

B.Sc. Chemistry Sem III Assignment (2024-25)

Paper: Physical Chemistry

- ❖ **This assignment is common to both Major and Minor students**
- ❖ **Use fair register to answer all the questions**

Mathematical Concepts and Computers:

Q 1. Write short notes on the following topics with examples where required:

Logarithmic relations, curve sketching, equations of straight lines and slopes, tracing of curves, differentiation of simple functions such as x , e^x , x^n , $\sin x$, $\log x$; maxima and minima, partial differentiation, integration of some useful functions, permutations and combinations, factorials and probability.

Q 2. Discuss binary number and their arithmetic operations with examples.

Gaseous State:

Q 1. Starting from postulates of kinetic theory of gases, derive the kinetic gas equation

$$PV = mN\bar{u}^2/3$$

Deduce the following gas laws from the kinetic gas equation

(i) Boyle's law; (ii) Charles law; (iii) Grahams law of effusion, and (iv) Avogadro's hypothesis

Q 2. (a) Explain the factors which led van der Waals to modify the ideal gas equation $PV=nRT$, and hence derive the van der Waals equation of state

$$(P + n^2a/V^2)(V-nb)=nRT$$

(i) What are the units of van der Waals constants a and b ? (ii) Do these constants depend upon temperature of the gas? (iii) From the given value of b for a real gas, how would you estimate the molecular diameter of a molecule of a given gas? (iv) Explain how the van der Waals equation of state accounts for the behaviour of real gases.

(b) Using the van der Waals equation, calculate the pressure exerted by 20.0 g of carbon dioxide in 1 dm³ vessel at 25 °C and compare this with the ideal gas value.

- Q 3.** (a) What is the virial equation of state? Express the following equations of states in the form of virial equation of state;
- (i) Van der Waals equation $(P + a/V_m^2)(V_m - b) = RT$
 - (ii) Berthelot's equation $(P + a/TV_m^2)(V_m - b) = RT$
 - (iii) Dieterici's equation $P\{\exp(a/V_m RT)\} (V_m - b) = RT$
- (b) Derive expressions for the second virial coefficient of the above equations of states.
- (c) What do you understand by the term 'compression factor Z' of a gas?
- Q 4.** (a) What is Boyle temperature? Show that at this temperature the second virial coefficient is zero. From this condition, calculate the value of Boyle temperature for van der Waals, Berthelot's and Dieterici's equations of states.
- (b) Explain why at Boyle temperature the van der Waals gases behave ideally over a wide range of pressures. Also explain why the initial slope of the compression factor $Z (= PV/RT)$ versus p curves is (i) positive if a gas is above its Boyle temperature, and (ii) negative if it is below its Boyle temperature.
- Q 5.** (a) Differentiate between the Andrew's isotherms and the van der Waals isotherms for carbon dioxide.
- (b) Define the terms critical temperature, critical pressure and critical volume. How are these quantities determined experimentally?
- (c) The van der Waals constants for HCl are $a = 371.843 \text{ kPa dm}^3 \text{ mol}^{-2}$ & $b = 40.8 \text{ cm}^3 \text{ mol}^{-1}$. Find the critical constants of this substance.
- Q 6.** What is the law of corresponding states? Derive the reduced equation of state for (i) van der Waals equation of state, and (ii) Dieterici's equation of state.
- Q 7.** (a) State Maxwell's law for the distribution of speeds among molecules of a gas. How does a change in temperature or pressure of a gas influence this distribution?
- (b) Following the Maxwell distribution of molecular speeds, derive the expressions for (i) root mean square speed, (ii) average speed, and (iii) most probable speed. Arrange these three speeds in order of increasing magnitude.
- (c) Following the Maxwell distribution of molecular speeds, derive the expressions for average kinetic energy.

