

West Bengal State University
B.A./B.Sc./B.Com. (Honours, Major, General) Examinations, 2012

PART - I

CHEMISTRY - HONOURS

Paper - II

Duration : 2 Hours]

[Full Marks : 50

*Candidates are required to give their answers in their own words as far as practicable.
 The figures in the margin indicate full marks.*

Answer four questions taking one from each Unit of CEMAT 12PA & 12PB.

CEMAT 12 PA

Answer any two questions taking one from each Unit.

UNIT - 1

1. a) The equation for the distribution of velocity of gas in one dimension is given by the equation : $\frac{dn_u}{n} = Ae^{-\beta u^2} du$.

Hence find the values of A and B.

$$\left[\text{Given : } \int_0^{\infty} e^{-bx^2} dx = \frac{1}{2} \sqrt{\frac{\pi}{b}} \quad \text{and} \quad \int_0^{\infty} x^n e^{-bx^2} dx = \frac{1}{4} \sqrt{\frac{\pi}{b^3}} \right] \quad 2 + 2$$

- b) Wall collision frequency of an ideal gas in a container decreases by 29.29 % when temperature is doubled at constant pressure. Justify the statement. 3
- c) The classical limit of molar heat capacities at constant volume for an ideal gas are about $54.041 \text{ JK}^{-1} \text{ mol}^{-1}$. Find the atomicity and shape of the gas molecules.

$$[\text{Given : } R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}] \quad 2$$

- d) Calculate the mean free path of a hydrogen molecule (ideal) at 298 K at the pressure of 10^{-5} torr.
- [Given : Collision diameter of H_2 gas = 270 pm and 1 atm. = 760 torr]
2. a) Assuming the expression for Maxwell's distribution of kinetic energies of ideal gas derive an equation to show that the fraction of molecules having energies greater than a specified value, ϵ , increases markedly with temperature. [Assume, $\epsilon \gg kT$].
- b) At what temperature most probable speed of hydrogen molecules will be twice that of helium molecules at 25°C ?
- c) Derive an equation to show how the most probable energy in the energy distribution curve depends on temperature.
- d) Derive an equation to show how the viscosity coefficient of an ideal gas depends on its mean free path.

UNIT - II

3. a) The initial slope of Z (compressibility factor) versus P (pressure) curve for H_2 is positive whereas that for CH_4 is negative at 0°C . Using a suitable expression for the slope of a van der Waals gas, explain the difference in nature of the slope.
- b) State the law of corresponding states. Show that at the corresponding states two van der Waals gases must have the same compressibility factors.
- c) For a growing air bubble at the end of a capillary tube immersed in a liquid, the pressure inside the bubble is maximum when the bubble is hemispherical. Justify / criticise the statement.

- d) Calculate the terminal speed of fall in glycerol (density 1.25 g cm^{-3}) at 25°C and 1 atm. pressure of a spherical steel ball of diameter 1.00 mm and density 7.8 g cm^{-3} .

[Given : η of glycerol at 25°C and 1 atm. pressure = 954 cp] 4

4. a) For a nonideal gas at a temperature above its Boyle temperature, if temperature is doubled at constant pressure its volume will be less than twice the volume. Justify or criticize. 2

- b) Surface tension is equal, both numerically and dimensionally, to the surface energy. Explain. 2

- c) Describe how the gas and liquid viscosities depend on temperature. Give the molecular explanation qualitatively for the difference in dependence of gas and liquid viscosities on temperature. 2 + 1

- d) At 20°C the interfacial tension between water and benzene is 35 mNm^{-1} . If $\gamma = 28.85 \text{ mNm}^{-1}$ for benzene and 72.75 mNm^{-1} for water (assuming that $\theta = 0$), calculate

- i) the work of adhesion between water and benzene
ii) the work of cohesion for benzene and for water. 3

