# DEPARTMENT OF CHEMISTRY <br> I. I. T. Bombay 

## CH-103: Chemistry I

2007-08

TUTORIAL SHEETS

## CH-103: Chemistry I, Semester 1, 2007-8 DEPARTMENT OF CHEMISTRY, I. I. T. Bombay

## COURSE CONTENTS:

Schrödinger equation, origin of quantization, applications of particle in a box problem; hydrogen atom, properties of atomic orbitals; many electron atoms; molecular orbital theory, bonding and energy levels of diatomic molecules $\mathrm{N}_{2}, \mathrm{O}_{2}, \mathrm{CO}$ and HF ; polyatomics; intermolecular forces; bonding in solids.

Hückel treatment of ethylene, butadiene and benzene, concept of aromaticity; configuration, molecular chirality and isomerism; conformation of alkanes and cycloalkanes; reactivity of carbonyl group (additions, addition-eliminations, reactions due to acidic proton, reactivity of acid halide, ester and amide); functional group interconversions involving oxidation and reduction.

Periodic properties: trends in size, electron affinity, ionization potential and electronegativity; Use of Ellingham diagram and thermodynamics in extraction of elements; transition metal chemistry: inorganic complexes, bonding theories, magnetism, bonding aspects and structural distortion; bioinorganic chemistry: storage and transport of proteins; introduction to organometallic reagents.

## REFERENCE BOOKS

i) Physical Chemistry by a) P.W. Atkins b) G. M. Barrow c) D. A. McQuarrie and J. D. Simon d) D. K. Chakrabarty and e) and IGNOU Chemistry booklets by H. V. Keer, A. Q. Contractor, B. L. Tembe (Editor), et al. on Atoms and Molecules, Inorganic Chemistry.
ii) www.cdeep.iitb.ac.in/nptel See the Engineering Chemistry-1 course among the core science courses.
iii) R. T. Morrison and R. N. Boyd, Organic Chemistry, 6th Edition, Prentice Hall India Pvt Ltd.
iv) L. G. Wade Organic Chemistry, 5th Edition, Pearson Education, Indian Branch.
v) G. Solomon and C. Fryhle, Organic Chemistry, 7th Edition, John Wiley \& Sons (Asia) Pvt Ltd.,
vi) Inorganic Chemistry by a) J. D. Lee, b) D. F. Shriver and P. W. Atkins.

SOME PHYSICAL CONSTANTS
Avogadro number, $\mathrm{N}_{\mathrm{A}}=6.023 \times 10^{23} \mathrm{~mol}^{-1}$ Velocity of light $\mathrm{c}=2.998 \times 10^{8} \mathrm{~ms}^{-1}$ Mass of electron, $\mathrm{m}_{\mathrm{e}}=9.108 \times 10^{-31} \mathrm{~kg}$. Electronic charge $\mathrm{e}=-1.602 \times 10^{-19} \mathrm{C}$ Faraday, $\mathrm{F}=96490 \mathrm{C}$ mole $^{-1} \quad$ Planck's constant, $\mathrm{h}=6.625 \times 10^{-34} \mathrm{Js}$ Mass of proton, $\mathrm{m}_{\mathrm{p}}=1.672 \times 10^{-27} \mathrm{~kg}$. Mass of neutron, $\mathrm{m}_{\mathrm{n}}=1.675 \times 10^{-27} \mathrm{~kg}$. Gas const. $\mathrm{R}=8.3145 \mathrm{JK}^{-1} \mathrm{~mole}^{-1}=1.98722 \mathrm{cal} \mathrm{K}^{-1} \mathrm{~mol}^{-1}=0.08206 \mathrm{~L} \mathrm{~atm} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}$ Boltzmann const. $\mathrm{k}_{\mathrm{B}}=1.38066 \times 10^{-23} \mathrm{~J} \mathrm{~K}^{-1}$, Atomic mass unit $=1.6606 \times 10^{-27} \mathrm{~kg}$ Permittivity of vacuum $\varepsilon_{0}=8.854 \times 10^{-12} \mathrm{C}^{2} /\left(\mathrm{N} \mathrm{m}^{2}\right)$ or J ${ }^{-1} \mathrm{C}^{2} \mathrm{~m}^{-1}$ $\left(1 / 4 \pi \varepsilon_{0}\right)=8.988 \times 10^{9} \mathrm{Nm}^{2} / \mathrm{C}^{2}$ Electron volt, $\mathrm{eV}=96.490 \mathrm{kJmole}^{-1}=8066 \mathrm{~cm}^{-1}$ Bohr radius $=0.5292$ Angstroms $=5.292 \times 10^{-11} \mathrm{~m}$
Bohr magneton $=\mathrm{eh} / 4 \pi \mathrm{~m}_{\mathrm{e}}=9.274 \times 10^{-24} \mathrm{~J} \mathrm{~T}^{-1}$

