53 (CY 201) ENCH

2014

ENGG. CHEMISTRY

Full Marks : 100

Time : Three hours

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

*Answer **any five** questions.*

1. *(a)* Fill in the blanks ***(any eight)*** : 1×8=8

   (i) Activation energy is ———— energy required to bring a chemical reaction.

   (ii) In Chichibabin reaction aromatic ———— reaction mechanism is observed.

   (iii) Retention of configuration is observed in ———— nucleophilic substitution reaction.

   (iv) The monomer of PP polymer is ————.

(v) Formaldehyde and ———— are the nonomers of Bakelite.

(vi) The number of phases of the reaction $CaCO_3(S) \rightleftharpoons CaO(S) + CO_2(g)$ is ————.

(vii) The unit of rate constant for 3rd order reaction is ————.

(viii) Components are minimum number of chemically ———— species which are needed to describe the composition of each phase in a system.

(ix) Carbocation is ———— hybridised.

(x) Buna-N-rubber is a copolymer. It contains ———— of acrylonitrile.

(b) What is number average molar mass of a macromolecule ? Give the mathematical form of number-average-molar mass $(\overline{M}_N)$ and weight-average-molar mass $(\overline{M}_W)$.

$1+\frac{1}{2}+\frac{1}{2} = 2$

(c) Explain each step of Terylene preparation with necessary chemical reactions. 2×3=6

(d) Equal number of molecules with $M_1 = 10{,}000$ and $M_2 = 30{,}000$ are mixed. Calculate $\overline{M}_N$ and $\overline{M}_W$. What is the heterogeneity index for the polymer ? 3+1=4

2. (a) What is neighbouring group participation of nucleophilic substitution reaction ?

Acetolysis of 4-methoxy-1-pentyl brosylate and 5-methoxy-2-pentyl brosylate give the same mixture of products because of neighbouring group participation. Explain the mechanism with appropriate reactions. 2+6=8

(b) For a 1st-order reaction

$$A \rightarrow P$$

Prove that $[A]=[A]_0 exp^{-kt}$; where k is the rate constant of the reaction. What will be the increase in rate of above reaction with $10^{\circ}C$ increase in temperature ? 4+1=5

(c) Distinguish between Buna-N-rubber and Buna-S-rubber. 4

(d) Calculate the ionic-strength of $BaSO_4$ in 0·01 molal solution. 3

3. (a) Distinguish between order and molecularity of a chemical reaction. 3+2=5

Find out the molecularity of the following reactions :

(i) $CH_3COOC_2H_5 + OH^{\ominus} \rightarrow CH_3COO^{\ominus} + C_2H_5OH$

(ii) $2Cl_2O \longrightarrow 2Cl_2 + O_2$

(iii) $2NO(g) + Cl_2(g) \longrightarrow 2NOCl(g)$

(iv) $C_{12}H_{22}O_{11} + H_2O \xrightarrow{H_3O^{\oplus}} C_6H_{12}O_6 + C_6H_{12}O_6$

(b) Prove that, for n^{th} order reaction ;

$$t_{1/2} \propto \frac{1}{a^{n-1}}$$

where, $t_{1/2}$ is the half-life period, a is the initial concentration of the reaction $nA \longrightarrow$ Products. 5

(c) In a particular reaction the time required to complete half of the reaction was found to increase nine times when the initial concentration of the reactant was reduced to one third. What is the order of the reaction ? Give *one* example of 2nd-order reaction. 3+1=4

(d) For the hydrolysis of sulphamic acid, $k_2 = 1{\cdot}16 \times 10^{-3}\ mol^{-1}\ dm^3 s^{-1}$ at $363K$, while $E_a = 127490\ Jmol^{-1}$.

From these data find $\Delta G^{\neq}$, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for the reaction at $363K$. 2+2+2

4. (a) What do you mean by Thermoplastic ? Give examples with appropriate chemical structure.

How can you differentiate thermoplastic from thermosetting plastic ? 2+2+2=6

(b) Complete the following polymerisation reactions : 2

(i) $nHOOC-(CH_2)_4-COOH + nH_2N-(CH_2)_6-NH_2 \rightarrow ?$

(ii) $n\ CH_2 = \underset{\displaystyle CH_3}{\overset{\displaystyle |}{CH}} \xrightarrow{\text{Zieglar-Natta Catalyst}} ?$

(c) The standard *emf* of the Daniell cell is $1{\cdot}1V$. Calculate the equilibrium constant for the reaction at $298K$. 3

(d) The *emf* of a standard cadmium cell is $1{\cdot}01832V$ at $298K$. The temperature coefficient of the cell is $-5{\cdot}0\times10^{-5}VK^{-1}$. Calculate ΔG, ΔH and ΔS for the cell reaction. 2+2+2=6

(e) Distinguish between galvanic cell and electrolytic cell. 3

5. (a) For a Ist-order reaction prove that

$$k = \frac{2{\cdot}303}{\Delta t} log \frac{c_1}{c_2}$$

where, k is the 1st order rate constant, c_1 and c_2 are the concentration of reactants at two instants differing by Δt. 4

(b) At a certain temperature ethyl acetate on saponification gave the following results :

$t(min)$	0	5	25	55
ml of $0{\cdot}1N$ CH_3COOH used to titrate 10 ml unreacted alkali.	16	10·2	4·3	2·3

Show that it is a 2nd-order reaction.

How much fraction of the ester will be decomposed in 40 minutes ? 4+2=6

(c) Write short notes on : 5×2=10

(i) Polystyrene

(ii) Bimolecular Nucleophillic Substitution $\left(S_N2\right)$

(iii) Saytzeff rule of elimination reaction.

(iv) Natural Rubber.

(v) Urea-formaldehyde resin.

6. *(a)* Write down the number of components, number of phases and evaluate the degrees of freedom for the following equilibria : $4\times2=8$

(i) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

(ii) $NH_4Cl(S) \rightleftharpoons NH_3(g) + HCl(g)$ when $\rho NH_3 \neq \rho HCl$.

(iii) A dilute solution of sulphuric acid in water.

(iv) Pure partly frozen acetic acid.

(b) Explain the instrumentation of Nuclear Magnetic Resonance Spectrometer. 6

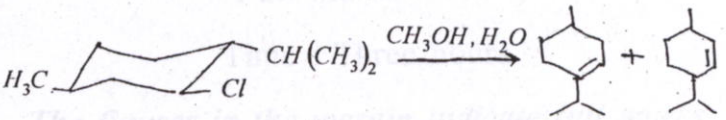
(c) Explain the dependence of rate constant on temperature with Arrhenius equation. 6

7. *(a)* Write the product formed in the following Electrophillic reaction with appropriate reaction mechanism :

$CH_3 - CH = CH_2 + HBr \longrightarrow ?$ 5

(b) What is unimolecular elimination reaction ? Distinguish between unimolecular elimination and unimolecular nucleophillic reaction. For the following reaction give the appropriate mechanism.

2+2+3=7



(c) Explain the one-component phase diagram of water-system.

Distinguish between phase diagram of water and carbon-dioxide.

What is meta-stable stage ? 4+3+1=8