FIRST B.SC. EXAMINATION, 2018

(2nd Semester, Old Syllabus)

CHEMISTRY (SUBSIDIARY)

PAPER - IVS

Time : Two hours   Full Marks : 50

Use a separate answerscript for each group.

GROUP - A

1. a) The reaction $A \rightarrow$ Products is "3/2" order with respect to A. Deduce the integrated rate law. Find the expression on half-life period.   3+2

   b) Consider two reactions I and II. The frequency factor of I is 100 times that of II ; the activation energy of I is 4.6 kcal higher than that of II. Show at 227ºC the rate constants have very nearly the same value.   3

   c) How can one determine the order of a reaction by method of half-life period ?   2

   d) What is 'turn over number'? How can one obtain the Michaelis constant (K_M) from a plot of r vs [S] ? The terms have their usual significance. What is the unit of K_M?   1+3+1

[Turn over

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iv) $Ph\ CH_2CHO \xrightarrow[Con.HCl]{EtSH}$ 1

v) $CH_3\ CH_2\ CO\ CH_3 \xrightarrow{Br_2,\ aq\cdot NaOH}$ 1

d) Write short notes on : $1\frac{1}{2} \times 2$

   i) Gatterman-Koch aldehyde synthesis

   ii) Reimer-Tiemann reaction

GROUP - C

3. a) Prove that the pH of an aqueous solution of ammonium cyanide is independent of its concentration.   4

   b) Justify the use of phenolphthalein ($pk_{in} = 9\cdot4$) as an indicator in the titration of benzoic acid ($K_a = 6\cdot3 \times 10^{-5}$) with standard NaOH solution.   5

   c) Derive the equation : $pH = pKa + \log \dfrac{[Salt]}{[Acid]}$ 4

   d) Write the Nernst equation for

   $$MnO_4^- + 8H^+ + 5e \rightarrow Mn^{2+} + 4H_2O$$ 2

   OR

   Find out the degree of hydrolysis and pH of a 0.02 (M) aqueous solution of ammonium chloride at 25ºC ($K_b = 1\cdot8 \times 10^{-5}$).   2

e) A zero order reaction must be multistep : Justify.

OR

Draw rate of reaction $(r(t))$ as a function of time (t) for a

first order reaction. 2

GROUP - B

2. a) i) Write one chemical method that can be used to distinguish primary, secondary, and tertiary alcohols. Illustrate with suitable example. 3

ii) Write a method of preparation of aldehyde using a reductive method. 1

iii) A compound on ozonolysis produces 2, 2–dimethyl-6-oxoheptanal. Write the structure of the starting compound. 1

b) Carry out the following transformations *(any two)* : 2×2

i) $PhCHO \rightarrow PhCH = CHCO_2H$

ii) $(CH_3)_2CCH_2CH_3 \rightarrow (CH_3)_2CH\ CH\ CH_3$
    with OH on the carbon (left), OH (right)

iii) $CH_3CH_2CN \rightarrow CH_3CH_2COCH_3$.

c) Predict the product(s) : answer question i - and *any three* from questions (ii - v) from the following :

i) $(CH_3)_2CO \xrightarrow[\text{II. } H_3O^+]{\text{I. } Mg/Et_2O} A \xrightarrow{\text{Con·}H_2SO_4} B$ 2

ii) $PhCOCH_3 \xrightarrow[CH_2Cl_2]{} $ 1

(reagent: chlorobenzene with CO_3H)

iii) $Ph\ COCH_3 \xrightarrow{SeO_2}$ 1