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THE OPEN UNIVERSITY OF SRI LANKA

B. Sc. Degree /Continuing Education Programme — Level 4

Final Examination — 2009/2010

CHU 2124/CHE 4124 — Physical Chemistry I

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

18th January 2010 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**; switch them off and leave them outside.
- Log tables and graph papers will be provided on request

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 = $10^{5} \ \mathrm{Pa}\left(\mathrm{N m^{-2}}\right)$

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Part A

1. Answer all the following parts, **(a) to (h)**

(a) Starting from the first law of thermodynamics, deduce a relationship that exists between the heat energy exchanged, q_p, and the change in enthalpy, ΔH, in an isobaric system

(State clearly any reasonable assumption/s that you need to make)

(20 marks)

(b) **Write down** the second law of thermodynamics in a mathematical form based on the entropy change that takes place in the **universe.**

(10 marks)

(c) Under what conditions will the following thermodynamic relationships apply:

(i) $dS = \frac{dq}{T}$ (ii) $dS = \frac{dq_{rev}}{T}$

(12 marks)

(d) **Define** "Thermal Capacity (C)" of a substance using a mathematical relationship. Under what conditions can the concept of thermal capacity be used?

(12 marks)

(e) Comment **briefly** on the statement "Endothermic processes are not always unnatural (non spontaneous) processes".

(12 marks)

(f) **Write down** the thermodynamic property which remains unchanged in a Joule-Thompson expansion.

(06 marks)

(g) **Define** "chemical potential (μ_i)" using a mathematical expression.

(08 marks)

(h) **Write down** (no proof required) a thermodynamic expression for the Gibbs free energy change, ΔG, for the process

$$pX + qY + rZ \rightleftarrows aC + bD$$

in the gaseous phase at a temperature ***J*** at the time when the partial pressures of ***X, Y, Z, C*** and ***D***, are *e, f, g, h, and i* respectively.

(equilibrium constant for the process at temperature ***J*** = ***L***; gas constant = R)

State any reasonable assumption/s you make.
Your answer should **not** include any symbol or quantity not included above.

(20 marks)

2 (a) Under what conditions, and to what type of systems can the following thermodynamically deducible equations apply

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

(ii) $\ln T + (\gamma - 1)\ln V = \text{constant}$

(iii) $\Delta S = nR\ln\left(\frac{P_1}{P_2}\right) + nC_{P,m}\ln\left(\frac{T_2}{T_1}\right)$

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

(v) $3H - G - 2U = 2PV + TS$

(vi) $\Delta S = \frac{\Delta H}{T}$

(vii) $\Delta G > 0$

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

(ix) $dA = -PdV - SdT$

(x) $dU = n\, C_{V,m}\, dT$

(40 marks)

(b) Attempt all the following parts, (i) - (iii). However, full marks will be given to those candidates scoring about 60 out of the allotted 80 marks. Pro-rata marks will be given to other candidates.

(i) 10^5 mol of a diatomic gas $[C_{v,,m} = (5R)/2]$ at 727 °C undergo a change of temperature to 227 °C by being subjected to a reversible adiabatic process. Final volume of the gas is 10^6 dm^3. Calculate

(α) the change in enthalpy, ΔH.

(β) the change in entropy, ΔS.

(γ) the initial volume of the gas.

If the initial molar entropy of the gas is 50 J mol^{-1} K^{-1} at 727 °C, calculate also the change in Gibbs Free Energy, ΔG, accompanying the process

(40 marks)

(ii) Define using a **mathematical** expression, the Joule Thompson Coefficient $(\mu_{J,T})$.

A gas has an upper inversion temperature of 200 °C and a lower inversion temperature of 20 °C. What can you qualitatively deduce about the values of the Joule Thompson Coefficient $(\mu_{J,T})$ at

(α) 35 °C

(β) 1000 °C

under standard atmospheric pressure. You are advised to draw an appropriate diagram in support of your answer.

