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# SOLVED PAPERS

# CHEMICAL SCIENCES

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# Chemical Sciences
## CSIR UGC-NET/JRF Exam.
### Solved Paper

# June 2012
# Chemical Science

### Useful Fundamental Constants

| | | |
|---|---|---|
| m | Mass of electron | $9.11 \times 10^{-31}$ Kg |
| h | Planck's constant | $6.63 \times 10^{-34}$ Jsec |
| e | Charge of electron | $1.6 \times 10^{-19}$ C |
| k | Boltzmann constant | $1.38 \times 10^{-23}$ J/k |
| c | Velocity of Light | $3.0 \times 10^{8}$ m/sec |
| $I_cV$ | $1.6 \times 10^{-14}$ J | |
| amu | $1.67 \times 10^{-27}$ kg | |
| G | $6.67 \times 10^{-11}$ Nm$^2$ kg$^{-2}$ | |
| $R_y$ | Rydberg constant | $1.097 \times 10^{7}$ m$^{-1}$ |
| $N_A$ | Avogadro number | $6.023 \times 10^{23}$ mole$^{-1}$ |
| $\varepsilon_0$ | $8.854 \times 10^{-12}$ Fm$^{-1}$ | |
| $\mu_0$ | $4\pi \times 10^{-7}$ Hm$^{-2}$ | |
| R | Molar Gas constant | 8.314 JK$^{-1}$ mole$^{-1}$ |

### List of the Atomic Weights of the Elements

| Element | Symbol | Atomic Number | Atomic Weight |
|---|---|---|---|
| Actinium | Ac | 89 | (227) |
| Aluminium | Al | 13 | 26.98 |
| Americium | Am | 95 | (243) |
| Antimony | Sb | 51 | 121.75 |
| Argon | Ar | 18 | 39.948 |
| Arsenic | As | 33 | 74.92 |
| Astatine | At | 85 | (210) |
| Barium | Ba | 56 | 137.34 |
| Berkelium | Bk | 97 | (249) |
| Beryllium | Be | 4 | 9.012 |
| Bismuth | Bi | 83 | 208.98 |
| Boron | B | 5 | 10.81 |
| Bromine | Br | 35 | 79.909 |
| Cadmium | Cd | 48 | 112.40 |
| Calcium | Ca | 20 | 40.08 |
| Californium | Cf | 98 | (251) |
| Carbon | C | 6 | 12.011 |
| Cerium | Ce | 58 | 140.12 |
| Cesium | Cs | 55 | 132.91 |
| Chlorine | Cl | 17 | 35.453 |
| Chromium | Cr | 24 | 52.00 |
| Cobalt | Co | 27 | 58.93 |
| Copper | Cu | 29 | 63.54 |
| Curium | Cm | 96 | (247) |
| Dysprosium | Dy | 66 | 162.50 |
| Einsteinium | Es | 99 | (254) |
| Erbium | Er | 68 | 167.26 |
| Europium | Eu | 63 | 151.96 |
| Fermium | Fm | 100 | (253) |
| Fluorine | F | 9 | 19.00 |
| Francium | Fr | 87 | (223) |
| Gadolinium | Gd | 64 | 157.25 |
| Gallium | Ga | 31 | 69.72 |
| Germanium | Ge | 32 | 72.59 |
| Gold | Au | 79 | 196.97 |
| Hafnium | Hf | 72 | 178.49 |
| Helium | He | 2 | 4.003 |
| Holmium | Ho | 67 | 164.93 |
| Hydrogen | H | 1 | 1.0080 |
| Indium | In | 49 | 114.82 |
| Iodine | I | 53 | 126.90 |
| Iridium | Ir | 77 | 192.2 |
| Iron | Fe | 26 | 55.85 |
| Krypton | Kr | 36 | 83.80 |
| Lanthanum | La | 57 | 138.91 |
| Lawrencium | Lr | 103 | (257) |
| Lead | Pb | 82 | 207.19 |
| Lithium | Li | 3 | 6.939 |
| Lutetium | Lu | 71 | 174.97 |
| Magnesium | Mg | 12 | 24.312 |
| Manganese | Mn | 25 | 54.94 |
| Mendelevium | Md | 101 | (256) |
| Mercury | Hg | 80 | 200.59 |
| Molybdenum | Mo | 42 | 95.94 |
| Neodymium | Nd | 60 | 144.24 |
| Neon | Ne | 10 | 20.183 |
| Neptunium | Np | 93 | (237) |
| Nickel | Ni | 28 | 58.71 |
| Niobium | Nb | 41 | 92.91 |
| Nitrogen | N | 7 | 14.007 |
| Nobelium | No | 102 | (253) |
| Osmium | Os | 76 | 190.2 |

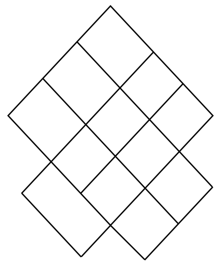
| | | | |
|---|---|---|---|
| Oxygen | O | 8 | 15.9994 |
| Palladium | Pd | 46 | 106.4 |
| Phosphorus | P | 15 | 30.974 |
| Platinum | Pt | 78 | 195.09 |
| Plutonium | Pu | 94 | (242) |
| Polonium | Po | 84 | (210) |
| Potassium | K | 19 | 39.102 |
| Praseodymium | Pr | 59 | 140.91 |
| Promethium | Pm | 61 | (147) |
| Protactinium | Pa | 91 | (231) |
| Radium | Ra | 88 | (226) |
| Radon | Rn | 86 | (222) |
| Rhenium | Re | 75 | 186.23 |
| Rhodium | Rh | 45 | 102.91 |
| Rubidium | Rb | 37 | 85.47 |
| Ruthenium | Ru | 44 | 101.1 |
| Samarium | Sm | 62 | 150.35 |
| Scandium | Sc | 21 | 44.95 |
| Selenium | Se | 34 | 78.96 |
| Silicon | Si | 14 | 28.09 |
| Silver | Ag | 47 | 107.870 |
| Sodium | Na | 11 | 22.9898 |
| Strontium | Sr | 38 | 37.62 |
| Sulfur | S | 16 | 32.064 |
| Tantalum | Ta | 73 | 180.95 |
| Technetium | Tc | 43 | (99) |
| Tellurium | Te | 52 | 127.60 |
| Terbium | Tb | 65 | 158.92 |
| Thallium | Tl | 81 | 204.37 |
| Thorium | Th | 90 | 232.04 |
| Thulium | Tm | 69 | 168.93 |
| Tin | Sn | 50 | 118.69 |
| Titanium | Tl | 22 | 47.90 |
| Tungsten | W | 74 | 183.85 |
| Uranium | U | 92 | 238.03 |
| Vanadium | V | 23 | 50.94 |
| Xenon | Xe | 54 | 131.30 |
| Ytterbium | Yb | 70 | 173.04 |
| Yttrium | Y | 35 | 88.91 |
| Zinc | Zn | 30 | 65.37 |
| Zirconium | Zr | 40 | 91.22 |

* Based on mass of $C^{12}$ at 12.00… . The ratio of these weights of those on the order chemical scale (in which oxygen of natural isotopic composition was assigned a mass of 16.0000…) is 1.000050. (Values in parentheses represent the most stable known isotopes).

## Part A

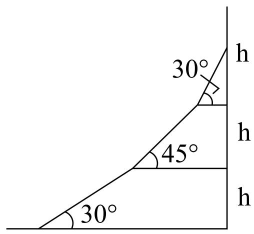
1. In still air, fragrance of a burning incense stick will be smelt by an observer quickest when the experiment is carried out at—
   (A) Low altitude and high air temperature
   (B) High altitude and low air temperature
   (C) Low altitude and low air temperature
   (D) High altitude and high air temperature

2. How many squares are there in this figure ?



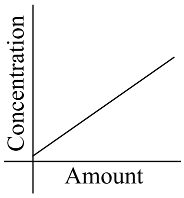
   (A) 9 (B) 14
   (C) 15 (D) 17

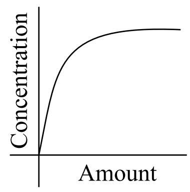
3. A mountain road has 3 sections of different slopes as shown. What is the average slope $m$ of the entire climb ?

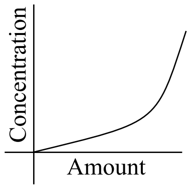


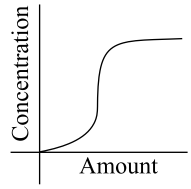

   (A) 1 (B) $\left(\frac{1}{3}\right) < m < \left(\frac{1}{2}\right)$
   (C) $1 < m < \sqrt{3}$ (D) $\left(\frac{1}{\sqrt{3}}\right) < m < 1$

4. Which of the following graphs shows the concentration of a sugar solution as a function of the cumulative amount of sugar added in the process of preparing a saturated solution (the temperature remaining constant) ?

(A) 

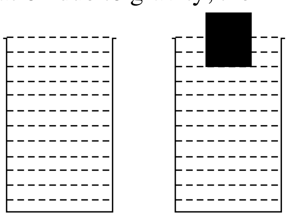

(B) 


(C) 


(D) 

5. There are sand-piles which are geometrically similar but of different heights. The ratio of the masses of the sand comprising two randomly chosen piles will be equal to the ratio of the—
(A) Pile heights
(B) Squares of the pile heights
(C) Cubes of the pile heights
(D) Cube-roots of the pile heights

6. There are two identical vessels of volume V each, one empty, and the other containing a block of wood of weight $w$. The vessels are then filled with water up to the brim. The two arrangements are shown as A and B in the figure. If the density of water is $\rho$ and $g$ is the acceleration due to gravity, then—



A B

(A) A and B have equal weights
(B) A is heavier than B by an amount $w$
(C) A is heavier than B by an amount $V\rho g - w$
(D) B is heavier than A by an amount $V\rho g - w$

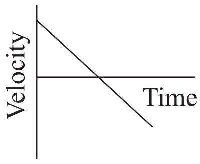
7. If the father has blood group O and the mother has blood group AB, what are the possible blood groups of their children ?
(A) O, AB, A (B) A, B
(C) A, O (D) B, AB

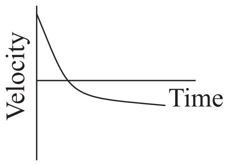
8. Nuclei of $^{32}P$ and $^{32}S$, accelerated through the same potential difference enter a uniform, transverse magnetic field (Z = 15 for P and Z = 16 for S). As they emerge from the magnetic field—
(A) Both nuclei emerge undeflected
(B) $^{32}P$ is deflected less than $^{32}S$
(C) $^{32}P$ is deflected more than $^{32}S$
(D) Both are equally deflected

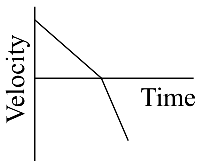
9. A person chewing a bubble gum did not experience ear pain in a jet plane while landing whereas another person not chewing a gum had ear pain. The reason could be—
(A) Chewing gum is a pain killer
(B) Chewing equilibrates pressure on both sides of the ear drum
(C) Chewing gum closes the ear drum
(D) Chewing distracts the person

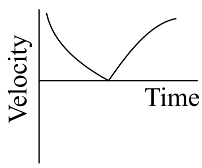
10. The reason why a lunar eclipse does not occur at every full moon is—
(A) The position of the sun is not favourable at all full moons
(B) The orbital planes of the moon and that of the earth are inclined to each other by a small angle
(C) The shape of the earth is not a perfect sphere
(D) The moon reflects only from one hemisphere

11. A boy throws a stone vertically upwards with a certain initial velocity. Which of the following graphs depicts the velocity as a function of time, if the acceleration due to gravity is assumed to be uniform and constant ?

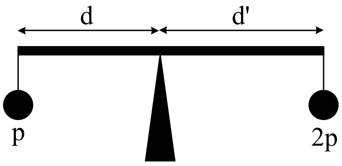
(A)



(B)



(C)



(D)



12. A rigid uniform bar of a certain mass has two bobs of the same size, but with different densities $\rho$ and $2\rho$ suspended identically from its ends.




When the bar is level on a fulcrum as shown in the figure, *d* and *d′* are related by—

(A) $2d = d'$ (B) $d > 2d'$

(C) $d = 2d'$ (D) $d < 2d'$

13. There are two points A and A′ on the equator at longitudes 0° and 90°E, and two other points B and B′ on the same longitudes, respectively, but at latitude 60°S. The distances (along the latitudes) between the points A, A′ and B, B′ are related by—

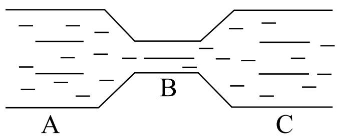
(A) AA′ = BB′

(B) AA′ = 2BB′

(C) $AA' = (\sqrt{3})\ BB'$

(D) $AA' = (\sqrt{2})\ BB'$

14.




Water is flowing through a tube as shown. The cross-sectional areas at A and C are equal, and greater than the cross-sectional are at B. If the flow is steady, then the pressure on the walls at B is—

(A) Less than that at A and that at C

(B) More than that at A and that at C

(C) Same as that at A and that at C

(D) More than that at A but less than that at C

15. Match the two lists—

| | **Raw Material** | | **Product** |
|---|---|---|---|
| (a) | Limestone | 1. | Porcelain |
| (b) | Gypsum | 2. | Glass |
| (c) | Silica sand | 3. | Plaster of Paris |
| (d) | Clay | 4. | Cement |

| | (a) | (b) | (c) | (d) |
|---|---|---|---|---|
| (A) | 1 | 2 | 3 | 4 |
| (B) | 4 | 3 | 2 | 1 |
| (C) | 1 | 3 | 4 | 2 |
| (D) | 4 | 1 | 3 | 2 |

16. The $^{14}C$ dating method is not usually used for dating organic substances older than–60,000 years, because—

(A) Such objects rarely contain carbon

(B) Such objects accumulated $^{14}C$ after their formation

(C) In those times there was no production of $^{14}C$

(D) Most of the $^{14}C$ in the sample would have decayed

17. A seismograph receives a S-wave 60 s after it receives the P-wave. If the velocities of P-and S-waves are 7 km/s and 6 km/s respectively, then the distance of the seismic focus from the seismograph is—

(A) 2520 km (B) 42 km

(C) 7070 km (D) 72 km

18. The decay of a radioactive isotope P produces a stable daughter isotope D. The ratio of the number of atoms of D to the number of atoms of P after 2 half lives would be—

(A) $\frac{1}{4}$ (B) $\frac{3}{4}$

(C) 3 (D) 2

19. The scatter plots represents the values measured by two similar instruments. Point A in the figure represents the true value. Which of the following is a correct description of the quality of these measurements ?

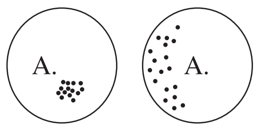



Fig. 1 Fig. 2

(A) Fig. 1 : good accuracy, good precision
Fig. 2 : good accuracy, good precision

(B) Fig. 1 : poor accuracy, poor precision
Fig. 2 : good accuracy, poor precision

(C) Fig. 1 : poor accuracy, good precision
Fig. 2 : poor accuracy, poor precision

(D) Fig. 1 : poor accuracy, poor precision
Fig. 2 : poor accuracy, good precision

20. Even though the concentration of $CO_2$ is the same at sea level and at high altitude, the photosynthetic rate is higher in a plant grown at sea level than in a plant (of the same species) grown at high altitude. The reason for this is—

(A) Light intensity is more at sea level
(B) Temperature is lower at higher altitude
(C) Atmospheric pressure is higher at sea level
(D) Relative humidity is higher at sea level

## Part B

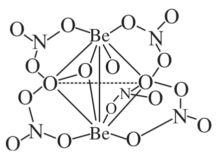
21. In the reactions (A) and (B),

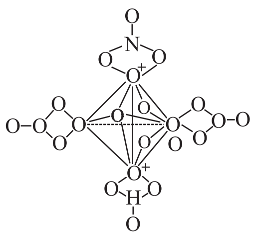
$$nH_2O + Cl^- \rightarrow [Cl\,(H_2O)_n]^- \quad \ldots(A)$$
$$6H_2O + Mg^{2+} \rightarrow [Mg\,(H_2O)_6]^{2+} \ldots(B)$$

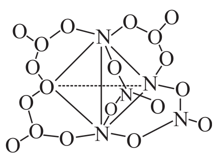
water behaves as—
(A) An acid in both (A) and (B)
(B) An acid in (A) and a base in (B)
(C) A base in (A) and an acid in (B)
(D) A base in both (A) and (B)

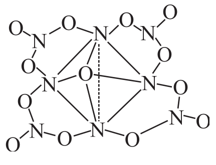
22. The size of the *d* orbitals in Si, P, S and Cl follows the order—
(A) Cl > S > P > Si
(B) Cl > P > S > Si
(C) P > S > Si > Cl
(D) Si > P > S > Cl

23. The correct structure of basic beryllium nitrate is—

(A) 

(B) 

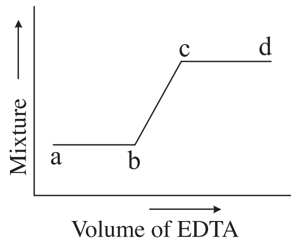
(C) 

(D) 

24. The total number of lone pairs of electrons in $I^-_3$ is—
(A) Zero (B) Three
(C) Six (D) Nine

25. If Mössbauer spectrum of $Fe(CO)_5$ is recorded in the presence of a magnetic field, the original spectrum with two lines changes into the one with—
(A) Three lines (B) Four lines
(C) Five lines (D) Six lines

26. The spectrophotometric response for the titration of a mixture of $Fe^{3+}$ and $Cu^{2+}$ ions against EDTA is given below :




The correct statement is—
(A) Volume *ab* ≡ [$Fe^{3+}$] and volume *cd* ≡ [$Cu^{2+}$]
(B) Volume *ab* ≡ [$Cu^{2+}$] and volume *cd* ≡ [$Fe^{3+}$]
(C) Volume *ab* ≡ [$Fe^{3+}$] and volume *cd* ≡ excess EDTA
(D) Volume *ab* ≡ [$Cu^{2+}$] and volume *cd* ≡ excess EDTA

27. In 'carbon-dating' application of radioisotopes, $^{14}C$ emits—
(A) β-particle (B) α-particle
(C) γ-radiation (D) Positron

28. The actual base pairs present in the double helical structure of DNA containing adenine (A), thymine (T), cytosine (C) and guanine (G), are—
(A) AG and CT
(B) AC and GT
(C) AG and AC
(D) AT and GC

29. The oxidation state of iron in *met*-hemoglobin is—
(A) Three (B) Two
(C) Four (D) Zero

30. The reactions of $Ni(CO)_4$ with the ligand L [L = $PMe_3$ or $P(OMe)_3$] yields $Ni(CO)_3$ L. The reaction is—
(A) Associative (B) Dissociative
(C) Interchange (Ia) (D) Interchange (Id)

31. As a ligand $Cl^-$ is—
(A) Only a σ-donor
(B) Only a π-donor
(C) Both a σ-donor and a π-donor
(D) a σ-donor and a π-acceptor

32. The correct *d*-electron configuration showing spin-orbit coupling is—
(A) $t_{2g}^6\, e_g^2$ (B) $t_{2g}^6\, e_g^0$
(C) $t_{2g}^4\, e_g^0$ (D) $t_{2g}^3\, e_g^2$

33. The correct statement for the aggregating nature of alkyl lithium (RLi) reagent is—
(A) The carbanion nucleophilicity increases with aggregation
(B) The observed aggregation arises from its electron deficient nature
(C) Carbanion nucleophilicity does not depend on aggregation
(D) The extent of aggregation is maximum in polar dative solvents

34. For the reaction, *trans*-$[IrCl(CO)(PPh_3)_2]$ + $Cl_2$ → *trans*-$[IrCl_3(CO)(PPh_3)_2]$, the correct observation is—
(A) $V_{CO}$ (product) > $V_{CO}$ (reactant)
(B) $V_{CO}$ (product) < $V_{CO}$ (reactant)
(C) $V_{CO}$ (product) = $V_{CO}$ (reactant)
(D) $V_{CO}$ (product) = $V_{CO}$ (free CO)

35. The nucleophilic attack on olefins under mild conditions—
(A) Is always facile
(B) Is more facile than electrophilic attack on olefins
(C) Is facile for electron-rich olefins
(D) Requires activation by coordination to metal

36. Among the following, the strongest oxidizing agent is—
(A) $[WO_4]^{2-}$ (B) $[CrO_4]^{2-}$
(C) $[MoO_4]^{2-}$ (D) $[ReO_4]^{-1}$

37. The least basic among the following is—
(A) $Al(OH)_3$ (B) $La(OH)_3$
(C) $Ce(OH)_3$ (D) $Lu(OH)_3$

38. For any operator A and its adjoint $A^+$, the incorrect statement is—
(A) $AA^+$ is hermitian
(B) $AA^+ + A^+A$ is hermitian
(C) $A + A^+$ is hermitian
(D) $A - A^+$ is hermitian

39. For hydrogen-like atom with a nuclear charge Z, the energy of orbital with principal quantum number '*n*' follows the relation—
(A) $E_n \propto n^2Z^2$ (B) $E_n \propto -\frac{Z^2}{n}$
(C) $E_n \propto -\frac{Z}{n}$ (D) $E_n \propto -\frac{Z^2}{n^2}$

40. The average value of the radius $\langle r\rangle$ in the 1*s* state of the hydrogen atom is ($a_o$ is Bohr radius)—
(A) $a_0$ (B) $1.5\, a_0$
(C) $0.75\, a_0$ (D) $0.5\, a_0$

41. Among the following, the correct statement is—
(A) The number of irreducible representations is equal to classes of symmetry operations
(B) The number of irreducible representations is equal to the order of the symmetry point group
(C) The irreducible representations contained in any point group are always of one dimension
(D) A symmetry point group may not contain a totally symmetric irreducible representation

42. For a diatomic molecule AB, the energy for the rotational transition from J = 0 to J = 1 state is $3.9\ cm^{-1}$. The energy for the rotational transition from J = 3 to J = 4 state would be—
(A) $3.9\ cm^{-1}$ (B) $7.8\ cm^{-1}$
(C) $11.7\ cm^{-1}$ (D) $15.6\ cm^{-1}$

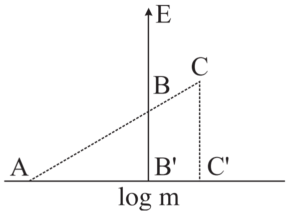
43. For the vibrational Raman spectrum of a homonuclear diatomic molecule, the selection rule under harmonic approximation is—
(A) $\Delta v = 0$ only (B) $\Delta v = \pm 1$ only
(C) $\Delta v = \pm 2$ only (D) $\Delta v = 0, \pm 1$

44. With increase in temperature, the Gibbs free energy for the adsorption of a gas on to a solid surface—
(A) Becomes more positive from a positive value
(B) Becomes more negative from a positive value
(C) Becomes more positive from a negative value
(D) Becomes more negative from a negative value

45. The vapour of a pure substance, when cooled under a pressure less than its triple-point pressure—
(A) Liquefies
(B) Liquefies first and then solidifies
(C) Solidifies directly
(D) Remains unchanged

46. The quantities, which are held fixed in a canonical ensemble are—
(A) N, T and P
(B) V, T and N
(C) N, V and E
(D) $\mu$, V and P

47. The correct value of $E^0$ of a half cell in the following graph of E *vs* log *m* (molality) is—




(A) CC′/AC′ (B) AB′
(C) BB′ (D) CC′

48. One of the assumptions made in the conventional activated complex theory is—
(A) Equilibrium is maintained between the reactants and the activated complex
(B) Equilibrium is maintained between the reactants and the products
(C) Equilibrium is maintained between the products and the activated complex
(D) Equilibrium is maintained between the reactants, the activated complex and the products

49. For a reaction, the rate constant *k* at 27°C was found to be :

$$k = 5{\cdot}4 \times 10^{11}\, e^{-50}$$

The activation energy of the reaction is—
(A) 50 J $mol^{-1}$
(B) 415 J $mol^{-1}$
(C) 15,000 J $mol^{-1}$
(D) 125,000 J $mol^{-1}$

50. During the addition polymerisation, the reaction proceeds via—
(A) Step-growth process
(B) Free-radical chain reaction
(C) Cascade process
(D) Addition reaction

51. How many atoms are there in an element packed in a *fcc* structure ?
(A) 1 (B) 2
(C) 4 (D) 8

52. The structure obtained when all the tetrahedral holes are occupied in a *fcc* structure, is of the type—
(A) NaCl (B) CsCl
(C) $CaF_2$ (D) ZnS

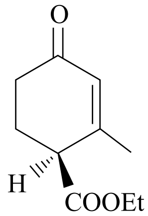
53. Dispersion of a solid in a liquid, a liquid in a gas and a liquid in a liquid are respectively known as—
(A) Aerosol, emulsion, sol
(B) Sol, aerosol, emulsion
(C) Emulsion, sol, aerosol
(D) aerosol, sol, emulsion

54. The data obtained from two sets of experiments A and B have the following characteristics :

| Experiment | A | B |
|---|---|---|
| Mean | 50 units | 100 units |
| Standard deviation | 2 units | 2 units |

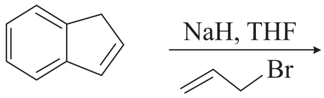
It may be concluded that—
(A) A is more precise than B
(B) A is less precise than B
(C) A and B are of the same precision
(D) Relative precision of A and B cannot be assessed

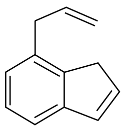
55. The IUPAC name of the compound given below is—

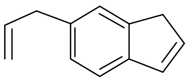


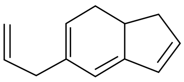
(A) ethyl (R)-2-methyl-4-oxocyclohex-2-enecarboxylate
(B) ethyl (S)-2-methyl-4-oxocyclohex-2-enecarboxylate
(C) (R)-4-ethoxycarbonyl-3-methylcyclohex-2-enone
(D) (S)-4-ethoxycarbonyl-3-methylcyclohex-2-enone

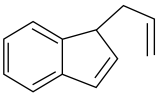
56. The major product formed in the following reaction is—



(A) 

(B) 

(C) 

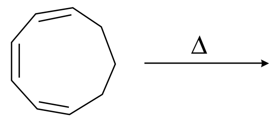
(D) 

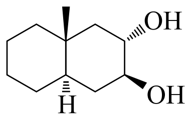
57. The number of signals that appear in the broad-band decoupled $^{13}C$ NMR spectrum of phenanthrene and anthracene, respectively, are—
(A) ten and four (B) ten and ten
(C) seven and four (D) seven and seven

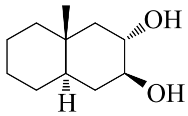
58. The co-enzyme that is involved in the reduction of a double bond in fatty acid biosynthesis is—
(A) NADH (B) Biotin
(C) Pyridoxal (D) $FADH_2$

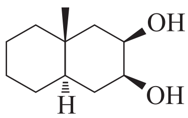
59. Epoxidation of (R)-cyclohex-2-enol with peracetic acid yields a 95 : 5 mixture of compounds A and B. Compounds A and B are—
(A) Enantiomers
(B) Diastercomers
(C) Constitutional isomers
(D) Homomers

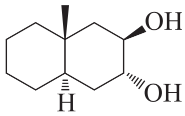
60. The major product formed in the following concerted reaction is—



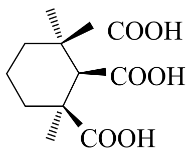
(A) 

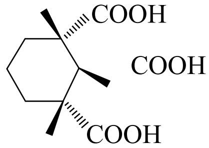
(B) 

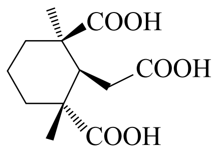
(C) 

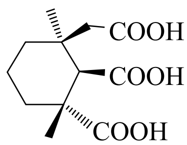
(D) 

61. The structure of *meso*-tricarboxylic acid that is formed on potassium permanganate oxidation of abietic acid is—

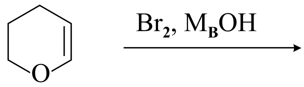
(A) 

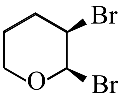
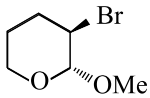
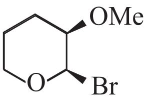
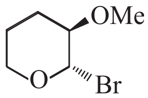
(B) 

(C) 

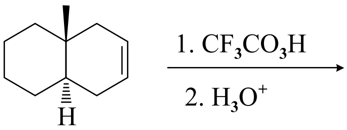
(D) 

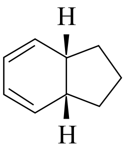
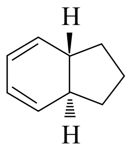
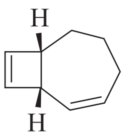
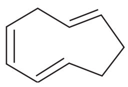
62. The major product formed in the following reaction is—




(A) 
(B) 
(C) 
(D) 

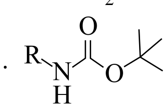
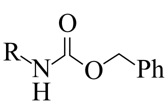
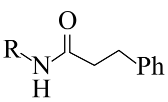
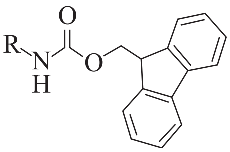
63. The major product formed in the following reaction is—




(A) 
(B) 
(C) 
(D) 

64. Among the following, the synthetic equivalent for acyl anion is—
(A) Nitroethane and base
(B) α-chloroacrylonitrile
(C) Ethylmagnesium bromide
(D) Acetyl chloride and triethylamine

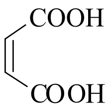
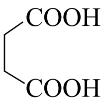
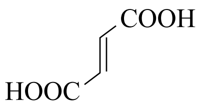
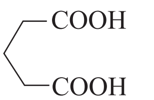
65. Among the following, the compound that undergoes deprotection easily on treatment with hydrogen in the presence of 10% Pd/C to generate RNH$_2$ is—

(A) 
(B) 
(C) 
(D) 

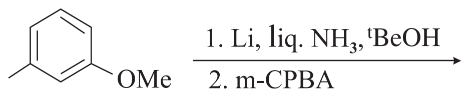
66. Among the following, the amino acid which is basic in nature is—
(A) Tyrosine (B) Asparagine
(C) Leucine (D) Arginine

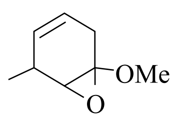
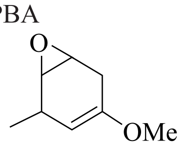
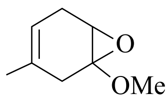
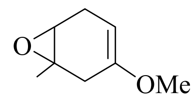
67. "Phosphorescence" is represented as—
(A) $T_1 \rightarrow S_0 + h\nu$ (B) $T_1 \rightarrow S_0 + \Delta$
(C) $S_1 \rightarrow S_0 + h\nu$ (D) $S_1 \rightarrow T_1 + \Delta$

68. Among the following diacids, the one that forms an anhydride fastest on heating with acetic anhydride is—

(A) 
(B) 
(C) 
(D) 

69. The major product formed in the following reaction sequence is—




(A) 
(B) 
(C) 
(D) 

70. In the 400 MHz $^1$H NMR spectrum, an organic compound exhibited a doublet. The two lines of the doublet are at δ 2.35 and 2.38 ppm. The coupling constant (J) value is—
(A) 3 Hz (B) 6 Hz
(C) 9 Hz (D) 12 Hz

# Part C

71. The strength of $p_n - d_2$ bonding in E—O (E = Si, P, S and Cl) follows the order—
(A) Si—O > P—O > S—O > Cl—O
(B) P—O > Si—O > S—O > Cl—O
(C) S—O > Cl—O > P—O > Si—O
(D) Cl—O > S—O > P—O > Si—O

72. In the following reactions carried out in liquid $NH_3$,
$$Zn(NH_2)_2 + 2KNH_2 \rightarrow K_2[Zn(NH_2)_4]$$
$$K_2[Zn(NH_2)_4] + 2NH_4NO_3 \rightarrow Zn(NH_2)_2 + 2KNO_3 + 4NH_3$$
$KNH_2$ and $NH_4NO_3$ act respectively as—
(A) Solvo-acid and solvo-base
(B) Solvo-base and solvo-acid
(C) Conjugate acid and conjugate base
(D) Conjugate base and conjugate acid

73. The pair of lanthanides with the highest third-ionization energy is—
(A) Eu, Gd (B) Eu, Yb
(C) Dy, Yb (D) Lu, Yb

74. The lanthanide (III) ion having the highest partition coefficient between tri-*n*-butylphosphate and concentrated $HNO_3$ is—
(A) La (III) (B) Eu (III)
(C) Nd (III) (D) Lu (III)

75. The quantitative determination of $N_2H_4$ with $KIO_3$ proceeds in a mixture of $H_2O/CCl_4$ as follows :
$$N_2H_4 + KIO_3 + 2HCl \longrightarrow N_2 + KCl + ICl + 3H_2O$$
The end point for the titrimetric reaction is—
(A) Consumption of $N_2H_4$
(B) ICl formation
(C) Disappearance of the yellow colour due to $Cl_2$ in $CCl_4$ layer
(D) Disappearance of the red colour due to $I_2$ in $CCl_4$ layer

76. Among the halides, $NCl_3$(A), $PCl_3$(B) and $AsCl_3$ (C), those which produce two different acids upon hydrolysis are—
(A) A and B (B) A and C
(C) B and C (D) A, B and C

77. The decreasing order of dipole moment of molecules is—
(A) $NF_3 > NH_3 > H_2O$
(B) $NH_3 > NF_3 > H_2O$
(C) $H_2O > NH_3 > NF_3$
(D) $H_2O > NF_3 > NH_3$

78. The cluster having arachno type structure is—
(A) $[Os_5(CO)_{16}]$ (B) $[Os_3(CO)_{12}]$
(C) $[Ir_4(CO)_{12}]$ (D) $[Rh_6(CO)_{16}]$

79. The carbonyl resonance in $^{13}C$ NMR spectrum of $(\eta^5\text{–}C_5H_5)\,Rh(CO)]_3$ ($^{103}Rh$, nuclear spin, I = 1/2, 100%) shows a triplet at – 65 °C owing to the presence of—
(A) Terminal CO (B) $\mu_2$– CO
(C) $\mu_3$– CO (D) $\eta^5$– $C_5H_5$

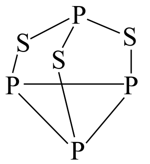
80. Low oxidation state complexes are often air-sensitive, but are rarely water sensitive because—
(A) Air is reducing in nature while water is inert
(B) Both air and water are oxidizing in nature
(C) Both air and water are not π-acceptors
(D) Complexes with low oxidation states will easily lose electrons to $O_2$ but will not bind to a π-donor molecule like $H_2O$

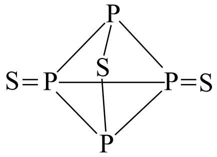
81. The metal complex that exhibits a triplet as well as a doublet in its $^{31}P$ NMR spectrum is—
(A) *mer*–$[IrCl_3(PPh_3)_3]$
(B) *trans*–$[IrCl(CO)(PPh_3)_2]$
(C) *fac*–$[IrCl_3(PPh_3)_3]$
(D) $[Ir(PPh_3)_4]^+$

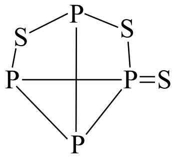
82. The complex that **does not** obey 18 electron rule is—
(A) $[(\eta^5\text{–}C_5H_5)RuCl(CO)(PPh_3)]$
(B) $[W(CO)_3(SiMe_3)(Cl)(NCMe)_2]$
(C) $[IrCl_3(PPh_3)_2(AsPh_2)]^-$
(D) $[O_s(N)Br_2(PMe_3)(NMe_2)]^-$

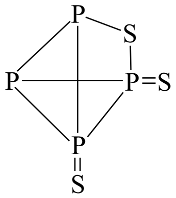
83. The number of spin-allowed ligand field transitions for octahedral Ni (II) complexes with $^3A_{2g}$ ground state is—
(A) Two (B) Three
(C) One (D) Four

84. The correct structure of $P_4S_3$ is—

(A) 

(B) 

(C) 

(D) 

85. The final product of the reaction $[Mn(CO)_6]^+$ + MeLi → is—

(A) $[Mn(CO)_6]^-$ Me

(B) $[Mn(CO)_5\ Me]$

(C) $[Mn(CO)_6]$

(D) $[(MeCO)\ Mn(CO)_5]$

86. The reaction that yields Li $[AlH_4]$ is—

(A) HCl (excess) + $AlCl_3$ + Li →

(B) $H_2$ + Al + Li →

(C) LiH (excess) + $AlCl_3$ →

(D) LiH (excess) + Al →

87. The number of microstates for $d^5$ electron configuration is—

(A) $21 \times 6^3$ (B) $14 \times 6^3$

(C) $7 \times 6^2$ (D) $28 \times 6^3$

88. The carbon-14 activity of an old wood sample is found to be 14.2 disintegrations $min^{-1}\ g^{-1}$. Calculate age of old wood sample, if for a fresh wood sample carbon–14 activity is 15.3 disintegrations $min^{-1}\ g^{-1}$ ($t_{1/2}$ carbon–14 is 5730 years), is—

(A) 5,000 years (B) 4,000 years

(C) 877 years (D) 617 years

89. The reaction $3[Rh_4(CO)_{12}] \rightarrow 2\ [Rh_6(CO)_{16}] + 4CO$ [25 °C, 500 atm CO] is—

(A) Exothermic as more metal-metal bonds are formed

(B) Endothermic as stronger metal carbonyl bonds are cleaved while weaker metal-metal bonds are formed

(C) Is entropically favorable but enthalpically unfavorable such that $\Delta G = 0$

(D) Thermodynamically unfavorable ($\Delta G > 0$)

90. A column is packed with 0.5 g of a strongly acidic ion exchange resin in $H^+$ form. A 1.0 M NaCl solution is passed through the column until the eluant coming out becomes neutral. The collected eluant is completely neutralized by 17 ml of 0.5 M NaOH. The ion exchange capacity of the resin is—

(A) 1.00 meq/g (B) 1.25 meq/g

(C) 1.50 meq/g (D) 1.75 meq/g

91. The molar extraction coefficient of B (MW = 180) is $4 \times 10^3$ lit $mol^{-1}\ cm^{-1}$. One litre solution of $C_1$ which contains 0.1358 g pharmaceutical preparation of B, shows an absorbance of 0.441 in a 1 cm quartz cell. The percentage (w/w) of B in the pharmaceutical preparation is—

(A) 10.20 (B) 14.60

(C) 20.40 (D) 29.12

92. The changes (from A–D given below) which occur when $O_2$ binds to hemerythrin are—

1. One iron atom is oxidized
2. Both the iron atoms are oxidized
3. $O_2$ binds to one iron atom and is also hydrogen bonded
4. $O_2$ binds to both the iron atoms and is also hydrogen bonded

(A) 2 and 3 (B) 2 and 4

(C) 1 and 4 (D) 1 and 3

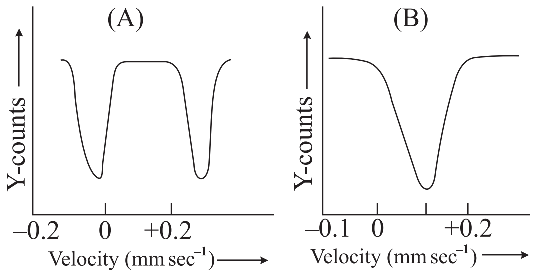
93. In photosynthetic systems the redox metalloproteins involved in electron transfer are cytochrome (cyt *b*), cytochrome *bf* complex (cyt *bf*) and plastocyanin (PC). The pathway of electron flow is—

(A) PC → cyt *b* → cyt *bf*

(B) cyt *bf* → cyt *b* → PC
(C) cyt *b* → cyt *bf* → PC
(D) PC → cyt *bf* → cyt *b*

94. The total numbers of fine and hyperfine EPR lines expected for octahedral high-spin Mn (II) complexes are respectively (I = 5/2 for Mn)—
(A) 3 and 30 (B) 5 and 33
(C) 5 and 30 (D) 4 and 24

95. The Mossbauer spectra of two iron complexes are shown below. They may arise from (i) high-spin iron (III), (ii) high-spin iron (II) and (iii) low-spin iron (III)




The correct matches of spectra (A) and (B) with the iron complexes are—
(A) A with (i) and B with (ii)
(B) A with (ii) and B with (i)
(C) A with (iii) and B with (ii)
(D) A with (ii) and B with (iii)

96. The probability of finding the particle in a one dimensional box of length L in the region between $\frac{L}{4}$ and $\frac{3L}{4}$ for quantum number $n = 1$ is—
(A) $\frac{1}{2}$ (B) $\frac{1}{2}+\frac{1}{\pi}$
(C) $\frac{1}{2}-\frac{1}{\pi}$ (D) $\frac{2}{3}$

97. A particle in three dimensional cubic box of length L has energy of $\frac{14h^2}{8mL^2}$. The degeneracy of the state is—
(A) 2 (B) 3
(C) 6 (D) 9

98. The following are the three statements about perturbation theory—
1. Second order perturbation correction to the ground state energy is ALWAYS negative.
2. Sum of the zeroth order and first order corrections to the ground state energy is ALWAYS greater than the exact ground state energy.
3. Sum of the zeroth order and first order corrections to the ground state energy is less than the exact ground state energy.

From the following which one is correct ?
(A) Only 1 is true
(B) Both 1 and 2 are true
(C) Only 3 is true
(D) Both 2 and 3 are true

99. Using Huckel molecular orbital approximation, the two roots of secular equation of ethene are—
(A) $\alpha + \sqrt{2}\beta, \alpha - \sqrt{2}\beta$
(B) $\alpha + \beta, \alpha$
(C) $\alpha + \beta, \alpha - \beta$
(D) $\alpha + 2\beta, \alpha - 2\beta$

100. For $H_2$ molecule in the excited state $\sigma^1{}_g\ \sigma^1{}_z$, the spin part of the triplet state with $ms = 0$ is proportional to—
(A) $\alpha(1)\,\beta(2)$
(B) $[\alpha(1)\,\beta(2) - \beta(1)\,\alpha(2)]$
(C) $\alpha(1)\,\alpha(2)$
(D) $[\alpha(1)\,\beta(2) + \beta(1)\,\alpha(2)]$

101. A square pyramidal, $MX_4$, molecule belongs to $C_{4V}$ point group. The symmetry operations are : E, $2C_4$, $C_2$, $2\sigma_Y$, and $2\sigma\Delta$. The trace for the reducible representation, when symmetry operations of $C_4$, applied to $MX_4$, is—
(A) 5 1 1 1 3 (B) 1 1 1 1 1
(C) 5 1 1 1 1 (D) 4 1 1 1 3

102. Character table of $C_{2V}$, point group is

| $C_2$ | E | $C_2$ | $\sigma_V$ | $\sigma_V$ | |
|---|---|---|---|---|---|
| $A_1$ | 1 | 1 | 1 | 1 | *z* |
| $A_2$ | 1 | 1 | –1 | –1 | – |
| $B_1$ | 1 | –1 | 1 | –1 | *x* |
| $B_2$ | 1 | –1 | –1 | 1 | *y* |

If the initial and final states belong to $A_1$ and $B_1$ irreducible representations respectively, the allowed electronic transition from $A_1$ to $B_1$ is—

(A) $z$-polarized (B) $y$-polarized
(C) $x$-polarized (D) $x, z$ polarized

103. Using cuvette of 0.5 cm path length, a $10^{-4}$ M solution of a chromophore shows 50% transmittance at certain wavelength. The molar extinction coefficient of the chromophore at this wavelength is (log 2 = 0.301)—

(A) 1500 $M^{-1}$ $cm^{-1}$ (B) 3010 $M^{-1}$ $cm^{-1}$
(C) 5000 $M^{-1}$ $cm^{-1}$ (D) 6020 $M^{-1}$ $cm^{-1}$

104. The set of allowed electronic transitions among the following is—

1. $^4\Sigma \rightarrow {}^2\Pi$ 2. $^3\Sigma \rightarrow {}^3\Pi$
3. $^1\Delta \rightarrow {}^1\Delta$ 4. $^2\Pi \rightarrow {}^2\Pi$
5. $^2\Sigma \rightarrow {}^3\Delta$

(A) 1, 2, 5 (B) 1, 3, 5
(C) 2, 3, 4 (D) 3, 4, 5

105. The following data were obtained from the vibrational fine structure in the vibronic spectrum of a diatomic molecule :

$$\omega_e = 512\ cm^{-1},\ \omega_e x_e \equiv 8\ cm^{-1}$$

where $\omega_e$ is the energy associated with the natural frequency of vibration and $x_e$ is the anharmonicity constant. The dissociation energy ($D_e$) of the molecule is—

(A) 4096 $cm^{-1}$ (B) 6144 $cm^{-1}$
(C) 8192 $cm^{-1}$ (D) 16384 $cm^{-1}$

106. An ideal gas was subjected to a reversible, adiabatic expansion and then its initial volume was restored by a reversible, isothermal compression. If '$q$' denotes the heat added to the system and '$w$' the work done by the system, then—

(A) $w < 0, q < 0$ (B) $w > 0, q < 0$
(C) $w < 0, q > 0$ (D) $w > 0, q > 0$

107. The gas phase reaction $2NO_2(g) \rightarrow N_2O_4(g)$ is an exothermic process. In an equilibrium mixture of $NO_2$ and $N_2O_4$, the decomposition of $N_2O_4$ can be induced by—

(A) Lowering the temperature
(B) Increasing the pressure
(C) Introducing an inert gas at constant volume
(D) Introducing an inert gas at constant pressure

108. Indicate which one of the following relations is not correct—

(A) $-\left(\frac{\partial T}{\partial V}\right)_S = \left(\frac{\partial \rho}{\partial S}\right)_V$

(B) $-\left(\frac{\partial T}{\partial \rho}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$

(C) $-\left(\frac{\partial S}{\partial V}\right)_T = -\left(\frac{\partial \rho}{\partial T}\right)_V$

(D) $-\left(\frac{\partial S}{\partial \rho}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$

109. The energy levels of the harmonic oscillator (neglecting zero point energy) are $\varepsilon_n = nh\nu$ for $n = 0, 1, 2, \ldots, \infty$. Assuming $h\nu = k_a T$, the partition function is—

(A) $e$ (B) $\frac{1}{e}$

(C) $1 - \frac{1}{e}$ (D) $\frac{1}{1-\frac{1}{e}}$

110. The correct entropy for 6 identical particles with their occupation number |0, 1, 2, 3| in four states is—

(A) $k_a \ln 6$ (B) $k_a \ln 12$
(C) $k_b \ln 60$ (D) $k_b \ln 720$

111. The correct Nernst equation for the concentration cell :

Pt |$H_2$ (P) | HCl $(a_\pm)_1$ | AgCl(S) | $\overparen{\text{Ag Ag}}$ | AgCl(S) | HCl $(a_\pm)_2$ | $II_2$ (P) | Pt without liquid junction would be—

(A) $E = \frac{2RT}{F} \text{Ln} \frac{(a_\pm)_1}{(a_\pm)_2}$

(B) $E = \frac{RT}{F} \text{Ln} \frac{(a_\pm)_2}{(a_\pm)_1}$

(C) $E = \frac{2RT}{F} \text{Ln} \frac{(a_\pm)_2}{(a_\pm)_1}$

(D) $E = \frac{RT}{2F} \text{Ln} \frac{(a_\pm)_2}{(a_\pm)_1}$

112. Main assumption(s) involved in the derivation of Debye-Huckel equation is(are) the validity of—

(A) Only Poisson equation

(B) Poisson equation and Boltzmann distribution

(C) Poisson equation, Boltzmann distribution and $|\pm Ze\phi| >> k_BT$

(D) Poisson equation, Boltzmann distribution and $|\pm Ze\phi| << k_BT$

113. In the base ($OH^-$) hydrolysis of a transition metal complex $[ML_6]^{Z+}$, the slope between $\log(k/k_0)$ and $\sqrt{1}$ is found to be –2.1. The charge on the complex is—

(A) +1 (B) +2
(C) +3 (D) +4

114. The rate law for one of the mechanisms of the pyrolysis of $CH_3CHO$ at 520 °C and 0.2 bar is Rate $= -k_2\left(\frac{k_1}{2kd}\right)^{1/2}[CH_3CHO]^{3/2}$

The overall activation energy $E_a$ in terms of the rate law is—

(A) $E_a(2) + E_a(1) + 2E_a(4)$

(B) $E_a(2) + \frac{1}{2}E_a(1) - E_a(4)$

(C) $E_a(2) + \frac{1}{2}E_a(1) - \frac{1}{2}E_a(4)$

(D) $E_a(2) - \frac{1}{2}E_a(1) + \frac{1}{2}E_a(4)$

115. In the Michaelis-Menten mechanism for enzyme kinetics, t he expression obtained is

$$\frac{V}{[E]_0\,[S]} = 1.4 \times 10^{12} - \frac{10^4\,V}{[E]_0}$$

The values of $k_3$ ($k_{cat}$, mol $L^{-1}s^{-1}$) and K (Michaelis constant, mol $L^{-1}$), respectively, are—

(A) $1.4 \times 10^{12}, 10^4$ (B) $1.4 \times 10^8, 10^4$
(C) $1.4 \times 10^8, 10^{-4}$ (D) $1.4 \times 10^{12}, 10^{-4}$

116. The most used acid catalyst in oil industry and the relevant process are respectively—

(A) Aluminophosphate and reforming
(B) Aluminosilicate and cracking
(C) Aluminosilicate and reforming
(D) Aluminophosphate and cracking

117. The wavelength and the spectral region for a single electron transfer across the band gap in a semiconductor ($E_g = 1{\cdot}98 \times 10^{-19}$ J) are—

[$h = 6.626 \times 10^{-34}$ Js, $c = 3 \times 10^8\ ms^{-1}$]

(A) 1000 nm, UV (B) 1000 nm, IR
(C) 500 nm, visible (D) 500 nm, FAR IR

118. The lattice parameter of an element stabilized in a *fcc* structure is 4.04 Å. The atomic radius of the element is—

(A) 2.86 Å (B) 1.43 Å
(C) 4.29 Å (D) 5.72 Å

119. The number-average molar mass ($\overline{M}_n$) and weight-average molar mass ($\overline{M}_w$) of a polymer are obtained respectively by—

(A) Osmometry and light scattering measurements
(B) Osmometry and viscosity measurements
(C) Light scattering and sedimentation measurements
(D) Viscosity and light scattering measurements

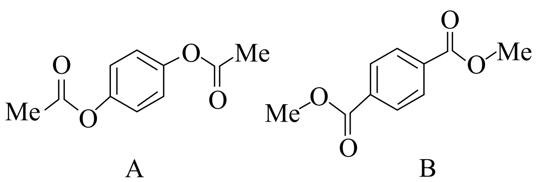
120. Two data sets involving the same variables X and Y are given below :

| X | 4.1 | 4.2 | 4.3 | 4.4 | 4.5 | 4.6 |
|---|---|---|---|---|---|---|
| Y (Set A) | 10.2 | 10.6 | 10.9 | 11.5 | 11.8 | 12.2 |
| Y (Set B) | 10.2 | 10.6 | 11.1 | 11.3 | 11.8 | 12.2 |

If the slopes and intercepts of the regression lines for the two sets are denoted by ($m_A$, $m_B$) and ($c_A$, $c_B$), respectively, then—

(A) $m_A > m_B, c_A > c_B$
(B) $m_A < m_B, c_A > c_B$
(C) $m_A > m_B, c_A < c_B$
(D) $m_A < m_B, c_A < c_B$

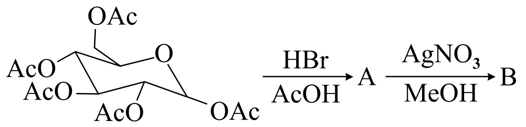
121. Compounds A and B exhibit two singlets, each in their $^1$H NMR spectra. The expected chemical shifts are at δ—

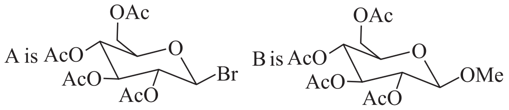



A B

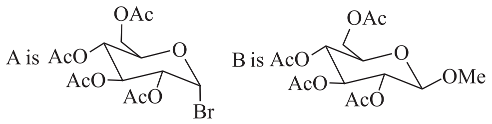
(A) 6.9 and 2.1 for A; 7.7 and 3.9 for B
(B) 7.7 and 3.9 for A; 6.9 and 2.1 for B
(C) 6.9 and 3.9 for A; 7·7 and 2.1 for B
(D) 7.7 and 2.1 for A; 6.9 and 3.9 for B

122. In the following reaction sequence, the major products A and B are—

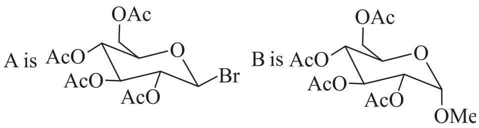


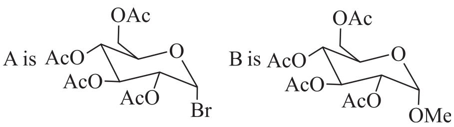

(A)




(B)

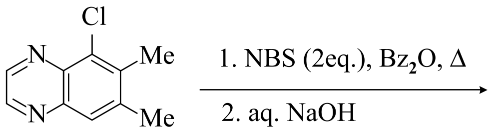


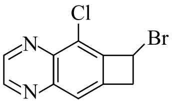

(C)

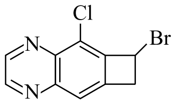


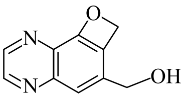

(D)

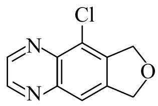
123. The structure of the tricyclic compound formed in the following two steps sequence is—



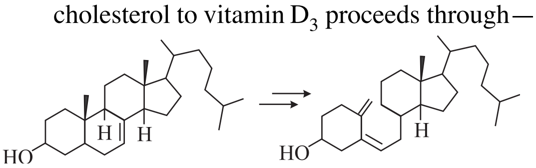

(A) 

(B) 

(C) 

(D) 

124. The two steps conversion of 7-dehydro-cholesterol to vitamin $D_3$ proceeds through—



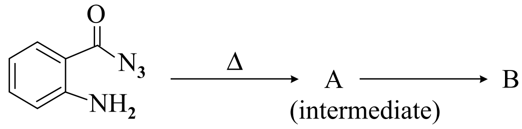

(A) Photochemical electrocyclic disrotatory ring opening; and thermal antarafacial [1, 7]-H shift

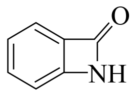
(B) Photochemical electrocyclic conrotatory ring opening; and thermal antarafacial [1, 7]-H shift

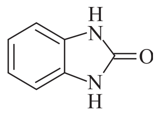
(C) Thermal electrocyclic conrotatory ring opening; and photochemical suprafacial [1, 7]-H shift

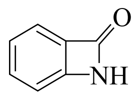
(D) Thermal electrocyclic disrotatory ring opening; and thermal suprafacial [1, 7]-H shift

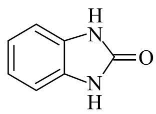
125. The intermediate A and the major product B in the following reaction are—



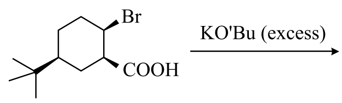

(A) A is acyl cation : B is 

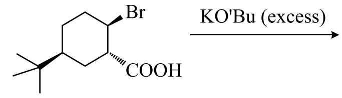
(B) A is acyl cation : B is 

(C) A is acyl nitrene : B is 

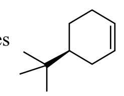
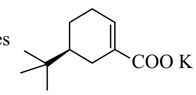
(D) A is acyl nitrene : B is 

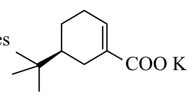
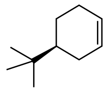
126. For the following two reactions A and B, the correct statement is—

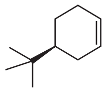
(A) 

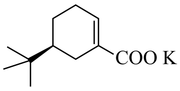

(B) 


(A)

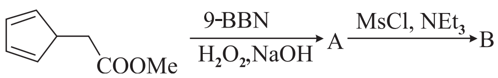
A gives  B gives 

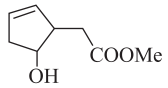
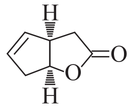
(B) A gives  B gives 

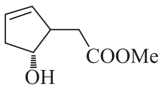
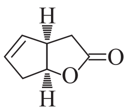
(C) both A and B give 

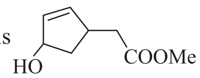
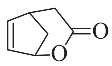
(D) both A and B give 

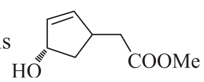
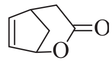

127. The major compound B formed in the reaction sequence given below exhibited a carbonyl absorption band at 1770 cm$^{-1}$ in the IR spectrum. The structures A and B are—




(A) A is  B is 

(B) A is  B is 

(C) A is  B is 

(D) A is  B is 

128. Consider the following reaction sequence starting with monoterpene α-pinene. Identify the correct statement—

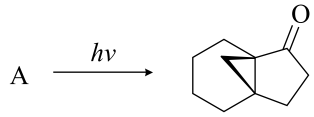
$$\underset{\alpha\text{-pinene}}{A} \xrightarrow{\text{alk } KMnO_4} \underset{\text{pinonic acid}}{B} \xrightarrow{NaOH/Br_2} \underset{\text{pinic acid}}{C}$$

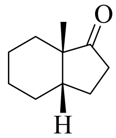
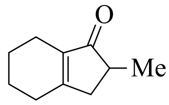
(A) A has a disubstituted double bond; B and C are dicarboxylic acids
(B) A has a trisubstituted double bond; B is a methyl ketone; and C is a dicarboxylic acid
(C) A has a disubstituted double bond; B is a methyl ketone; and C is a dicaroxylic acid
(D) A has an exocyclic double bond; B and C are monocarboxylic acids

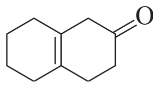
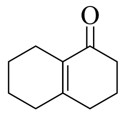
129. The major product formed when (3R, 4S)-3, 4-dimethylhexa-1, 5-diene is heated at 240 °C is—

(A) (2Z,6Z)-octa-2,6-diene
(B) (2E,6E)-octa-2,6-diene
(C) (2E,6Z)-octa-2,6-diene
(D) (3Z,5E)-octa-3,5-diene

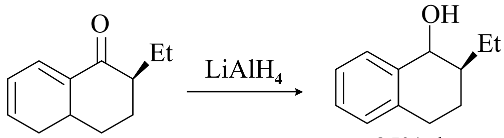
130. Structure of the starting material A in the following photochemical Norrish reaction, is—




(A)  (B) 

(C)  (D) 

131. Considering the following reaction, among *a–c*, the correct statements are—

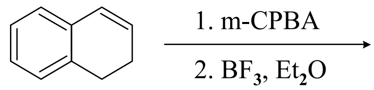


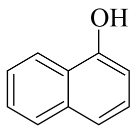
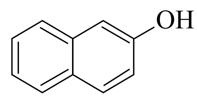

85% de

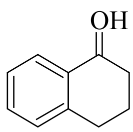
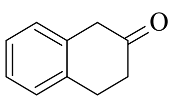
1. The carbonyl group has enantiotopic faces;
2. The hydride attack is *re*-facial;
3. It is a diastereoselective reduction

(A) 1 and 2 only (B) 1 and 3 only
(C) 2 and 3 only (D) 1, 2 and 3

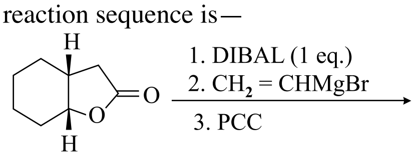
132. The major product formed in the following reaction sequence is—

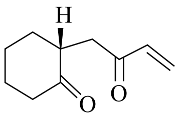


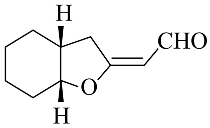

(A)  (B) 

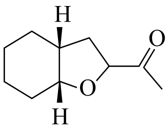
(C)  (D) 

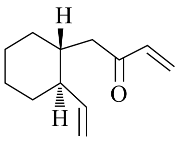
133. The major product formed in the following reaction sequence is—



(A) 

(B) 

(C) 

(D) 

134. Match the following—

**Compound**

(a) Acetic acid

(b) Acetonitrile

(c) Acetone

(d) Carbon tetrachloride

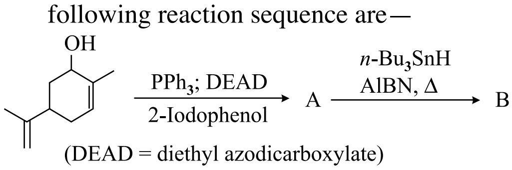
**$^{13}C$ NMR chemical shift (δ ppm)**

1. 95 2. 115

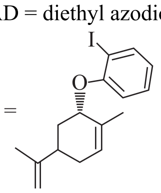
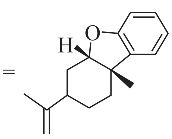
3. 175 4. 205

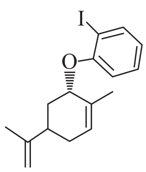
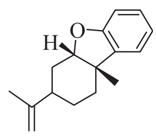
| | (a) | (b) | (c) | (d) |
|---|---|---|---|---|
| (A) | 3 | 2 | 4 | 1 |
| (B) | 3 | 4 | 1 | 2 |
| (C) | 1 | 2 | 4 | 3 |
| (D) | 3 | 1 | 2 | 4 |

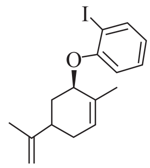
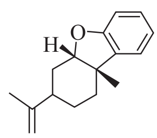
135. The major products A and B in the following reaction sequence are—

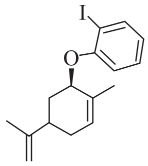
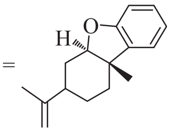



(DEAD = diethyl azodicarboxylate)

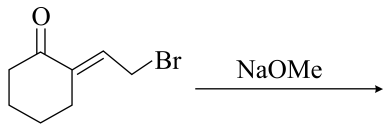
(A) A =  B = 

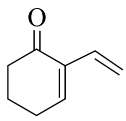
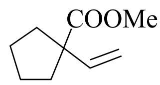
(B) A =  B = 

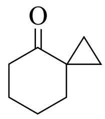
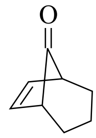
(C) A =  B = 

(D) A =  B = 

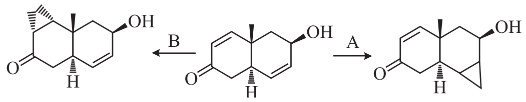
136. The major product formed in the following reaction is—




(A)  (B) 

(C)  (D) 

137. The reagents A and B in the following reactions are—



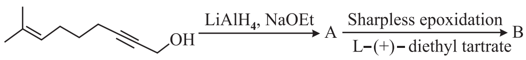

(A) A = $CH_2I_2$,Zn–Cu; B = $Me_4S^+I$, NaH

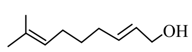
(B) A = $CH_2I_2$,Zn–Cu; B = $Me_3S^+(O)I^-$, NaH

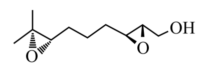
(C) A = $Me_3S^+I^-$,NaH; B = $Me_3S^+(O)I^-$, NaH

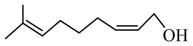
(D) A = $Me_3S^+(O)I^-$,NaH; B = $CH_2I_2$, Zn–Cu

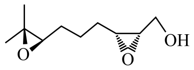
138. The major products A and B formed in the following reaction sequence are—

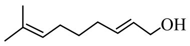


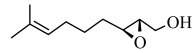

(A) A = 

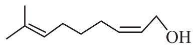
B = 

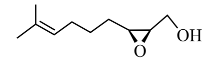
(B) A = 

B = 

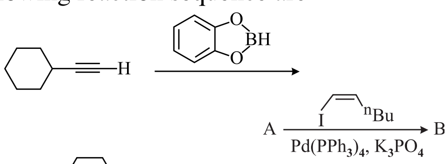
(C) A = 

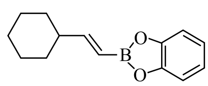
B = 

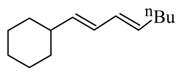
(D) A = 

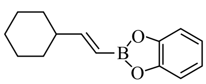
B = 

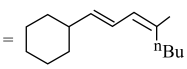
139. The major products A and B formed in the following reaction sequence are—

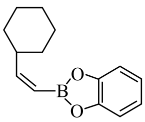
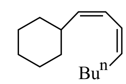


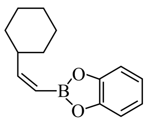
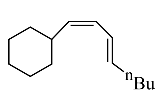
(A) A = 

B = 

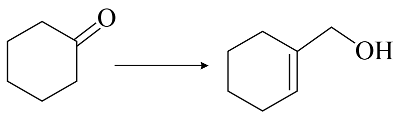
(B) A = 

B = 

(C) A =  B = 

(D) A =  B = 

140. The correct reagent combination/reaction sequence for effecting the following conversion is—



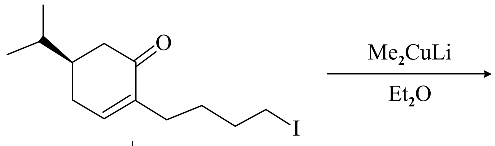
(A) (a) $Me_3SiCH_2OMe$, BuLi; (b) $H_3O^+$; (c) $NaBH_4$, MeOH

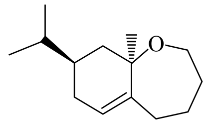
(B) (a) $Ph_3P^+CH_2OMeCl^-$, BuLi; (b) $H_3O^+$; (c) $NaBH_4$, MeOH

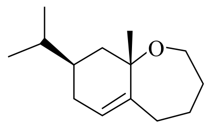
(C) (a) $NH_2NHTs$; (b) NaOEt; (c) ClCOOEt

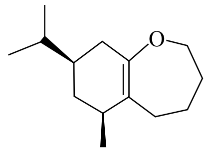
(D) (a) $NH_2NHTs$; (b) 2eq. $^n$BuLi; (c) HCHO

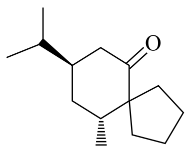
141. The major product formed in the following reaction is—



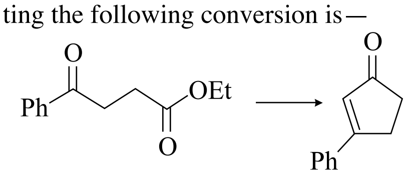
(A) 

(B) 

(C) 

(D) 

142. The correct sequence of reagents for effecting the following conversion is—



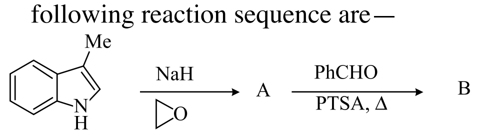
(A) (a) $(CH_2OH)_2$, PTSA, Δ; (b) $CO_2Ti\langle_{Cl}\rangle AlMe_2$ (Tebbe's reagent); (c) $H_3O^+$; (d) KOH

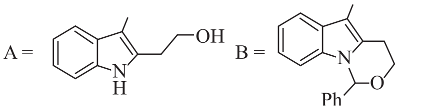
(B) (a) $(CH_2OH)_2$, PTSA, Δ; (b) $Ph_3P–CH_2$; (c) $H_3O^+$; (d) KOH

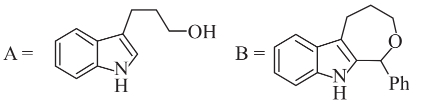
(C) (a) $CO_2Ti\langle_{Cl}\rangle AlMe_2$ (Tebbe's reagent); (b) $H_3O^+$; (c) KOH

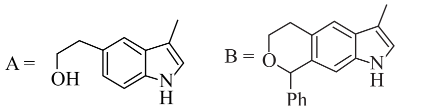
(D) (a) $Ph_3P–CH_2$; (b) $H_3O^+$; (c) KOH

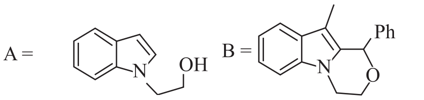
143. The major products A and B formed in the following reaction sequence are—



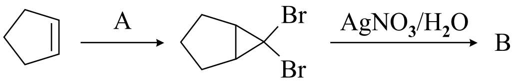
(A) 

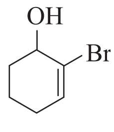
(B) 

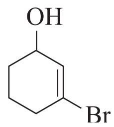
(C) 

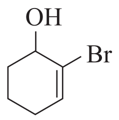
(D) 

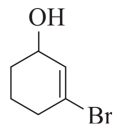
144. The reagent A required and the major product B formed in the following reaction sequence are—



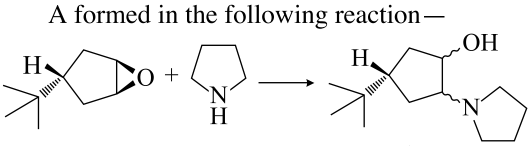
(A) A = $CH_2Br_2$ and KO$^t$Bu B = 

(B) A = $CH_2Br_2$ and KO$^t$Bu B = 

(C) A = $CHBr_3$ and KO$^t$Bu B = 

(D) A = $CHBr_3$ and KO$^t$Bu B = 

145. Among the choices, the correct statement for A formed in the following reaction—



A

(A) A is a single enantiomer
(B) A is a racemic mixture
(C) A is a mixture of two diastereomers
(D) A is a mixture of two epimers

# Answers with Explanations

1. (D)
2. (C) Total number of squares are 15.
3. (D) 4. (B) 5. (C) 6. (A) 7. (B)
8. (B)
9. (B) Chewing equilibrates the pressure on both side of the ear drum.
10. (A) 11. (A) 12. (D) 13. (B) 14. (A)
15. (B) In the most general sense of the word, a cement is a binder, a substance that sets and hardens independently, and can bind other materials together. The word "cement" traces to the Romans, who used the term *opus caementicium* to describe masonary resembling modern concrete that was made from crushed rock with burnt lime as binder.
16. (D) Radiocarbon dating (usually referred to as simply carbon dating) is a radiometric dating method that uses the naturally occurring radioisotope carbon-14 ($^{14}C$) to estimate the age of carbon-bearing materials up to about 58,000 to 60,000 years. Raw *i.e.*, uncalibrated, radiocarbon ages are usually reported in radiocarbon years "Before Present" (BP), with "present" defined as AD 1950. Such raw ages can be calibrated to give calendar dates. One of the most frequent uses of radiocarbon dating is to estimate the age of organic remains from archaeological sites. When plants fix atmospheric carbon dioxide ($CO_2$) into organic material during photosynthesis they incorporate a quantity of $^{14}C$ that approximately matches the level of this isotope in the atmosphere (a small difference occurs because of isotope fractionation, but this is corrected after laboratory analysis.
17. (A) 18. (C) 19. (C) 20. (C) 21. (B)
22. (D) 23. (A) 24. (D) 25. (D) 26. (C)
27. (A) Carbon 14, unlike carbon 12 and carbon 13, is radioactive; meaning that over time the carbon 14 atoms will decay. When the isotope carbon 14 decays it gives off a beta particle and in doing so becomes nitrogen 14. The amount of carbon 12 and carbon 13, however, remains constant.
28. (D) The base pairing-rules for DNA are that, only the Nitrogen Bases of DNA which are;

Adenine "*A*"-which only pairs with-Thymine "*T*", and Cytosine "*C*"-which only pairs with-Guanine "*G*" can only pair to one another within that sequence.

