

2013

CHEMISTRY

(Major)

Paper : 2.1

Full Marks : 60

Time : 2½ hours

*The figures in the margin indicate full marks
for the questions*

1. Answer in brief :

1×7=7

- (a) Give the schematic plot of compressibility factor against pressure at a definite temperature to show the difference between ideal gas and real gas.
- (b) Indane gas used for cooking in houses consists mainly of butane and propane. Does each of these two gases have critical temperature higher than 298 K?
- (c) Out of nematic, smectic and cholesteric liquid crystal phases, state which is the most ordered one?

- (d) State why liquid is less compressible than gas.
- (e) Liquid crystal display consists of a liquid crystal sandwiched between two thin glass plates with provision for applying electric field. State what change occurs in the liquid crystal phase when electric field is applied.
- (f) Write the cell reaction that takes place in the cell
$$\text{Pt (s)} | \text{H}_2 \text{ (g)} | \text{H}^+ \text{ (c}_1\text{)} || \text{H}^+ \text{ (c}_2\text{)} | \text{H}_2 \text{ (g)} | \text{Pt (s)}$$
- (g) Calculate the value of $\text{p}K_a$ of the acid whose dissociation constant is 2.0×10^{-5} .

2. Answer the following questions : 2×4=8

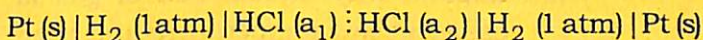
- (a) Discuss the effect of temperature on the distribution of molecular speeds. Draw necessary graphs to show this effect.
- (b) A liquid A has half the surface tension of the liquid B. Again the density of the liquid A is twice that of B. If in a capillary tube A rises to the height of 10 cm, what will be the rise of B in the same tube at the same temperature?

(c) Explain why K^+ has higher ion mobility than Li^+ .

(d) Write the reaction that takes place in Ag-AgCl electrode. Also write Nernst equation for the same.

3. (a) Discuss about the Ostwald viscometer method for the determination of viscosity of a liquid. How does viscosity of a liquid vary with temperature? 4+1=5

(b) Deduce an expression for the e.m.f. of the concentration cell with transference : 5



Or

Write short notes on dry cell and lead storage battery. $2\frac{1}{2} \times 2 = 5$

(c) Deduce the expressions for critical constants P_c , T_c and V_c in terms of the van der Waals constants. Can a van der Waals gas be liquefied for which the value of the van der Waals constant a is zero? 4+1=5

Or

Explain what you mean by collision cross-section. Define mean free path and find an expression for this. How does the mean free path vary with pressure? $2+2+1=5$

4. (a) Answer either (i), (ii) and (iii) or (iv) and (v):

(i) Deduce the equation of corresponding states. 4

(ii) Using the principle of equipartition of energy, deduce an expression for the energy of 1 mol CO_2 (g) at temperature T K. 4

(iii) Explain why liquefaction of gas is easier at low temperature and high pressure. 2

Or

(iv) Write the two main causes of deviation from ideal gas behaviour. Explain how van der Waals modified the ideal gas equation. $2+4=6$

(v) Deduce an expression for the thermal conductivity of monatomic gas by using kinetic theory of gases. 4

(b) (i) Using the concept of chemical potential, prove that the elevation of boiling point of a dilute solution containing non-volatile non-electrolyte solute is proportional to the molal concentration of the solution. 5

(ii) Explain why effervescence is observed when a soda water bottle is opened. 2

(iii) 122 g of benzoic acid is dissolved in 1000 g of benzene at a definite temperature. The vapour pressure of pure benzene is 0.876 atm at that temperature. Assuming that the benzoic acid dimerises completely, calculate the vapour pressure of the solution (temperature constant). 3

(c) Answer either (i), (ii) and (iii) or (iv), (v) and (vi) :

(i) Deduce Stokes-Einstein equation relating diffusion coefficient and viscosity of the medium. 5

(ii) A moving boundary experiment was carried out with 20 mol m^{-3} NaCl solution in water. In the

experiment, a current of 0.0016 A moved the boundary through a distance of 0.06 m in 34 minutes and 30 seconds. The radius of the tube used in the experiment is 1.88×10^{-3} m. Calculate the transport number of Na^+ ion. 3

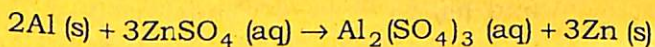
- (iii) Calculate the ionic strength of the solution which is 0.1 M in KCl and 0.2 M in K_2SO_4 . 2

Or

- (iv) Discuss in brief about the Debye-Hückel theory of strong electrolyte leading to Debye-Hückel-Onsager equation. 5

- (v) Calculate the mean ionic activity coefficient of 0.01 M Na_2SO_4 solution in water at 298 K. 3

- (vi) Calculate the standard free energy change associated with the reaction



Given :

$$E_{\text{Al}^{3+}|\text{Al}}^{\circ} = -1.66 \text{ V} \text{ and } E_{\text{Zn}^{2+}|\text{Zn}}^{\circ} = -0.76 \text{ V}$$

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2013

CHEMISTRY

(Major)

Paper : 2.2

(Organic Chemistry)

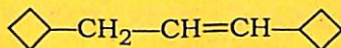
Full Marks : 60

Time : 2½ hours

The figures in the margin indicate full marks
for the questions

1. Answer the following questions : 1×7=7

(a) Write IUPAC name of



(b) Give an example, where S_N1 reaction does not follow the first-order kinetics.

