PH.D ENTRANCE TEST.
MODEL QUESTION PAPER.
SUBJECT:- CHEMISTRY.

Marks for each section are indicated in the right hand side.

SECTION: I [10]

($h = 6.626 \times 10^{-34}$ Js, $N_A = 6.023 \times 10^{23}$ mol^{-1}, $C = 3 \times 10^8$ $m.s^{-1}$, $R = 8.314$ $JK^{-1}mol^{-1}$, $k = 1.38 \times 10^{-23}$ JK^{-1})

1. Give the expression of Schrodinger equation for a particle outside of a one dimensional box.

2. Differentiate covalent bond and covalent-coordinate bond.

3. Define the term magnetic susceptibility.

4. Propose mechanism for the formation of phenyl diazonium chloride from aniline.

5. Give IUPAC name to the dicarbonyl compound which leads to 2,3-dimethylcyclohex-2-en-1-one upon aldol condensation.

6. X-Ray crystallography is a powerful tool for structure determination of a new compoun(d) Why do we still bother with other spectroscopic methods?

7. Define pharmacophore.

8. What is polydispersity index ? How much it would be for monodisperse polymer ?

9. What are radiative capture reactions ? Give two examples.

10. How accuracy and precision of triple distilled water can be determined ?

SECTION:II [40]

Select the correct answer in the following:

1. Which of the following is correct order of increasing 15B value of the complexes?
   (i). $[Ni(NCS)_6]^{3-}$
   (ii). $[Ni(CN)_6]^{3-}$
   (iii). $[Ni(F)_6]^{3-}$
   (iv). $[Ni(H_2O)_6]^{3+}$

   (a) (iii) < (i) < (ii) < (iv)
   (b) (iii) < (ii) < (i) < (iv)
   (c) (iii) < (iv) < (i) < (ii)
   (d) (ii) < (i) < (iv) < (iii)

2. Which of the following is correct order of decreasing number of the microstate present in the terms?
   (i). ^4F
   (ii). ^1G
   (iii). ^4P
   (iv). ^3H
   (a) (iv) > (i) > (ii) > (iii)
   (b) (iii) > (ii) > (i) > (iv)
   (c) (iv) > (i) > (iii) > (ii)
   (d) (iv) > (ii) > (iii) > (i)

3. The technique of electron spin resonance spectroscopy can only be applied to the species having:
   (a) All paired electron
   (b) One or more unpaired electrons
   (c) No unpaired electrons
   (d) Three paired and no unpaired electrons

4. The commutator $[L_x, L_+]$ is equal to:
   (a) $\hbar \hat{L}_-$ (b) $\hbar \hat{L}_y$ (c) $-\hbar \hat{L}_z$ (d) $-\hbar \hat{L}_-$

5. Below Neel temperature substance behave like :
   (a) Paramagnetic
   (b) Antiferromagnetic
   (c) Ferromagnetic
   (d) Ferrimagnetic

6. The pair having similar geometry is:
   (a) $[Pt(Cl)_4]^{2-}$, XeF_4
   (b) SiF_4, SF_4
   (c) SF_4, XeF_4
   (d) $[FeCl_4]^{2-}$, $[Pt(Cl)_4]^{2-}$

7. Match the coordination compound in List-I with an appropriate pair of characteristics from List -II and select the correct answer using the code given below the lists.

List-I		List-II	
P.	$[Co(F)_6]^{3-}$	1.	2.78 B.M., d^2sp^3 hybridization
Q.	$[Co(NH_3)_6]^{3+}$	2.	2.78 B.M., sp^3d^2 hybridization
R.	$[V(NH_3)_6]^{3+}$	3.	Zero B.M., d^2sp^3 hybridization
S.	$[Ni(NH_3)_6]Cl_2$	4.	4.90 B.M., sp^3d^2 hybridization

	P	Q	R	S
(a)	4	3	1	2
(b)	1	3	4	2
(c)	3	1	2	4
(d)	2	4	1	3

8. The conversion from methanol to acetic acid is catalyzed by
(a) $[Rh(CO)_2I_2]^{2-}$ (c) $[Rh(CO)_2I_2]^{+}$
(b) $[Rh(CO)_2I_2]^{-}$ (d) $[Rh(CO)_2I_2]$

9. Match the List -I and List-II and select the correct answer using the code given below the lists.

List-I **Class of elements**		List- I **Elements**	
P.	Alkaline earth metals	**1.**	Te
Q.	Nobel gases	**2.**	Rn
R.	Chalcogens	**3.**	At
S.	Halogens	**4.**	Sr