- e) Give the SI units of van der Waals constant a and b . 2

CEMAT 12 PB

UNIT - 1

5. a) Identify the following systems as open, closed or isolated system.
- A system surrounded by a rigid, impermeable and diathermic wall.
 - A system surrounded by a non-rigid, impermeable and adiabatic wall.
- b) Prove that :
- $$\mu_{JT} = \frac{1}{C_p} \left[T \left(\frac{\partial V}{\partial T} \right)_P - V \right] \quad [\mu_{JT} = \text{Joule - Thomson coefficient}]$$
- c) Show by schematic diagrams that for the same change in state of a gas, the two stage expansion produces more work than the single stage expansion could possibly produce.
- d) At 25°C and 1 atm. pressure the heat of combustion of (CH₂)₃ [cyclopropane] is - 2090 kJ mol⁻¹. Under the same conditions the heat of formation of CO₂ and H₂O (l) are - 393.0 and - 285.0 kJ mol⁻¹ respectively. Find heat of formation of (CH₂)₃ at 25°C and 1 atm. pressure.
- e) 1.0 m³ of an ideal monatomic gas at 273.2 K and 10 atm. is expanded adiabatically and irreversibly to a final pressure of 1 atm. Find final temperature, ΔU and w.
6. a) Show that for reversible adiabatic change of an ideal gas, TV^{γ-1} = constant [γ = $\frac{\bar{C}_p}{\bar{C}_v}$].
- b) Represent Carnot cycle through T - S diagram and characterise the different steps. Also find out the expression of efficiency in terms of area.

c) Prove that : $\left(\frac{\partial S}{\partial V}\right)_T = \frac{\alpha}{\beta}$

[α = coefficient of thermal expansion,

β = coefficient of compressibility].

d) Calculate the entropy change accompanying the freezing of one mole of water at 25°C to ice at - 10°C at 1 atm. pressure.

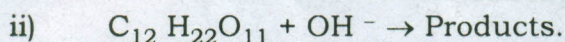
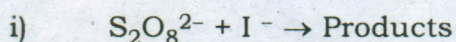
[Given : Heat of fusion of ice at its fusion point (0°C) is 6.00 kJ mol⁻¹, the heat capacity of ice is 36.82 JK⁻¹ mol⁻¹ and heat capacity of liquid water is 75.31 JK⁻¹ mol⁻¹]

UNIT - II

7. a) What is the unit of pre-exponential factor for a first order reaction ? Is it temperature independent ? Explain.

b) Based on Lindemann mechanism show that unimolecular decomposition of a gas may follow 1st order kinetics under a specific condition.

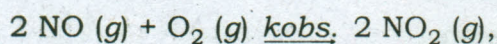
c) Draw the schematic plots of $\log k$ vs $\sqrt{\mu}$ for the following reactions in dilute solutions.



Indicate slope in each plot. [k = rate constant, μ = ionic strength].

d) For a reaction, $A + B \rightarrow$ products, at 37°C, order with respect to each reactant is one. The initial concentration of each reactant is 0.1 M. If initial rate is 1.64×10^{-5} M s⁻¹, find the time for the rate to drop to one fourth of its initial value.

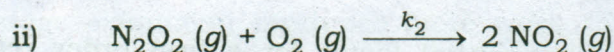
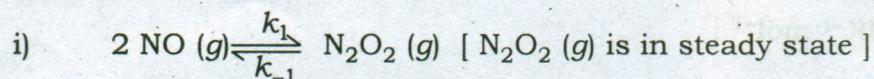
8. a) The oxidation $\text{NO}(g)$ to form $\text{NO}_2(g)$ according to,



reveals a rate law of the form,

$$\frac{1}{2} \frac{d[\text{NO}_2]}{dt} = k_{\text{obs}} [\text{NO}]^2 [\text{O}_2].$$

Based on a proposed mechanism as,



derive the rate law and compare with the experimental one.

- b) A reversible reaction, $A \xrightleftharpoons[k_b]{k_f} C$, is first order in both the forward (f) and back (b) directions. Derive the integrated rate law and compare with that for 1st order reaction.

- c) At 25°C the inversion of aqueous sucrose solution at a constant $[\text{H}^+]$ proceeds with constant half-life. When $[\text{H}^+]$ is made 10-fold, the reaction proceeds with constant half-life, which is $\frac{1}{10}$ th to the previous value. Find order with respect to sucrose and H^+ . The rate law is expressed as : $-\frac{d[\text{sucrose}]}{dt} = k [\text{sucrose}]^\alpha [\text{H}^+]^\beta$, α & β are orders with respect to sucrose and H^+ respectively.

- d) For the reaction, $A + B \rightarrow \text{Products}$, doubling the concentrations of A and B , the initial rate increases to 8-fold whereas doubling the concentration of A , the initial rate increases by 4-fold. Find orders with respect to A and B in the rate law, $r = k [A]^\alpha [B]^\beta$, where α and β are orders with respect to A and B respectively.

2

Part III

3

back

1st

3+1

needs

with

spect

=

H+

3