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# THE OPEN UNIVERSITY OF SRI LANKA

**B. Sc. Degree /Continuing Education Programme — Level 4**
**Final Examination — 2010/2011**
**CHU 2124/CHE 4124 — Physical Chemistry I**

2 hours

| 6th January 2011 | 1.00 p.m. — 3.00 p.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 $(N_A)$ | = | $6.023\times10^{23}\ \mathrm{mol^{-1}}$ |
| 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 | = | $10^{5}\ \mathrm{Pa}\left(\mathrm{N\,m^{-2}}\right)$ |

## Part A

1 (a) Write down the mathematical form of the second law of thermodynamics based on the entropy change that takes place in an experimental **system**.
**Deduce** the second law based on the entropy change that concurrently takes place in the **universe.**

(14 marks)

(b) State, in a mathematical form, the third law of thermodynamics

(08 marks)

(c) Write down the mathematical expressions that **define**
(i) chemical potential ($\mu_i$)
(ii) the Joule – Thompson coefficient ($\mu_{JT}$)

(14 marks)

(d) Deduce the Maxwell relationship that can be obtained from the thermodynamic expression
$d\mathbf{B} = \mathrm{M}d\mathbf{Y} - \mathrm{L}d\mathbf{X}$
where **B, L, M, X** and **Y** are all thermodynamic properties

(16 marks)

(e) Under what conditions and/or to what kind of systems can the following thermodynamically deducible equations apply?

(i) $S - nR\ln P + n\,C_{P,m}\ln T = \text{constant}$

(ii) $\Delta G < 0$

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

(iv) $(1-\gamma)\ln P + \gamma\ln T = \text{constant}$

(32 marks)

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

(i) the standard free energy change, $\Delta G^o$, 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 $T_2$.

(16 marks)

2. (a) (i) The freezing point depression $\Delta T$ for a dilute solution (of an involatile solute in a volatile solvent) is given by an expression of the type

$$\Delta T = \frac{RT_o^2 Y}{X}$$

where R is the gas constant and $T_o$ is the freezing point of the solvent.
Identify the terms Y and X.

(16 marks)

(ii) Pure benzene (relative molecular mass = 78) freezes at 5.80 °C. A solution of 0.23 g of phenyl acetic acid ($C_6H_5CH_2COOH$) in 4.4 g of benzene freezes at 4.87 °C. The enthalpy of fusion of benzene is 9.9 kJ $mol^{-1}$.

Use the above data to calculate the (apparent) relative molecular mass of phenyl acetic acid.

(36 marks)

(iii) The (theoretical) relative molecular mass of phenyl acetic acid is 136. How can you account for the apparent calculated value in (ii) above being different from the theoretical value?

(16 marks)

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

$$\ln K = 20.00 - \left[\frac{750}{T/K}\right]$$

Calculate $\Delta G°$ for this reaction at 57 °C.

(32 marks)

3. (a) In a pressure flask at 27 °C, there is 100 moles of a gas (assumed to behave ideally) which could be any one of the four gases; neon, oxygen, carbon dioxide, sulphur dioxide.

When this gas was expanded adiabatically from 3 to 4 $dm^3$, the maximum decrease of temperature that could be obtained was 27.4 °C.

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

(ii) Use the value of $\gamma$ from (i) to identify which one of the four gases are present.

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

(65 marks)

(b) The vapour pressure of a liquid at various temperatures are given in the following table.

| Temperature/°C | 25 | 45 | 65 |
|---|---|---|---|
| Vapour Pressure/$10^5$ N $m^{-2}$ | 0.195 | 0.429 | 0.837 |

Calculate, as accurately as possible, the mean molar enthalpy of vapourisation of the liquid, $\Delta H_m$, in the given temperature range. State the assumptions you have made during the above calculation.

(35 marks)

## Part B

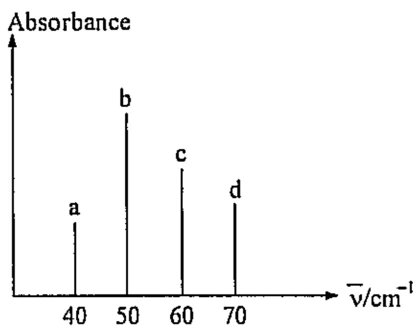
4. (a) Assume that a molecule of $H^{35}Cl$ behaves as a rigid rotor as far as its rotational motion is considered.

(i) Write down a mathematical relationship between the rotational energy of a $H^{35}Cl$ molecule and its rotational constant and identify all the parameters in it.

(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)

(b) Assume that a molecule of $H^{35}Cl$ behaves as a harmonic oscillator as far as its vibrational motion is considered.

(i) Write down a mathematical relationship between the vibration energy of a $H^{35}Cl$ molecule and its equilibrium vibration frequency and identify all the parameters in it.

(ii) Write down a mathematical relationship between the force constant of a $H^{35}Cl$ molecule and its equilibrium vibration frequency and identify all the parameters in it.

