[Time: Three Hours] **[Marks:100]**

Please check whether you have got the right question paper.

N.B: **1) All** questions are **Compulsory.**

2) Figures to the **right** indicate **full** marks

3) **Use** of logarithmic table/non-programmable calculator is **allowed.**

Q. 1) Select the most appropriate choice for the following: (40 M)

1) To be physically acceptable, a quantum mechanical wave function must be:
   a) An integer
   b) A multiple of ħ
   c) A real number
   d) Part of continuum

2) Consider the hypothetical reaction $A + 2B \rightarrow AB_2$.
   It follows the rate law: rate = k [A] [B]. Hence, the rate determining step is:
   a) $A + B \rightarrow AB$
   b) $A + 2B \rightarrow AB_2$
   c) $AB + B \rightarrow AB_2$
   d) $AB + A \rightarrow A_2 + B$

3) For the reaction: $2A + B \rightarrow D + E$ the following mechanism has been proposed:
   $A + B \rightarrow C + D$ (Slow)
   $A + C \rightarrow E$ (Fast)
   The rate law expression for the reaction is:
   a) Rate = k $[A]^2$ [B]
   b) Rate = k [A] [B]
   c) Rate = k [A] [C]
   d) Rate = k $[A]^2$ [B] [C]

4) In a reaction mechanism, the rate determining step is the _____
   a) Fastest and has the lowest activation energy
   b) Slowest and has the highest activation energy
   c) Fastest and has the highest activation energy
   d) Slowest and has the lowest activation energy

5) The solubility product of a salt is equal to the square of its solubility. The ratio of cations to anions in the salt is _____
   a) 1:2
   b) 1:3
   c) 2:3
   d) 1:1

6) Which of the following statements is false regarding the reaction: $A_{(g)} \leftrightarrow B_{(g)}$
   a) The reaction can achieve the lowest possible free energy by going to completion
   b) At equilibrium, $\Delta G = 0$
   c) At equilibrium, $G_A = G_B$
   d) None of the above

7) The effect that tends to retard the mobilities of the ions in solution s:
   a) Asymmetry effect
   b) Relaxation effect
   c) Refractive index
   d) Viscosity

8) How many atoms are there in an element packed in a bcc structure?
   a) 08
   b) 04
   c) 02
   d) 01

9) When a salt is added to a solution of another salt having a common ion, the degree of dissociation, α _____
   a) Increases
   b) Remains the same
   c) Decreases
   d) None of these

10) One of the assumption made in the conventional activated complex theory is:
   a) Equilibrium is maintained between the activated complex and products
   b) Equilibrium is maintained between the reactants and products
   c) Equilibrium is maintained between the reactants and activated complex and also between products and activated complex
   d) Equilibrium is maintained between the reactants and activated complex

11) Olefin hydrogenation using Wilkinson's catalyst initiates with:
   a) olefin addition to $Rh(PPh_3)_2Cl$
   b) olefin addition to $Rh(PPh_3)_3Cl$
   c) a phosphine dissociation from $Rh(PPh_3)_3Cl$
   d) a phosphine addition to $Rh(PPh_3)_2Cl$

12) Which metal complex ion is expected to be subject to a Jahn-Teller distortion?
   a) $[Cr(OH_2)_6]^{3+}$
   b) $[Cr(NH_3)_6]^{2+}$
   c) $[Cr(CN)_6]^{3-}$
   d) $[Cr(bpy)_3]^{2+}$

13) Which one of the following cubic cell contains only one atom?
   a) Simple cubic cell
   b) Face centered cubic cell
   c) Body centered cubic cell
   d) none of these

14) Marcus-Hush theory applies to:
   a) any electron transfer reaction of consideration
   b) outer-sphere electron transfer in redox reactions
   c) inner-sphere electron transfer in redox reactions
   d) all biological redox reactions

15) Which one of the following molecules/ions is square planar
   a) CH_4
   b) NH_4^+
   c) PCl_4^+
   d) XeF_4

16) The perchloric acid molecule contains:
   a) 13 lone pairs, 1 π bond, and 4 σ bonds.
   b) 9 lone pairs, no π bonds, and 6 σ bonds.
   c) 8 lone pairs, 2 π bonds, and 7 σ bonds.
   d) 11 lone pairs, no π bonds, and 5 σ bonds.