## CH - 103 TUTORIALS

## CH - 103 TUTORIAL - 1

1. What inference can be drawn about the structure of an atom from Rutherford's experiment on scattering of $\alpha$ particles by a gold foil? List the processes/phenomena that could not be explained by classical physics.
2. In photoelectric effect phenomenon, how do the following parameters vary with increasing frequency of incident radiation: (a) Photocurrent and (b) Kinetic energy of photoelectrons.
3. What are the postulates of Bohr's theory for the structure of hydrogen atom? Which of them are consistent with the uncertainty principle? Rationalise.
4. Derive an expression for - (a) the radius of first Bohr orbit (b) energy of an electron in the first Bohr orbit. Calculate their respective values from known constants.
5. a) What total amount of energy (in Joules) would be required to shift all the electrons from the first Bohr orbit to the sixth orbit in one mole of hydrogen atoms? b) Through what distance would each electron have to move? c) If the electrons returned to their initial state, what would be the wavelength of emitted light?
6. An alpha ( $\alpha$ ) particle and a free electron, each initially at rest, combine to form $\mathrm{He}^{+}$ion in its ground state, with the emission of a photon. Estimate the energy of this photon.
7. At $115^{\circ} \mathrm{K}$, atoms of vapourised sodium (at wt 23) have a rms velocity of about $700 \mathrm{~ms}^{-1}$. What is the de Broglie wavelength of sodium atoms at this velocity?
8.a) With what speed must an electron travel in order to have a de Broglie wavelength of 0.1 nm ? b) Through what potential difference must the electron be accelerated to give it this velocity?
8. What is the de Broglie wavelength for (a) rifle bullet of mass 1.0 g and velocity $300 \mathrm{~ms}^{-1}$, (b) 70 kg person running at a speed of $10 \mathrm{~ms}^{-1}$.
9. A small communication satellite weighs 1470 g and is traveling at a velocity of $7500 \mathrm{~cm} / \mathrm{s}$. If the uncertainty in its velocity ( $\Delta \mathrm{v}$ ) is $10 \mathrm{~cm} / \mathrm{s}$. what uncertainty will be associated in locating the satellite?
10. a) If the position of speck of dust mass 1 micro gram is known within $10^{-3}$ mm , what is the indeterminacy in its momentum and velocity?
(b) If an electron in a hydrogen atom is confined to a region of size 53 picometer (pm) from the nucleus, what is the indeterminacy in its momentum and velocity?
12) Analogous to The Schrödinger equation $\mathrm{H} \psi=\mathrm{E} \psi$ (which is a basis for molecular structure and spectroscopy), other operator equations are written as Operator * function $=$ number * function. The number is called an eigenvalue and the function, the eigenfunction. Suggest eigenfunctions and eigenvalues for operators $\mathrm{d} / \mathrm{dx}, \mathrm{d}^{2} / \mathrm{dx}^{2}, \partial^{2} / \partial \mathrm{y}^{2}+\partial^{2} / \partial \mathrm{z}^{2}+\partial^{2} / \partial \mathrm{x}^{2},\left(\mathrm{~h} / 2 \pi\right.$ i) $\partial / \partial \varphi, \int \mathrm{dx}$. All molecular energy levels are the solutions of appropriate Schrödinger or other operator equations.

