2022

CHEMISTRY — HONOURS

Paper : CC-2

Full Marks : 50

The figures in the margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

Write the answers to ***Physical Chemistry*-1 (Group-A)** and ***Organic Chemistry*-1B (Group-B)** questions in *separate answer books*.

Group - A

(Physical Chemistry - 1)

Answer ***question no.* 1** (compulsory) and ***any five*** questions from the rest (***question nos.* 2 to 9**).

1. Answer the following questions : 1×8

(a) For a real gas, which one is expected to be higher between T_B and T_C? Why?

(b) Real gases, at high pressure, are hard to compress.— Explain.

(c) Define 'flux' with an example. Is it a vector quantity or scalar?

(d) How does 'Diffusion Coefficient' vary with temperature and pressure?

(e) What is the order of a unimolecular elementary reaction? Justify briefly.

(f) At 0°C temperature and 1 atm pressure the mean free path of an ideal gas is 10^{-7} m. Calculate the radius of the gas molecule.

(g) State the principle of equipartition of energy.

(h) What would be the type of the slope (positive or negative) in the Z vs. P plot at a constant temperature in the limit of zero pressure for a van der Waals gas whose $b < \frac{a}{RT}$?

2. (a) Starting from Maxwell's molecular Kinetic energy distribution function, derive an expression for the most probable kinetic energy, $\epsilon_{\text{most probable}}$. Is $\epsilon_{\text{most probable}} = \frac{1}{2} m (C_{\text{most probable}})^2$? Comment.

(b) For a triatomic gas, $\gamma = \frac{C_p}{C_v} = 1.66\overline{6}$ ... show that the molecule is non-linear. 3+2

3. (a) Draw the theoretical (van der Waals) and experimental P-V isotherm for a real gas below the critical temperature explaining the difference in nature between the two.

   (b) Calculate the % of gas molecules (behaving ideally) that are expected to have kinetic energy less than 6.5 kJ mol^{-1} at 250 K. 3+2

4. (a) The molecules of a gas are confined to move in a plane, the speed distribution function being expressed as :

$$\frac{dn_c}{n} = \left(\frac{m}{kT}\right) e^{-mc^2/2kT} c\, dc.$$

   Calculate the probability of a molecule having a kinetic energy equal to or greater than a given value ϵ'.

   (b) The coefficient of viscosity, η of H_2 at 0°C and 1 atm is 8.53 μPaS. Find η of D_2 at 0°C and 1 atm. Assume that $\sigma_{H_2} = \sigma_{D_2}$. 3+2

5. (a) The decomposition of Ozone : $2O_3 \rightarrow 3O_2$ proceeds through the following steps :

$$O_3 \underset{k-1}{\overset{k_1}{\rightleftharpoons}} O_2 + O$$

$$O + O_3 \xrightarrow{k_2} 2O_2 \text{ (slow)}$$

   Obtain the rate expression for the reaction in terms of the individual rate constants using steady state approximation.

   (b) How does the time required for a first-order reaction to go to 99% completion relate to the half-life of the reaction? 3+2

6. (a) The hydrolysis of a substance is catalysed specifically by hydrogen ions, the rate constant being given by

$$k(S^{-1}) = 4.70\times10^{-2}\times[H^+] \text{ (mol dm}^{-3}).$$

   When the substance is dissolved in a 1.0×10^{-3}(M) solution of an acid HA, the rate constant is 3.2×10^{-5} S^{-1}. Calculate the dissociation constant of the acid HA.

   (b) Find out the terminal velocity of a raindrop of radius 0.01 cm falling through air of viscosity coefficient 1.85×10^{-4} poise. Neglect the density of air in comparison to that of water (density of water = 1g cm^{-3}). 3+2

7. (a) Although the virial equation of state of a real gas coincides with that of the perfect gas at $P \rightarrow 0$, not all its properties necessarily coincide with those of a perfect gas in that limit.— Justify with the example of variation of compressibility factor (Z).

   (b) Assuming the intermolecular attraction to be negligible for a gas, and its molar volume at 0°C and 100 atm pressure is 1.107×10^{-2} times the volume at NTP, calculate the molecular diameter of the gas. 3+2

8. (a) A layer of oil, 1.5 mm thick is placed between two microscopic slides. A force of 5.5×10^{-4}N is required to glide one slide over the other at a speed of 1 cm/s when their contact area is 12 sqcm. Calculate the coefficient of viscosity of the oil.