17) Hemocyanin contains

a) a dinuclear copper core and binds dioxygen in the cuprous state.
b) a dinuclear copper core and binds dioxygen in the cupric state.
c) a mononuclear copper core and binds dioxygen in the cuprous state
d) a mononuclear copper core and binds dioxygen in the cupric state

18) Total number of geometrical isomers for the complex $[RhCl(CO)(PPh_3)(NH_3)]$is

a) 1
b) 2
c) 3
d) 4

19) The shape of XeF_4 molecules is based on VBT is having_____

a) 4 bond pairs
b) 4 bonds pairs and 1lone pair
c) 4 bonds pairs and 2 lone pairs
d) 4 Bonds pairs and 4 lone pairs

20) Choose the 16 e– complex from the following:

a) $Ni(CO)_4$
b) $Rh(PPh_3)_3Cl$
c) $Fe(CO)_5$
d) $(\eta^6\text{-}C_6H_6)_2Cr$

21) Among the compounds a)-d) the one that can be used as a formyl anion equivalent in the presence of a strong base is:

a) Ethylene
b) Nitroethane
c) 1 , 3-Dithiane
d) 1, 4-dithiane

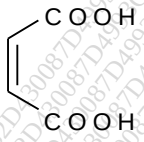
22) The number of nodes present in the HOMO of 1 , 3, 5-Hexatriene in its ground state is:

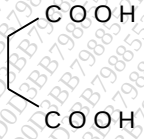
a) One
b) Two
c) Three
d) Four

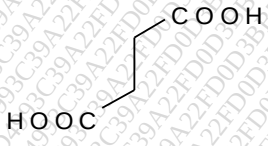
23) The reactive position of Nicotinamide Adenine Dinucleotide (NAD) in biological redox reaction is:

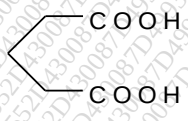
a) 2-position of Pyridine ring
b) 6-position of the Pyridine ring
c) 4-position of the Pyridine ring
d) 5-position of the Pyridine ring

24) Among the following diacids, the one that forms an anhydride fastest on heating with acetic anhydride is:

a) 

b) 

c) 

d) 

25) The number of signals that appear in the broad band decoupled ^{13}C-NMR spectrum of Phenanthrene and Anthracene respectively are:

a) Ten and four

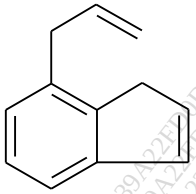
b) Ten and ten

c) Seven and four

d) Seven and seven

26) The major product formed in the following reaction is:

a)



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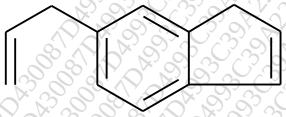

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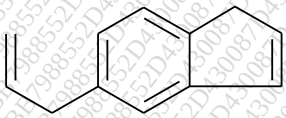
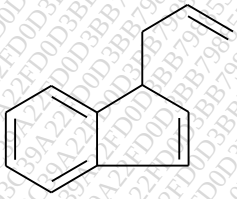


d)



27) For Oestrone, among the statements A to C, the correct ones are:

A. It is a steroidal hormone

B. It has two hydroxyl groups

C. It has one ketone and one phenolic group

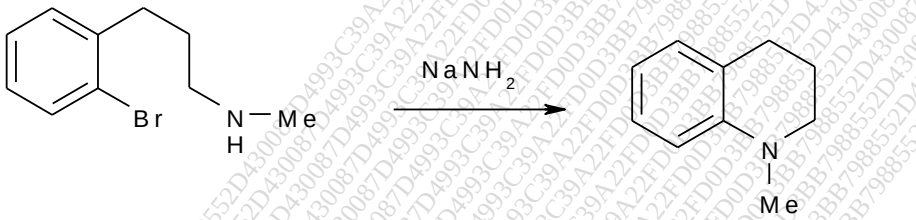
a) A, B and C

b) A and B

c) A and C

d) B and C

28) The reactive intermediate involved in the following reaction is:



a) A carbocation

b) A carbanion

c) A free radical

d) An aryne

29) The heterocyclic ring present in the amino acid Histidine is:

a) Pyridine

b) Tetrahydro pyrrole

c) Indole

d) Imidazole

30) The Gauche conformation ($\phi = 60^\circ$) of n-butane possesses:

a) Plane of symmetry; and is achiral

b) C_2 axis of symmetry; and is chiral

c) Center of symmetry; and is achiral

d) Plane of symmetry; and is chiral

31) In a reversed phase HPLC

a) A hydrophilic stationary phase is combined with a non-polar mobile phase

b) A hydrophilic stationary phase is combined with a polar mobile phase

c) A hydrophobic stationary phase is combined with a non-polar mobile phase

d) A hydrophobic stationary phase is combined with a polar mobile phase

32) Which ion will be deflected most in the magnetic field of a mass spectrometer?

a) $^{53}Cr^{2+}$

b) $^{53}Cr^{+}$

c) $^{52}Cr^{+}$

d) $^{52}Cr^{2+}$

33) A Karl Fischer titration is used to determine:

a) The pH of a water sample

b) The water content of the sample

c) The alcohol content of blood

d) The concentration of Cl_2 in a water sample

34) The purpose of the flame in flame atomic-absorption spectroscopy is to:

a) Purify the sample

b) Desolvate and atomize the analyte atoms in a sample

c) Excite the analyte atoms

d) Ionize the analyte atoms

35) Compound Z absorbs light of wavelength 320 nm. A 1.0×10^{-3} mol dm^{-3} solution of a compound Z gives an absorbance reading of 0.145 when placed in a solution cell of path length 1 cm. what is the value of the molar extinction (absorption) coeficient of Z?

a) 15 $dm^3\,mol^{-1}\,cm^{-1}$

b) 1500 $dm^3\,mol^{-1}\,cm^{-1}$

c) 1.5×10^{-4} mol $dm^{-3}\,cm^{-1}$

d) 150 $dm^3\,mol^{-1}\,cm^{-1}$

36) Which one of the following compounds does not absorb light in the UV/visible spectrum?

a) Aspirin
b) Paracetamol
c) Chloral hydrate
d) Phenobarbitone

37) Result of analysis of a metal by complexometric titration were: 7.146, 7.098, 7.256, 6.942 and 6.593. If Q_{90} for N = 5 is 0.64, comment on the lowest value and highest value.

a) The lowest value is acceptable and highest value is to be rejected
b) The lowest value is rejected and highest value is acceptable
c) Both are to be rejected
d) Both are acceptable

38) Which statement is true about polarography?

a) The diffusion current is caused by solution stirring
b) The addition of supporting electrolytes is necessary for a migration current
c) The diffusion current is proportional to the square root of the concentration of the electroactive species
d) The magnitude of the diffusion current is proportional to concentration of electroactive species

39) For EDTA titrations, the analyte solution and titrant solution are buffered at same pH, for which of the following reasons?

I. The conditional formation constant is affected By pH
II. The fraction of EDTA in Y^{-4} form varies with pH
III. When EDTA reacts to form metal complex, H^+ is a product in most cases

a) I and III only
b) II and III only
c) I and II only
d) I, II and III

40) Fajan's method of titrimetric analysis involves detection of the end point on the basis of which one of the following?

a) Color change
b) Appearance of a precipitate
c) Neutralization reaction
d) Adsorption phenomenon

Q. 2) Attempt **Any Three** of the following questions:

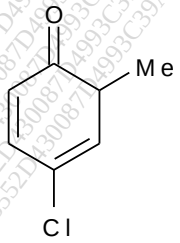
A. i. Explain the kinetics of free radical addition polymerization. (5M)

ii. Give a brief account of homogeneous and heterogeneous catalysis. (5M)