29. (A) 30. (B)

31. (C) In coordination chemistry, a ligand is an ion or molecule that binds to a central metal atom to form a coordination complex. The bonding between metal and ligand generally involves formal donation of one or more of the ligand's electron deficient pairs. The nature of metal-ligand bonding can range from covalent to ionic. Furthermore, the metal-ligand bond order can range from one to three. Ligands are viewed as Lewis bases, although rare cases are known involving Lewis acidic "ligands".

32. (C) 33. (B) 34. (A) 35. (D)

36. (B) Chromate salts contain the chromate anion, $CrO_4^{2-}$. Dichromate salts contain the dichromate anion, $Cr_2O_7^{2-}$. They are oxyanions of chromium in the oxidation state +6. They are moderately strong oxidizing agents.

37. (A) For hydrogen and other nuclei stripped to one electron, the energy depends only upon the principal quantum number *n*.

$$E_n = \frac{-13.6\, Z^2\, eV}{n^2}$$

This fits the hydrogen spectrum unless you take a high resolution look at fine structure where the electron spin and orbital quantum numbers are involved. At even higher resolutions, there is a tiny dependence upon the orbital quantum number in the Lamb shift.

38. (D) 39. (D) 40. (B) 41. (A) 42. (D)

43. (B) 44. (C)

45. (C) In thermodynamics, the **triple point** of a substance is the temperature and pressure at which the three phases (gas, liquid and solid) of that substance coexist in thermodynamic equilibrium. For example, the triple point of mercury occurs at a temperature of –38.8344°C and a pressure of 0.2 $mP_a$.

In addition to the triple point between solid, liquid and gas, there can be triple points involving more than one solid phase, for substances with multiple polymorphs. Helium-4 is a special case that presents a triple point involving two different fluid phases. In general, for a system with *p* possible phases, there are triple points.

$$\binom{p}{3} = \frac{1}{6} p\,(p-1)\,(p-2)$$

46. (B) 47. (C)

48. (A) The key assumption of Activated Complex Theory (ACT), that the AC is in thermodynamic equilibrium with the reactants, needs to be reconsidered. This is because the formation of the AC is slower than its collapse to product. However, this can be remedied by assuming that the AC is formed in a rapid pre-equilibrium as a thermally activated species, which collapses to products in a slow step involving the diffusion of another AC molecule (or solvent in the case of a unimolecular reaction).

49. (D)

50. (B) Additional Polymerization : A chemical reaction in which simple molecules (monomers) are added to each other to form long-chain molecules (polymers) without by products. The molecules of the monomer join together to form a polymeric product in which the molecular formula of the repeating unit is identical with that of the monomer. The molecular weight of the polymer so formed is thus the total of the molecular weights of all of the combined monomer units.

51. (C) First, consider the atoms at the 8 corners. Each corner atom is occupied by 8 unit cells, which means 1/8 of the atom is actually in one unit cell. There are 8 of these corner atoms, so $8\left(\frac{1}{8}\right) = 1$.

Next, consider the atoms at the 6 faces of the unit cell. Each face atom is occupied by 2 unit cells, which means 1/2 of the atom is in one unit cell. There are 6 of these face atoms, so 6 (1/2) = 3.

Add up the two values… 1 + 3 = 4

So, there are 4 atoms contained in a face-centered.

52. (C) Liquids, solids and gases all may be mixed to form colloidal dispersions.

**Aerosols :** solid or liquid particles in a gas.

**Examples :** Smoke is a solid in a gas. Fog is a liquid in a gas.

**Sols :** solid particles in a liquid. Example : Milk of Magnesia is a sol with solid magnesium hydroxide in water.

**Emulsions :** liquid particles in liquid. Example : Mayonnaise is oil in water.

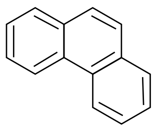
**Gels :** liquids in solid. Examples : gelatin is protein in water. Quicksand is sand in water.

53. (B)  54. (B)

55. (B) As ester is first priority group compared to ketone and alkene, it will go in first priority and after applying Cahn-Prelog Rule (A molecule may contain any number of stereo centers and any number of double bonds, and each gives rise to two possible configurations) option 2 is correct.

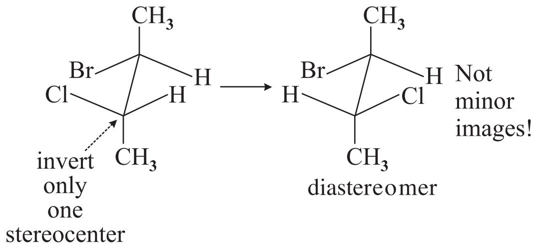
56. (D) Due to the generation of allelic and benzylic carbonium that is resonance stabilized so it will attack on the bromo allyl in very facile condition that's why product 4 is formed as major product.

57. (C) In the phenathrene there are 7 types of magnetically equivalent while in anthracene there are 4 types of magnetically equivalent carbons. **Phenanthrene** is a polycyclic aromatic hydrocarbon composed of three fused benzene rings. The name *phenanthrene* is a composite of phenyl and anthracene. In its pure form, it is found in cigarette smoke and is a known irritant, photo-sensitizing skin to light. Phenanthrene appears as a white powder having blue fluorescence.



58. (D)

59. (B) Due to generation of two chiral centers by epoxidation it will generate diastereomers. A diastereomer is simply any stereoisomer that is not an enantiomer. Technically, *cis-trans* isomers are diastereomers. However, typically the term is reserved for stereoisomers that differ at some but not all stereocenters.




Diastereomers formed by inverting some but not all stereocenters

60. (A)  61. (B)

62. (B) Due to the *cis* bromonium addition and after that SN2 reaction of OMe - gives the product two due to oxygen lone pair.

63. (D)  64. (A)  65. (B)  66. (D)  67. (A)

68. (A)

69. (C) Due to Birch reduction first intermediate is the one which prefers the formation of product 3 as para directing strength of methyl group is more than that of methoxy.

70. (D)  71. (D)  72. (A)  73. (B)  74. (D)

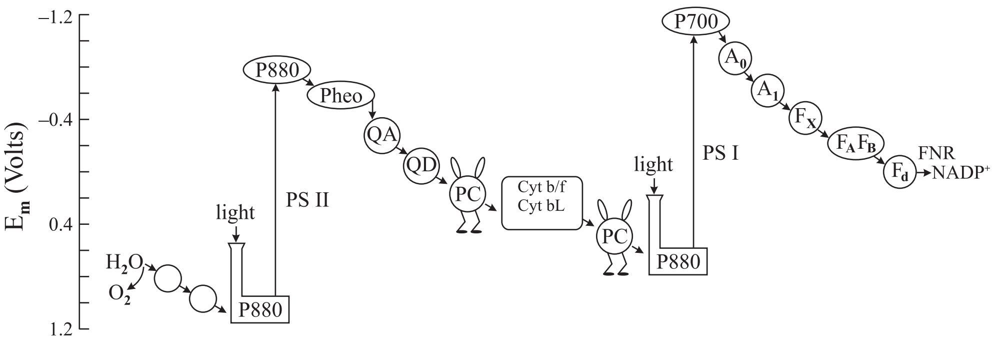
75. (D)  76. (C)  77. (C)  78. (B)  79. (B)

80. (D)  81. (A)  82. (D)  83. (B)  84. (A)

85. (D)  86. (C)  87. (C)  88. (D)  89. (B)

90. (D)  91. (A)  92. (A)

93. (C)



94. (C) 95. (B) 96. (B) 97. (C) 98. (B)
99. (C) 100. (D) 101. (A) 102. (C) 103. (D)
104. (C) 105. (C) 106. (B) 107. (D) 108. (B)
109. (D) 110. (C)
111. (B) The two (ultimately equivalent) equations for these two cases (half-cell, full cell) are as follows :

$E_{red} = E^{\theta}{}_{red} - \frac{RT}{zF} \ln \frac{a_{Red}}{a_{Ox}}$ (half-cell reduction potential)

$E_{cell} = E^{\theta}{}_{cell} - \frac{RT}{zF} \ln Q$ (total cell potential)

112. (D) 113. (B) 114. (C) 115. (C) 116. (B)
117. (B) 118. (B) 119. (A) 120. (C) 121. (A)
122. (B) 123. (D) 124. (B) 125. (D) 126. (B)
127. (B)
128. (B) A has a trisubstituted double bond which is endocyclic and after $KMnO_4$ oxidation it gives B a methyl ketone and after the reaction with NaOH and $Br_2$ gives dicarboxylic acid C.
129. (C)
130. (C) This is the Norrish type reaction in which abstraction of gama hydrogen takes place by the formation of double bond that gives product 3.
131. (C) The hydride ion attacks from the lower face of the plane that is called *re facial* and it reduces the ketone that results in another chiral centre so it will be diastereoselective reduction.
132. (D)
133. (A) In case of DIBAL reaction opening of lactam took place because here is only 1 equation DIBAL is used so further reduction of aldehyde is not possible second reaction is Grignard on aldehyde group which give secondary allelic alcohol which on oxidation with PCC gives ketone.
134. (A) 135. (A) 136. (B)
137. (B) The alpha beta unsaturated ketones on reaction with Ch2I2 Zn–Cl give cyclopropyl on alpha beta unsaturated bond on the other hand alpha beta unsat alcohols on reaction with tetramethyl sulphonium iodide in presence of hydride gives cyclopropane at alpha beta unsat positions.
138. (C) Reaction with LAH gives *cis* ally alcohol which on sharpless epoxidation gives up epoxide.
139. (B) The hydroboration of alkynes gives *trans* hydroborene due to steric hindrance of bulkier cyclopropyl and hydroborating group which on further substitution gives same side conjugated alkene.
140. (D) A simple stark examine reaction after that anionic attack on formaldehyde gives the alcohol.
141. (D) 142. (A)
143. (D) Abstraction of H from indolic N attacks on oxirane giving product 4A which after addition with benzaldehyde gives product 4B.
144. (C) 145. (B)

# Chemical Sciences
## CSIR UGC-NET/JRF Exam.
### Solved Paper

# December 2012
# Chemical Science

Time : 3 Hours] [Maximum Marks : 200

## Direction

1. This Test Booklet contains one hundred and forty five (20 Part 'A' + 50 Part 'B' + 75 Part 'C') Multiple Choice Questions (MCQs). You are required to answer a maximum of 15, 35 and 25 questions from part 'A', 'B' and 'C' respectively. If more than required number of questions are answered, only first 15, 35 and 25 questions in Parts 'A', 'B' and 'C' respectively, will be taken up for evaluation.
2. Each question in Part 'A' and 'B' carries 2 marks and Part 'C' questions carry 4 marks each respectively. There will be negative marking @ 25% for each wrong answer.
3. Below each question in Part 'A', 'B' and 'C' four alternatives or responses are given. Only one of these alternatives is the 'correct' option to the question. You have to find, for each question, the correct or the best answer.

## Useful Fundamental Constants

| | | |
|---|---|---|
| m | Mass of electron | $9.11 \times 10^{-31}$ kg |
| h | Planck's constant | $6.63 \times 10^{-34}$ J-sec |
| e | Charge of electron | $1.6 \times 10^{-19}$ C |
| K | Boltzmann constant | $1.38 \times 10^{-23}$ J/K |
| c | Velocity of Light | $3.0 \times 10^{8}$ m/sec |
| IeV | $1.6 \times 10^{-19}$ J | |
| amu | $1.67 \times 10^{-27}$ kg | |
| G | $6.67 \times 10^{-11}$ Nm$^2$ kg$^{-2}$ | |
| $R_y$ | Rydberg constant | $1.097 \times 10^{7}$ m$^{-1}$ |
| $N_A$ | Avogadro number | $6.023 \times 10^{23}$ mole$^{-1}$ |
| $\varepsilon_0$ | $8.854 \times 10^{-12}$ Fm$^{-1}$ | |
| $\mu_0$ | $4\pi \times 10^{-7}$ Hm$^{-1}$ | |
| R | Molar Gas constant | 8.314 JK$^{-1}$ mole$^{-1}$ |

## List of the Atomic Weights of the Elements

| Element | Symbol | Atomic Number | Atomic Weight |
|---|---|---|---|
| Actinium | Ac | 89 | (227) |
| Aluminium | Al | 13 | 26.98 |
| Americium | Am | 95 | (243) |
| Antimony | Sb | 51 | 121.75 |
| Argon | Ar | 18 | 39.948 |
| Arsenic | As | 33 | 74.92 |
| Astatine | At | 85 | (210) |
| Barium | Ba | 56 | 137.34 |
| Berkelium | Bk | 97 | (249) |
| Beryllium | Be | 4 | 9.012 |
| Bismuth | Bi | 83 | 208.98 |
| Boron | B | 5 | 10.81 |
| Bromine | Br | 35 | 79.909 |
| Cadmium | Cd | 48 | 112.40 |
| Calcium | Ca | 20 | 40.08 |
| Californium | Cf | 98 | (251) |
| Carbon | C | 6 | 12.011 |
| Cerium | Ce | 58 | 140.12 |
| Cesium | Cs | 55 | 132.91 |
| Chlorine | Cl | 17 | 35.453 |
| Chromium | Cr | 24 | 52.00 |
| Cobalt | Co | 27 | 58.93 |
| Copper | Cu | 29 | 63.54 |
| Curium | Cm | 96 | (247) |
| Dysprosium | Dy | 66 | 162.50 |
| Einsteinium | Es | 99 | (254) |
| Erbium | Er | 68 | 167.26 |
| Europium | Eu | 63 | 151.96 |
| Fermium | Fm | 100 | (253) |
| Fluorine | F | 9 | 19.00 |
| Francium | Fr | 87 | (223) |
| Gadolinium | Gd | 64 | 157.25 |
| Gallium | Ga | 31 | 69.72 |
| Germanium | Ge | 32 | 72.59 |
| Gold | Au | 79 | 196.97 |
| Hafnium | Hf | 72 | 178.49 |

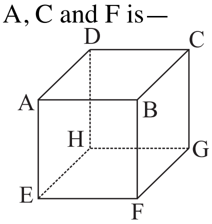
| | | | |
|---|---|---|---|
| Helium | He | 2 | 4.003 |
| Holmium | Ho | 67 | 164.93 |
| Hydrogen | H | 1 | 1.0080 |
| Indium | In | 49 | 114.82 |
| Iodine | I | 53 | 126.90 |
| Iridium | Ir | 77 | 192.2 |
| Iron | Fe | 26 | 55.85 |
| Krypton | Kr | 36 | 83.80 |
| Lanthanum | La | 57 | 138.91 |
| Lawrencium | Lr | 103 | (257) |
| Lead | Pb | 82 | 207.19 |
| Lithium | Li | 3 | 6.939 |
| Lutetium | Lu | 71 | 174.97 |
| Magnesium | Mg | 12 | 24.312 |
| Manganese | Mn | 25 | 54.94 |
| Mendelevium | Md | 101 | (256) |
| Mercury | Hg | 80 | 200.59 |
| Molybdenum | Mo | 42 | 95.94 |
| Neodymium | Nd | 60 | 144.24 |
| Neon | Ne | 10 | 20.183 |
| Neptunium | Np | 93 | (237) |
| Nickel | Ni | 28 | 58.71 |
| Niobium | Nb | 41 | 92.91 |
| Nitrogen | N | 7 | 14.007 |
| Nobelium | No | 102 | (253) |
| Osmium | Os | 76 | 190.2 |
| Oxygen | O | 8 | 15.9994 |
| Palladium | Pd | 46 | 106.4 |
| Phosphorus | P | 15 | 30.974 |
| Platinum | Pt | 78 | 195.09 |
| Plutonium | Pu | 94 | (242) |
| Polonium | Po | 84 | (210) |
| Potassium | K | 19 | 39.102 |
| Praseodymium | Pr | 59 | 140.91 |
| Promethium | Pm | 61 | (147) |
| Protactinium | Pa | 91 | (231) |
| Radium | Ra | 88 | (226) |
| Radon | Rn | 86 | (222) |
| Rhenium | Re | 75 | 186.23 |
| Rhodium | Rh | 45 | 102.91 |
| Rubidium | Rb | 37 | 85.47 |
| Ruthenium | Ru | 44 | 101.1 |
| Samarium | Sm | 62 | 150.35 |
| Scandium | Sc | 21 | 44.95 |
| Selenium | Se | 34 | 78.96 |
| Silicon | Si | 14 | 28.09 |
| Silver | Ag | 47 | 107.870 |
| Sodium | Na | 11 | 22.9898 |
| Strontium | Sr | 38 | 87.62 |
| Sulphur | S | 16 | 32.064 |
| Tantalum | Ta | 73 | 180.95 |
| Technetium | Tc | 43 | (99) |
| Tellurium | Te | 52 | 127.60 |
| Terbium | Tb | 65 | 158.92 |
| Thallium | Tl | 81 | 204.37 |
| Thorium | Th | 90 | 232.04 |
| Thulium | Tm | 69 | 168.93 |
| Tin | Sn | 50 | 118.69 |
| Titanium | Ti | 22 | 47.90 |
| Tungsten | W | 74 | 183.85 |
| Uranium | U | 92 | 238.03 |
| Vanadium | V | 23 | 50.94 |
| Xenon | Xe | 54 | 131.30 |
| Ytterbium | Yb | 70 | 173.04 |
| Yttrium | Y | 39 | 88.91 |
| Zinc | Zn | 30 | 65.37 |
| Zirconium | Zr | 40 | 91.22 |

* Based on mass of $C^{12}$ at 12.00… . The ratio of these weights of those on the order chemical scale (in which oxygen of natural isotopic composition was assigned a mass of 16.0000…) is 1.000050. (Values in parentheses represent the most stable known isotopes).

# Part–A

1. Which of the following numbers is the largest ?
$2^{3^4}, 2^{4^3}, 3^{2^4}, 3^{4^2}, 4^{2^3}, 4^{3^2}$.
(A) $2^{3^4}$ (B) $3^{4^2}$
(C) $4^{3^2}$ (D) $4^{2^3}$

2. The cube ABCDEFGH in the figure has each edge equal to $a$. The area of the triangle with vertices at A, C and F is—




(A) $\frac{\sqrt{3}}{4}a^2$ (B) $\frac{\sqrt{3}}{2}a^2$
(C) $\sqrt{3}\,a^2$ (D) $2\sqrt{3}\,a^2$

3. What is the number of distinct arrangements of the letters of the word UGC-CSIR so that U and I cannot come together ?
(A) 2520 (B) 720
(C) 1520 (D) 1800

4. Suppose the sum of the seven positive numbers is 21. What is the minimum possible value of the average of the squares of these numbers ?
(A) 63 (B) 21
(C) 9 (D) 7

5. Let $A = \dfrac{1^{13} + 2^{13} + 3^{13} + \cdots + 100^{13}}{100}$,

$B = \dfrac{1^{13} + 3^{13} + 5^{13} + \cdots + 99^{13}}{50}$,

$C = \dfrac{2^{13} + 4^{13} + 6^{13} + \cdots + 100^{13}}{50}$,

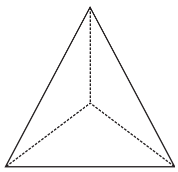
Which of the following is true ?

(A) $B < C < A$ (B) $A < B < C$
(C) $B < A < C$ (D) $C < A < B$

6. A circle of radius 5 units in the XY plane has its centre in the first quadrant, touches the $x$-axis and has a chord of length 6 units on the $y$-axis. The coordinate of its centre are—

(A) (4, 6) (B) (3, 5)
(C) (5, 4) (D) (4, 5)

7. A wire of length 6 metres is used to make a tetrahedron of each edge 1 metre, using only one strand of wire for each edge. The minimun number of times the wire has to be cut is—



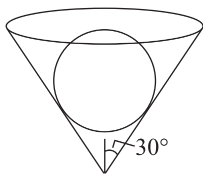
(A) 2 (B) 3
(C) 1 (D) 0

8. If the sum of the next two terms of the series below is $x$, what is the value of $\log_2 x$ ?

2, – 4, 8, – 16, 32, – 64, 128, …………

(A) 128 (B) 10
(C) 256 (D) 8

9.




A conical vessel with semi-vertical angle 30° and height 10·5 cm has a thin lid. A sphere kept inside it touches the lid. The radius of the sphere (in cm) is—

(A) 3·5 (B) 5
(C) 6·5 (D) 7

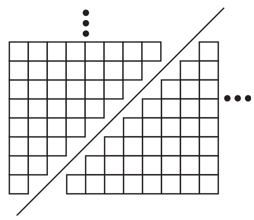
10. Amar, Akbar and Anthony are three friends, one of whom is a doctor, another is an engineer and the third is a professor. Amar is not an engineer. Akbar is the shortest. The tallest person is a doctor. The engineer's height is the geometric mean of the heights of the other two. Then which of the following is true ?

(A) Amar is a doctor and he is the tallest
(B) Akbar is a professor and he is tallest
(C) Anthony is an engineer and he is shortest
(D) Anthony is a doctor and he is the tallest

11. If 100 cats catch 100 mice in 100 minutes, then how long will it take for 7 cats to catch 7 mice ?

(A) 100/7 minutes (B) 100 minutes
(C) 49/100 minutes (D) 7 minutes

12. What does this digram demonstrate ?



(A) $1 + 2 + 3 + \cdots + n = \dfrac{n \cdot (n+1)}{2}$

(B) $1^2 + 2^2 + 3^2 + \cdots + n^2 = \dfrac{n \cdot (n+1) \cdot (2n+1)}{2}$

(C) $1 + 3 + \cdots + (2n + = -1) = n^2$

(D) $2^2 + 4^2 + \cdots + (2n)^2 = \dfrac{2 \cdot n(n+1) \cdot (2n+1)}{3}$

13. Suppose there are socks of N different colours in a box. If you take out one sock at a time, what is the maximum number of socks that you have to take out before a matching pair is found ? Assume that N is an even number.

(A) N (B) N + 1
(C) N – 1 (D) N/2

14. At what time after 4 O' clock, the hour and the minute hands will lie opposite to each other ?

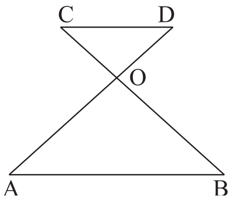
(A) $4 - 50' - 31''$ (B) $4 - 52' - 51''$
(C) $4 - 53' - 23''$ (D) $4 - 54' - 33''$

15. Which of the following curves just touches the $x$-axis ?

(A) $y = x^2 - x + 1$

(B) $y = x^2 - 2x + 2$
(C) $y = x^2 - 10x + 25$
(D) $y = x^2 - 7x + 12$

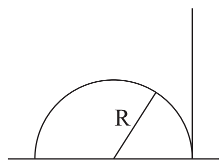
16.




If AB is paralleled to CD and AO = 2OD, then the area of triangle OAB is bigger than the area of triangle OCD by a factor of—

(A) 2 (B) 3
(C) 4 (D) 8

17.




A semi-circular arch of radius R has a vertical pole put on the ground together with one of its legs. An ant on the top of the arch finds the angular height of the tip of the pole to be 45°. The height of the pole is—

(A) $\sqrt{2}$R (B) $\sqrt{3}$R
(C) $\sqrt{4}$R (D) $\sqrt{5}$R

18. Suppose we make N identical smaller spheres from a big sphere. The total surface area of the smaller spheres is X times the total surface area of the big sphere, where X is—

(A) $\sqrt{N}$ (B) 1
(C) $N^{1/3}$ (D) $N^3$

19. What is the next number in the sequence 24, 30, 33, 39, 51, ········ ?

(A) 57 (B) 69
(C) 54 (D) 81

20. Four lines are drawn on a plane with no two parallel and no three concurrent. Lines are drawn joining the points of intersection of the previous four lines. The number of new lines obtained this way is—

(A) 3 (B) 5
(C) 12 (D) 2

# Part–B

21. For an odd nucleon in '*g*' nuclear orbital and parallel to I, spin and parity are—

(A) 9/2 and (+) (B) 7/2 and (+)
(C) 9/2 and (–) (D) 7/2 and (–)

22. For the deposition of Pb by electroplating, the best suited compound among the following is—

(A) $PbCl_2$ (B) $PbSO_4$
(C) $Pb(Et)_4$ (D) $Pb(BF_4)_2$

23. Appropriate reasons for the deviation form the Beer's law among the following are—

1. Monochromaticity of light
2. Very high concentration of analyte
3. Association of analyte
4. Dissociation of analyte

(A) 1, 2 and 4 (B) 2, 3 and 4
(C) 1, 3 and 4 (D) 1, 2 and 3

24. Which one of the following shows the highest solubility in hot concentrated aqueous NaOH?

(A) $La(OH)_3$ (B) $Nd(OH)_3$
(C) $Sm(OH)_3$ (D) $Lu(OH)_3$

25. In the vibrational spectrum of $CO_2$, the number of fundamental vibrational modes common in both infrared and Raman are—

(A) three (B) two
(C) one (D) zero

26. The light pink colour of $[Co(H_2O)_6]^{2+}$ and the deep blue colour of $[CoCl_4]^{2-}$ are due to—

(A) MLCT transition in the first and d-d transition in the second
(B) LMCT transitions in both
(C) d-d transitions in both
(D) d-d transition in the first and MLCT transition in the second

27. In $Mo_2(S_2)_6]^{2-}$ cluster the number of bridging $S_2^{2-}$ and coordination number of Mo respectively, are—

(A) 2 and 8 (B) 2 and 6
(C) 1 and 8 (D) 1 and 6

28. $^1$H NMR spectrum of HD would show—

(A) a singlet
(B) a doublet

(C) a triplet with intensity ratio : 1 : 2 :1

(D) a triplet with intensity ratio 1 : 1 : 1

29. The number of possible isomers of $[Ru(PPh_3)_2(acac)_2]$ (acac = acetylacetonate) is—

(A) 2 (B) 3

(C) 4 (D) 5

30. The total number of Cu – O bonds present in the crystalline copper (II) acetate monohydrate is—

(A) 10 (B) 6

(C) 8 (D) 4

31. The electronegativity difference is the highest for the pair—

(A) Li, Cl (B) K, F

(C) Na, Cl (D) Li, F

32. Which ones among $CO_3^{2-}$, $SO_3$, $XeO_3$ and $NO_3^-$ have planar structure ?

(A) $CO_3^{2-}$, $SO_3$ and $XeO_3$

(B) $SO_3$, $XeO_3$ and $NO_3^-$

(C) $CO_3^{2-}$, $XeO_3$ and $NO_3^-$

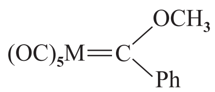
(D) $CO_3^{2-}$, $SO_3$ and $NO_3^-$

33. The substitution of $\eta^5$ – Cp group with nitric oxide is the easiest for—

(A) $\eta^5 - Cp_2Fe$ (B) $\eta^5 - Cp_2CoCl$

(C) $\eta^5 - Cp_2Ni$ (D) $\eta^5 - Cp_2Co$

34. The molecule




obeys 18 e rule. The two 'M' satisfying the condition are—

(A) Cr, $Re^+$ (B) Mo, V

(C) V, $Re^+$ (D) Cr, V

35. The correct set of the biologically essential elements is—

(A) Fe, Mo, Cu, Zn (B) Fe, Cu, Co, Ru

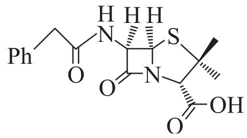
(C) Cu, Mn, Zn, Ag (D) Fe, Ru, Zn, Mg

36. The number of lines exhibited by a high resolution EPR spectrum of the species, $[Cu(ethylenediamine_2]^{2+}$ is [Nuclear spin (I) of Cu = 3/2 and that of N = 1]—

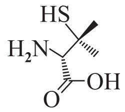
(A) 12 (B) 15

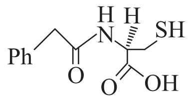
(C) 20 (D) 36

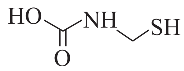
37. Degradation of penicillin G—

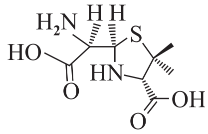



gives penicillamine that can utilize nitrogen, oxygen or sulfur atoms as donors to bind with lead(II), mercury(II) or copper(II). The structure of penicillamine is—

(A)



(B)



(C)



(D)



38. The molecule that has an $S_6$ symmetry element is—

(A) $B_2H_6$ (B) $CH_4$

(C) $PH_5$ (D) $SF_6$

39. The electric dipole allowed transition in a $d^2$ atomic system is—

(A) $^3F \rightarrow {}^1D$ (B) $^3F \rightarrow {}^1P$

(C) $^3F \rightarrow {}^3D$ (D) $^3F \rightarrow {}^3P$

40. When a hydrogen atom is placed in an electric field along the $y$-axis, the orbital that mixes most with the ground state $1s$ orbital is—

(A) $2s$ (B) $2p_x$

(C) $2p_y$ (D) $2p_z$

41. For water, $\Delta H_{vap} \approx 41$ kJ mol$^{-1}$. The molar entropy of vaporization at 1 atm pressure is approximately—

(A) 410 J K$^{-1}$ mol$^{-1}$ (B) 110 J K$^{-1}$ mol$^{-1}$

(C) 41 J K$^{-1}$ mol$^{-1}$ (D) 11 J K$^{-1}$ mol$^{-1}$

42. If A and B are non-commuting hermitian operators, all eigenvalues of the operator given by the commutator [A, B] are—

(A) complex (B) real

(C) imaginary (D) zero

43. The value of the commutator $[x, p_x^2]$ is given by—
(A) $2i$ (B) $2i\hbar$
(C) $2i\hbar x$ (D) $2i\hbar p_x$

44. The correlation coeffcient between two arbitrary variable $x$ and $y$ is zero, if—
(A) $\langle xy \rangle = \langle yx \rangle$ (B) $\langle x^2 \rangle = \langle x \rangle^2$
(C) $\langle y^2 \rangle = \langle y \rangle^2$ (D) $\langle xy \rangle = \langle yx \rangle \langle y \rangle$

45. A Carnot engine takes up 90 J of heat from the source kept at 300 K. The correct statement among the following is—
(A) it transfers 60 J of heat to the sink at 200 K
(B) it transfers 50 J of heat to the sink at 200 K
(C) it transfers 60 J of heat to the sink at 250 K
(D) it transfers 50 J of heat to the sink at 250 K

46. The relative population in two states with energies $E_1$ and $E_2$ satisfying Boltzman distribution is given by $n_1/n_2 = (3/2)\ \exp.[-(E_1 - E_2)/K_BT]$. The relative degeneracy $g_2/g_1$ is—
(A) 2 (B) 2/3
(C) 3/2 (D) 3

47. The Daniell cell is—
(A) $Pt_I(s)|Zn(s)|Zn^{2+}(aq)||Cu^{2+}(aq)|Cu(s)|Pt_{II}(s)$
(B) $Pt_I(s)|Zn(s)|Zn^{2+}(aq)||Ag^{+}(aq)|Ag(s)|Pt_{II}(s)$
(C) $Pt_I(s)|Fe(s)|Fe^{2+}(aq)||Cu^{2+}(aq)|Cu(s)|Pt_{II}(s)$
(D) $Pt_I(s)|H_2(g)|H_2SO_4(aq)||Cu^{2+}(aq)|Cu(s)|Pt_{II}(s)$

48. If the concept of *half-life* is generalized to *quarter-life* of a first order chemical reaction, it will be equal to—
(A) $ln\ 2/k$ (B) $ln\ 4/k$
(C) $4/k$ (D) $1/4k$

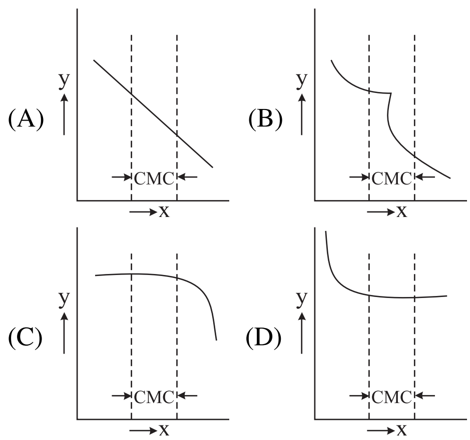
49. Kohlrausch's law is applicable to a dilute solution of—
(A) potassium chloride in hexane
(B) acetic acid in water
(C) hydrochloric acid in water
(D) benzoic acid in benzene

50. A dilute silver nitrate solution is added to a slight excess of sodium iodide solution. A solution of AgI is formed whose surface adsorbs—
(A) $I^-$ (B) $NO_3^-$
(C) $Na^+$ (D) $Ag^+$

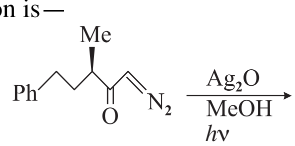
51. The absorption spectrum of $O_2$ shows a vibrational structure that becomes continuum at 56875 $cm^{-1}$. At the continuum, it dissociates into one ground state atom ($O_g$) and one excited state atom ($O_e$). The energy difference between $O_e$ and $O_g$ is 15125 $cm^{-1}$. The dissociation energy (in $cm^{-1}$) of ground state of $O_2$ is—
(A) $\frac{56875}{15125}$ (B) $\frac{15125}{56875}$
(C) 72000 (D) 41750

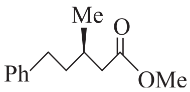
52. The angle between the two planes represented by the Miller indices (110) and (111) in a simple cubic lattice is—
(A) 30° (B) 45°
(C) 60° (D) 90°

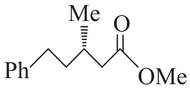
53. The correct representation of the variation of molar conductivity ($y$-axis) with surfactant concentration ($x$-axis) is [CMC = Critical Micelle Concentration]—

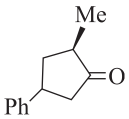


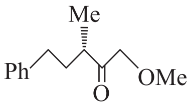

54. The major product formed in the following reaction is—



(A) 

(B) 

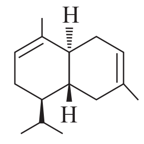
(C) 

(D) 

55. If the $pK_a$ value for *p*-methoxybenzoic acid is 4·46 and that of benzoic acid is 4·19, the $\sigma_{para}$ for methoxy group is—

(A) 8·65 (B) 4·32
(C) 0·27 (D) –0·27

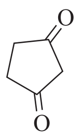
56. The biosynthetic precursor of cadinene is—

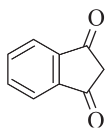


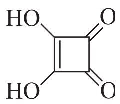
**Cadinene**

(A) shikimic acid (B) mevalonic acid
(C) arachidonic acid (D) prephenic acid

57. The correct order of acidity of the compounds A-C is—

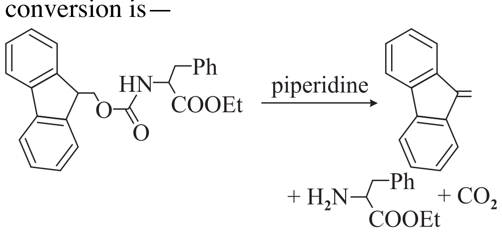

**A**


**B**


**C**

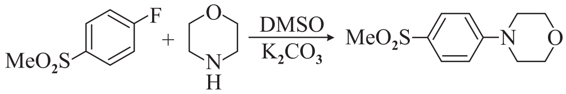
(A) A > B > C (B) B > C > A
(C) C > A > B (D) B > A > C

58. The mechanism involved in the following conversion is—



(A) $E_2$-elimination (B) $E_1$-elimination
(C) *syn*-elimination (D) E1cb-elimination

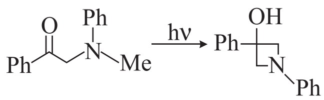
59. The correct statement(s) A-D are given for the following reaction. The correct one(s) is (are)—



1. aromatic *ipso* substitution reaction
2. aromatic nucleophilic substitution
3. aromatic electrophilic substitution
4. aromatic free radical substitution

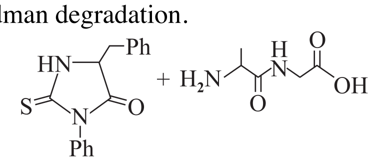
(A) 1 and 2 only
(B) 1 and 3 only
(C) 3 and 4 only
(D) 3 only

60. The following photochemical transformation proceeds through



(A) Norrish type I reaction
(B) Norrish type II reaction
(C) Barton reaction
(D) Paterno-Buchi reaction

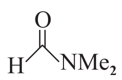
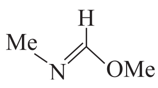
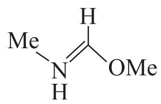
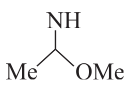
61. A tripeptide gives the following products on Edman degradation.



The tripeptide is—

(A) Phe-Ala-Gly (B) Phe-Gly-Ala
(C) Ala-Gly-Phe (D) Gly-Ala-Phe

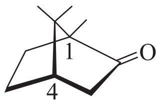
62. In the $^1H$ NMR spectrum recorded at 293 K, an organic compound ($C_3H_7NO$), exhibited signals at δ 7·8 (1 H, s), 2·8 (3 H, s) and 2·6 (3 H, s). The compound is—

(A) 
(B) 
(C) 
(D) 

63. In the IR spectrum of *p*-nitrophenyl acetate, the carbonyl absorption band appears at—

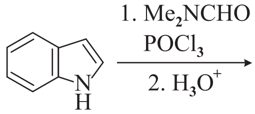
(A) 1670 $cm^{-1}$ (B) 1700 $cm^{-1}$
(C) 1730 $cm^{-1}$ (D) 1760 $cm^{-1}$

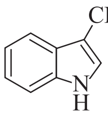
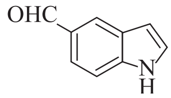
64. The absolute configuration at the two chiral centres of (–)-camphor is—

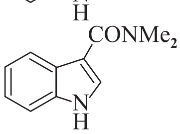
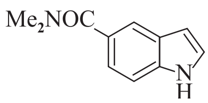


(A) 1R, 4R (B) 1R, 4*s*
(C) 1*s*, 4R (D) 1*s*, 4*s*

65. The major product formed in the following reaction is—



(A)  (B) 

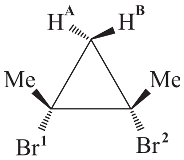
(C)  (D) 

66. The first person to separate a racemic mixture into individual enantiomers is—
(A) J. H. Van't Hoff (B) L. Pasteur
(C) H. E. Fischer (D) F. Wöhler

67. Consider the following statements for [18]-annulene :
1. it is aromatic
2. the inner protons resonate at δ 9·28 in its $^1$H NMR spectrum
3. there are six protons in the shielded zone.

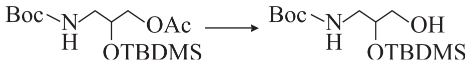
The correct statements are—
(A) 1, 2, 3 (B) 1 and 2 only
(C) 2 and 3 only (D) 1 and 3 only

68. In the compound given below, the relation between $H^A$, $H^B$, and between $Br^1$, $Br^2$ is—



(A) $H^A$, $H^B$ are enantiotropic; and $Br^1$, $Br^2$ are diastereotopic
(B) $H^A$, $H^B$ are diastereotopic; and $Br^1$, $Br^2$ are enantiotropic
(C) $H^A$, $H^B$ are diastereotopic; and $Br^1$, $Br^2$ are homotopic
(D) $H^A$, $H^B$ are enantiotropic; and $Br^1$, $Br^2$ are homotopic

69. The most appropriate reagent to effect the following chemoselective conversion is—



(A) HCl, EtOH, reflux
(B) $Bu_4NF$
(C) $K_2CO_3$ MeOH
(D) $CF_3COOH$, EtOH, rt

70. Among the following, an example of a 'Green Synthesis' is—
(A) synthesis of malachite green
(B) Friedel-Craft's acylation of anisole with $Ac_2O$/anhydrous $AlCl_3$
(C) Jones' oxidation of benzyl alcohol to benzoic acid
(D) Diels-Alder reaction of furan and maleic acid in water

# Part–C

71. The recoil energy of a Mössbauer nuclide of mass 139 amu is 2·5 Mev. The energy emitted by the nucleus in keV is—
(A) 12·5 (B) 15·0
(C) 20·5 (D) 25·0

72. Complexes of general formula, *fac*-$[Mo(CO)_3(phosphine)_3]$ have the C-O stretching bands as given below :

Phosphines : $PF_3$ (A); $PCl_3$ (B); $P(Cl)Ph_2$ (C); $PMe_3$ (D)

v(CO), $cm^{-1}$ : 2090 (i); 2040 (ii); 1977 (iii); 1945 (iv)

The correct combination of the phosphine and the streching frequency is—
(A) (A – i) (B – ii) (C – iii) (D – iv)
(B) (A – ii) (B – i) (C – iv) (D – iii)
(C) (A – iv) (B – iii) (C – ii) (D – i)
(D) (A – iii) (B – iv) (C – i) (D – ii)

73. On subjecting 9·5 ml solution of $Pb^{2+}$ of X M to polorographic measurements, $I_d$ was found to be 1 μA. When 0·5 ml of 0·04 M $Pb^{2+}$ was added before the measurement, the $I_d$ was found to be 1·25 μA. The molarity X is—
(A) 0·0035 (B) 0·0400
(C) 0·0067 (D) 0·0080

74. Match each item from the List-I (compound in solvent) with that from the List-II (its behaviour) and select the correct combination using the codes given below—

**List-I**

(a) $CH_3COOH$ in pyridine

(b) $CH_3COOH$ in $H_2SO_4$

(c) $HClO_4$ in $H_2SO_4$

(d) $SbF_5$ in HF

**List-II**

1. Strong acid 2. Weak acid
3. Strong base 4. Weak base

**Codes :**

| | (a) | (b) | (c) | (d) |
|---|---|---|---|---|
| (A) | 1 | 2 | 3 | 4 |
| (B) | 2 | 1 | 3 | 4 |
| (C) | 3 | 4 | 2 | 1 |
| (D) | 4 | 2 | 3 | 1 |

75. Structure of a carborane with formula, $C_2B_4H_8$ is formally derived from—

(A) *Closo*-borane (B) *Nido*-borane
(C) *Arachno*-borane (D) *Conjuncto*-borane

76. Boric acid is a weak acid in aqueous solution. But its acidity increases significantly in the presence of ethylene glycol, because—

(A) ethylene glycol releases additional $H^+$

(B) $B(OH)_4^-$ is consumed in forming a compound with ethylene glycol

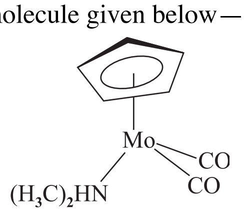
(C) ethylene glycol neutralizes $H^+$ released by boric acid

(D) Boric acid dissociates better in the mixed-solvent

77. Coordination number of 'C' in $Be_2C_3$ whose structure is correlated with that of $CaF_2$, is—

(A) 2 (B) 4
(C) 6 (D) 8

78. For the molecule given below—




Consider the following statements about its room temperature spectral data :

1. $^1H$ NMR has singles at 5·48 and 3·18 ppm.
2. $^1H$ NMR has multiplet at 5·48 and singlet at 3·18 ppm.
3. IR has CO stretching bands at 1950 and 1860 $cm^{-1}$.
4. IR has only one CO stretching band at 1900 $cm^{-1}$.

The correct pair of statements is—

(A) 1 and 3 (B) 2 and 3
(C) 1 and 4 (D) 2 and 4

79. In the cluster $[Co_3(CH)(CO)_9]$ obeying 18e rule, the number of metal-metal bonds and the bridging ligands respectively, are—

(A) 3 and 1 CH (B) 0 and 3 CO
(C) 3 and 1 CO (D) 6 and 1 CH

80. Consider the ions Eu(III), Gd(III), Sm(III) and Lu(III). The observed and calculated magnetic moment values are closest for the pair—

(A) Gd (III), Lu (III)
(B) Eu (III), Lu (III)
(C) Sm (III), Gd (III)
(D) Sm (III), Eu (III)

81. Silicates with continuous 3D framework are—

(A) *Neso*-silicates (B) *Soro*-silicates
(C) *Phyllo*-silicates (D) *Tecto*-silicates

82. The correct spinel structure of $Co_3O_4$ is—

(A) $(Co^{2+})_t(2Co^{3+})_oO_4$
(B) $(Co^{3+})_t(Co^{2+}Co^{3+})_oO_4$
(C) $(Co^{2+}Co^{3+})_t(Co^{3+})_oO_4$
(D) $(2Co^{3+})_t(Co^{2+})_oO_4$

83. In the solid state, the $CuCl_5^{3-}$ ion has two types of bonds. There are—

(A) three long and two short
(B) two long and three short
(C) one long and four short
(D) four long and one short

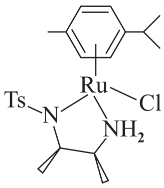
84. In metalloenzymes, the metal centers are covalently linked through the side chains of the amino acid residues. The correct set of

amino-acids which are involved in the primary coordination spheres of metalloenzymes is—

(A) Ala, Leu, His (B) Glu, His, Cys
(C) Leu, Glu. Cys (D) Ala, His, Glu

85. Consider the catalyst in Column-I and reaction in Column-II :

**Column-I**

(a) [(R)-BINAP]$Ru^{2-}$
(b) $[Rh(CO)_2I_2]^-$
(c) $Pd(PPh_3)_4$
(d) 


**Column-II**

1. Hydroformylation
2. Asymmetric hydrogenation
3. Asymmetric hydrogen transfer
4. Heck coupling

The best match of a catalyst of Column-I with the reaction under Column-II is—

**Codes :**

| | (a) | (b) | (c) | (d) |
|---|---|---|---|---|
| (A) | 2 | 1 | 4 | 3 |
| (B) | 1 | 2 | 3 | 4 |
| (C) | 3 | 1 | 4 | 2 |
| (D) | 4 | 3 | 2 | 1 |

86. A solution of 2·0 g of brass was analysed for Cu electrogravimetrically using Pt-gauze as electrode. The weight of Pt-gauze changed from 14·5 g to 16·0 g. The percentage weight of Cu in brass is—

(A) 50 (B) 55
(C) 60 (D) 75

87. The platinum complex of $NH_3$ and $Cl^-$ ligands is an anti-tumour agent. The correct isomeric formula of the complex and its precursor are—

(A) *cis*–$Pt(NH_3)_2Cl_2$ and $PtCl_4^{2-}$
(B) *trans*–$Pt(NH_3)_2Cl_2$ and $PtCl_4^{2-}$
(C) *cis*–$Pt(NH_3)_2Cl_2$ and $Pt(NH_3)_4^{2+}$
(D) *trans*–$Pt(NH_3)_2Cl_2$ and $Pt(NH_3)_4^{2+}$

88. Successive addition of NaCl, $H_3PO_4$, KSCN and NaF to a solution of $Fe(NO_3)_3{\cdot}9H_2O$ gives yellow, colourless, red and again colourless solutions due to the respective formation of—

(A) $[Fe(H_2O)_5Cl]^{2+}$, $[Fe(H_2O)_5(PO_4)]$, $[Fe(H_2O)_5(SCN)]^{2+}$, $[Fe(H_2O)_5F]^{2+}$
(B) $[Fe(H_2O)_4Cl(OH)]^{1+}$, $[Fe(H_2O)_5(PO_4)]$, $[Fe(H_2O)_5(SCN)]^{2+}$, $[Fe(H_2O)_5F]^{2+}$
(C) $[Fe(H_2O)_5Cl]^{2+}$, $[Fe(H_2O)_6]^{3+}$, $[Fe(H_2O)_5(SCN)]^{2+}$, $[Fe(H_2O)_5F]^{2+}$
(D) $[Fe(H_2O)_5Cl]^{2+}$, $[Fe(H_2O)_5(PO_4)]$, $[Fe(H_2O)_5(SCN)]^{2+}$, $Fe(H_2O)_4(SCN)F]^{1+}$

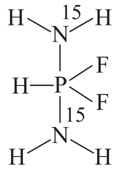
89. Which one of following will not undergo oxidative addition by methyl iodide ?

(A) $[Rh(CO)_2I_2]^-$
(B) $[Ir(PPh_3)_2(CO)Cl]$
(C) $[\eta^5\text{–}CpRh(CO)_2]$
(D) $[\eta^5\text{–}Cp_2Ti(Me)(Cl)]$

90. In hydroformylation reaction using $[Rh(PPh_3)_3(CO)(H)]$ as the catalyst, addition of excess $PPh_3$ would—

(A) increase the rate of reaction
(B) decrease the rate of reaction
(C) not influence the rate of reaction
(D) stop the reaction

91. Find out the number of lines in the $^{31}P$ NMR signal for—




(A) 3 (B) 6
(C) 18 (D) 90

92. The rate of exchange of $OH_2$ present in the coordination sphere by $^{18}OH_2$ of, (i) $[Cu(OH_2)_6]^{2+}$; (ii) $[Mn(OH_2)_6]^{2+}$; (iii) $[Fe(OH_2)_6]^{2+}$; (iv) $[Ni(OH_2)_6]^{2+}$, follows an order—

(A) (i) > (ii) > (iii) > (iv)
(B) (i) > (iv) > (iii) > (ii)
(C) (ii) > (iii) > (iv) > (i)
(D) (iii) > (i) > (iv) > (ii)

93. Based on the behaviour of the metalloenzymes, consider the following statements :
1. In the enzymes, the zinc activates $O_2$ to form peroxide species.
2. In the enzymes, the zinc activates $H_2O$ and provides a zinc bound hydroxide.
3. In the oxidases, the iron activates $O_2$ to break the bonding between the two oxygens.
4. Zinc ion acts as a nucleophile and attacks at the peptide carbonyl.

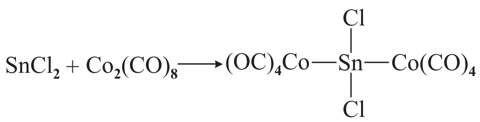
The set of correct statements is—
(A) 1 and 2 (B) 2 and 3
(C) 3 and 4 (D) 1 and 4

94. $Fe^{2+}$–porphyrins fail to exhibit reversible oxygen transport and cannot differentiate CO from $O_2$. However, the haemoglobin is free both these pitfalls. Among the following :
1. $Fe^{2+}$–porphyrins undergo μ–oxodimer formation and the same is prevented in case of the haemoglobin.
2. Fe–CO bond strength is much low in case of haemoglobin when compared to the $Fe^{2+}$–porphyrins.
3. While Fe–CO is linear, Fe-$O_2$ is bent and is recognized by haemoglobin.
4. The interlinked four monomeric units in the haemoglobin are responsible to overcome the pitfalls.

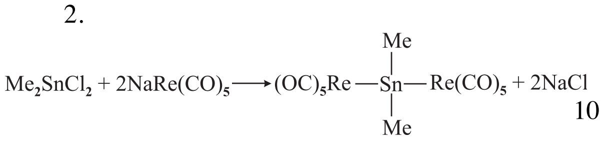
The correct set of statements is—
(A) 1 and 2 (B) 1 and 3
(C) 3 and 4 (D) 2 and 4

95. Reactions A and B are, termed as respectively—

1.



2.