	P	Q	R	S
(a)	4	2	1	3
(b)	3	1	4	2
(c)	1	3	2	4
(d)	2	4	3	1

10. Which of the following compound, first used in chemotherapy of syphilis?
(a) Organo zinc (c) Organo lithium
(b) Organo silicon (d) Organo mercury

11. The term symbol for N_2^+ molecule is:
(a) $^1\pi_g$ (b) $^1\Sigma_g$ (c) $^2\Sigma_g$ (d) $^2\Sigma_u$

12. Consider the following sets of quantum numbers:

	n	l	m	s
(i)	3	0	0	+1/2
(ii)	2	2	1	-1/2
(iii)	4	3	-2	+1/2
(iv)	1	0	-1	-1/2
(v)	3	2	3	+1/2

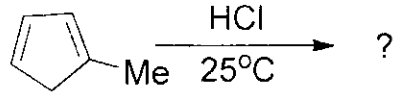
Which of the following sets of quantum numbers is NOT possible?

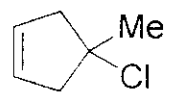
(a) (iii) (iv), and (v) (c)(iv),(i) (iv), and (v)
(b) (i),(ii) (iv), and (v) (d) (ii) (iv), and (v)

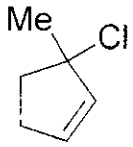
13. If charge of central metal ion is less than stability will be:

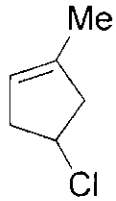
(a) More Increases (c) Decreases
(b) Increases (d) Remain same

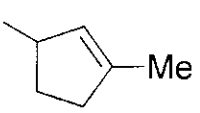
14. What should be the probable product in the following reaction?



(a) 

(b) 

(c) 

(d) 

15. Which of the following is a chemoselective oxidizing agent for C=C double bond?

(a) H_2CrO_4 (c) OsO_4
(b) $KMnO_4$ (d) $Pb(OAc)_4$

16. The sailors in the search of America who joined Columbus suffered from scurvy because

(a) they had excess of sea-food. (c) resveratrole in red wine affected them badly.
(b) they missed ascorbic acid in their diet. (d) hygienic conditions in ship were very inferior.

17. Petroleum ether is_____.

(a) a mixture of alkanes (c) methoxy ethane
(b) ethoxy ethane (d) methoxy methane

18. Which of the following compounds does not contain a carbon atom at the aldehyde oxidation level?

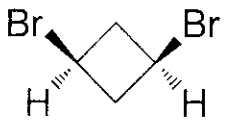
(a) propannitrile (c) dichloromethane
(b) 2-butanone (d) 2.2-dimethoxypropane

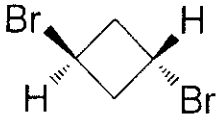
19. ^{13}C NMR spectrum of propanol recorded using $CDCl_3$ shows four signals. Which of the following option can be correctly assigned to carbon-1 of the molecule?

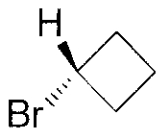
(a) 12.5 ppm (c) 58.7 ppm
(b) 18.3 ppm (d) 77 ppm

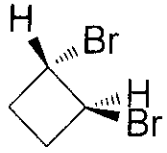
20. Infra-red spectrum of p-hydroxyacetanilide shows three typical absorptions at 3330 cm^{-1}(sharp band), 3300-3000 cm^{-1} (broad band) and 2920 cm^{-1} (sharp band). These bands are best assigned as
(a)Hydrogen bonded -OH stretching, N-H stretching and C-H stretching
(b) N-H stretching, Hydrogen bonded -OH stretching and C-H stretching
(c) Non- Hydrogen bonded -OH stretching, N-H stretching and C-H stretching
(d) Non- Hydrogen bonded -OH stretching, Hydrogen bonded -OH stretching and N-H stretching

21. Which of the following molecules do not possess any diastereotopic hydrogen atoms?

(i) 

(ii) 

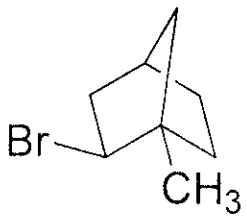
(iii) 

(iv) 

(a) i, ii and iii
(b)ii,iii and iv
(c) i, ii and iv
(d) Only ii

22. Aniline on nitration with HNO_3 and H_2SO_4 in a ratio of 1:3 will yield ortho-, meta- and para-isomers in the ratio of _____.
(a) 1:33:66
(b) 1:66:33
(c) 33:1:66
(d) 66:1:33

23. What is the correct absolute configuration of the following molecules?



(a) 1R,2S,4R
(b) 1R,2R,4S
(c) 1S,2R,4S
(d) 1S,2S,4R

24. CH_2=CH-CHO is a product of _____.
(a) base catalyzed aldol of acetaldehyde and formaldehyde
(b) acid catalyzed dehydration of glycerol
(c) acetaldehyde and methylene iminium ion
(d) all of the above reactions

