

2022

## CHEMISTRY — HONOURS

Paper : CC-1

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 **Inorganic Chemistry-1 (Group-A)** and **Organic Chemistry-1A (Group-B)** questions in *separate answer books*.

## Group - A

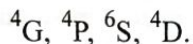
## (Inorganic Chemistry - 1)

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

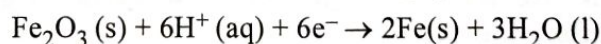
1. Answer the following questions :

1×8

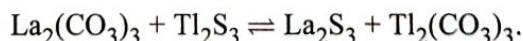
- (a) Write down a set of quantum numbers that uniquely defines  $4d_{z^2}$  when the external magnetic field is applied along  $z$  axis.
- (b) Predict the number of maxima when a curve is plotted between  $4\pi r^2 R^2(r)$  vs.  $r$  for 5d orbital.
- (c) Predict the increasing order of energy among the following R-S terms :



- (d) Identify the acid and base using suitable theory :  $2HF + PF_5 \rightleftharpoons H_2F^+ + PF_6^-$
- (e) Indicate whether the pH of an aqueous solution of NaCN at 25°C is greater or lesser than 7.
- (f) Identify with reason whether the below-mentioned reaction is a double decomposition reaction or a redox reaction :  $CuH + HCl = CuCl + H_2$ .
- (g) Write the Nernst equation for the reduction of  $Fe_2O_3(s)$  :



- (h) Predict the direction of the following equilibrium using HSAB concept :

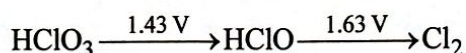
2. (a)  $Cu^{2+}$  ion readily liberates iodine from iodide ion in acid medium but not in presence of ethylenediamine.— Justify.  $\left[ E_{Cu^{2+}/Cu^+}^\circ = 0.15V, E_{Cu^{2+}/CuI}^\circ = 0.87V, E_{\frac{1}{2}I_2/I^-}^\circ = 0.54V \right]$ 

- (b) Discuss the physical significance of magnetic quantum number.

3+2

Please Turn Over

3. (a) Although  $\text{N}(\text{CH}_3)_3$  is a stronger base than  $\text{NH}_3$ , the adduct of the latter is more stable than the former with  $\text{B}(\text{CH}_3)_3$ . Explain.
- (b) Determine the ground state term symbol for Chromium (Atomic No. 24). 3+2
4. (a) How will you titrate an aqueous solution of acetic acid potentiometrically against an aqueous solution of  $\text{NaOH}$ ? Show the expected titration curve for the neutralisation reaction.
- (b) Predict and justify the correct order of basicity :  $\text{CH}_3^-$ ,  $\text{NH}_2^-$ ,  $\text{F}^-$ ,  $\text{OH}^-$ . 3+2
5. (a) From the following Latimer diagram predict whether hypochlorous acid ( $\text{HClO}$ ) will disproportionate or not in aqueous solution :



- (b) Which member of the following pairs is the stronger acid? Give reason(s) for your choice.
- (i)  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  or  $[\text{Ga}(\text{H}_2\text{O})_6]^{3+}$
- (ii)  $\text{H}_2\text{CrO}_4$  or  $\text{HMnO}_4$  3+2
6. (a) Choose and justify :
- (i) more basic :  $[\text{Fe}(\text{CN})_6]^{3-}$  or  $[\text{Fe}(\text{CN})_6]^{4-}$
- (ii) more acidic in gas phase :  $\text{PH}_3$  or  $\text{NH}_3$
- (iii) stronger acid :  $\text{HSO}_3\text{F}$  or  $[\text{SbF}_5(\sim 14 \text{ mol } \%) + \text{HSO}_3\text{F}]$
- (b) Electronic configuration of Cr is  $[\text{Ar}] 3d^5 4s^1$  rather than  $[\text{Ar}] 3d^4 4s^2$ . Justify on the basis of exchange energy. 3+2
7. (a) Establish Nernst equation for  $\text{MnO}_4^-/\text{Mn}^{2+}$  system in acid medium and explain why  $\text{Cl}^-$  is oxidized by  $\text{MnO}_4^-$  only at low pH ( $< 6$ ) and not in neutral medium.
- $$\left[ E_{\text{MnO}_4^-/\text{Mn}^{2+}}^\circ = 1.51 \text{ V}; E_{\frac{1}{2}\text{Cl}_2/\text{Cl}^-}^\circ = 1.36 \text{ V} \right]$$
- (b)  $\text{SiO}_2$  is added to a molten mixture of  $\text{Fe} + \text{FeO}$ . Predict the change in acidity. 3+2
8. (a) The 3s and 3p orbitals have identical energies in the hydrogen atom, but in the chlorine atom their energies are much different. Explain.
- (b) Balance the following redox reaction by ion-electron method :
- (i)  $\text{KMnO}_4 + \text{H}_2\text{C}_2\text{O}_4 + \text{H}_2\text{SO}_4 = \text{MnSO}_4 + \text{CO}_2 + \text{K}_2\text{SO}_4 + \text{H}_2\text{O}$
- (ii)  $\text{MnO}_4^- + \text{H}_2\text{SO}_3 \rightarrow \text{Mn}^{2+} + \text{HSO}_4^-$ . 3+2
9. (a) The value of  $K_{\text{sp}}$  for  $\text{AgCl}$  is  $1.77 \times 10^{-10}$  (at 298 K). Compare the solubility of  $\text{AgCl}$  in water and in  $0.0100 \text{ mol dm}^{-3}$  hydrochloric acid.
- (b) Why dilute hydrochloric acid is used for the precipitation of cations in analytical group 1? 3+2