## CH-103 TUTORIAL - 2

13. a) Calculate the energies in Joules for $n=1$ and $n=2$ for an electron in a one dimensional box of length of 0.1 nm .
b) If the length of the molecule is 1.0 nm , what is the probability of finding the electron between
(i) $\mathrm{x}=0.049$ and 0.051 and (ii) $\mathrm{x}=0$ and 0.020 ( x in nm)
14. Hexatriene, $\mathrm{H}_{2} \mathrm{C}=\mathrm{CH}-\mathrm{CH}=\mathrm{CH}-\mathrm{CH}=\mathrm{CH}_{2}$, is a "linear" molecule of length 7.3 $\AA$. The six pi electrons are free to move along the entire length of the molecule. Using a one dimensional potential well model for this molecule, calculate the values for the first four energy levels. What will be the longest wavelength of radiation absorbed which will excite the electron from the highest filled to the lowest unfilled energy level? Compare this value with the experimental value of 258 nm . What do you conclude from this?
15. An electron moves in a rectangular box of edge lengths $\mathrm{a}, \mathrm{b}$ and c along $\mathrm{x}, \mathrm{y}$, $z$ axes respectively. Write the expression for the energy and the wave function of the electron. If the electron is confined in a cubic box of side 'a' plot the energy values (in terms of $\mathrm{h}^{2} / 8 \mathrm{ma}^{2}$ ) showing the degenerate energy levels. The solutions of the particle in a box problem or a particle in a confined region find applications in nanochemistry.
16. Assuming the ground state wave function for hydrogen atom to be $\Psi(\mathrm{R}, \theta, \varphi)$ $=\mathrm{N} \exp \left(-\mathrm{R} / \mathrm{a}_{\mathrm{o}}\right)$, find the normalization constant N .
Use $\int x^{n} e^{-a x}{ }_{d x}=n!/ a^{n+1}$
What is the formula for the volume element in spherical polar coordinates? Why do we need spherical coordinates for the hydrogen atom problem and not for a particle in a box problem?
17. From the wave function of 1s orbital, account for the fact that the probability of finding the electron is the same anywhere on the surface of a sphere of radius $r$ (where $r$ is the distance of electron from the nucleus).
$\Psi_{\text {ls }}=(1 / \pi)^{1 / 2}\left(\mathrm{Z} / \mathrm{a}_{\mathrm{o}}\right)^{3 / 2} \exp \left(-\mathrm{Zr} / \mathrm{a}_{\mathrm{o}}\right)$.
18.a) Draw the radial part of wave function $\mathrm{R}(\mathrm{r})$ against r for 1 s , 2 s and 3 s orbitals. b) Show that if $R^{2}(r)$ for ls orbital is plotted as a function of $r$, the maximum lies at the origin. c) Show that if $4 \pi r^{2} R^{2}$ is plotted as a function of $r$, the graph should have a maximum.
18. If the radial part of the wave function $R(r)$ for a hydrogen like atom is $\mathrm{R}=2\left(\mathrm{Z} / \mathrm{a}_{\mathrm{o}}\right)^{3 / 2} \exp \left(-\mathrm{Zr} / \mathrm{a}_{\mathrm{o}}\right)$, show mathematically that the radial probability $\left(4 \pi r^{2} R^{2}\right)$ has a maximum at $r=a_{0} / Z$.
19. The 2 s orbital has a node. From the radial wave function $R(2 s)=(2 \sqrt{ } 2)^{-1}$ $\left(\mathrm{Z} / \mathrm{a}_{0}\right)^{3 / 2}\left(2-\mathrm{Zr} / \mathrm{a}_{\mathrm{o}}\right) \mathrm{e}^{-\mathrm{Zr} / 2 \mathrm{a}} \mathrm{o}$. Find the value of r at which the node occurs in a hydrogen atom. What are the locations of the nodes for a 3s orbital.
20. Sketch qualitatively the radial probability distribution ( $4 \pi r^{2} R^{2}$ ) curves for the following orbitals : 1s, $2 \mathrm{~s}, 2 \mathrm{p}, 3 \mathrm{~s}, 3 \mathrm{p}, 3 \mathrm{~d}$ in hydrogen atom.

22 Sketch the polar plot for $\mathrm{s}, \mathrm{p}_{\mathrm{z}}$ and $\mathrm{d}_{\mathrm{z}} 2$ orbitals.
23. Where is the probability of finding an electron in 1 s and $2 \mathrm{p}_{\mathrm{z}}$ orbital greatest?
24. What are the formulae for the radial electron densities in the 2 s and 2 p states?
25. Explain the variation of ionization energy in the second period of the periodic table. Use the concept of an effective charge.
26. How does the size of the atom vary in a period $(\rightarrow)$ and in a group $(\downarrow)$ ? Explain.
27. How does the ionization energy of elements vary in a period $(\rightarrow)$ and in a group $(\downarrow)$ ? Explain.

