



UNIVERSITY OF KELANIYA - SRI LANKA
FACULTY OF SCIENCE

Bachelor of Science General Degree Examination – November 2023

Academic Year 2021/2022 – Semester I

CHEM 21682 & CHEM 21512 (Repeat) – Basic Physical Chemistry II

Number of Questions: Four (04)

Time: Two (02) hours

Number of pages: Four (04)

Answer all questions.

Planck's constant (h)	=	$6.626 \times 10^{-34} \text{ J s}$
Speed of light (c)	=	$2.98 \times 10^8 \text{ m s}^{-1}$
Charge of an electron (e)	=	$1.602 \times 10^{-19} \text{ C}$
Mass of an electron (m_e)	=	$9.11 \times 10^{-31} \text{ kg}$
Avogadro's number (L)	=	$6.022 \times 10^{23} \text{ mol}^{-1}$
Universal gas constant (R)	=	$8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
Permittivity of free space (ϵ_0)	=	$8.84 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$
Boltzmann constant (K)	=	$1.3806488 \times 10^{-23} \text{ J K}^{-1}$
1 atm	=	$1.01 \times 10^5 \text{ N m}^{-2} = 760 \text{ mmHg} = 760 \text{ Torr}$

1. (a) (i) Using only one diagram illustrate the electronic, rotational, and vibrational energy levels of a diatomic molecule.
(ii) List the different regions of the electromagnetic spectrum and state the type of molecular transitions that occur in each region.
(10 marks)
- (b) Explain the occurrence of Lyman, Balmer and Paschen series in the atomic spectrum using the selection rules which govern the transition of electrons between energy levels of hydrogenic atoms.
(10 marks)
- (c) Sketch and name the normal modes of vibrations of CO_2 and SO_2 molecules and identify the IR active modes of each.
(20 marks)
- (d) The fundamental and first two overtones in the vibrational spectrum of the OH radical occur at 3569.8 , 6974.6 , and 10217.8 cm^{-1} , respectively
Find the equilibrium vibrational frequency of OH radical and the anharmonicity constant.
Derive values for the force constant and zero-point energy of the OH radical.
[H = 1.008 amu , O = 15.999 amu]
(40 marks)

- (c) (i) What is Russel-Saunders's coupling (L-S coupling)?
 (ii) Determine the atomic term symbols arising due to $3s^1 3p^1$ electron configuration. (20 marks)

2. (a) Rotational absorption lines of $^1\text{H}^{35}\text{Cl}$ gas were found at the following wavenumbers (cm^{-1}) 83.32, 104.13, 124.73, 145.37, 165.89, 186.23, 206.60, and 226.86. Calculate the moment of inertia and the bond length of the molecule. [H = 1.0078 amu, Cl = 34.9688 amu] (35 marks)

- (b) For the following subshells give the values of the quantum numbers (n , l and m_l) and the number of orbitals in each subshell.
 (i) $2p$ (ii) $3d$ (iii) $4f$ (10 marks)

- (c) State the key differences between physisorption and chemisorption processes. (10 marks)

- (d) The data below are for the chemisorption of hydrogen on copper at 25°C (V is the volume of gas corresponding to the standard temperature and pressure).

P/Torr	0.19	0.97	1.90	4.05	7.50	11.95
V/ cm^3	0.042	0.163	0.221	0.321	0.441	0.471

- (i) Confirm that the above data fit the Langmuir Isotherm. (20 marks)
 (ii) Calculate the value of Langmuir constant (K) and adsorption volume corresponding to complete monolayer coverage (V_∞). (10 marks)
 (e) Considering colloidal systems explain the followings,
 (i) the sky and the sea look blue in colour?
 (ii) the formation of river delta
 (iii) the electro-dialysis process used in purification of blood of kidney patients. (15marks)

3. The wave function (Ψ) for a particle in one-dimensional infinite potential box ($V = 0$ for $0 \leq x \leq L$, and infinite elsewhere) is given by $\Psi = A \sin kx + B \cos kx$, where A and B are constants and k is related to the energy (E) of the particle by $k = \sqrt{\frac{2mE}{\hbar^2}}$. If the mass of the particle is ' m ', and $\hbar = \frac{h}{2\pi}$ where h is the Planck constant,

(a) obtain expressions for A , B , and k in terms of the width of the box L . You may use the boundary conditions and the normalization condition. Hence, write expressions for the energy (E) and the wave function (Ψ) in terms of L .