(A) Insertion, Metathesis
(B) Metathesis, Insertion
(C) Oxidative addition, Metathesis
(D) Oxidative addition, Insertion

96. A metal crystallizes in f.c.c. structure with a unit cell side of 500 pm. If the density of the crystal is 1·33 g/cc, the molar mass of the metal is close to—
(A) 23 (B) 24
(C) 25 (D) 26

97. The activation energy for the bimolecular reaction A + BC → AB + C is $E_0$ in the gas phase. If the reaction is carried out in a confined volume of $\lambda^3$, the activation energy is expected to—
(A) remain unchanged
(B) increase with decreasing λ
(C) decrease with decreasing λ
(D) oscillate with decreasing λ

98. In a many-electron atom, the total orbital angular momentum (L) and spin (S) are good quantum numbers instead of the individual electron orbital ($l_1, l_2$) and spin ($s_1, s_2$) angular momenta in the presence of—
(A) inter-electron repulsion
(B) spin-orbit interaction
(C) hyperfine couping
(D) external magnetic field

99. The packing fraction of a simple cubic lattice is close to—
(A) 0·94 (B) 0·76
(C) 0·52 (D) 0·45

100. The number of IR active vibrational modes of pyridine is—

| $C_{2v}$ | $E_2$ | $C_2$ | $\sigma_v$ | $\sigma'_v$ | |
|---|---|---|---|---|---|
| $A_1$ | 1 | 1 | 1 | 1 | $z$ |
| $A_2$ | 1 | 1 | –1 | –1 | $R_z$ |
| $B_1$ | 1 | –1 | 1 | –1 | $x, R_y$ |
| $B_2$ | 1 | –1 | –1 | 1 | $y, R_x$ |

(A) 12 (B) 20
(C) 24 (D) 33

101. One of the excited states of Ti has the electronic configuration $[Ar]4s^2\ 3d^1\ 4p^1$. The number of microstates with zero total spin (S) for this configuration is—
(A) 9 (B) 15
(C) 27 (D) 60

102. For the reaction $A_2 \rightleftharpoons 2A$ in a closed container, the relation between the degree of dissociation ($\alpha$) and the equilibrium constant $K_p$ at a fixed temperature is given by—
(A) $\alpha = [K_p / (K_p + 4p)]$
(B) $\alpha = [K_p / (K_p + 4p)]^{1/2}$
(C) $\alpha = [K_p + 4p) / K_p]$
(D) $\alpha = [(K_p + 4p) / K_p]^{1/2}$

103. The fugacity of a gas depends on pressure and the compressibility factor Z (= $p\bar{V}$ /RT) through the relation [$\bar{V}$ is the molar volume]—

$$f = p \cdot exp \left[\int_0^p \frac{Z-1}{p} dp\right]$$

For most gases at temperature T and up to moderate pressure, this equation shows that—
(A) $f < p$, if $T \to 0$ (B) $f < p$, if $T \to \infty$
(C) $f > p$, if $T \to 0$ (D) $f = p$, if $T \to 0$

104. The internal pressure $(\partial U/\partial V)_T$ of a real gas is related to be compressibility factor $Z = p\bar{V}/RT$ by [$\bar{V}$ is the molar volume]—
(A) $(\partial U/\partial V)_T = RT\,(\partial Z/\partial V)_T$
(B) $(\partial U/\partial V)_T = RT / (\bar{V}\,Z)$
(C) $(\partial U/\partial V)_T = (RT^2 / \bar{V})\,(\partial Z/\partial T)_V$
(D) $(\partial U/\partial V)_T = (\bar{V} / RT^2)\,(\partial Z/\partial T)_V$

105. Suppose, the ground stationary state of a harmonic oscillator with force constant $k$ is given by $\psi_o = \exp[-Ax^2]$
Then, A should depend on $k$ as—
(A) $A \propto k^{-1/2}$ (B) $A \propto k$
(C) $A \propto k^{1/2}$ (D) $A \propto k^{1/3}$

106. Combining two real wave functions $\phi_1$ and $\phi_2$, the following functions are constructed : $A = \phi_1 + \phi_2$, $B = \phi_1 + i\phi_2$, $C = \phi_1 - i\phi_2$, $D = i(\phi_1 + \phi_2)$. The correct statement will then be—
(A) A and B represent the same state
(B) A and C represent the same state
(C) A and D represent the same state
(D) B and D represent the same state

107. Crystal **A** diffracts from (111) and (200) planes but not from (110) plane, while the Crystal **B** diffracts from (110) and (200) planes but not from the (111) plane. From the above, we may conclude that—
(A) **A** has fcc lattice while **B** has bcc lattice
(B) **A** has bcc lattice while **B** has fcc lattice
(C) **A** and **B** both have fcc lattice
(D) **A** and **B** both have bcc lattice

108. The decomposition of $NH_3$ on Mo surface follows Langmuir-Hinshelwood mechanism. The decomposition was carried out at low pressures. The initial pressure of $NH_3$ was $10^{-2}$ torr. The pressure of $NH_3$ was reduced to $10^{-4}$ torr in 10 minutes. The rate constant of decomposition of $NH_3$ is—
(A) $9{\cdot}9 \times 10^{-4}$ torr min$^{-1}$
(B) $0{\cdot}4606$ min$^{-1}$
(C) $9{\cdot}9 \times 10^{-3}$ torr min$^{-1}$
(D) $0{\cdot}693$ min$^{-1}$

109. A polymer sample has the following composition.

| Number of molecules | Molecular weight |
|---|---|
| 10 | 1000 |
| 50 | 2000 |
| 40 | 4000 |

The polydispersity Index (P.D.I.) of the polymer is—
(A) $\frac{85000}{27}$ (B) $\frac{85}{81}$
(C) $\frac{850}{729}$ (D) $\frac{729}{850}$

110. The equilibrium constant for an electrochemical reaction $2Fe^{3+} + Sn^{2+} \rightleftharpoons 2Fe^{2+} + Sn^{4+}$ is [$E^0$ ($Fe^{3+}$ / $Fe^{2+}$) = 0·75V, $E^0$ ($Sn^{4+}$ / $Sn^{2+}$) = 0·15V, (2·303RT / F) = 0·06V]—
(A) $10^{10}$ (B) $10^{20}$
(C) $10^{30}$ (D) $10^{40}$

111. A bacterial colony grows most commonly by cell division. The change in the population due to cell division in an actively growing colony is $dN = \lambda_g N\,dt$. The population of bacterial colony at time $t$ is [$N_0 = N(t = 0)$]—
(A) $N_0\,\lambda_g t$ (B) $N_0\,exp[-\lambda_g t]$
(C) $N_0\,exp[\lambda_g t]$ (D) $N_0\,(\lambda_g t)^2$

112. The Arrhenius parameters for the thermal decomposition of NOCl, $2NOCl(g) \rightarrow 2NO(g) + Cl_2(g)$, are $A = 10^{13}$ $M^{-1}$ $s^{-1}$, $E_a$ = = 105 kJ mol$^{-1}$ and RT = 2·5 kJ mol$^{-1}$. The enthalpy (in kJ mol$^{-1}$) of the activated complex will be—
(A) 110 (B) 105
(C) 102·5 (D) 100

113. The rotational partition function of $H_2$ is—

(A) $\sum_{J=0,1,2,\ldots} (2J+1)e^{-\beta hcBJ(J+1)}$

(B) $\sum_{J=1,3,5,\ldots} (2J+1)e^{-\beta hcBJ(J+1)}$

(C) $\sum_{J=0,2,4,\ldots} (2J+1)e^{-\beta hcBJ(J+1)}$

(D) $\frac{1}{4}\left[\sum_{J=0,2,4,\ldots} (2J+1)e^{-\beta hcBJ(J+1)} + 3\sum_{J=1,3,5,\ldots} (2J+1)e^{-\beta hcBJ(J+1)}\right]$

114. The potential in Debye-Hückel theory is proportional to—

(A) $1/kr$ (B) $exp[-kr]$
(C) $\exp[-kr]/r$ (D) $kr$

115. The vibrational frequency and anharmonicity constant of an alkali halide are 300 $cm^{-1}$ and 0·0025, respectively. The positions (in $cm^{-1}$) of its fundamental mode and first overtone are respectively—

(A) 300, 600 (B) 298·5, 595·5
(C) 301·5, 604·5 (D) 290, 580

116. The adsorption of a gas is described by the Langmuir isotherm with the equilibrium constant K = 0·9 $kPa^{-1}$ at 25°C. The pressure (in kPa) at which the fractional surface coverage is 0·95, is—

(A) 1/11·1 (B) 21·1
(C) 11·1 (D) 42·2

117. The energy of a harmonic oscillator in its ground state is $\frac{1}{2}\hbar\omega$. According to the virial theorem, the average kinetic (T) and potential (V) energies of the above are—

(A) $T = \frac{1}{4}\hbar\omega;\ V = \frac{1}{4}\hbar\omega$

(B) $T = \frac{1}{8}\hbar\omega;\ V = \frac{3}{8}\hbar\omega$

(C) $T = \hbar\omega;\ V = -\frac{1}{2}\hbar\omega$

(D) $T = \frac{3}{8}\hbar\omega;\ V = \frac{1}{8}\hbar\omega$

118. The energy of a hydrogen atom in a state is $\frac{-hcR_H}{25}$ ($R_H$ = Rydberg constant). The degeneracy of the state will be—

(A) 5 (B) 10
(C) 25 (D) 50

119. The trial wave function of a system is expanded as $\psi_t = c_1\phi_1 + c_2\phi_2$. The matrix elements of the Hamiltonian are $\langle\phi_1|H|\phi_1\rangle = 0$; $\langle\phi_1|H|\phi_2\rangle = 2\cdot0 = \langle\phi_2|H|\phi_1\rangle$ and $\langle\phi_2|H|\phi_2\rangle = 3\cdot0$. The approximate ground-state energy of the system from the linear variational principle is—

(A) –1·0 (B) –2·0
(C) +4·0 (D) +5·0

120. One molecular orbital of a polar molecule AB has the form $C_A\psi_A + C_B\psi_B$ , where $\psi_A$ and $\psi_B$ are normalized atomic orbitals of centred on A and B, respectively. The electron in this orbital is found on atom B with a probability of 90%. Neglecting the overlap between $\psi_A$ and $\psi_B$, a possible set of $C_A$ and $C_B$ is—

(A) $C_A = 0\cdot95, C_B = 0\cdot32$
(B) $C_A = 0\cdot10, C_B = 0\cdot90$
(C) $C_A = -0\cdot95, C_B = 0\cdot32$
(D) $C_A = 0\cdot32, C_B = 0\cdot95$

121. 4-Hydroxybenzoic acid exhibited signals at δ 171, 162, 133, 122 and 116 ppm in its broadband decoupled $^{13}C$ NMR spectrum. The correct assignment of the signals is—

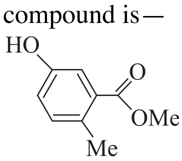
(A) δ 171 (C–4), 162 (COOH), 133 (C–3 & 5), 122 (C-1) and 116 (C-2 & 6)
(B) δ 171 (COOH), 162 (C-4), 133 (C–2 & 6), 122 (C-1) and 116 (C-3 & 5)
(C) δ 171 (C–4), 162 (COOH), 133 (C–2 & 6), 122 (C-1) and 116 (C-3 & 5)
(D) δ 171 (COOH), 162 (C–4), 133 (C–3 & 5), 122 (C-1) and 116 (C-2 & 6)

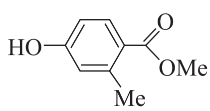
122. An organic compound ($C_9H_{10}O_3$) exhibited the following spectral data :

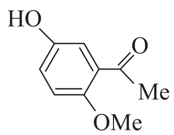
IR : 3400, 1680 $cm^{-1}$;

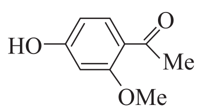
$^1H$ NMR : δ 7·8 (1 H, d, J = 8 Hz), 7·0 (1 H, d, J = 8 Hz), 6·5 (1 H, s), 5·8 (1 H, s, $D_2O$ exchangeable), 3·9 (3 H, s), 2·3 (3 H, s).

The compound is—

(A) 


(B) 


(C) 

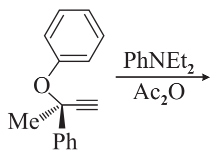

(D) 

123. The $[\alpha]_D$ of a 90% optically pure 2-arylpropanoic acid solution is +135°. On treatment with a base at RT for one hour, $[\alpha]_D$ changed to +120°. The optical purity is reduced to 40% after 3 hours. If so, the optical purity of the solution after 1 hour, and its $[\alpha]_D$ after 3 hours, respectively, would be—

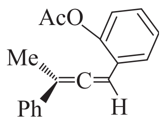
(A) 80%; and 60° (B) 70%; and 40°

(C) 80%; and 90° (D) 70%; and 60°

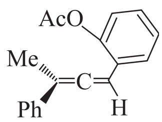
124. In the following pericyclic reaction, the structure of the allene formed and its configuration are—



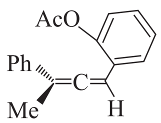

(optically pure)

(A) 

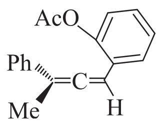
R

(B) 

S

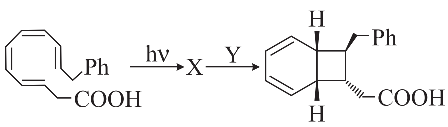
(C) 

R

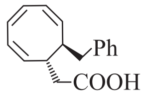
(D) 

S

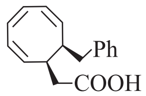
125. In the following sequence of pericyclic reactions X and Y are—



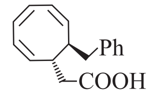

X Y

(A) 

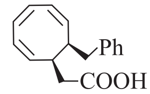
hν / DIS

(B) 

hν / CON

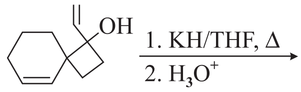
(C) 

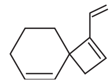
Δ / DIS

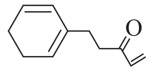
(D) 

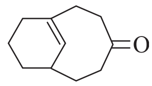
Δ / CON

126. The major product formed in the following reaction is—



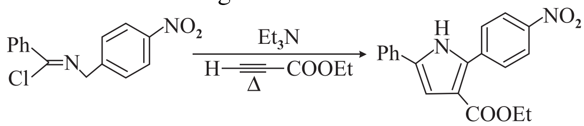

(A) 

(B) 


(C) 


(D) 


127. The following conversion involves—



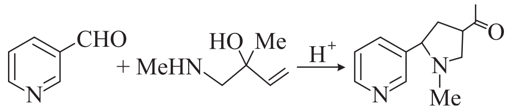

(A) a 1, 3-dipolar species as reactive intermediate and a cycloaddition.

(B) a carbenium ion as reactive intermediate, and a cycloaddition

(C) a 1, 3-dipolar species as reactive intermediate, and an aza Wittig reaction

(D) a carbanion as reactive intermediate, and an aza Cope rearrangement

128. The following transformation involves—




(A) an iminium ion, [3, 3]-sigmatropic shift and Mannich reaction

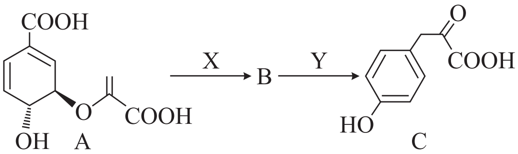
(B) a nitrenium ion, [3, 3]-sigmatropic shift and Michael reaction

(C) an iminium ion, [1, 3]-sigmatropic shift and Mannich reaction

(D) a nitrenium ion, [1, 3]-sigmatropic shift and Michael reaction

129. With respect to the following biogenetic conversion of chorismic acid (A) to 4-

hydroxyphenylpyruvic acid (C), the correct statement is—




(A) X is Claisen rearrangement; Y is oxidative decarboxylation
(B) X is Fries rearrangement; Y is oxidative decarboxylation
(C) X is Fries rearrangement; Y is dehydration
(D) X is Claisen rearrangement; Y is dehydration

130. Match the following—

**List-I**

(a) β-amyrin (b) squalene
(c) morphine (d) ephedrine

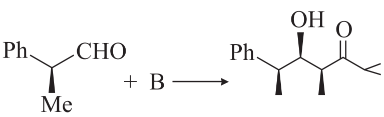
**List-II**

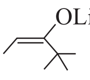
1. alkaloid, secondary alcohol
2. alkaloid, phenol
3. triterpene, secondary alcohol
4. acyclic triterpene, polyene

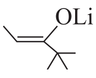
**Codes :**

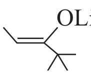
| | (a) | (b) | (c) | (d) |
|---|---|---|---|---|
| (A) | 3 | 4 | 2 | 1 |
| (B) | 2 | 1 | 3 | 4 |
| (C) | 3 | 2 | 4 | 1 |
| (D) | 1 | 4 | 2 | 3 |

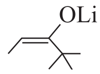
131. In the following reaction, the structure of B, and the mode of addition are—



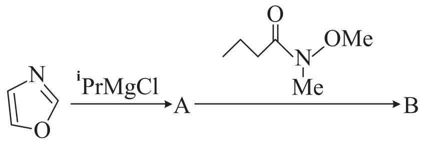

(A)  Re-Si facial

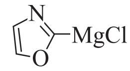
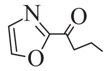
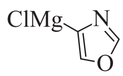
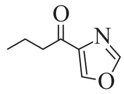
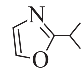
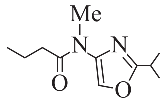
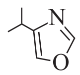
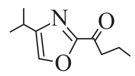
(B)  Re-Re facial

(C)  Re-Si facial

(D)  Si-Si facial

132. In the following reaction A and B are—




| | (A) | (B) |
|---|---|---|
| (A) |  |  |
| (B) |  |  |
| (C) |  |  |
| (D) |  |  |

133. Match the following biochemical transformations with the coenzymes involved—

**List-I**

(a) α-ketoglutarate to glutamic acid
(b) uridine to thymidine
(c) pyruvic acid to acetyl coenzyme A

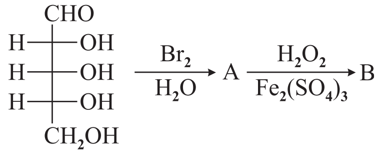
**List-II**

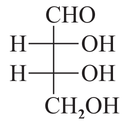
1. tetrahydrofolate
2. NADH
3. thiamine pyrophosphate
4. pyridoxamine

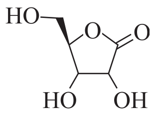
**Codes :**

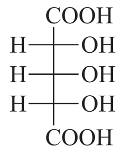
| | (a) | (b) | (c) |
|---|---|---|---|
| (A) | 4 | 1 | 3 |
| (B) | 1 | 2 | 4 |
| (C) | 2 | 1 | 3 |
| (D) | 4 | 2 | 3 |

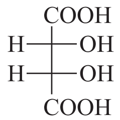
134. The structure of the major product B formed in the following reaction sequence is—



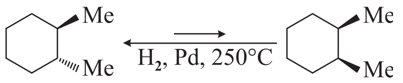
(A) 

(B) 

(C) 

(D) 

135. Given the energy of each gauche butane interaction is 0·9 k-cal/mol, ΔG value of the following reaction is—

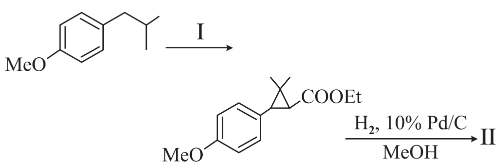



(e, e conformer)

(A) 0·9 k-cal/mol (B) 1·8 k-cal/mol

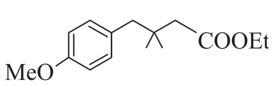
(C) 2·7 k-cal/mol (D) 3·6 k-cal/mol

136. In the following reaction, the reagent I and the major product II are—

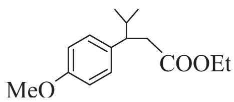



I II

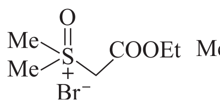
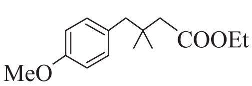
(A)

$N_2CHCOOEt$, $Cu(acac)_2$ 

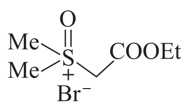
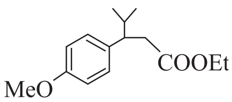
(B)

$N_2CHCOOEt$, $Cu(acac)_2$ 

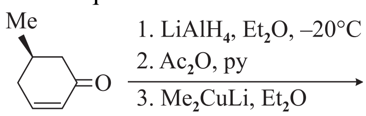
(C)

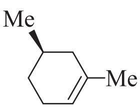
NaH,  

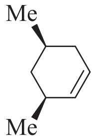
(D)

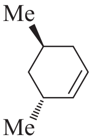
NaH,  

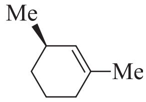
137. The major product formed in the following reaction sequence is—




(A) 

(B) 

(C) 

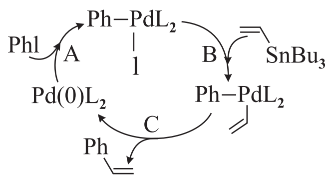
(D) 

138. 12·0 g of acetophenone on reaction with 76·2 g of iodine in the presence of aq. NaOH gave solid A in 75% yield. Approximate amount of A obtained in the reaction and its structure are—

(A) 80 g, $CI_4$ (B) 40 g, $CI_4$

(C) 60 g, $CHI_3$ (D) 30 g, $CHI_3$

139. Consider the following reaction mechanism.




The steps A, B and C, respectively, are—

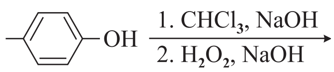
(A) oxidative addition; transmetallation; reductive elimination

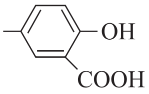
(B) oxidative addition; carbopalladation; β-hydride elimination

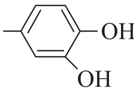
(C) carbopalladation; transmetallation; reductive elimination

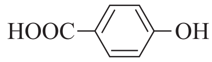
(D) metal halogen exchange; transmetallation; metal extrusion

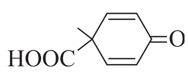
140. The major product formed in the following reaction sequence is—



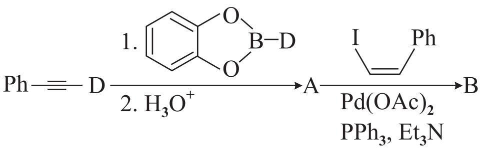

(A) 

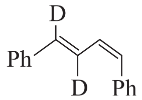
(B) 

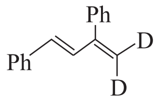
(C) 

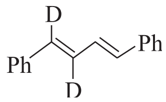
(D) 

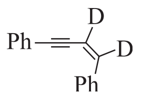
141. The major product B formed in the following reaction sequence is—



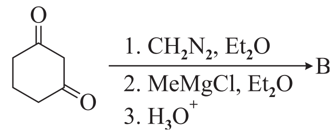

(A) 

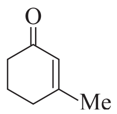
(B) 

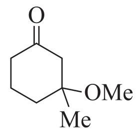
(C) 

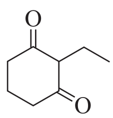
(D) 

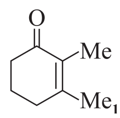
142. The major product B formed in the following reaction sequence is—



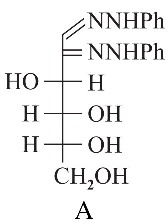

(A) 

(B) 

(C) 

(D) 

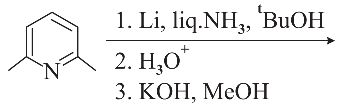
143. The osazone A could be obtained from—

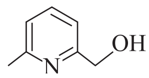


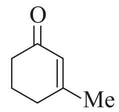
A

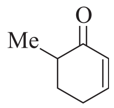
(A) glucose and mannose
(B) mannose and galactose
(C) gulose and fructose
(D) galactose and fructose

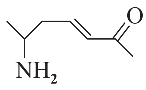
144. The major product formed in the following reaction is—



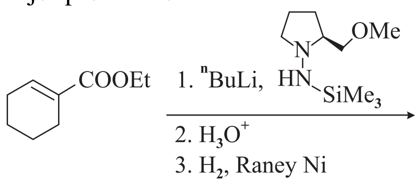

(A) 

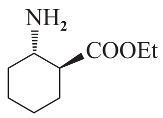
(B) 

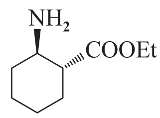
(C) 

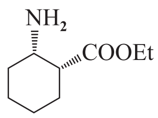
(D) 

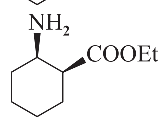
145. In the following enantioselective reaction, the major product formed is—




(A) 

(B) 

(C) 

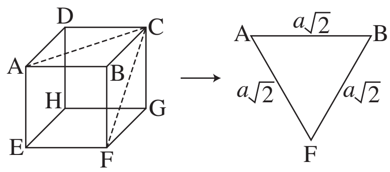
(D) 

# Answers with Explanations

## Part–A

1. (A) $2^{3^4} = 2^{81}$, $2^{4^3} = 2^{64}$, $3^{2^4} = 3^{16}$, $3^{4^2} = 3^{16}$, $4^{2^3} = 4^8 = 2^{16}$, $4^{3^2} = 4^9 = 2^{18}$.
Therefore, $2^{3^4}$ is the largest.

2. (B)



Equilateral triangle is formed with diagonal.

$$\therefore \quad \text{Area ACF} = \frac{\sqrt{3}}{4}(\text{Side})^2$$

$$= \frac{\sqrt{3}}{4}(a\sqrt{2})^2$$

$$= \frac{\sqrt{3}}{2}a^2$$

3. (D) Total number of distinct arrangements

$$= \frac{|\underline{7}}{|\underline{2}} = 2520$$

Number of arrangements when U and I come together

$$= \frac{|\underline{6}}{|\underline{2}} \times 2 = 720$$

Thus, the no. of arrangements when U and I cannot come together

$$= 2520 - 720$$
$$= 1800$$

4. (C) Let numbers are $a, b, c, d, e, f, g$

Given, $a + b + c + d + e + f + g = 21$

$\because$ Arithematic Progression $\geq$ Geometrical Progression

$$\text{A.P.} = \text{G.P.}$$

(When all the numbers are equal)

Now, $$\frac{a + b + c + d + e + f + g}{7} = 3$$

If $a = b = c = d = e = f = g = 3$

$$\Rightarrow \frac{a^2 + b^2 + c^2 + d^2 + e^2 + f^2 + g^2}{7} = 9$$

5. (C) $50B = 1^{13} + 3^{13} + 5^{13} + \ldots 99^{13}$ ...(1)

$50C = 2^{13} + 4^{13} + 6^{13} + \ldots 100^{13}$ ...(2)

Each term of (2) is greater to term of (1)

Then, $50C > 50B \Rightarrow C > B$

Now, $100A = 1^{13} + 2^{13} + 3^{13} + 4^{13} + \ldots 100^{13}$

$100A = 50B + 50C$

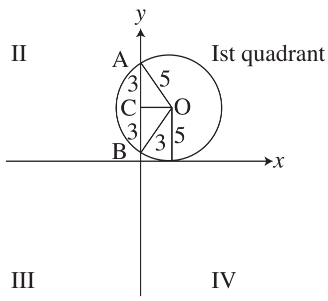
$2A = B + C$

Therefore, $2A > 2B$ and $2A < 2C$

Then, $A > B$ and $A < C$

Therefore, $B < A < C$

6. (D) In right angled triangle BOC

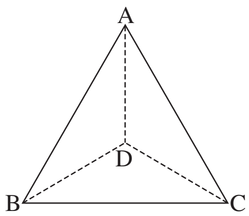



$$OB^2 = OC^2 + BC^2$$
$$5^2 = OC^2 + 3^2$$
$$OC = \pm 4$$
$$\Rightarrow \quad OC = 4$$

–ve not taken in first quadrant

So, centre is (4, 5).

7. (C) The minimum single cut is required because wire ABCDB = 5 m



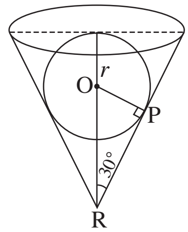

and Wire AD = 1m

8. (D) 2, – 4, 8, –16, 32, – 64, 128, – 256, 512

$$-256 + 512 = x$$
$$x = 256$$
$$\log_2 x = \log 256$$
$$= \log_2 2^8$$
$$\log_2 x = 8 \quad \boxed{\log_2 2 = 1}$$

9. (A) Let $r$ is radius, then

$$OR = 10{\cdot}5 - r$$




In Δ OPR

$$\sin 30° = \frac{OP}{OR} \Rightarrow \frac{r}{10{\cdot}5 - r} = \frac{1}{2}$$
$$\Rightarrow \quad 0{\cdot}5 = \frac{r}{10{\cdot}5 - r}$$
$$\Rightarrow \quad 2 = \frac{10{\cdot}5}{r} - 1$$
$$\Rightarrow \quad 3 = \frac{10{\cdot}5}{r}$$
$$\Rightarrow \quad r = 3{\cdot}5$$

10. (A) Amar Doctor (tallest)

(Shortest) Akbar Engineer $e^2 = dp$

Anthony Professor

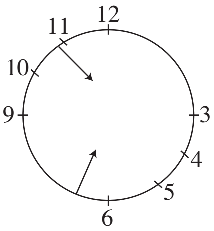
Therefore, Amar is a doctor and he is the tallest.

11. (B) If 100 cats catch 100 mice in 100 minutes, then 7 cates will catch 7 mice also in 100 minutes.

12. (A) Each half diagram shows increase in one unit, thus $1 + 2 + 3 + \ldots + n = \frac{n(n+1)}{2}$.

13. (B) Since, socks is in pair, so atleast N + 1 number of socks would be taken out.

14. (D)



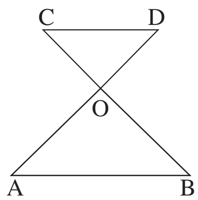

4 – 54′ – 33″

15. (C) When curve touches the $x$-axis, $y = 0$ for real $x$.

$$\therefore \quad 0 = x^2 - 10x + 25$$
$$\Rightarrow \quad (x-5)^2 = 0$$
$$\Rightarrow \quad x = 5$$

No other option have real value of $x$.

16. (C) AB // CD




Let OD = $r$

Thus, ∠ COD = ∠ AOB

and ∠ DCO = ∠ ABO

Therefore, Δ OCD and Δ OBA are symmetric triangle

$$\text{Thus, } \frac{\text{Area of triangle } \Delta \text{ OAB}}{\text{Area of triangle } \Delta \text{ OCD}} = \left(\frac{\text{AO}}{\text{OD}}\right)^2$$
$$= \left(\frac{2\text{OD}}{\text{OD}}\right)^2$$
$$= 4$$

17. (*)

18. (C) Let $r$ is the radius of small sphere and R is the radius of big sphere.

$$\text{Thus, } \frac{4}{3}\pi R^3 = N\frac{4}{3}\pi r^3$$

$$\text{Volume of sphere} = \frac{4}{3}\pi\,(\text{radius})^3$$

$$\Rightarrow \quad R^3 = Nr^3$$
$$\Rightarrow \quad \left(\frac{r}{R}\right)^3 = \frac{1}{N}$$

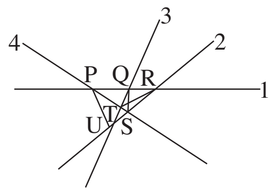
$$\text{Also,} \quad 4\pi R^2 \cdot X = N(4\pi r^2)$$
$$\Rightarrow \quad R^2 X = Nr^2$$
$$\Rightarrow \quad X = \left(\frac{r}{R}\right)^2 N$$
$$= \left(\frac{1}{N}\right)^{2/3} \cdot N$$
$$\Rightarrow \quad X = N^{1-2/3} = N^{1/3}$$

19. (A) 24 30 33 39 51 57

2 + 4 = +6 | 3 + 0 = +3 | 3 + 3 = +6 | 3 + 9 = +12 | 5 + 1 = +6

Thus, the next number is 57.

20. (A) No parallel and No concurrent lines.




New lines are PU, QS and RT.

## Part–B

21. (A) Like atomic and molecular orbital, there are also nuclear orbital with same rules. We know that

Unitary operator have two parity,

$$P = \pm 1$$

When even serial number (azimuthal quantum No.) is found for orbital, it is positive (P) and *vice-versa*. We know that spin for orbitals are

| Orbitals | Serial No. (Azimuthal Quantum No.) | Parity | Spin |
|---|---|---|---|
| $s$ | 0 | + | $\frac{1}{2}$ |
| $p$ | 1 | – | $\frac{3}{2}$ |
| $d$ | 2 | + | $\frac{5}{2}$ |
| $f$ | 3 | – | $\frac{7}{2}$ |
| $g$ | 4 | + | $\frac{9}{2}$ |
| $h$ | 5 | – | $\frac{11}{2}$ |

22. (D) Electroplating is a process that uses electrical current to reduce dissolved metal cations so that they form a coherent metal coating on an electrode.

Also, $PbCl_2$ and $PbSO_4$ are ionic and insoluble in cold water $Pb(Et)_4$ is toxic.

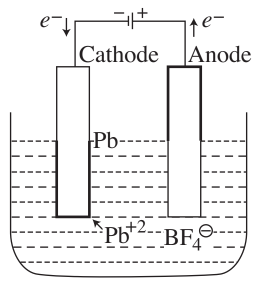



**Fig : Electroplating of a Metal with Lead in a $Pd(BF_4)_2$ bath**

It is generally agreed that electro deposited metals are crystalline and external appearance depends mainly on the rate at which the crystal grow and on the rate of the formation of fresh nuclei.

23. (B) Beer's law is,

$$\log\left(\frac{I_0}{I}\right) = ecl = A$$

Since, absorbance is directly proportional to concentration, very high concentration of analyte deviates the Beer's law. Further Association or dissociation of analyte increases or decreases the concentration of analyte, so it also cause deviation.

24. (D) In Lanthanoids in (+3) oxidation state shows decrease in size when we go down from La to Lu.

In hot concentrated aqueous NaOH, OH have small size and strongly binds with $Lu^{+3}$ and forms $[Lu(OH)_6]^{-3}$. That is the reason $Lu(OH)_3$ shows the highest solubility in hot concentrated aqueous NaOH.

25. (D) The structure of $CO_2$ is

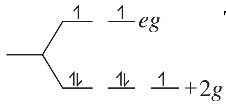
$$\overleftarrow{O}=C=\overrightarrow{O} \text{ Symmetric}$$

Since, symmetric stretching gives no change in dipole moment so it is IR-inactive mode.

Since, $CO_2$ is centrosymmetric molecule, therefore all the modes that is inactive in IR, are active in Raman.

Therefore, there are no fundamental vibrational modes common in both IR and Raman spectra.

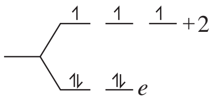
26. (C) $[CO(H_2O)_6]^{2+}$, $d^7$ system




Transition from + g to eg

Octahedral environment

$[COCl_4]^{2-}$, $d^7$ system

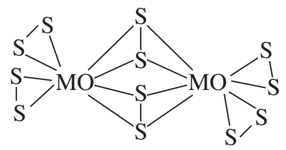



Transition from e to + 2

So, both complexes show d-d transition.

27. (A) $[MO_2(S_2)_6]^{-2}$

$S_2^{2-}$ is $2e^-$ donor




Briolging $S_2^{-2}$ ligand are 2 and coordination number are 8.

28. (D) For D, I = 1

Multiplicity = 2nI + 1

n = No. of D atom

I = spin of D atom

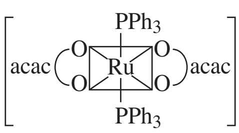
Therefore, M = 2 × 1 × 1 + 1

= 3

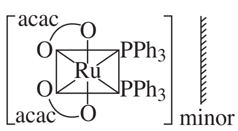
and Intensity ratio will be non-pascal.

So, [1]H NMR spectrum of HD gives a triplet with intensity ratio 1 : 1 : 1.

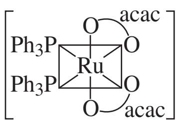
29. (B) $[Ru(PPh_3)_2(acac)_2]$ (acac = acetylacetonate)




Trans



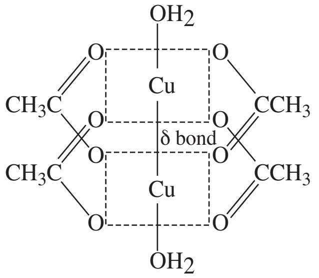

Cis-d




Cis-l

3 possible isomer are shown above.

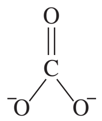
30. (A) This complex exists or dimer and structure is



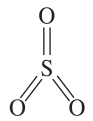

There are 10 Cu-O bond presents in this complex.

31. (B) Among the given elements K has least electronegativity and F has most electronegativity. Therefore, the electronegativity difference is greater in K and F.

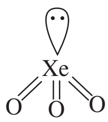
32. (D)



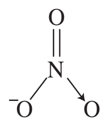
$sp^2$-hybridization
Trigonal planar



$sp^2$-hybridization
Trigonal planar



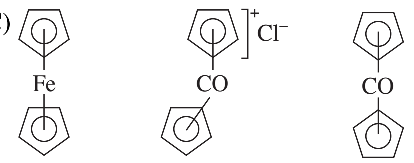
$sp^3$-hybridization
Trigonal pyramidal



$sp^2$-hybridization
Trigonal planar

Therefore, $CO_3^{2-}$, $SO_3$ and $NO_3^-$ have planar structure.

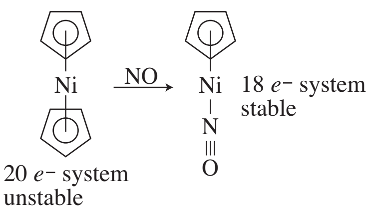
33. (C)




18°-$e^-$ system stable | $18e^-$ system stable | $19e^-$ system unstable

But $C_p$ is not replaceable with NO in this case.

Therefore,




34. (A) $(OC)_5M=C(OCH_3)(Ph)$

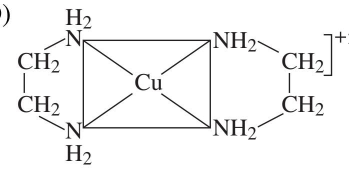
This is an example of metal carbene complex. Since, the molecule obeys $18e^-$ rule and carbene is $2e^-$ donor.

Therefore, we need a metal with $6e^-$.

This is only Cr and $Re^+$ pair.

35. (A) Fe is found in haemoglobin myoglobin and cytrochromes. Mo is for nitrogen fixation. Cu for heamocyanin and Zn for metalloenzymes.

36. (D)




I of Cu = $\frac{3}{2}$, I of N = 1

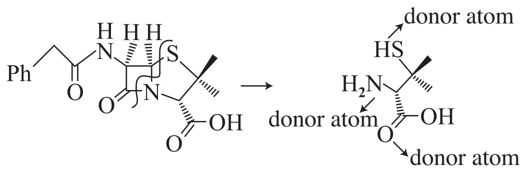
Therefore,

$$(2n_1I_1 + 1)(2n_2I_2 + 1) = \left(2 \times 1 \times \frac{3}{2} + 1\right)(2 \times 4 \times 1 + 1) = 36$$

$n_1$ = no. of Cu atom, $I_1$ = I of Cu

$n_2$ = no. of N atom, $I_2$ = I of N.

37. (A) Degradation of penicillin G




Penicillamine can utilize N, O, S atoms as donors to bind with Pb(II), Hg(II) and Cu(II).

38. (D) $B_2H_6 \rightarrow D_{2h}$ point group and $S_2$ axis

$CH_4 \rightarrow T_d$ point group and $S_4$ axis

$PH_5 \rightarrow D_3h$ point group and $S_3$ axis

$SF_6 \rightarrow O_h$ point group and $S_6$ axis

(symmetry element)

39. (C) For electronic transition selection rule is, $\Delta S = O$, $\Delta l = \pm 1$ and $\Delta J = 0, \pm 1$

For $d^2$, $^3F \rightarrow {}^3D$ is allowed transition.

Because $\Delta S = 0$, $\Delta l = -1$.

40. (C) When a hydrogen atom is placed in an electric field along the $y$-axis, electron density will be oriented along $y$-axis and therefore $2p_y$ orbital mixes most with the ground state $1s$ orbital.

41. (B) For water, $\Delta H_{vap} \approx 41 kJ\ mol^{-1}$
For vaporization, $T_b = 273 + 100 = 373\ K$
Therefore, molar entropy of vaporization,

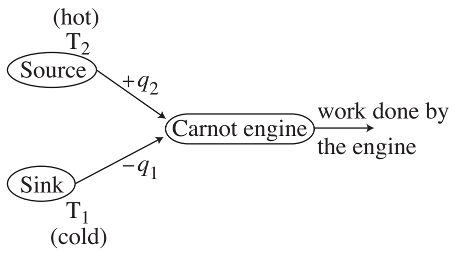
$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T_b} = \frac{41 \times 1000 J\ mol^{-1}}{373 K} \approx 109{\cdot}9\ J\ K^{-1}\ mol^{-1}$$

42. (C) For commuting operators,
$$[A, B] = 0$$
For non-commuting hermitian operators, there is always a real value multiplie with $i$ is found. Therefore, it is always imaginary.

43. (D) $$[x, p_x^2] = i\hbar{\cdot}2p_x = 2i\hbar p_x$$
It is non-commuting operator.

44. (D) The correlation coefficient between two arbitrary variables $x$ and $y$ is given by
$$r = \frac{n[\Sigma xy - \Sigma x\ \Sigma y]}{\sqrt{[n\Sigma x^2 - (\Sigma x)^2]\ [n\Sigma y^2 - (\Sigma y)^2]}} = 0$$
$$\Rightarrow \quad \Sigma xy = \Sigma x \Sigma y$$
or, $<xy> = <x><y>$

45. (A) $$T_2 = 300\ K$$
$$q_2 = 90\ J$$




We know $$\frac{q_2 - q_1}{q_2} = \frac{T_2 - T_1}{T_2}$$
$$\therefore \quad q_2 - q_1 = 90 \times \left(\frac{300 - 200}{300}\right) = 30$$
$$q_1 = 60\ J$$

46. (B) Boltzman Distribution law is
$$\frac{n_i}{n_J} = \frac{g_i}{g_J} e^{-(E_i - E_J)/K_BT}$$
and given that $$\frac{n_1}{n_2} = \left(\frac{3}{2}\right) e^{-(E_1 - E_2)/K_BT}$$
$$\therefore \quad \frac{g_1}{g_2} = \frac{3}{2}$$
$$\Rightarrow \quad \frac{g_2}{g_1} = \frac{2}{3}$$

47. (A) In the Daniell cell, Copper and Zinc electrodes are immersed in a solution of Copper (II) sulphate and Zinc sulphate respectively.
Oxidation → $Zn(s) \rightarrow Zn^{+2}(aq) + 2e^-$ at anode
Reduction → $Cu^{+2}(aq) + 2e^- \rightarrow Cu(s)$ at cathode
Overall cell $r^h$ is
$Zn(s) + Cu^{+2}(aq) \rightarrow Zn^{+2}(aq) + Cu(s)$

48. (B) We know that for first order reaction,
$$A_+ = A_0 e^{-k_1 +}$$
According to question,
$$\frac{A_0}{4} = A_0 e^{-K_1 + 1/4}$$
$$\Rightarrow \quad \frac{1}{4} = \frac{1}{e^{K_1 + 1/4}}$$
$$\Rightarrow \quad 4 = e^{K_1 + 1/4}$$
$$\Rightarrow \quad ln\ 4 = K_{1 + 1/4}$$
$$\Rightarrow \quad t_{1/4} = \frac{ln\ 4}{K_1}$$

49. (C) According to Kohlrausch's law at infinite dilution, when dissociation is complete, each ion makes a definite contribution towards molar conductance of the electrolyte irrespective of the nature of the other ion with which it is associated and the molar conductance at infinite dilution for any electrolyte is given by the sum of the contribution of the two ions.
In given option, only HCl in $H_2O$ completely dissociated and contributes equal ion.

50. (A) A dilute silver nitrate solution is added to a slight excess of sodium iodide solution, a negatively charged solution of silver iodide is formed.

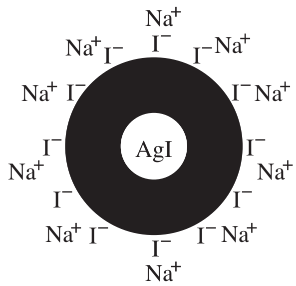



**Fig. : Electrical property of colloid based on concept of electrical double layer**

$AgNO_3 + NaI \rightarrow AgI + NaNO_3$

The negatively charged AgI attracts $Na^+$ and repels $NO_3^-$.

Therefore, $Na^+$ try to form a rigid layer with $I^-$.

51. (D) We know that,

Dissociation energy,

$$D_e = E_{max} - E_0$$

$E_0$ is ground state energy

It is clear from question that

$$E_{max} = 56875 \text{ cm}^{-1}$$

and $$E_0 = 15125$$

$\therefore$ $$D_e = 56875 - 15125 = 41750 \text{ cm}^{-1}$$

52. (*) The angle between two planes having miller indices $(h_1k_1l_1)$ and $(h_2k_2l_2)$ is given as

$$\cos\theta = \frac{h_1h_2 + k_1k_2 + l_1l_2}{\sqrt{h_1^2 + k_1^2 + l_1^2}\sqrt{h_2^2 + k_2^2 + l_2^2}}$$

$$\Rightarrow \cos\theta = \frac{|X| + |X| + OX}{\sqrt{1^2 + 1^2 + 0^2}\sqrt{1^2 + 1^2 + 1^2}}$$

$$= \frac{2}{\sqrt{2}\cdot\sqrt{3}} = \frac{\sqrt{2}}{\sqrt{3}}$$

$$\theta = \cos^{-1}(0\cdot816)$$

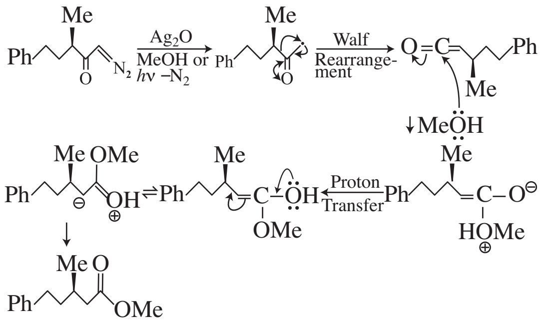
$$\Rightarrow \theta = 35\cdot31$$

All options are incorrect.

53. (B) The molar conductance of an ionic surfactant of the type $Na^+R^-$ in water is plotted against the square root of the normality of the solution. The curve obtained, instead of being the smoothly decreasing curve characteristic of ionic electrolytes of this type, has a sharp break in it at low concentrations. This sharp break in the curve accompanied by reduction in the conductance of the solution, indicating a sharp increase in the mass per unit charge of the material in soluton, is interpreted as evidence for the formation of miceller at that point from the unassociated molecular of surfactant with part of the charge of the micelle neutralized by associated counter ions.

$$\log \text{CMC} = -a \log c_i + b$$

54. (A)

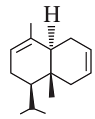
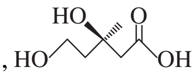



55. (D) We know that,

$$\log \frac{K_{P\text{-}OMe}}{K_{COOH}} = \sigma$$

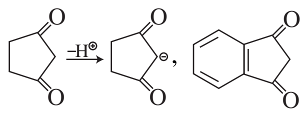
$$\sigma = \log K_{P\text{-}OMe} - \log K_{COOH}$$
$$= -\log K_{COOH} - (-\log K_{P\text{-}OMe})$$
$$= P^{K_{a(COOH)}} - P^{K_{a(P\text{-}OMe)}}$$
$$= 4\cdot19 - 4\cdot46$$
$$\sigma = -0\cdot27$$

Electron releasing group have –ve σ value.

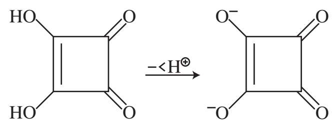
56. (B) Biosynthetic precursor of Cadinene  is mevalonic acid, .



57. (C)



| A | B |
|---|---|
| more acidic with reactive methylene gp | aromatic ring makes proton less acidic due to $e^-$ withdrawing nature |

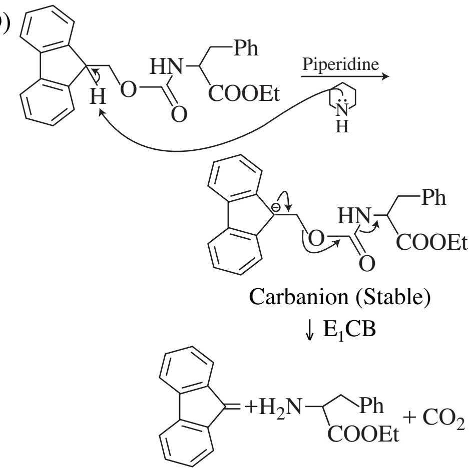



C

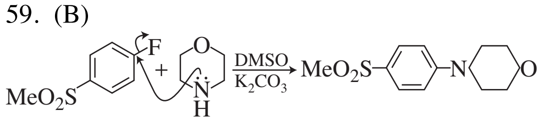
acidic like $H_2SO_4$ aromatic in nature

Therefore, C > A > B

58. (D)

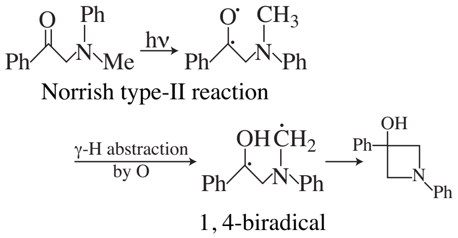


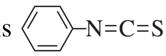

59. (B)



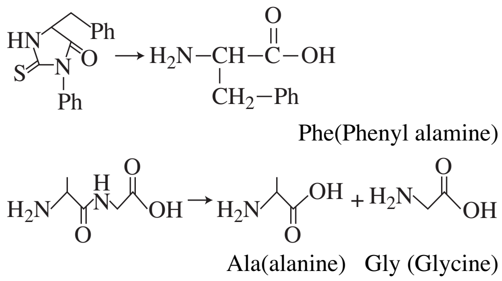

This reaction is aromatic *ipso* substitution and aromatic nucleophilic substitution.

60. (B)




61. (A) Edman's reagent is 


Phenyisothio cyanate




Therefore, the sequence is Phe-Ala-Gly, Since Edman degradation occur from N-T-A From N-terminal to Acid terminal.

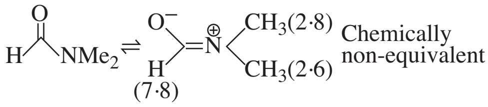
62. (A) $C_3H_7NO$

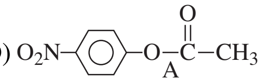
$$DBE = \frac{\text{No. of C-atoms} + 2 - \text{No. of H-atoms} + \text{No. of N-atoms}}{2}$$

$$= \frac{6+2-7+1}{2} = 1$$

δ 7·8(1H, s)
δ 2·8(3H, s)
δ 2·6(3H, s)

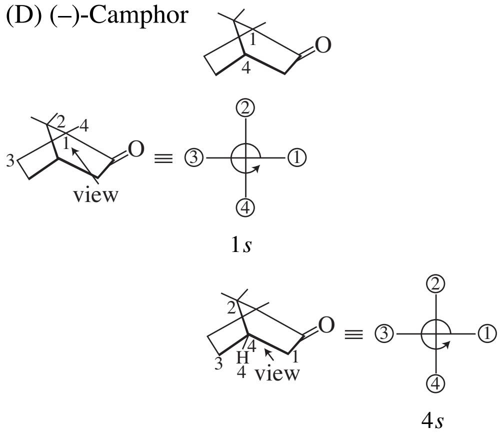
From the above observation the structure of compound is




63. (D) 

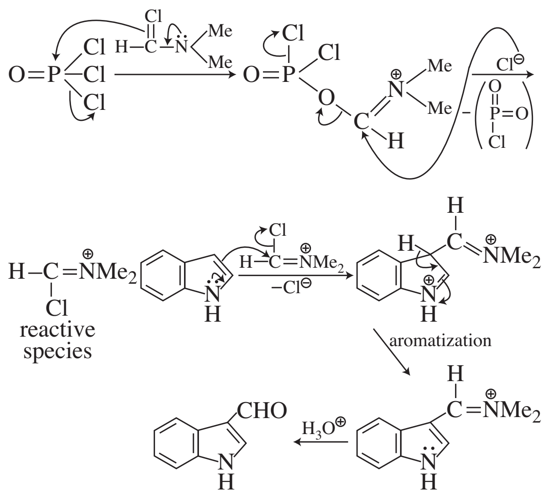

Normally, ester groups show absorption at 1750 – 1770 in phenyl acetate, is shower absorption at 1765 but in compound (A) due to conjugation with ring and O-atom absorption decreases and it appears at 1761 $cm^{-1}$.

64. (D) (–)-Camphor



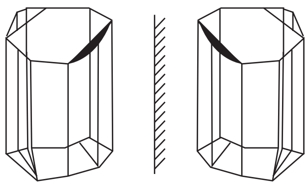

Absolute configuration is 1*s*, 4*s*.

65. (A) This reaction is Vielsmeir-Haac Reaction.



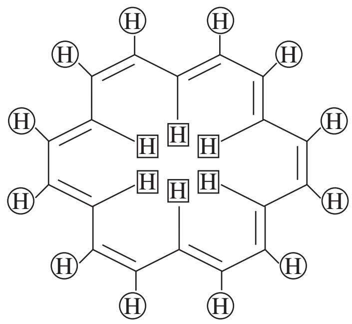
66. (B) The first person to separate a racemic mixture into individual enantiomers is L. Pasteur.

Pasteur separated the left and right crystal shapes from each other to form two piles of crystals; in solution one form rotated light to the left, the other to the right, while an equal mixture of the two forms cancelled each other's effect and does not rotate the polarized light.



Mirror image

67. (D)



[18]-Annulene

* aromatic, planar

* shows aromatic substitution

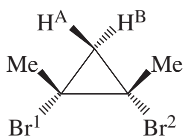
* 12[H] outer, deshielded zone δ = 9·28

* 6[H] inner, shielded zone δ = –3·0

* 37 k-cal/mol resonance energy

* diatropic

68. (B)

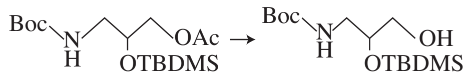



Molecule has a plane of symmetry bisecting $H^A$ and $H^B$ reflecting $Br^1/Br^2$ and $CH_3/CH_3$.

(a) $Br^1$ and $Br^2$ are reflected by plane, so they are enantiotropic to each other.

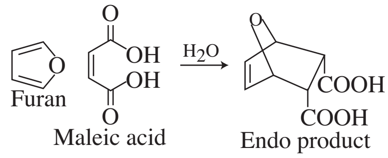
(b) $H^A$ and $H^B$ are bisecting by plane. Hence, they are diastereotopic to each other.

69. (C)




The hydrolysis of ester is faster in alkaline medium therefore the correct one is $K_2CO_3$, MeOH.

70. (D) Diels-Alder reaction of furan and maleic acid in water is an example of 'Green Synthesis'.




## Part–C

71. (D) Recoil energy,

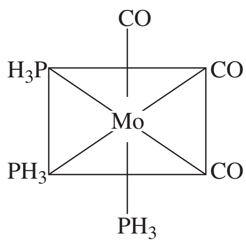
$$E_r = \frac{E^2}{2Mc^2}$$

or, $$E_r = \frac{536E^2}{M} \text{ eV}$$

$$E = \sqrt{\frac{2{\cdot}5 \times 10^6 \times 139 \times 931{\cdot}5}{536}}$$

$$= 24{\cdot}57 \text{ keV}$$

72. (A) CO is π-acid ligand and have tendency to back-bonding with metal.




Electron donating phosphine group increase $e^-$ density on metal and back bonding with M and CO becomes strong. As a result of this C = O bond becomes weak.

Therefore, stretching frequency, $\upsilon_{C=0}$ decreases.

| Phosphine | V(CO) ($cm^{-1}$) |
|---|---|
| $PF_3$ (A) | 2090 (i) |
| $PCl_3$ (B) | 2040 (ii) |
| $P(Cl)Ph_2$ (C) | 1977 (iii) |
| $PMe_3$ (D) | 1945 (iv) |

73. (C) $I_d = K(C^* - C)$

where ($C^*$—C) is concentration gradient and K is constant $I_d$ α concentration (mol $ml^{-1}$)

$$\begin{cases} C_1 = \dfrac{X}{9{\cdot}5} \\ C_2 = \dfrac{0{\cdot}04}{0{\cdot}5} \end{cases}$$

$$\frac{Id_1}{Id_2} = \frac{C_1}{C_2}$$

$$\Rightarrow \quad X = 0{\cdot}0067$$

74. (C) (A) $CH_3COOH$ in pyridine
Strong base

$\rightarrow CH_3COO^- + C_5H_5\overset{\oplus}{N}H$ solvocation

(B) $CH_3COOH$ in $H_2SO_4$
Strong base

$\rightarrow CH3CO\overset{\oplus}{O}H_2 + HSO_4^-$ solvo anion

(C) $HClO_4$ in $H_2SO_4$

$\rightarrow ClO_4^- + H_3S^+O_4$ (weak acid)

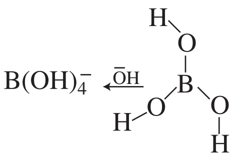
(D) $SbF_5$ in HF $\rightarrow SbF_6^- + H_2F^+$ strong acid
2 mole

75. (B) $C_2B_4H_8$ = (BH) × 4 + (CH) × 2 + 2
= 2 × 4 + 3 × 2 + 2
= $16e^-$ or $8e^-$ pair
or $(m + 2)e^-$ pair (Nido)

—BH contributes $2e^-s$ to framework.

—CH contributes $3e^-s$ to framework.

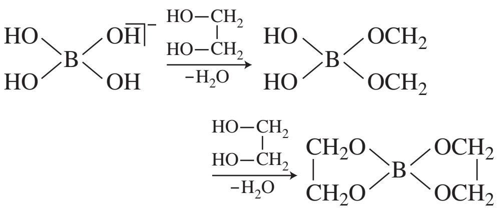
76. (B) Boric acid is a weak acid in aq. solution.




with HO—CH₂—

$CH_2$—OH

$B(OH)_4^-$ consumed in forming a compound with ethylene glycol.

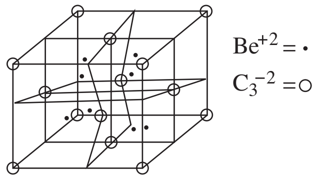



77. (D) $Be_2C_3$ structure is correlated with $CaF_2$.

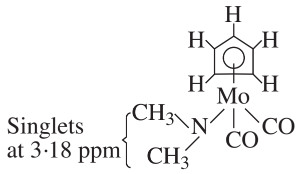
Therefore, $Be^{+2}$ in tetrahedral voids.

Since, molecules have FCC arrangement.

Thus, $Be^{+2}$ have 4 coordination number and $C_3^{-2}$ have 8 coordination number.




78. (A)




All 5-protons *r* are equal and resonate at 5·48 ppm.

Also, both CO are is different environment, therefore gives two signal at 1950 and 1860 $cm^{-1}$.

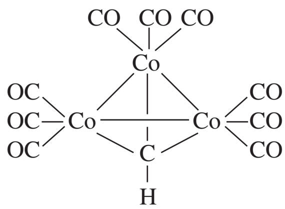
79. (A) —CH is $3e^-$ donor ligand.

No. of M—M bond

$$= \frac{18 \times 3 - (9 \times 3 + 9 \times 2 + 3)}{2}$$

$$= \frac{54 - 48}{2} = 3$$

Therefore, structure of $[CO_3(CH)(CO)_9]$




Thus, No. of M—M bond = 3

and Bridging ligand = 1

80. (A) Since, $Gd^{+3}$ and $Lu^{+3}$ have $4f^7$ and $4f^{14}$ electronic configuration. Therefore, no orbital contribution observed and magnetic moment value is closest w.r.t. observed and calculated.

81. (D) Neso-silicates = ortho silicates $SiO_4^{-2}$ unit

Soro-silicates = $Si_2O_7^{-2}$ unit

Tecto-silicates = $SiO_2$ unit and 3D framework

82. (A) The structure of $Co_3O_4$ is normal spinel.

In normal spinel the $Co^{+2}$ ions occupy tetrahedral voids and $Co^{+3}$ ions occupy octahedral voider.

Therefore structure is,

$$(Co^{+2})_t\,(2Co^{+3})_O O_4$$

For Inverse spinel structures it is

$$(Co^{+3})_t\,(Co^{+2}\;Co^{+3})_O\;O_4$$

83. (A) In the solid state, the $CuCl_5^{3-}$ ion have trigonal bipyramidal geometry and *d*-orbitals are

$$d_{z}^{1} > d_{xy}^{2} = d_{x^2-y^2}^{2} > d_{xz}^{2} = d_{yz}^{2}$$

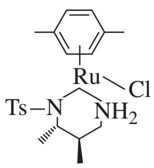
The two ligands on the *z*-axis and three are in between *xy* plane and directly in path of orbitals lobe and feels. There are four $e^-$s in $d_{xz}^2$ and $d_{yz}^2$ and repel each other, due to this bond length becomes long. Thus, three long and two short bond is found.

84. (B) In metalloenzymes, the metal centers are covalently linked through the side chains of the amino acid residues. Therefore Glu, His Cys are involved in the primary coordination spheres of metalloenzymes.

85. (A) [R-BINAP]$Ru^{2-}$ is used for Asymmetric hydrogenation.

$[Rh(CO)_2I_2]^-$ for Hydroformylation

$[Pd(PPh_3)_4]$ for Heck coupling.



for Asymmetric hydrogen transfer

86. (D) The weight of pt-gauze as electrode is changed as

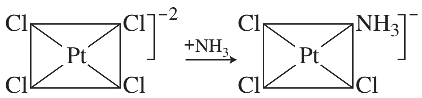
$$= 16{\cdot}0 - 14{\cdot}5$$
$$= 1{\cdot}5\text{g}$$

Thus, weight of Cu is 2·0 g brass is 1·5 g.

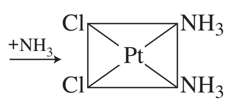
Therefore, percentage weight of Cu in brass

$$= \frac{1{\cdot}5}{2{\cdot}0} \times 100$$
$$= 75\%$$

87. (A)

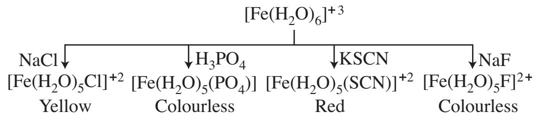



$Cl^-$ have trans effect > $NH_3$




Cis-platin
(anti-tumour agent)

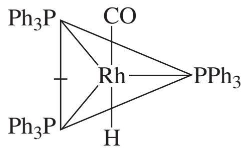
88. (A) In solution $Fe(NO_3)_3{\cdot}9H_2O$ exists as $[Fe(H_2O)_6]^{+3}{\cdot}(NO_3^-)_3{\cdot}3H_2O$




89. (D) For oxidative addition reaction, metal should have $e^-$ rich and have tendency to charge its oxidation state.

Therefore, $[\eta^5 - Cp_2Ti(Me)Cl]$ do not have tendency to show oxidative addition reaction.

90. (B)

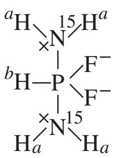



In hydroformylation reaction, 16$e^-$ species is reactive catalysts. Due to excess $PPh_3$, it becomes 20 $e^-s$ species and lost it catalytic reactivity.

So, the rate of reaction decreases in the presence of excess $PPh_3$.

91. (D)

| Species | I |
|---|---|
| $^{1}H$ | $\frac{1}{2}$ |
| $^{15}N$ | $\frac{1}{2}$ |
| $^{19}F$ | $\frac{1}{2}$ |
| $^{31}P$ | $\frac{1}{2}$ |




No. of lines

$$= (2n_1I_1 + 1)\,(2n_2I_2 + 1)\,(2n_3I_3 + 1)\,(2n_4I_4 + 1)$$

2N 2F 4H 1H

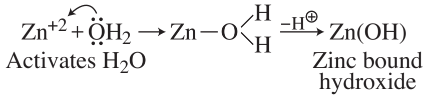
$$= \left(2 \times 2 \times \frac{1}{2} + 1\right)\left(2 \times 2 \times \frac{1}{2} + 1\right)\left(2 \times 4 \times \frac{1}{2} + 1\right)\left(2 \times 1 \times \frac{1}{2} + 1\right)$$

$$= 3 \times 3 \times 5 \times 2$$
$$= 90$$

92. (A) Since in $[Cu(H_2O)_6]^{+2}$, John-Teller distortion observed, so rate of exchange is fast.

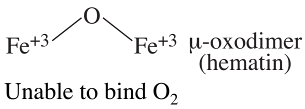
Rest of others are 3*d*-series dipositive metal cations. Thus, rate of exchange with $^{18}H_2O$ decreases with decrease in size and increase in atomic number.

93. (B) Since, Zn is a lewis acid, so




In oxidases an enzyme that catalyse the reduction of $O_2$ to $H_2O$ or $H_2O_2$, the iron activates $O_2$ to break the bonding between the two oxygen's.

94. (B) $Fe^{+2}$-porphyrins fail to exhibit reversible oxygen transport and cannot differentiate CO from $O_2$. However, the haemoglobin is free from both these pitfalls.

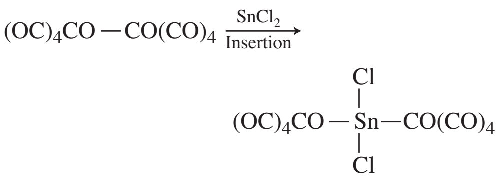



* $Fe^{+2}$-porphyrins undergo μ-oxodimer formation and the same is prevented in case of haemoglobin.

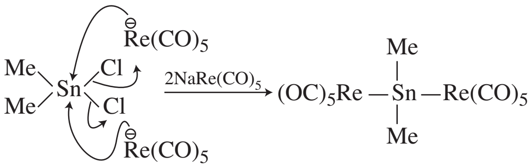
$*_1$ Fe-CO is linear, Fe—$O_2$ is bent recognized by haemoglobin.

95. (A) $SnCl_2$ behaves as a carbene and it insert into the CO—CO bond.

Insertion :




Metathesis :




96. (C) We know that,

Density $p = \frac{nM}{Na^3}$

where $n$ is no. of particles per unit cell

M = Molar Mass

N = Avogadro's number

$a$ = edge length of cube

$$\therefore \ M = \frac{pNa^3}{n}$$

$$= \frac{(1{\cdot}33 \text{g cm}^{-3})\ (6{\cdot}023 \times 10^{23} \text{ mole}^{-1})\ (500 \times 100^{-10} \text{ cm})^3}{4}$$

M = 25

97. (C) Bimolecular reaction

$$A + BC \rightarrow AB + C$$

There will be greater possibilities of collisions between molecule when volume is smaller and therefore activation energy decreases with decreasing λ.

98. (A) There is a strong electron-electron *i.e.*, inter-electron repulsion in many-electron atom. Due to this the orbital angular momentum ($l_1$, $l_2$) and sign angular momentum ($s_1$, $s_2$) are couple together to for total orbital angular momentum (L) and (S).

99. (C) Packing fraction

$$= \frac{\text{(No. of particles per unit cell)} \times \text{(Volume of 1 particle)}}{\text{Total volume of unit cell}}$$

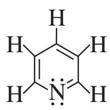
For simple cubic lattice

$$= \frac{1 \times \frac{4}{3}\pi r^3}{a^3}$$

$$= \frac{4}{3} \times \frac{22}{7} \times \frac{r^3}{(2r)^3}$$

$$= 0{\cdot}52$$

100. (C)




Order of group = 4 ($C_{2v}$ = 2 × 2 = 4)

| $C_{2v}$ | E | $C_2$ | $\sigma_V(xz)$ | $\sigma_V'(yz)$ | √ |
|---|---|---|---|---|---|
| $A_1$ | 1 | 1 | 1 | 1 | $z$ |
| $A_2$ | 1 | 1 | –1 | –1 | $R_z$ |
| $B_1$ | 1 | –1 | 1 | –1 | $x, R_y$ |
| $B_2$ | 1 | –1 | –1 | 1 | $y, R_x$ |
| No. of unshifted atoms | 11 | 3 | 3 | 11 | |
| Character per atoms | 3 | –1 | 1 | 1 | |
| Reducible Representation | 33 | –3 | 3 | 11 | |

$$\text{No. of } A_1 = \frac{1}{4}[33 \times 1 \times 1 + (-3) \times 1 \times 1 + 3 \times 1 \times 1 + 11 \times 1 \times 1] = 11$$

$$\text{No. of } A_2 = \frac{1}{4}[33 \times 1 \times 1 + (-3) \times 1 \times 1 + 3 \times (-1) \times 1 + 11 \times (-1) \times +1] = 4$$

$$\text{No. of } B_1 = \frac{1}{4}[33 \times 1 \times 1 + (-3) \times (-1) \times 1 + 3 \times 1 \times 1 + 11 \times (-1) \times 1] = 7$$

No. of $B_2 = \frac{1}{4}[33 \times 1 \times 1 + (-3)(-1) \times 1 + 3 \times (-1) \times 1 + 11 \times 1 \times 1] = 11$

Therefore,

$$\text{R.R.}, \tau_{red} = 11A_1 + 4A_2 + 7B_1 + 11B_2$$

$$\tau_{trans} = B_1 + B_2 + A_1$$

(Right side of box)

$$\tau_{rot} = B_2 + B_1 + A_2$$

$$\therefore \quad \tau_{vib} = 10A_1 + 3A_2 + 5B_1 + 9B_2$$

Since, $A_2$ is not IR-active.