25. Which of the following statements are NOT correct for hydroboration of alkenes?
(i) It gives syn alcolhol.
(ii) It is a concerted process.
(iii)It is regeoselective to provide boron to the olefinic carbon having less capability to stabilize carbocation.
(iv)addition to alkene occurs from the hindered side.
(a) (i) & (iv)
(b) (i) & (iii)
(c) (ii),(iii) & (iv)
(d) (iv) only

26. A mixture of enantiomers [+A and –A] has observed specific rotation of -60°. The specific rotation of pure dextro isomer is 100°. What is the % amount of isomer +A present in the given mixture?
(a) 20% (b) 80% (c) 60% (d) 40%

27. Thexyl borane does not prefer to undergo migration during H_2O_2 oxidation because
(a) $Na_2CO_3.1.5\ H_2O_2$ is a mild oxidizing agent. (c) it involves migration of a 3° carbon.
(b) a secondary carbon is involved in migration. (d) it distorts the cage structure.

28. The point group D_{nh} has:

(a) n two–fold axes
(b) n-fold principal axis
(c) n-fold principal axis and a horizontal plane
(d) n-fold principal axis, n two–fold axis perpendicular to principal axis and a horizontal plane

29. The half life of a substance in a reaction varies inversely with its initial concentration, then the order of a reaction is:

(a) zero
(b) second
(c) first
(d) third

30. Which of the following is a proper representation of canonical partition function ?

(a) $Z = \sum e^{\beta E_j}$
(b) $Z = e^{-\beta E_j}$
(c) $Z = 1 / \sum e^{-\beta E_j}$
(d) $Z = (e^{-\beta E_j})^{-1}$

31. In Debye – Huckel theory, the activity coefficient of each of the ions of an electrolyte are:

(a) product value
(b) mean value
(c) additive value
(d) fraction value

32. Number average molar mass of a polymer can be determined by:

(a) colligative property
(b) elevation of boiling point
(c) osmosis
(d) all the above

33. A FCC lattice gives reflections with indices of :

(a) all even numbers
(b) all odd numbers
(c) even numbers and a zero
(d) both **a** and **b**

34. In a β^+ decay:

(a) proton is converted to neutron
(b) neutron is converted to proton
(c) α particle is converted to proton
(d) none of the above

35. Michaelis - Menten equation gives rate laws of :

(a) homogeneously catalyzed reaction
(b) heterogenously catalyzed reaction
(c) phosphorylation reaction
(d) acid catalyzed reaction

36. AgCl in water is an example of :

(a) lyophobic colloid
(b) lyophilic colloid
(c) hydrophilic colloid
(d) hydrophobic colloid

37. Raman shift measures :

(a) molecular vibrational difference
(b) molecular energy level difference
(c) molecular rotational difference
(d) molecular motion difference

38. Carnot cycle defines:

(a) a reversible cycle
(b) two isothermal steps at different temperatures
(c) two adiabatic steps
(d) all the above

39. At a low temperature, for an isothermal process:

(a) $\Delta G^0 = \Delta H^0$
(b) $\Delta G^0 \approx \Delta H^0$
(c) $\Delta G^0 = - T\Delta S^0$
(d) $\Delta G^0 = \Delta H^0 - T\Delta S^0$

40. At the triple point of water:

(a) F = 0
(b) F = 1
(c) F = 2
(d) F = 3

SECTION:III

[25]

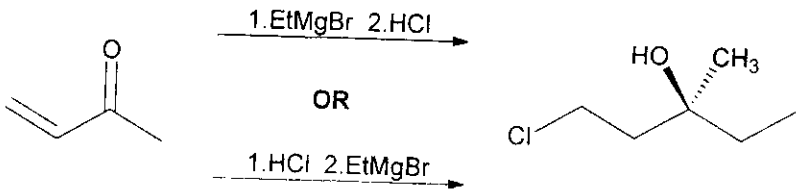
1.(a) Write the formula for the complex dichlorobis(ethylenediamine) cobalt(III) ion. Draw its geometrical and optical isomers. 3

1.(b) Identify the ground term from each set of terms: 2
(i) ^{3}G, ^{3}F, ^{1}H, ^{3}H
(ii) ^{4}G, ^{3}F, ^{2}H, ^{4}P