(iii) What is the specific selection rule in the vibrational spectroscopy of $H^{35}Cl$.

(iv) Starting with the equation for the vibrational energy level derive an expression for the position of line/s in the IR spectrum of $H^{35}Cl$.

(v) How many lines are there in the IR spectrum of $H^{35}Cl$?

(vi) Calculate the position of line/s in the IR spectrum of $H^{35}Cl$ if the force constant of the H-Cl bond is $516.0\ N\ m^{-1}$. Relative atomic masses: $H = 1$ and $^{35}Cl = 35$.

(50 marks)

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5. (a) 4.5 g of water is mixed with 92.0 g of pure ethanol (density = $9.0 \times 10^5$ g $m^{-3}$)

(relative atomic masses : H =1.0; O = 16.0; C= 12.0)

(i) Identify the solvent and the solute in the above system.

(ii) Calculate the mole fraction of the solvent.

(20 marks)

(b) (i) Write down the Clausius – Clapeyron expression that relates vapour pressure to the boiling point
(ii) The boiling point of n-Hexane at Pressure of 1 atm. is 69 °C. Given that the enthalpy of vapourisation is 30 kJ $mol^{-1}$, calculate its vapour pressure (in N $m^{-2}$) at 50 °C

(25 marks)

(c) Two liquids, 46.0 g of toluene and 80.0 g of a compound X, were mixed together at 25 $^{O}$C. The vapour pressures of pure toluene and pure X at this temperature are reported as 50 torr and 30 torr respectively. The total vapour pressure of the mixture is found to be 40 torr.
By writing down the relevant mathematical expressions, calculate the molar mass of X (in g $mol^{-1}$).
[Assume that this mixture behaves as an ideal solution; molar mass of toluene = 92.0 g $mol^{-1}$]

(25 marks)

(d) At standard atmospheric pressure, a liquid A [relative atomic mass 32 and boiling point 75 °C] and water form a constant boiling mixture (boiling point 120 °C) of composition 64 % by mass of A. This is a fully miscible system at all compositions. (H=1.0; O = 16.0)

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

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

(30 marks)

6 (a) A student collected a steam distillate at 98 °C and 760 torr pressure. This distillate contains water (B) and a compound A (of relative molar mass 90) which are immiscible at 98 °C. At this temperature, the vapour pressure of water is 720 torr and that of A is 40 torr above the respective liquid phases. Using the expression given below (where the symbols used have their standard meanings) or otherwise, calculate the weights of water and A that are expected to separate out when the total weight of the distillate is 115 g. (Assume that the amount of A and/or B in the gas phase is negligible)

$$\frac{W_A}{W_B} = \frac{M_A P_A^o}{M_B P_B^o}$$

(20 marks)

(b) It is found that a metal A (Melting Point = 500 °C) and metal B (Melting Point = 1000 °C) forms a compound, $AB_2$, with a congruent Melting Point of 750 °C Two eutectics, whose compositions are given as $X_B = 0.2$ and $X_B = 0.8$, are formed with the Melting Points at 250 °C, and 350 °C respectively ($X_B$ = mole fraction of B)

(i) Sketch a clearly labeled phase diagrams (identify all regions) based on the above data.

(ii) Sketch cooling curves corresponding to a melt of composition $X_B = 0.2$ and $X_B = 0.5$

(30 marks)

(c) (i) Write down a mathematical equation relating the number of photons crossing a unit area (perpendicular to the direction of propagation) in unit time in a beam of electromagnetic radiation to its intensity and identify all the parameters in it.

(ii) The intensity of a beam of light of wavelength $20\ \text{nm}$ is $3.4 \times 10^5\ \text{W m}^{-2}$. Calculate the number of photons crossing an area (perpendicular to the direction of propagation of the beam) of $2\ \text{cm}^2$ in $3\ \text{s}$.

(18 marks)

(d) (i) Write down Beer – Lambert law in equation form and identify all the parameters in it.

(ii) Define an absorption spectrum of a chemical compound in a solution.

(iii) Using Beer – Lambert law briefly describe how an absorption spectrum originates.

(iv) Two compounds, X and Y, do not react with each other and dissolve in a solvent Z. A student prepared a solution of X in Z of concentration $0.03\ \text{mol dm}^{-3}$. In a spectroscopic experiment this solution showed an absorbance of 2 in a sample cell of path length $1.00\ \text{cm}$ with radiation of wavelength $770\ \mu\text{m}$. He then dissolved some Y in the above mentioned solution so that the concentration of Y in the solution was $0.05\ \text{mol dm}^{-3}$. Calculate the absorbance of the solution of X and Y in the same sample cell with the same radiation at $25^0\text{C}$. The molar extinction coefficient of Y in Z at wavelength $770\ \mu\text{m}$ at $25^0\text{C}$ is $50.00\ \text{dm}^3\ \text{mol}^{-1}\ \text{cm}^{-1}$.

(32 marks)