West Bengal State University

B.A./B.Sc./B.Com (Honours, Major, General) Examinations, 2015

PART – I

CHEMISTRY — HONOURS

Paper – II

Duration : 2 Hours] [Full Marks : 50

The figures in the margin indicate full marks.

CEMAT-12-PA

Answer any *two* questions taking *one* from each Unit.

UNIT – I

1. a) The Maxwell's speed distribution is given as

$$P(c) = Ac^2 e^{-mc^2/(2kT)}$$

What does $P(c)$ mean ? Find the dimension of A.

Find $\left\langle \frac{1}{C} \right\rangle$ [Given : $\int_0^\infty x \exp(-\beta x^2) dx = \frac{1}{(2\beta)}$] 1 + 1 + 3

b) What do you mean by 'collision diameter' ? Derive a relation between mean free path (λ) and collision diameter of a gas. How does λ depend on T and P ? 1 + 3 + 1

c) Apply the equipartition principle to calculate $\gamma (\approx C_p / C_v)$ for a linear, tri-atomic, ideal gas. What is the limiting value of γ when the number of atoms in the molecules becomes very large ? 2 + 1

2. a) Obtain an expression for the distribution of translational kinetic energy from Maxwell's distribution of speed. How does it differ if the gas is changed from Helium to Argon ? 4 + 1

b) Calculate the number of binary collision per c.c. of $N_2(g)$ per second, at 2 atm, 30°C. The bond length of the gas molecules is 1·87 Å. 3

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c) Two flasks A and B have equal volumes. A is maintained at 300 K and B at 600 K. A contains hydrogen gas and B has equal mass of methane gas. Assuming ideal behaviour for both the gases, calculate (i) the ratio of mean free path in two containers [The collision diameter of methane may be assumed to be twice as that of hydrogen], (ii) the ratio of coefficient of viscosity in two flasks. 5

UNIT – II

3. a) Explain the term 'contact angle' and indicate explicitly the factors which govern its value when a liquid comes in contact with a solid in a gaseous atmosphere. 4

b) At room temperature iodine is solid, bromine is liquid, chlorine and fluorine are gaseous. Can you explain this on the basis of intermolecular attraction ? 2

c) Write the unit and dimension of van dar Waals constants 'a' and 'b'. 1 + 1

d) A steel ball of density 7·9 g/c.c. having diameter of 4 mm is dropped into a column of liquid. It takes 55 seconds to fall through a distance of 1 m. Calculate the viscosity of the liquid. [Given, the density of the liquid is 1·10 g/c.c.] 3

e) What do you mean by 'Boyle temperature' ? 1

4. a) Give the graphical representation of a van der Waals gas explaining the different regions and parts.

Explain critical temperature (T_c) with reference to the curve. 3 + 2

b) What is 'virial equation of state' ? What does the second viral coefficient (B_{2v}) signify ? 2

c) What are viscosity and viscosity coefficient ? Explain the unit of the coefficient. 3

d) Derive Laplace's equation for excess pressure inside a spherical bubble, suspended in air. 2

CEMAT-12-PB

Answer any *two* questions taking *one* from each Unit.

UNIT – I

5. a) For a constant pressure process, $\Delta H = q_p$. Does it follow that q_p is a state function ? 2

b) Why does C_p exceeds C_v for an ideal gas ? Give a molecular explanation. 2

c) Show that $C_p - C_v = \frac{T\alpha^2 V}{\kappa}$, where α = coefficient of volume expansion; κ = coefficient of compressibility. 4

d) At 25°C the coefficient of thermal expansion of water is $\alpha = 2 \cdot 07 \times 10^{-4} K^{-1}$ and the density is 0·9970 g/cm^3. If the temperature of 200 g of water is raised from 25°C to 50°C under a constant pressure of 101 kPa, calculate w. Calculate also q, ΔH and ΔU. (Given , $C_p = 75 \cdot 30$ JK^{-1}mol^{-1}) 3

e) A spontaneous polymerisation must be an exothermic process." Justify or criticize. 2

6. a) "C_v is independent of pressure for a gas obeying equation of state $P(V - nb) = nRT$." Justify or criticize. 2

b) Show the equivalence of Kelvin-Planck and Clausius statements of the second law of thermodynamics. 4

c) Show that for a van der Waals gas, $\frac{\alpha}{\kappa} = \frac{R}{V - b}$ where, α = coefficient of volume expansion; κ = coefficient of compressibility. 3

d) Draw a Carnot cycle in H *vs* T and U *vs* S diagram. 2

e) A Carnot cycle heat engine does 2·50 kJ of work per cycle and has an efficiency of 45%. Find the temperatures of the two reservoirs between which the Carnot engine is operating. 2

UNIT – II

7. a) For a consecutive reaction $A \rightarrow B \rightarrow C$, obtain a relation for the time at which the concentration of B will be maximum in terms of rate constants of individual steps. Assume all the reaction steps are first order. 4

b) "Second order reaction is never completed." Justify or criticize. 2

c) The rate constant of a reaction is experimentally found to decrease with increase in temperature. Is there any contradiction with Arrhenius rate equation ? 2

d) Show that if A undergoes two simultaneous reactions (parallel reactions) to produce B and C according to the reactions $A \rightarrow B$ and $A \rightarrow C$, then the observed activation energy (E_a) for the disappearance of A is given by the equation $E_a = \frac{k_1 E_1 + k_2 E_2}{k_1 + k_2}$, where k_1 and k_2 are the first order rate constants of the individual step and E_1 and E_2 are activation energies of the two steps. 4

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8. a) "Unimolecular reactions are not always first order." Justify it using Lindemann's theory. 3

b) "Zero order reaction must be a multi-step reaction." Justify or criticize. 2

c) Consider a reaction $A \rightarrow$ Products, which is one-half order with respect to A.

i) Derive the integrated form of rate equation.

ii) Write the unit of rate constant (k).

iii) Decide what function should be plotted to determine the rate constant. Also show the plot. $2 + \frac{1}{2} + (1 + \frac{1}{2})$

d) "Activation energy of a reaction can never be zero or negative." Justify or criticize. 3