## CH-103 TUTORIAL -3

28. What are the Hamiltonians for $\mathrm{Li}, \mathrm{B}$ and N atoms?
29) Why is the function $1 \mathrm{~s}(1)+1 \mathrm{~s}(2)$ not a wavefunction for the helium atom?
30) The He atom has a total spin of zero in the ground state, while in its excited state, its total spin can be zero or one. What are the suitable combinations of spin-orbitals leading to these spin values? Write an effective Schrödinger equation for each of the electron in He .
31. What is the shielding constant ( S ) of one of the two electrons from the other in helium atom?
I.E of $\mathrm{He}=2.372 \times 10^{6} \mathrm{~J} / \mathrm{mol}, \quad$ I.E of $\mathrm{H}=1.313 \times 10^{6} \mathrm{~J} / \mathrm{mol}$
32. Calculate the shielding constant of one of the two electrons in $\mathrm{Li}^{+}$and $\mathrm{Al}^{+11}$ ions respectively. ( Z for $\mathrm{A} 1=13$, and for $\mathrm{Li}=3$ ). How does this value compare with the one obtained in question number 31? What conclusions can one draw from these values? (I.E. of $\mathrm{Li}^{+}=7.3 \mathrm{MJ} / \mathrm{mol}$, I.E. of $\mathrm{Al}^{+11}=201.27 \mathrm{MJ} / \mathrm{mol}$
33. In a lithium atom, if the inner electrons completely shield the outer electron from the nucleus, what would be the ionization energy? The observed I.E. value is $0.52 \mathrm{MJ} / \mathrm{mole}$. How effective are the two inner electrons ( $/ \mathrm{s}^{2}$ ) in their shielding action on the outer electron.
34. The spectral line corresponding to the transition $2 p \rightarrow 2 s$ in lithium has been observed at $\lambda=671 \mathrm{~nm}$. Calculate the shielding constant due to two 1 s electrons for a $2 p$ electron and compare this value with that obtained in question 33. (I.E. of $\mathrm{Li}=0.52 \mathrm{MJ} / \mathrm{mole})$.
35. Estimate the relative size of neutral lithium atom and lithium ion. (Shielding constant $\mathrm{S}=1.74, \mathrm{Z}$ for $\mathrm{Li}=3$ ).
36. The ionization energy of $\mathrm{Li}, \mathrm{Be}^{+}, \mathrm{B}^{+2}$ and $\mathrm{C}^{+3}$ is $0.52,1.756,3.658,6.221$ $\mathrm{MJ} / \mathrm{mol}$ respectively. Plot a graph of square root of the ionization energy versus the nuclear charge for the above elements. Explain the observed relationship with the help of Bohr's expression for the binding energy of an electron in a one electron atom.
37. Write the Schrödinger equation for the hydrogen molecule ion. How would you choose the wave function for this molecule?
38. Write the Schrödinger equation for $\mathrm{Li}_{2}$ and HF.
39. Write the wave function for hydrogen molecule using valence bond theory and molecular orbital theory. What is the difference between the two wave functions?
40. Explain why the formation of hydrogen molecule ion is not possible according to valence bond theory? Compute the value of the contour of the molecular orbital in $\mathrm{H}_{2}{ }^{+}$on two circular contours perpendicular to the molecular axis; one contour containing an atom at the center and another contour bisecting the internuclear axis.
41. Sketch the bonding and antibonding MOs formed from $p_{x}, p_{y}$ and $p_{z}$ orbitals. Indicate approximate values of the MOs on the contours of the MOs.
42. Write the M.O. configuration of the following molecules $\mathrm{Li}_{2}, \mathrm{~N}_{2}, \mathrm{~F}_{2}$ and CO. What is the bond order for each molecule?

## CH-103 TUTORIAL - 4

43. The bond dissociation energy of $\mathrm{N}_{2}$ is $1837 \mathrm{~kJ} /$ mole and that of CO is 2081 $\mathrm{kJ} / \mathrm{mole}$. On the basis of M.O. theory, account for the difference in bond energy.
44. The binding energy of $\mathrm{N}_{2}{ }^{+}$is less than that of $\mathrm{N}_{2}$ whereas the binding energy of $\mathrm{O}_{2}{ }^{+}$is greater than that of $\mathrm{O}_{2}$. Explain on the basis of M.O. configurations.
45. Which of the following molecules will have the smallest bond length: $\mathrm{F}_{2}, \mathrm{~N}_{2}$, $\mathrm{O}_{2}$ ? Why?
46. What hybrid orbitals are formed from the combination of s and p orbitals? What is the resulting geometry in each case? (Use $\mathrm{BeCl}_{2}, \mathrm{BC1}_{3}$ and $\mathrm{CC1}_{4}$ molecules as examples). What do the coefficients of the AOs in the hybrid orbitals signify? Rationalise the values of the coefficients of the above hybrid orbitals. Using the coefficients, compute the angles between the hybrid orbitals.
47. Molecular nitrogen and acetylene $\left(\mathrm{C}_{2} \mathrm{H}_{2}\right)$ are isoelectronic (14 electrons in each) and both have a triple bond. Using the structure of $\mathrm{N}_{2}$ an analogue, predict the geometry of acetylene. What hybrid orbitals are used by the carbon atoms?
48. Draw the overlap diagram for $\mathrm{C}_{2} \mathrm{H}_{4}$
49. When a hydrogen atom (A) approaches a hydrogen cation (B) hydrogen molecule ion is formed. Draw the energy diagram as a function of internuclear distance ( $\mathrm{r}_{\mathrm{AB}}$ ), for (i) bonding, (ii) antibonding molecular orbitals.
50. Discuss the main features of (a) ionic (b) covalent, (c) metallic solids, (c) molecular solids and e) hydrogen bonding. Comment on their electronic energy level diagrams. What are the different intermolecular forces responsible for each one of these?