- Q 8.** (a) Derive and explain the terms collision diameter (σ), mean free path (λ), collision number (Z_1) and collision frequency (Z_{11}). Discuss the effects of temperature and pressure on these terms.
- (b) The collision diameter for helium is 207 pm and for methane, 414 pm. How does the mean free path for He compare with that for CH₄, under the same conditions?
- (c) Calculate the value of σ , λ , Z_1 and Z_{11} for nitrogen molecules at 25 °C and at pressure of 10^{-3} mmHg. given that b for nitrogen is $39.1 \text{ cm}^3 \text{ mol}^{-1}$

Solid State:

Q 1. Explain the following: (a) Haüy's idea of unit cell, (b) Space lattice, (c) Unit cell, (d) Law of constancy of interfacial angles (e) Law of rational indices. (f) Law of constancy of symmetry.

Q 2. (a) What are the Miller indices and Weiss indices?

(b) Compute the Miller indices for a face having intercepts on the three axes as

(i) $a : \frac{1}{3} b : \frac{1}{2} c$ (ii) $\frac{1}{2} a : \frac{1}{4} b : \infty c$ (iii) $a : b : \infty c$ (iv) $2a : 2b : 3c$

(c) Show, with the help of diagrams, the planes in cubic unit cells having the following Miller indices:

- (i) Primitive cubic cell (100), (110) and (111)
 (ii) Face-centred cubic cell (200), (220) and (111)
 (iii) Body-centred cubic cell (200), (100) and (222)

(d) Show qualitatively or otherwise that the interplanar distance in a cube having Miller indices (hk) is given by

$$d_{hkl} = \frac{a}{(h^2 + k^2 + l^2)^{1/2}}$$

where a is the edge length of the cube.

Q 3. (a) Derive the Bragg's equation $n\lambda = 2d \sin\theta$ for the reflection of X-rays from the faces of a crystal and show that it can be written as $\lambda = 2d_{hkl} \sin\theta$

(b) Explain why one should employ monochromatic X-rays in studying the reflections from the faces of the crystals. What would happen if, instead, polychromatic X-rays are employed?

(c) Explain Laue's method and powder method of diffraction.

Q 4. (a) Determine the crystal structure of NaCl, KCl and CsCl.

(b) Calculate the density of diamond from the fact that it has a face-centred cubic structure with two atoms per lattice point and a unit cell edge of 356.9 pm.

Liquid State, Liquid Crystal and Colloidal State:

Q 1. (a) Discuss the general characteristics of liquid and compare them with those of gases and solids.

(b) Define the term vapour pressure of a liquid. With the help of energy distribution of molecules in a liquid, explain why the vapour pressure of a liquid increases with increase in temperature and why a liquid cools down on evaporation.

(c) State and explain Trouton's law.

Q 2. (a) What are liquid crystals? List their characteristics.

(b) Describe the structures and main characteristics of 1. Smectic liquid crystals 2. Nematic liquid crystals and 3. Cholesteric liquid crystals

(c) Explain Thermography and seven segment cells

Q 3. (a) How do the kinetic, optical, and electrical properties collectively influence the stability of colloids

(a) State Hardy-Schulze law and describe its significance in the coagulation and stabilization of colloidal particles.

(b) Define the gold number and explain how it quantifies the protective action of colloids.

Q 4. What are the different types of emulsions? Describe their preparation methods and explain the function of emulsifiers in maintaining emulsion stability.

Q 5. What are gels? Classify different types of gels, explain their preparation methods, and discuss their properties.

Chemical Kinetics and Catalysis:

Q 1. Distinguish between: (i) Average rate and instantaneous rate. (ii) Order and molecularity.

Q 2. (a) Derive integrated rate expression for zero order, first order, second order, pseudo-order reactions.

(b) Outline the methods which are employed to determine the order of a reaction

(c) Define the term half-life. Show that for a first-order reaction, half-life has a constant value.

Q 3. The radioactive decay follows the first-order kinetics. If half of a sample disintegrates in 1590 years, what is the rate constant for the disintegration?

Q 4. Briefly outline the experimental methods of studying chemical kinetics viz. conductometric, potentiometric, optical methods, polarometry and spectrophotometry

Q 5. (a) What effect does temperature has on the rate of chemical reactions?

(b) Arrhenius equation is

$$k = A \exp(-E_a/RT)$$

Explain the term A and E_a , involved in the above expression.