## Group - B

## (Organic Chemistry - 1A)

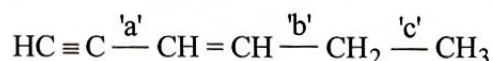
Answer **question no. 10** (compulsory) and **any three** questions from the rest (**question nos. 11 to 15**).

10. (a) Calculate DBE (Double Bond Equivalent) for the molecular formula  $C_6H_7N$ .

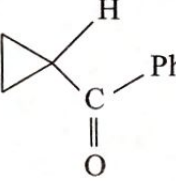
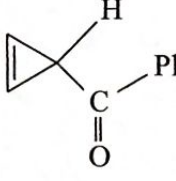
(b) Draw the canonical forms of  $\overset{+}{>C}-\ddot{O}Me$ . Identify the most stable structure. 1+1



11. (a) Draw the orbital picture of  $CH_2=CH-CH\ddot{O}$ , mentioning the hybridization of all the carbon and oxygen atoms present in the molecule.

(b) Arrange the following C - C bonds 'a', 'b' and 'c', in increasing order of bond length giving proper reasons. 3+2



12. (a) Represent the  $\pi$  M.O. diagram of cyclobutadiene. How can you predict the antiaromatic nature of the molecule from the diagram?

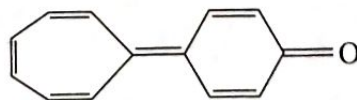
(b) Compare the acidities of  and  and justify. 3+2

13. (a) When -I is treated with silver perchlorate in propionic acid (solvent), the molecule is rapidly solvolysed but under same condition -I undergoes no solvolysis at all. Explain the observation.

(b) Tertiary butanol is miscible in water in all proportions but *n*-butanol is partly miscible. Explain. 3+2

14. (a) 1,3-Butadiene is a conjugated diene whereas 2,3-ditertiarybutyl-1,3-butadiene behaves like a non-conjugated one. Explain.

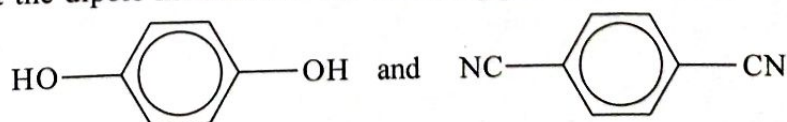
(b) Explain why free rotation is possible about the double bond between rings of the following compound— 3+2



15. (a) Give one example of each type of the following reactions :

(i) Pericyclic reaction (ii) Substitution reaction (iii) Elimination reaction.

(b) Comment about the dipole moments of the following pair of molecules. 3+2



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  $0^\circ\text{C}$  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,  $\gamma = \frac{C_p}{C_v} = 1.666\bar{6}$  ... show that the molecule is non-linear.

3+2

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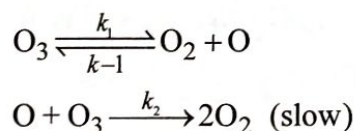
3. (a) Draw the theoretical (van der Waals) and experimental P-V isotherm for a real gas below the critical temperature explaining the difference in nature between the two.
- (b) Calculate the % of gas molecules (behaving ideally) that are expected to have kinetic energy less than  $6.5 \text{ kJ mol}^{-1}$  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  $\epsilon'$ .

- (b) The coefficient of viscosity,  $\eta$  of  $\text{H}_2$  at  $0^\circ\text{C}$  and 1 atm is  $8.53 \mu\text{PaS}$ . Find  $\eta$  of  $\text{D}_2$  at  $0^\circ\text{C}$  and 1 atm. Assume that  $\sigma_{\text{H}_2} = \sigma_{\text{D}_2}$ . 3+2
5. (a) The decomposition of Ozone :  $2\text{O}_3 \rightarrow 3\text{O}_2$  proceeds through the following steps :



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

$$k(\text{S}^{-1}) = 4.70 \times 10^{-2} \times [\text{H}^+] \text{ (mol dm}^{-3}\text{)}.$$