Therefore, total IR active vibration modes are

$$10 + 5 + 9 = 24$$

101. (B) ${}_{22}Ti$ – [Ar] $4s^2\,3d^1\,4p^1$

Excited state

$$\text{No. of microstates} = \frac{\lfloor 4l + 2}{\lfloor 4l + 2 - q \; \lfloor q}$$

where $l$ is azimuthal quantum no. of valence shell and $q$ is no. of $e^-$s in valence shell

$$= \frac{\lfloor 4 \times 1 + 2}{\lfloor 4 + 2 - 2 \; \lfloor 2}$$

$$= \frac{6 \times 5 \times \lfloor 4}{\lfloor 4 \times 2 \times 1}$$

$$= 15$$

102. (B) $A_2 \rightleftharpoons 2A$

at $t = 0$: 1, 0

at equilibrium: $1 - \alpha$, $2\alpha$

Since, $P_A = X_A P \Rightarrow X_A = \frac{2\alpha}{1 - \alpha + 2\alpha} = \frac{2\alpha}{1 + \alpha}$

$$P_{A_2} = X_{A_2} P$$

$$\Rightarrow X_{A_2} = \frac{1 - \alpha}{1 - \alpha + 2\alpha} = \frac{1 - \alpha}{1 + \alpha}$$

$$\text{Thus, } K_p = \frac{P_A^2}{P_{A_2}} = \frac{\left(\frac{2\alpha}{1 + \alpha}\right)^2 P^2}{\left(\frac{1 - \alpha}{1 + \alpha}\right) P} = \frac{4\alpha^2}{1 - \alpha^2} P$$

$$(1 - \alpha^2) K_p = 4\alpha^2 p$$

$$K_p - K_p\alpha^2 - 4\alpha^2 p = 0$$

$$\Rightarrow \quad \alpha = \left[\frac{K_p}{(K_p + 4p)}\right]^{1/2}$$

$$K_p = \alpha^2 (K_p + 4p)$$

103. (A)

$$Z = \frac{p\bar{V}}{RT}$$

$$f = p \cdot e^{\int_0^p \left(\frac{Z-1}{P}\right) dp}$$

For Van der Waal gas

$$f = pe^{Pb/RT}$$

$\Rightarrow$ If $T \to \infty, f = p$

If $T \to 0$, then $f < p$.

104. (C)

$$Z = \frac{p\bar{V}}{RT}$$

$$\Rightarrow \quad p = \frac{ZRT}{\bar{V}}$$

$$\Rightarrow \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{\bar{V}}\left[\left(\frac{\partial Z}{\partial T}\right)_V T + Z\right]$$

$$i.p. = \left(\frac{\partial U}{\partial V}\right)_T$$

$$= T\left(\frac{\partial P}{\partial T}\right)_V - p$$

$$= T\frac{R}{\bar{V}}\left[\left(\frac{\partial Z}{\partial T}\right)_V \cdot T + Z\right] - p$$

$$= \frac{RT^2}{\bar{V}}\left(\frac{\partial Z}{\partial T}\right)_V + \frac{ZRT}{\bar{V}} - p$$

$$\left\{\because \frac{ZRT}{\bar{V}} = p\right.$$

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{RT^2}{\bar{V}}\left(\frac{\partial Z}{\partial T}\right)_V$$

105. (C) Harmonic Oscillator wave function is given as :

$$\psi_n(x) = N_n H_n\, e^{-\alpha x^2/2}$$

and given wave function is

$$\psi_0 = e^{-Ax^2}$$

Thus, $A \propto \frac{\alpha}{2}$

Since, $\alpha = \left(\frac{k\mu}{\hbar^2}\right)^{1/2}$

Therefore, $A \propto k^{1/2}$

106. (C)

$$A = \phi_1 + \phi_2$$

$$D = i(\phi_1 + \phi_2)$$

Combing two real wave functions $\phi_1$ and $\phi_2$, constructed functions $\phi_1 + \phi_2$ and $i(\phi_1 + \phi_2)$ represent the same state because if the two function multiplied by any constant, no effect on the state and on the energy because multiply only in eigen value, not in energy and no effect on wave function.

107. (A) For BCC, $h + k + l$ should be even FCC, $h, k, l$ all either even or odd

where 0 is even number.

Thus, A has $f_{CC}$ lattic while B has bcc lattice.

108. (B) At low pressure, Langmuir-Hinshelwood mechanism follows first order kinetics.

$$\therefore \quad K_1 = \frac{2 \cdot 303}{T} \log_{10} \frac{P_0}{P_f}$$

$$= \frac{2 \cdot 303}{10} \log_{10} \frac{10^{-3}}{10^{-4}}$$

$$= \frac{2 \cdot 303}{10} \times 2$$

$$= 0 \cdot 4606 \text{ min}^{-1}$$

109. (C) $$\overline{M}_n = \frac{n_1M_1 + n_2M_2 + n_3M_3}{n_1 + n_2 + n_3}$$

$$= \frac{10 \times 1000 + 50 \times 2000 + 40 \times 4000}{10 + 50 + 40}$$

$$= 2700$$

$$\overline{M}_w = \frac{n_1M_1^2 + n_2M_2^2 + n_3M_3^2}{n_1M_1 + n_2M_2 + n_3M_3}$$

$$= \frac{85000}{27}$$

Therefore,

$$\text{P.D.I.} = \frac{\overline{M}_w}{\overline{M}_n}$$

$$= \frac{85000}{27} \cdot \frac{1}{2700} = \frac{850}{729}$$

110. (B) $2 \times (Fe^{+3} + e^- \rightarrow Fe^{+2})$ reduction at cathode

$Sn^{+2} \rightarrow Sn^{+4} + 2e^-$ Oxidation at anode

$$2Fe^{+3} + Sn^{+2} \rightarrow 2Fe^{+2} + Sn^{+4}$$

$$E^0_{Cell} = E_{cathode} - E_{anode}$$

$$= 0 \cdot 75V - 0 \cdot 15V$$

$$= 0 \cdot 60V$$

Thus, $$E^0_{Cell} = \frac{2 \cdot 303RT}{nF} \log K_{eq}$$

$$\log K_{eq} = \frac{0 \cdot 60V \times 2}{0 \cdot 06V} = 20$$

$$K_{eq} = 10^{20}$$

111. (C) $$dN = \lambda_g N dt$$

Integrating it with appropriate limits

$$\int_{N_0}^{N} \frac{dN}{N} = \lambda_g \int_0^t dt$$

$$[ln\, N]_{N_0}^{N} = \lambda_g t$$

$$N = N_0 e^{\lambda_g t}$$

112. (D) $2NOCl(g) \rightarrow 2NO(g) + Cl_2(g)$

$$\Delta H = E_a + (\Delta n_g^* - 1)RT$$

$$\Delta n_g^* = -1 \text{ (Bimolecular reaction)}$$

$$\therefore \quad \Delta H = 105 \text{ kJ mol}^{-1} + (-1 - 1) \times 2 \cdot 5 \text{ kJ mol}^{-1}$$

$$= 100 \text{ kJ mol}^{-1}$$

113. (D) Rotational partition function of $H_2$

$$q_r = \frac{1}{4}\Big[\sum_{J = 0, 2, 4} (2J + 1)\, e^{-\beta hc\, BJ(J+1)} + 3 \sum_{J = 1, 3, 5} (2J + 1)\, e^{-\beta hc\, BJ(J+1)}\Big]$$

114. (C) The potential in Debye Hückel theory is

$$\psi_r = \frac{Z_i e_0}{q} \frac{e^{-kr}}{r}$$

$$\psi_r \propto \frac{e^{-kr}}{r}$$

115. (B) Fundamental vibration :

$$\Delta\tilde{E}_{0 \rightarrow 1} = \tilde{\upsilon}_e(1 - 2x_e)$$

$$= 300(1 - 2 \times 0 \cdot 0025)$$

$$= 298 \cdot 50 \text{ cm}^{-1}$$

First overtones

$$\Delta\tilde{E}_{0 \rightarrow 2} = 2\tilde{v}_e (1 - 3x_e)$$

$$= 2 \times 300(1 - 3 \times 0 \cdot 0025)$$

$$= 595 \cdot 50 \text{ cm}^{-1}$$

116. (B) According to Langmuir Isotherm, fractional surface coverage is given as :

$$\frac{1}{\theta} = \frac{1}{K_{eq}P} + 1$$

$$\Rightarrow \quad \frac{1}{\theta} - 1 = \frac{1}{K_{eq}\, P}$$

$$\Rightarrow \quad P = \frac{\theta}{(1 - \theta)K_{eq}}$$

$$= \frac{0 \cdot 95}{0 \cdot 05 \times 0 \cdot 9}$$

$$= 21 \cdot 1$$

117. (A) According to virial theorem for simple harmonic oscillator, the kinetic energy and potential energy is equal and half of the total energy.

$$E = K + U \qquad \because U = K$$

$$\frac{\hbar w}{2} = 2K$$

$$K = \frac{\hbar w}{4} = U$$

118. (C) Energy of a hydrogen atom in a state is

$$\frac{-hcR_H}{h^2} = \frac{-hCR_H}{25} \left(\because E = -13{\cdot}6 \cdot \frac{Z^2}{n^2}\right)$$

Degeneracy $= n^2 = 25$

119. (A) $\psi_t = c_1\phi_1 + c_2\phi_2$

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = 0$$

$$\because S_{11} = 1, S_{22} = 1, S_{12} = S_{21} = 0$$

$H_{11} = \langle\phi_1 | \hat{H} | \phi_1\rangle = 0$, $H_{12} = H_{21} = \langle\phi_1 | \hat{H} | \phi_2\rangle = 2{\cdot}0 = \langle\phi_2 | \hat{H} | \phi_1\rangle$, $H_{22} = \langle\phi_2 | \hat{H} | \phi_2\rangle = 3{\cdot}0$

$$\therefore \begin{vmatrix} 0 - E & 2 - 0 \\ 2 - 0 & 3 - E \end{vmatrix} = -3E + E^2 - 4 = 0$$

$$E^2 - 3E - 4 = 0$$

$$\Rightarrow E^2 - 4E + E - 4 = 0$$

$$\Rightarrow (E + 1)(E - 4) = 0$$

Since, ground state energy is lowest.

Thus, $E = -1{\cdot}0$

120. (D) Polar molecule AB $\rightarrow$ $A^+B^-$ has molecular orbital $C_A\psi_A + C_B\psi_B$

$$C_A^2 + C_B^2 = 1 \text{ (normalization)}$$

Since, $C_B^2 = 90\%$

$$= \frac{90}{100} = 0{\cdot}9$$

$$\Rightarrow C_B = 0{\cdot}95$$

$$C_A^2 = 10\%$$

$$= \frac{10}{100} = 0{\cdot}1$$

$$\Rightarrow C_A = 0{\cdot}32$$

$$\Rightarrow C_A = 0{\cdot}32, C_B = 0{\cdot}95$$

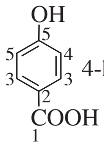
121. (B) δ 171 at COOH

δ 162 at C-4

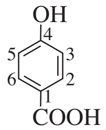
δ 133 at C-2 and C-6

δ 122 at C-1

δ 116 at C-3 and C-5



4-hydroxy benzoic acid



122. (D) $C_9H_{10}O_3$

$$DBE = \frac{18 + 2 - 10}{2}$$

$$= 5 \text{ double bond or ring}$$

IR : 3400, 1680 $cm^{-1}$

$^1H$ NMR :

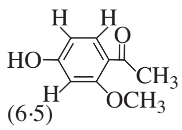
δ 7·8 (1H, d, J = 8Hz) } aromatic protons
7·0 (1H, d, J = 8 Hz) } with *m*-position

6·5 (1H, S) aromatic proton with O-position to —OH to —$OCH_3$

5·8 (1H, S, $D_2O$ exchangeable) —OH

3·9 (3H, S) with electronegative atom like oxygen.

2·3 (3H, S) adjacent to carbonyl group.



123. (A) Since, specific rotation $[\alpha]_D$ of a 90% optically pure 2-arylpropanoic acid is +135°.

So, 100% optically pure isomer will show $\frac{135}{90} \times 100 = 150° [a]_D$.

After one hour $[\alpha]_D$ reduced to 120°

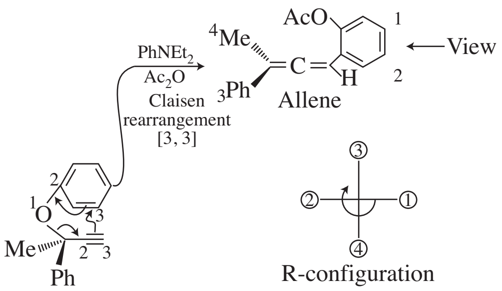
$$\text{Thus, Optical purity} = \frac{120}{150} \times 100$$

$$= 80\%$$

After 3 hours optical purity is reduced to 40%.

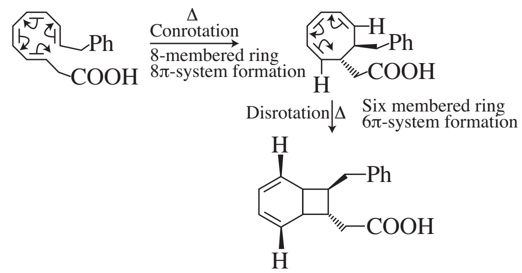
So, Specific rotation $= \dfrac{150 \times 40}{100} = 60°$

124. (A)

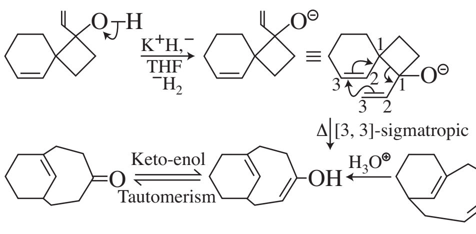



Thermal condition, so retention in configuration w.r.t. Me and Ph.

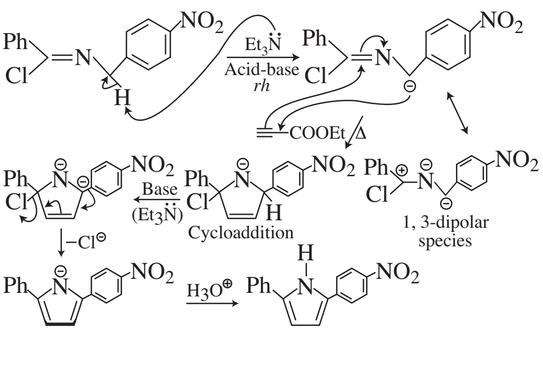
125. (C)



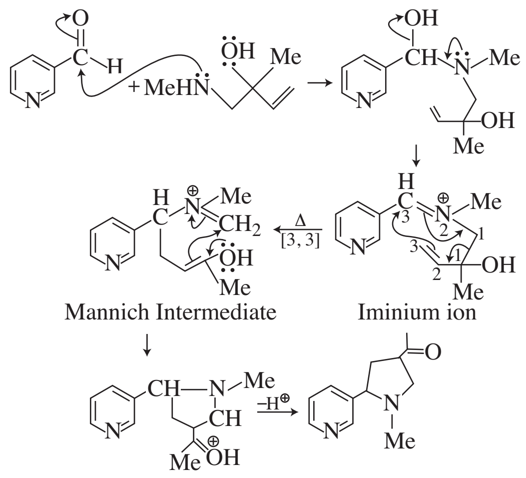

126. (C)



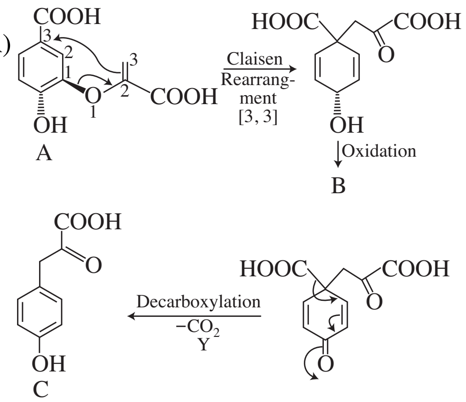

127. (A)




128. (A)

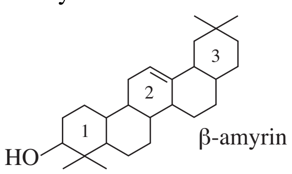



129. (A)

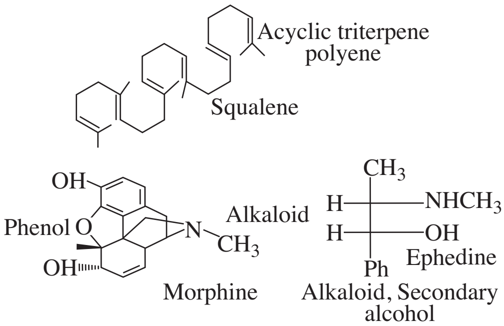



Claisen rearrangement followed by oxidative decarboxylation.

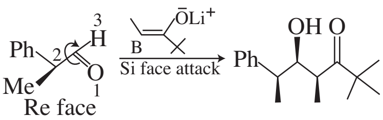
130. (A)




Triterpene and Secondary alcohol.

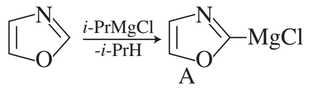


131. (C)

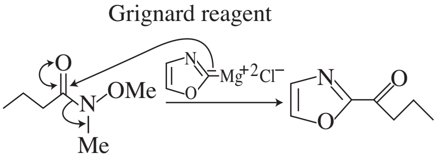



Re face of carbonyl and Si-face of enolate, syn product will be formed.

132. (A)




Grignard reagent



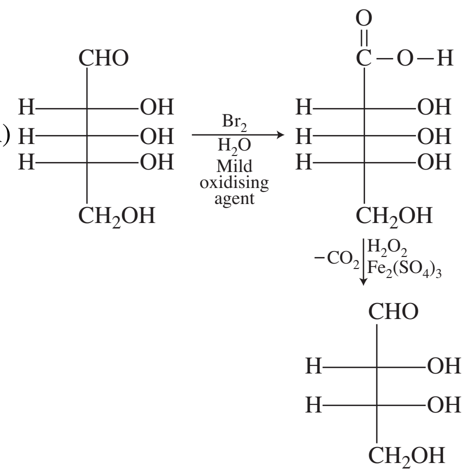

133. (A) α-Ketoglutarate $\xrightarrow{\text{Pyridoxamine}}$ Glutamic acid

Uridine $\xrightarrow{\text{Tetrahydrofolate}}$ Thymidine

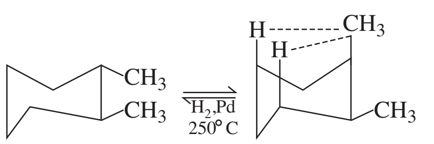
Pyruvic acid $\xrightarrow[\text{Pyrophosphate}]{\text{Thiamine}}$ Acetyl coenzyme A

(For structure see Lehninger text book)

134. (A)




135. (B)




No. 1, 3 interaction

Two, H/Me 1, 3 interaction

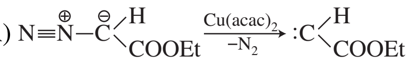
Since, 1 gauche butane interaction energy = 0·9 k-cal/mol.

So, ΔG for given reaction

= 2 × 0·9 k-cal/mol

= 1·8 k-cal/mol

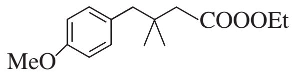
136. (A)




Carbene

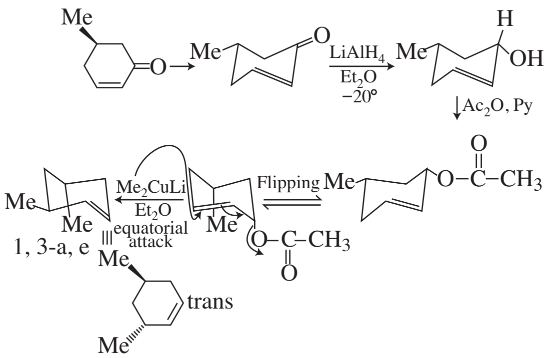

hydrogenolysis

MeOH↓$H_2$, 10% Pd/C




least hindered bond will be break

137. (C)



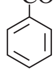

138. (D)

$NaOH + I_2 \rightarrow NaOI + HI$

$PhCOCH_3 + 3NaOI \rightarrow PhCOCI_3 + 3NaOH$

$PhCOCI_3 + NaOH \rightarrow PhCOONa + CHI_3$

$COCH_3$ M.w.t. = 120 M.w.t. = 394



12g $CHI_3$

120g acetophenone gives 394g iodoform.

12g acetophenone willl give

$$\frac{394}{120} \times 12 = 39{\cdot}4\text{g}$$

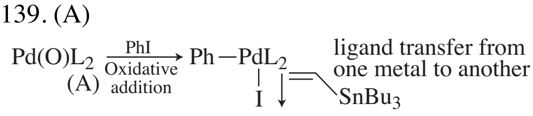
Since, yield is 75%

So, 12g acetophenone will give

$$= \frac{39{\cdot}4 \times 75}{100}$$

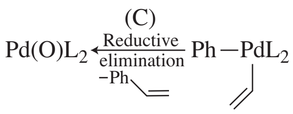
$$= 29{\cdot}5 \text{ g } CHI_3$$

139. (A)

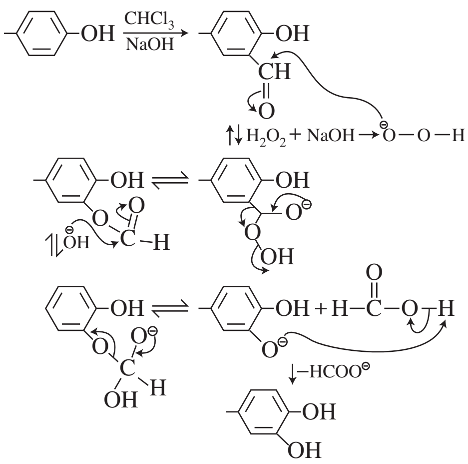



Oxidation state increased by two units.

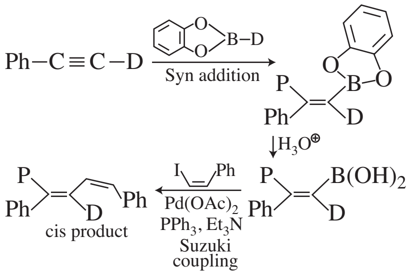
(B) Transmetallation



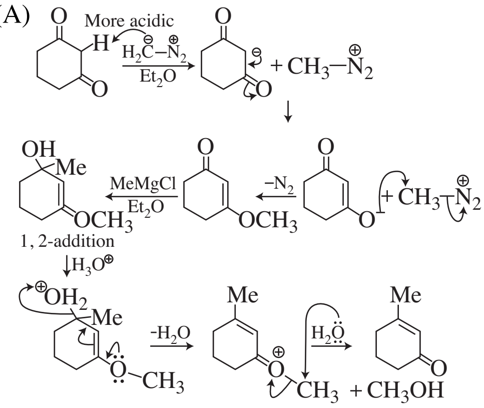
140. (B) This is Reimer-Tiemann Reaction



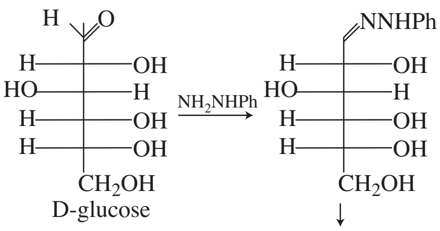

141. (A)

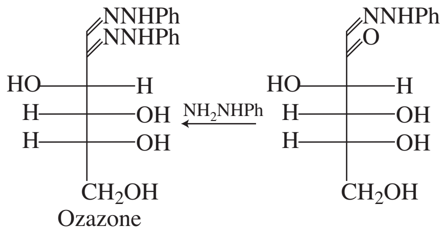


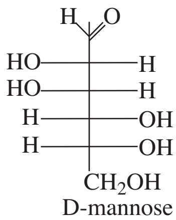

142. (A)



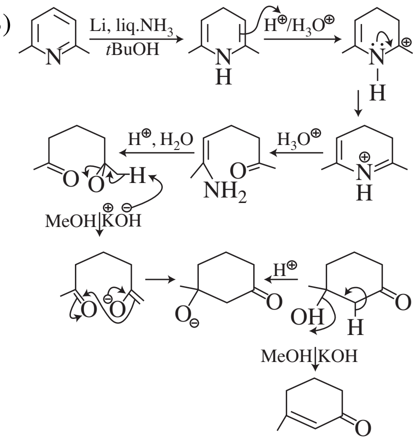

143. (A)



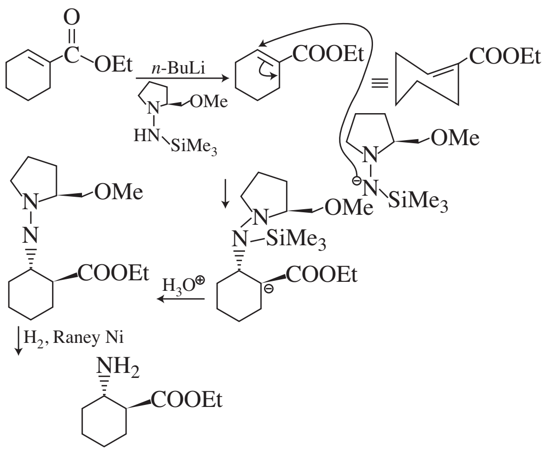




144. (B)




145. (*) Doubtful question ?



# Chemical Sciences
## CSIR UGC-NET/JRF Exam.
### Solved Paper

# June 2013
# Chemical Sciences

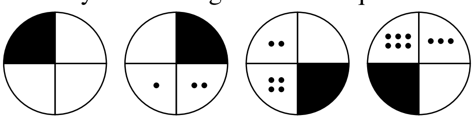
## PART A

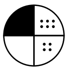
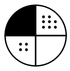
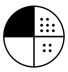
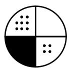
1. During an evening party, when Ms. Black, Ms. Brown and Ms. White met, Ms. Brown remarked, "It is interesting that our dresses are white, black or brown, but for each of us the name does not match the colour of the dress !". Ms. White replied, "But your white dress does not suit you !". Pick the correct answer.
   (A) Ms. White's dress was brown
   (B) Ms. Black's dress was white
   (C) Ms. White's dress was black
   (D) Ms. Black's dress was black

2. Of all the triangles that can be inscribed in a semicircle of radius R with the diameter as one side, the biggest one has the area—
   (A) $R^2$ (B) $R^2\sqrt{2}$
   (C) $R^2\sqrt{3}$ (D) $2R^2$

3. A square pyramid is to be made using a wire such that only one strand of wire is used for each edge. What is the minimum number of times that the wire has to be cut in order to make the pyramid ?
   (A) 3 (B) 7
   (C) 2 (D) 1

4. Identify the next figure in the sequence—

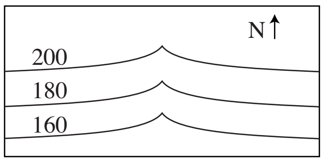


   (A)  (B) 
   (C)  (D) 

5. In a customer survey conducted during Monday to Friday, of the customers who asked for child care facilities in super markets, 23% were men and the rest, women. Among them, 19.9% of the women and 8.8% of the men were willing to pay for the facilities—
   1. What is the ratio of the men to women customers who wanted child care facilities ?
   2. If the survey had been conducted during the weekend instead, how will the result change ?

   With the above data—
   (A) Only 1 can be answered
   (B) Only 2 can be answered
   (C) Both 1 and 2 can be answered
   (D) Neither 1 nor 2 can be answered

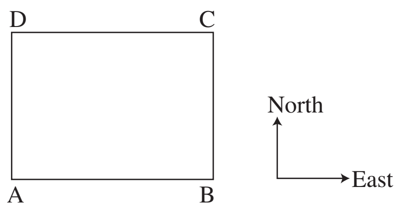
6. The map given below shows contour lines which connect points of equal ground surface elevation in a region. Inverted 'V' shaped portions of contour lines represent a valley along which a river flows. What is the downstream direction of the river ?




Scale = 1 : 5000

   (A) North (B) South
   (C) East (D) West

7. During a summer vacation, of 20 friends from a hostel, each wrote a letter to each of all others. The total number of letters written was—
   (A) 20 (B) 400
   (C) 200 (D) 380

8. 

A person has to cross a square field by going from A to C. The person is only allowed to move towards the east or towards the north or use a combination of these movements. The total distance travelled by the person—

(A) depends on the length of each step
(B) depends on the total number of steps
(C) is different for different paths
(D) is the same for all paths

9. A crow is flying along a horizontal circle of radius R at a height R above the horizontal ground. Each of a number of men on the ground found that the angular height of the crow was a fixed angle $\theta$ (< 45°) when it was closest to him. Then all these men must be on a circle on the ground with a radius—

(A) $R + R \sin \theta$ (B) $R + R \cos \theta$
(C) $R + R \tan \theta$ (D) $R + R \cot \theta$

10. How many pairs of positive integers have gcd 20 and lcm 600 ?
(gcd = greatest common divisor; lcm = least common multiple)

(A) 4 (B) 0
(C) 1 (D) 7

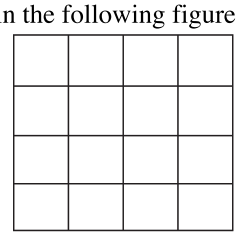
11. Two integers are picked at random from the first 15 positive integers without replacement. What is the probability that the sum of the two numbers is 20 ?

(A) $\frac{3}{4}$ (B) $\frac{1}{21}$
(C) $\frac{1}{105}$ (D) $\frac{1}{20}$

12. A daily sheet calendar of the year 2013 contains sheets of 10 × 10 cm size. All the sheets of the calendar are spread over the floor of a room of 5 m × 7.3 m size. What percentage of the floor will be covered by these sheets ?

(A) 0.1 (B) 1
(C) 10 (D) 100

13. How many rectangles (which are not squares) are there in the following figure ?



(A) 56 (B) 70
(C) 86 (D) 100

14. Define $a \otimes b = \text{lcm}(a, b) + \text{gcd}(a, b)$ and $a \oplus b = a^b + b^a$. What is the value of $(1 \oplus 2) \otimes (3 \oplus 4)$ ? Here lcm = least common multiple and gcd = greatest common divisor—

(A) 145 (B) 286
(C) 436 (D) 572

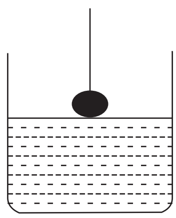
15. There is an equilateral triangle in the XY plane with its centre at the origin. The distance of its sides from the origin is 3.5 cm. The area of its circumcircle in $cm^2$ is—

(A) 38.5 (B) 49
(C) 63.65 (D) 154

16. What is the value of $\frac{1}{1 \times 2} + \frac{1}{2 \times 3} + \frac{1}{3 \times 4} + \ldots$ to $\infty$ ?

(A) $\frac{2}{3}$ (B) 1
(C) 2 (D) $\infty$

17. A sphere of iron of radius R/2 fixed to one end of a string was lowered into water in a cylindrical container of base radius R to keep exactly half the sphere dipped. The rise in the level of water in the container will be—

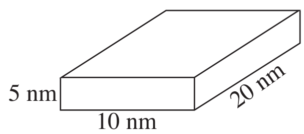


(A) R/3 (B) R/4
(C) R/8 (D) R/12

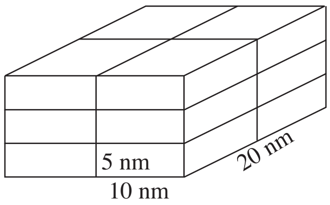
18. Choose the largest number—

(A) $2^{500}$ (B) $3^{400}$
(C) $4^{300}$ (D) $5^{200}$

19. A crystal grows by stacking of unit cells of 10 × 20 × 5 nm size as shown in the diagram given below. How many unit cells will make a crystal of 1 $cm^3$ volume ?



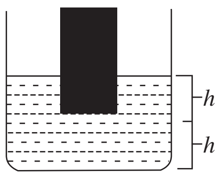

**Unit cell (not to scale)**




**Crystal (not to scale)**

(A) $10^6$ (B) $10^9$
(C) $10^{12}$ (D) $10^{18}$

20. A solid cylinder of basal area A was held dipped in water in a cylindrical vessel of basal area 2A vertically such that a length *h* of the cylinder is immersed. The lower tip of the cylinder is at a height *h* from the base of the vessel. What will be the height of water in the vessel when the cylinder is taken out ?




(A) $2h$ (B) $\frac{3}{2}h$
(C) $\frac{4}{3}h$ (D) $\frac{5}{4}h$

## PART B

21. Which of the following pairs has the highest difference in their first ionization energy ?
(A) Xe, Cs (B) Kr, Rb
(C) Ar, K (D) Ne, Na

22. The ligand in uranocene is—
(A) $C_8H_8^{2-}$ (B) $C_5H_5^{2-}$
(C) $C_6H_6$ (D) $C_4C_4^{2-}$

23. In metal–olefin interaction, the extent of increase in metal → olefin π-back-donation would—
(A) Lead to a decrease in C = C bond length
(B) Change the formal oxidation state of the metal
(C) Change the hybridisation of the olefin carbon from $sp^2$ to $sp^3$
(D) Increase with the presence of electron donating substituents on the olefin

24. The oxidation state of molybdenum in $[(\eta^7\text{–tropylium})\ Mo\ (CO_3]^+$ is—
(A) +2 (B) +1
(C) 0 (D) –1

25. The reaction of $[PtCl_4]^{2-}$ with two equivalents of $NH_3$ produces—
(A) *cis*-$[Pt(NH_3)_2Cl_2]$
(B) *trans*-$[Pt(NH_3)_2Cl_2]$
(C) Both *cis*-$[Pt(NH_3)_2Cl_2]$ and *trans*-$[Pt(NH_3)_2Cl_2]$
(D) *cis*-$[Pt(NH_3)_2Cl_4]^{2-}$

26. The electronic transition responsible for the colour of the transition metal ions is—
(A) $d_\pi \rightarrow d_\sigma$ (B) $d_\pi \rightarrow d_{\sigma*}$
(C) $d_\pi \rightarrow d_{\pi*}$ (D) $d_\sigma \rightarrow d_{\pi*}$

27. The number of metal-metal bonds in $[W_2(OPh)_6]$ is—
(A) 1 (B) 2
(C) 3 (D) 4

28. The Mulliken symbols for the spectroscopic states arising from the free-ion term F are—
(A) $T_{2g} + E_g$ (B) $T_{1g} + T_{2g} + T_{1u}$
(C) $T_{1g} + T_{2g} + A_{2g}$ (D) $A_{1g} + T_{2g} + T_{1g}$

29. Which of the following is used as propellant for whipping creams ?
(A) $N_2O$ (B) NO
(C) $N_2O_3$ (D) $N_2O_5$

30. Flame proof fabrics contain—
(A) $H_2NC(O)NH_2{\cdot}Na_2SO_4$
(B) $H_2NC(S)NH_2{\cdot}Na_2SO_4$
(C) $H_2NC(O)NH_2{\cdot}H_3PO_4$
(D) $H_2NC(S)NH_2{\cdot}H_3PO_4$

31. Among the compounds A–D, those which hydrolyse easily are—
(A) $NCl_3$ (B) $NF_3$
(C) $BiCl_3$ (D) $PCl_3$

32. The coordination geometry of copper(II) in the type I copper protein plastocyanin is—
(A) Square planar
(B) Tetrahedral
(C) Octahedral
(D) Distorted tetrahedral

33. The metal ions present in the active site of nitrogenase enzyme co-factor are—
(A) Fe, Mo (B) Fe, W
(C) Fe, Cu (D) Fe, Ni

34. The reaction $[(CO)_5\ Mn(Me)] + CO \rightarrow [(CO)_5\ Mn\{(C(O)Me\}]$ is an example for—
(A) Oxidation addition
(B) Electrophilic substitution
(C) Nucleophilic substitution
(D) Migratory insertion

35. The number of EPR signals observed for octahedral Ni (II) complexes is—
(A) One (B) Two
(C) Three (D) Zero

36. For neutron activation analysis of an element, the favourable characteristics of both the target and the product are from the following—
1. High neutron cross-section area of target
2. Long half-life of the product
3. Low neutron cross-section area of target
4. Low half-life time of the product

The correct characteristics from the above are—
(A) 1 and 2 (B) 2 and 3
(C) 3 and 4 (D) 1 and 4

37. The concentrations of a species A undergoing the reaction $A \rightarrow P$ is 1.0, 0.5, 0.33, 0.25 mol $dm^{-3}$ at $t = 0$, 1, 2 and 3 seconds, respectively. The order of the reaction is—
(A) Two (B) One
(C) Zero (D) There

38. The difference in energy levels of $n = 2$ and $n = 1$ of a particle in a one dimensional box is 6 units of energy . In the same units, what is the difference in energy levels of $n = 3$ and $n = 2$ for the above system ?
(A) 4 (B) 5
(C) 9 (D) 10

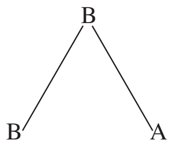
39. The wave function $\psi$ of a certain system is the linear combination

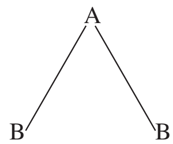
$$\psi = \sqrt{\frac{1}{4}}\psi_1 + \sqrt{\frac{3}{4}}\psi_2$$

where $\psi_1$ and $\psi_2$ are energy eigen functions with eigen values (non-degenerate) $E_1$ and $E_2$, respectively. What is the probability that the system energy will be observed to be $E_1$ ?
(A) $\sqrt{\frac{3}{16}}$ (B) $\frac{3}{4}$
(C) $\frac{1}{4}$ (D) $\sqrt{\frac{1}{4}}$

40. What is the atomic term symbol for helium atom with electronic configuration $1s^2$ ?
(A) $^2S_{1/2}$ (B) $^1P_0$
(C) $^1S_0$ (D) $^1S_1$

41. A molecule contains the following symmetry operations : E, $2C_6$, $2C_3$, $C_2$, $3\sigma_d$, $3\sigma_v$. The number of classes and order of the symmetry point group is—
(A) 3, 12 (B) 5, 12
(C) 6, 12 (D) 6, 6

42. A triatomic molecule of the type $AB_2$ shows two IR absorption lines and one IR-Raman line. The structure of the molecule is—
(A) B–B–A (B) B–A–B
(C) 

(D) 


43. In NMR spectroscopy, the product of the nuclear '$g$' factor ($g_N$), the nuclear magneton ($\beta_N$) and the magnetic field strength ($B_0$) gives the—
(A) Energy of transition from $\alpha$ to $\beta$ state
(B) Chemical shift
(C) Spin-spin coupling constant
(D) Magnetogyric ratio

44. An aqueous mixed solution of NaCl and HCl is exactly neutralized by an aqueous NaOH solution. The number of components in the final mixture is—
(A) 1 (B) 2
(C) 3 (D) 4

45. The lowest pressure at which the liquid phase of a pure substance can exist is known as—
(A) Critical point pressure
(B) Super-incumbent pressure
(C) Triple-point pressure
(D) Saturation vapour pressure

46. A chemical reaction involving non-linear molecule + non-linear molecule $\rightleftharpoons$ non-linear activated complex. The number of vibrational degrees of freedom in the activated complex, containing N atoms, is—
(A) 3N – 5 (B) 3N – 6
(C) 3N – 7 (D) 3N – 8

47. Calculate the total number of microstates for 6 identical particle with their occupation numbers {1, 2, 3} in three states is—
(A) 6 (B) 12
(C) 60 (D) 720

48. If the concentration ($c$) is increased to 4 times its original value ($c$), the change in molar conductivity for strong electrolytes is (where $b$ is Kohlrausch constant)—
(A) 0 (B) $b\sqrt{c}$
(C) $2b\sqrt{c}$ (D) $4b\sqrt{c}$

49. In atom recombination reactions—
(A) $E_a = 0, \Delta S^{\#} = +ve, \Delta H^{\#} = +ve$
(B) $E_a = 0, \Delta S^{\#} = -ve, \Delta H^{\#} = -ve$
(C) $E_a = +ve, \Delta S^{\#} = -ve, \Delta H^{\#} = -ve$
(D) $E_a = +ve, \Delta S^{\#} = +ve, \Delta H^{\#} = +ve$

50. In the Lindemann mechanism of unimolecular reactions, the observed order at low concentration is—
(A) 0.5 (B) 1
(C) 1.5 (D) 2

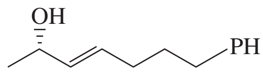
51. The aggregation of surfactant molecules is known as—
(A) Micelles (B) Clusters
(C) Gel (D) Colloid

52. The coordinates for the atoms in a body-centred cubic unit cell are—
(A) (0, 0, 0) and (1/2, 0, 0)
(B) (0, 0, 0) and (1/2, 1/2, 1/2)
(C) (0, 0, 0) and (0, 1/2, 0)
(D) (0, 0, 0) and (0, 0, 1/2)

53. The interplanar distance (Å) for (100) plane in a cubic structure with the lattice parameter of 4 Å is—
(A) 1 (B) 2
(C) 4 (D) 8

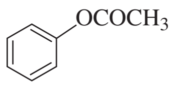
54. The correlation coefficient of two parameters is found to be –0.99. It may be concluded that the two parameters are—
(A) Strongly correlated
(B) Almost uncorrelated
(C) Connected by a cause-effect relationship
(D) Not connected by a cause-effect relationship

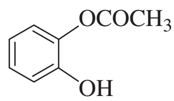
55. The IUPAC name for the compound given below is—

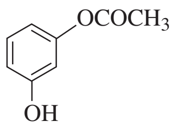


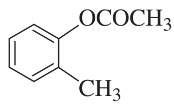

(A) (2R, 3Z)-7-phenylhept-3-en-2-ol
(B) (2S,3Z)-7-phenylhept-3-en-2-ol
(C) (2R,3E)-7-phenylhept-3-en-2-ol
(D) (2S,3E)-7-phenylhept-3-en-2-ol

56. Among the following esters, the one that undergoes acid hydrolysis fastest is—

(A) 

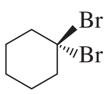
(B) 

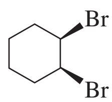
(C) 

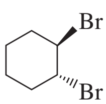
(D) 

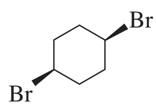

57. Reaction of cyclohexyl benzyl ether with hydrogen in the presence of 10% Pd/C yields—
(A) cyclohexanol and toluene
(B) cyclohexanol and benzyl alcohol
(C) cyclohexane and benzyl alcohol
(D) cyclohexane and toluene

58. Among the following dibromocyclohexanes, the one that reacts fastest with sodium iodide to give cyclohexene is—

(A) 

(B) 

(C) 

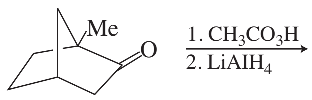
(D) 

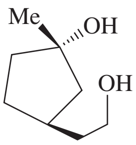
59. Match the following drugs with their medicinal activity—

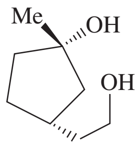
| | | | |
|---|---|---|---|
| (a) | 5-fluorouracil | 1. | Anti-bacterial |
| (b) | Amoxicillin | 2. | Cholesterol |
| | lowering | 3. | Anticancer |
| | | 4. | Anti-inflammatory |

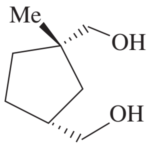
| | (a) | (b) |
|---|---|---|
| (A) | 1 | 2 |
| (B) | 4 | 3 |
| (C) | 3 | 4 |
| (D) | 3 | 1 |

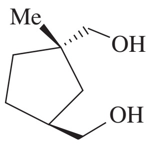
60. The major product formed in the following reaction sequence is—




(A) 


(B) 

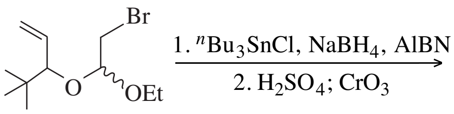

(C) 

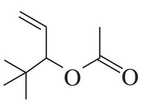

(D) 

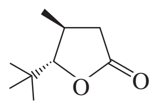

61. The biosynthetic precursor for the steroids is—

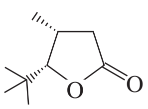
(A) Secologanin
(B) Shikimic acid
(C) Mevalonic acid
(D) α-ketoglutaric acid

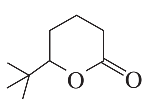
62. The major product formed in the following reaction sequence is—



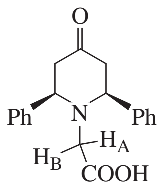

(A) 

(B) 

(C) 

(D) 

63. In the compound given below, the hydrogens marked A and B are—

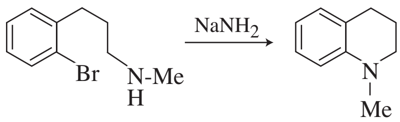



(A) Homotopic (B) Isotopic
(C) Enantiotopic (D) Diastereotopic

64. In the IR spectrum, the absorption band due to carbonyl group in phenyl acetate appears at—

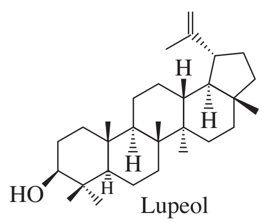
(A) 1800 $cm^{-1}$ (B) 1760 $cm^{-1}$
(C) 1710 $cm^{-1}$ (D) 1660 $cm^{-1}$

65. The reactive intermediate involved in the following reaction is—




(A) A carbocation (B) A carbanion
(C) A free radical (D) An aryne

66. Number of isoprene units present in lupeol is—



Lupeol

(A) Two (B) Four
(C) Six (D) Eight

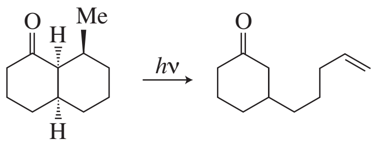
67. The heterocyclic ring present in the amino acid histidine is—

(A) Pyridine (B) Tetrahydropyrrole
(C) Indole (D) Imidazole

68. The *gauche* conformation (φ = 60°) of *n*-butane posseses—

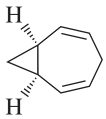
(A) Plane of symmetry; and is achiral
(B) $C_2$-axis of symmetry; and is chiral
(C) Centre of symmetry; and is achiral
(D) Plane of symmetry; and is chiral

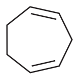
69. The following photochemical conversion proceeds through—

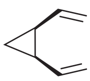


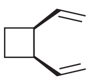

(A) Barton reaction
(B) Paterno-Buchi reaction
(C) Norrish type I reaction
(D) Norrish type II reaction

70. Among the following dienes, the one that undergoes a degenerate Cope rearrangement is—

(A) 


(B) 

(C) 

(D) 

## PART C

71. A radioisotope $^{41}Ar$ initially decays at the rate of 34,500 disintegrations/minute, but decay rate falls to 21,500 disintegrations/minute after 75 minutes. The $t_{1/2}$ for $^{41}Ar$ is—

(A) 90 minutes (B) 110 minutes
(C) 180 minutes (D) 220 minutes

72. The orders of reactivity of ligands, $NMe_3$, $PMe_3$ and CO with complexes $MeTiCl_3$ and $(CO)_5$ MO (thf) are—

(A) CO > $PMe_3$ > $NMe_3$ and CO > $NMe_3$ > $PMe_3$
(B) $PMe_3$ > CO > $NMe_3$ and $NMe_3$ > CO > $PMe_3$
(C) $NMe_3$ > $PMe_3$ > CO and CO > $PMe_3$ > $NMe_3$
(D) $NMe_3$ > CO > $PMe_3$ and $PMe_3$ > $NMe_3$ > CO

73. The number of lone-pairs are identical in the pairs—

(A) $XeF_4$, $ClF_3$ (B) $XeO_4$, $ICl_4^-$
(C) $XeO_2F_2$, $ICl_4^-$ (D) $XeO_4$, $ClF_3$

74. Among the following, those can act as Mossbauer nuclei are—

1. $^{129}I$ 2. $^{57}Co$
3. $^{57}Fe$ 4. $^{121}Sb$

(A) 1, 2, 3 and 4
(B) 2, 3 and 4 only
(C) 1, 2 and 4 only
(D) 1, 3 and 4 only

75. Which of the pairs will generally result in tetrahedral coordination complexes, when ligands are $Cl^-$ or $OH^-$—

1. Be(II), Ba(II) 2. Ba(II), Co(II)
3. Co(II), Zn(II) 4. Be(II), Zn(II)

(A) 1 and 2 (B) 2 and 3
(C) 3 and 4 (D) 1 and 4

76. Silica gel contains $[CoCl_4]^{2-}$ as an indicator. When activated, silica gel becomes dark blue while upon absorption of moisture, its colour changes to pale pink. This is because—

(A) Co(II) changes its coordination from tetrahedral to octahedral
(B) Co(II) changes its oxidation state to Co(III)
(C) Tetrahedral crystal field splitting is NOT equal to octahedral crystal field splitting
(D) Co(II) forms kinetically labile while Co(III) forms kinetically inert complexes

77. For the metalloprotein hemerythrin, the statement that is not true is—

(A) There are two iron centers per active site
(B) Both iron centres are hexacoordinated in the active state
(C) One iron is hexacoordinated while the other is pentacoordinated in the active state
(D) It is found in marine invertebrates

78. For a tetragonally distorted Cr(III) complex, zero-field splitting results in the following number of Kramers doublets—

(A) 1 (B) 2
(C) 3 (D) 4

79. Intense band at 15000 $cm^{-1}$ in the UV-visible spectrum of $[Bu_4N]_2$ $Re_2Cl_8$ is due to the transition—

(A) $\pi \rightarrow \pi^*$ (B) $\delta \rightarrow \delta^*$
(C) $\delta \rightarrow \pi^*$ (D) $\pi \rightarrow \delta^*$

80. Electron change in reduction of $Ce(SO_4)_2$, $KMnO_4$, $HNO_2$ and $I_2$ with hydrazine in acidic medium, respectively is—
(A) 1e, 1e, 2e and 4e
(B) 1e, 3e, 2e and 4e
(C) 2e, 3e, 1e and 4e
(D) 2e, 4e, 1e and 3e

81. The compound that will behave as an acid in $H_2SO_4$ is—
(A) $CH_3COOH$ (B) $HNO_3$
(C) $HClO_4$ (D) $H_2O$

82. Among the oxides of nitrogen, $N_2O_3$, $N_2O_4$ and $N_2O_5$, the compound(s) having N–N bond is/are—
(A) $N_2O_4$ and $N_2O_5$
(B) $N_2O_3$ and $N_2O_5$
(C) $N_2O_3$ and $N_2O_4$
(D) $N_2O_5$ only

83. The treatment of PhBr with *n*-BuLi yields—
(A) 2*n*-BuPh + $Br_2$ + $Li_2$
(B) PhPh + octane + 2LiBr
(C) *n*-BuPh + LiBr
(D) PhLi + *n*-BuBr

84. Though cyclobutadiene ($C_4H_4$) is highly unstable and readily polymerizes in its free state, its transition metal complexes could be isolated because—
(A) It engages in long-range interaction with transition metals
(B) It gains stability due to formation of $C_4H_4^{2-}$ on binding to transition metals
(C) Its polymerization ability reduces in presence of transition metal
(D) It becomes stable in presence of transition metals due to formation of $C_4H_4^{2+}$

85. Identify the order representing increasing π-acidity of the following ligands—
$C_2F_4$, $NEt_3$, CO and $C_2H_4$
(A) $CO < C_2F_4 < C_2H_4 < NEt_3$
(B) $C_2F_4 < C_2H_4 < NEt_3 < CO$
(C) $C_2H_4 < NEt_3 < CO < C_2F_4$
(D) $NEt_3 < C_2H_4 < C_2F_4 < CO$

86. The species with highest magnetic moment (spin only value) is—
(A) $VCl_6^{4-}$
(B) $(\eta^5\text{–}C_5H_5)_2Cr$
(C) $[Co(NO_2)_6]^{3-}$
(D) $[Ni(EDTA)]^{2-}$

87. The number of metal-metal bonds in $Ir_4(CO)_{12}$ is—
(A) 4 (B) 6
(C) 10 (D) 12

88. Three bands in the electronic spectrum of $[Cr(NH_3)_6]^{3+}$ are due to the following transitions :
1. $^4A_{2g} \rightarrow {^4T_{1g}}$ 2. $^4A_{2g} \rightarrow {^4T_{2g}}$
3. $^4A_{2g} \rightarrow {^2E_g}$
Identify the correct statement about them—
(A) Intensity of 1 is lowest
(B) Intensity of 3 is lowest
(C) Intensities of 1, 2 and 3 are similar
(D) Intensities of 2 and 3 are similar

89. Identify the pairs in which the covalent radii of elements are almost similar—
1. Nb, Ta 2. Mo, W
3. La, Lu 4. Sc, Y
(A) 1 and 2 only
(B) 1 and 3 only
(C) 2 and 3 only
(D) 1, 2 and 3 only

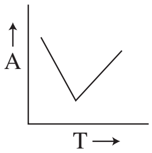
90. Consider the following lanthanide(III) ions :
1. Nd(III) 2. Gd(III)
3. Dy(III)
The magnetic moment closest to the spin only value is(are) for—
(A) 2 only (B) 1 and 2 only
(C) 1 and 3 only (D) 2 and 3 only

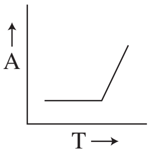
91. The $\Delta_t$ of the following complexes—
1. $[CoCl_4]^{2-}$
2. $[CoBr_4]^{2-}$ and
3. $[Co(NCS)_4]^{2-}$ follows the order
(A) 3 > 1 > 2 (B) 1 > 2 > 3
(C) 2 > 1 > 3 (D) 3 > 2 > 1

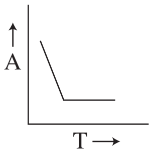
92. In complexometric titration

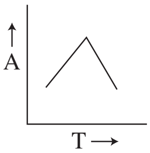
S(substrate) + T(titrant) $\rightarrow$ P(product)

The end point is estimated spectrophotometrically. If S and P have $\varepsilon = 0$, the shape of the titration curve would look like—

(A) 


(B) 


(C) 


(D) 


93. Identify the chiral complexes from the following—

1. $[Cr(EDTA)]^-$ 2. $[Ru(bipy)_3]^{3+}$
3. $[PtCl(diene)]^+$

(A) 1 only (B) 1 and 2 only
(C) 1 and 3 only (D) 2 and 3 only

94. Distribution ratio of 'A' between $CHCl_3$ and water is 9.0. It is extracted with several, 5 mL aliquot of $CHCl_3$. The number of aliquots needed to extract 99.9% of 'A' from its 5 mL aqueous solution are—

(A) 2 (B) 3
(C) 4 (D) 5

95. The correct equilibrium order for the interconversion of different forms of $SiO_2$ is—

(A) Tridymite $\rightleftharpoons$ quartz $\rightleftharpoons$ cristobalite $\rightleftharpoons$ liquid $SiO_2$

(B) Quartz $\rightleftharpoons$ tridymite $\rightleftharpoons$ cristobalite $\rightleftharpoons$ liquid $SiO_2$

(C) Quartz $\rightleftharpoons$ cristobalite $\rightleftharpoons$ tridymite $\rightleftharpoons$ liquid $SiO_2$

(D) Cristobalite $\rightleftharpoons$ tridymite $\rightleftharpoons$ quartz $\rightleftharpoons$ liquid $SiO_2$

96. The rate equation for the reaction, $2AB + B_2 \rightarrow 2\,AB_2$, is given by

$$\text{rate} = k\,[AB]\,[B_2]$$

A possible mechanism consistent with this rate law is—

(A) $2AB + B_2 \xrightarrow{\text{slow}} 2AB_2$

(B) $AB + AB \rightleftharpoons A_2B_2$ (fast)

$A_2B_2 + B_2 \xrightarrow{\text{slow}} 2AB_2$

(C) $AB + B_2 \xrightarrow{\text{slow}} AB_3$

$AB_3 + AB \xrightarrow{\text{fast}} 2AB_2$

(D) $AB + B_2 \rightleftharpoons AB_3$ (fast)

$AB_3 + AB \xrightarrow{\text{slow}} 2AB_2$

97. Observe the following statements—

1. In the $H_2$–$O_2$ reaction, explosion occurs when the rate of chain branching exceeds that of chain termination.
2. The order of the reaction, $nA \rightarrow$ products, is 2.5. For this reaction, $t_{1/2} \propto [A]_0^{-3/2}$
3. Unimolecular gas phase reactions are second order at low pressure but become first order at high pressure.

Which of the following is correct ?

(A) 1, 2 and 3 are correct
(B) Only 2 is correct
(C) Only 3 is correct
(D) 1 and 2 are correct

98. For the particle-in-a-box problem in (0, L), an approximate wave function is given as $x\,(L/2 - x)\,(L - x)$. The average energy $\bar{E}$ for such a state will obey—

(A) $\frac{h^2}{8mL^2} < \bar{E}\ \frac{h^2}{2mL^2}$ (B) $\bar{E} > \frac{h^2}{2mL^2}$

(C) $\frac{h^2}{4mL^2} < \bar{E} < \frac{h^2}{2mL^2}$ (D) $0 < \bar{E} < \frac{h^2}{8mL^2}$

99. For two variables $x$ and $y$, the following data set is given :

| $x$ | $y$ |
|---|---|
| –1 | 1 |
| 0 | 2 |
| 1 | 3 |

The correct statement for the covariance A and correlation coefficient B of $x$ and $y$ is—

(A) A = 2/3, B = 1
(B) A = –2/3, B =1
(C) A = –2/3, B = –1
(D) A = 0, B = 0

100. The hydrogenic orbital with the form of the radial function
$r^2$ ($\alpha_1 - r$) ($\alpha_2 - r$) exp [$-\beta r$], where $\alpha_1\alpha_2$ and $\beta$ are constants, may be identified as a—
(A) 3*d* orbital (B) 4*f* orbital
(C) 5*d* orbital (D) 5*f* orbital

101. The operator $[x, [x, p^2]]$ is identical with—
(A) $[px, [x, p]]$ (B) $[xp, [x, p]]$
(C) $-[p, [x^2, p]]$ (D) $[x, [x^2, p]]$

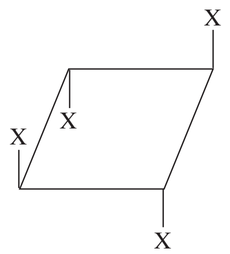
102. For the particle-in-a-box problem in (0, L), the value of $\langle x^3 \rangle$ in the $n \rightarrow \infty$ limit would be—
(A) $L^3/6$ (B) $L^3/3$
(C) $L^3/4$ (D) $L^4/4$

103. Identity the Mulliken notation for the following irreducible representation

| E | $E_n$ | $^nC_2$ | $i$ | $\sigma_h$ |
|---|---|---|---|---|
| 1 | 1 | –1 | –1 | –1 |

(A) $A'_{1u}$ (B) $A''_{2u}$
(C) $B'_{2u}$ (D) $A'_{2u}$

104. Identify the point group symmetry of the following molecule (all C–C bond lengths are equal)—




(A) $C_{2v}$ (B) $S_4$
(C) $D_{2d}$ (D) $D_{4d}$

105. The ground state term symbol for N*b* (atomic number 41) is $^6D$. The electronic configuration corresponding to this term symbol is—
(A) [Kr] $4d^3\ 5s^2$ (B) [Kr] $4d^4\ 5s^1$
(C) [Kr] $4d^5\ 5s^0$ (D) [Kr] $4d^3\ 5s^1 5p^1$

106. In the presence of an external magnetic field (normal Zeeman effect), the transition $^1D_2 \rightarrow {}^1P_1$ splits into—
(A) 9 lines (B) 8 lines
(C) 7 lines (D) 6 lines

107. Identify the Hückel determinant for cyclobutadiene—

(A) $\begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{vmatrix}$

(B) $\begin{vmatrix} \alpha - E & \beta & 0 & \beta \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ \beta & \beta & 0 & \alpha - E \end{vmatrix}$

(C) $\begin{vmatrix} \alpha - E & \beta & 0 & \beta \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ \beta & 0 & \beta & \alpha - E \end{vmatrix}$

(D) $\begin{vmatrix} \alpha - E & \beta & 0 & \beta \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{vmatrix}$

108. On mixing 120 mL of 0.05 M $CH_3COOH$ and 40 mL of 0.05 M of NaOH, the pH of the solution is—
($pK_a = -\log K_a$)
(A) $pK_a + 0.69$ (B) $pK_a + 0.301$
(C) $pK_a$ (D) $pK_a - 0.69$

109. A system consists of gaseous $H_2$, $O_2$, $H_2O$ and $CO_2$ where the amount of $CO_2$ is specified and the equilibrium constant for the reaction $2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g)$ is known. The number of degrees of freedom of the system is—
(A) 2 (B) 3
(C) 4 (D) 5

110. "Colloids are thermodynamically unstable with reference to bulk but kinetically stable". Identify the correct pair—

| **Statements** | **Reasons** |
|---|---|
| (a) Thermodynamically | (c) Interfacial surface tension |
| (b) Kinetically stable | (d) Electrical double layer |

(A) (a) ↔ (d) and (b) ↔ (c)
(B) (a) ↔ (c) and (b) ↔ (d)
(C) (a) ↔ (c) and (b) ↔ (c)
(D) (a) ↔ (d) and (b) ↔ (d)

111. An AX system gave 4 lines at 4.72, 4.6, 1.12 and 1.0 ppm away from TMS using an nmr spectrometer operating at 100 MHz. What are the values of $J_{AX}$ (in Hz) and $\delta_{AX}$ (in ppm), respectively ?

