53 (CY 201) ENCH

2012 C
2013
(May)

ENGG. CHEMISTRY

Paper : CY 201

Full Marks : 100

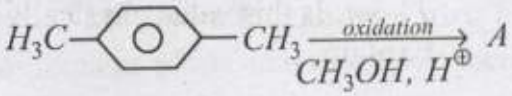
Pass Marks : 30

Time : Three hours

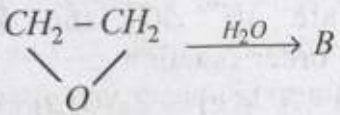
The figures in the margin indicate full marks for the questions.

*Answer **any five** questions.*

1. *(a)* What do you mean by Polymerisation ? Write the product formed of the reaction



$$H_3C-C_6H_4-CH_3 \xrightarrow[CH_3OH,\ H^{\oplus}]{oxidation} A$$



$$CH_2-CH_2 \xrightarrow{H_2O} B$$

$$A + B \xrightarrow{-H_2O} C$$; where product C is a condensation polymer. 2+1+1+2=6

Contd.

(b) Write short notes on : Buna–*S*–rubber and Buna–*N*–rubber.
What is the main difference between these two rubbers ? 2+2+1=5

(c) Explain the osmotic pressure method of determining the molecular mass a polymer. Draw a plot of reduced osmotic pressure versus concentration of polymer. 3+2=5

(d) How intrinsic viscosity is related to molecular weight polymer ?
Calculate the approximate concentration of myosin in water which would have a viscosity at $1 \cdot 5 \cdot [\eta] = 217 cm^3 g^{-1}$. 1+3=4

2. (a) What do you mean by pseudofirst order reaction ? Distinguish between molecularity and order of a reaction. 2+3=5

(b) What is the value of the rate constant, predicted by the Arrhenius equation if $T \to \infty$. Is this value physically reasonable ? Explain. 2+2=4

(c) Calculate $\Delta H^{\neq}$, $\Delta G^{\neq}$ and $\Delta S^{\neq}$ for the second order reaction
$NO_2(g) + NO_2(g) \to 2\,NO(g) + O_2(g)$ at $500K$. Given $A = 2 \cdot 0 \times 10^9 S^{-1}$. The energy of activation is $111\,K\,Jmol^{-1}$. 5

(d) What is the expression for pre-exponential factor or Arrhenius constant of the following reaction according to Collission theory ?

$$A + B \rightarrow P$$

It is found that for the reaction $NO + Cl_2 \rightarrow NOCl + Cl$ that $A = 4 \cdot 0 \times 10\, L\, mol^{-1} s^{-1}$ at $298K$. Use $\sigma(NO) = 0 \cdot 42\, nm^2$ and $\sigma(Cl_2) = 0 \cdot 93\, nm^2$ estimate the ρ-factor for the reaction. 2+4=6

3. (a) What do you mean by degree of freedom ? Give the number of degrees (F) of freedom of the following systems : 2+1+1=4

(i) water, allowing for its autoprotolysis

(ii) aqueous acetic acid

(b) Both H_2O and CO_2 can be drawn by one component phase-diagram. But there is a difference in the phase-diagram of H_2O and CO_2. Why this difference exist explain with the phase-diagram. 2+2+1=5

(c) Distinguish between hexagonal closed-packed structure and cubic closed-packed structure. 3

(d) Write short notes on : 3+3=6

(i) Hund's rule of maximum multiplicity.

(ii) Bohr's spectrum of H^3-atom.

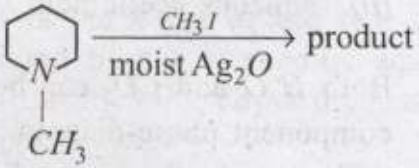
(e) Find out the conjugate acid-base pair in the following reaction : 2

$$H_2SO_4 + H_2O \rightleftharpoons H_3O^{\oplus} + HSO_4^{\ominus}$$

4. (a) Explain the bimolecular nucleophilic substitution reaction with a suitable example.

Distinguish between SN^1 and SN^2 reaction. 4+2=6

(b) Name the product formed in the following reaction with reaction mechanism 2+3=5



(c) Write short notes on : 2×3=6

(i) Addition Reaction

(ii) Substitution Reaction

(d) Which can be expected to have the higher dissociation energy ? 1½+1½=3

(i) N_2 or $N_2^{\oplus}$

(ii) F_2 or $F_2^{\oplus}$

5. (a) The E.M.F of the standard weston cell written as

$Cd(Hg),\ CdSO_4 \cdot \frac{8}{3} H_2O(S) \| \ CdSO_4\ (sat)$, $Hg_2SO_4(s),\ Hg$ in which cell reaction is

$$Cd(Hg) + Hg_2SO_4(S) + \frac{8}{3} H_2O(l) \rightarrow CdSO_4 . \frac{8}{3} H_2O(S) + 2Hg(l)$$

is $1 \cdot 0185 V$ at $25^{\circ} C$. Calculate ΔG°, ΔS° and ΔH° for the cell reaction if $\left(\partial E^{\circ} / \partial T\right)_P$ for the cell is $5 \cdot 00 \times 10^{-5} VK^{-1}$. 5

(b) Calculate the ionic strength of

(i) $0 \cdot 15$ *molal* KCl solution

(ii) a solution which is $0 \cdot 1$ *molal* in KCl and $0 \cdot 2$ *molal* in K_2SO_4. 2+3=5

(c) What is the Debye-Huckel limiting law ? Calculate the mean activity coefficient $(\gamma \pm)$ of $NaCl$ at a molality $0 \cdot 01$. 2+3=5

(d) Write short notes on : 3+2=5

(i) Glass Electrode

(ii) Calomel Electrode.

6. (a) Explain the Instrumentation of Nuclear Magnetic Resonance Spectrometer.

At a magnetic flux density $1 \cdot 65T$, the frequency of separation between protons in benzene and tetramethyl silane is $510 \cdot 5Hz$. What is the chemical shift in δ and τ-scale ? 5+5=10

(b) What is the ratio of the number of proton spins in the lower state to the number in the higher state in a magnetic field of $2T$ at temperature $25^{\circ}C$?

What is the increasing order of chemical shift of the following ?

CH_3I, CH_3Br, CH_3Cl, CH_3F

Explain the reason behind this.

5+3+2=10

7. *(a)* For the displacement reaction,

$$\left[Co(NH_3)_5Cl\right]^{2+} + H_2O \rightarrow \left[Co(NH_3)_5(H_2O)\right]^{3+} + Cl^{\ominus}$$

The rate constant is given by

$$ln\left[k/\left(min^{-1}\right)\right] = \frac{-1106 \cdot 7k}{T} + 31 \cdot 33$$

Evaluate k, E and A for the chemical reaction at $25^{\circ}C$. 5

(b) Write short notes on : 2×4=8

(i) Number-average molecular weight

(ii) Weight-average molecular weight

(iii) Z-average molecular weight

(iv) Viscosity-average molecular weight.

(c) A solution contains equal number of particles with molar masses $10,000\,gmol^{-1}$ and $20,000\,gmol^{-1}$, respectively. Calculate $\overline{Mn}$ and $\overline{Mm}$. 2+3=5

(d) Define phase, components and degree of freedom with a suitable example. 2