## CH - 103 Tutorial 5

51. (a) Draw the occupied $\pi$-MOs of $1,3,5$-hexatriene and identify the number of nodes in each MOs. (b) Explain why the lowest occupied $\pi$-MO of benzene is lower in energy than the lowest energy $\pi$-MOs of 1,3,5-hexatriene.
52. In each of the given cases, identify (i) the nucleophile and the electrophile (ii) show using 'electron-pushing' arrows how the following reaction happens (iii) what kind orbitals (such as $n, \sigma, \sigma^{*}, \pi, \pi^{*}$ or AO) of the nucleophile and the electrophile are involved in these reactions.

53. From each of the resonance structures that follow, designate the one that would contribute most to the hybrid and explain your choice.
a)

b) $\stackrel{\oplus}{\mathrm{C}} \mathrm{H}_{2}-\mathrm{N}\left(\mathrm{CH}_{3}\right)_{2} \longleftrightarrow \mathrm{CH}_{2} \stackrel{\oplus}{\mathrm{~N}}\left(\mathrm{CH}_{3}\right)_{2}$
54. As part of your analysis of linear $\pi$ conjugated systems, account for the following observations.

The UV absorption band shifts progressively to longer wavelength in proceeding from ethylene to butadiene to linear hexatriene, and then to even further lower energy visible regions of electromagnetic spectrum in the case of carotenes.
55. Label following compounds as aromatic or antiaromatic

1

2

3

4

5
56. (a) Draw the HOMO and LUMO of ethylene and 1,3-butadiene. (b) Identify the important orbitals that are involved in the reaction as shown below,

57. These aromatic systems are constituents of different carbon allotropes. Explain.


58. Which $-\mathrm{CH}_{3}$ group will be relatively more acidic? The one bonded to cyclohexane or the one bonded to benzene (as in toluene)? Explain.
59. Write the order of the rate of formation of carbocations from the following iodo compounds. Justify your answer.
a)

b)

c)

*60. In the following two examples, analyze the effects of molecular geometry and symmetry on the interaction of p-orbitals to form the $\pi$ molecular orbitals. On this basis deduce possible rules regarding geometric, symmetric and electronic requirements for an aromatic system?
a)


b)


CH - 103 Tutorial 6
61. Draw all constitutional isomers of $\mathrm{C}_{3} \mathrm{H}_{6} \mathrm{DCl}$. Which of these are chiral ?
62. Locate any plane of symmetry or center of symmetry in each one of the following. Which one is chiral and which one achiral?
a) (E) -1,2-Dichloroethene
b) cis -1,2-dichlorocyclopropane
c) (Z) -1,2-Dichloroethene
d) trans -1,2-dichlorocyclopropane
63. A meso stereoisomer is possible for one of the following. Which one?
a) 2,3-dibromopentane
b) 2,4-dibromopentane
c) 3-bromo-2-pentanol
d) 4-bromo-2 -pentanol
64. List the substituents in each of the following sets in order of priority from highest to lowest.
a) $-\mathrm{Cl},-\mathrm{OH},-\mathrm{SH},-\mathrm{H}$
b) $-\mathrm{CH}_{3},-\mathrm{CH}_{2} \mathrm{Br},-\mathrm{CH}_{2} \mathrm{Cl},-\mathrm{CH}_{2} \mathrm{OH}$
c) $-\mathrm{H},-\mathrm{OH},-\mathrm{CHO},-\mathrm{CH}_{3}$
d) $-\mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2},-\mathrm{C}\left(\mathrm{CH}_{3}\right)_{3},-\mathrm{H},-\mathrm{CH}=\mathrm{CH}_{2}$
e) $-\mathrm{H},-\mathrm{N}\left(\mathrm{CH}_{3}\right)_{2},-\mathrm{OCH}_{3},-\mathrm{CH}_{3}$
65. Assign absolute configurations as R or S and write the Fischer projection for each.
a)

b)

c)

d)

66. Draw three - dimensional representations of
a) R enantiomer of
b) S enantiomer of


67. Classify each of the following objects as to whether it is chiral or achiral.
a) screw driver
b) a cricket bat
c) a golf club
d) an ear
e) a hammer
f) a screw
68. Identify the relationship in each of the following pairs as constitutional isomers, diastereomers, enantiomers or identical.
a)


b)


c)


d)


69. (a) Assign the configuration of glycidol (given below). (b) This optically pure enantiomer has $[\alpha]=+12^{\circ}$ (neat, without solvent). What would be the measured rotation of a sample of this compound if it is contaminated by its enantiomer such that $25 \%$ of the sample is its enantiomer?