(A) 12 and 3.6 (B) 6 and 3.6

(C) 12 and 2.86 (D) 6 and 2.86

112. The equilibrium population ratio ($n_j/n_i$) of a doubly-degenerate energy level ($E_j$) lying at energy 2 units higher than a lower nondegenerate energy level ($E_i$), assuming $k_BT$ = 1 unit, will be—

(A) $2e^{-2}$ (B) $2e^2$

(C) $e^2$ (D) $e^{-2}$

113. Which of the following statements is true for a cyclic process ?

(A) $\oint dq = 0$

(B) $\oint dw = 0$

(C) Heat can be completely converted into work

(D) Work can be completely converted into heat

114. Identify, from the following, the correct ionic strengths for (a) a 0.01 molal solution of NaCl and (b) a 0.01 molal solution of $Na_2SO_4$—

(A) (a) 0.010 mol kg$^{-1}$ (b) 0.010 mol kg$^{-1}$

(B) (a) 0.010 mol kg$^{-1}$ (b) 0.030 mol kg$^{-1}$

(C) (a) 0.010 mol kg$^{-1}$ (b) 0.025 mol kg$^{-1}$

(D) (a) 0.010 mol kg$^{-1}$ (b) 0.015 mol kg$^{-1}$

115. A system has 100 degenerate energy levels and 100 bosons are kept in it. Find the entropy of the system at equilibrium—

(A) $10^{-2}$ $k_B$ (B) $10^2$ $k_B$

(C) 460.6 $k_B$ (D) 4.606 $k_B$

116. Which is correct Nernst equation for redox reaction O + $ne$ $\rightleftharpoons$ R ?

(A) $E = E^0 - \frac{RT}{nF} \ln \frac{[O]}{[R]}$

(B) $\frac{[O]}{[R]} = e^{\frac{nF}{RT}(E - E^0)}$

(C) $\frac{[O]}{[R]} = e^{-\frac{nF}{RT}(E - E^0)}$

(D) $\frac{[O]}{[R]} = e^{\frac{RT}{nF}(E - E^0)}$

117. A plane of spacing $d$ shows first order Bragg diffraction at angle $\theta$. A plane of spacing $2d$—

(A) Shows Bragg diffraction at $2\theta$

(B) Shows Bragg diffraction at $\theta/2$

(C) Shows Bragg diffraction at $\sin^{-1}\left(\frac{\sin\theta}{2}\right)$

(D) Shows Bragg diffraction at $\sin^{-1}\left(\frac{\sin 2\theta}{2}\right)$

118. In the formation of $H_2$ molecule from 2H atoms placed at positions A and B, and separated by a distance $r_{AB}$, a part of the spatial wave function is—

$$\varphi_A(1)\, \varphi_A(2) + \varphi_B(1)\, \varphi_B(2)$$

(A) This is a covalent term and is important as $r_{AB} \to \infty$

(B) This is an ionic term and is important as $r_{AB} \to \infty$

(C) This is a covalent term and is important as $r_{AB} \to 0$

(D) This is an ionic term and is important as $r_{AB} \to 0$

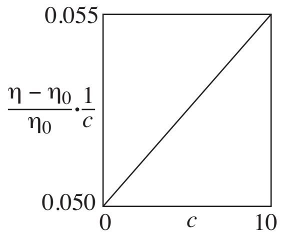
119. A 0.1 M solution of compound A shows 50% transmittance when a cell of 1 cm width is used at $\lambda_1$ nm. Another 0.1 M solution of compound B gives the optical density value of 0.1761 using 1 cm cell at $\lambda_1$ nm. What will be the transmittance of a solution that is simultaneously 0.1 M in A and 0.1 M in B using the same cell and at the same wavelength ?

(log 20 = 1.301; log 30 = 1.4771; log 50 = 1.699)

(A) 33.3% (B) 50%

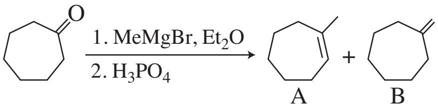
(C) 66.7% (D) 70%

120. Using standard equation for intrinsic viscosity $[\eta] = K\overline{M}_v^a$, for a solution of polymer and any information from the graph identify viscosity-average molar mass ($\overline{M}_v$) [given that $a = 0.5$, $K = 5 \times 10^{-5}$ Lg$^{-1}$].



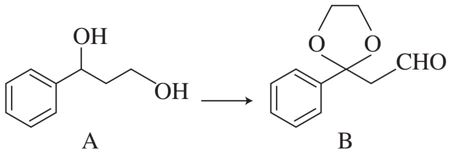

(A) $10^3$ g/mol (B) $10^4$ g/mol
(C) $10^5$ g/mol (D) $10^6$ g/mol

121. Among the following, the correct statement for the following reaction is—



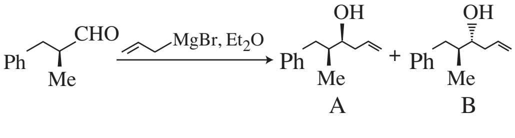

(A) A is the major product and it will have five signals in the proton decoupled $^{13}C$ NMR spectrum
(B) A is the minor product and it will have eight signals in the proton decoupled $^{13}C$ NMR spectrum
(C) B is the major product and it will have five signals in the proton decoupled $^{13}C$ NMR spectrum
(D) B is the minor product and it will have five signals in the proton decoupled $^{13}C$ NMR spectrum

122. For the following three step conversion of A to B, the appropriate sequence of reactions is—



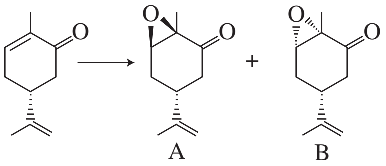

(A) $MnO_2$; $(CH_2OH)_2$/*p*-TSA; PCC
(B) PCC; $MnO_2$; $(CH_2OH)_2$/*p*-TSA
(C) PCC; $(CH_2OH)_2$/*p*-TSA; Jones' reagent
(D) Jones' reagent; $(CH_2OH)_2$/*p*-TSA; $MnO_2$

123. Which one of the following statements is true for the following transformation ?



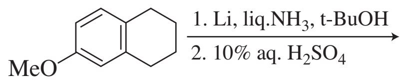

(A) A is the major product and it is Cram product
(B) A is the major product and it is anti-Cram product
(C) B is the major product and it is a Cram product
(D) B is the major product and it is anti-Cram product

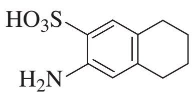
124. Which one of the following statements is true for the following transformation ?

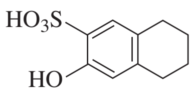


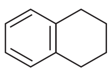

(A) Suitable reagent is *m*-CPBA and B is the major product
(B) Suitable reagent is *m*-CPBA and A is the major product
(C) Suitable reagent is aq. $H_2O_2$/NaOH and B is the major product
(D) Suitable reagent is aq. $H_2O_2$/NaOH and A is the major product

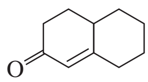
125. The compound formed in the following reaction sequence is—



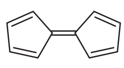
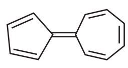

(A) 

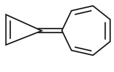
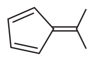

(B) 


(C) 

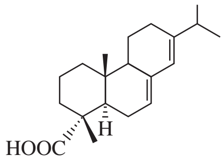
(D) 

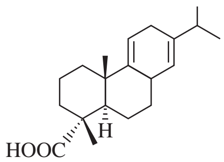

126. Among the following compounds, the one which has highest dipole moment is—

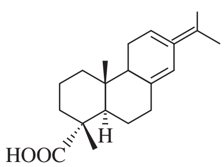
(A)  (B) 

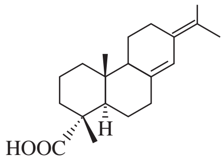
(C)  (D) 

127. In the UV-Vis spectrum, a diterpenoid exhibited a $\lambda_{max}$ at 275 nm. The compound, among the choices given below, is—

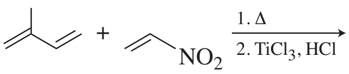
(A) 

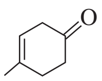
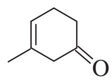
(B) 

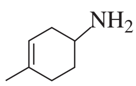
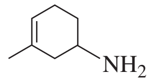
(C) 

(D) 

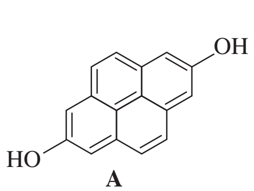
128. The major product formed in the following reaction is—



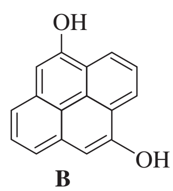
(A) 
(B) 

(C) 
(D) 

129. In the broadband decoupled $^{13}C$ NMR spectrum, the number of signals appearing for the two pyrenediols A and B, respectively, are—



**A**



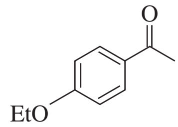
**B**

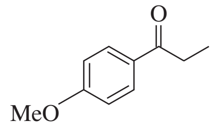
(A) Eight and eight (B) Eight and sixteen

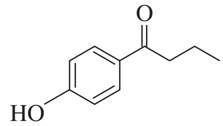
(C) Five and ten (D) Five and eight

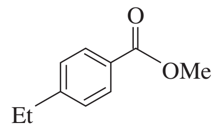
130. An organic compound exhibited the following $^1H$ NMR spectral data :

δ 7.80 (2, H, d, J = 8 Hz), 6.80 (2 H, d, J = 8 Hz), 4.10 (2 H, q, J = 7.2 Hz); 2.4 (3 H, s), 1.25 (3 H, t, J = 7.2Hz). The compound, among the choices given below, is—

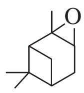
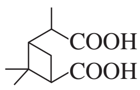
(A) 

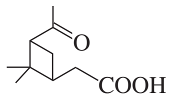
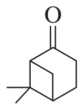
(B) 

(C) 

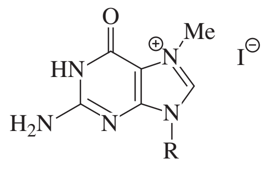
(D) 

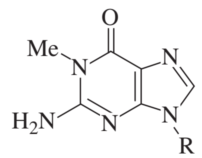
131. α-Pinene on reaction with dilute alkaline $KMnO_4$ produces a diol, which on further oxidation with chromium trioxide gives product A, which undergoes a positive haloform test. The compound A is—

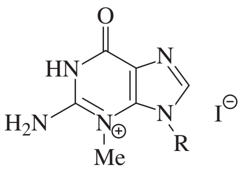
(A) 
(B) 

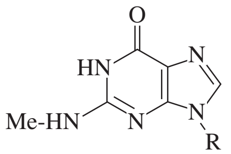
(C) 
(D) 

132. The major product formed in the reaction of guanosine with one equivalent of methyl iodide is—

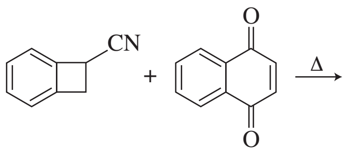
(A) 

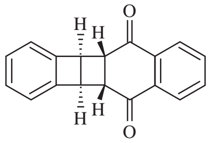
(B) 

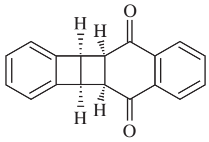
(C) 

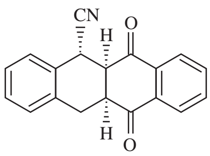

(D) 

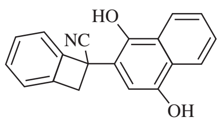

133. The major product formed in the following reaction is—



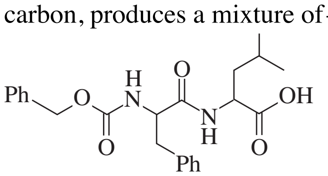

(A) 

(B) 

(C) 


(D) 


134. Reaction of the dipeptide, given below, with hydrogen in the presence of 10% palladium over carbon, produces a mixture of—



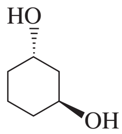

(A) Gly-Leu + toluene + carbon dioxide

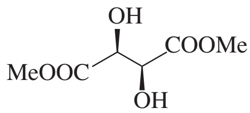
(B) Phe-Leu + toluene + carbon dioxide

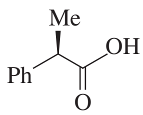
(C) Phe-Leu + benzyl alcohol + carbon dioxide

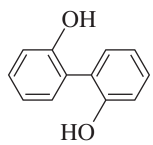
(D) Gly-Leu + benzyl alcohol + carbon dioxide

135. Among the following, the most suitable reagent for carrying out resolution of racemic 3-methylcyclohexanone is—

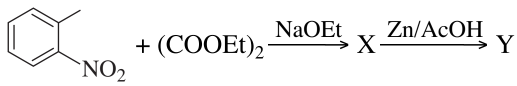
(A) 

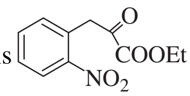

(B) 

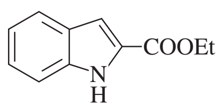

(C) 

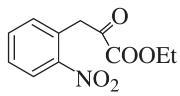

(D) 

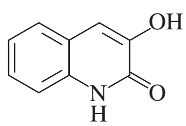

136. In the following reaction sequence, structures of the major products X and Y are—

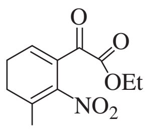
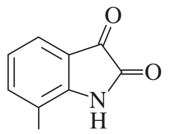


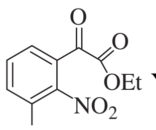
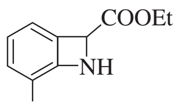

(A) X is 


Y is 

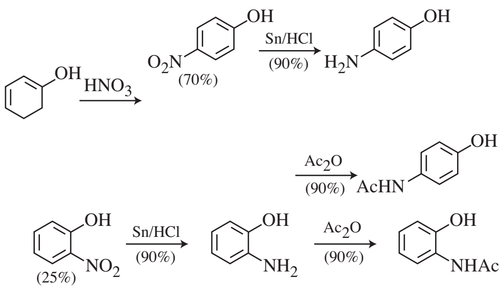

(B) X is 


Y is 

(C) X is  Y is 

(D) X is  Y is 

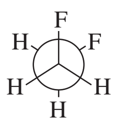
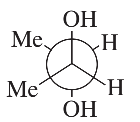
137. Consider the following reaction sequence :

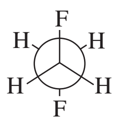
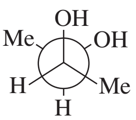


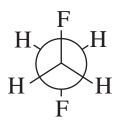
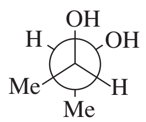

The overall yield for the formation of *p*-hydroxyacetanilide and *o*-hydroxyacetanilides from phenol, respectively, are approximately—

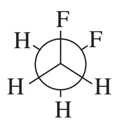
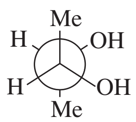
(A) 57 and 20% (B) 57 and 68%
(C) 83 and 68% (D) 83 and 20%

138. The most stable conformations of 1, 2–difluoroethane and *dl*-2,3-butanediol are—

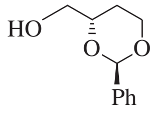
(A)  and 

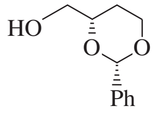
(B)  and 

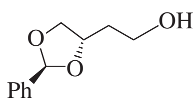
(C)  and 

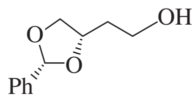
(D)  and 

139. Reaction of (S)-1,2,4-butanetriol with benzaldehyde in the presence of a catalytic amount of *p*-TSA furnished the major product A. The structure of A is—

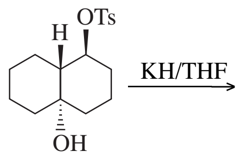
(A) 

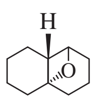
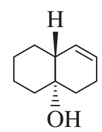
(B) 

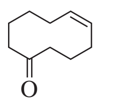
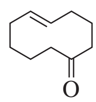
(C) 

(D) 

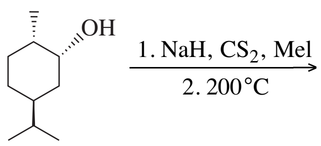
140. The major product formed in the following reaction is—

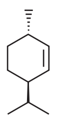
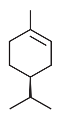


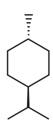
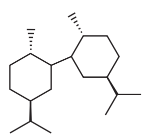

(A)  (B) 

(C)  (D) 

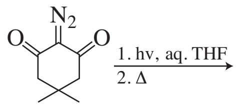
141. The major product formed in the following reaction is—

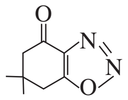
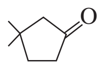


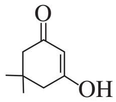
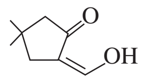

(A)  (B) 

(C)  (D) 

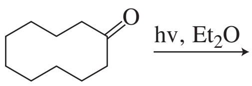
142. The major product formed in the following reaction is—

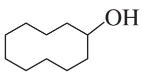
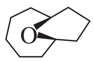


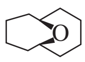
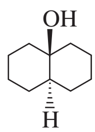

(A)  (B) 

(C)  (D) 

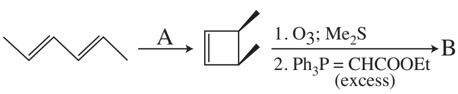
143. The major product formed in the following reaction is—

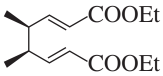


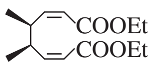

(A)  (B) 

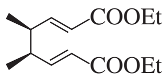
(C)  (D) 

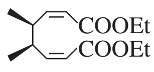
144. Predict the condition A and the structure of the major product B in the following sequence—



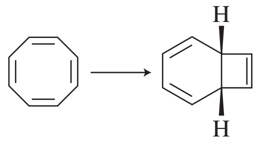

(A) A is *hv* B is 

(B) A is *hv* B is 

(C) A is Δ B is 

(D) A is Δ B is 

145. The most appropriate mode of cyclisation in the following transformation is—




(A) Con-rotatory in photochemical; and dis-rotatory in thermal conditions
(B) Con-rotatory in thermal; and dis-rotatory in photochemical conditions
(C) Con-rotatory in thermal; and con-rotatory in photochemical conditions
(D) Dis-rotatory in photochemical; and dis-rotatory in thermal conditions

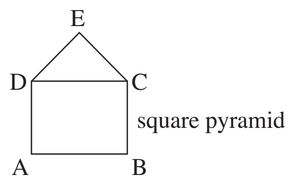
# Answers with Hints

## Part–A

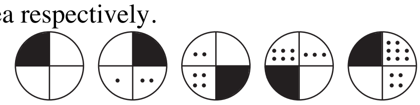
1. (C) Ms. Black → brown; Ms. Brown → white; Ms. White → black

| Ms. Black | Ms. Brown | Ms. White |
|---|---|---|
| ↓ | ↓ | ↓ |
| brown | white | black |

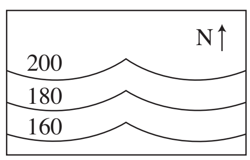
Each bears different colour dress according to their name.
2. (A)
3. (D)




Only one cut is required as ABCEDA is formed without cut and then after one cut CD is made.
4. (C) For every next figure, dark cut is rotating clockwise with one part adjacent to next and small circles are increasing 2 and 1 adjacent to dark area and next after adjacent to dark area respectively.



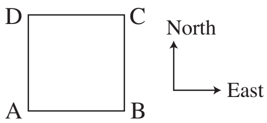
5. (A)
6. (B)




Since inverted 'V' shaped portions of contour lines represent a valley along which a river flows and that direction is north according to given figure. Thus, the downstream direction of the river is south.

7. (D)

8. (D)




Since, there is square and allowed only to North and East direction move the total distance travelled by the person is same for all paths.

9. (D) 10. (A) 11. (B) 12. (C) 13. (B)

14. (C) 15. (D) 16. (B) 17. (D) 18. (B)

19. (D) 20. (B)

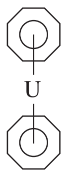
## Part–B

21. (D) As we go down the group in periodic table for sodium family, the number of electrons increases and their attraction towards nucleus increases and removal of $e^-$ become difficult. So Na loses $e^-$ s very easily.

In the case of inert gas family, Ne has its complete octet, strongly connected with nucleus $e^-$ attraction and do not give $e^-$s to lose easily.

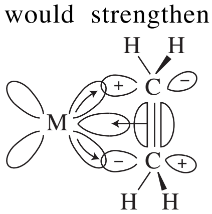
Thus Na, Ne pair have highest difference in their first ionization energy in given option.

22. (A) The structure of uranocene is $U^{+4} (C_8H_8^{-2})_2$.



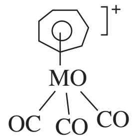

Most stable actenocene.

23. (C) In Metal-Olefin interaction, the extent of increase in metal → Olefin π-back donation would strengthen the Metal-Olefin bond




which produces a increase in C = C bond length and somewhat single bond character which results a change in hybridisation from $sp^2$ to $sp^3$.

24. (C) $[(n^7\text{–tropylium}) Mo(CO)_3]^+$

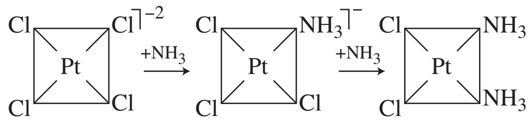



In zero oxidation state of Mo, complex have 18 $e^-$ (stable)

$$7 + 6 + 6 - 1 = 18$$

tropylium is a $7e^-$ donor ligand in neutral method.

25. (A)

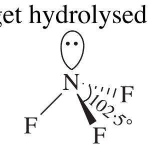



Cis-platin (anticancer drug)

$Cl^-$ have more trans directing ability than $NH_3$.

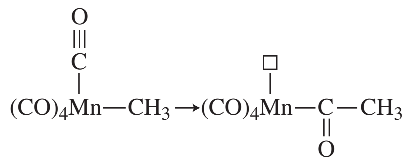
26. (A) 27. (C) 28. (C) 29. (A) 30. (C)

31. (C) Among given compounds $NF_3$ is not hydrolyse easily because, the more electronegative F atom strongly attracts the $e^-$s present in N atom and they are no longer available to get hydrolysed.

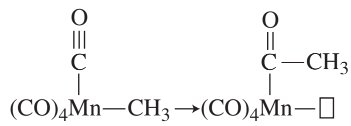



32. (D) 33. (A)

34. (D)




(Co insertion)




(methyl migration)

□ = vacant site

So overall migratory insertion.

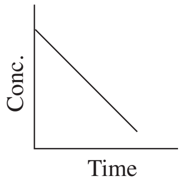
35. (A)

36. (A) Neutron activation analysis is a sensitive multi-element analytical technique used for both qualitative and quantitative analysis of major, minor, trace and rare elements. It requires high neutron cross-section area of target and long half-life of the product.

37. (C) $A \rightarrow P$

$$\text{rate} = -\frac{d[A]}{dt}$$

$$\Rightarrow \quad [A]_t = [A]_0 - n\,Kt$$




From given observation, we find this graph and it indicates that order of reaction is zero.

38. (D) For a particle in a one dimensional box energy is given as

$$E_n = \frac{n^2h^2}{8\,ma^2}$$

where $a$ is length of box, $m$ is mass of particle. Thus,

$$E_1 = \frac{h^2}{8\,ma^2}$$

and $$E_2 = \frac{4h^2}{8\,ma^2}$$

So, $$E_2 - E_1 = \frac{3h^2}{8\,ma^2}$$
$$= 6 \text{ units of energy}$$

Therefore, $$E_3 - E_2 = (9-4)\frac{h^2}{8\,ma^2}$$
$$= 5 \times 2$$
$$= 10 \text{ units of energy}$$

39. (C)

40. (C) $2^{He}$ : $1S^2$    1S
⇅

Electronic term symbol $= {}^{2S+1}L_J$

$$S = \frac{n}{2} = 0$$
$$\Rightarrow \quad 2S + 1 = 1$$
$$L = 0\,(S)$$
$$J = 0$$

Thus, term symbol for He $= {}^1S_0$

41. (C) Symmetry operation : $E, {}^2C_6, {}^2C_3, C_2, 3\sigma_d, 3\sigma_v$ symmerty operations with different symmetry element is equal to number of classes

$= 6$

order of the symmetry point group

$= 1 + 2 + 2 + 1 + 3 + 3$

$= 12$

42. (B) In triatonic centrosymmetric molecule, the vibrational mode which are active in IR, are inactive in Raman and *vice-versa*. Thus $AB_2$ molecule showing two IR absorption lines and one IR–Raman line have following structure—

$$\overleftarrow{B} - A - \overrightarrow{B}$$

asymmetric stretching and bending → IR active symmetric stretching → IR-Raman active

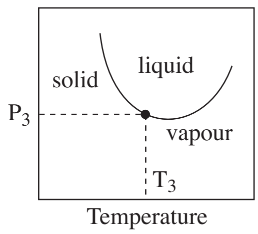
43. (A) In NMR spectroscopy energy of transition from α to β state is given as :

$$V_{\alpha \rightarrow \beta} = g_N\beta_N B_0$$

44. (B) $\underset{(aq)}{NaCl + HCl} \xrightarrow[\text{Neutralization}]{\text{aq. NaOH}} \underset{\text{2 components}}{2\,NaCl + H_2O}$

There are no HCl and NaOH in final mixture.

45. (C)




The lowest pressure at which the liquid phase of a pure substance can exist is known as 'Triple-point pressure'.

46. (C)

47. (C) Number of microstates

$$= \frac{\lfloor n}{\lfloor n_1 \,\lfloor n_2 \,\lfloor n_3 \,\ldots\ldots}$$

where $n$ is total identical particles and $n_1$, $n_2$, $n_3$ are occupation number.

Thus, $$= \frac{\lfloor 6}{\lfloor 1 \,\lfloor 2 \,\lfloor 3}$$
$$= \frac{6 \times 5 \times 4 \times \lfloor 3}{1 \times 2 \times 1 \times \lfloor 3}$$
$$= 60$$

48. (B)    49. (B)

50. (D) Lindeman Mechanism :

$$A + A \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} A^* + A$$
$$A^* \xrightarrow{K_2} D$$

Rate of formation of product $= K_2\,[A^*]$

Applying SSA on $[A^*]$

$$\frac{d[A^*]}{dt} = K_1[A]^2 - K_{-1}[A^*]\ [A] - K_2[A]^* = 0$$

$$[A^*] = \frac{K_1[A]^2}{K_{-1}[A] + K_2}$$

$$\text{Rate} = \frac{K_2K_1[A]^2}{K_{-1}[A] + K_2}$$

If $K_2 >> K_{-1}[A]$ at low concentration

$$\text{Rate} = K_1[A]^2$$

Second order kinetics.

51. (A)
52. (B) When coordinates are changed with one axis, the unit cell is simple cubic, when changes with two axis, it is face-centred cubic.

Thus, when coordinates are changed with three axis, the unit cell is body centred cubic.

$(0, 0, 0)$ to $\left(\frac{1}{2}, 0, 0\right)$ – simple cubic

$(0, 0, 0)$ to $\left(\frac{1}{2}, \frac{1}{2}, 0\right)$ – f.c.c.

$(0, 0, 0)$ to $\left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right)$ – b.c.c.

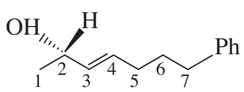
53. (C) For cubic system, interplanar distance is given as

$$d_{hkl}^2 = \frac{a^2}{h^2 + k^2 + l^2}$$

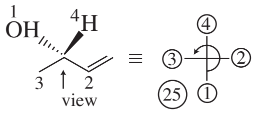
Thus, $$d_{100}^2 = \frac{4^2}{1^2 + 0^2 + 0^2} = 16$$

$\Rightarrow$ $$d_{100} = 4\ \text{Å}$$

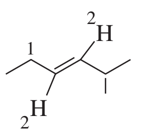
54. (A)
55. (D)




For, 2-position




For, 3–position

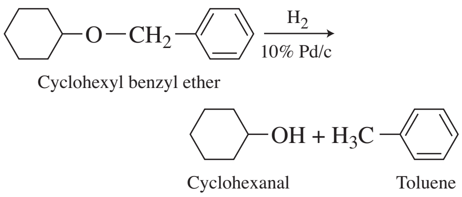


≡ 3E

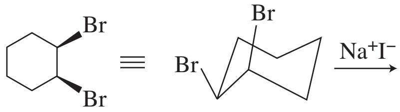
Thus, IUPAC Name is originated as

(2S, 3E)–7–Phenylhept-3-en-2-ol

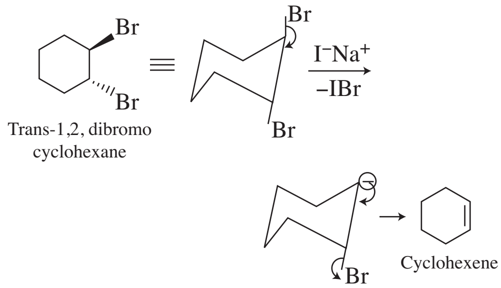
56. (B)
57. (A)



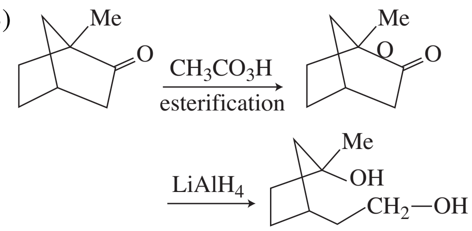

58. (C)



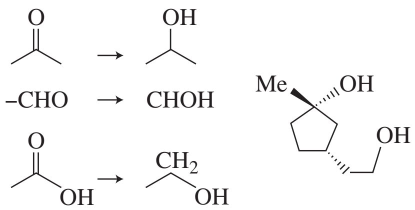

no available position to form cyclohexene



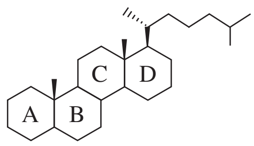

59. (D)
60. (B)




$LiAlH_4$ reduces as

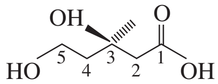



61. (C) Steroids are type of organic compound that contains a characteristic arrangement of four cycloalkane ring that are joined to each other as—



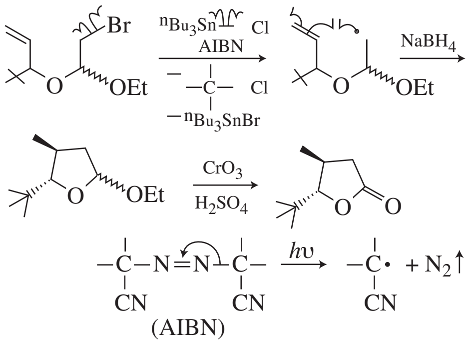

cholestane, a polytypical steroid skeleton

Mevalonic Acid—

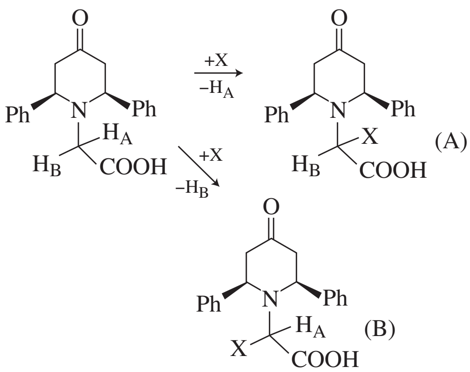



(3R)–3, 5–Dihydroxy-3-methyl pentanoic acid used as biosynthetic precursor for steroids.

62. (B)



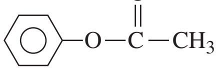

63. (C)




Structures (A) and (B) have non-superimposable mirror images,

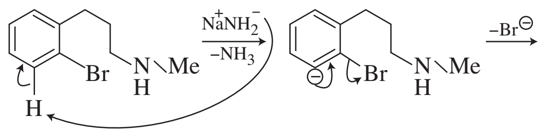
Thus, $H_A$ and $H_B$ are enantiotopic

64. (B)



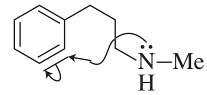

Ester group have carbonyl stretching frequency at 1765 to 1770. But due to phenyl ring, —O—atom involves in conjugation and – CO frequency decreases to 1760 cm$^{-1}$.

65. (D)

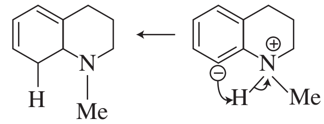



Proceeds through aryne intermediate

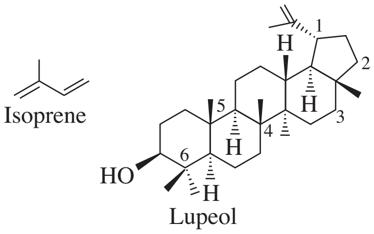
(aryne)
Benzyne intermediate




Six-membered ring is stable

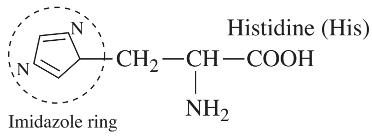



66. (C)

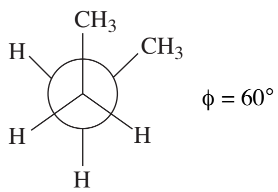



Six isoprene units in Lupeol is identified.

67. (D)



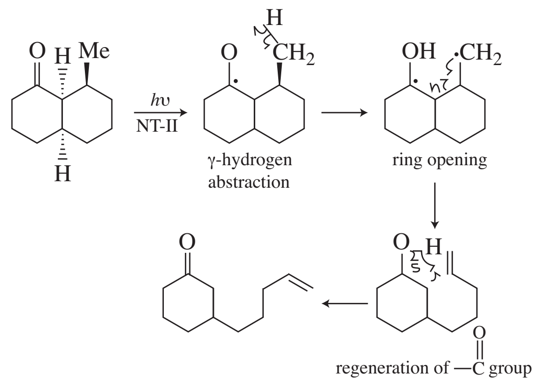

68. (B) Gauche conformation of *n*-butane with 60° dihedral angle (ϕ)



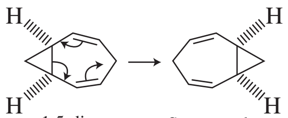

Staggered

$C_2$–axis bisects molecule with one methyl at each side (front & back) and is chiral, no plane of symmetry, no centre of symmetry.

69. (D)



70. (A)



1,5-diene      Same product

A molecular rearrangement in which the principal product is indistinguishable (in the absence of isotopic labelling) from the principal reactant, is known as 'degenerate rearrangement'.

## Part–C

71. (B) Initial decay,

$$N_O = 34500 \text{ disintegrations/minute}$$

After 75 minutes,

$$N_t = 21500 \text{ disintegrations/minute}$$

We know that, disintegration constant,

$$\lambda = \frac{2{\cdot}303}{t}\log\left(\frac{N_O}{N_t}\right)$$

$$= \frac{2{\cdot}303}{75}\log\left(\frac{34500}{21500}\right)$$

$$= 0{\cdot}00626$$

And, also $$t_{1/2} = \frac{0{\cdot}693}{\lambda} = \frac{0{\cdot}693}{0{\cdot}00626}$$

$$= 110{\cdot}7 \text{ minute}$$

72. (C) Since $MeTiCl_3$ have no $e^-$s for back donation with π-accepting ligands like $PMe_3$ and CO, therefore, It reacts in order

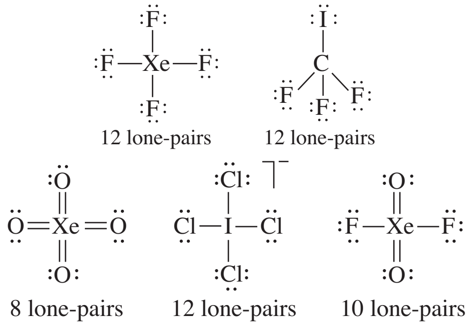
$$NMe_3 > PMe_3 > CO$$

(more π-accepting tendency)

Now, in $(CO)_5Mo(thf)$, Mo have sufficient $e^-$s and vacant site to react with π-acceptor ligand Thus, the order is

$$CO > PMe_3 > NMe_3$$

73. (A) In given option, only I is correct, if we consider only attached molecules lone-pairs,




74. (D) Mössbauer spectra are shown by nuclei which have value of I > O and also have different value of I in excited and ground state of nucleus.

Among given molecule, only $^{57}Co$ nuclei are mössbauer inactive because it decays as

$$^{57}_{27}Co \xrightarrow{1e^-} {}_{26}Fe^{57}$$

which is M.B. active, $^{129}I$ and $^{121}Sb$ is also active.

75. (C)

76. (A) $[CoCl_4]^{-2} \xrightarrow[\text{(H}_2\text{O) excess}]{\text{moisture}} [Co(H_2O)_6]^{+2}$

dark blue tetrahedral +2 O.S.     pale pink octahedral +2 O.S.

Tetrahedral complexes are darker in colour.

77. (B)    78. (B)

79. (B) $[Bu_4N]_2 Re_2Cl_8 \rightarrow 2\,NBu_4^+ + Re_2Cl_8^{-2}$

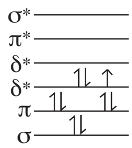
$R_e$ : $5d^5\,6s^2$

$R_e^{+++}$ : $5d^4$

$\sigma^2\pi^4\delta^2 \rightarrow \sigma^2\pi^4\delta^1\delta^{*1}$

15000 $cm^{-1}$

(Royal blue)




$\delta \rightarrow \delta^*$ transition

80. (A)

81. (C) (base) $CH_3COOH + H_2SO_4$

$$\rightarrow CH_3CO\overset{\oplus}{O}H_2 + HSO_4^-$$

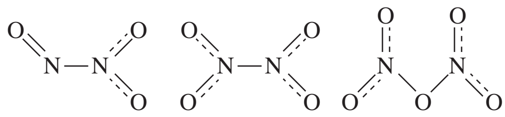
(base) $HNO_3 + H_2SO_4 \rightarrow H_2NO_3^{\oplus} + HSO_4^-$

(acid) $HClO_4 + H_2SO_4 \rightarrow ClO_4^- + H_3^{\oplus}SO_4^-$

behaves as acid

(base) $H_2O + H_2SO_4 \rightarrow H_3O^{\oplus} + HSO_4^-$

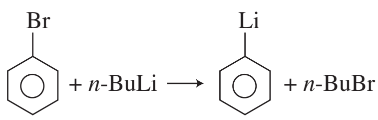
82. (C)

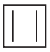


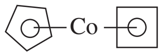
$N_2O_3$     $N_2O_4$     $N_2O_5$

$N_2O_3$ and $N_2O_4$ have N–N bond.

83. (D)



84. (B)  highly unstable and readily polymerises in its free state when binds with transition metal complexes, it gains stability due to formation of $C_4H_4^{2-}$, like




$18e^-$ species

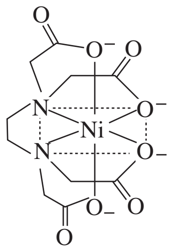
$4e^-$ donor
(stable)

85. (D) Among the given ligand CO is most π-acid ligand. Between $C_2H_4$ and $C_2F_4$, $C_2F_4$ has more tendency to behave as π-acid ligand due to more electronegative F atoms which holds $e^-$ density towards F atoms and alkene behaves as a better π-accepting position from metal. $NEt_3$ has very little behaviour towards π-back bonding. Thus, the order is

$$NEt_3 < C_2H_4 < C_2F_4 < CO$$

86. (A)

| $VCl_6^{-2}$ | $(\eta^5-C_5H_5)_2$ Cr | [Ni (EDTA)]$^{-2}$ |
|---|---|---|
| — — $e_g$ | — — $e_{1g}$ | ↿ ↿ $e_g$ |
| ↿ ↿ ↿ $t_{2g}$ | ↿ $a_{1g}$ | ⥮ ⥮ ⥮ $t_{2g}$ |
| | ⥮ ↿ $e_{2g}$ | |
| $\mu$ = 3·9 BM | $\mu$ = 2·9 BM | III $\mu$ = 2·9 BM |




— — $e_g$
⥮ ⥮ ⥮ $t_{2g}$

$[Co(NO_2)_6]^{-3}$ $\mu = 0$

Thus, $VCl_6^{-2}$ has highest magnetic moment.

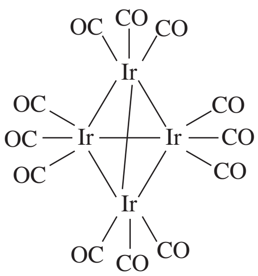
87. (B) Metal-Metal bonds

$$= \frac{n \times 18 - \text{Total no. of valence } e^- \text{s in complex}}{2}$$

$n$ = total no. of metals

$Ir_4(CO)_{12}$, CO is $2e^-$ donor ligand

Ir have 9 $e^-$s in valence shell



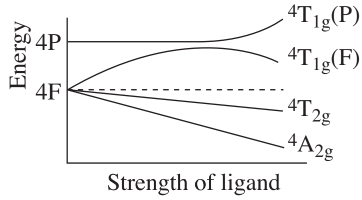

18 $e^-$ species
(Stable)

Thus,

$$\text{M–M bonds} = \frac{4 \times 18 - (4 \times 9 + 2 \times 12)}{2}$$

$$= \frac{72 - 60}{2} = 6$$

88. (B)




$[Cr(NH_3)_6]^{+3}$

$Cr^{+3}$ :

| +2 | +1 | 0 | −1 | −2 |
|---|---|---|---|---|
| 1 | 1 | 1 | | |

$2S + 1 = 4$

$L = 3$ (F)

$^4F$

$^4A_{2g} \longrightarrow {}^4T_{2g}$, $\longrightarrow {}^4T_{1g}$ } strong bands

Thus, $^4A_{2g} \rightarrow {}^2E_g$ intensity is lowest

89. (A) Due to lanthanide contraction, the covalent radii of Nb(1·34 Å), Ta(1·34Å) and Mo(1·29), W(1·30) are almost similar.

$$\text{Chemical Reactivity} = f\left(\frac{\text{Charge}}{\text{Radius}}\right)$$

No increase in covalent radii due to L.C.

90. (B) $\mu_S = \sqrt{n(n+2)}$

$$\text{Gd (III)}: \mu_S = \sqrt{\frac{7}{2}\left(\frac{7}{2}+2\right)} = \sqrt{\frac{7}{2} \times \frac{11}{2}}$$

$$= \frac{\sqrt{77}}{2} = 4{\cdot}38$$

$$\text{Nd (III)}: \mu_S = \sqrt{\frac{3}{2} \times \frac{7}{2}} = \frac{\sqrt{21}}{2} = 2{\cdot}29$$

91. (A) As strong field ligand have high crystal field stabilisation energy, according to spectrochemical series of ligand, the given ligand in order

$$Br^- < Cl^- < NCS^-$$

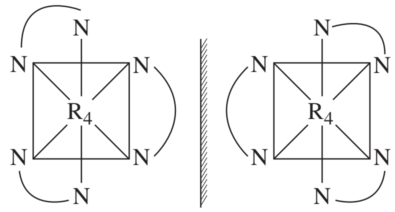
Thus, $\Delta_t$ of given complexes follow the order :

$$[Co(NCS)_4]^{-2} > [CoCl_4]^{-2} > [CoBr_4]^{-2}$$

92. (C)

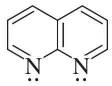
93. (B) (A) $[Cr(EDTA)]^-$ is a chiral molecule, having *d-l* pair (enanntiones) see structure of question 86 (iv)

(B)




Enantiomers (*d*–*l* pair)

where N⌒N = bypyridine




Optically active

(C) $[Pt\ Cl\ (diene)]^+$ has square planar structures so it is a chiral.

94. (C) 95. (B)

96. (C) $2\,AB + B_2 \rightarrow 2\,AB_2$

rate is given as :

$$\text{rate} = K\,[AB]\,[B_2]$$

According to this rate law, mechanism is

$$AB + B_2 \xrightarrow[K_1]{\text{slow}} AB_3$$

$$AB_3 + AB \xrightarrow[K_2]{\text{fast}} 2\,AB_2$$

$$\text{rate} = K_1\,[AB]\,[B_2],$$

slowest step is rate determining step.

97. (A) (i) As reaction proceed, pressure of system increases and radical become closer, so rate of propagation become fast. At a certain point radicals value become infinite and this responsible for explosion due to increase in pressure.

(ii)

$$nA \rightarrow P\ (\text{products})$$

$$\text{rate} = K\,[A]^{5/2}$$

$$\frac{d\,[A]}{dt} = nK\,[A]^{5/2}$$

$$+\int_{Ao}^{At} \frac{d\,[A]}{[A]^{5/2}} = -\,nK\int_0^t dt$$

Integrating it gives,

$$+\int_{Ao}^{A} \frac{A^{5/2+1}}{-5/2+1} = -\,n\,Kt$$

$$-\frac{2}{3}\,[A^{-3/2}]_{A_o}^{A_t} = -\,n\,Kt$$

$$\frac{2}{3}\,[[A_t]^{-3/2} - [A_0]^{-3/2}] = n\,Kt$$

$$[A_t]^{-3/2} = \frac{3}{2}\,([A]_0^{-3/2} + n\,Kt)$$

$$\left[\frac{A_0}{2}\right]^{-3/2} = \frac{3}{2}\,([A]_0^{-3/2} + \frac{3}{2}\,nK\,t_{1/2}$$

$$+\,[A_0]^{-3/2} = n\,Kt_{1/2}$$

$$t_{1/2} \propto [A]_0^{-3/2}$$

(iii) According to Lindeman theory, Unimolecular reactions (gas phase) are second order at low pressure and become first order at high pressure.

98. (B) 99. (A)

100. (C)

Radial function $= r^2\,(\alpha_1 - r)(\alpha_2 - r)\,e^{-\beta r}$

Indicater that $r^2 = r^l$

$\Rightarrow$ $1 = 2$ means *d*-orbital

Since it have two nodes, $r = \alpha_1$ and $r = \alpha_2$

Thus, orbital (hydrogenic) is identified as 5*d* because radial node

$= n - l - 1$

$= 5 - 2 - 1$

$= 2$

101. (C) $[x, (x, p^2)] = [x, i\hbar\,.\,2p]$

$= x\,.\,2p\,i\hbar - 2i\hbar\,px = 0$

$-\,[p\,[x^2, p]] = -\,[p, -\,i\hbar\,.\,2x]$

$= -\,[-\,i\hbar\,.\,2x\,.\,p - (-p\,.\,i\hbar\,.\,2x)]$

$= +\,2i\hbar\,xp - 2\,i\hbar\,xp = 0$

102. (C) Wave function,

$$\Psi_{(x)} = \sqrt{\frac{2}{L}}\,\sin\left(\frac{n\pi x}{L}\right)$$

Thus, $<x^3>$

$$= \int_0^L \Psi(x)\,x^3\,.\,\Psi(x)^*\,dx$$

$$= \frac{2}{L}\int_0^L \sin^2\left(\frac{n\pi x}{L}\right).\,x^3\,dx)$$

$$= \frac{L^3}{4}$$

103. (B)

| E | $C_n$ | $nC_2$ | $i$ | $\sigma_h$ |
|---|---|---|---|---|
| 1 | 1 | – 1 | – 1 | – 1 |

If below principle axis is + ve sign, there is A notation in irreducible representation.

If below $C_2$ : – ve, then 2

If below $\sigma_h$ : – ve then double dash "

If below $i$ : – ve then $u$

Thus, overall irreducible representation = $A''_{24}$

104. (C)

105. (B) $_{41}Nb$ : [Kr] $4d^4\ 5s^1$

4d: 1 1 1 1 _ (+2 −1 0 −1 −2); 5s: 1 (0)

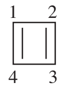
$$2S + 1 = 6$$
$$L = +2 \times 1 = 2\ D$$

Thus, ground state term symbol = $^6D$

106. (A)

107. (C)

$$\begin{array}{c|cccc|} & 1 & 2 & 3 & 4 \\ 1 & x & 1 & 0 & 1 \\ 2 & 1 & x & 1 & 0 \\ 3 & 0 & 1 & x & 1 \\ 4 & 1 & 0 & 1 & x \end{array}$$



$$\because\ x = \frac{\alpha - E}{\beta}$$

$$\Rightarrow\ E = \alpha - \beta x$$

$\therefore$ Huckel determinant

$$= \begin{vmatrix} \frac{\alpha - E}{\beta} & 1 & 0 & 1 \\ 1 & \frac{\alpha - E}{\beta} & 1 & 0 \\ 0 & 1 & \frac{\alpha - E}{\beta} & 1 \\ 1 & 0 & 1 & \frac{\alpha - E}{\beta} \end{vmatrix}$$

$$= \begin{vmatrix} \alpha - E & \beta & 0 & \beta \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ \beta & 0 & \beta & \alpha - E \end{vmatrix}$$

108. (C)

120 mL of 0·05 M $CH_3COOH$

40 mL of 0·05 M NaOH

moles of $H^+$ = 0·05 × 120 = 6·0 mM

moles of $\bar{O}H$ = 0·05 × 40 = 2·0 mM

remaining $H^+$ = 4 mM

$$[H^+]_{net} = \frac{4 \times 10^{-3}}{160 \times 10^{-3}} = \frac{4}{160} = \frac{1}{40}$$
$$= 0{\cdot}025 \text{ mole } l^{-1}$$
$$pH = -\log(2{\cdot}5 \times 10^{-2})$$
$$= 2 + \log 2{\cdot}5 = 2{\cdot}39$$

109. (B) 110. (B)

111. (C) AX system gives 4 lines at 4·72, 4·6, 1·12 and 1·0 ppm 100 MHz instrument is given.

$J_{AX}$ = (difference between any two adjacent peaks) × (instrument frequency)
= (4·72 – 4·60) ppm × 100 MHz
= 0·12 ppm × 100 MHz
= 12 Hz

$$\delta_{AX} = \frac{4{\cdot}72 + 4{\cdot}60 + 1{\cdot}12 + 1{\cdot}00}{4}$$
$$= \frac{11{\cdot}44}{4} = 2{\cdot}86 \text{ ppm}$$

112. (A) $$\frac{n_j}{n_i} = g\, e^{-(E_j - E_i)/K_BT}$$

Since $g$ = 2 (doubly-degenerate)

and $E_j - E_i$ = 2 units

$K_BT$ = 1 unit

Thus, $$\frac{n_j}{n_i} = 2e^{-2}$$

113. (D)

114. (B) Ionic strength is given as

$$I = \frac{1}{2} \sum_{i=0}^{i} m_i z_i^2$$

$m_i$ is molality of ion and $z_i$ is charge

Thus, for NaCl

$Z_+ = 1,$

$Z_- = 1,$

$m_+ = 0{\cdot}01 \text{ mol} = m_-$

$$I = \frac{1}{2}(0{\cdot}01 \times 1^2 + 0{\cdot}01 \times 1^2)$$
$$= \frac{0{\cdot}02}{2} = 0{\cdot}010 \text{ mol kg}^{-1}$$

For $Na_2SO_4$

$Z_+ = 1,\ Z_- = 2$

$m_+ = 2 \times 0{\cdot}01 = 0{\cdot}02,$

$m_- = 0{\cdot}01$ molal

$$I = \frac{1}{2}(0{\cdot}02 \times 1^2 + 0{\cdot}01 \times 2^2)$$
$$= \frac{0{\cdot}02 + 0{\cdot}04}{2}$$
$$= 0{\cdot}030 \text{ mol kg}^{-1}$$

115. (B)

116. (B) $$O + ne^- \rightleftharpoons R$$

$$E = E^\circ - \frac{RT}{nF} ln \frac{[R]}{[O]}$$

(According to Nernst equation)

Thus, $$E - E^\circ = -\frac{RT}{nF} ln \frac{[R]}{[O]}$$

$$\frac{nF}{RT}(E - E^\circ) = -\ln\frac{[R]}{[O]}$$

$$\Rightarrow \quad \frac{[O]}{[R]} = e^{\frac{-nF}{RT}(E - E^\circ)}$$

117. (C) We know Bragg equation that

$$2d \sin\theta = n\lambda$$

where $n$ = order of diffraction

Given that $2d \sin\theta = \lambda$ ...(1)

A plane of spacing $2d$ shows

$$2 . 2d \sin\phi = \lambda$$

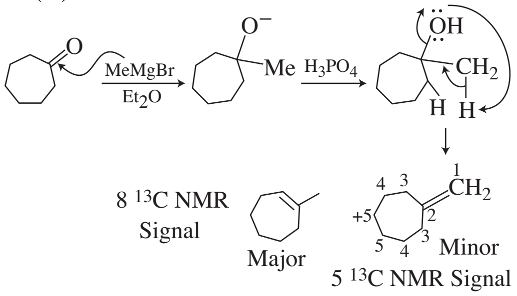
From (1), $4d \sin\phi = 2d \sin\theta$

$$\sin\phi = \frac{\sin\theta}{2}$$

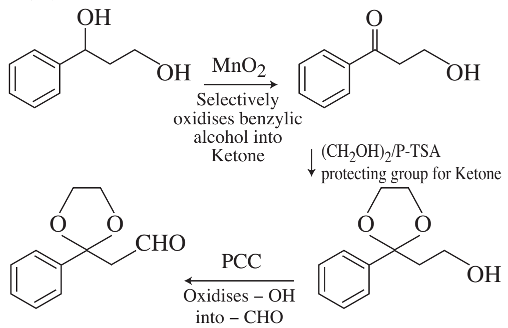
$$\Rightarrow \quad \phi = \sin^{-1}\left(\frac{\sin\theta}{2}\right)$$

118. (D) 119. (A) 120. (D)

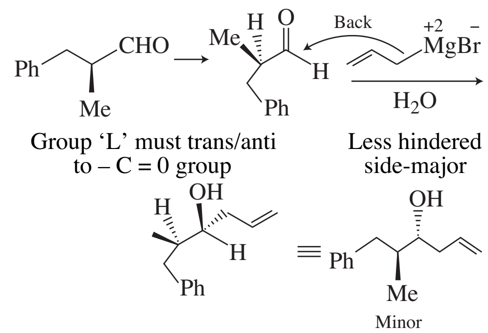
121. (D)

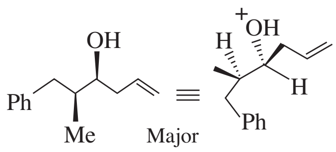



122. (A)




123. (A)

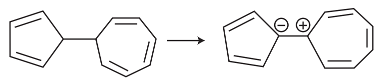



Cram product (front side attack)

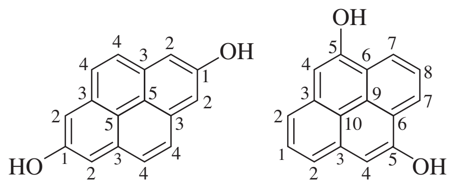
124. (D) 125. (D)

126. (B) Among all the options, only option (B) have aromaticity character after charge distribution or keeps in that position and this leads to highest dipole moment in its.



aromatic compound

(C) The broadband decoupled $^{13}$C NMR spectrum.



Five signals    Ten signals

127. (C) 128. (A) 129. (C)

130. (A) $^1$H NMR spectral data is given as

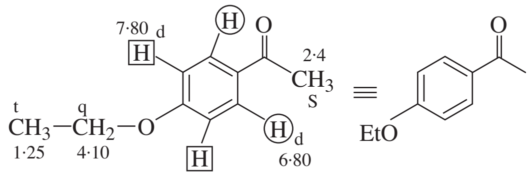
δ 7·80 (2H, d, J = 8Hz) — aromatic *m*-hydrogens w.r.t. > C = 0 group

6·80 (2H, d, J = 8 Hz) — aromatic *o*–hyrogens w.r.t. > C = 0 group

4·10 (2H, q, J = 7·2 Hz) — – $CH_2$ environment adjacent to electronegative group

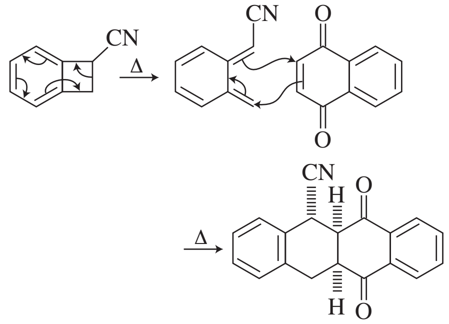
1·25 (3H, t, J = 7·2 Hz) — J value indicates that coupling with – $CH_2$ group

2·4 (3H, S) — adjacent to > C = 0 group or benzylic position

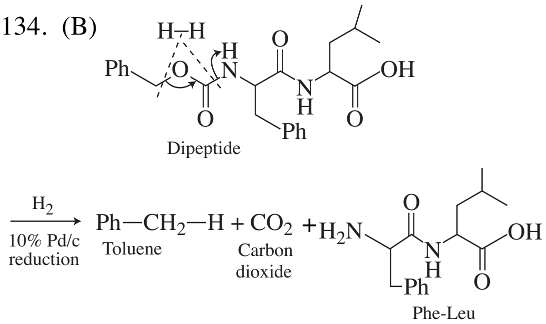


131. (C) 132. (A)

133. (C)



134. (B)




135. (B) 136. (A)

137. (A) Let overall phenol is $x$

Thus, overall formation of *p*-hydroxyacetanilide

$$= x \times \frac{70}{100} \times \frac{90}{100} \times \frac{90}{100} \times 100$$

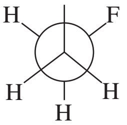
$$= \frac{x \times 567}{1000} \times 100 = 56{\cdot}7\%$$

And, overall formation of *o*–hydroxyacetanilide

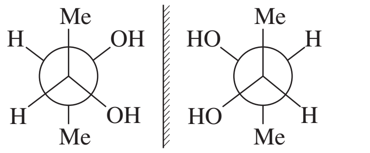
$$= x \times \frac{25}{100} \times \frac{90}{100} \times \frac{90}{100} \times 100$$

$$= 20{\cdot}25\%$$

138. (D)



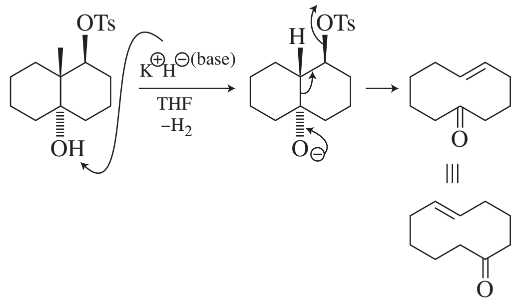
1, 2–difluoroethane most stable conformation due to $\phi = 60°$ (staggered)



$\theta = 60°$ (gauche/staggered) *dl*–2, 3–butanediol

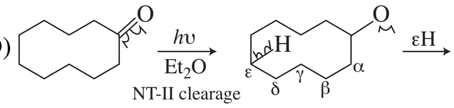
139. (B)

140. (D)

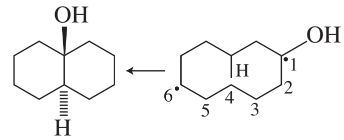


141. (A) 142. (B)

143. (D)

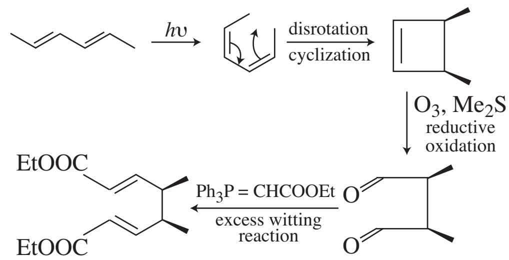



abstraction due to ring cyclisation

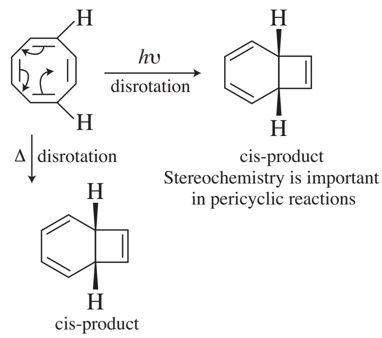


ring cyclisation (6-membered) is important in this case

144. (A)




145. (D)



# CSIR UGC-NET/JRF Exam., December 2013 Solved Paper

# Chemical Sciences

## PART–A

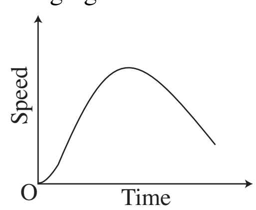
1. A cylinder of radius 1 cm and height 1 cm is broken into three pieces. Which of the following must be true ?
   (A) At least one piece has volume equal to 1 $cm^3$
   (B) At least two pieces have equal volumes
   (C) At least one piece has volume less than 1 $cm^3$
   (D) At least one piece has volume greater than 1 $cm^3$

2. For real number $x$ and $y$, $x^2 + (y - 4)^2 = 0$. Then the value of $x + y$ is—
   (A) 0 (B) 2
   (C) $\sqrt{2}$ (D) 4

3. Every time a ball falls to ground, it bounces back to half the height it fell from. A ball is dropped from a height of 1024 cm. The maximum height from the ground to which it can rise after the tenth bounce is—
   (A) 102·4 cm (B) 1·24 cm
   (C) 1 cm (D) 2 cm

4. A farmer gives 7 full, 7 half-full and 7 empty bottles of honey to his three sons and asks them to share these among themselves such that each of them gets the same amount of honey and the same number of bottles. In how many ways can this be done ? (bottles cannot be distinguished otherwise, they are sealed and cannot be broken)—
   (A) 0 (B) 1
   (C) 2 (D) 3

5. A car is moving along a straight track. Its speed is changing with time as shown.




   Which of the following statements is correct ?
   (A) The speed is never zero
   (B) The acceleration is zero once on the path
   (C) The distance covered initially increases and then decreases
   (D) The car comes back to its initial position once

6. If $a + b + c + d + e = 10$ (all positive numbers), then the maximum value of $a \times b \times c \times d \times e$ is—
   (A) 12 (B) 32
   (C) 48 (D) 72

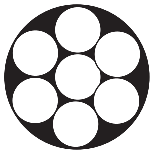
7. How many nine-digit positive integers are there, the sum of squares of whose digits is 2 ?
   (A) 8 (B) 9
   (C) 10 (D) 11

8. A circle of radius 7 units lying in the fourth quadrant touches the $x$-axis at (10, 0). The centre of the circle has coordinates—
   (A) (7, 7) (B) (– 10, 7)
   (C) (10, – 7) (D) (7, – 7)

9. One of the four—A, B, C and D committed a crime. A said, “I did it.” B said, “I didn’t.” C said, “B did it.” D said, “A did it.” Who is lying ?
   (A) A (B) B
   (C) C (D) D

10. What is the arithmetic mean of $\frac{1}{1 \times 2}, \frac{1}{2 \times 3}, \frac{1}{3 \times 4}, \frac{1}{4 \times 5}, \ldots, \frac{1}{100 \times 101}$ ?
   (A) 0·01 (B) $\frac{1}{101}$
   (C) 0·00111… (D) $\frac{\frac{1}{49 \times 50} + \frac{1}{50 \times 51}}{2}$

11. A circle circumscribes identical, closepacked circles of unit diameter as shown. What is the total area of the shaded portion ?