(20 marks)

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

$C_4H_9COOH(l)$ = -500; $CO_2(g)$ = - 400 ;

Given that the standard enthalpy of combustion of $C_4H_9COOH(l)$ at 300 K is 3500 kJ mol^{-1}, calculate the standard enthalpy of dissociation of water according to the equation

$$2H_2O(l) \dashrightarrow 2H_2(g) + O_2(g)$$

(20 marks)

3. Attempt all the following parts, **(a) – (d)**. However, full marks for this question will be given to those who score 100 out of the allotted 124 marks.

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

(i) the variation of the standard enthalpy change, ΔH^o, of a reaction with temperature at a given pressure.

(ii) the variation of the equilibrium constant, K_P, of a reaction with temperature T written in the form

$$\left(\frac{\partial \ln K_P}{\partial T}\right)_P =$$

(iii) the variation of the vapour pressure of a univariant system with temperature.

(iv) the variation of the Gibbs free energy of a reaction with temperature and known as the Gibbs – Helmholtz equation.

(24 marks)

(b) The temperature dependence of the vapour pressure of the solid and liquid forms of a given compound X are given respectively by the equations

$$\log_{10} \mathrm{P/torr} \;=\; 12 \;-\frac{2500}{T/K} \quad \text{(solid)}$$

$$\log_{10} \mathrm{P/torr} \;=\; 6 \;-\frac{1800}{T/K} \quad \text{(liquid)}$$

(i) What do you understand by "the triple point of X"?

(ii) Deduce the temperature corresponding to the triple point of X.

(iii) Calculate the enthalpy of vaporization of X.

Indicate clearly any reasonable assumption/s that you make.

(40 marks)

(c) The thermodynamic properties **C, L, M, E, X** and **Y** are relevant to a given thermodynamic system for which the following thermodynamic expressions apply:

$$\mathbf{dC} = -\,\mathbf{MdY} \;-\; \mathbf{XdL}$$
$$\mathbf{dE} = \;\mathbf{YdM} \;-\; \mathbf{XdL}$$

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

(ii) Show that $\mathbf{X} = \mathbf{Y}\left(\frac{\partial X}{\partial Y}\right)_L - \left(\frac{\partial E}{\partial L}\right)_Y$

(iii) If **XL** = **ZQY**, where **Z** and **Q** are constants, show that $\left(\frac{\partial E}{\partial L}\right)_Y = 0$

(30 marks)

(d) The standard molar enthalpy of formation , ΔH^o_f, for the reaction

$$N_2(g) + O_2(g) \text{ -----> } 2NO(g)$$

is 100 kJ mol^{-1}. Standard molar entropies, S°, of the relevant gases are given below.

Gas	S^o / J K^{-1} mol^{-1}
$N_2(g)$	190
$O_2(g)$	200
NO(g)	210

(i) Calculate the standard entropy of formation, ΔS^o_f, for the reaction.

(ii) Predict the temperature above which the above reaction will become spontaneous under standard conditions. (You could assume that ΔH^o_f and ΔS^o_f are independent of the temperature)

(30 marks)

Part B

4. (a) Define the following as applied in molecular spectroscopy.
   - (i) Number density of photons in a beam of radiation
   - (ii) Absorption spectrum
   - (iii) Transmittance of a sample

(12 marks)

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

(09 marks)

(c) (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 25^0C. 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 25^0C is 66.0 dm^3 mol^{-1} cm^{-1}.

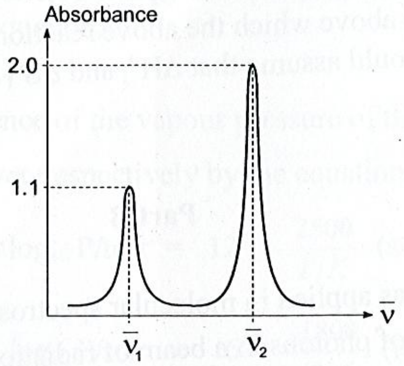
(α) Calculate the absorbance of the solution in the sample cell for radiation of frequency, 4.5×10^2 Hz at 25^0C. State assumption/s, if any, you make in this calculation.