(c) What type of graph do you expect between $\log(k/k^0)$ and $1/T$? What is its slope?

Q 6. (a) Describe the collision theory of bimolecular gaseous reactions. Show that it leads to the rate expression

$$r = p \left\{ \pi \sigma_{AB}^2 \left(\frac{8k_B T}{\pi \mu} \right)^{1/2} N_A^* N_B^* \right\} \exp(-E_0/RT)$$

Explain the significance of the term p in the above expression. The factor p is usually less than 1. Explain, why it is so.

(b) Compare the rate constants as given by Arrhenius equation and the collision theory

Q 7. (a) Describe the activated complex theory (transition state theory). Show that it leads to the rate expression

$$r = \left(K^\ddagger \frac{RT}{N_A h} \right) [A][B]$$

where the various symbols have their usual meanings

(b) Show that

$$k_2 = \frac{RT}{N_A h} K^\ddagger = \frac{RT}{c^\circ N_A h} \exp(-\Delta^\ddagger H^\circ / RT) \exp(\Delta^\ddagger S^\circ / R)$$

(c) Compare the rate constants as given by Arrhenius equation and the activated complex theory and show that

$$\begin{aligned} E_a &= \Delta^\ddagger E^\circ + RT \\ E_a &= \Delta^\ddagger H^\circ + (1 - \Delta^\ddagger \nu_g) RT \\ A &= \frac{RT}{c^\circ N_A h} \exp(\Delta^\ddagger S^\circ / R) \exp(1 - \Delta^\ddagger \nu_g) \\ &= \nu_{\text{vib}} \exp(\Delta^\ddagger S^\circ / R) \exp(1 - \Delta^\ddagger \nu_g) \end{aligned}$$

where ν_{vib} is the frequency of decomposition of the activated complex.

Q 8. (a) What is meant by the term catalyst? Give general characteristics of catalytic reactions.

(b) What are buffer solutions? Derive Henderson's equation

(c) What is hydrolysis of salt? Explain the hydrolysis of different types of salts

Thermodynamics and Thermochemistry:

Q 1. The first law of thermodynamics is essentially a law of conservation of energy and is written as

$$dU = dq + dw$$

(i) Explain the symbols involved in this expression.

(ii) Prove mathematically that q and w are not state functions.

Q 2. (a) Define heat capacity of a system.

Using the first law of thermodynamics, show that

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V \quad \text{and} \quad C_P = \left(\frac{\partial H}{\partial T} \right)_P$$

(b) Derive the following relations:

$$C_P - C_V = \left[P + \left(\frac{\partial U}{\partial V} \right)_T \right] \left(\frac{\partial V}{\partial T} \right)_P; \quad C_P - C_V = \left[V - \left(\frac{\partial H}{\partial P} \right)_T \right] \left(\frac{\partial P}{\partial T} \right)_V$$

$$C_P - C_V = \left[V + \left(\frac{\partial H}{\partial T} \right)_P \left(\frac{\partial T}{\partial P} \right)_H \right] \left(\frac{\partial P}{\partial T} \right)_V$$

$$C_P - C_V = T \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_P = TV \alpha^2 / \kappa_T = -T \frac{(\partial P / \partial T)_V^2}{(\partial P / \partial V)_T}$$

Q 3. (a) Starting from the definition of Joule-Thomson coefficient, derive the relations

$$\mu_{JT} = - \frac{1}{C_P} \left(\frac{\partial H}{\partial P} \right)_T = \frac{1}{C_P} \left[T \left(\frac{\partial V}{\partial T} \right)_P - V \right]$$

(b) Show that $\mu_{JT} = 0$ for an ideal gas.

(c) What is an inversion temperature?

Q 4. Calculate w , q , dU & dH for the expansion of ideal gases under isothermal and adiabatic conditions for reversible process.

Q 5. Explain the following

- (a) Hess's Law of heat summation and its applications
- (b) Heat of reaction at constant pressure and at constant volume
- (c) Enthalpy of neutralization, Bond dissociation energy
- (d) Kirchhoff's equation