P =$$

(07 marks)

(d) 50 mol of oxygen gas ($C_{v,m} = \frac{5R}{2}$) at 300K are expanded irreversibly and adiabatically from an initial pressure of 200 atmospheres against a constant external pressure X until the final pressure of the system is X. The final temperature of the system was found to be 275 K.

Calculate
(i) the change in enthalpy, ΔH
(ii) the value of X.

(30 marks)

02. (a) Write down (**no proof required**) the mathematical expressions that can be derived for
(i) the variation of the enthalpy change, ΔH, of a reaction with temperature.
(ii) the variation of the equilibrium constant, K_p of a process with temperature.
(iii) the Gibbs free energy change, ΔG, in the chemical process represented by the balanced expression.

$$\ell C + m D + n E \Leftrightarrow a A$$

where ℓ, m, n represent stoichiometric coefficients for the reactants and a the stoichiometric coefficient for the product. The activities of C,D,E & A are w,x,y & z respectively.

Equilibrium constant for the reaction at the experimental temperature T = K.

(iv) predicting the variation of the vapour pressure of a univarient system with temperature.

(24 marks)

(b) The enthalpy change accompanying the formation of one mole of ammonia, $NH_3(g)$ from its elements at 300K is – 46 kJ.

Assuming ideal gas behaviour, calculate the molar internal energy of formation of ammonia at 300K.

(25 marks)

(c) The Joule-Thompsor Coefficient, μ_{JT}, can be expressed through the equation.

$$\mu_{JT} = -\frac{1}{C_P}\left(\frac{\partial H}{\partial P}\right)_T$$

(i) What can you say about the value of $\left(\frac{\partial H}{\partial P}\right)_T$ for

(α) gaseous sulphur dioxide

(β) gaseous oxygen.

(7 marks)

(ii) The value of μ_{JT} for gaseous sulphur dioxide can be taken as constant at 1.15K atm^{-1} up to 50 atmosphere pressure. Calculate the change of enthalpy, ΔH, that would occur when 50 moles of SO_2 at 25^{0}C and 10 atmosphere pressure are compressed isothermally to 30 atmosphere pressure.

($C_{p,m}$ for SO_2 = 25 J K^{-1}mol^{-1})

(26 marks)

(iii) Use the Clapeyron equation.

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

to establish the fact that the **freezing** of water at its standard melting point takes place with an increase in volume (ΔV)

(18 marks)

03. (a) The vapour pressure of liquid ozone is 16.6 kN m^{-2} at 130K and 166.0 kN m^{-2} at 150K. Calculate the standard boiling point of ozone.

You may state & use any reasonable assumption for your calculation.

(30 marks)

(b) 100 moles of a monatomic ideal gas $\left[C_{v,m} = \frac{3R}{2}\right]$ is heated from 127^{0}C to 427 ^{0}C at constant pressure. Calculate the entropy change ΔS, that occurs during this heating process.

Given that the molar entropy of the gas at 127^{0}C is 100 J K^{-1}mol^{-1}, calculate also the Gibbs free energy change, ΔG, that takes place during the heating process.

(35 marks)

(c) Assuming that the thermodynamic properties **B,L,M, x** and **y** are relevant to a given closed system and that the thermodynamic equation.

$$\mathbf{B = L\ dx - M\ dy}$$

applies to this system,

Write down the corresponding Maxwell type relationship.

(10 marks)

(d) 1000 moles of liquid water is converted into water vapour at its standard boiling point of 373K under one standard atmosphere pressure. The density of water at 373 K can be assumed to be 1000 kg m^{-3} while the water vapour can be assumed to behave as an ideal gas. The enthalpy of vaporization of water at 373K = 40 kJ mol^{-1}.

Calculate the,

(i) change of entropy , ΔS

(ii) change of Gibbs free energy, ΔG

accompanying the process.

(25 marks)

PART – B

4. (a) Write down two effects that lead to a finite (non-zero) width of a peak in an absorption spectrum.

(12 marks)

(b) Write down the following as applied in the IR spectroscopy of a diatomic molecule which behaves as a harmonic oscillator.

(i) gross selection rule and

(ii) the specific selection rule

(18 marks)

(c) (i) Consider a heterogeneous diatomic molecule which behaves as a harmonic oscillator.

(α) Write down an expression for the vibrational energy of the molecule and identify all the terms in it.

(β) Deduce an expression that gives the location of a peak in the IR absorption spectrum of the molecule.

(ii) The strongest peak in the IR absorption spectrum of $^{14}N^{16}O$ is centred at $1876.06\ cm^{-1}$. Stating any assumption/s you make, calculate the following for $^{14}N^{16}O$.