70. (a) Identify the chiral centres in cholesterol and (b) predict the number of theoretically possible stereo isomers.

*71. A pair of diastereomeric bromides $\mathbf{A}$ and $\mathbf{B}$ is given below. (i) Draw the conformational diagram for compounds $\mathbf{A}$ and $\mathbf{B}$. (ii) Which one of these is capable of
undergoing elimination reaction upon treatment with a base?
A



## CH - 103 Tutorial 7

72. Given the following partial structure, add a substituent X to $\mathrm{C}-1$ so that it satisfies the indicated stereochemical requirements

a) Anti to A
b) Gauche to A
c) Trans to B
d) Cis to $B$
73. Sketch an approximate potential energy diagram for rotation about C-C bond in 2,2-dimethylpropane.
74. Draw the most stable conformation for the following two compounds.
a)

b)

75. Assign $\mathrm{E}, \mathrm{Z}$ configuration for the following geometrical isomers.


76. Assign the following pairs of compounds as constitutional isomers, diastereomers, enantiomers or identical.
a)


b)


77. Draw the preferred conformations of the following compounds.
a)

b) $\mathrm{HOCH}_{2} \mathrm{CH}_{2} \mathrm{OH}$
78. A certain natural product having $[\alpha]_{\mathrm{D}}+40.3^{\circ}$ was isolated. Two structures have been independently proposed for this compound. Which one do you think is more likely to be correct? Why?


79. 2-Isopropyl 5-methylcyclohexanol (menthol) is used to flavour various foods and tobacco. Draw the conformational structure of menthol with the configuration as indicated.

80. Assign the relative configuration ( D or L ) of the following compounds.
a)


*81. Draw the conformational structures of the following compounds (Hint: the trivial names of the compounds are indicative of the nature of bonding between cyclopropane ring(s) and cyclohexane ring).


Triaxane


Peraxane
*82. How many cyclohexanes need to be joined in forming the hydrocarbon adamantane $\left(\mathrm{C}_{10} \mathrm{H}_{16}\right)$ ? What is the nature of ring fusion in this molecule and what is the conformation of each cyclohexane? Compare the structure with that of diamond?

## CH - 103 Tutorial 8

83. Suggest an appropriate mechanism that will account for the formation of $\mathbf{A}$ and $\mathbf{B}$ as given below,

84. Explain how a protection-deprotection method will be helpful in effecting following transformation

85. Propose a mechanism of the given reaction. How do you classify this reaction?

86. Complete the following reactions by identifying the product
(i)


(ii)


(iii)



(iv)

87. Write four important products of following Claisen ester condensation reaction


$\xrightarrow[\text { (ii) } \mathrm{H}^{+}, \mathrm{H}_{2} \mathrm{O}]{\text { (i) } \mathrm{C}_{2} \mathrm{H}_{5} \mathrm{ONa}, \mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH}}$
88. Acetone dissolved in isotopically labeled water $\left(\mathrm{H}_{2} \mathrm{O}^{18}\right)$ converts slowly into $\left(\mathrm{CH}_{3}\right)_{2} \mathrm{C}=\mathrm{O}^{18}$. The rate of isotope incorporation increases progressively if the solution is made more and more acidic. Explain why?
89. Bromination of acetone is accelerated under both acidic and alkaline pH . Write the reaction mechanisms and account for the observed rate accelerations.
90. An excess of racemic acid $\mathrm{CH}_{3} \mathrm{CHClCOOH}$ is allowed to react with (S)-2-methyl-1butanol to form the ester,


Upon careful distillation of the reaction mixture, three fractions are obtained, each of which is optically active. Draw stereochemical formulas of the compound or compounds making up each fraction.
*91. Paraldehyde (structure given below) used as a sedative or hypnotic agent can be prepared from acetaldehyde in presence of an acid catalyst. Propose a mechanism for the formation of paraldehyde.

*92. The substrates shown differ vastly in their reactivity towards water. The intrinsically sluggish substrates can however also be made to react if either hydronium or hydroxide ion is used as the catalyst. Explain. Compare the mechanisms of uncatalyzed and catalyzed reactions.