(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.

(γ) Using the results of the above calculations, calculate the rate of absorption of radiation energy by the sample if the cross sectional area of the sample, perpendicular to the beam, is 1.0 cm^2.

(50 marks)

(d) 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 $E_1 = 1.00\times10^{-20}$ J. State assumption/s, if any, you make in this calculation.

(29 marks)

5. (a) What is meant by "an intensive variable"? Give two examples.

(10 marks)

(b) Sketch a clearly labeled "Temperature (boiling point) vs Composition" phase diagram for an ideal binary mixture of two liquids.

(12 marks)

(c) The pure vapour pressures (P^o) of Benzene and Toluene have the following values in the temperature range between their two boiling points and at a pressure of one (1) bar. Toluene and Benzene are assumed to form an ideal binary mixture at all compositions.

T/°C(Boiling Point)	80	90	95	100	110
P^o(benzene)/bar	1.00	1.30	1.50	1.80	-
P^o(toluene)/bar	-	0.50	0.60	0.75	1.00

(i) **Calculate** (where relevant) the compositions of the vapour and liquid phases in terms of the mole fraction of Benzene (**X_B** in the liquid phase; **Y_B** in the vapour phase) at each of the above temperatures (Hint: The total pressure is always equal to 1 bar).

(ii) **Generate** the relevant table of values required to plot the "Boiling point vs Composition" phase diagram.

(iii) Given that $X_B = 0.1$ and $Y_B = 0.19$ when the boiling point of the mixture is 105 °C, determine the corresponding vapour pressures of pure benzene and pure toluene at this temperature.

(45 marks)

(d) (i) What is meant by **"eutectic composition"** with respect to a binary system?

(ii) The phase diagram for Mg-Cu at constant pressure shows that two compounds are formed: $MgCu_2$ which melts at 800 °C and Mg_2Cu which melts at 600 °C. Considering the composition in terms of mole % Mg, three eutectics are observed at 20% (700 °C), 60% (550 °C) and 80% (400 °C). The melting point of pure Cu is 1100 °C and that of Mg is 650 °C. Sketch the phase diagram for this system and label all regions/points clearly.
(rel. atomic masses: Mg = 24.0; Cu = 63.5)

(33 marks)

6 (a) Write down a relationship between the number of photons crossing a unit area, placed perpendicular to a beam of monochromatic radiation, in unit time and the intensity of the beam and, identify all the parameters in it.

(10 marks)

(b) A student obtained a (parallel) beam of radiation by merging two monochromatic (parallel) beams of radiation, X and Y, of frequencies 3.50×10^{12} Hz and 8.30×10^{12} Hz, respectively. The intensity of the resultant, non-monochromatic, beam was found to be 4.10×10^{-5} W m^{-2}. In beam X, he found the number of photons crossing a unit area, placed perpendicular to the beam, in one second to be 6.18×10^{15}. Calculate the number of photons crossing a unit area, placed perpendicular to the beam, in one second in beam Y.

(40 marks)

(c) A solution is made by mixing 4.0 g of **C** [relative molar mass = 40] and 100.0 ml of **D** (Density = 900 kg m^{-3} and relative molar mass = 60).
(i) Calculate the mole fraction of **C.**
(ii) Identify the solute and the solvent in the above solution; explain your choice.

(15 marks)

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

(ii) When 20.0 g of **A** and 30.0 g of **B** are mixed, two layers, labeled as **p** and **q**, are formed. The layer **p** contains 20 % of **A** by weight while the layer **q** contains 70% of A by weight.
Calculate the weight of **A** in the layer **p**.

(35 marks)