B. Predict the number of unpaired electrons, the spin-only magnetic moments at 25˚C for each of the following: (10M)

i. $[Fe(CN)_6]^{4-}$
ii. $[Ru(NH_3)_6]^{3+}$
iii. $[Cr(NH_3)_6]^{2+}$
iv. $[EuCl_6]^{4-}$
v. $[PtCl_4]^{-2}$

C. i. Calculate λmax for the following compound: (5M)



ii. Explain with mechanism Biginelli Condensation. (5M)

D. i. In what way, does Fourier Transform Spectroscopy differ from conventional IR spectroscopy? What are the advantages of Fourier Transform instruments? (4M)

ii. What do you understand by theoretical plate concept and how HETP affects the separation of HPLC column? (3M)

iii. Discuss the classification of Ion selective electrodes, with suitable examples. (3M)
In what respect do these electrodes differ from ion specific electrodes?

E. i. State the postulates of quantum mechanics. (3M)

ii. A metal crystallizes with a face-centered cubic lattice. The edge of the unit cell is 408 pm. Calculate the number of atoms in the unit cell and diameter of the metal atom. (For FCC, edge = $r / \sqrt{8}$) (2M)

iii. Explain Heck reaction with mechanism. (2M)

iv. A solution of 500 cm^3 of 1 x 10^{-3} M $NiCl_2$ (aq) is titrated with 1 x 10^{-3} M EDTA in a solution of 0.1 M ammonia at pH 1.0. Calculate P_{Ni} when 25.0 cm^3 of titrant solution is added. (α_{Ni}^{2+} = 1.34 x 10^{-4} at pH 11.0) (3M)

Q. 3) Answer **Any Two** of the following questions:

A. i. Describe the characteristic features of catalysis. (8M)
Calculate the activation energy of a reaction whose rate constant is doubled by 10° rise in temperature in the vicinity of 300 K. (R = 8.314 JK^{-1} mol^{-1})

ii. State the Schrodinger wave equation and explain the terms involved. (7M)
Which of the following functions are eigen function of the operator $\mathbf{d^2/dx^2}$?

i. $\sin 4x$
ii. $9x^3$

B. i. Discuss the various steps in the reaction catalysed by the enzyme monooxygenase (Cytochrome P450). (5M)

ii. Calculate the total electron count, polyhedral electron count and predict the structures of the following organometallic compounds. (5M)

a) $[Rh(CO)_{16}]$
b) $[FeC(CO)_{15}]$
c) $[Os_5C(CO)_{12}]^{-2}$
d) $[Ru_5C(CO)_{16}]$
e) $[Os_6(CO)_{18}]^{-2}$

iii. On the basis of the concept of hybridization, derive the wave function for the hybrid orbitals formed in the molecule of CH_4. (5M)

C. i. How will you convert Cholesterol into 16-DPA? (5M)

ii. Explain the following with mechanism: (6M)
a) Hunsdiecker reaction
b) Cope rearrangement

iii. Give an example of AB and A_2X_2 spin systems. (4M)

D. i. Polarography is a highly elegant technique invented by Jaroslav Heyrovsky for which he received the Nobel Prize in 1959.

a. What is the unique feature of polarography which separates it from other Electroanalytical techniques? (2M)

b. Sketch a polarogram and label two important details of the polarographic wave on your diagram. (3M)

c. Calculate the concentration of Cd(II) ions in a solution which gave a diffusion current of 31.52 μA.
Given: Diffusion coefficient of Cd(II) = 6.9×10^{-6} cm^2 s^{-1}
Drop time = 5 seconds, rate flow of mercury = 4 mg s^{-1} (3M)

ii. a. The observed λmax values for phenol and phenolate ion are 211 nm and 235 nm respectively while in the case of aniline and anilinium ion, values are 230 nm and 203 nm respectively. Explain. (4M)

b. Name the various types of radiochemical methods. Discuss any one. (3M)