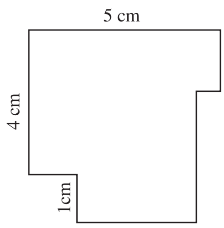


(A) 2 (B) $2\pi$
(C) 1/2 (D) $\pi/2$

12. There are 2 hills, A and B, in a region. If hill A is located N30°E of hill B, what will be the direction of hill B when observed from hill A ? (N 30°E means 30° from north towards east).
(A) S 30°W (B) S 60°W
(C) S 30°E (D) S 60°E

13. What is the next number in the following sequence ?
39, 42, 46, 50, ……
(A) 52 (B) 53
(C) 54 (D) 55

14. What is the perimeter of the given figure, where adjacent sides are at right angles to each other ?




(A) 20 cm
(B) 18 cm
(C) 21 cm
(D) Cannot be determined

15. Three fishermen caught fishes and went to sleep. One of them woke up, took away one fish and 1/3rd of the remainder as his share, without others' knowledge. Later, the three of them divided the remainder equally. How many fishes were caught ?
(A) 58 (B) 19
(C) 76 (D) 88

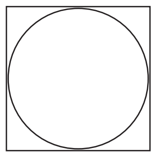
16. $(25 \div 5 + 3 - 2 \times 4) + (16 \times 4 - 3) =$
(A) 61 (B) 22
(C) 41/24 (D) 16

17. Consider the sequence of ordered sets of natural numbers—
{1}, {2, 3}, {4, 5, 6}, …
What is the last number in the $10^{th}$ set ?
(A) 10 (B) 19
(C) 55 (D) 67

18. A student buys a book from an online shop at 20% discount. His friend buys another copy of the same book in a book fair for ₹ 192 paying 20% less than his friend. What is the full price of the book ?
(A) ₹ 275 (B) ₹ 300
(C) ₹ 320 (D) ₹ 392

19. 366 players participate in a knock-out tournament. In each round all competing players pair together and play a match, the winner of each match moving to the next round. If at the end of a round there is an odd number of winners, the unpaired one moves to the next round without playing a match. What is the total number of matches played ?
(A) 366 (B) 282
(C) 365 (D) 418

20. What does the diagram establish ?



**Note**—The diagram is a circle inside a square.
(A) $\pi > 3$
(B) $\pi \geq 2\sqrt{2}$
(C) $\pi < 4$
(D) $\pi$ is closer to 3 than to 4

## PART–B

21. The boiling point of a solution of non-volatile solid is higher than that of the pure solvent. It always indicates that—
(A) the enthalpy of the solution is higher than that of the pure solvent
(B) the entropy of the solution is higher than that of the pure solvent
(C) the Gibbs free energy of the solution is higher than that of the pure solvent
(D) the internal energy of the solution is higher than that of the pure solvent

22. When Frenkel defects are created in an otherwise perfect ionic crystal, the density of the ionic crystal—
(A) increases
(B) decreases
(C) remains same
(D) oscillates with the number of defects

23. The correct thermodynamic relation among the following is—
(A) $\left(\frac{\partial U}{\partial V}\right)_S = -P$ (B) $\left(\frac{\partial H}{\partial V}\right)_S = -P$
(C) $\left(\frac{\partial G}{\partial V}\right)_S = -P$ (D) $\left(\frac{\partial A}{\partial V}\right)_S = -S$

24. The molecule in which the bond order increases upon addition of an electron is—
(A) $O_2$ (B) $B_2$
(C) $P_2$ (D) $N_2$

25. The volume of a gas adsorbed on a solid surface is 10·0 mL, 11·0 mL, 11·2 mL, 14·5 mL and 22·5 mL at 1·0, 2·0, 3·0, 4·0 and 5·0 atm. pressure, respectively. These data are best represented by—
(A) Gibbs's isotherm
(B) Langmuir isotherm
(C) Freundlich isotherm
(D) BET isotherm

26. A compound of M and X atoms has a cubic unit cell. M atoms are at the corners and body centre position and X atoms are at face centre positions of the cube. The molecular formula of the compound is—
(A) MX (B) $MX_2$
(C) $M_3X_2$ (D) $M_2X_3$

27. The angle at which the first order Bragg reflection is observed from (110) plane in a simple cubic unit cell of side 3·238 Å, when chromium $K_\alpha$ radiation of wavelength 2·29 Å is used, is—
(A) 30° (B) 45°
(C) 60° (D) 90°

28. Michael Faraday observed that the colour of colloidal suspensions of gold nanoparticles changes with the size of the nanoparticles. This is because—
(A) gold forms complex with the solvent
(B) band gap of gold changes with size of the nanoparticle
(C) gold in nanocrystalline form undergoes transmutation to other elements
(D) colloidal suspensions diffract light

29. A reactor contains a mixutre of $N_2$, $H_2$ and $NH_3$ in equilibrium ($K_P$ = 3·75 $atm^{-2}$). If sufficient he is introduced into the reactor to double the total pressure, the value of $K_P$ at the new equilibrium would be—
(A) 0·94 $atm^{-2}$ (B) 3·75 $atm^{-2}$
(C) 7·50 $atm^{-2}$ (D) 15·00 $atm^{-2}$

30. Electrolysis of an aqueous solution of 1·0 M NaOH results in—
(A) Na at the cathode and $O_2$ at the anode
(B) $H_2$ at the cathode and $O_2$ at the anode
(C) Na and $H_2$ at the cathode and $O_2$ at the anode
(D) $O_2$ at the cathode and $H_2$ at the anode

31. In a potentiometric titration, the end point is obtained by observing—
(A) change in colour
(B) jump in potential
(C) increase in current
(D) increase in turbidity

32. The orbital with two radial and two angular nodes is—
(A) 3*p* (B) 5*d*
(C) 5*f* (D) 8*d*

33. The energy of 2*s* and 2*p* orbitals is the same for—
(A) Li (B) $Li^{2+}$
(C) $Be^{2+}$ (D) $H^-$

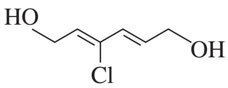
34. If a homonuclear diatomic molecule is oriented along the Z-axis, the molecular orbital formed by linear combination of $P_x$ orbitals of the two atoms is—
(A) $\sigma$ (B) $\sigma^*$
(C) $\pi$ (D) $\delta$

35. In the mechanism of reaction, $H_2 + Br_2 \rightarrow 2HBr$, the first step is—
(A) dissociation of $H_2$ into H-radicals
(B) dissociation of $Br_2$ into Br-radicals
(C) reaction of H-radical with $Br_2$
(D) reaction of Br-radical with $H_2$

36. The cell voltage of Daniel cell $[Zn]ZnSO_4(aq)||CuSO_4(aq)[Cu]$ is 1·07 V. If reduction potential of $Cu^{2+}$ [Cu is 0·34 V, the reduction potential of $Zn^{2+}$ |Zn is—
(A) 1·41 V (B) – 1·41 V
(C) 0·73 V (D) – 0·73 V

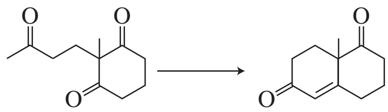
37. According to Arrhenius equation ($k$ = rate constant and T = temperature)—
(A) In $k$ decreases linearly with 1/T
(B) In $k$ decreases linearly with T
(C) In $k$ increases linearly with 1/T
(D) In $k$ increases linearly with T

38. The IUPAC name of the compound given below is—




(A) (2E, 4E)-3-chlorohexa-2, 4-diene-1, 6-diol
(B) (2Z, 4E)-3-chlorohexa-2, 4-diene-1, 6-diol
(C) (2Z, 4Z)-4-chlorohexa-2, 4-diene-1, 6-diol
(D) (2E, 4Z)-4-chlorohexa-2, 4-diene-1, 6-diol

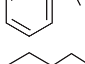
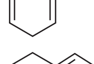
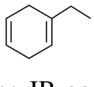
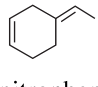
39. A suitable organocatalyst for enantioselective synthesis of Wieland-Miescher ketone (A) is—



A (optically active)

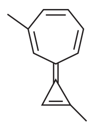
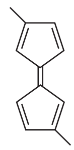
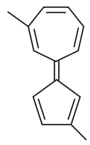
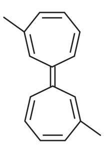
(A) (–)-proline (B) (+)-menthone
(C) guanidine (D) (+)-BINOL

40. The major product formed in the reaction of styrene with an excess of lithium in liquid ammonia and $t$-butylalcohol is—

(A)  (B) 
(C)  (D) 

41. In the IR spectrum of $p$-nitrophenyl acetate, the carbonyl absorption band appears at—
(A) 1660 $cm^{-1}$ (B) 1700 $cm^{-1}$
(C) 1730 $cm^{-1}$ (D) 1770 $cm^{-1}$

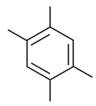
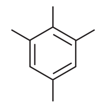
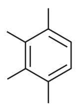
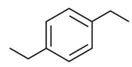
42. Amongst the following, the compound which has the lowest energy barrier for the *cis-trans* isomerisation is—

(A)  (B) 
(C)  (D) 

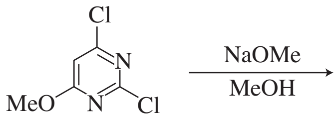
43. For estrone, among the statements A-C, the correct ones are—
1. it is a steroidal hormone
2. it has two hydroxyl groups
3. it has one ketone and one hydroxyl groups

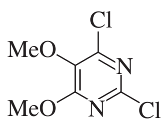
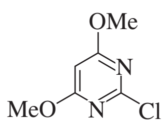
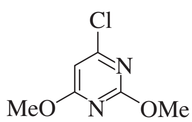
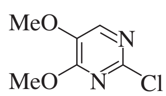
(A) 1, 2 and 3 (B) 1 and 2
(C) 1 and 3 (D) 3 and 3

44. An organic compound having the molecular formula $C_{10}H_{14}$ exhibited two singlets in the $^1$H NMR spectrum, and three signals in the $^{13}$C NMR spectrum. The compound is—

(A)  (B) 
(C)  (D) 

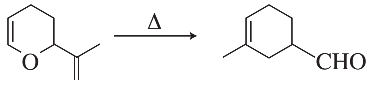
45. The major product formed in the following reaction is—




(A)  (B) 
(C)  (D) 

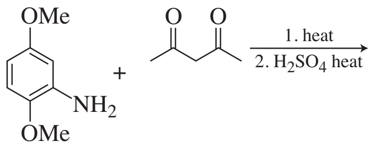
46. L-DOPA is used for the treatment of—
    (A) tuberculosis
    (B) Parkinson's disease
    (C) diabetes
    (D) cancer

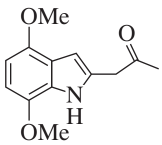
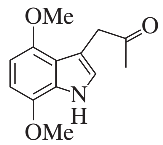
47. The following reaction proceeds through a—

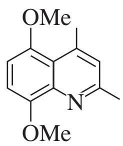
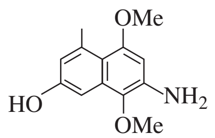


    (A) 1, 3-sigmatropic rearrangement
    (B) 2, 3-sigmatropic rearrangement
    (C) 3, 3-sigmatropic rearrangement
    (D) 3, 5-sigmatropic rearrangement

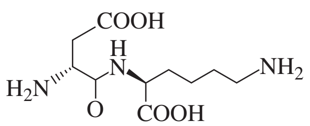
48. The major product formed in the following reaction is—



(A)  (B) 

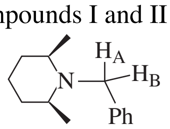
(C)  (D) 

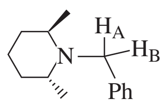
49. The constituent amino acids present in the following dipeptide, respectively, are—



    (A) (R)-aspartic acid and (S)-lysine
    (B) (S)-aspartic acid and (R)-lysine
    (C) (R)-glutamic acid and (S)-arginine
    (D) (S)-glutamic acid and (S)-arginine

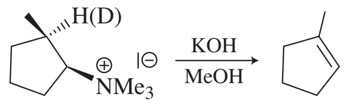
50. The two benzylic hydrogens $H_A$ and $H_B$ in the compounds I and II, are—


**(I)**


**(II)**

    (A) diastereotopic in I and enantiotopic in II
    (B) diastereotopic in II and enantiotopic in I
    (C) diastereotopic in both I and II
    (D) enantiotopic in both I and II

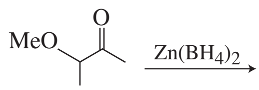
51. Deuterium kinetic isotope effect for the following reaction was found to be 4·0. Based on this information, mechanism of the reaction is—

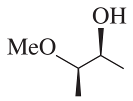
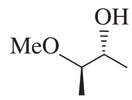


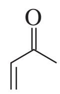
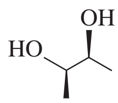
    (A) $E_1$ (B) $E_2$
    (C) $E_{1CB}$ (D) Free radical

52. The number of nodes present in the highest occupied molecular orbital of 1, 3, 5-hexatriene in its ground state is—
    (A) one (B) two
    (C) three (D) four

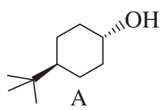
53. The major product formed in the following reaction is—

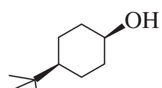


(A)  (B) 

(C)  (D) 

54. For acylation with acetic anhydride/triethylamine, and oxidation with chromium trioxide of the *trans*- and *cis*-alcohols A and B, the correct statement is—


A


B

    (A) A undergoes acylation as well as oxidation faster than B
    (B) B undergoes acylation as well as oxidation faster than A
    (C) A undergoes acylation faster than B, whereas B undergoes oxidation faster than A
    (D) B undergoes acylation faster than A, whereas A undergoes oxidation faster than B

55. Patients suffering from Wilson's disease have—
(A) low level of Cu-Zn superoxide dismutase
(B) high level of Cu-Zn superoxide dismutase
(C) low level of copper-storage protein, ceruloplasmin
(D) high level of copper-storage protein, ceruloplasmin

56. High dose of dietary supplement $ZnSO_4$ for the cure of Zn deficiency—
(A) reduces myoglobin
(B) increases iron level in blood
(C) increases copper level in brain
(D) reduces copper, iron and calcium levels in body

57. The bond order of the metal-metal bond in the dimeric complex $[Re_2Cl_4(PMe_2Ph)_4]^+$ is—
(A) 4·0 (B) 3·5
(C) 3·0 (D) 2·5

58. Among the molten alkali metals, the example of an immiscible pair (in all proportions) is—
(A) K and Na (B) K and Cs
(C) Li and Cs (D) Rb and Cs

59. Among the following, an example of a hypervalent species is—
(A) $BF_3{\cdot}OEt_2$ (B) $SF_4$
(C) $[PF_6]^-$ (D) $Sb_2S_3$

60. Commonly used scintillator for measuring γ-radiation is—
(A) Nal(Al) (B) NaI(Tl)
(C) CsI(Tl) (D) CsI(Al)

61. A sample of Aluminium ore (having no other metal) is dissolved in 50 mL of 0·05 MEDTA. For the titration of unreacted EDTA, 4 mL of 0·05 M. $MgSO_4$ is required. The percentage of Al in the sample is—
(A) 27 (B) 31
(C) 35 (D) 40

62. Which of the following is not suitable as catalyst for hydroformylation ?
(A) $HCo(CO)_4$
(B) $HCo(CO)_3PBu_3$
(C) $HRh(CO)(PPh_3)_3$
(D) $H_2Rh(PPh_3)_2Cl$

63. In a cluster, $H_3CoRu_3(CO)_{12,}$ total number of electrons considered to be involved in its formation is—
(A) 57 (B) 60
(C) 63 (D) 72

64. Among the following the correct acid strength trend is represented by—
(A) $[Al(H_2O)_6]^{3+}$ < $[Fe(H_2O)_6]^{3+}$ < $[Fe(H_2O)_6]^{2+}$
(B) $[Fe(H_2O)_6]^{3+}$ < $[Al(H_2O)_6]^{3+}$ < $[Fe(H_2O)_6]^{2+}$
(C) $[Fe(H_2O)_6]^{2+}$ < $[Fe(H_2O)_6]^{3+}$ < $[Al(H_2O)_6]^{3+}$
(D) $[Fe(H_2O)_6]^{2+}$ < $[Al(H_2O)_6]^{3+}$ < $[Fe(H_2O)_6]^{3+}$

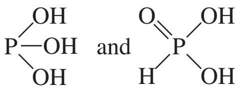
65. An octahedral metal ion $M^{2+}$ has magnetic moment of 4·0 B.M. The correct combination of metal ion and *d*-electron configuration is given by—
(A) $Co^{2+}$, $t_2g^5$ $e_g^2$
(B) $Cr^{2+}$, $t_2g^4$ $e_g^2$
(C) $Mn^{2+}$, $t_2g^3$ $e_g^1$
(D) $Fe^{2+}$, $t_2g^4$ $e_g^2$

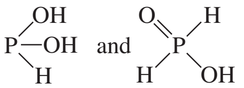
66. The reaction of $FeCl_3{\cdot}6H_2O$ with $SOCl_2$ yields—
(A) $FeCl_2$(s), $SO_2$(g) and HCl(g)
(B) $FeCl_3$(s), $SO_2$(g) and HCl(I)
(C) $FeCl_2$(s), $SO_3$(g) and HCl(g)
(D) $FeCl_3$(s), $SO_2$(g) and HCl(g)

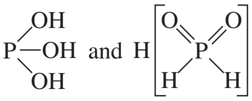
67. Treatment of $ClF_3$ with $SbF_5$ leads to the formation of a/an—
(A) polymeric material
(B) covalent cluster
(C) ionic compound
(D) Lewis acid-base adduct

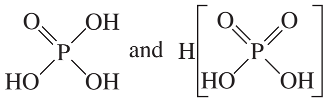
68. According to VSEPR theory, the geometry (with lone pair) around the central iodine in $I_3^+$ and $I_3^-$ ions respectively are—
(A) tetrahedral and tetrahedral
(B) trigonal bipyramidal and trigonal bipyramidal
(C) tetrahedral and trigonal bipyramidal
(D) tetrahedral and octahedral

69. Two tautomeric forms of phosphorus acid are—

(A) 

(B) 

(C) 

(D) 

70. The reason for the chemical inertness of gaseous nitrogen at room temperature is best given by its—

(A) high bonding energy only
(B) electronic configuration
(C) HOMO-LUMO gap only
(D) high bond energy and HOMO-LUMO gap

## PART–C

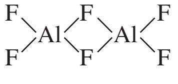
71. The reactive position of nicotinamide adenine dinucleotide (NAD) in biological redox reactions is—

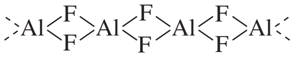
(A) 2-position of the pyridine ring
(B) 6-position of the pyridine ring
(C) 4-position of the pyridine ring
(D) 5-position of the pyridine ring

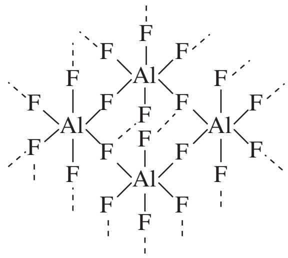
72. The electrophile $Ph_3C^+$ reacts with $[(\eta^5 - C_5H_5)Fe(CO)_2\ (CDMe_2)]^+$ to give a product A. The product A is formed because—

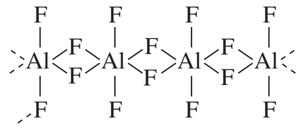
(A) Fe is oxidised
(B) alkyl is substituted with $Ph_3C$
(C) Fe-Ph bond is formed
(D) alkyl is converted to alkene

73. The solid state structure of aluminum fluoride is—

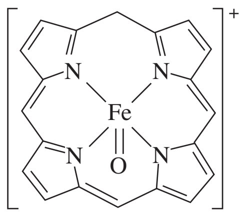
(A) 

(B) 

(C) 

(D) 

74. Oxidised form of enzyme catalase (structure A), prepared by the reaction of $[Fe(P)]^+$ (P = porphyrin) with $H_2O_2$, has green color because—

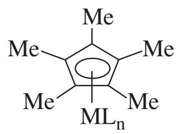


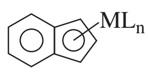
A (substituents on ring are removed for clarity)

(A) oxidation state of iron changed from $Fe^{III}$ to $Fe^{IV}$
(B) porphyrin ring is oxidized by one electron
(C) $\pi$ - $\pi^*$ transition appears in the visible region
(D) $Fe^{IV}$ is coordinated with anionic tyrosinate ligand in axial position

75. Substitution of L with other ligands will be easiest for the species—

(A) 

(B) 

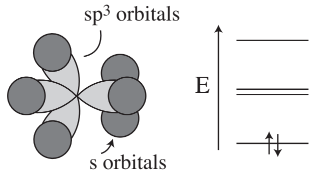
(C) 

(D) 

76. The ground state terms of $Sm^{3+}$ and $Eu^{3+}$, respectively, are—

(A) $7_{F_0}$ and $6_{H_{5/2}}$ (B) $6_{H_{5/2}}$ and $7_{F_0}$
(C) $2_{F_{5/2}}$ and $5_{I_4}$ (D) $7_{F_6}$ and $2_{F_{7/2}}$

77. The orbital interactions shown below represent




(A) $CH_3$—Al interactions in $Al_2(CH_3)_6$
(B) B—H interactions in $B_2H_6$
(C) $CH_3$—Li interactions in $Li_4(CH_3)_4$
(D) $CH_3CH_2$—Mg interactions in $EtMgBr{\cdot}(OEt_2)_2$

78. Compounds $K_2Ba[Cu(NO_2)_6]$ (A) and $Cs_2Ba[Cu(NO_2)_6]$ (B) exhibit tetragonal elongation and tetragonal compression, respectively. The unpaired electron in A and B are found respectively, in orbitals—
(A) $d_{z^2}$ and $d_{x^2-y^2}$ (B) $d_{x^2-y^2}$ and $d_{z^2}$
(C) $d_{z^2}$ and $d_{z^2}$ (D) $d_{x^2-y^2}$ and $d_{x^2-y^2}$

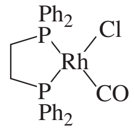
79. Among the following, the correct statement is—
(A) CH is isolobal to $Co(CO)_3$
(B) $CH_2$ is isolobal to $Ni(CO)_2$
(C) CH is isolobal to $Fe(CO)_4$
(D) $CH_2$ is isolobal to $Mn(CO)_4$

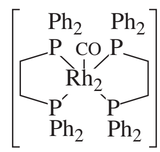
80. In Mossbauer experiment, a source emitting at 14·4 Kev ($3{\cdot}48 \times 10^{18}$ Hz) had to be moved towards absorber at 2·2 mm $s^{-1}$ for resonance. The shift in the frequency between the source and the absorber is—
(A) 15·0 MHz (B) 20·0 MHz
(C) 25·5 MHz (D) 30·0 MHz

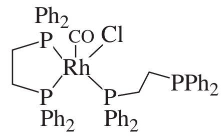
81. In the atomic absorption spectroscopic estimation of Fe(III) using $O_2/H_2$ flame, the absorbance decreases with the addition of—
(A) $CO_3^{2-}$ (B) $SO_4^{2-}$
(C) EDTA (D) $Cl^-$

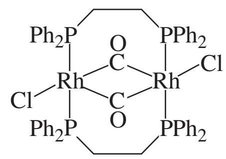
82. $MnCr_2O_4$ is likely to have a normal spinel structure because—
(A) $Mn^{2+}$ will have a LFSE in the octahedral site whereas the $Cr^{3+}$ will not
(B) Mn is in + 2 oxidation state and both the Cr are in + 3 oxidation state
(C) Mn is in + 3 oxidation state and 1 Cr is in + 2 and the other is in + 3 state
(D) $Cr^{3+}$ will have a LFSE in the octahedral site whereas the $Mn^{2+}$ ion will not

83. Reaction of $Ph_2PCH_2CH_2PPh_2$ with $[RHCl(CO)_2]_2$ in a 2 : 1 molar ratio gives a crystalline solid A. The IR spectrum of complex A shows $\nu_{CO}$ at 1985 $cm^{-1}$. The $^{31}P\{^1H\}$ NMR spectrum of A consists of two doublets of doublets of equal intensities ($^{103}Rh$ is 100% abundant and I = $^1/_2$). The structure of complex A is—

(A) 


(B) 


(C) 


(D) 


84. In a polarographic estimation, the limiting currents (μA) were 0·15, 4·65, 9·15 and 27·15 when concentrations (mM) of Pb(II) were 0, 0·5, 1·0 and 3·0, respectively. An unknown solution of Pb(II) gives a limiting current of 13·65 μA. Concentration of Pb(II) in the unknown is—
(A) 1·355 mM (B) 1·408 mM
(C) 1·468 mM (D) 1·500 mM

85. The gases $SO_2$ and $SO_3$ were reacted separately with ClF gas under ambient conditions. The major products expected from the two reactions respectively, are—
(A) $SOF_2$ and $ClOSO_2F$
(B) $SOF_2$ and $SO_2F_2$
(C) $SO_2ClF$ and $SO_2F_2$
(D) $SO_2ClF$ and $ClOSO_2F$

86. In a specific reaction, hexachlorocyclotriphosphazene, $N_3P_3Cl_6$ was reacted with a metal fluoride to obtain mixed halo derivatives namely $N_3P_3Cl_5F(1)$, $N_3P_3Cl_4F_2(2)$, $N_3P_3Cl_3F_3(3)$, $N_3P_3Cl_2F_4(4)$, $N_3P_3ClF_5(5)$.

Compositions among these which can give isomeric products are—

(A) 1, 2 and 3
(B) 2, 3 and 4
(C) 3, 4 and 5
(D) 5, 1 and 2

87. Xenon forms several fluorides and oxofluorides which exhibit acidic behavior. The correct sequence of descending Lewis acidity among the given species is represented by—

(A) $XeF_6 > XeOF_4 > XeF_4 > XeO_2F_2$
(B) $XeOF_4 > XeO_2F_2 > XeOF_4 > XeF_6$
(C) $XeF_4 > XeO_2F_2 > XeOF_4 > XeF_6$
(D) $XeF_4 > XeF_6 > XeOF_4 > XeO_2F_2$

88. Among the following clusters, A = $[(H)Co_6(CO)_{15}]^-$, B = $[(H)_2Os_6(CO)_{18}]$, C = $[(H)_2Os_5(CO)_{16}]$

H is encapsulated in—

(A) A only
(B) B only
(C) B and C only
(D) A and B only

89. Number of isomeric derivatives possible for the neutral *closo*-carborane, $C_2B_{10}H_{12}$ is—

(A) three (B) two
(C) four (D) six

90. The correct statement regarding the terminal/bridging CO groups in solid $CO_4(CO)_{12}$ and $Ir_4(CO)_{12}$ is—

(A) both have equal number of bridging CO groups
(B) number of bridging CO groups in $CO_4(CO)_{12}$ is 4
(C) the number of terminal CO groups in $Co_4(CO)_{12}$ is 8
(D) the number of bridging CO groups in $Ir_4(CO)_{12}$ is zero

91. Among the following the correct combination of complex and its colour is—

| | **Complex** | **Colour** |
|---|---|---|
| (A) | $[Co(CN)_4]^{2-}$ | Red |
| (B) | $[CoCl_4]^{2-}$ | Orange |
| (C) | $[Co(NCS)_4]^{2-}$ | Blue |
| (D) | $[CoF_4]^{2-}$ | Yellow |

92. On reducting $Fe_3(CO)_{12}$ with an excess of sodium, a carbonylate ion is formed. The ion is isoelectronic with—

(A) $[Mn(CO)_5]^-$ (B) $[Ni(CO)_4]$
(C) $[Mn(CO)_5]^+$ (D) $[V(CO)_6]^-$

93. The correct statement for ozone is—

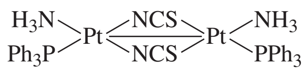
(A) It absorbs radiations in wavelength region 290–320 nm
(B) It is mostly destroyed by NO radical in atmosphere
(C) It is non-toxic even at 100 ppm level
(D) Its concentration near poles is high due to its paramagnetic nature

94. The most appropriate structure for the complex $[Pt_2(NH_3)_2(NCS)_2(PPh_3)_2]$ is—

(A) 


(B) 

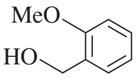

(C) 

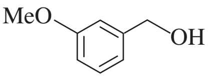

(D) 

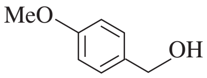

95. For higher boranes 3*c*-2*e* 'BBB' bond may be a part of their structures. In $B_5H_9$, the number of such electron deficient bond(s) present is/are—

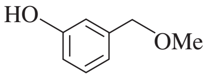
(A) four (B) two
(C) zero (D) one

96. An organic compound ($C_8H_{10}O_2$), which does not change the color of ferric chloride solution, exhibited the following $^1H$ NMR spectral data : δ 7·3 (1 H, *t*, J = 8 Hz), 7·0 (1 H, *d*, J = 8 Hz), 6·95 (1 H, s), 6·9 (1 H, *d*, J = 8 Hz), 5·3 (1 H, brs, $D_2O$ exchangeable), 4·6 (2 H, s), 3·9 (3 H, s). Structure of the compound is—

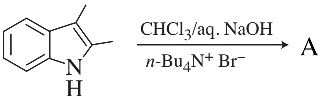
(A) 

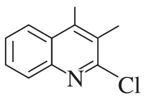

(B) 

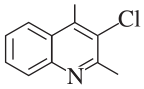

(C) 

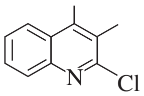

(D) 

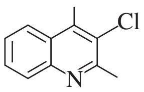

97. In the following reaction, the intermediate and the major product A are—




(A) CHCl and 


(B) CHCl and 

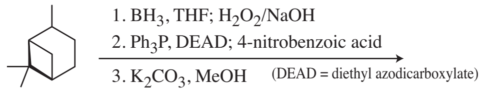

(C) $CCl_2$ and 

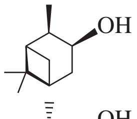

(D) $CCl_2$ and 

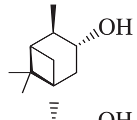

98. Methyl 4-oxopentanoate exhibited signals at δ 208, 172, 51, 37, 32 and 27 ppm in its $^{13}C$ NMR spectrum. The signals due to the methoxy, Cl, C4 and C5 carbons are—

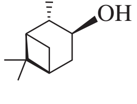
(A) OMe - 32; Cl - 208; C4 - 172; C5 - 51
(B) OMe - 51; Cl - 208; C4 - 172; C5 - 32
(C) OMe - 32; Cl - 172; C4 - 208; C5 - 51
(D) OMe - 51; Cl - 172; C4 - 208; C5 - 32

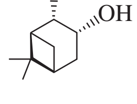
99. The major product formed in the following reaction sequence is—



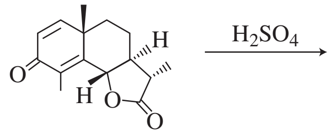

(A) 

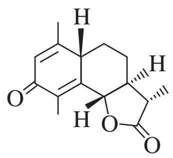

(B) 

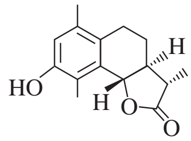

(C) 

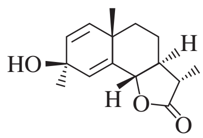

(D) 

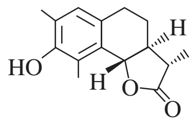

100. The major product formed in the sulfuric acid mediated rearrangement of the sesquiterpene santonin A is—



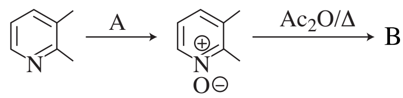

(A) 

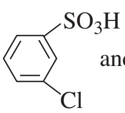
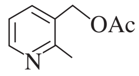

(B) 

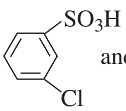
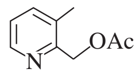

(C) 

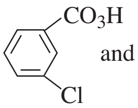
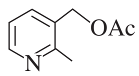

(D) 

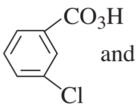
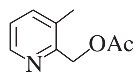

101. In the following transformation, the reagent A and the major product B, respectively, are—




(A)  and 

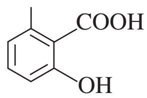

(B)  and 


(C)  and 


(D)  and 

102. The peptide A on reaction with I-fluoro-2, 4-dinitrobenzene followed by exhaustive hydrolysis gave phenylalanine, alanine, serine and N-(2,4-dinitrophenyl)glycine. On the other hand, peptide A after two cycles of Edman degradation gave Phe-Ser as the product. The structure of the peptide A is—
(A) Phe-Ser-Ala-Gly
(B) Phe-Ser-Gly-Ala
(C) Gly-Ala-Phe-Ser
(D) Ala-Gly-Phe-Ser

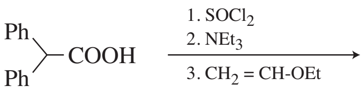
103. The compound B (labeled) is precursor for biosynthesis of the natural product A. The labeled carbons in the product A are—

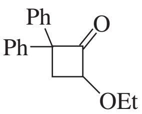
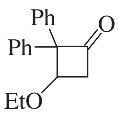
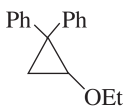
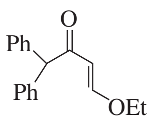

A

$Me^{14}COOH$
B

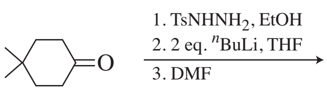
(A) C1, C3, C5 and Me
(B) C2, C4, C6 and Me
(C) C2, C4, C6 and COOH
(D) C1, C3, C5 and COOH

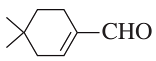
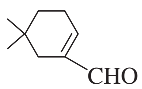
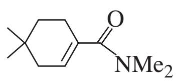
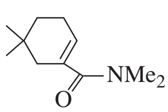
104. The major product formed in the following reaction sequence is—



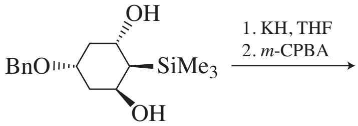
(A) 
(B) 
(C) 
(D) 

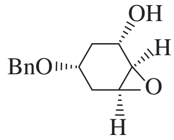
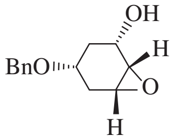
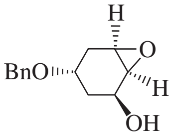
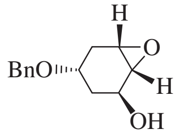
105. The major product formed in the following reaction sequence is—



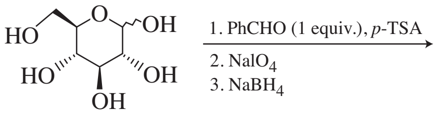
(A) 
(B) 
(C) 
(D) 

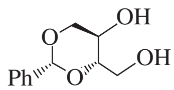
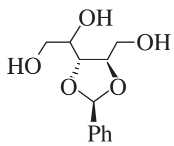
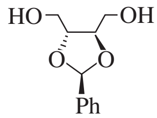
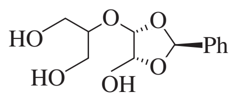
106. The major product formed in the following reaction sequence is—



(A) 
(B) 
(C) 
(D) 

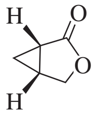
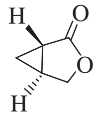
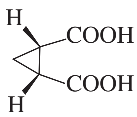
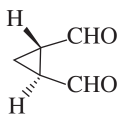
107. The major product formed in the following reaction sequence is—



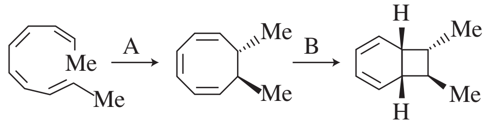
(A) 
(B) 
(C) 
(D) 

108. The major product formed in the following reaction sequence is—

*cis*-but-2-ene-1,4-diol $\xrightarrow[\text{2. PCC, } CH_2Cl_2]{\text{1. } CH_2I_2\text{, Zn-Cu, } CH_2Cl_2}$

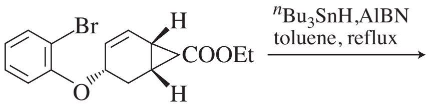
(A) 
(B) 
(C) 
(D) 

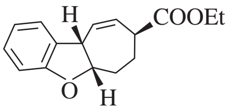
109. The conditions A-B, required for the following pericyclic reactions are—

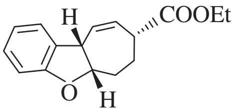


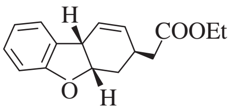
(A) A - Δ; B - Δ (B) A - hv; B - Δ
(C) A - hv; B - hv (D) A - Δ; B - hv

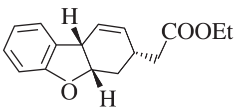
110. The major product formed in the following reaction sequence is—



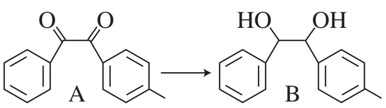

(A) 

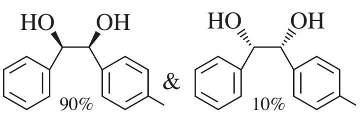
(B) 

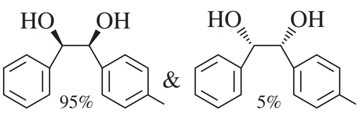
(C) 

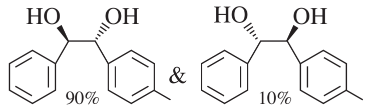
(D) 

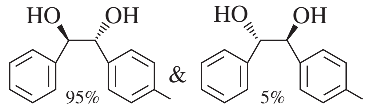
111. Stereoselective reduction of the dione A with a chiral reducing agent provides the corresponding diol B in 100% diastereoselectivity and 90% ce favouring R,R-configuration. The composition of the product is—



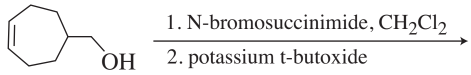
(A) 

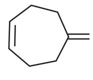
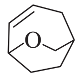

(B) 

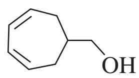
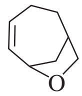

(C) 


(D) 

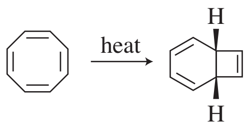

112. The major product formed in the following reaction sequence is—




(A)  (B) 

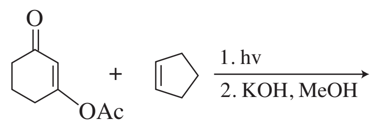
(C)  (D) 

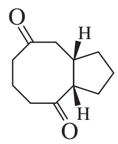
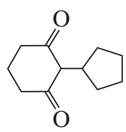
113. The number of π electrons participating and the pericyclic mode in the following reaction are—

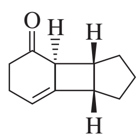
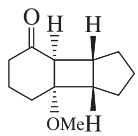



(A) 4 and conrotatory
(B) 4 and disrotatory
(C) 6 and conrotatory
(D) 6 and disrotatory

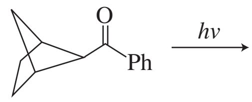
114. The major product formed in the following reaction sequence is—

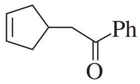
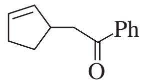


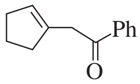
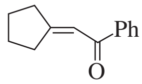

(A)  (B) 

(C)  (D) 

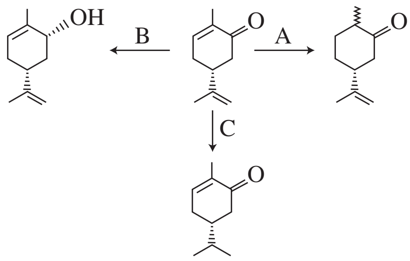
115. The major product formed in the following photochemical reaction is—



(A)  (B) 

(C)  (D) 

116. The most suitable reagent combination of A-C, required in the following conversions are—



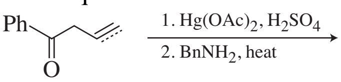
(A) A = Li/liq. $NH_3$; B = $NaBH_4$, $CeCl_3.7H_2O$; C = $H_2$, $(PH_3P)_3RhCl$

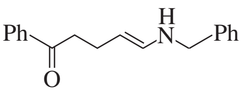
(B) A = Li/liq. $NH_3$; B = $NaBH_4$, $CeCl_3.7H_2O$; C = $H_2$, 10% Pd/C

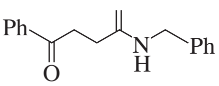
(C) A = $NaBH_4$, $CeCl_3.7H_2O$; B = Li/liq. $NH_3$; C = $H_2$, $(Ph_3P)_3RhCl$

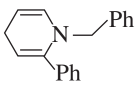
(D) A = $NaBH_4$, $CeCl_3.7H_2O$; B = Li/liq. $NH_3$; C = $H_2$, 10% Pd/C

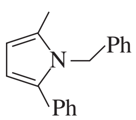
117. The major product formed in the following reaction sequence is—



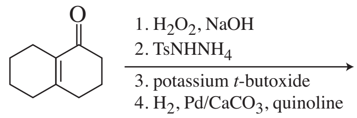
(A) 

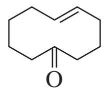
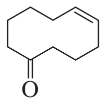
(B) 

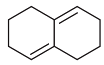
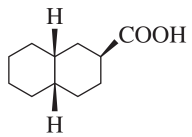
(C) 

(D) 

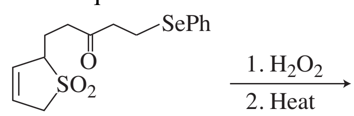
118. The major product formed in the following reaction sequence is—

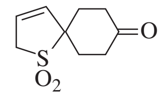
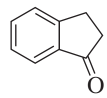


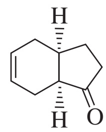
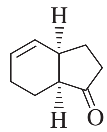
(A)  (B) 

(C)  (D) 

119. The major product formed in the following reaction sequence is—

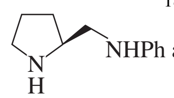


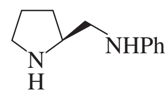
(A)  (B) 

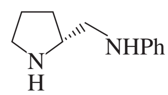
(C)  (D) 

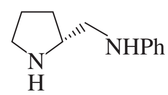
120. The major product B formed in the following reaction sequence, and overall yield of its formation are—

(S)-glutamic acid $\xrightarrow[180\,°C\ 60\%]{\text{aniline}}$ A $\xrightarrow[80\%]{LiAlH_4}$ B

(A)  and 48%

(B)  and 70%

(C)  and 48%

(D)  and 70%

121. Metallic gold crystallizes in *fcc* structure with unit cell dimension of 4·00 Å. The atomic radius of gold is—

(A) 0·866 Å (B) 1·414 Å

(C) 1·732 Å (D) 2·000 Å

122. A first order gaseous reaction is 25% complete in 30 minutes at 227°C and in 10 minutes at 237°C. The activation energy of the reaction is closest to (R = 2 cal $K^{-1}$ $mol^{-1}$)—

(A) 27 kcal $mol^{-1}$ (B) 110 kcal $mol^{-1}$

(C) 55 kcal $mol^{-1}$ (D) 5·5 kcal $mol^{-1}$

123. The most probable value of $r$ for an electron in 1s orbital of hydrogen atom is—

(A) $a_0/2$ (B) $a_0$

(C) $\sqrt{2}\, a_0$ (D) $3a_0/2$

124. The quantum mechanical virial theorem for a general potential $V(x, y, z)$ is given by $\left\langle x\frac{\partial V}{\partial x} + y\frac{\partial V}{\partial y} + z\frac{\partial V}{\partial z}\right\rangle = 2(T)$ where T is the kinetic energy operator and < > indicates expectation value. This leads to the following relation between the expectation value of kinetic energy and potential energy for a quantum mechanical harmonic oscillator problem with potential $V = \frac{1}{2}k_xX^2 + \frac{1}{2}k_yY^2 + \frac{1}{2}k_zZ^2$—

(A) $\langle T\rangle = \langle V\rangle$ (B) $\langle T\rangle = -\frac{1}{2}\langle V\rangle$

(C) $\langle T\rangle = \frac{1}{2}\langle V\rangle$ (D) $\langle T\rangle = -\langle V\rangle$

125. Consider a particle in a one dimensional box of length '$a$' with the following potential—

$V(x) = \infty \quad x < 0$

$V(x) = \infty \quad x > a$

$V(x) = 0 \quad 0 \le x \le a/2$

$V(x) = V_1 \quad a/2 \le x \le a$

Starting with the standard particle in a box hamiltonian as the zeroth order Hamiltonian and the potential of $V_1$ from '$a/2$' to '$a$' as a perturbation, the first-order energy correction to the ground state is—

(A) $V_1$ (B) $V_1/4$

(C) $-V_1$ (D) $V_1/2$

126. The energy for a single electron excitation in cyclopropenium cation in Huckel theory is—

(A) β (B) 2β

(C) 3β (D) 4β

127. The molecule that has the smallest diffusion coefficient in water is—

(A) Glucose (B) Fructose

(C) Ribose (D) Sucrose

128. In the reaction between NO and $H_2$ the following data are obtained—

Experiment I : $P_{H_2}$ = Constant

| | | | |
|---|---|---|---|
| $P_{NO}$ (mm of Hg) | 359 | 300 | 152 |
| $-\frac{dP_{NO}}{dt}$ | 1·50 | 1·03 | 0·25 |

Experiment II : $P_{NO}$ = Constant

| | | | |
|---|---|---|---|
| $P_{H_2}$ (mm of Hg) | 289 | 205 | 147 |
| $-\frac{dP_{H_2}}{dt}$ | 1·60 | 1·10 | 0·79 |

The orders with respect to $H_2$ and NO are—

(A) 1 with respect to NO and 2 with respect to $H_2$

(B) 2 with respect to NO and 1 with respect to $H_2$

(C) 1 with respect to NO and 3 with respect to $H_2$

(D) 2 with respect to NO and 2 with respect to $H_2$

129. The angular momentum operator $\hat{L}_y$ is—

(A) $-\frac{h}{i}(y\partial/\partial z - z\partial/\partial y)$

(B) $\frac{h}{i}(z\partial/\partial x - x\partial/\partial z)$

(C) $\frac{-ih}{2m}\frac{\partial}{\partial x}$

(D) $\frac{h}{i}(z\partial/\partial x - y\partial/\partial y)$

130. Both NaCl and KCl crystallize with the *fcc* structure. However, the X-ray powder diffraction pattern of NaCl corresponds to the *fcc* structure whereas, that of KCl corresponds to simple cubic structure. This is because—

(A) $K^+$ and $Cl^-$ are isoelctronic

(B) $Na^+$ and $Cl^-$ are isoelctronic

(C) $K^+$ and $Cl^-$ are disordered in the crystal lattice

(D) KCl has anti-site defects

131. Consider a two-dimensional harmonic oscillator with potential energy $V(x, y) = \frac{1}{2} k_x X^2 + \frac{1}{2} k_y Y^2$. If $\Psi_{ax}(x)$ and $\Psi_{ny}(y)$ are the eigensolutions and $E_{nx}$ and $E_{ny}$ are the eigenvalues of harmonic oscillator problem in $x$ and $y$ direction with potential $\frac{1}{2} k_x X^2$ and $\frac{1}{2} k_y Y^2$, respectively, the wave functions and eigenvalues of the above two-dimensional harmonic oscillator problem are—

(A) $\Psi_{nx,ny} = \Psi_{nx}(x) + \Psi_{ny}(y)$
$E_{nx,ny} = E_{nx} + E_{ny}$

(B) $\Psi_{nx,ny} = \Psi_{nx}(x)\,\Psi_{ny}(y)$
$E_{nx,ny} = E_{nx}\,E_{ny}$

(C) $\Psi_{nx,ny} = \Psi_{nx}(x)\,\Psi_{ny}(y)$
$E_{nx,ny} = E_{nx} + E_{ny}$

(D) $\Psi_{nx,ny} = \Psi_{nx}(x) + \Psi_{ny}(y)$
$E_{nx,ny} = E_{nx}\,E_{ny}$

132. An element exists in two crystallographic modifications with FCC and BCC structures. The ratio of the densities of the FCC and BCC modifications in terms of the volumes of their unit cells ($V_{FCC}$ and $V_{BCC}$) is—

(A) $V_{BCC} : V_{FCC}$ (B) $2V_{BCC} : V_{FCC}$

(C) $V_{BCC} : 2V_{FCC}$ (D) $V_{BCC} : \sqrt{2}\, V_{FCC}$

133. For an electronic configuration of two non-equivalent $\pi$ electrons $[\pi^1, \pi^1]$, which of the following terms is not possible ?

(A) $^1\Sigma$ (B) $^3\Sigma$

(C) $^3\Delta$ (D) $^3\Phi$

134. Given $\gamma\,(^1H) \simeq 2{\cdot}7 \times 10^8\ T^{-1}S^{-1}$. The resonance frequency of a proton in magnetic field of 12·6 T is close to ($\pi$ = 3·14)—

(A) 60 MHz (B) 110 MHz

(C) 540 MHz (D) 780 MHz

135. The atomic masses of fluorine and hydrogen are 19·0 and 1·0 amu, respectively (1 amu = $1{\cdot}67 \times 10^{-27}$ kg). The bond length of HF is 2·0 Å. The moment of inertia of HF is—

(A) $3{\cdot}2 \times 10^{-47}$ kg m$^2$

(B) $6{\cdot}4 \times 10^{-47}$ kg m$^2$

(C) $9{\cdot}6 \times 10^{-47}$ kg m$^2$

(D) $4{\cdot}8 \times 10^{-47}$ kg m$^2$

136. The chemical potential ($\mu_i$) of the $i^{th}$ component is defined as—

(A) $\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{T,P}$ (B) $\mu_i = \left(\frac{\partial H}{\partial n_i}\right)_{T,P}$

(C) $\mu_i = \left(\frac{\partial A}{\partial n_i}\right)_{T,P}$ (D) $\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P}$

137. The transition that is allowed by $x$-polarized light in trans-butadiene is—

(The character table for $C_{2h}$ is given below)

| $C_{2h}$ | E | $C_2$ | $i$ | $\sigma_h$ | |
|---|---|---|---|---|---|
| $A_g$ | 1 | 1 | 1 | 1 | $R_x, x^2, y^2, z^2, xy$ |
| $B_g$ | 1 | – 1 | 1 | – 1 | $R_x, R_y, xz, yz$ |
| $A_u$ | 1 | 1 | – 1 | – 1 | $z$ |
| $B_u$ | 1 | – 1 | – 1 | 1 | $x, y$ |

(A) $^1A_u \rightarrow {}^1A_u$ (B) $^1A_u \rightarrow {}^1B_g$

(C) $^1B_u \rightarrow {}^1B_g$ (D) $^3B_g \rightarrow {}^1A_g$

138. The masses recorded when a substance is weighted 4 times are 15·8, 15·4, 15·6 and 16·0 mg. The variance (square of the standard deviation) is closest to—

(A) 0·02 (B) 0·05

(C) 0·10 (D) 0·20

139. The heat capacity of 10 mol of an ideal gas at a certain temperature is 300 $JK^{-1}$ at constant pressure. The heat capacity of the same gas at the same temperature and at constant volume would be—

(A) 383 $JK^{-1}$ (B) 217 $JK^{-1}$

(C) 134 $JK^{-1}$ (D) 466 $JK^{-1}$

140. Work ($w$) involved in isothermal reversible expansion from $V_i$ to $V_f$ of $n$ moles of an ideal gas is—

(A) $w = -nRT \text{ In } (V_f/V_i)$

(B) $w = nRT\,(V_f/V_i)$

(C) $w = -nRT\,(V_f/V_i)$

(D) $w = nRT \log(V_f/V_i)$

141. The Maxwell's relationship derived from the equation dG = VdP – SdT is—

(A) $\left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial S}{\partial P}\right)_T$

(B) $\left(\frac{\partial P}{\partial V}\right)_T = \left(\frac{\partial T}{\partial S}\right)_P$

(C) $\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$

(D) $\left(\frac{\partial P}{\partial V}\right)_T = -\left(\frac{\partial T}{\partial S}\right)_P$

142. The number of ways in which four molecules can be distributed in two different energy levels is—

(A) 6 (B) 3

(C) 16 (D) 8

143. Consider the cell—

Zn | $Zn^{2+}$ ($a$ = 0·01) || $Fe^{2+}$ ($a$ = 0·001), $Fe^{3+}$ ($a$ = 0·01) | Pt

Ecell = 1·71 V at 25°C for the above cell. The equilibrium constant for the reaction :

$Zn + 2Fe^{3+} \rightleftharpoons Zn^{2+} + 2Fe^{2+}$ at 25°C would be close to—

(A) $10^{27}$ (B) $10^{54}$

(C) $10^{81}$ (D) $10^{40}$

144. The molecule with the smallest rotation partition function at any temperature among the following is—

(A) $CH_3$-C ≡ C-H (B) H-C ≡ C-H

(C) H-C ≡ C-D (D) D-C ≡ C-D

145. The limiting molar conductivities of NaCl, NaI and RbI are 12·7, 10·8 and 9·1 mS $m^2$ $mol^{-1}$, respectively. The limiting molar conductivity of RbCl would be—

(A) 32·6 mS $m^2$ $mol^{-1}$

(B) 7·2 mS $m^2$ $mol^{-1}$

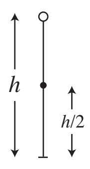
(C) 14·4 mS $m^2$ $mol^{-1}$

(D) 11·0 mS $m^2$ $mol^{-1}$

## Answers with Hints

1. (D) 2. (D)

3. (C) A ball is dropped from a height of 1024 cm.




∴ The maximum height from the ground to which it can rise after the tenth bounce

$$\frac{1024}{2 \times 2 \times 2 \times 2 \times 2 \times 2 \times 2 \times 2 \times 2 \times 2} = 1 \text{ cm}$$

4. (C)

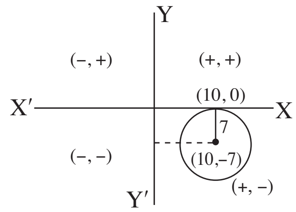
5. (B) We know that

$$\text{acceleration} = \frac{\text{Change in velocity}}{\text{Change in time}}$$

∴ the graph represents, acceleration is 0 once on path.

6. (B) 7. (A)

8. (C) It is clear from figure, the centre of circle is (10, –7)




9. (C) A said, "I did it."

B said, "I didn't."

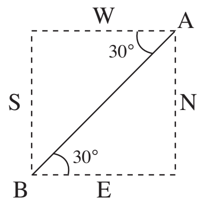
C said, "B did it."

D said, "A did it."

Thus, it is clear from statements that C is lying.

10. (B) 11. (D)

12. (A) Hill A is located N30° E of hill B.




Thus, according to question, direction of hill B from A = S 30° W.

13. (D) 14. (A)

15. (B) Of all the options given in question only 19 is correct because $(19 - 1) \times \frac{1}{3} = 6$, 7 fish is taken by one fisherman.

∴ 19 – 7 = 12 is divided equally among all the three with 4 fishes.

16. (A) $(25 \div 5 + 3 - 2 \times 4) + (16 \times 4 - 3)$

$= (5 + 3 - 2 \times 4) + (16 \times 4 - 3)$

$= (5 + 3 - 8) + (64 - 3)$

$= (8 - 8) + (64 - 3)$

$= 0 + 61 = 61$

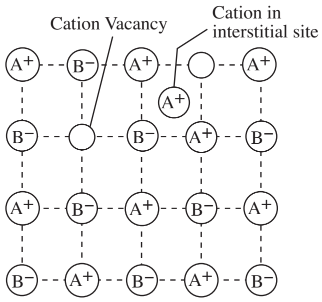
17. (C) {1}, {2, 3}, {4, 5, 6}

in every set 1 number increases proceeded to words higher natural number.

Thus, last number in 10th set is 55.

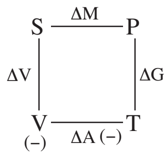
18. (B) 19. (C) 20. (C) 21. (B)

22. (C) Since displacement of cation takes place, so no effect on density.




23. (A) From this rule, given in figure we know

$$dU = TdS - PdV$$

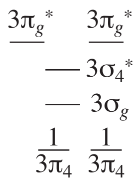



Differentiating w.r.t. V at constant S

$$\therefore \quad \left(\frac{\partial U}{\partial V}\right)_S = -P$$

24. (B) We know that for $B_2$. M.O. diagram is

$(1\sigma_g^2)\ (1\sigma_4{}^{*2})\ (2\sigma_g^2)\ (2\sigma_4{}^{*2})$




Addition of an $e^-$ increases the value of bond order due to extra $e^-$ will go into bonding-orbital.

25. (D)

26. (D) M atoms are at the corners

$$= \frac{1}{8} \times 8$$

$$= 1$$

and at body centre position = 1

$$\therefore \quad M = 2$$

X atoms are at face centre positions

$$= \frac{1}{2} \times 6$$

$$= 3$$

$$\therefore \quad X = 3$$

Thus, formula of compound = $M_2X_3$

27. (B) According to Bragg's Law,

$$n\lambda = 2d \sin\theta$$

$$\therefore \quad \sin\theta = \frac{n\lambda}{2d}$$

(first order diffraction, $n = 1$)

$$\sin\theta = \frac{2{\cdot}29\ \text{Å} \times \sqrt{2}}{2 \times 3{\cdot}238\ \text{Å}}$$

$$= \frac{1}{2} = \sin 45°$$

$$\left(\because d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}\right)$$

$$\boxed{\theta = 45°}$$

28. (B)

29. (B) Mixture of $N_2, H_2$ & $NH_3$,

$$K_p = 3{\cdot}75\ \text{atm}^{-2}$$

He is introduced into the reactor to double the total pressure. The addition of inert gas

$$N_2 + 3H_2 \rightarrow 2NH_3$$

$K_p \propto (P_{total})$

$\therefore$ new $K_p$,

$$\therefore \quad K_p' = (P_{total})$$

$$= P_{total}$$

$$\therefore \quad K'_p = 3{\cdot}75 = 3{\cdot}75\ \text{atm}^{-2}$$

30. (B) Consider ionization as

$$NaOH \rightleftharpoons Na^+(aq) + \bar{O}H(aq)$$

water also dissociates into ions

$$H_2O(l) \rightleftharpoons H^+(aq) + \bar{O}H(aq)$$

Since reduction potential of $H^+$ is higher than $Na^+$

at cathode

$$H^+(aq) + e^- \rightarrow \tfrac{1}{2}H_2(g)$$

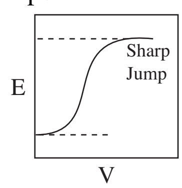
at anode, $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

Net reaction,

$NaOH(aq) + H_2O(l)$

$$\rightarrow Na^+(aq) + \bar{O}H(aq) + \frac{1}{2}H_2(g) + \frac{1}{2}O_2(g)$$

31. (B) In potentiometric titration, EMF measurement is done. The end point is observed after sharp jump in potential.



32. (B) We know that

angular node = value of $l$

and radial node

$$n - l - 1 = 2$$
$$n - l = 3$$

$\therefore$ 5*d* orbital have 2 radial & 2 angular nodes.

33. (B) 34. (C)

35. (B) $H_2 + Br_2 \rightarrow 2HBr$

First step – initiation

$$Br_2 \xrightarrow{K_1} 2\overset{\circ}{Br}$$

dissociation of $Br_2$ into $\overset{\circ}{Br}$ radicals

$$\left.\begin{array}{l} H_2 + \overset{\bullet}{Br} \xrightarrow{K_2} HBr + \overset{\circ}{H} \\ \overset{\circ}{H} + Br_2 \xrightarrow{K_3} HBr + \overset{\circ}{Br} \end{array}\right\} \text{propagation}$$

$HBr + \overset{\circ}{Br} \xrightarrow{K_4} \overset{\circ}{H} + Br_2$ – inhibition (not important)

$2\overset{\circ}{Br} \xrightarrow{K_5} Br^2$ – termination

36. (D) Daniel cell

$Zn|ZnSO_4(aq)||CuSO_4(aq)|Cu^7$

$$E = 1{\cdot}07 \text{ V}$$

half cell reactions are

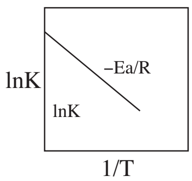
$Zn(s) \rightarrow Zn^{+2} + 2e^-$ at anode

$Cu^{+2} + 2e^- \rightarrow Cu(s)$ at cathode

$$\because \quad E = E_c - E_a$$
$$1{\cdot}07 = 0{\cdot}34 - E_{z_n^{+2}/Z_n}$$
$$\Rightarrow \quad E_{z_n^{+2}/Z_n} = -0{\cdot}73 \text{ V}$$

37. (A) According to Arrhenius equation,

$$K = Ae^{-Ea/RT}$$

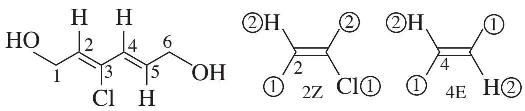



$$lnK = ln\,A - \frac{Ea}{RT}$$

hint – $\boxed{y = mx + c}$

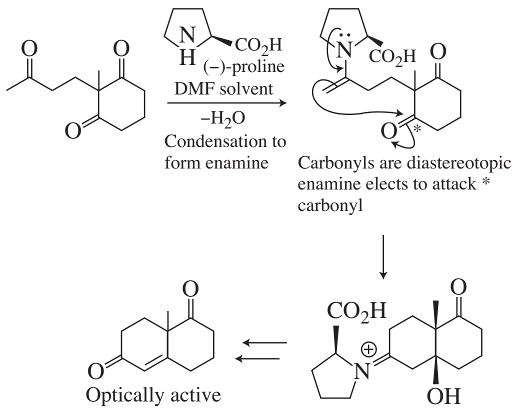
*ln*K decreases linearly with $\frac{1}{T}$ ·

38. (B)

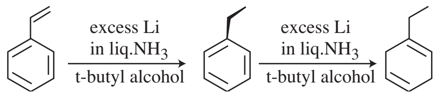



(2Z, 4E)-3-chlorohexa-2, 4-diene-1, 6-dial

39. (A)

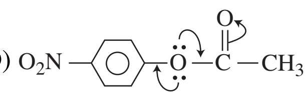



40. (C)




alkyl gp acts $e^-$ releasing group, facilitate the formation of ortho & meta hydrogenated product.

41. (D)

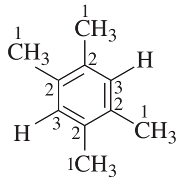



P-nitro phenyl acetate

esters show band at 1760 – 1780 $cm^{-1}$

42. (C) 43. (C)

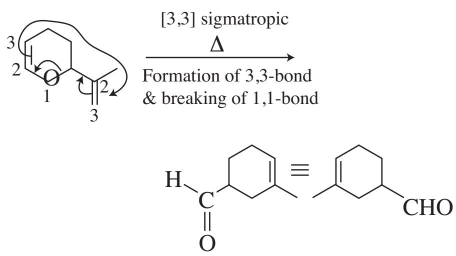
44. (A) $C_{10}H_{14}$, DBE $= \dfrac{20 + 12 - 14}{2} = 4$




two singlets in $^1$H NMR
three signals in $^{13}$C NMR

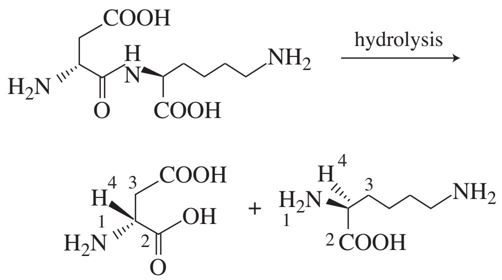
45. (C) 46. (B)

47. (C)



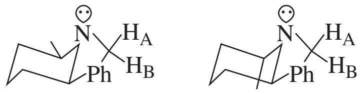

48. (C)

49. (A)



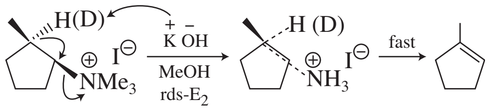

(R) - aspartic acid (S) - lysine

50. (B)

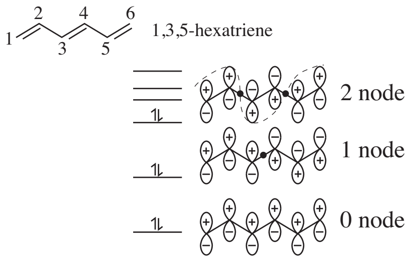



(I) enantiotopic (II) diastereotopic

51. (B) 'C—H' or 'C—D' bond cleavage in T.S.—Primary Kinetic isotope effect




52. (B)




53. (A) 54. (C) 55. (C) 56. (D)

57. (B) dimeric complex $[Re_2Cl_4(PMe_2Ph)_4]^+$

Oxidation state

$$2x - 4 = +1$$

$$x = 2{\cdot}5$$

$$\therefore \quad \text{Bond order} = \frac{1}{2}$$

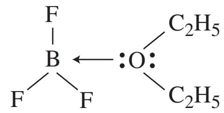
(B.M.O's $e^-s$ – ABMO's $e^-s$)

$$= \frac{1}{2}(8-1)$$

$$= 3{\cdot}5$$

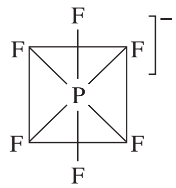
58. (C)

59. (C)




Coordination bond

$\ddot{S}F_4$ $sp^3d$




P : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$

5 valence $e^-s$

This compound have hypervalent covalent bond.

60. (B) 61. (B)

62. (D) $2RCH = CH_2 + 2CO + H_2 \xrightarrow{CO_2(CO)_8}$

$RCH_2CH_2CHO + RCH_2—CH_3$ with $HC = O$ on the $CH_2$

In hydroformylation reaction, we need one or two mole of CO from catalyst to give product by migratory insertion. Thus, the given option $H_2RH(PPh_3)_2Cl$ is not suitable as catalyst for hydroformylation.