(b) Explain briefly whether viscosity has any effect on the rate of diffusion. 3+2

9. (a) The expression for rate constant of a reaction is given by $\log K = A - \frac{B}{T} + C\log T$.

Find the expression for activation energy of the reaction.

(b) The half-life of decomposition of a compound is 45 minutes. If the initial concentration is halved, the half-life becomes 90 minutes. What is the order of the decomposition reaction? Justify your answer. 3+2

Group - B

[Organic Chemistry - (1B)]

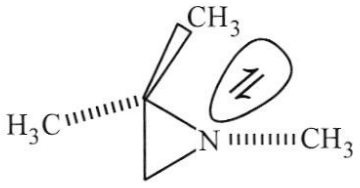
Answer ***question no.* 10** (compulsory) and ***any three*** questions from the rest (***question nos.* 11 to 15**).

10. (a) Represent *meso*-tartaric acid in Fischer projection formula and convert it to Newmann Projection.

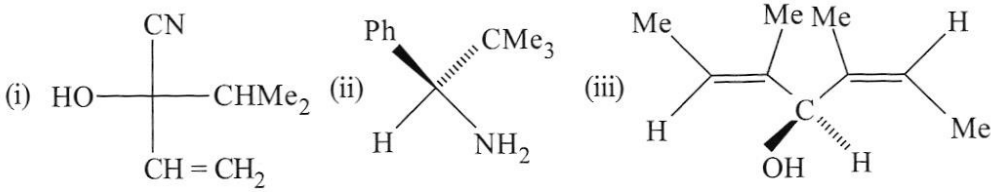
(b) Draw the orbital picture of diphenyl carbene. 1+1

11. (a) Write down all the possible conformers of active butane-2-3-diol. Indicate the most stable conformer giving proper reason.

(b) Is this aziridine compound resolvable? Explain. 3+2

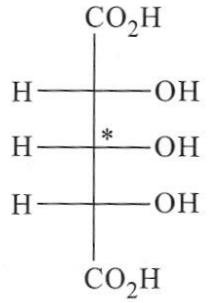


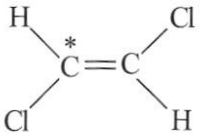
12. (a) Assign *R*/*S* descriptor of the following showing priority sequence of the ligands :

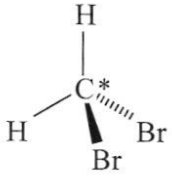


(b) Draw the Fischer projection of active 2,3-dihydroxybutanoic acid. Convert it to Newmann Projection (staggered only). 3+2

13. (a) Designate the marked (*) centres of the following compounds as stereogenic/non-stereogenic, chirotopic/achirotopic with reasons :

(i) 

(ii) 

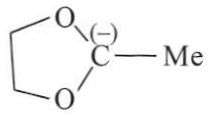
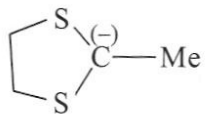
(iii) 

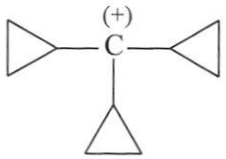
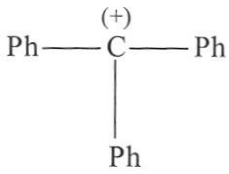
(b) Write the structure of the following :

(i) 2*R*, 3*r**, 4*S*–2,3,4-trichloropentane

(ii) *syn*-$CH_3CH(OH)CH(CH_3)COPh$ 3+2

14. (a) Comment on the stability of the following pairs with reason :

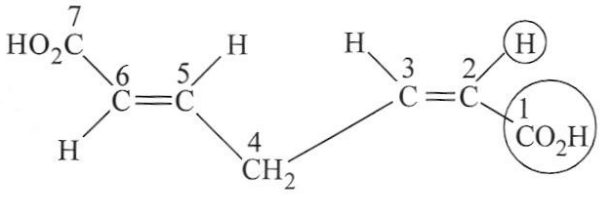
(i)  and 

(ii)  and 

(b) Indicate the symmetry elements present in the following compounds :

(i) $CHCl_3$ (ii) $CH_2 = C = CH_2$ 3+2

15. (a) The following compound (A) can be named as (2*Z*, 5*E*)-2,5-heptadienedioic acid or (2*E*, 5*Z*)-2,5-heptadienedioic acid. Which one is correct? What should be the name of the compound if the encircled groups are mutually exchanged?



A

(b) Define non-classical carbocation with one example. 3+2