53 (CY 201) ENCH

2014

ENGG. CHEMISTRY

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

   (i) The monomer of perpex is ————.

   (ii) The minimum energy required to bring a chemical reaction is ————.

   (iii) In an elimination reaction the more substituted alkene is identified by ———— rule.

   (iv) Walden inversion is observed in ———— nucleophilic substitution.

(v) In Chichibabin reaction _____ mechanism is observed.

(vi) The unit of rate constant of $\frac{9}{2}$th order reaction is _____.

(vii) In absence of catalyst, a mixture of $H_2O(g)$, $H_2(g)$ and $O_2(g)$ at room temperature is a _____ component system.

(viii) For the reaction

$$NH_4Cl(S) \rightleftharpoons NH_3(g) + HCl(g),\ P_{NH_3} \rightleftharpoons P_{HCl}$$

the degree of freedom is _____.

(ix) The half life period of 2nd-order reaction of type $2A \rightarrow$ product is _____.

(x) For same reaction type, the value of $k_{35°C}/k_{25°C}$ = _____ ;

where $k_{35°C}$ and $k_{25°C}$ are rate constants at $35°C$ and $25°C$.

(b) Arrange the following in increasing order : $1 \times 3 = 3$

(i) primary alkyl halide, secondary alkyl halide, tertiary alkyl halide (on the basis of E-2 elimination).

(ii) 3°-carbocation, 1°-carbocation, 2°-carbocation (on basis of stability)

(iii) $k_{45^\circ C}, k_{65^\circ C}, k_{25^\circ C}, k_{35^\circ C}$ (on the basis of rate constant with respect to temperature)

(c) Complete the following reaction with suitable mechanism for elemination reaction.

$$CH_3 - \underset{\displaystyle Br}{\underset{|}{CH}} - CH_2 - CH_3 \xrightarrow[CH_3OH]{CH_3O^{\ominus}}$$

Explain the major product formation with the help of Saytzeff-rule. 5

(d) Distinguish between unimolecular nucleophilic substitution reaction and bimolecular nucleophilic substitution reaction.

Give the energy-profile diagram for each of the reaction. 2+2=4

2. (a) A protein sample consists of an equimolar mixture of haemoglobin $\left(M = 15 \cdot 5\, kg\, mol^{-1}\right)$, ribonuclease $\left(M = 13 \cdot 7\, kg\, mol^{-1}\right)$ and myoglobin $\left(M = 17 \cdot 2\, kg\, mol^{-1}\right)$. Calculate the number-average and mass-average masses. Which is greater ? 5

(b) For a Ist-order reaction 3+3=6

$$A \longrightarrow P$$

prove that $[A] = [A]_0\, exp^{-kt}$

where k is the rate constant of the reaction.

Draw the plot of $[A]/[A]_0$ versus time *(t)*.

(c) For the second-order reaction $A + 3B \rightarrow P$,

where P stands for the product, the differential rate equation is 7

$$\frac{dx}{dt} = k_2(a-x)(b-3x).$$

Find out the value of k_2 if

$$\frac{1}{(a-x)(b-3x)} = \frac{1}{(3a-b)}\left[\frac{3}{b-3x} - \frac{1}{a-x}\right]$$

(d) Give the mechanism for Chichibabin reaction by aromatic nucleophilic substitution. 2

3. *(a)* Define ionic strength of a solution. Find out the ionic strength of the following electrolytes 2+3=5

$$KNO_3,\ K_3[Fe(CN)_6],\ Na_2SO_4.$$

(b) Calculate the mean activity $a\pm$, mean molality $b\pm$, $\gamma\pm$ of $CdCl_2$ in 0·01 molal solution. γ_+ and γ_- may be assumed to be 0·5 and 0·8 respectively. 5

(c) What is the *e.m.f* of the cell which have $\Delta G = -100 kJ/mol$ and $v = 1$? 2

(d) Give the derivation for Nernst equation. 4

(e) Give the expression for Debye-Hückel Limiting Law. Calculate the mean ionic activity coefficient of 0·01 $mol\,L^{-1}\,NaCl$ aqueous solution at $298k (A = 0{\cdot}509)$. 4

4. (a) Complete the following reactions with appropriate structures : 2×3=6

(i) 1, 3-butadiene + Styrene $\rightarrow$ SBR

(ii) Glutamic acid + hexamethylene diammine $\rightarrow$ polymer (condensation)

(iii) phenol + formaldehyde $\rightarrow$ Bakelite.

(b) What do you mean by Intrinsic viscosity ? What is the value of Mark-Houwink exponent ? 2+1=3

(c) How rate constant of a reaction depends on temperature ? Explain.

Prove that 3+4=7

$$\log k = \frac{Ea}{2{\cdot}303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

where, $K = \frac{k_2}{k_1}$.

(d) Give *two* examples of 2nd-order reaction of type $2A \rightarrow P$.

What is pseudounimolecular reaction ?

2+2=4

5. (a) The intrinsic viocosity of a polymer at $20°C$ is $180\,cm^3/g$. If $[\eta]$ is related to the viscosity average molar mass $\overline{M}_{vise}$ by the expression :

$$[\eta] = 3{\cdot}60 \times 10^{-2} \left(\overline{M}_{visc.}\right)^{0{\cdot}64}$$

Calculate $\overline{M}_{visc.}$ 5

(b) Draw the phase-diagram for one-component water system. 4+2=6

Prove that the vapour-pressure of meta-stable state is greater than the stable state.

(c) Define chemical-shift in nuclear magnetic resonance spectroscopy. 3

(d) The standard *e.m.f* of the cell 2×3=6

$$Pt(S)|H_2(g)|HBr(aq)|AgBr(S)|AgCl(S)$$

was measured over a range of temperatures and the data were fitted to the following polynomial :

$$E^{o}(v)=0{\cdot}07131-4{\cdot}99\times10^{-4}(T-298)-3{\cdot}45\times10^{-6}(T-298)^2$$

Evaluate the standard reaction Gibbs energy, enthalpy and entropy at 298*k*.

6. (a) Write short notes on : 2×5=10

(i) Octane number

(ii) Carbonization of coal

(iii) Water gas

(iv) Natural gas

(v) Urea-formaldehyde-resin.

(b) Explain the protective measures against corrosion. 4

(c) At a certain temperature ethylacetate on saponification gave the following results :

t (*min*)	0	5	25	55	120
ml of 0·1*N* CH_3COOH used to titrate 10*ml* of unreacted alkali	16	10·2	4·3	2·3	1·1

Show that it is a second-order reaction of type $2A \longrightarrow P$. 6

7. (a) What is the difference between Galvanic cell and Daniel cell ? 2

(b) Define phase, component and degrees of freedom. 3

(c) Prove that $P^H + P^{OH} = 14$ 2

(d) Write the full form of 3

(i) NMR

(ii) ESR

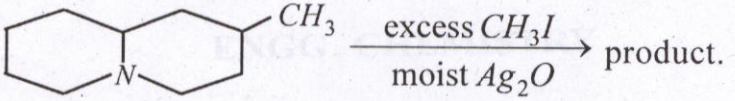
(iii) UV-Viz-spectroscopy

(e) Give the polymerisation reaction of natural rubber. 2

(f) Prove that : for Ist-order reaction $t_{1/2} = 0{\cdot}693/k$; where $t_{1/2} \rightarrow$ half-life period and

$k \rightarrow$ rate constant. 3

(g) Give the mechanism of the following elimination reaction 5



give the structure and IUPAC nomenclature of the product.