63. (B) $H_3CORu_3(CO)_{12}$

Total No. of $e^-s$ :— 3 + 9 + (8 × 3) + (12 × 2)

= 60 (valence $e^-s$)

64. (D) For aqua ion complex, acidity is more when (1) small size & (ii) greater charge

65. (A) $Co^{+2}$, Octahedral, ↿ ↿ $e_g$

$d^7$, system ⥮ ⥮ ↿ $t_{2g}$

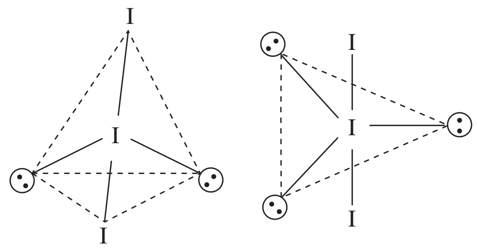
M.M. ≃ 3·9 B.M.

66. (D)

67. (C) $ClF_3 + SbF_5 \rightarrow SbF_6^- + ClF_2^+$

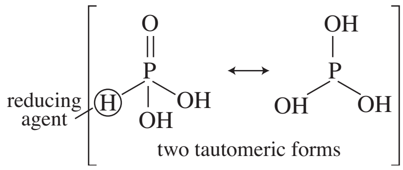
base acid ionic product

68. (C)



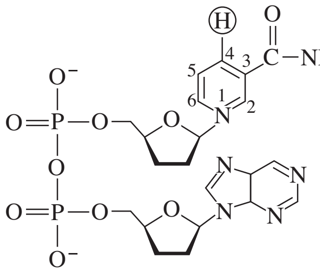

Tetrahedral ($I_3^+$) Trigonal bipyromidal ($I_3^-$)

69. (A) Phosphorus Acid (ortho)




70. (D)

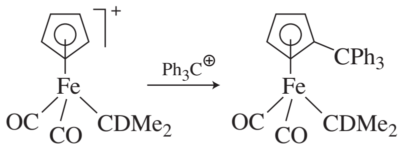
71. (C)



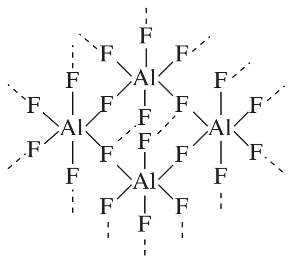

Nicotinamide adenine dinucleotide (NAD)

4-position of pyridine ring is most favourable position for nucleophilic attack in this case

72. (D)




73. (C) In solid state, Alluminium flouride have three-dimensional network structure unlike $AlCl_3$ (dimeric)



74. (B) 75. (C)

76. (B) $Sm^{+3}, f^5$ system

| +3 | +2 | +1 | 0 | −1 | −2 | −3 |
|---|---|---|---|---|---|---|
| 1 | 1 | 1 | 1 | 1 | | |

$$S = 5/2$$
$$2S + 1 = 6$$
$$L = +3 + 2 + 1 + 0 - 1$$
$$= 5(H)$$
$$\therefore J = L - S$$
(less than half-filled orbital)
$$= 5/2$$

For $Sm^{+3}$, we have ground state term symbol, $^{2S+1}L_J = \boxed{^6H_{5/2}}$ $Eu^{+3}$, $f^6$ system

| | | | | | | |
|---|---|---|---|---|---|---|
| 1 | 1 | 1 | 1 | 1 | 1 | |

$$S = \frac{6}{2} = 3$$

$2S + 1 = 7$, $L = 3$ (F), $J = 0$

$\therefore \boxed{^7F_0}$

77. (C)

78. (B) $K_2Ba[Cu(NO_2)_6]$
(A)

– tetragonal elongation ($Z_{out}$)

unpaired $e^-$ will go in $d_{x^2-y^2}$ orbital.

Thus, orbital order –

$d_{x^2-y^2} > d_{z^2} > d_{xy} > d_{xz} = d_{yz}$

$Cs_2Ba[Cu(NO_2)_6]$
(B)

– tetragonal compression ($Z_{in}$)

$$d_{z^2} > d_{x^2-y^2} > d_{xz} = d_{yz} > d_{xy}$$

unpaired $e^-$ will go in $dz^2$ orbital.

79. (A) In C—H, the three valency of C is remain and in $Co(CO)_3$, $15e^-$ system also have lack of $3e^-s$ for 18 electronic system.
So, CH & $Co(CO)_3$ are isolobal.

80. (C) We know that, Doppler shift in frequency,

$$\Delta\upsilon = \upsilon\frac{\upsilon}{c}$$

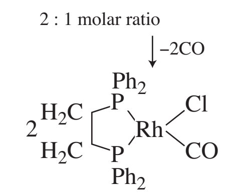
$$\therefore \Delta\upsilon = \frac{3{\cdot}48 \times 10^{18}\text{ Hz} \times 2{\cdot}2\text{ ms}^{-1}}{3 \times 10^{11}\text{ ms}^{-1}}$$
$$= 2{\cdot}55 \times 10^7\text{ Hz}$$
$$= 25{\cdot}5\text{ MHz}$$

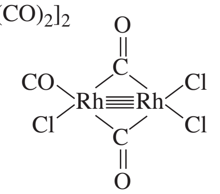
81. (B)

82. (D) $MnCr_2O_4$ – normal spinel structure $(Mn^{+2})_{Td}(Cr_2^{+3})_O O_4$ because $Cr^{+3}$ will have a LFSE in octahedral site whereas $Mn^{+2}$ ion will not.

83. (A)

$Ph_2PCH_2CH_2PPh_2 + [RhCl(CO)_2]_2$



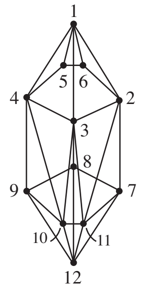




$\upsilon_{CO}$ = 1985 (terminal Co)

$CH_2$ couple with P to form doublet and this doublet with another $CH_2$ gives doublets of doublets.

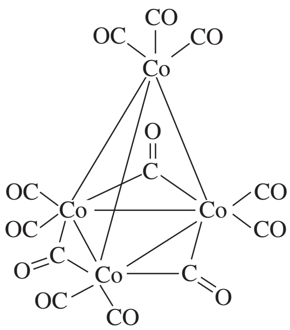
84. (D) 85. (D) 86. (B) 87. (A) 88. (A)

89. (A) Closo-carborane – $C_2B_{10}H_{12}$
    (i) 1, 2–ortho isomer
    (ii) 1, 7–meta
    (iii) 1, 12–para




90. (D)

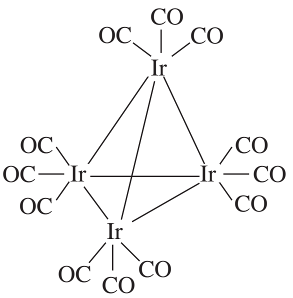
$Co_4(CO)_{12}$




$$\text{M–M bond} = \frac{72 - (24 + 36)}{2} = 6$$

Terminal CO = 9
bridging CO = 3

$Ir_4(CO)_{12}$

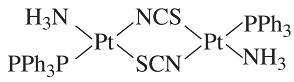



$$\text{M–M bond} = \frac{72 - (24 + 36)}{2} = 6$$

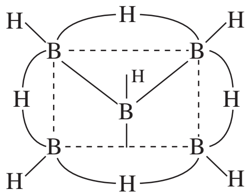
Terminal CO = 12
bridging CO = 0

91. (C) 92. (B) 93. (A)

94. (C) Pt complexes are $16e^-$ species generally, therefore there is not Pt-Pt bond formation & structure is NCS is coordinated with both side N & S with $2e^-$ donation




95. (D) For higher borones 3C–2e 'BBB' bond may be a part of their structures. For $B_5H_9$ Styx code : 4120

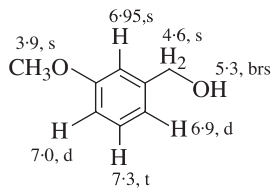


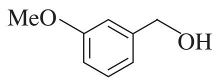

96. (B) $C_8H_{10}O_2$,

$$\text{DBE} = \frac{16 + 2 - 10}{2} = 4 \text{ (one ring)}$$

δ7·3 (1H, + J = 8Hz)
7·0 (1H, *d* J = 8Hz)
6·95 (1H, S)
6·9 (1H, *d*, J = 8Hz)
5·3 (1H, brs, $D_2O$ exchangeable)
4·6 (2H, S)
3·9 (3H, S)

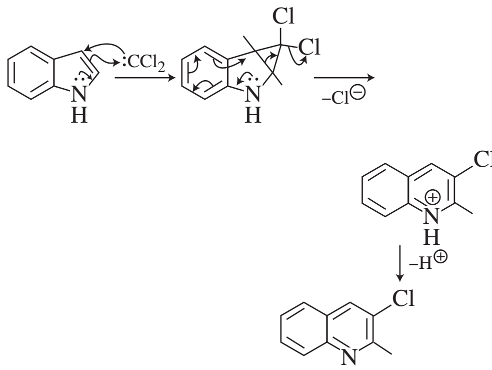
3 double bond

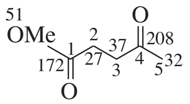


correct structure

97. (D) $CHCl_3 \xrightarrow[-H_2O]{\text{aq.NaOH}^{\ominus}} \overset{\ominus}{C}Cl_3 \xrightarrow{-Cl^{\ominus}} :CCl_2$



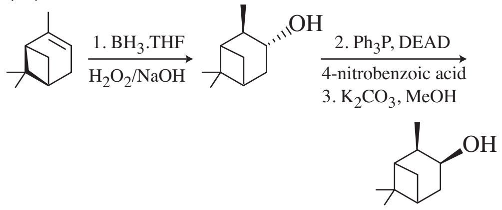
98. (D) 

Methy-4-Oxopentanoate

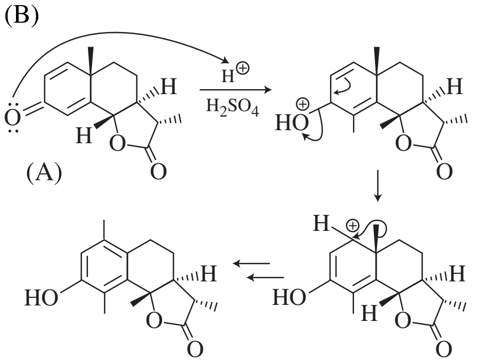
$^{13}$C NMR spectrum data suggest

OMe – 51, $C_1$ = 172, $C_4$ = 208, $C_5$ = 32

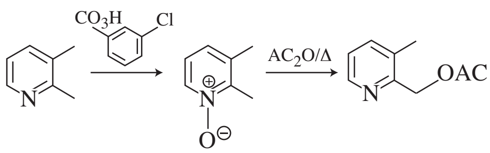
99. (A)



100. (B)

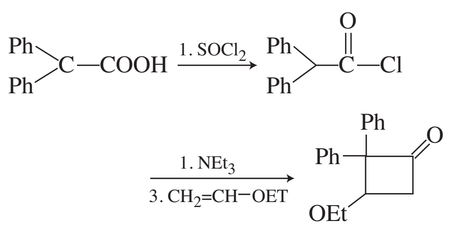


101. (D)



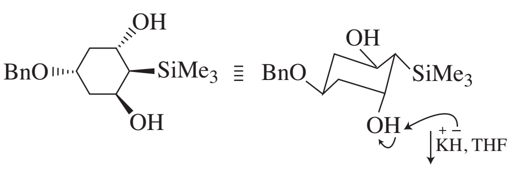
102. (C)

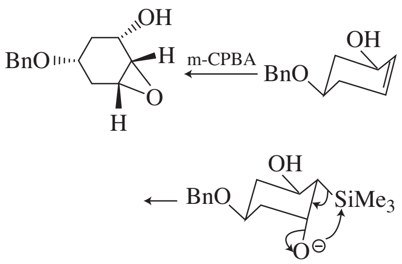
103. (C)

104. (B) 

105. (A)

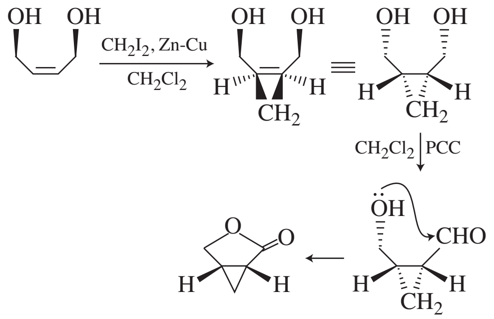
106. (B)

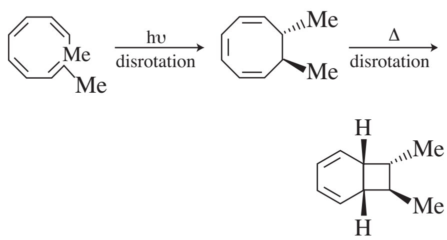


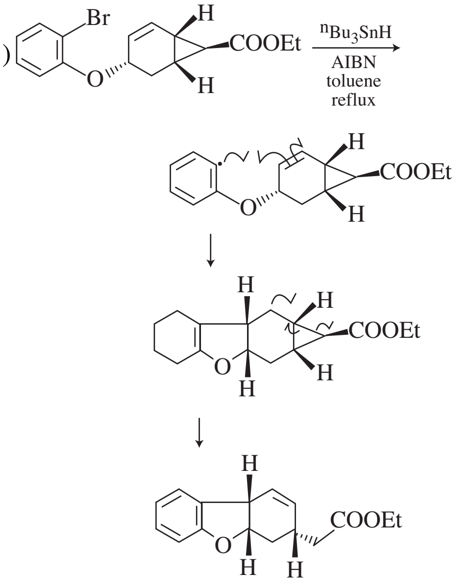


107. (A)

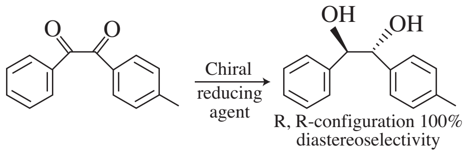
108. (A)



109. (B) 

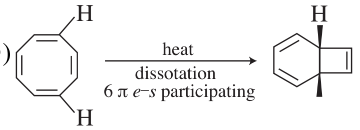
110. (D) 

111. (D)



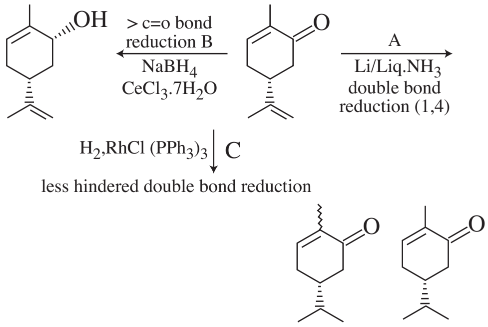

90% ee means 95% R,R–configured product.

112. (B)

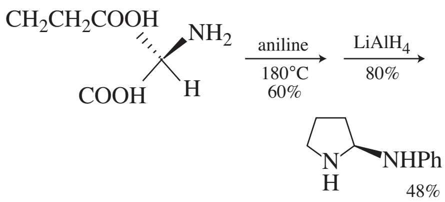
113. (D) 


114. (A) 115. (B)

116. (A)




117. (D) 118. (B) 119. (D)

120. (A) 


121. (B) Unit cell dimension, $a = 4{\cdot}00$Å

atomic radius in fcc structure is given by

$$r = \frac{a}{2\sqrt{2}} = \frac{4}{2\sqrt{2}}$$

$$= 1{\cdot}414 \text{ Å}$$

122. (C)

123. (B) The most probable value of $r$ for $e^-$ is $1s$ orbital of Hydrogen

$$r_{mp} = P(r) = R(r)^2 \cdot r^2$$

$$\Rightarrow 4\frac{d}{dr}(e^{-2r} \cdot r^2) = 0$$

$$(\because R_{1s} = 2 \cdot e^{-r})$$

$$r_{mp} = 1 = a_0$$

expectation value, $\langle r \rangle = \frac{3a_0}{2}$

124. (A) Its first option,

$\langle T \rangle = \langle V \rangle$, all explanations are true.

125. (D) 126. (C) 127. (D)

128. (B) From given data, it is clear that

rate $\propto [NO]^2$

and rate $\propto [H_2]$

Thus, orders are 2 w.r.t. NO and 1 w.r.t. $H_2$.

129. (B) The angular momentum operator $\hat{L}_y$ is

$$\hat{L}_y = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$$

$$= -\frac{i \cdot i}{i}\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$$

$$= \frac{\hbar}{i}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) \qquad (i^2 = -1)$$

130. (A) NaCl & KCl crystallize with fcc structure

NaCl — fcc

KCl — simple cubic

because $K^+$ and $Cl^-$ are iso electronic and form simple cubic structure simply.

131. (C) $V_{(x,y)} = \frac{1}{2}k_x X^2 + \frac{1}{2}k_y Y^2$

Thus, $\psi_{nx,ny} = \psi_{nx}(x).\psi_{ny}(y)$

and $E_{nx}, E_{ny} = E_{nx} + E_{ny}$

132. (B) We know

$$\rho = \frac{nM}{NV}$$

$$\therefore \quad \rho_{FCC} = \frac{4M}{NV_{FCC}}$$

and $$\rho_{BCC} = \frac{2M}{NV_{BCC}}$$

$$\therefore \quad \frac{\rho_{FCC}}{\rho_{BCC}} = \frac{4M}{NV_{FCC}} \cdot \frac{NV_{BCC}}{2M}$$

$$= \frac{2V_{BCC}}{V_{FCC}}$$

133. (D) $\pi^1\ \pi^1$

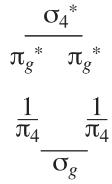
For this, we have

$\Lambda = 0(\Sigma)$

$2\Sigma + 1 = 1 \text{ or } 3$

$= 1\ \pi$

$= 2\ \Delta$




There is no term symbol like 3ϕ because it has $\Lambda = 3$ which is not possible in this case.

134. (C) We know that angular frequency,

$$\omega = \gamma B_0$$

where $\gamma$ is gynomagnetic ratio & $B_0$ = magnetic field.

Thus, $\omega = 2{\cdot}7 \times 10^8\ T^{-1}S^{-1} \times 12{\cdot}6T$

$= 34{\cdot}02 \times 10^8$ Hz

$\therefore$ resonance frequency,

$$\upsilon = \frac{\omega}{2\pi} = \frac{34{\cdot}02 \times 10^8 \text{ Hz}}{2 \times 3{\cdot}14}$$

$= 5{\cdot}14 \times 10^8$ Hz

$= 514$ MHz

135. (B) Moment of Inertia,

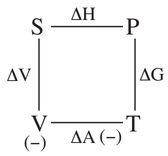
$$J = \mu r^2$$

$$I = \frac{m_1 m_2}{m_1 + m_2} \times r^2$$

$$= \frac{19}{20} \times 2 \times 2 \times 10^{-20}\ m^2 \times 1{\cdot}67 \times 10^{-27} \text{ kg}$$

$= 6{\cdot}6 \times 10^{-47}$ kgm$^2$

136. (D) The chemical potential is given as




$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P}$$

at constant temp. & pressure.

137. (B) The transition that is $x$-polarised light in trans-butadiene is for

$$^1A_u \rightarrow {}^1B_u$$

$$A_u \begin{pmatrix} x & B_u \\ y & B_u \\ z & A_u \end{pmatrix} B_u = \begin{matrix} 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 \\ 1 & -1 & 1 & -1 \end{matrix}$$

$\rightarrow$ $x$-polarised (all + ve)

138. (B)

139. (B) $n = 10$ mol, $C_P = 300\ JK^{-1}$, $C_V$ = ?

$\therefore\ C_P - C_V = nR$

$C_V = C_P - nR$

$= 300 - 10 \times 8{\cdot}314\ JK^{-1}$

$= 217\ JK^{-1}$

140. (A) Isothermal reversible expansion work,

$$w = -nRT\, ln\left(\frac{V_f}{V_i}\right)$$

– sign for expansion,

If compression then + (positive) sign.

141. (C) Maxwell's relationships are

(i) $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

(ii) $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$

(iii) $\left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S$

(iv) $\left(\frac{\partial P}{\partial S}\right)_V = -\left(\frac{\partial T}{\partial V}\right)_S$

142. (C)

143. (B) $Zn/Zn^{+2}$ ($a$= 0·01) || $Fe^{+2}$ ($a$ = 0·001), $Fe^{+3}$ ($a$ = 0·01)/Pt $E_{cell}$ = 1·71V

$$Zn + 2Fe^{+3} \rightleftharpoons Zn^{+2} + 2Fe^{+2}$$

$$Zn \rightarrow Zn^{+2} + 2e^-$$

$$2Fe^{+3} \xrightarrow{2e^-} 2Fe^{+2}$$

$$\therefore \quad \log k_{eg} = \frac{n \times E_{cell}}{0{\cdot}0591}$$

$$= \frac{2 \times 1{\cdot}7100}{0{\cdot}0591} \approx 54$$

$$k_{eg} = 10^{54}$$

144. (B) All explanation are correct, but option is (B) H—C ≡ C—H – smallest partition function, less molecular mass.

145. (D) Limiting molar conductivities of reactant

$= \lambda^{\infty}$ of product

$\therefore$ NaI + RbCl $\rightarrow$ NaCl + RbI mSm$^2$ mol$^{-1}$

10·8 12·7 9·1

$\therefore\ \lambda_{RbCl} = 12{\cdot}7 + 9{\cdot}1 - 10{\cdot}8$

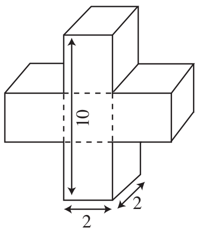
$= 11{\cdot}0$ mSm$^2$ mol$^{-1}$

## Chemical Sciences
### CSIR-UGC NET/JRF Exam.
**Solved Paper**

# June 2014
# Chemical Sciences

## PART A

1. The following diagram shows 2 perpendicularly inter-grown prismatic crystals (twins) of identical shape and size. What is the volume of the object shown (units are arbitrary) ?




(A) 60 (B) 65
(C) 72 (D) 80

2. Suppose in a box there are 20 red, 30 black, 40 blue and 50 white balls. What is the minimum number of balls to be drawn, without replacement, so that you are certain about getting 4 red, 5 black, 6 blue and 7 white balls ?

(A) 140 (B) 97
(C) 104 (D) 124

3. In the growing years of a child, the height increases as the square root of the age while the weight increases in direct proportion to the age. The ratio of the weight to the square of the height in this phase of growth—

(A) is constant
(B) reduces with age
(C) increases with age
(D) is constant only if the weight and height at birth are both zero

4. Students in group A obtained the following marks : 40, 80, 70, 50, 60, 90, 30. Students in group B obtained 40, 80, 35, 70, 85, 45, 50, 75, 60 marks. Define dispersion (D) = (maximum marks – minimum marks), and

relative dispersion (RD) = $\frac{\text{dispersion}}{\text{mean}}$. Then,

(A) RD of group A = RD of group B
(B) RD of group A > RD of group B
(C) RD of group A < RD of group B
(D) D of group A < D of group B

5. In 450 g of pure coffee powder 50 g of chicory is added. A person buys 100 g of this mixture and adds 5 g of chicory to that. What would be the rounded-off percentage of chicory in this final mixture ?

(A) 10 (B) 5
(C) 14 (D) 15

6. The time gap between the two instants, one before and one after 12·00 noon, when the angle between the hour hand and the minute hand is 66°, is—

(A) 12 min (B) 16 min
(C) 18 min (D) 24 min

7. Suppose

$$x \,\Delta\, y = (x - y)^2$$
$$x \text{ o } y = (x + y)^2$$
$$x * y = (x \times y)^{-1}$$
$$x \cdot y = x \times y$$

+, – and × have their usual meanings. What is the value of

[(197 o 315) – (197 Δ 315)} · (197 * 315) ?

(A) 118 (B) 512
(C) 2 (D) 4

8. If A × B = 24, B × C = 32, C × D = 48 then A × D—

(A) cannot be found (B) is a perfect square
(C) is a perfect cube (D) is odd

9. If all horses are donkeys, some donkeys are monkeys and some monkeys are men, then which statement must be true ?
   (A) All donkeys are men
   (B) Some donkeys may be men
   (C) Some horses are men
   (D) All horses are also monkeys

10. A rectangular area of sides 9 and 6 units is to be covered by square tiles of sides 1, 2 and 5 units. The minimum number of tiles needed for this is—
   (A) 3 (B) 11
   (C) 12 (D) 15

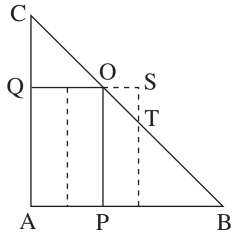
11. Suppose $n$ is a positive integer. Then $(n^2 + n)(2n + 1)$—
   (A) may not be divisible by 2
   (B) is always divisible by 2 but may not be divisible by 3
   (C) is always divisible by 3 but may not be divisible by 6
   (D) is always divisible by 6

12. There is a train of length 500 m, in which a man is standing at the rear end. At the instant the rear end crosses a stationary observer on a platform, the man starts walking from the rear to the front and the front to the rear of the train at a constant speed of 3 km/hr. The speed of the train is 80 km/hr. The distance of the man from the observer at the end of 30 minutes is—
   (A) 41·5 km (B) 40·5 km
   (C) 40·0 km (D) 41·0 km

13. Three identical flat equilateral-triangular plates of side 5 cm each are placed together such that they form a trapezium. The length of the longer of the two parallel sides of this trapezium is—
   (A) $5\sqrt{\frac{3}{4}}$ cm (B) $5\sqrt{2}$ cm
   (C) 10 cm (D) $10\sqrt{3}$ cm

14. An archer climbs to the top of a 10 m high building and aims at a bird atop a tree 17 m away. The line of sight from the archer to the bird makes an angle of 45° to the horizontal. What is the height of the tree ?
   (A) 17 m (B) 27 m
   (C) 37 m (D) 47 m

15. Consider a right-angled triangle ABC where AB = AC = 3. A rectangle APOQ is drawn inside it, as shown, such that the height of the rectangle is twice its width. The rectangle is moved horizontally by a distance 0·2 as shown schematically in the diagram (not to scale).




What is the value of the ratio $\frac{\text{Area of } \Delta ABC}{\text{Area of } \Delta OST}$ ?
   (A) 625 (B) 400
   (C) 225 (D) 125

16. 80 gsm paper is cut into sheets of 200 mm × 300 mm size and assembled in packets of 500 sheets. What will be the weight of a packet ? (gsm = $g/m^2$)
   (A) 1·2 kg (B) 2·4 kg
   (C) 3·6 kg (D) 4·8 kg

17. Find the missing letter

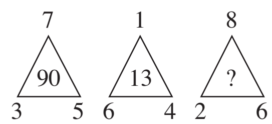
| | | | |
|---|---|---|---|
| A | B | C | D |
| F | I | L | O |
| K | P | U | Z |
| P | W | D | ? |

   (A) P (B) K
   (C) J (D) L

18. A merchant buys equal numbers of shirts and trousers and pays Rs. 38,000. If the cost of 3 shirts is Rs. 800 and that of a trouser is Rs. 1,000, then how many shirts were bought ?
   (A) 60 (B) 30
   (C) 15 (D) 10

19. Consider the set of numbers $\{17^1, 17^2, \ldots, 17^{300}\}$. How many of these numbers end with the digit 3 ?
   (A) 60 (B) 75
   (C) 100 (D) 150

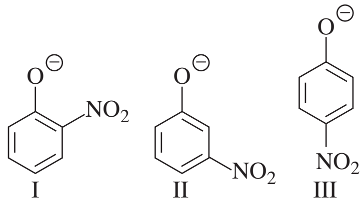
20. Find the missing number in the triangle.



(A) 16 (B) 96
(C) 50 (D) 80

## PART B

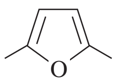
21. The correct order of basicity for the following anions is—

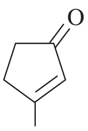


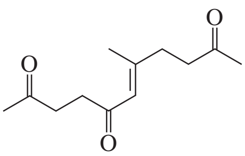

I II III

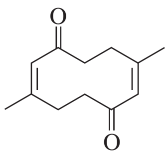
(A) II > III > I (B) I > II > III
(C) II > I > III (D) III > II > I

22. The major product formed in the reaction of 2, 5-hexanedione with $P_2O_5$ is—

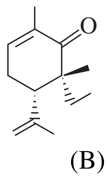
(A) 


(B) 


(C) 

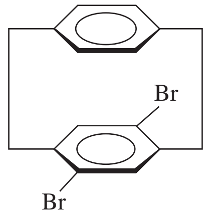

(D) 


23. The absolute configuration of the two stereogenic (chiral) centres in the following molecule is—




(A) 5R, 6R (B) 5R, 6S
(C) 5S, 6R (D) 5S, 6S

24. The correct statement about the following molecule is—




(A) molecule is chiral and possesses a chiral plane
(B) Molecule is chiral and possesses a chiral axis
(C) Molecule is achiral as it possesses a plane of symmetry
(D) Molecule is achiral as it possesses a centre of symmetry

25. Consider the following statements about *cis*- and *trans*-decalins—
1. *cis*-isomer is more stable than *trans*-isomer
2. *trans*-isomer is more stable than *cis*-isomer
3. *trans*-isomer undergoes ring-flip
4. *cis*-isomer undergoes ring-flip

The correct statements among the above are—
(A) 2 and 4 (B) 1 and 3
(C) 1 and 4 (D) 2 and 3

26. In bis (dimethylglyoximato) nickel(II), the number of Ni—N, Ni—O and intramolecular hydrogen bond(s), respectively, are—
(A) 4, 0 and 2 (B) 2, 2 and 2
(C) 2, 2 and 0 (D) 4, 0 and 1

27. Among the following species, (1) Ni(II) as dimethylglyoximate, (2) Al(III) as oxinate, (3) Ag(I) as chloride, those that precipitate with the urea hydrolysis method are—
(A) 1, 2 and 3 (B) 1 and 2
(C) 1 and 3 (D) 2 and 3

28. If an enzyme fixes $N_2$ in plants by evolving $H_2$, the number of electrons and protons associated with that, respectively are—
(A) 6 and 6 (B) 8 and 8
(C) 6 and 8 (D) 8 and 6

29. The particles postulated to always accompany the positron emission among—
(1) neutrino, (2) anti-neutrino, (3) electron, are—
(A) 1, 2 and 3 (B) 1 and 2
(C) 1 and 3 (D) 2 and 3

30. Toxicity of cadmium and mercury in the body is being reversed by proteins, mainly using the amino acid residue—
(A) Glycine (B) Leucine
(C) Lysine (D) Cysteine

31. $NiBr_2$ reacts with $(Et)(PH)_2P$ at – 78°C in $CS_2$ to give red compound, 'A', which upon standing at room temperature turns green to give compound, 'B', of the same formula. The measured magnetic moments of 'A' and 'B' are 0·0 and 3·2 BM, respectively. The geometries of 'A' and 'B' are—
(A) Square planar and Tetrahedral
(B) Tetrahedral and Square planar
(C) Square planar and Octahedral
(D) Tetrahedral and Octahedral

32. The correct non-linear and iso-structural pair is—
(A) $SCl_2$ and $I_3$ (B) $SCl_2$ and $I_3^+$
(C) $SCl_2$ and $ClF_2^-$ (D) $I_3^+$ and $ClF_2^-$

33. Ozone present in upper atmosphere protects people on the earth—
(A) due to its diamagnetic nature
(B) due to its blue colour
(C) due to absorption of radiation of wavelength at 255 nm
(D) by destroying chlorofluoro carbons

34. If L is a neutral monodentate ligand, the species, $[AgL_4\}^{2+}$, $[AgL_6\}^{2+}$ and $[AgL_4]^{3+}$ respectively are—
(A) paramagnetic, paramagnetic and diamagnetic
(B) paramagnetic, diamagnetic and paramagnetic
(C) diamagnetic, paramagnetic and diamagnetic
(D) paramagnetic, diamagnetic and diamagnetic

35. Chromite ore on fusion with sodium carbonate gives—
(A) $Na_2CrO_4$ and $Fe_2O_3$
(B) $Na_2Cr_2O_7$ and $Fe_2O_3$
(C) $Cr_2(CO_3)_3$ and $Fe(OH)_3$
(D) $Na_2CrO_4$ and $Fe_2(CO_3)_3$

36. The ligand(s) that is (are) fluxional in $[(\eta^5 - C_5H_5)(\eta^1 - C_5H_5)Fe(CO)_2]$ in the temperature range 221 – 298 K, is (are)—
(A) $\eta^5 - C_5H_5$
(B) $\eta^1 - C_5H_5$
(C) $\eta^5 - C_5H_5$ and CO
(D) $\eta^1 - C_5H_5$ and CO

37. $[CoL_6]^{3+}$ is red in colour whereas $[CoL'_6]^{3+}$ is green. L and L′ respectively corresponds to—
(A) $NH_3$ and $H_2O$
(B) $NH_3$ and 1, 10-phenanthroline
(C) $H_2O$ and 1, 10-phenanthroline
(D) $H_2O$ and $NH_3$

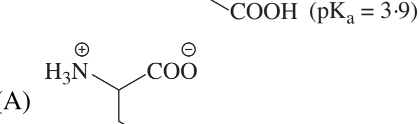
38. The oxidation state of Ni and the number of metal–metal bonds in $[Ni_2(CO)_6]^{2+}$ that are consistent with the 18 electrons rule are—
(A) Ni(– II), 1 bond (B) Ni(IV), 2 bonds
(C) Ni(–I), 1 bond (D) Ni(IV), 3 bonds

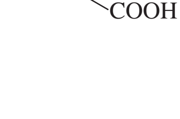
39. Structures of $SbPh_5$ and $PPh_5$ respectively are—
(A) trigonal bipyramidal, square pyramidal
(B) square pyramidal, trigonal bipyramidal
(C) trigonal bipyramidal, trigonal bipyramidal
(D) square pyramidal, square pyramidal

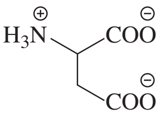
40. The typical electronic configurations of the transition metal centre for oxidative addition are—
(A) $d^0$ and $d^8$ (B) $d^5$ and $d^8$
(C) $d^8$ and $d^{10}$ (D) $d^5$ and $d^{10}$

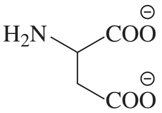
41. Gelatin added during the polarographic measurement carried out using dropping mercury electrode—
(A) reduces streaming motion of Hg drop
(B) decreases viscosity of the solution
(C) eliminates migrating current
(D) prevents oxidation of Hg

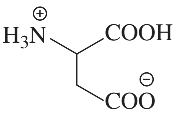
42. The $pK_a$ values of the following salt of aspartic acid are indicated below. The predominant species that would exist at pH = 5 is—



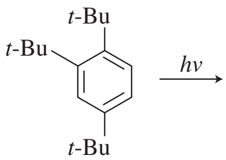

(A)


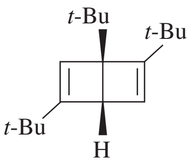
(B) 

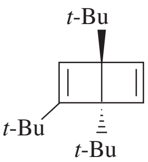

(C) 

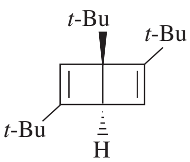

(D) 

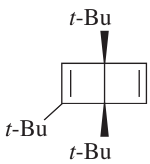

43. The major product formed in the following photochemical reaction is—




(A) 


(B) 


(C) 


(D) 


44. The pair of solvents in which $PCl_5$ does NOT ionize is—

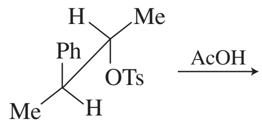
(A) $CH_3CN, CH_3NO_2$

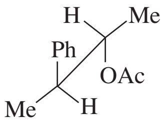
(B) $CH_3CN, CCl_4$

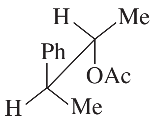
(C) $C_6H_6, CCl_4$

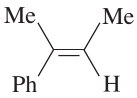
(D) $CH_3CN, C_6H_6$

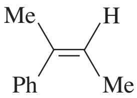
45. The major product formed in the following reaction is—



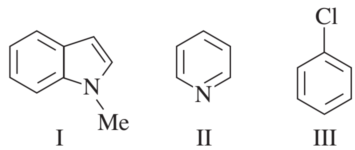

(A) 


(B) 


(C) 


(D) 


46. The correct order for the rates of electrophilic aromatic substitution of the following compounds is—




I II III

(A) I > II > III (B) II > I > III

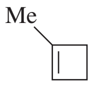
(C) III > II > I (D) I > III > II

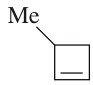
47. The commutator of the kinetic energy operator, $\hat{T}_x$ and the momentum operator, $\hat{p}_x$ for the one-dimensional case is—

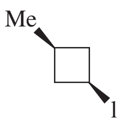
(A) $i\hbar$ (B) $i\hbar \frac{d}{dx}$

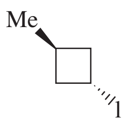
(C) 0 (D) $i\hbar x$

48. The major product formed in the reaction of *trans*-1-bromo-3-methylcyclobutane with sodium iodide in DMF is—

(A) 


(B) 


(C) 


(D) 

49. When Si is doped with a Group V element—
(A) donor levels are created close to the valence band
(B) donor levels are created close to the conduction band
(C) acceptor levels are created close to the valence band
(D) acceptor levels are created close to the conduction band

50. The symmetry point group of propyne is—
(A) $C_3$ (B) $C_{3v}$
(C) $D_3$ (D) $D_{3d}$

51. For a first order reaction A → products, the plot of $\ln\left(\frac{[A]_t}{[A]_0}\right)$ *vs*. time, where $[A]_0$ and $[A]_t$ refer to concentrations at time $t = 0$ and $t$ respectively, is—
(A) a straight line with a positive slope passing through origin
(B) a straight line with a negative slope passing through origin
(C) an exponential curve asymptotic to the time axis
(D) a curve asymptotic to the $\ln\left(\frac{[A]_t}{[A]_0}\right)$ axis

52. In radical chain polymerization the quantity given by 'the rate of monomer depletion, divided by the rate of propagating radical formation' is called—
(A) kinetic chain length
(B) propagation efficiency
(C) propagation rate constant
(D) polymerization time

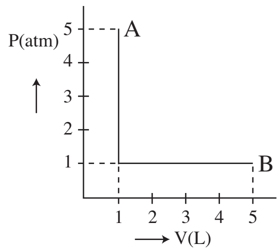
53. Number of rotational symmetry axes for triclinic crystal system is—
(A) 4 (B) 3
(C) 1 (D) 0

54. Generally, hydrophobic colloids are flocculated efficiently by ions of opposite type and high charge number. This is consistent with the—
(A) peptization principle
(B) Krafft theory
(C) Hardy-Schulze rule
(D) Langmuir adsorption mechanism

55. Examine the following first order consecutive reactions. The rate constant (in $s^{-1}$ units) for each step is given above the arrow mark—
1. $P \xrightarrow{10^5} Q \xrightarrow{10^8} R$
2. $P \xrightarrow{10^5} Q \xrightarrow{10^3} R$
3. $P \xrightarrow{10^7} Q \xrightarrow{10^7} R$
4. $P \xrightarrow{10^2} Q \xrightarrow{10^6} R$

Steady-state approximation can be applied to—
(A) 1 only (B) 3 only
(C) 2 and 3 only (D) 1 and 4 only

56. The figure below represents the path followed by a gas during expansion from A → B. The work done is (L atm.)



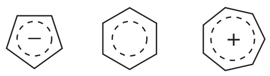

(A) 0 (B) 9
(C) 5 (D) 4

57. An aqueous solution of an optically pure compound of concentration 100 mg in 1 mL of water and measured in a quartz tube of 5 cm length was found to be – 3°. The specific rotation is—
(A) – 30° (B) – 60°
(C) – 6° (D) + 6°

58. Two phases (α and β) of a species are in equilibrium. The correct relations observed among the variables, T, $p$ and μ are—
(A) $T_\alpha = T_\beta, p_\alpha \neq p_\beta, \mu_\alpha = \mu_\beta$
(B) $T_\alpha \neq T_\beta, p_\alpha = p_\beta, \mu_\alpha = \mu_\beta$
(C) $T_\alpha = T_\beta, p_\alpha = p_\beta, \mu_\alpha = \mu_\beta$
(D) $T_\alpha = T_\beta, p_\alpha = p_\beta, \mu_\alpha \neq \mu_\beta$

59. The number of configurations in the most probable state, according to Boltzmann formula is—
(A) $e^{S/k_B}$ (B) $e^{-S/k_B}$
(C) $e^{-E/k_BT}$ (D) $e^{-\Delta G/k_BT}$

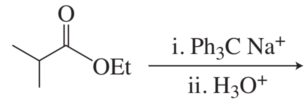
60. The correct match of the ′HNMR chemical shifts (δ) of the following species/compounds is—

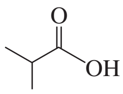


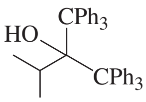
I II III

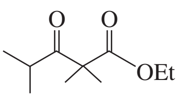
(A) I : 5·4; II : 7·2; III : 9·2
(B) I : 9·2; II : 7·2; III : 5·4
(C) I : 9·2; II : 5·4; III : 7·2
(D) I : 7·2; II : 9·2; III : 5·4

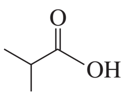
61. The major products formed in the following reaction are—




(A)  + $Ph_3C–CH_2CH_3$

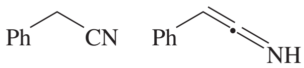
(B)  + EtOH

(C)  + EtOH

(D)  + $CH_2{=}CH_2$

62. In a Diels-Alder reaction, the most reactive diene amongst the following is—
(A) (4E)-1, 4-hexadiene
(B) (4Z)-1, 4-hexadiene
(C) (2E, 4E)-2, 4-hexadiene
(D) (2Z, 4Z)-2, 4-hexadiene

63. Consider the statements about the following structures **X** and **Y**.



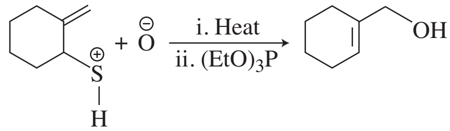
X Y

1. **X** and **Y** are resonance structures
2. **X** and **Y** are tautomers
3. **Y** is more basic than **X**
4. **X** is more basic than **Y**

The correct statement(s) among the above is (are)—

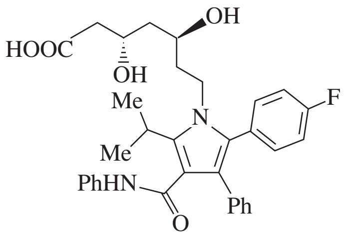
(A) 1 and 3 (B) Only 3
(C) 2 and 4 (D) 2 and 3

64. Pericyclic reaction involved in one of the steps of the following reaction sequence is—




(A) [1, 3] sigmatropic shift
(B) [3, 3] sigmatropic shift
(C) [1, 5] sigmatropic shift
(D) [2, 3] sigmatropic shift

65. Atorvastatin (structure given below) is a—




(A) cholesterol lowering drug
(B) blood sugar lowering drug
(C) anti-plasmodial drug
(D) anti-HIV drug

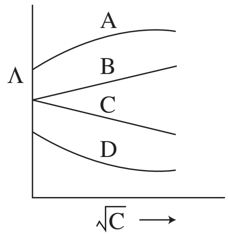
66. The maximum bond order obtained from the molecular orbitals of a transition metal dimer, formed as linear combinations of *d*-orbitals alone, is—
(A) 3 (B) 4
(C) 5 (D) 6

67. The term symbol that is NOT allowed for the $np^2$ configuration is—
(A) $^1D$ (B) $^3P$
(C) $^1S$ (D) $^3D$

68. If the ionization energy of H atom is $x$, the ionization energy of $Li^{2+}$ is—
(A) $2x$ (B) $3x$
(C) $9x$ (D) $27x$

69. If temperature is doubled and the mass of the gaseous molecule is halved, the rms speed of the molecule will change by a factor of—
(A) 1 (B) 2
(C) $\frac{1}{2}$ (D) $\frac{1}{4}$

70. In the graph below, the correct option, according to Kohlrausch law is—




(A) A is a weak electrolyte and B is a strong electrolyte
(B) A is a strong electrolyte and B is a weak electrolyte
(C) C is a strong electrolyte and D is a weak electrolyte
(D) C is a weak electrolyte and D is a strong electrolyte

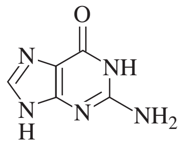
## PART C

71. Reduction of $[Ru(NH_3)_5$ (isonicotinamide)$]^{3+}$ with $[Cr(H_2O)_6]^{2+}$ occurs by inner sphere mechanism and rate of the reaction is determined by dissociation of the successor complex. It is due to the—
(A) inert ruthenium bridged to inert chromium centre
(B) inert ruthenium bridged to labile chromium centre
(C) labile ruthenium bridged to inert chromium centre
(D) labile ruthenium bridged to labile chromium centre

72. Consider the second order rate constants for the following outer-sphere electron transfer reactions
$[Fe(H_2O)_6]^{3+}/[Fe(H_2O)_6]^{2+}$ 4·0 $M^{-1}$ $sec^{-1}$
$[Fe(phen)_3]^{3+}/[Fe(Phen)_3]^{2+}$ $3·0 \times 10^7$ $M^{-1}$ $sec^{-1}$
(phen = 1, 10-phenanthroline)
The enhanced rate constant for the second reaction is due to the fact that—
(A) The 'phen' is a π-acceptor ligand that allows mixing of electron donor and acceptor orbitals that enhances the rate of electron transfer
(B) The 'phen' is a π-donor ligand that enhances the rate of electron transfer
(C) The 'phen' forms charge transfer complex with iron and facilitates the electron transfer
(D) The 'phen' forms kinetically labile complex with iron and facilitates the electron transfer

73. The compound $[Re_2(Me_2PPh)_4Cl_4]$ (M) having a configuration of $\sigma^2\pi^4,\delta^2\delta^{*2}$ can be oxidized to $M^+$ and $M^{2+}$. The formal metal – metal bond order in M, $M^+$ and $M^{2+}$ respectively are—
(A) 3·0, 3·5 and 4·0 (B) 3·5, 4·0 and 3·0
(C) 4·0, 3·5 and 3·0 (D) 3·0, 4·0 and 3·5

74. In low chloride ion concentration, the anticancer drug cis-platin hydrolyses to give a diaquo complex and this binds to DNA via adjacent guanine




(guanine)

The co-ordinating atom of guanine to Pt(II) is—
(A) N1 (B) N3
(C) N7 (D) N9

75. The $^{19}F$-NMR spectrum of $ClF_3$ shows—
(A) doublet and triplet for a T-shaped structure
(B) singlet for a trigonal planar structure
(C) singlet for a trigonal pyramidal structure
(D) doublet and singlet for a T-shaped structure

76. The low temperature (–98°C) $^{19}F$ NMR spectrum of $SF_4$ shows doublet of triplets. It is consistent with the point group symmetry—
(A) $C_{3v}$ (B) $C_{4v}$
(C) $T_d$ (D) $C_{2v}$

77. Amongst organolithium (A), Grignard (B) and organoaluminium (C) compounds, those react with $SiCl_4$ to give compound containing Si — C bond are—
(A) A and B (B) B and C
(C) A and C (D) A, B and C

78. In its electronic spectrum, $[V(H_2O)_6]^{3+}$ exhibits two absorption bands, one at 17,800 ($\upsilon_1$) and the second at 25,700 ($\upsilon_2$) $cm^{-1}$. The correct assignment of these bands, respectively is—

(A) $\upsilon_1 = {}^3T_{1g}(F) \rightarrow {}^3T_{2g}(F)$

$\upsilon_2 = {}^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$

(B) $\upsilon_1 = {}^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$

$\upsilon_2 = {}^3T_{1g}(F) \rightarrow {}^3T_{2g}(P)$

(C) $\upsilon_1 = {}^3A_{2g} \rightarrow {}^3T_{1g}(F)$

$\upsilon_2 = {}^3A_{2g} \rightarrow {}^3T_{2g}(F)$

(D) $\upsilon_1 = {}^3A_{2g} \rightarrow {}^3T_{2g}(F)$

$\upsilon_2 = {}^3A_{2g} \rightarrow {}^3T_{1g}(F)$

79. Reactions of elemental As with hot and conc. $HNO_3$ and $H_2SO_4$, respectively, give—

(A) $As_4O_6$ and $As_2(SO_4)_3$

(B) $As(NO_3)_5$ and $As_2(SO_4)_3$

(C) $As_4O_6$ and $H_3AsO_4$

(D) $H_3AsO_4$ and $As_4O_6$

80. The total valence electron count and the structure type adopted by the complex $[Fe_5(CO)_{15}C]$ respectively, are—

(A) 74 and *nido* (B) 60 and *closo*

(C) 84 and *arachno* (D) 62 and *nido*

81. 1H NMR spectrum of $[\eta^5\text{–}C_5H_5)Rh(C_2H_4)_2]$ at – 20°C shows a typical AA 'XX' pattern in the olefinic region. On increasing the temperature to ~70°C, the separate lines collapse into a single line which is due to—

(A) free rotation of the ethylene ligand about the metal-olefin bond

(B) intramolecular exchange between the ethylene ligands

(C) intermolecular exchange between the ethylene ligands

(D) change in hapticity of the cyclopentadienyl ligand

82. The nuclides among the following, capable of undergoing fission by thermal neutrons, are—

1. $^{233}U$ 2. $^{235}U$

3. $^{239}Pu$ 4. $^{232}Th$

(A) 1, 2 and 4 (B) 1, 3 and 4

(C) 2, 3 and 4 (D) 1, 2 and 3

83. The use of dynamic inert atmosphere in thermogravimetric analysis (TGA)—

(A) decreases decomposition temperature

(B) decreases weight loss

(C) reduces rate of decomposition

(D) increases weight loss

84. The correct statements for hollow cathode lamp (HCL) from the following are—

1. HCL is suitable for atomic absorption spectroscopy (AAS)
2. lines emitted from HCL are very narrow
3. the hardening of lamp makes it unsuitable for AAS
4. transition elements used in the lamps have short life

(A) 1, 2 and 3 (B) 2, 3 and 4

(C) 3, 4 and 1 (D) 4, 1 and 2

85. Identify the correct statement about $[Ni(H_2O)_6]^{2+}$ and $[Cu(H_2O)_6]^{2+}$

(A) all Ni–O and Cu–O bond lengths of individual species are equal

(B) Ni–O (equatorial) and Cu–O (equatorial) bond lengths are shorter than Ni–O (axial) and Cu–O (axial) ones respectively

(C) all Ni–O bond lengths are equal whereas Cu–O(equatorial) bonds are shorter than Cu–O(axial) bonds

(D) all Cu–O bond lengths are equal whereas Ni–O(equatorial) bonds are shorter than Ni–O(axial) bonds

86. Reaction of nitrosyl tetrafluoroborate to Vaska's complex gives complex A with $\angle$M–N–O = 124°. The complex A and its N–O stretching frequency are, respectively—

(A) $[IrCl(CO)(NO)(PPh_3)_2]BF_4$, 1620 $cm^{-1}$

(B) $[IrCl(CO)(NO)_2(PPh_3)](BF_4)_2$, 1720 $cm^{-1}$

(C) $[IrCl(CO)(NO)_2(PPh_3)](BF_4)_2$, 1520 $cm^{-1}$

(D) $[IrCl(CO)(NO)(PPh_3)_2]$, 1820 $cm^{-1}$

87. The correct order of decreasing electronegativity of the following atoms is—

(A) As > Al > Ca > S

(B) S > As > Al > Ca

(C) Al > Ca > S > As

(D) S > Ca > As > Al

88. A 1 : 2 mixture of $Me_2NCH_2CH_2CH_2PPh_2$ and KSCN with $K_2[PdCl_4]$ gives a square planar complex A. Identify the correct pairs of donor atoms *trans* to each other in complex A from the following combinations—

1. P, N
2. N, S
3. P, S
4. N, N

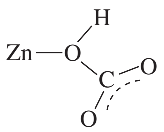
(A) 1 and 2 (B) 1 and 4
(C) 2 and 3 (D) 3 and 4

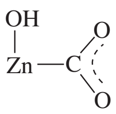
89. For a low energy nuclear reaction, $^{24}Mg(d, \alpha)^{22}Na$, the correct statements from the following are—

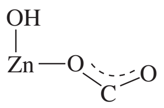
1. kinetic energy of *d* particle is not fully available for exciting $^{24}Mg$
2. total number of protons and neutrons is conserved
3. Q value of nuclear reaction is much higher in magnitude relative to heat of chemical reaction
4. threshold energy is ≤ Q value

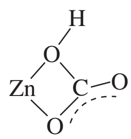
(A) 1, 2 and 3 (B) 1, 2 and 4
(C) 2, 3 and 4 (D) 1, 3 and 4

90. At pH 7, the zinc(II) ion in carbonic anhydrase reacts with $CO_2$ to give—

(A) 


(B) 


(C) 


(D) 


91. Molybdoenzymes can both oxidize as well as reduce the substrates, because—

(A) Mo(VI) is more stable than Mo(IV)
(B) Mo(IV) can transfer oxygen atom to the substrate and Mo(VI) can abstract oxygen atom from the substrate
(C) conversion of Mo(VI) to Mo(IV) is not favoured
(D) Mo(VI) can transfer oxygen atom to the substrate and Mo(IV) can abstract oxygen atom from the substrate

92. A comparison of the valence electron configuration of the elements, Sm and Eu suggests that—

(A) Sm is a better one electron reductant than Eu
(B) Sm is a better one electron oxidant than Eu
(C) facile oxidation state is +2 for both the elements
(D) both of these display similar redox behaviour

93. The cooperative binding of $O_2$ in hemoglobin is due to—

(A) a decrease in size of iron followed by changes in the protein conformation
(B) an increase in size of iron followed by changes in the protein conformation
(C) a decrease in size of iron that is NOT accompanied by the protein conformational changes
(D) an increase in size of iron that is NOT accompanied by the protein conformational changes

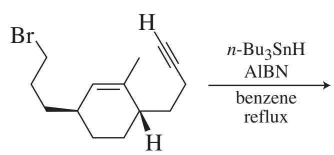
94. Amongst the following which is not isolobal pairs—

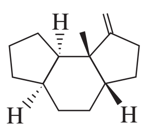
(A) $Mn(CO)_5, CH_3$ (B) $Fe(CO)_4, O$
(C) $Co(CO)_3, R_2Si$ (D) $Mn(CO)_5, RS$

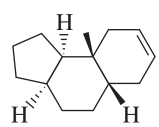
95. The correct order of the size of S, $S^{2-}$, $S^{2+}$ and $S^{4+}$ species is—

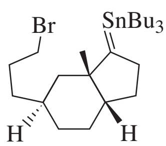
(A) $S > S^{2+} > S^{4+} > S^{2-}$
(B) $S^{2+} > S^{4+} > S^{2-} > S$
(C) $S^{2-} > S > S^{2+} > S^{4+}$
(D) $S^{4+} > S^{2-} > S > S^{2+}$

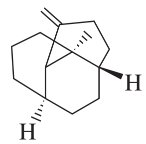
96. The major product formed in the following reaction is—



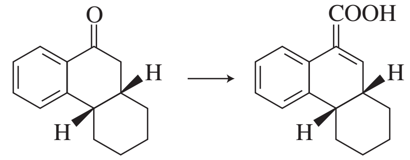

(A) 


(B) 


(C) 

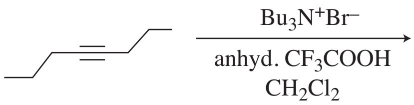

(D) 

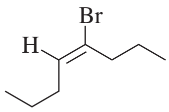
97. The correct combination of reagents to effect the following conversion is—

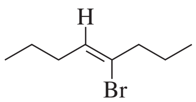


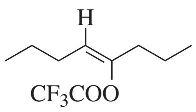
(A) (i) $Ph_3P^+CH_2OMeCl^-$, BuLi; (ii) $H_3O^+$; (iii) Jones' reagent
(B) (i) $H_2N$–NHTs; (ii) BuLi (2 equiv.); (iii) DMF
(C) (i) $H_2N$–NHTs; (ii) BuLi (2 equiv.); (iii) $CO_2$
(D) (i) $ClCH_3CO_2Et$, LDA; (ii) $BF_3 \cdot OEt_2$; (iii) DMSO, $(COCl)_2$, $Et_3N$ – 78°C to rt

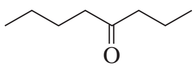
98. The major product formed in the following reaction is—



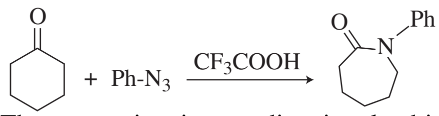

(A) 

(B) 

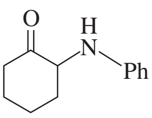
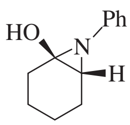
(C) 

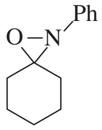
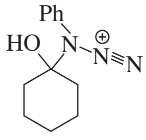
(D) 

99. Consider the following reaction.

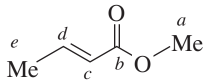



The appropriate intermediate involved in this reaction is—

(A) 
(B) 

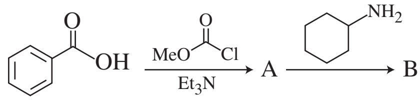
(C) 
(D) 

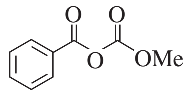
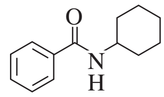
100. The correct $^{13}C$ NMR chemical (δ) shift values of carbons labeled a-e in the following ester are—

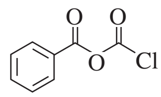
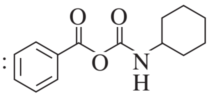


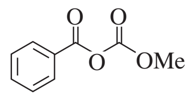
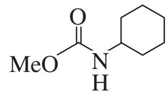
(A) a : 19; b : 143; c : 167; d : 125; e : 52
(B) a : 52; b : 143; c : 167; d : 125; e : 19
(C) a : 52, b : 167; c : 143; d : 125; e : 19
(D) a : 52, b : 167; c : 125; d : 143; e : 19

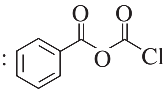
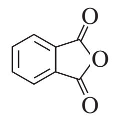
101. The products A and B in the following reaction sequence are—



(A) A :  B : 

(B) A :  B : 

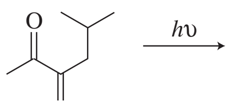
(C) A :  B : 

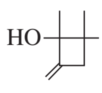
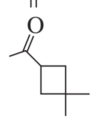
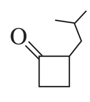
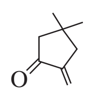
(D) A :  B : 

102. The biosynthesis of isopentenyl pyrophosphate from acetyl CoA involves—
1. Four molecules of acetyl CoA
2. Three molecules of ATP
3. Two molecules of NADPH
4. Two molecules of lipoic acid

The correct options among these are—
(A) 1, 2 and 4 (B) 1 and 2
(C) 2 and 3 (D) 1, 3 and 4

103. Amongst the following, the major products formed in the following photochemical reaction are—

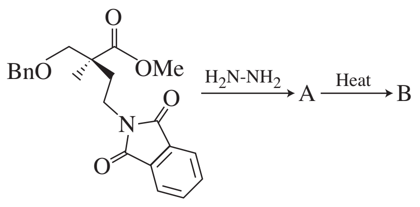


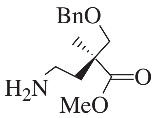
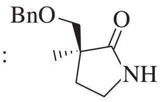
   

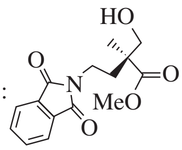
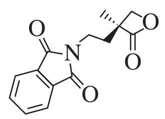
(1) (2) (3) (4)

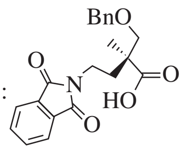
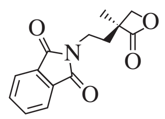
(A) 1 and 3 (B) 2 and 3
(C) 1 and 4 (D) 1 and 2

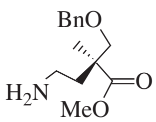
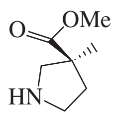
104. The products A and B in the following reaction sequence are—



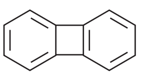
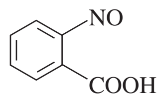

(A) A :  B : 

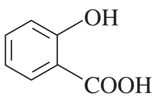
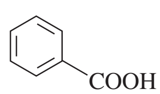
(B) A :  B : 

(C) A :  B : 

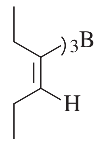
(D) A :  B : 

105. Anthranilic acid, on treatment with *iso*-amyl nitrite furnishes a product which displays a strong peak at 76 (m/e) in its mass spectrum. The structure of the product is—

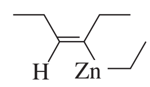
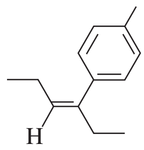
(A)  (B) 

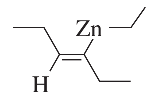
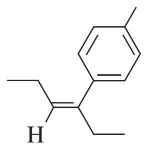
(C)  (D) 

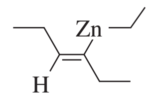
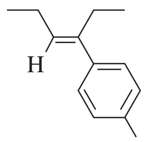
106. The organoborane X, when reacted with $Et_2Zn$ followed by $p$-iodotoluene in the presence of catalytic amount of $Pd(PPh_3)_4$ furnishes a trisubstituted alkene. The intermediate and the product of the reaction, respectively, are—

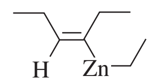
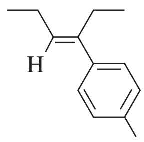


**X**

(A)  and 

(B)  and 

(C)  and 

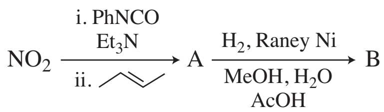
(D)  and 

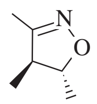
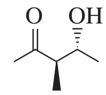
107. Using Boltzmann distribution, the probability of an oscillator occupying the first three levels ($n$ = 0, 1 and 2) is found to be $p_0 = 0{\cdot}633$, $p_1 = 0{\cdot}233$ and $p_2 = 0{\cdot}086$.

