00116

The Open University of Sri Lanka
B. Sc. Degree /Continuing Education Programme — Level 4
Final Examination — 2012/2013
CHU 2124/CHE 4124 — Physical Chemistry I

2 hours

26th July 2013	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)	=	$8.314\ \text{J}\,\text{K}^{-1}\text{mol}^{-1}$
Avogadro constant (N_A)	=	$6.023\times10^{23}\ \text{mol}^{-1}$
Faraday constant (F)	=	$96{,}500\ \text{C}\,\text{mol}^{-1}$
Planck's constant (h)	=	$6.63\times10^{-34}\ \text{J}\,\text{s}$
Velocity of light (c)	=	$3.0\times10^{8}\ \text{m}\,\text{s}^{-1}$
Protonic charge (e)	=	$1.602\times10^{-19}\ \text{C}$
Standard atmospheric pressure	=	$10^{5}\ \text{Pa}\left(\text{N}\,\text{m}^{-2}\right)$

Part A

1.(a) (i) Starting from the first law of Thermodynamics, derive the following Gibbs relationship applicable to reversible processes in closed systems where only PV work is possible.

$$dG = VdP - SdT$$

(ii) Write down the Maxwell relationship corresponding to the above Gibbs relationship

(iii) Write down the variation of the Gibbs free energy of a reaction with temperature, known as Gibbs – Helmholtz equation.

(50)

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

$$\ln K = 20.00 - [750/T/K].$$

Calculate ΔG° for this reaction at 57°C. (20)

12

(c) For a reaction at 500K, $\Delta H^o < 0$ and $\Delta S^o > 0$.
Deduce whether at 500K,
(i) the reaction will occur spontaneously under atmospheric pressure
(ii) K is less than 1

(30)

2 . (a) (i) Define the term "Joule-Thompson Coefficient (μ_{JT})" using a mathematical expression
(ii) Define "thermal capacity" of a system by writing down a mathematical expression. Clearly indicate the type of system to which this is applicable.

(20)

(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.

(20)

(c) 10^5 moles of nitrogen ($C_{p,m} = 7R/2$) occupying a volume of 100 dm^3 at a temperature of 627 °C (state X) undergo a change of temperature to 127 °C (state Y) by being subjected to a reversible adiabatic expansion.
Calculate
(i) change in internal energy, ΔU
(ii) Change in entropy, ΔS

(20)

(d) Under what conditions and/or to what type of systems can the following thermodynamically deducible expressions apply.
(i) $(1-\gamma)\ln P + \gamma \ln T = constant$
(ii) $\Delta S \leq 0$
(iii) $\Delta G = \Delta H - T\Delta S$
(iv) $\Delta T = K.m$
(v) $\Delta S = \dfrac{\Delta H}{T}$

(40)

2. (a) The standard enthalpy of formation ΔH_f^o for the reaction
$N_{2(g)} + O_{2(g)} \rightarrow 2NO_{(g)}$ is 90 kJ mol^{-1}. Standard molar entropies of the three gases in J K^{-1} mol^{-1} are given below;

$N_{2(g)} = 190$; $O_{2(g)} = 200$; $NO_{(g)} = 210$

(i) Calculate the standard entropy of formation for the reaction.
(ii) Predict the temperature at which the above reaction will become spontaneous under standard conditions. Assume that ΔH^o and ΔS^o are independent of temperature.

(40)

(b) Write down (no proof required) the equations representing the variation of vapour Pressure with temperature for,
(i) Any univariant system involving two phases
(ii) Any univariant system involving two phases, where one phase is an ideal gas

(iii) The vapour pressures of sulphur dioxide, in equilibrium with solid and liquid phases, are given by the equations;

$$\ln P\ (\text{solid})/\text{Pa} = 29.28 - 4308\ \text{K}/T$$
$$\ln P\ (\text{liquid})/\text{Pa} = 24.05 - 3284\ \text{K}/T$$

where T is the thermodynamic temperature. Calculate ,

(i) the temperature and pressure of the triple point of sulphur dioxide.

(ii) the enthalpy and the entropy of sublimation of sulphur dioxide at the triple point.

(60)

Part B

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

(i) Raoults Law (ii) Phase rule (16)

(b) 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 A in the liquid phase is 0.25, the vapour pressure of the system is 3.0×10^5 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)

(c) The normal boiling points of pure liquids, X and Y, respectively, are 160 °C and 200 °C. An equi-molar mixture of X and Y 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.

(iii) With the aid of the above sketch, briefly outline the result of carrying out fractional distillation corresponding to a composition of a mixture where the mole fraction of X = 0.25

(48)

5. (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 the 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)

(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)

(c) (i) Write down the relationship between (frequency or wave number) separation between adjacent lines in the microwave spectrum of a diatomic molecule and the rotational constant, B.

(ii) Write down the relationship between the bond length and B and identify all the parameters in it.

(iii) Two consecutive lines in the microwave spectrum of a gaseous diatomic molecule PQ appears at $75.624\ \text{cm}^{-1}$ and $100.832\ \text{cm}^{-1}$. What is the bond length, P–Q, if PQ behaves as a rigid rotor.?
[Relative atomic masses: P = 27.00, Q = 1.00]

(60)

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)

(b) A student obtained a (parallel) beam of radiation by merging two monochromatic (parallel) beams of radiation, X and Y, of frequencies $3.50\times10^{12}\,\text{Hz}$ and $8.30\times10^{12}\,\text{Hz}$, respectively. The intensity of the resultant, non-monochromatic, beam was found to be $4.10\times10^{-5}\,\text{W m}^{-2}$. 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)

(c) 4.6 g of formic acid is mixed with 50.00 ml of pure ethanol (density = $9.0\ \text{x}10^5\ \text{g m}^{-3}$)

(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)

(d) Metal A (M.Pt = 600 °C) and Metal B (M.Pt = 1200 °C) form a simple eutectic system at elevated temperatures with a eutectic composition at a temperature of 300 °C. The eutectic composition is given in terms of mole fraction of A (x_A) where $x_A = 0.4$

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

(ii) Sketch a cooling curve corresponding to an equimolar mixture of A and B; identify important phase changes occurring during the cooling process.

(35)