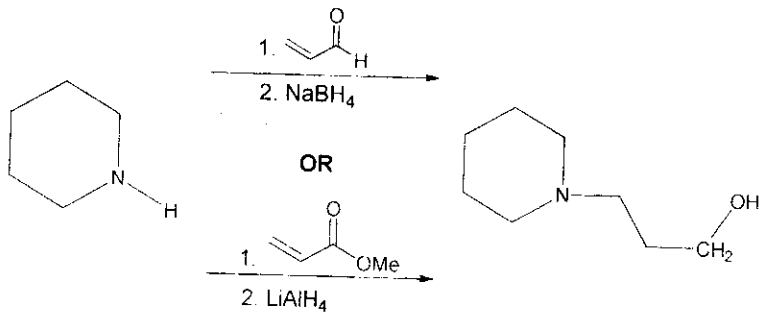
2.(a) Explain the structure of $[Co_4(CO)_{12}]$. 03

2.(b) Write the IUPAC names for $Hg[Co(NCS)_4]$ and $[Pt(NH_3)_4\ (NO_2)(Cl)]SO_4$. 02

3.(a) Which of the following routes shown below could actually lead to the product formation? Why? 03



3.(b) For preparation of the shown aminoalcohol two routed are propose(d) Which route is more likely to succeed? Why? 02

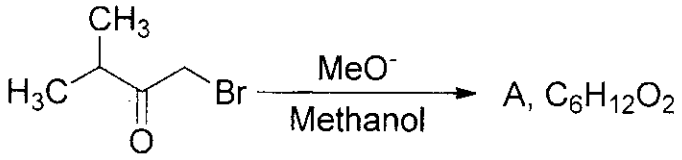


4.a Suggest correct structure for the product A interpreting the spectroscopic data given below. 03

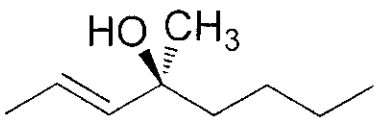
IR, ϑ : 1745 cm^{-1} very prominent band

^{13}C NMR, δ : 179, 52, 39, 27 ppm

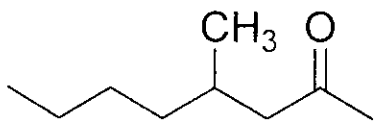
^{1}H NMR, δ : 1.2 (s), 3.7 (s)



4.(b) How could you synthesize following two products from a common substrate 3-penten-2-one by choice of proper reagent? 02



Product-A



Product-B

5.(a) What is electrical double layer ? Give its features as per Gouy – Chapman model. 03

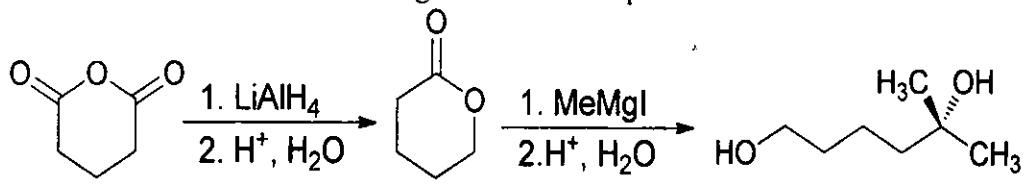
5.(b) For H_2O (*l*) at 100 °C and 1 atm, $\rho = 0.958$ g/cm^3. Find the specific volume of H_2O (*l*) at 100 °C and 1 atm. 02

SECTION:IV

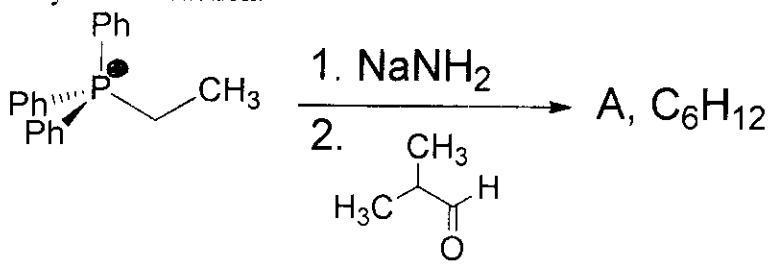
[25]

1. Explain Jahn Teller theorem. Describe the symmetrical and unsymmetrical arrangement of t_{2g} and e_g electrons in strong field and weak field octahedral complexes. Discuss the condition for no distortion, slight distortion and strong distortion in high-spin and low-spin octahedral complexes. 07

2.(a) Give mechanism for the following reaction and explain. 04



2.(b) The following reaction between a phosphonium salt, base and an aldehyde gives a hydrocarbon A, C_6H_{12}. Give correct structure for the product and comment on the stereochemistry of the reaction. 03



3.(a) Give Arrhenius equation and explain how one can find E_a of a reaction. 03

(b) Derive Nernst equation. **04**

4. Discuss the reasons responsible for global warming. 04

Rough work