When the substance is dissolved in a  $1.0 \times 10^{-3} \text{ (M)}$  solution of an acid HA, the rate constant is  $3.2 \times 10^{-5} \text{ S}^{-1}$ . 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  $1.85 \times 10^{-4}$  poise. Neglect the density of air in comparison to that of water (density of water =  $1 \text{ g cm}^{-3}$ ). 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  $0^\circ\text{C}$  and 100 atm pressure is  $1.107 \times 10^{-2}$  times the volume at NTP, calculate the molecular diameter of the gas. 3+2

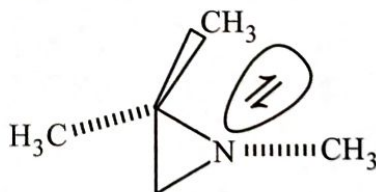
8. (a) A layer of oil, 1.5 mm thick is placed between two microscopic slides. A force of  $5.5 \times 10^{-4}$  N is required to glide one slide over the other at a speed of 1 cm/s when their contact area is 12 sqcm. Calculate the coefficient of viscosity of the oil.
- (b) Explain briefly whether viscosity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

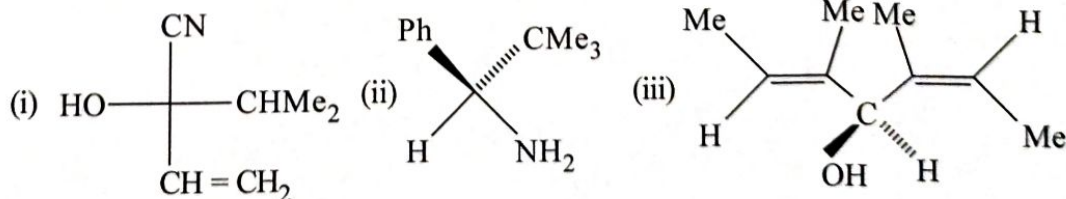
#### [Organic Chemistry - (1B)]

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

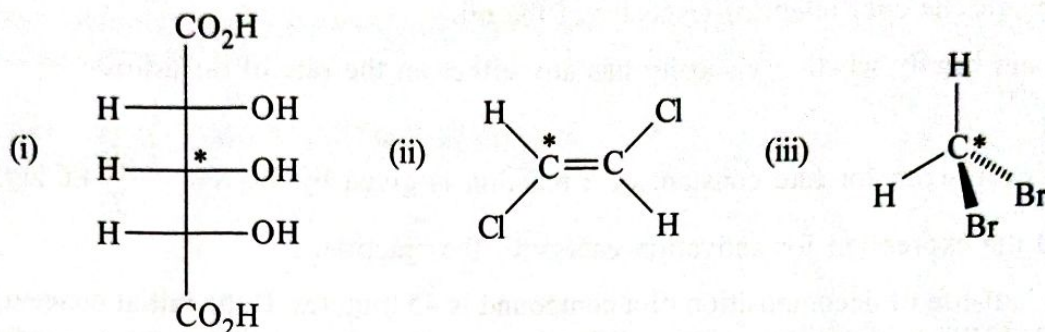


12. (a) Assign *R/S* descriptor of the following showing priority sequence of the ligands :



- (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 :

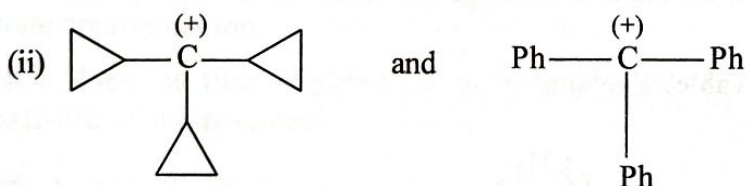
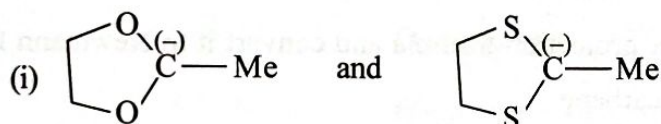


- (b) Write the structure of the following :

- (i)  $2R, 3R^*, 4S$ -2,3,4-trichloropentane  
 (ii) *syn*- $\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{CH}_3)\text{COPh}$

3+2

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

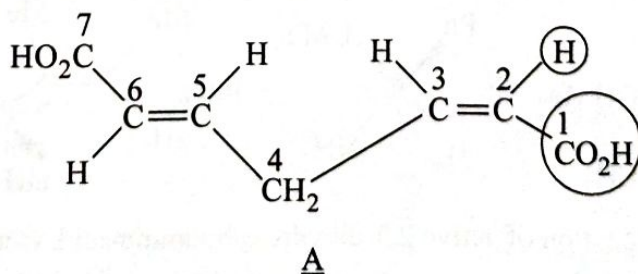


- (b) Indicate the symmetry elements present in the following compounds :

- (i)  $\text{CHCl}_3$  (ii)  $\text{CH}_2 = \text{C} = \text{CH}_2$

3+2

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



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

3+2