*93. Propose a detailed mechanism for following reaction.


CH 103 Tutorial No. 9
101. If the element with $Z=114$ is discovered, in which group would you expect to find it? What would be its electronic configuration and the IUPAC name?
102. How many unpaired electrons would be there in $\mathrm{Gd}^{3+}$ ?
103. Which metal has the lowest melting point and why? Which metal has the highest melting point and why?
104. Account for the large decrease in electron affinity between Lithium and beryllium despite the increase in nuclear charge.
105. The +4 oxidation state of lead $(\mathrm{Pb})$ is much more strongly oxidizing than that of tin $(\mathrm{Sn})$. Reason out.
106. Arrange these atoms in the order of increasing ionization energy: $\mathrm{As}, \mathrm{Sn}, \mathrm{Ca}, \mathrm{Se}, \mathrm{Al}$.
107. Why are the metals Al and Ti not produced by pyrometallurgical extraction of $\mathrm{Al}_{2} \mathrm{O}_{3}$ and $\mathrm{TiO}_{2}$ ?
108. Using the Ellingham diagram of oxides, determine whether Aluminum can be used to reduce MgO .
109. Ellingham diagram predicts a negative $\Delta \mathrm{G}^{\mathrm{o}}$ value for the reduction of $\mathrm{Cr}_{2} \mathrm{O}_{3}$ with Al at room temperature. In fact the reduction is carried out at a much higher temperature. Suggest an explanation.
110. What is the reducing species in the self-reduction of CuS ore?
111. Can carbon be used as a reducing agent for the reduction of the metal sulfide ores?
112. Is there any correlation between the heats of formation of the metal oxides and their position in the electrochemical series? Comment.
113. Account for the fact that the roasting of PbS in air gives PbO whereas that of HgS gives Hg .
114. Sodium metal is produced commercially by the electrolysis of a mixture of $40 \% \mathrm{NaCl}$ and $60 \% \mathrm{CaCl}_{2}$. What is the role of $\mathrm{CaCl}_{2}$ in this process? Will Ca also be produced along with Na ?
115. How is very pure silicon obtained for Semiconductor application?

## CH-103 Tutorial No. 10

116. Draw all possible isomers of (a) octahedral $\left[\mathrm{RuCl}_{2}\left(\mathrm{NH}_{3}\right)_{4}\right]$, (b) square planar $\left[\operatorname{IrH}(\mathrm{CO})\left(\mathrm{PR}_{3}\right)_{2}\right]$ (c) Octahedral $\left[\mathrm{IrCl}_{3}\left(\mathrm{PEt}_{3}\right)_{3}\right]$, (d) $\left[\mathrm{Ru}(\text { bipy })_{3}\right]^{2+}$
117. Write the formula for (a) pentaamminechlorocobalt(III)chloride, (b) $\mu$ hydrooxobis(pentaamminechromium(III)chloride)
118. Crystalline AgO is diamagnetic. Explain.
119. Draw structures of the following complexes using the valence bond approach:
(a) $\mathrm{Ni}(\mathrm{CO})_{4}$,
(b) $\left[\mathrm{Ni}(\mathrm{CN})_{4}\right]^{2-}$
(c) $\left[\mathrm{CoCl}_{4}\right]^{2-}$
(d) $\mathrm{OsO}_{4}$
(e) $\mathrm{VOCl}_{3}$
(f) $\left[\mathrm{Pt}\left(\mathrm{NH}_{3}\right)_{4}\right]^{2+}$
(g) $\left[\mathrm{Ag}\left(\mathrm{NH}_{3}\right)_{2}\right]^{+}$,
(h) $\left[\mathrm{Pt}_{\left.\left(\mathrm{PPh}_{3}\right)_{4}\right]}\right.$
(i) $\left[\mathrm{Cr}_{2} \mathrm{O}_{7}\right]^{2-}$
120. Which electron configuration, high-spin or low spin, of a $d^{5}$ transition metal complex would be favored by the application of high pressure and why?
121. Suggest a reason for the fact that a number of tetrahedral $\operatorname{Co}(\mathrm{II})$ complexes are stable, whereas the corresponding $\mathrm{Ni}(\mathrm{II})$ complexes are not.
122. Using crystal field stabilization energy as the criterion, indicate whether you expect the following spinels to be normal or inverse: $\mathrm{Fe}_{3} \mathrm{O}_{4}, \mathrm{Co}_{3} \mathrm{O}_{4}$.
123. Determine configuration (in terms of $\mathrm{t}_{2 \mathrm{~g}}{ }^{\mathrm{m}} \mathrm{e}_{\mathrm{g}}{ }^{\mathrm{n}}$ or $\mathrm{e}^{\mathrm{m}} \mathrm{t}_{2}{ }^{\mathrm{n}}$ ), the number of unpaired electrons, and the CFSE (in terms of $\Delta_{o}$ or $\Delta_{t}$ ) for each of the following complexes.
(a) tetrahedral $\left[\mathrm{FeCl}_{4}\right]^{2-}$
(b) $\mathrm{W}(\mathrm{CO})_{6}$
124. The $\mathrm{Cr}^{2+}$ ion in $\mathrm{CrF}_{2}$ is surrounded by six fluoride ions. Of these, four are at a distance of $\sim 2.00 \AA$ while the other two are at a distance of $2.43 \AA$ from the metal ion. Explain this observation.