(20 marks)

(b). (i). Write expressions for energy (E), wave function (Ψ) and the probability density (P) separately for a particle in the first three lowest energy states.

(ii). Draw separate diagrams showing the variations of the wave functions and the probability densities with x for the first three lowest energy states.

(30 marks)

(c). (i). If the potential box is 3-dimensional with each side L , write the expression for the energy of a particle in the state represented by n_x , n_y and n_z . **Derivation is not required.**

($V = 0$ for $0 \leq x \leq L, 0 \leq y \leq L, 0 \leq z \leq L$, and infinite elsewhere)

(10 marks)

(ii). Write the expression for the energy of the particle in the first excited state.

(iii). What is the degeneracy of the first excited state?

(iv). Write the wave functions correspond to the degenerate states.

(40 marks)

4. (a). (i). Using the harmonic oscillator model, show that for a particle vibrating in one dimension, the energy required to excite the particle to a neighbouring energy level does not depend on the energy levels between which the transition takes place.

(ii). For a harmonic oscillator consisting of a particle of mass 1.33×10^{-25} kg, the difference in adjacent energy levels is 4.82×10^{-21} J. Calculate the force constant of the oscillator.

(35 marks)

(b) (i) Starting from $dG = -SdT + VdP$ relation, derive the Clapeyron equation for the

solid \rightleftharpoons liquid equilibrium.

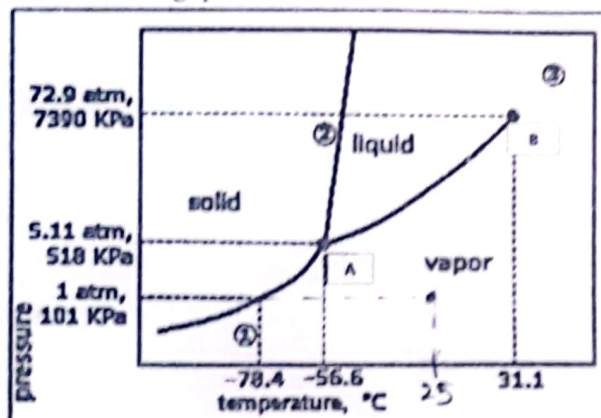
(10 marks)

- (ii) Molar volume of a certain solid is $142.0 \text{ cm}^3/\text{mol}$ at 1.00 atm and the melting temperature is 427 K at this pressure. When pressure is 1.2 MPa the molar volume changed to $152 \text{ cm}^3/\text{mol}$ while the melting point changes to 440 K . Calculate the enthalpy change associated with it using the approximation to the Clapeyron equation below.

$$P_2 - P_1 = \frac{\Delta H}{\Delta V_m} \ln \frac{T_2}{T_1}$$

(10 marks)

- (c) Considering the diagram phase diagram of a pure substance A given below, answer to the question following questions.



- (i) Label points A and B.

(05 marks)

- (ii) Identify the stable phase of the substance A at 1 atm pressure and room temperature of 25°C and state the phase transition occur at 1 atm pressure.

(10 marks)

- (iii) State Gibbs Phase rule and define all terms.

(10 marks)

- (iv) Apply phase rule to following to find the degree of freedom

- (I) line 2 on the melting point curve
- (II) point A

(10 marks)

- (d) Sketch a phase diagram of a High boiling azeotropic solution of a binary mixtures.

(10 marks)