

Ph.D. Programme in Chemistry

Model Question Paper

RESEARCH APTITUDE ASSESSMENT TEST

Time : 2 Hours

Max. Marks : 75

I. Part A: Multiple Choice Questions 30 x 1 mark = 30 marks

Choose the correct Response viz., A, B, C, D or E for the Questions from 1 - 30 which carry ONE mark each. Please NOTE that an **incorrect response** will attract **negative marking**. (For Multiple Choice question with 5 options, $\frac{1}{4}$ th mark shall be deducted for an incorrect answer.)

1. The first half-life of a zeroth order reaction is 200s. The duration of the next half- life is ()
A) 200s B) 100s C) 400s D) 50s E) cannot be predicted

2. Consider the following parallel reactions: ()
A \rightarrow B, rate constant k_1 , activation energy 45.3kJmol^{-1}
B \rightarrow C, rate constant k_2 , activation energy 69.8kJmol^{-1}
If the rate constants are equal at 320 K, the temperature at which $k_1/k_2 = 2$, is
A) 298 K B) 250 K C) 273 K D) 310 K E) 225 K

3. Oxygen for metabolism is taken up by Haemoglobin(Hb) to form oxyhaemoglobin(HbO_2) according to the simplified equation ()
 $\text{Hb(aq)} + \text{O}_2(\text{aq}) \rightarrow \text{HbO}_2(\text{aq})$

Where the second order rate constant is $2.1 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ at 37°C . For an average adult, the concentrations of Hb and O_2 in the blood and in the lungs are $8 \times 10^{-6}\text{M}$ and $1.5 \times 10^{-6}\text{M}$ respectively. The rate of formation of HbO_2 is

- A) $5 \times 10^{-5}\text{Ms}^{-1}$ B) $5 \times 10^{-4}\text{Ms}^{-1}$ C) $2.5 \times 10^{-5}\text{Ms}^{-1}$
D) $1 \times 10^{-4}\text{Ms}^{-1}$ E) $2.5 \times 10^{-4}\text{Ms}^{-1}$
4. The NMR signal of a compound is found to be 240Hz downfield from the TMS peak using a spectrometer operating at 60MHz. The chemical shift δ in ppm relative to TMS is ()
A) 2 ppm B) 3 ppm C) 5 ppm
D) 4 ppm E) 6 ppm

5. Which one of the following compounds is coloured? ()
 A) benzene B) naphthalene C) anthracene
 D) cyclohexane E) tetracene

6. Which one of the following compounds/ ions has point group D_3 ? ()
 A) $[\text{CoF}_6]^{3-}$ B) $[\text{CoCl}_6]^{3-}$ C) $[\text{Co}(\text{en})_3]^{3+}$
 D) $[\text{Co}(\text{gly})_3]$ E) $[\text{CoBr}_6]^{3-}$

7. Crystallisation of sodium acetate from a super saturated solution occurs spontaneously. Which one of the following is true from this observation? ()
 A) $\Delta G = -ve, \Delta S = -ve, \Delta H = -ve$ B) $\Delta G = -ve, \Delta S = -ve, \Delta H = +ve$
 C) $\Delta G = -ve, \Delta S = +ve, \Delta H = -ve$ D) $\Delta G = +ve, \Delta S = -ve, \Delta H = -ve$
 E) $\Delta G = -ve, \Delta S = +ve, \Delta H = +ve$

8. Consider the following system at equilibrium ()

$$\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$$

The number of phases (P), components(C) and degrees of freedom are

A) P= 3, C=1,F= 0 B) P= 3, C=2,F= 1 C) P= 3, C=3,F= 2
 D) P= 2, C=1, F= 1 E) P= 2, C=2,F= 2

9. Among the following molecules identify the one whose symmetry number is 12. ()
 A) BF_3 B) SO_2 C) CHCl_3 D) CH_4 E) NH_3

10. Using the following standard reduction potentials, ()

$$\text{Cu}^{2+} + 2\text{e} \rightarrow \text{Cu}, E_1^0 = 0.342 \text{ V}$$

$$\text{Cu}^{2+} + \text{e} \rightarrow \text{Cu}^+, E_2^0 = 0.153 \text{ V}$$
 the standard reduction potential for $\text{Cu}^+ | \text{Cu}$, calculated is
 A) 0.495 V B) 0.189 V C) -0.189V
 D) 0.531V E) 0.248 V

11. Which one of the following species/molecules can be detected by ESR spectroscopy? ()
 A) Nitric oxide B) Methane C) Ethane D) Ethylene E) Methyl carbocation

12. $[\text{M}+2]^+$ peak of 33% abundance is observed in the mass spectrum of ()
 A) Iodobenzene B) Fluorobenzene C) Phenol
 D) Bromobenzene E) Chlorobenzene

13. In the ^{13}C NMR spectrum a peak at $\sim\delta 175$ is observed. The compound is ()
 A) Paracetamol B) p-Aminophenol C) Phenol
 D) Catechol E) Resorcinol
14. Which one of the following techniques is the most suitable to study the composition of lemon grass oil? ()
 A) HPLC B) GC-MS C) TGA D) IR E) NMR
15. Among the following identify the most stable dimethylcyclohexane. ()
 A) cis-1,2 B) trans-1,2 C) cis-1,3
 D) trans-1,4 E) cis-1,4
16. to 30.

Part - B

II. Answer any 9 of the following in about 150 words each in the sheets provided with the question paper:

(9 x 5 = 45 marks)

1. The pre-exponential factor and activation energy for the hydrolysis of t-butyl chloride are $2.1 \times 10^{16} \text{ s}^{-1}$ and 102 kJmol^{-1} , respectively. Calculate the values of ΔS^{\ddagger} and ΔH^{\ddagger} at 286 K for the reaction.

2. The hydrolysis of urea,

$$(\text{NH}_2)_2\text{CO} + \text{H}_2\text{O} \rightarrow 2\text{NH}_3 + \text{CO}_2$$
 has been studied by many researchers. At 100°C , the pseudo first order rate constant is $4.2 \times 10^{-5} \text{ s}^{-1}$. The reaction is catalyzed by the enzyme urease, which at 21°C has a rate constant of $3 \times 10^4 \text{ s}^{-1}$. If the enthalpies of activation for the uncatalyzed and catalyzed reactions are 134 kJmol^{-1} and 43.9 kJmol^{-1} , respectively, calculate the temperature at which the nonenzymatic hydrolysis of urea would proceed at the same rate as the enzymatic hydrolysis at 21°C .

3. a) What is the probability of locating a particle in a one dimensional box between $a/4$ and $3a/4$, where 'a' is the length of the box. Assume the particle to be in the lowest level.
 b) Explain in terms of their electron configurations, why Fe^{2+} is more easily oxidized to Fe^{3+} than Mn^{2+} to Mn^{3+} .

(3+2=5marks)

4. Construct the character table for water molecule of C_{2v} point group.
5. Sketch the COSY (^1H - ^1H) NMR spectrum of nicotinic acid(pyridine-3-carboxylic acid).
6. to 12.

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