## CH - 103 Tutorial No. 11

125. How will you calculate the magnetic moment ( $\mu$, B.M.) from molar susceptibility $\left(\chi_{\mathrm{m}}\right)$ ?
126. The following complexes have the indicated effective magnetic moments. Describe the structure and bonding of the complexes on the basis of the $\mu_{\text {eff }}$ values.
$\mathrm{K}_{2} \mathrm{NiF}_{6} \quad 0.0 ; \quad \mathrm{Ni}\left(\mathrm{NH}_{3}\right)_{2} \mathrm{Cl}_{2} \quad 3.3 ; \quad \mathrm{Ni}\left(\mathrm{PEt}_{3}\right) \mathrm{Cl}_{2} \quad 0.0 ; \quad \mathrm{Ni}\left(\mathrm{Ph}_{3} \mathrm{AsO}_{2}\right)_{2} \mathrm{Cl}_{2}$ 3.95 .
127. Name the transition metal configurations (both in octahedral and tetrahedral environments) which are expected to have orbital contribution to the magnetic moment?
128. Which one would you expect to have greater magnetic moment: $\mathrm{CoCl}_{4}{ }^{2-}$ or $\mathrm{CoF}_{6}{ }^{4-}$ ? Why?
129. Which one would you expect to have greater magnetic moment: $\mathrm{CoCl}_{4}{ }^{2-}$ or $\mathrm{CoI}_{4}{ }^{2-}$ ? Why?
130. Calculate $\mu_{\text {eff }}$ for $\mathrm{Dy}_{2}\left(\mathrm{SO}_{4}\right)_{3} \cdot 8 \mathrm{H}_{2} \mathrm{O}$.
131. Calculate $\mu_{\text {eff }}$ for $\mathrm{Gd}^{3+}$.
132. What are storage and transport proteins? Draw the structure of porphin.
133. Why is $\mathrm{CN}^{-}$toxic ion to humans?
134. What is the role of globular protein in oxygen transport?
135. What is the "Cooperative effect"?
136. Why are all the oxygen carriers that contain iron and porphyrins are found inside the cells?
137. Why is the size of high spin $\mathrm{Fe}(\mathrm{II})$ larger than low spin $\mathrm{Fe}(\mathrm{II})$ ?
138. What prevents synthetic iron porphyrins from functioning as $\mathrm{O}_{2}$ carriers?
139. Oxygen $\left(\mathrm{O}_{2}\right)$ is a $\sigma$-donor and a $\pi$-acceptor. CO is also an example of this type of ligand. Can you use these facts to propose a mechanism for CO poisoning.

## CH - 103 Tutorial No. 12

140. What is the essential condition for a compound to be called as an organometallic compound?
141. What is C-H acidity? How is this important for the preparation of organolithium compounds.
142. Reaction of benzene with n-butyllithium produces phenyllithium and n-butane. But the reaction of phenyllithium with n-butane does not yield n-butyllithium. Why?
143. What is the reaction of alkyllithium with nitriles?
144. What are metallocenes? How is ferrocene prepared?
145. Why are organolithium compounds always associated (form aggregates) in solid state and in solution?
146. What do you mean by kinetic stability? How does this affect organometallic chemistry?
147. Why are organometallic compounds sensitive to air (oxygen) and moisture $\left(\mathrm{H}_{2} \mathrm{O}\right)$ ?
148. Give a synthetic methodology to obtain Grignard reagents?
149. State and explain Schlenk equiblirium.
150. What is the role of zinc in Reformatsky reaction?
151. How does one synthesize dialkylboranes? How do these compounds react with olefins?
152. Describe the structure of methyllithium.
153. Why organometallic compounds are preferred as reagents / catalysts in organic synthesis?