(c) What is partial rate factor?

(d) What does the term 'topocity' signify?

(e) Why only α -H atoms in saturated carbonyl compounds take part in the aldol condensation?

(f) What are homotopic ligands?

(g) Arrange the following hydrocarbons in order of their increasing acid strengths :



2. Answer the following questions : 2×4=8

- (a) Discuss the relative stabilities of different conformations of cyclohexane.
- (b) What is the requirement for showing prochirality?
- (c) Give two examples of molecules containing enantiotropic H-atoms.
- (d) How are the H-atoms at a prochiral centre distinguished from one another?

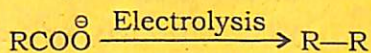
3. Answer any three questions : 5×3=15

- (a) (i) Explain why chlorine ($-\text{Cl}$) in chlorobenzene is an *o*, *p*-director, but a deactivator at the same time. 2
- (ii) How will you trap a benzyne intermediate? 1
- (iii) Write down the mechanism of Chichibabin reaction of pyridine. 2
- (b) Give an example of $\text{Ar S}_{\text{N}}1$ reaction. What is the mechanism involved? What are the evidences in support of this mechanism? 1+2+2=5
- (c) (i) Explain why substitution via benzyne mechanism is not possible when the adjacent positions of the leaving group are blocked. 3
- (ii) Aniline is more reactive than acetanilide towards electrophilic substitution. Why? 2

- (d) (i) How will you prepare *meta*-nitrotoluene from benzene? 2
(ii) What is o/p ratio? What are the factors influencing o/p ratio? 1+2=3

4. Answer any *three* questions : 10×3=30

- (a) (i) Propose a mechanism of the following reaction :



What are the evidences in support of the proposed mechanism?

1½+1½=3

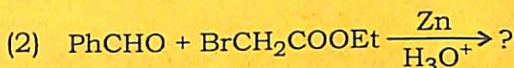
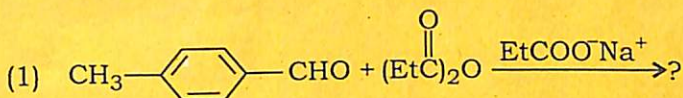
- (ii) Starting from benzene diazonium chloride, synthesise nitrobenzene. 2
(iii) When excess alcohol vapours are passed over conc. H₂SO₄ at 130 °C–140 °C, an ether is formed. What is the mechanism involved in this reaction? 2
(iv) How can you distinguish between 1°, 2°- and 3°-amines by Hofmann mustard oil test? 3
(b) (i) Show, mechanistically, that a 1°-alcohol can be selectively converted into an aldehyde by Swern oxidation. 3
(ii) Convert CH₃Br into C₃H₈ involving Corey-House synthesis. 2

- (iii) Discuss the mechanism of Tollens' reaction. 3
- (iv) The rate of hydrolysis of $(\text{CH}_3)_3\text{CBr}$ in 50% aqueous methanol is thousand times faster than that in pure methanol. Explain. 2
- (c) (i) Glycolization of olefins can be stereospecifically controlled to yield either *cis*- or *trans*-1, 2-glycol. Explain. 3
- (ii) Distinguish between Hofmann's rule and Saytzeff rule. 3
- (iii) An organic compound A with molecular formula, $\text{C}_5\text{H}_{12}\text{O}$ reacts with sodium metal to produce H_2 gas. Compound A reacts with Lucas reagent (anhydrous $\text{ZnCl}_2 + \text{conc. HCl}$) and produces turbidity immediately. When vapours of compound A are passed over alumina (Al_2O_3), it is converted into compound B. Compound B, on ozonolysis, forms compounds C and D. Compounds C and D give coloured p.p.t. with Brady's reagent. Compound C forms silver mirror with Tollens' reagent, while compound D does not respond to this test. Identify compounds A to D and write all the chemical equations involved. 4

Or

What is Wittig reaction? What is its mechanism? Give its one synthetic application. 1+2+1=4

- (d) (i) What are the products of the following condensation reactions? Name the condensation reaction in each case : 2+2=4



- (ii) When toluene is treated with DCl at -78°C , no deuterium is exchanged and the solution does not conduct electricity. What is the structure of the complex? 2
- (iii) What is Nef reaction? Explain its mechanism. 2
- (iv) *o*-nitrobenzaldehyde undergoes the benzoin condensation, but *p*-nitrobenzaldehyde does not. Why? 2

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