(α) Classical vibration frequency,

(β) Zero point energy

(γ) Force constant of the bond

[Relative atomic masses: $^{14}N = 14$ and $^{16}O = 16$]

(70 marks)

5 (a) List three factors that affect the molar extinction coefficient of a pure substance in solution.

(12 marks)

(b) List two microscopic parameters of a sample of a pure compound that determine the height of an absorption peak of the sample at a particular frequency of radiation.

(08 marks)

(c) (i) Write down an equation relating the number density of photons in a monochromatic beam of radiation to its intensity and identify all the terms in it.

(ii) Starting with the above equation deduce an expression for the number density of photons of a beam of non-monochromatic radiation having photons of frequency ν_1 and ν_2 only. The intensity of the beam is I and the fraction of energy of the beam carried by photons of frequency ν_1 is x.

(iii) A non-monochromatic beam of radiation of intensity 3×10^{-5} W m^{-2} consists of photons of frequencies 5×10^{10} Hz and 6×10^{11} Hz only. One third (1/3) of the energy of the beam is carried by the photons of frequency 6×10^{11} Hz. Calculate the number density of photons in this beam of radiation.

(30 marks)

(d) Liquid A (relative molar mass = 64;boiling point 80 °C) and Water form a fully miscible binary system at all compositions. At standard atmospheric pressure, liquid A and water form a constant boiling mixture (boiling point 120 °C) of composition 64 % by mass of A.

(i) What is meant by "constant boiling mixture"?

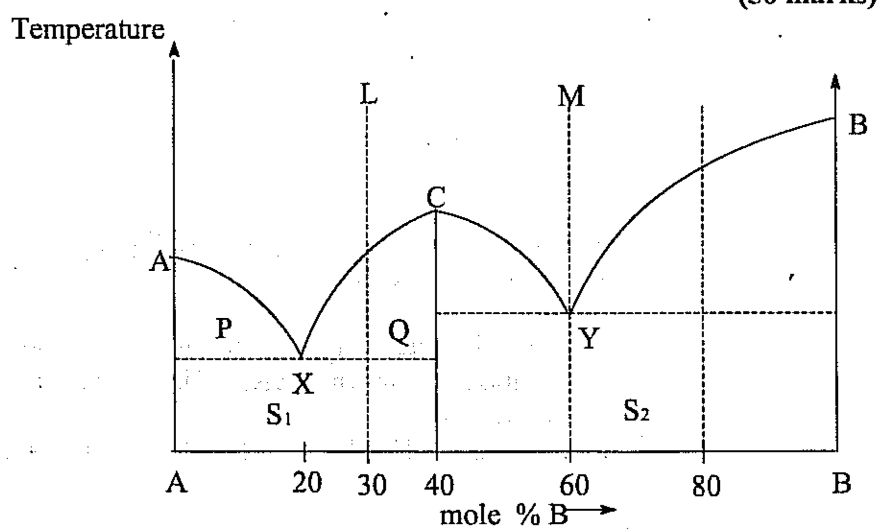
(ii) Sketch and label fully the boiling point / composition phase diagram (composition in terms of **mole fraction of A**) for this system.

(iii) Calculate the mole fraction of A corresponding to the constant boiling composition.

(iv) Explain the outcome of fractional distillation of an equimolar mixture of A and water.

(50 marks)

6.



(a) The **Temperature vs Composition** phase diagram given above corresponds to that of a system consisting of two metals, A and B

(i) Identify, clearly, the regions/points represented by all the symbols (A, B, -----etc) in the above diagram.

(ii) Sketch the cooling curves corresponding to

(α) a melt corresponding to the composition at C

(β) a melt corresponding to the composition at L

(γ) a melt corresponding to the composition at M

Explain the shape of the cooling curves that you have drawn in (β) and (γ) in terms of the phase rule.

(50 marks)

(b) (i) Derive the expression $P = X_B (P^o_B - P^o_A) + P^o_A$ which represents the total vapor pressure (P) of an ideal binary system comprising two liquids A and B. [standard notations have been used; marks will be awarded for writing down all relevant mathematical expressions in the above derivation].

(ii) Two liquids, 46.0 g of methylbenzene and 80.0 g of a compound C, were mixed together at room temperature. The vapour pressures of pure methylbenzene and pure C at this temperature are 50 torr and 30 torr respectively. If the total vapour pressure of the mixture is 42 torr,

(I) calculate the molar mass of C (in g mol^{-1}) and,

(II) calculate, the vapour composition corresponding to the above mixture at room temperature.

(Assume ideal behaviour and total miscibility under all compositions)

(iii) "A binary system consisting of the liquid M / liquid N shows negative deviation from Raoult's law."

Explain this statement with the aid of the relevant "Pressure vs Composition" graph which also includes the one corresponding to an ideal system.

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

(50 marks)

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