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Your Roll No.....

5186

B.Sc. (Physical Sciences/Life Sciences)

(Semester III) B

CHEMISTRY—Paper CHPT-303

(Physical Chemistry-2/Organic Chemistry-3)

(Admissions of 2010 and onwards)

Time : 3 *Hours* *Maximum Marks* : 70

(Write your Roll No. on the top immediately on receipt of this question paper.)

Use separate answer-sheet for Section A and Section B.

Section A

Attempt *three* questions in all.

Question No. 1 is compulsory.

Use of calculator is allowed.

$R = 8.314\ JK^{-1}\ mol^{-1}$, $F = 96487C$.

1. Explain any *five* of the following :

   (*a*) The variation of molar conductivity with dilution for weak and strong electrolytes. 3

(*b*) The conductometric titration of a weak acid with a strong base. 3

(*c*) Reversible and irreversible cells taking *one* example each. 3

(*d*) The principle of steam distillation. 3

(*e*) Congruent and incongruent melting points. 3

(*f*) Gas-ion electrode taking the example of hydrogen electrode. 3

(*g*) Phases, components and degrees of freedom taking *one* example. 3

(*h*) Vapour pressure-composition curve of an ideal solution. 3

2. (*a*) State Nernst distribution law and show that it is in agreement with the phase rule requirements. 3

(*b*) An aqueous solution contains 0.20 g of aspirin in 30 cm^3 of solution. 20 cm^3 of ether is added to this solution, the mixture is then shaken well and allowed to come to equilibrium at 298 K. The distribution coefficient is 4.7 at this temperature in favour of ether. How much aspirin remains in the aqueous phase ? If the extraction is carried out with two successive 10 cm^3 portions of ether, calculate the quantity of aspirin remaining unextracted in the aqueous solution. 4

(*c*) Explain a system with an upper CST by drawing a temperature-composition diagram. 3

3. (*a*) Give the thermodynamic derivation of the Gibbs phase rule. 3

(*b*) Draw and label the phase diagram of the sulphur system. Explain the various equilibria occurring in the system. 5

(*c*) The vapour pressure of a liquid A is 60 torr at 310 K and 300 torr at 360 K. Calculate the molar heat of vapourisation of A. 2

4. (*a*) Explain the moving boundary method of determination of transport number of an ion. 4

(*b*) An aqueous solution of aniline hydrochloride 0.1 M has a molar conductivity of 120.0 S cm^2 mol^{-1}. On the addition of some aniline to this solution, the molar conductivity decreases to 102.0 S cm^2 mol^{-1}. The molar conductivity of HCl of the same concentration is 410 S cm^2 mol^{-1}. Calculate the degree of hydrolysis and the hydrolysis constant of aniline hydrochloride. 4

(*c*) Define ionic mobility and give its SI unit. 2

5. (*a*) Give a method for the experimental determination of emf of a cell. 3

(*b*) Derive expressions for calculating ΔG, ΔH and ΔS from emf of a cell. 3

(*c*) For the cell : 4

$$Hg(l)|Hg_2Cl_2(s)\left|\begin{matrix}\text{sat. solution}\\ KCl\end{matrix}\right\|\left.\begin{matrix}H^+, Q, QH_2\\ pH = 4.0\end{matrix}\right|Pt(s)$$

Write the electrode reduction reactions and the cell reaction.

Calculate the emf of the cell at 25°C.

Given :

$E_{SCE} = 0.244$ V and

$E^0 Q, QH_2, H^+ \,|\, Pt = 0.700$ V at 25°C.

Section B

Attempt any *three* questions.

1. (*a*) Give examples of the following reactions : 6

(*i*) Hell-Volhard-Zelinsky reaction

(*ii*) Reformatsky reaction

(*iii*) Perkin condensation.

(*b*) Giving reasons arrange the following carboxylic acids in increasing order of their reactivity towards reaction with CH_3OH in presence of acid : 2

$$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{\underset{|}{CH}}}-COOH,\ CH_3CH_2CH_2COOH,\ CH_3COOH$$

(*c*) An organic carboxylic acid 'A', molecular formula $C_2H_4O_2$, gives 'B' upon treatment with $SOCl_2$. 'B' when treated with NH_3 forms 'C', 'B' also reacts with CH_3OH to form 'D'.

Giving reactions, identify 'A', 'B', 'C' and 'D'. How will you convert 'D' into A ? 4

2. (*a*) How is ethylacetoacetate prepared ? Write the structures for Keto and Enol forms of ethylacetoacetate and give one evidence for existence of each of the two forms. 2+3

(*b*) How is ethylacetoacetate used to prepare the following ? 6

(*i*) Crotonic acid

(*ii*) Methylacetic acid

(*iii*) 2-Butanone.

3. (*a*) Complete the following reactions and identify the major product formed in each case : 1

(*i*) $$(CH_3)_2\overset{\oplus}{N}(CH_2CH_2CH_3)CH_2CH_3O\overset{\ominus}{H} \xrightarrow{\Delta} ?$$

(*ii*) $$CH_3\underset{\substack{| \\ Br}}{C}HCH_2CH_3 \xrightarrow[\Delta]{alc\ KOH} ?$$

(*b*) Which out of the two amines, aniline and dimethyl amine will react with $CHCl_3$ and alc. KOH ? 2

(*c*) How will you convert : 8

(*i*) Phthalimide into methylamine

(*ii*) Aniline into sulphanilic acid

(*iii*) Benzenediazonium chloride into p-Hydroxy-azobenzene

(*iv*) Acetamide into methylamine.

4. (*a*) How will you convert ? 6

(*i*) Aldopentase into Aldohexose

(*ii*) Glucose into Fructose.

(*b*) Write short notes on any *two* of the following : 6

(*i*) Ruff degradation

(*ii*) Mutarotation

(*iii*) Open chain structure for glucose

(*iv*) Structure of sucrose.