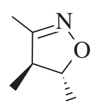
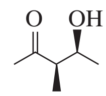
The probability of finding an oscillator in energy levels $n \geq 3$ is—

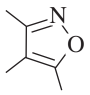
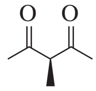
(A) 0·032 (B) 0·048
(C) 0·952 (D) 1·000

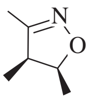
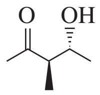
108. The major products A and B in the following reaction sequence are—



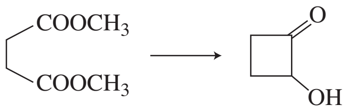

(A) A :  B : 

(B) A :  B : 

(C) A :  B : 

(D) A :  B : 

109. The correct combination of reagents required to effect the following conversion is—



(A) (i) Na, xylene, $Me_3SiCl$, heat; (ii) $H_3O^+$

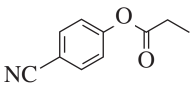
(B) (i) Na, xylene, heat; (ii) $H_2O_2$, NaOH

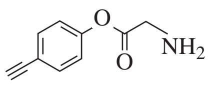
(C) (i) NaOEt, EtOH; (ii) Na, xylene, heat

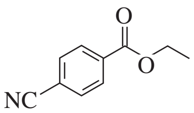
(D) (i) $TiCl_3$, Zn-Cu, $Me_3SiCl$, heat; (ii) $H_3O^+$

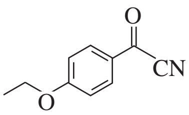
110. An organic compound gives following spectral data :

IR : 2210, 1724 $cm^{-1}$; $^1$H NMR : δ 1·4 (*t*, J = 7·1 Hz, 3H), 4·4 (*q*, J = 7·1 Hz, 2H), 7·7 (*d*, J = 8·0 Hz, 2H), 8·2 (*d*, J = 7·0 Hz, 2H); $^{13}$C NMR : δ 16, 62, 118, 119, 125, 126, 127, 168. The compound is—

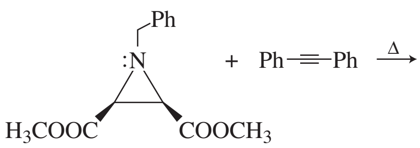
(A) 

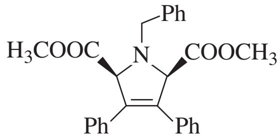
(B) 

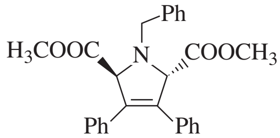
(C) 

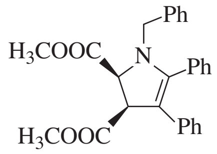
(D) 

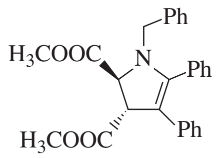
111. The major product formed in the following reaction is—



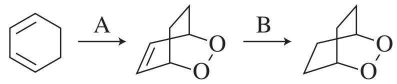
(A) 

(B) 

(C) 

(D) 

112. The correct combination of reagents for effecting the following sequence of reactions is—



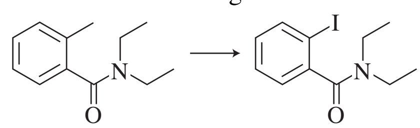
(A) A = $O_3/O_2$; B = $K^+$ $^-$OOC–N=N–COO$^-$ $K^+$, AcOH

(B) A = $O_2$, Rose Bengal, *h*υ; B = $K^+$ $^-$OOC–N=N–COO$^-$$K^+$, AcOH

(C) A = $O_2$, Rose Bengal, *h*υ; B = $H_2$, Pd/C

(D) A = $O_2$, Rose Bengal, Δ; B = $H_2$, Pd/C

113. The correct combination of reagents required to effect the following conversion is—



(A) $I_2$, $HNO_3$

(B) *s*-BuLi, – 78°C followed by KI

(C) NaOEt followed by $ICH_2CH_2I$

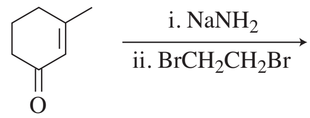
(D) *s*-BuLi, – 78°C followed by $ICH_2CH_2I$

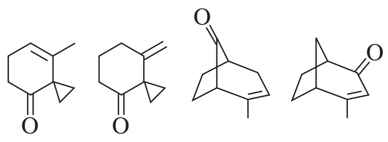
114. Consider a particle confined in a cubic box. The degeneracy of the level, that has an energy twice that of the lowest level, is—

(A) 3 (B) 1

(C) 2 (D) 4

115. Only two products are obtained in the following reaction sequence. The structures of the products from the list I-IV are—

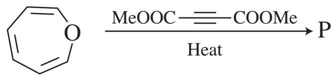


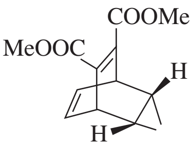



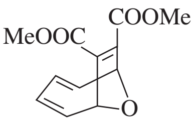

I II III IV

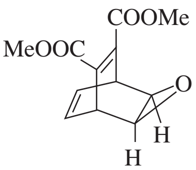
(A) I and II
(B) II and IV
(C) I and III
(D) III and IV

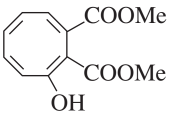
116. The major product A formed in the following reaction is—



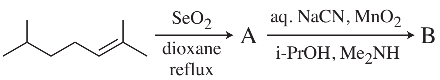

(A) 

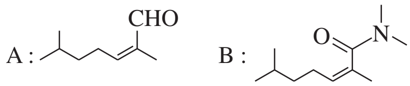

(B) 

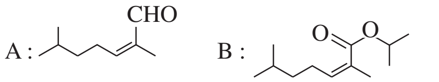

(C) 

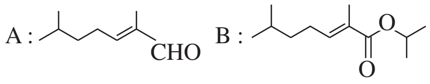

(D) 

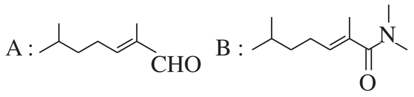

117. The products A and B in the following reaction sequence are—




(A) 


(B) 


(C) 


(D) 

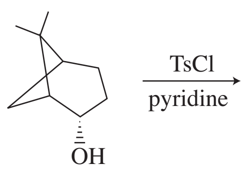

118. The spatial part of the wave function of the atom in its ground state is $1s(1)1s(2)$. The spin part would be—

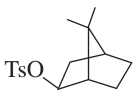
(A) $\alpha(1)\alpha(2)$
(B) $\beta(1)\beta(2)$
(C) $\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \beta(1)\alpha(2)]$
(D) $\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$

119. The number of phases, components and degrees of freedom, when Ar is added to an equilibrium mixture of NO, $O_2$ and $NO_2$ in gas phase are, respectively,

(A) 1, 3, 5 (B) 1, 4, 5
(C) 1, 3, 4 (D) 1, 4, 4

120. The major product formed in the following reaction is—




(A) 


(B) 


(C) 


(D) 

121. A particle in a one dimensional harmonic oscillator in $x$-direction is perturbed by a potential $\lambda x$ ($\lambda$ is number). The first-order correction to the energy of the ground state—

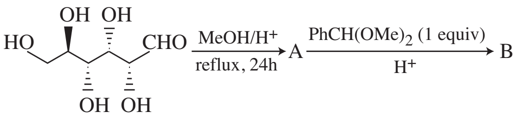
(A) is zero

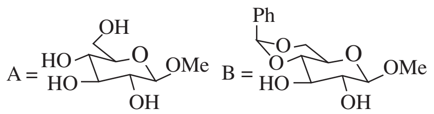
(B) is negative

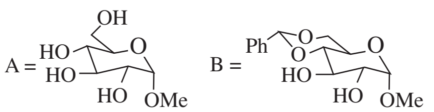
(C) is positive

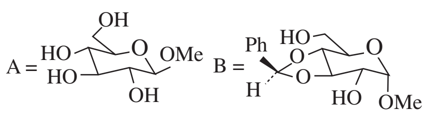
(D) may be negative or positive but NOT zero

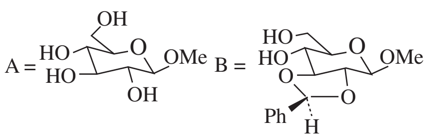
122. The products A and B in the following sequence of reactions are—



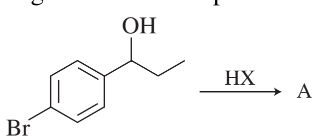

(A) 

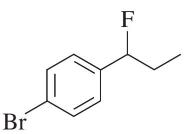
(B) 

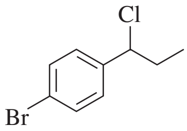
(C) 

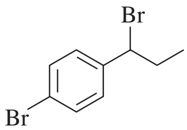
(D) 

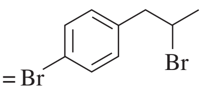
123. The mass spectrum of the product A, formed in the following reaction, exhibits M, M + 2, M + 4 peaks in the ratio of about 1 : 2 : 1. The reagent HX and the product P are—




(A) HX = HF and P = 

(B) HX = HCl and P = 

(C) HX = HBr and P = 

(D) HX = HBr and P = 

124. Match the following natural products in column A with their structural features in column B.

| | **Column A** | | **Column B** |
|---|---|---|---|
| (a) | Colchicine | 1. | Tetrahydrooxepine |
| (b) | Strychnine | 2. | Phenanthrene |
| (c) | Quinine | 3. | Tropolone |
| (d) | Ephedrine | 4. | Phenylethylamine |
| | | 5. | Quionoline |
| | | 6. | Benzofuran |

Identify the correct match from the following—

| | (a) | (b) | (c) | (d) |
|---|---|---|---|---|
| (A) | 3 | 1 | 5 | 4 |
| (B) | 6 | 1 | 2 | 5 |
| (C) | 1 | 4 | 6 | 4 |
| (D) | 3 | 1 | 5 | 6 |

125. A particle in a one-dimensional box (potential zero between 0 to $a$ and infinite outside) has the ground state energy $E_0 = \frac{0{\cdot}125h^2}{ma^2}$. The expectation value of the above Hamiltonian with $\psi(x) = x(x-a)$ yields an energy $E_1$. Using a linear combination of two even functions $x(x-a)$ and $x^2(x-a)^2$, we obtain variational minimum to the ground state energy as $E_2$. Which of the following relations holds for $E_0$, $E_1$ and $E_2$ ?

(A) $E_0 < E_1 < E_2$

(B) $E_0 < E_2 < E_1$

(C) $E_1 < E_0 < E_2$

(D) $E_2 < E_0 < E_1$

126. The dissociation constant of a weak acid HX at a given temperature is $2{\cdot}5 \times 10^{-5}$. The pH of 0·01 M NaX at this temperature is—

(A) 7·3 (B) 7·7

(C) 8·3 (D) 8·7

127. The ground state energy of hydrogen atom is – 13·598 eV. The expectation values of kinetic energy, $\langle T \rangle$ and potential energy, $\langle V \rangle$, in units of eV, are—

(A) $\langle T \rangle = 13{\cdot}598, \langle V \rangle = -27{\cdot}196$

(B) $\langle T \rangle = -27{\cdot}196, \langle V \rangle = 13{\cdot}598$

(C) $\langle T \rangle = -6{\cdot}799, \langle V \rangle = -6{\cdot}799$

(D) $\langle T \rangle = 6{\cdot}799, \langle V \rangle = -20{\cdot}397$

128. If $\psi = 0{\cdot}8\ \varphi_A + 0{\cdot}4\ \varphi_B$ is a normalized molecular orbital of a diatomic molecule AB, constructed from $\varphi_A$ and $\varphi_B$ which are also normalized, the overlap between $\varphi_A$ and $\varphi_B$ is—

(A) 0·11 (B) 0·31

(C) 0·51 (D) 0·71

129. At a given temperature consider

$Fe_2O_3(s) + 3CO(g) \rightleftharpoons 2Fe(s) + 3CO_2(g)$; $K_1 = 0{\cdot}05$

$2CO_2(g) \rightleftharpoons 2CO(g) + O_2(g)$; $K_2 = 2 \times 10^{-12}$

The equilibrium constant for the reaction

$2Fe_2O_3(s) \rightleftharpoons 4Fe(s) + 3O_2$ is—

(A) $1 \times 10^{-13}$ (B) $2 \times 10^{-38}$

(C) $4 \times 10^{-15}$ (D) $2 \times 10^{-24}$

130. In a bomb calorimeter, the combustion of 0·5 of compound A (molar mass = 50 g mol$^{-1}$) increased the temperature by 4 K. If the heat capacity of the calorimeter along with that of the material is 2·5 kJ K$^{-1}$, the molar internal energy of combustion, in kJ, is—

(A) 1000 (B) – 1000

(C) 20 (D) – 20

131. The translational, rotational and vibrational partition functions for a molecule are—

$f_{\text{translation}} \simeq 10^{10}$ m$^{-1}$, $f_{\text{rotation}} \simeq 10$, $f_{\text{vibration}} \simeq 1$, $(k_BT/h) \simeq 10^{13}$ at room temperature,

$NA \simeq 6 \times 10^{23}$

Using the approximate data given above, the frequency factor (A) for a reaction of the type : *atom + diatomic molecule → nonlinear transition state → product,* according to the conventional transition state theory is—

(A) $2 \times 10^{3}$ (B) $6 \times 10^{7}$

(C) $2 \times 10^{12}$ (D) $6 \times 10^{13}$

132. The interplanar spacing of (110) planes in a cubic unit cell with lattice parameter $a$ = 4,242 Å is—

(A) 3 Å (B) 6 Å

(C) 7·35 Å (D) 2·45 Å

133. A compound $A_xB_y$ has a cubic structure with A atoms occupying all the corners of the cube as well as all the face center positions. The B atoms occupy four tetrahedral voids. The values of $x$ and $y$ respectively, are—

(A) 4, 4 (B) 4, 8

(C) 8, 4 (D) 4, 2

134. The number of lines in the ESR spectrum of $CD_3$ is (the spin of D is 1)—

(A) 1 (B) 3

(C) 4 (D) 7

135. The C = O bond length is 120 pm in $CO_2$. The moment of inertia of $CO_2$ would be close to (masses of C and O are $1{\cdot}9 \times 10^{-27}$ kg and $2{\cdot}5 \times 10^{-27}$ kg, respectively)—

(A) $1{\cdot}8 \times 10^{-45}$ kg m$^2$

(B) $3{\cdot}6 \times 10^{-45}$ kg m$^2$

(C) $5{\cdot}4 \times 10^{-45}$ kg m$^2$

(D) $7{\cdot}2 \times 10^{-45}$ kg m$^2$

136. The fluorescence lifetime of a molecule in a solution is $5 \times 10^{-9}$ s. The sum of all the noradiative rate constants ($\Sigma k_{nr}$)for the decay of excited state is $1{\cdot}2 \times 10^{8}$ s$^{-1}$. The fluorescence quantum yield of the molecule is—

(A) 0·1 (B) 0·2

(C) 0·4 (D) 0·6

137. Solutions of three electrolytes have the same ionic strength and different dielectric constants as 4, 25 and 81. The corresponding relative magnitude of Debye-Huckel screening lengths of the three solutions are—

(A) 4, 25 and 81

(B) 2, 5 and 9

(C) 1/2, 1/5 and 1/9

(D) 1, 1 and 1

138. Simple Hückel molecular orbital theory—

(A) considers electron-electron repulsion explicitly

(B) distinguishes *cis*-butadiene and *trans*-butadiene

(C) distinguishes *cis*-butadiene and cyclobutadiene

(D) has different coulomb integrals for non-equivalent carbons

139. For the nondissociative Langmuir type adsorption of a gas on a solid surface at a particular temperature, the fraction of surface coverage is 0·6 at 30 bar. The Langmuir isotherm constant (in $bar^{-1}$ units) at this temperature is—

(A) 0·05 (B) 0·20

(C) 2·0 (D) 5·0

140. For a set of 10 observed data points, the mean is 8 and the variance is 0·04. The 'standard deviation' and the 'coefficient of variation' of the data set are, respectively—

(A) 0·005, 0·1% (B) 0·02, 0·2%

(C) 0·20, 2·5% (D) 0·32, 1·0%

141. In the Lineweaver-Burk plot of (initial rate)$^{-1}$ *vs*. (initial substrate concentration)$^{-1}$ for an enzyme catalyzed reaction following Michaelis-Menten mechanism, the *y*-intercept is 5000 $M^{-1}$ s. If the initial enzyme concentration is $1 \times 10^{-9}$ M, the turnover number is—

(A) $2·5 \times 10^3$ (B) $1·0 \times 10^4$

(C) $2·5 \times 10^4$ (D) $2·0 \times 10^5$

142. The $E \otimes E$ direct product in $D_3$ point group contains the irreducible representations

| $D_3$ | E | $2C_3$ | $3C_2$ |
|---|---|---|---|
| $A_1$ | 1 | 1 | 1 |
| $A_2$ | 1 | 1 | – 1 |
| $E_2$ | 2 | – 1 | 0 |

(A) $A_1 + A_2 + E$ (B) $2A_1 + E$

(C) $2A_2 + E$ (D) $2A_1 + 2A_2$

143. The result of the product $C_2(x)$ $C_2(y)$ is—

(A) E (B) $\sigma_{xy}$

(C) $C_2(z)$ (D) *i*

144. Given

1. $Fe(OH)_2$ (s) + $2e^-$ → Fe(s) + $2OH^-$ (aq); $E° = – 0·877$ V
2. $Al^{3+}$ (aq) + $3e^-$ → Al(s); $E° = – 1·66$V
3. AgBr(aq) + $e^-$ → Ag(s) + $Br^-$ (aq); $E° = 0·071$ V

The overall reaction for the cells in the direction of spontaneous change would be—

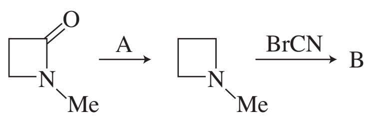
(A) Cell with A & B : Fe reduced
Cell with A & C : Fe reduced

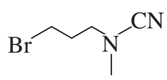
(B) Cell with A & B : Fe reduced
Cell with A & C : Fe oxidized

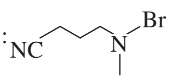
(C) Cell with A & B : Fe oxidized
Cell with A & C : Fe oxidized

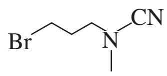
(D) Cell with A & B : Fe oxidized
Cell with A & C : Fe reduced

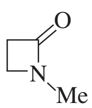
145. The reagent **X** used and the major product **Y** formed in the following reaction sequence are—




(A) A : $LiAH_4$ B : 


(B) A : $LiAH_4$ B : 


(C) A : $NaBH_4$ B : 


(D) A : $H_2$/Pd-C B : 

## Answers with Hints

1. (C)  2. (D)

3. (D) According to question,

$$h \propto \sqrt{\text{age}}$$

$$\therefore \quad h^2 \propto \text{age}$$

$$\text{and} \quad w \propto \text{age}$$

$$\text{Thus,} \quad \frac{w}{h^2} = 1 \text{ (constant)}$$

if weight and height at birth are both zero.

4. (B) Mean of A

$$= \frac{40 + 80 + 70 + 50 + 60 + 90 + 30}{7} = 60$$

Dispersion of A = 90 – 30 = 60

relative dispersion (RD) of A

$$= \frac{60}{60} = 1$$

Now, Mean of B

$$= \frac{40 + 80 + 35 + 70 + 85 + 45 + 50 + 75 + 60}{9}$$

= 60

dispersion of B = 85 – 35 = 50

$$\text{RD of B} = \frac{50}{60} = 0{\cdot}83$$

Thus, RD of A > RD of B.

5. (C)  6. (D)

7. (D) $\{(197 + 315)^2 - (197 - 315)^2\} \cdot (197 \times 315)^{-1}$

$$= + 4 \times 197 \times 315 \times \frac{1}{197 \times 315} = 4$$

8. (B) $\frac{A \times B}{B \times C} \times C \times D = \frac{24}{32} \times 48$

$$\Rightarrow \quad A \times B = \frac{3}{4} \times 48$$

$$= 3 \times 12$$

$$= 36 = (6)^2$$

⇒ Perfect square.

9. (B) horses = donkeys ...(1)

some donkeys = monkeys ...(2)

some monkeys = men ...(3)

go through options, eq. (1), (2) and (3) gives Some donkeys may be men.

10. (C) area of rectangle = 54 units

perimeter of square tiles = 4, 8, 20

Thus, minimum no. of tiles needed = 12.

11. (D) $(n^2 + n)(2n + 1)$, $n$ is a + ve integer

$n = 1$, $(1 + 1)(2 + 1) = 6$

$n = 2$, $6 \times 5 = 30$

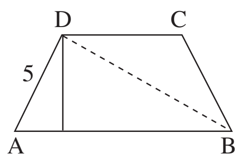
$n = 3$, $12 \times 7 = 84$

A number is divisible by 6, when it is also divisible by 2 and 3.

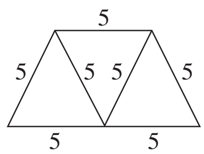
Thus, it is always divisible by 6.

12. (B)

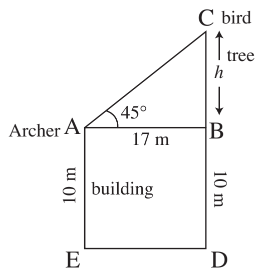
13. (C) Length of longer of two parallel sides of trapezium $= 5 \times 2 = 10$ cm




Trapezium




14. (B) Figure clearly indicates that we have to find out BC + BD = $h$ + BD




$$\text{Thus,} \quad \tan 45° = \frac{BC}{AB}$$

$$1 = \frac{h}{17} \Rightarrow h = 17$$

Thus, height of tree

$$h + BD = 17 + 10$$

$$= 27 \text{ m}$$

15. (C) Area of ΔABC

$$= \frac{1}{2} \times AB \times AC$$

$$= \frac{1}{2} \times 3 \times 3 = \frac{9}{2}$$

In rectangle, $h = 2b$

Thus, $OS = \frac{b}{2}$

$= \frac{0{\cdot}2 + 0{\cdot}2}{2} = 0{\cdot}2$

and $ST = 0{\cdot}2$

Area of $\Delta OST = \frac{1}{2} \times OS \times ST$

$= \frac{1}{2} \times 0{\cdot}2 \times 0{\cdot}2$

Thus, value of ratio

$$= \frac{\frac{1}{2} \times 3 \times 3}{\frac{1}{2} \times 0{\cdot}2 \times 0{\cdot}2}$$

$= 225$

16. (B)

17. (B) $A \overset{+1}{\rightarrow} B \overset{+1}{\rightarrow} C \overset{+1}{\rightarrow} D$

$F \overset{+3}{\rightarrow} I \overset{+3}{\rightarrow} L \overset{+3}{\rightarrow} O$

$K \overset{+5}{\rightarrow} P \overset{+5}{\rightarrow} U \overset{+5}{\rightarrow} Z$

$P \overset{+7}{\rightarrow} W \overset{+7}{\rightarrow} D \overset{+7}{\rightarrow} K$

18. (B) Price of one shirt $= \frac{800}{3}$

Price of one trousers = 1,000

Thus, go through options—

Thus, price of 30 shirts

$= \frac{800 \times 30}{3} = 8{,}000$

and that of 30 trousers

$= 1{,}000 \times 30 = 30{,}000$

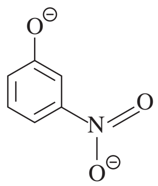
Total $= 30{,}000 + 8{,}000$

$= 38{,}000$

Thus, right option is 30.

19. (B) 20. (D)

21. (A)

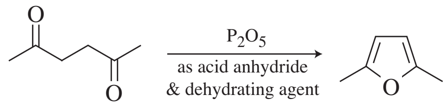



Mesomerism is not possible in case of m-substitution, hence basicity increases due to availability of electrons.

In case of o and $p$ – substitution – $NO_2$ group acts as electron withdrawing group with mesomeric effect and it is more dominant with $p$-substitution. Hence, the order of basicity is—

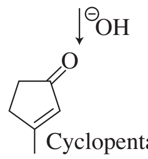
II > III > I

22. (A)



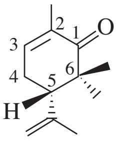

2,5-hexanedione
intramolecular aldol

furan



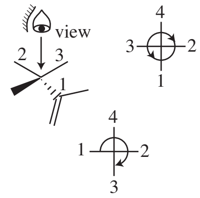

Cyclopentanone

23. (C)

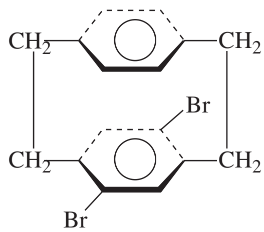



For 5-position

For 6-position



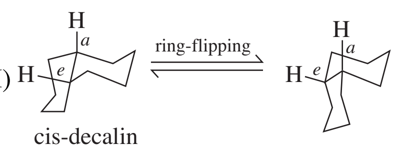

24. (A)




Due to chiral plane molecule is chiral.

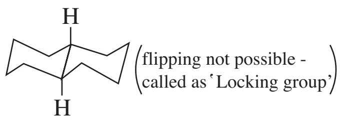
25. (A) (CSIR gave option (D), but it is wrong)

(I)




cis-decalin

(II)



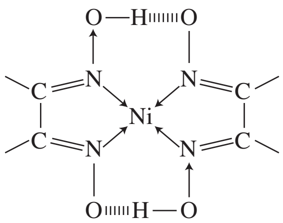

trans-decalin

Two factors are responsible for less stability of (I)

(i) non-bonding interaction in concave area.

(ii) 1,3-diaxial interaction with atoms or groups.

26. (A) Structure of bis (dimethylglyoximato) nickel (II)



Ni – N bond = 4
Ni – O bond = 0
H – bonds = 2
(intramolecular)

27. (B) 28. (B)

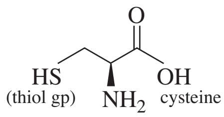
29. (D) Positron (positive electron) result from the transformation of a proton to a neutron.

$${}^{1}_{1}P \rightarrow {}^{1}_{0}n + {}^{0}_{1}e + \bar{\upsilon}$$

proton neutron positron anti-neutrino

anti-neutrino balance the spiner. When the positron is ejected from the nucleur it very quickly collides with an electron in the surroundings. Sometimes positron emission also gives positron and neutrino with characteristic energy spectrum.

30. (D) The thiol group has a high affinity for heavy metals, so that proteins containing cysteine, such as metallo thionein, will bind metals such as Hg & Cd, Pb tightly and removes toxicity of such metals.




31. (A)

$$NiBr_2 \xrightarrow[-78°C \text{ in } CS_2]{2(Et)(Ph)_2P} [NiBr_2{\cdot}P(Ph)_2(Et)]$$

M.M. = 0·0 A (Red)

Square planar ($dsp^2$)

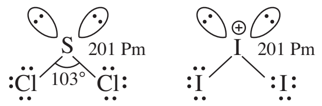
↓ room temperature

tetrahedral ($sp^3$) $[NiBr_2{\cdot}P(Ph)_2(Et)]$ green, B

$sp^3$

M.M. = 3·2 BM (two unpaired $e^-$ + orbital contribution)

32. (B)

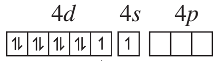



non-linear and iso-structural pair

33. (C) Ozone absorbs UV-B. UV-B (255 nm) would otherwise damage the DNA of all DNA-based life on/near Earth's Surface. It acts as a greenhouse sunlight can come in but it can't go out. Ozone protects earth by keeping it warm. Ozone is a protectant in upper atmosphere but if found in lower atmosphere where we live, it is poisonous.

34. (A) $[AgL_4]^{2+}$ Ag(II) $[AgL_6]^{2+}$ Ag(II) $[AgL_4]^{3+}$ Ag(III)

4d 4s 4p



unpaired $e^-$ paramagnetic

Same octahedral

diamagnetic (no unpaired $e^-$)

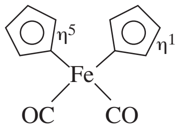
35. (A) $FeCr_2O_4 \xrightarrow[Na_2CO_3]{\text{fusion}} Na_2[CrO_4] + Fe_2O_3$

Chromite ore sodium chromate

Spinel— $Fe^{II}(Cr^{III})_2O_4$ ↓

$$\underset{\text{pure chromium}}{2Cr} \xleftarrow[-Al_2O_3]{2Al} Cr_2O_3 \xleftarrow[-Na_2CO_3,\ -CO]{2C} Na_2Cr_2O_7$$

36. (B)




(Fluxional) (221-298 K)

37. (A) $[Co(NH_3)_6]^{+3}$ – $d^6$ system, Red colour

L = $NH_3$

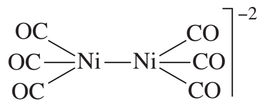
$[Co(H_2O)_6]^{+3}$ – $d^6$ system, green colour

L′ = $H_2O$

38. (C) $[Ni_2(CO)_6]^{-2}$

$$\text{M–M bond} = \frac{36-(12+20+2)}{2} = 1$$

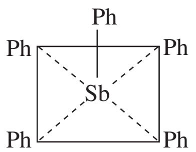
Ni (– I) state

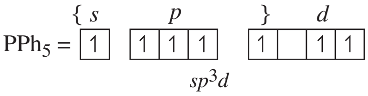


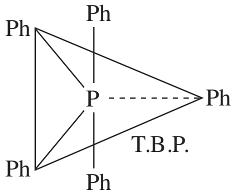

18 $e^-$ system

39. (B) $SbPh_5$

Shows square pyramidal structure due to prior availability of *d*-orbital




40. (C) For an oxidative addition reaction to occur :

(i) non-bonding $e^-$ density on the metal

(ii) Two vacant coordination site

(iii) A metal with stable O.S. separated by 2 units.

Thus, $d^8$ and $d^{10}$ is correct option.

41. (A) Gelatin is added during the polaroghaphic measurement carried out using droping mercury electrode to—

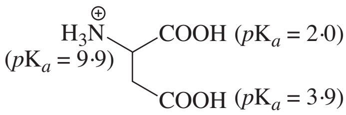
(i) reduce streaming motion of falling Hg drop

(ii) increase $I_d$

(iii) increase $E_{1/2}$

(iv) eliminate residual current

42. (B)




aspartic acid

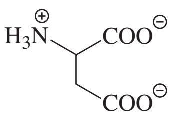
At pH = 5 (acidic character),

But we know that

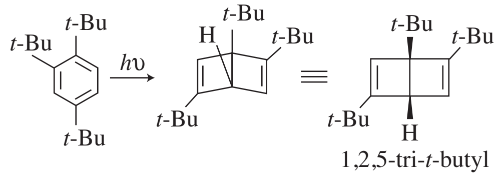
lower $pK_a$ = strong acid

higher $pK_a$ = weak acid

Therefore, the species exist at pH = 5 is—



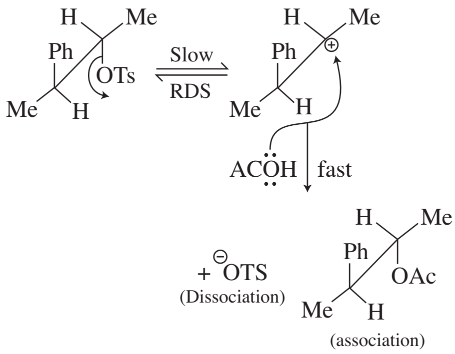

43. (A) 1, 2, 4-tri-*t*-butyl benzene gives the 1,2,5-tri-*t*-butyl Dewar structure. The driving force for the reaction is probably the relief of steric compression of the *t*-butyl groups. While the ring closure could be regarded as an allowed disrotatory closure of a 4N-system, the orbital symmetry rules for aliphatic systems cannot be arbitrarily extended to aromatic systems.




1,2,5-tri-*t*-butyl Dewar structure

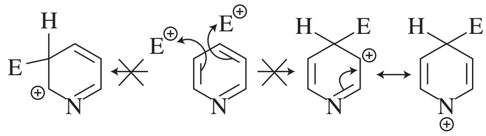
44. (C) Eliminate options, all given options have polar solvents except option (C). So the right answer is C. Benzene and carbon tetra chloride are non-polar solvents and do not ionize $PCl_5$.

45. (A)



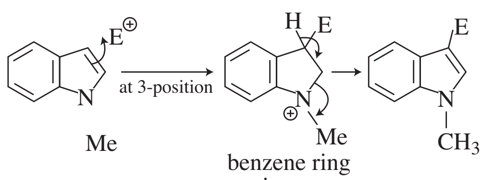

Due to planar structure of carbocation, attack at both side is possible.

46. (D)

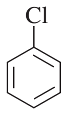



unstable electron deficient cation

unstable $e^-$ deficient cation




Thus, I > III > II ⇒ rate of electrophilic aromatic substitution.



is deactivating towards further EASR.

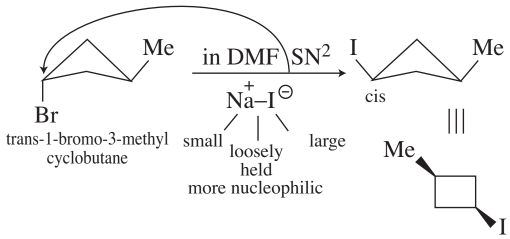
47. (C) $[\hat{T}_x \hat{P}_x] = \hat{T}_x \hat{P}_x - \hat{P}_x \hat{T}_x = 0$

(same axis operator in this case do not commute)

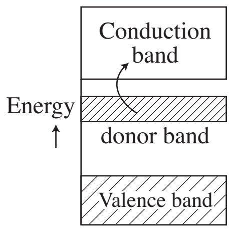
$$\therefore \quad \hat{T}_x = -\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2}$$

$$\hat{P}_x = -i\hbar\frac{d}{dx}$$

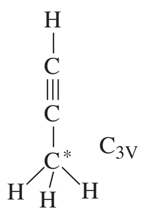
48. (C)




49. (B) Group V element is added to the Si. The fifth electron on Group V element is not bonded and excited into conduction band where they act as charge carriers (extrinsic conduction)




50. (B) One $C_3$ axis (passing through the $C^*$ and — C ≡ C — H group and also through the centre of the triangle formed by joining the three hydrogen atoms), $\sigma_n$ absent, $3\sigma_v$ present (each passing through $C^*$, —C ≡ C—H group and one of the H atoms, and bisecting the line joining the other two H atoms).



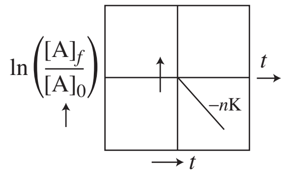

Complete list of symmetry elements — E, $C_3^1$ $C_3^2$, $3\sigma_v$ point group— $C_{3v}$

51. (B) A → products, First order reaction

We know that

$$[A]_f = [A]_0\, e^{-nKt}$$

$$\therefore \quad \ln\left(\frac{[A]_f}{[A]_0}\right) = -nKt$$




Straight line with –ve slope passing through origin.

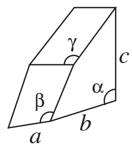
52. (A) The kinetic chain length can be defined as the average number of monomer moleculers consumed by each effective free radical generated by initiator.

$$\upsilon = \frac{\text{rate of propagation}}{\text{rate of initiation}}$$

$$= \frac{\text{rate of propagation}}{\text{rate of termination}}$$

rate of initiation = rate of monomer depletion.

53. (D) Triclinic crystal system-most unsymmetrical exists in primitive form ($a \neq b \neq c$, $\alpha \neq \beta \neq \gamma \neq 90°$)




**Examples** : $K_2Cr_2O_7$, $CuSO_4{\cdot}5H_2O$, $H_3BO_3$

So, no rotational symmetry axis is found.

54. (C) **Hardy-Schulze Rule—**

(1) Coagulation is brought about by ions having opposite charge to that of the sol.

(2) The efficacy of an ion to cause coagulation depends upon its valency (high charge).

(3) The minimum concentration of an electrolyte required to cause coagulation or flocculation of a sol is called its flocculation value (millimoles per litre) efficacy varies directly as the square of the valency of the ion.

55. (D) In the state of steady approximation, reactions are investigated under such conditions that the slowest rate-determining step

does not exist, one assumes the steady state approximation (s.s.a.) for the transient, *i.e.*, short-lived intermediate.

In case of consecutive $r^n$, $K_1 \neq K_2$, so (3) is wrong and in (2), $K_1 > K_2$ which is not possible due to long lifetime of Q. So (1) and (4) shows s.s.a.

56. (D) Expansion against a particular constant external pressure, $P_{ext} \propto P$

Then, Work done

$$W = -\int_{V_1}^{V_2} P^{ext}\, dv \quad \text{[expansion (–)]}$$

$$W = -P^{ext}(V_2 - V_1)$$

$$= -1(5-1) = -4$$

–ve sign only indicates expansion.

57. (B) Specific rotation is given by

$$[\alpha]_\lambda^T = \frac{\alpha}{Cl}$$

$\alpha = -3°$, C = 100 mg in 1 mL = 0·1 g in 1 mL

$l$ = 5 cm = 0·5 dm (decimeter)

$$\therefore \quad [\alpha]_\lambda^T = \frac{-3}{0{\cdot}1 \times 0{\cdot}5} = -60°$$

58. (C) Two phases ($\alpha$ and $\beta$) of a species are in equilibrium. Then following conditions—

(i) Thermal Equilibrium

$$\Rightarrow \quad T_\alpha = T_\beta$$

(ii) Mechanical equilibrium

$$\Rightarrow \quad P_\alpha = P_\beta$$

(iii) Chemical Equilibrium

$$\Rightarrow \quad \mu_\alpha = \mu_\beta$$

59. (A) The Boltzmann formula for the entropy,

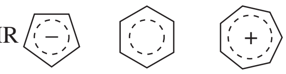
$$S = K_B \ln W$$

where W is number configurations in the most probable state of the system

$$\therefore \quad \ln W = \frac{S}{K_B}$$

$$\Rightarrow \quad \boxed{W = e^{S/K_B}}$$

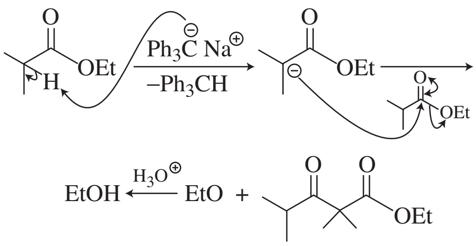
60. (A) $^1$HNMR



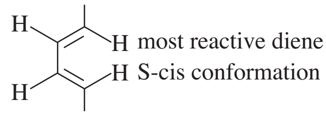
| δ | 5·4 | 7·2 | 9·2 |
|---|---|---|---|
| | I | II | III |

In Benzene, Hydrogens are deshielded by the large anisotropic field generated by the $e^{-s}$ in the ring's II system. I, III also show ring current.

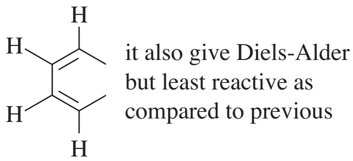
61. (C)




62. (C) (2E, 4E) – 2, 4-hexadiene

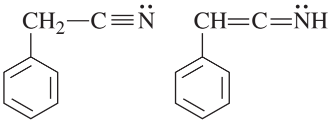



(2*z*, 4*z*) – 2, 4-hexadiene




Other two options are not working well for D–A reaction.

63. (D)

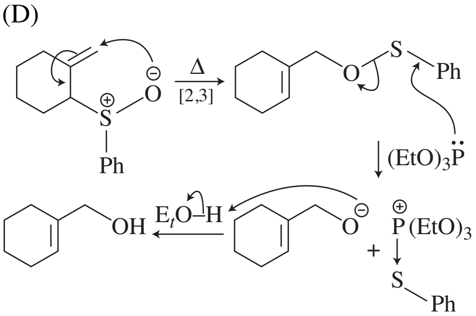


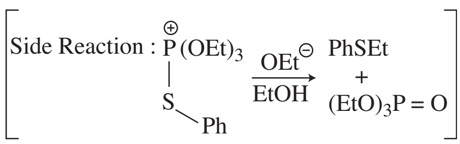

X Y

Clearly, X and Y are toutomers because sharing of H takes place with hetero atom.

Y is more basic due to availability of electrons on N-atom and forming ability of $NH_2$ with external source.

64. (D)



65. (A)   66. (C)

67. (D) $np^2$ configuration

*np*

| ↿ | ↿ | | $2S + 1 = 3$, $L = 1(P)$ | $^3P$ |
|---|---|---|---|---|
| +1 | 0 | −1 | | |
| ⇅ | | | $2S + 1 = 1$, $L = 2$ | $^1D$ |
| | ⇅ | | $2S + 1 = 1$, $L = 0$ | $^1S$ |

$^3D$ is not possible for $np^2$ configuration.

68. (C) According to Bohr, ionization energy of H and H like atom is given by

$$E_n = -\frac{2\pi^2 Z^2 me^4}{(4\pi\varepsilon_0)^2 n^2 h^2}$$

Thus, $E_n \propto Z^2$ (Z = atomic number)

For $Li^{+2}$, $Z = 3$

And for H, $E_n = x$

Therefore, $E_n$ for $Li^{+2} = 9x$

69. (B) Root Mean Square Speed of the molecule is

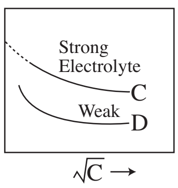
$$C_{rms} = \left(\frac{3RT}{M}\right)^{1/2}$$

$$C_{rms} \propto \left(\frac{T}{M}\right)^{1/2}$$

$T = 2T^1$, $M = \frac{1}{2}M^1$

$$\therefore \quad C_{rms} = \left(\frac{2}{\frac{1}{2}}\right)^{1/2} = (4)^{1/2} = 2$$

70. (C) Strong electrolyte—




linear increase with dilution, curve can be extrapolated and the value of $\Lambda_m^\infty$ can be determined.

Weak electrolyte—

Variation is non-linear, initially very slow, as C approaches zero increase become very fast but never approaches limiting value (Y-axis).

71. (B) [CSIR gave wrong answer option (A)]

$[Ru(NH_3)_5(\text{isonicotinamide})]^{3+}$ (Inert) $+ [Cr(H_2O)_6]^{2+}$ (Labile) $\xrightarrow[\text{sphere mechanism}]{\text{inner}}$

isonicotinamide can act as a bridge for electron transfer.

72. (A) $[Fe(H_2O)_6]^{3+}$

For outer electron transfer reaction :

(i) electron transfer from $t_{2g}$ takes place.

(ii) spin state should be same.

(iii) not much difference in bond length.

(iv) unsaturated π-acceptor ligand (mixing of $e^-$ donar and acceptor orbitals).

The presence of all the above factors in $[Fe(Phen)_3]^{+3}$ makes it's reaction faster than $[Fe(H_2O)_6]^{3+}$.

73. (A) $[Re_2(Me_2PPh)_4Cl_4]$

Configuration : $\sigma^2 \pi^4 \delta^2 \delta^{*2}$

| | $Re_2[Me_2PPh)_4Cl_4]$ | $(M^+)$ | $(M^{+2})$ |
|---|---|---|---|
| δ* | ⇅ | ↿ | — |
| δ | ⇅ | ⇅ | ⇅ |
| π | ⇅ ⇅ | ⇅ ⇅ | ⇅ ⇅ |
| σ | ⇅ | ⇅ | ⇅ |
| | (M) 3·0 | 3·5 | 4·0 |

$$M—M \text{ bond order} = \frac{BMO - ABMO}{2} = \frac{8-2}{2} = 3 \text{ for M}$$

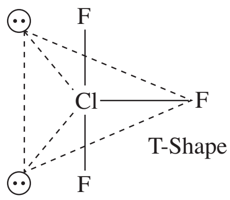
74. (C) Cis-isomer is active at low concentration

$cis–PT\ (NH_3)_2Cl_2 + H_2O \rightleftharpoons cis\text{-}[Pt(NH_3)_2Cl\ (H_2O)]^+ + Cl^\ominus$

Pt binds at 7-position of guanine.

When a self-complementary aligomer (a portion of a DNA chain) reacts with the *cis* isomer, two adjacent guaniners are bound and Watson-Crick base pairing is disrupted [See also James E. Huheey–Page No.-700].

75. (A)



$^{19}F$ NMR spectrum

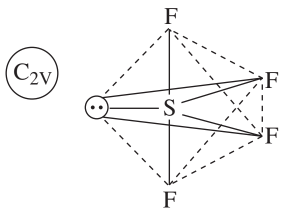
Two axial F

$$2 \times 2 \times \frac{1}{2} + 1 = 3 \text{ (triplet)}$$

equatorial F.

$$2 \times 1 \times \frac{1}{2} + 1 = 2 \text{ (doublet)}$$

76. (D) low temp. $^{19}F$ NMR spectrum of $SF_4$—doublet of triplets

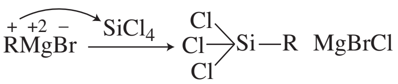



equatorial $F = 2 \times 2 \times \frac{1}{2} + 1 = 3$

axial $F = 2 \times 2 \times \frac{1}{2} + 1 = 3$

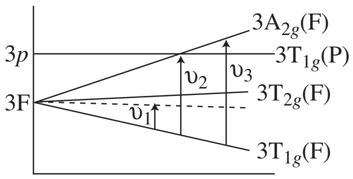
One $C_2$ axis is present (passes through S and bisects the line joining the two F atoms each. No. $\sigma_h$.2$\sigma_V$ present (molecular plane and the plane bisecting the line joining the two F atoms passing through S).

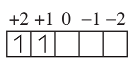
Complete list of symmetry elements = E, $C_2$, 2$\sigma_V$

77. (D) 


like this, all compounds given in question form Si—C bond due to $R^{\ominus}$ species which attacks at Si centre.

78. (A) $[V(H_2O)_6]^{3+}$, $d^2$ system



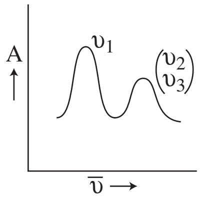




$$2S + 1 = 3 \quad ^3F, ^3P$$

$$L = 3(F)$$

[$^3T_{1g}$ (F) → $^3A_{2g}$ (F) – not observed low intensity and high energy portion of spectrum]

Observed spectrum




$$\upsilon_1 = {}^3T_{1g}(F) \rightarrow {}^3T_{2g}(F)$$

$$\upsilon_2 = {}^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$$

79. (D)

80. (A) $[Fe_5(CO)_{15}C]$

Total valence electron count

$= 8 \times 5 + 15 \times 2 + 4$

$= 74$

structure type $= 40 + 30 + 4$

$= 74 - 60 = 14$

$= 7e^-$ pair

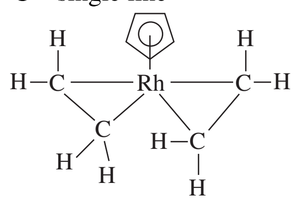
$= (m + 2)$ = Nido

81. (A) $[(\eta^5 - C_5H_5)\,Rh\,(C_2H_4)_2]$

at – 20°C shows $^1H$ NMR

typical $AA^1$ $XX^1$ pattern

at ~ 70°C – single line




due to free rotation of the ethylene ligand about the metal-olefin bond.

82. (D) Very heavy nuclei have a lower binding energy per nucleon than nuclei with an intermediate mass. $U^{233}$ and $U^{235}$ are used as fission by thermal neutrons.

$$^{238}_{92}U + ^{1}_{0}n \rightarrow ^{239}_{92}U \xrightarrow[t_{1/2} = 23{\cdot}5 \text{ min}]{\beta} ^{239}_{93}Np$$

$$\xrightarrow[t_{1/2} = 2{\cdot}3 \text{ days}]{\beta} ^{239}_{94}Pu$$

All isotopes of Pu are fissile and used as a nuclear fuel.

83. (A) 84. (A)

85. (C) $[Ni(H_2O)_6]^{2+}$ is $d^8$ system and have regular octahedral geometry (all Ni–O bond lengths are equal). Whereas $[Cu(H_2O)_6]^{2+}$ is

$d^9$ system, shows **large John-Teller distortion** with $Z_{out}$ (tetragonally elongated). Therefore, Cu–O (equatorial) bonds are shorter than Cu–O (axial) bonds.

86. (A) $Ir(Ph_3P)_2(CO)Cl + \overset{+}{N}OBF^-_4 \rightarrow$

$$[Ir(Ph_3P)_2\,(CO)\,(NO)Cl]^+BF_4^-$$
Square pyramidal

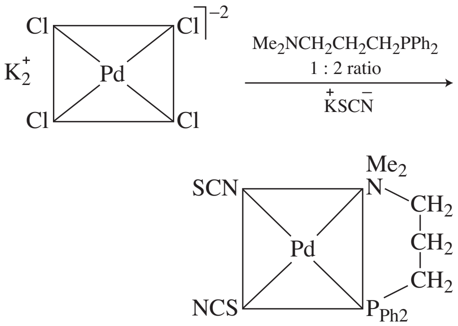
bent nitrosyl ligand, $\angle M–N–O = 124°$ at apical position 1 $e^-$ donor, less $e^-$ density on metal, high Bond Order, so N—O stretching frequency, $\upsilon_{NO} \simeq 1620\ cm^{-1}$.

87. (B) Across the period from left to right, electro-negativity increases.

Down the group, electronegativity decreases combining both factors, we have the order

S > As > Al > Ca

88. (A)




On warming,

S–bonded isomer is converted to the N-bonding isomer, which is presumably slightly more stable.

So, P opposite to N and S opposite to N.

89. (A) ${}^{24}_{12}Mg + {}_1H^2 \xrightarrow{(d,\,\alpha)} {}^{22}_{11}Na + {}_2He^4$

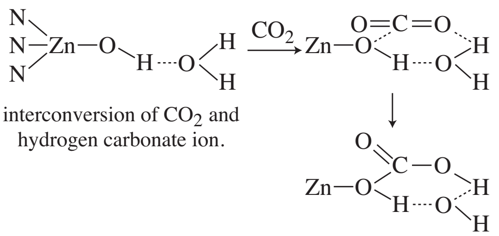
Denterium

(i) Q >> heat of chemical reaction.

(ii) total no. of P and $n$ is conserved.

(iii) no enough energy in d-particle.

90. (A) At PH = 7




interconversion of $CO_2$ and hydrogen carbonate ion.

91. (D)

92. (B) $Sm^{+2}$ : [Xe] $4f^6$

$Eu^{+2}$ : [Xe] $4f^7$

Thus, Sm is better oxidant (oxidising agent) statement 1, 3 and 4 are wrong.

$Sm^{+2} + e^- \rightarrow Sm^{+1}$ : [Xe] $4f^7$

93. (A) (i) Binding of dioxygen molecule

$$PFe^{II} + O_2 \rightleftharpoons PFe^{II}\,O_2 \leftrightarrow PFe^{III}O_2^-$$

(ii) Forming μ-peroxo complex with second heme

$$PFe^{II}O_2 + Fe^{II} \rightarrow PFe^{III}—O—O—Fe^{III}P$$

(iii) $PFe^{III}—O—O—Fe^{III}\,P \rightarrow 2PFe^{III}—O\cdot \leftrightarrow 2PFe^{IV} = O$

(iv) $2Fe^{IV} = O + PFe^{II} \rightarrow PFe^{III}—O—Fe^{III}\,P$

(decrease in size, $Fe^{+2} \rightarrow Fe^{+3}$)

Followed by changes in protein conformation takes place.

94. (C) Isolobal pairs – electronically equivalent groups

$Mn(CO)_5 = 7 + 10 = 17$
$CH_3 = 6 + 3 = 9$
less than 1 for inertness

$Fe(CO)_4 = 8 + 8 = 16$
O = 8
less than 2 for inert gas configuration

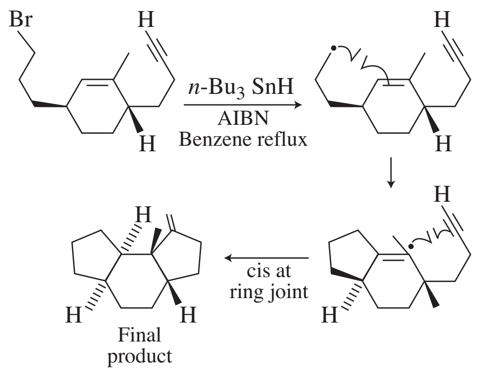
| | | |
|---|---|---|
| $Mn(CO)_5 = 17$ | $Co(CO)_3 = 9 + 6 = 15$ | different |
| RS = 17 | $R_2Si = 4 + 2 = 6$ | |

95. (C) anion > atom > cation – order of size

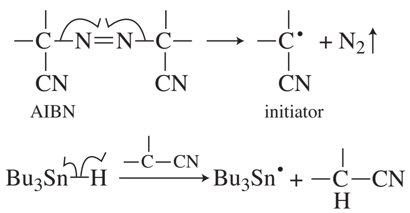
Therefore, $S^{2-} > S > S^{2+} > S^{4+}$

Due to increased ionic radii in anions.

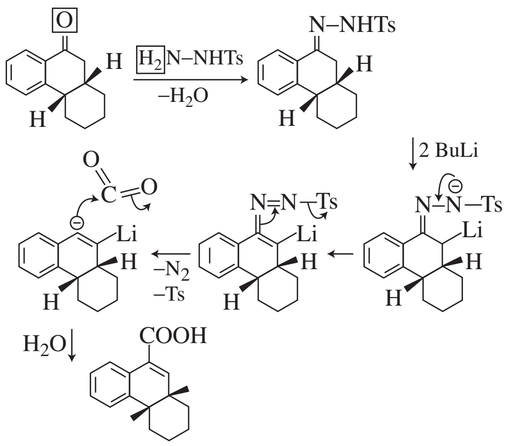
96. (A)



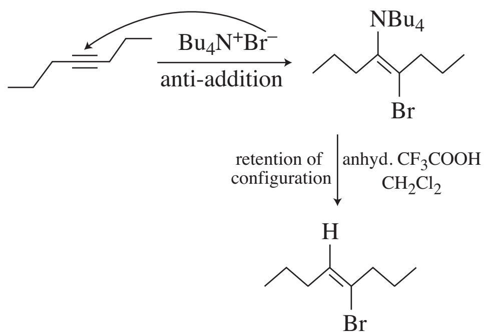
Side $R^h$



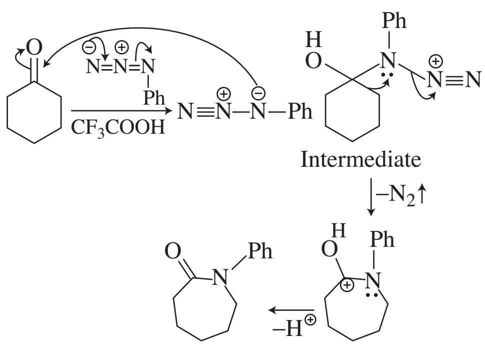
97. (C)



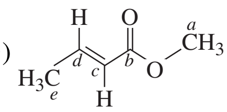
98. (B)



99. (D)



100. (D)



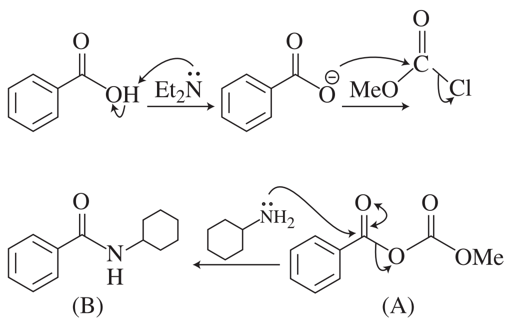
> C = O group shows maximum value around 170 alkene carbon – 120 – 150 (almost)

Me(a) adjacent to electronegative –O atom (more value).

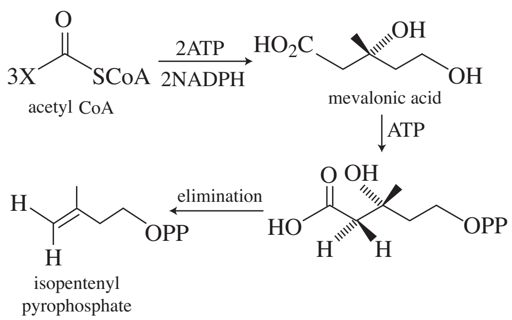
In case of *c* and *d* there is α, β-unsaturated carbonyl case and (*d*) carbon have more value due to more deshielding effect.

Thus, *a* : 52; *b* : 167; *c* : 125; *d* : 143; *e* : 19

101. (A)



102. (C)



there is no role of lipoic acid.

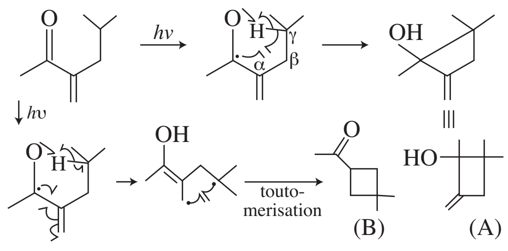
ATP – 3 molecules

NADPH – 2 molecules

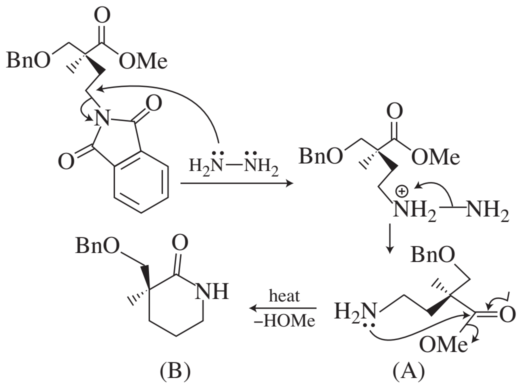
acetyl CoA – 3 molecules.

{PP = pyrophosphate group transferred from ATP}

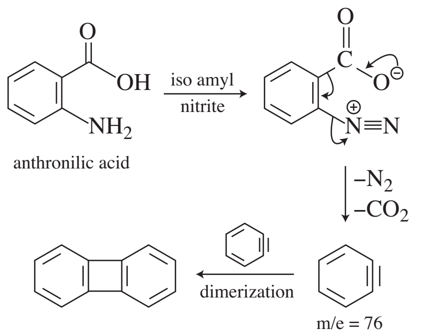
103. (D)



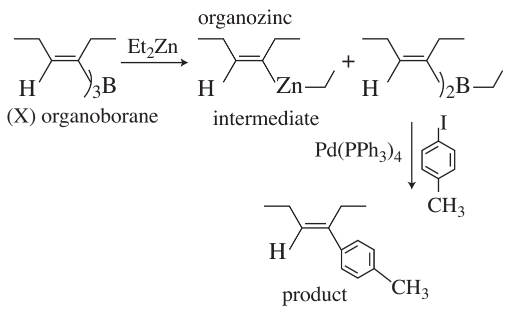

104. (A)




105. (A)

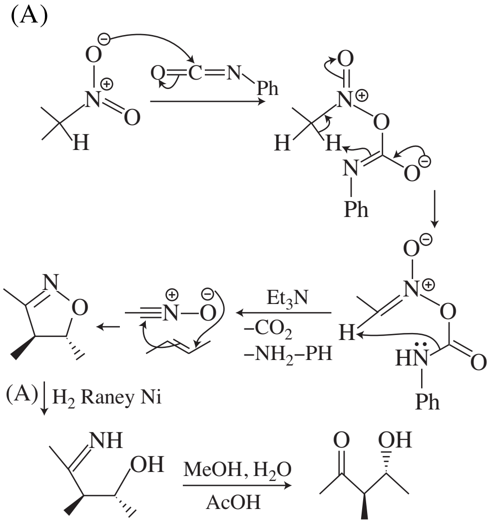



106. (D)

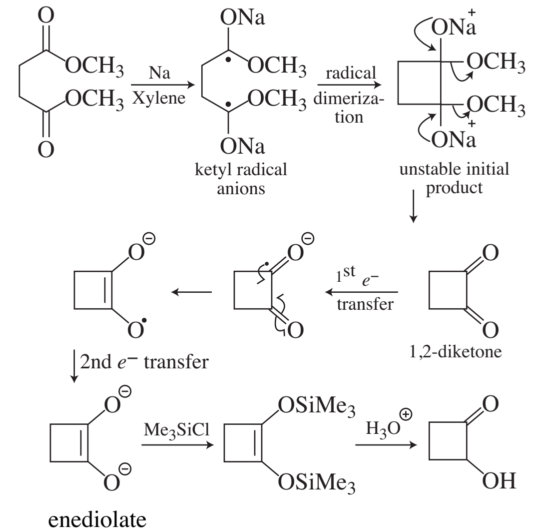



107. (B)

108. (A)




109. (A)




110. (C) IR : 2210 cm$^{-1}$

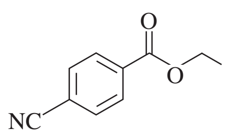
(presence of ≡ bond C ≡ C, C ≡ N)

$^{13}$CNMR : 8 types of C–atom.

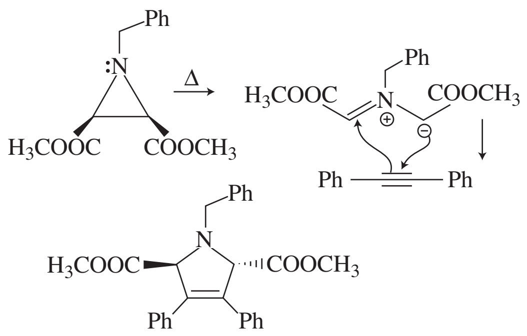
δ 1·4 ($t$, J = 7·1 Hz, 3H)
δ 4·4 ($q$, J = 7·1 Hz, 2H) 〉 —$CH_2$—$CH_3$ with O

δ 7·7 ($d$, J = 7·0 Hz, 2H)
δ 8·2 ($d$, J = 7·0 Hz, 2H) 〉 aromatic protons

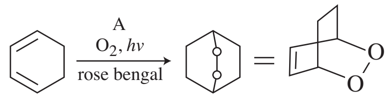
Thus, we have structure :



111. (B)

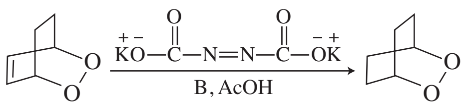



112. (B)



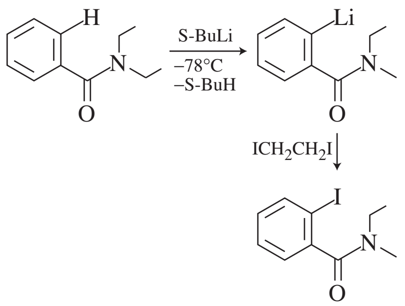

Rose Bengal is used in synthetic chemistry to generate singlet oxygen from triplet oxygen, which reacts with an alkene.

A : $O_2$, Rose Bengal, $h\upsilon$




($H_2$, Pd/C – not useful here)

113. (D)




Strong base like LDA and Buhi can abstract H attached with benzene ring.

114. (A) Energy of a particle confined in cubic box is

$$E_{3D} = (n_x^2 + n_y^2 + n_z^2)\frac{h^2}{8ma^2}$$

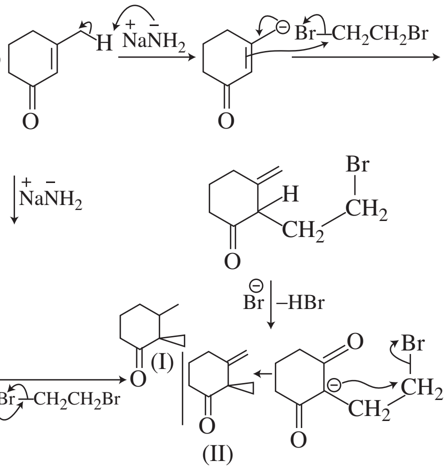
Let $$K = \frac{h^2}{8ma^2}$$

Thus, the degeneracy of the level, E = σK, twice that of the lowest level = 3

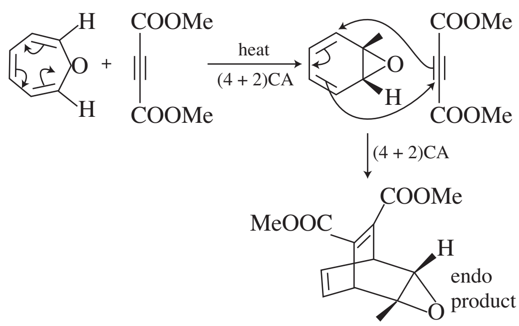
(2, 1, 1) (1, 1, 2) (1, 2, 1) ——— E = 6K

(1, 1, 1) ——— E = 3K

115. (A)

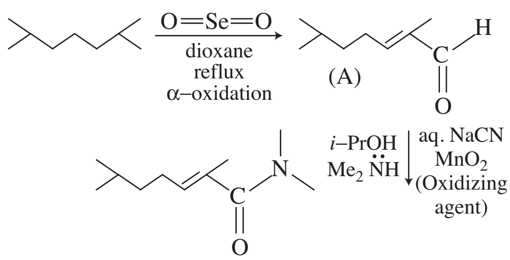



116. (A)




Stable due to secondary interaction between double bond and lone pair of electrons on oxygen atom.

117. (D)




118. (D) The four normalized two electrons spin eigen functions with correct exchange properties are—

Symmetric : $\begin{cases} \alpha(1)\,\alpha(2) \\ \beta(1)\,\beta(2) \\ [\alpha(1)\,\beta(2) + \beta(1)\,\alpha(2)]/\sqrt{2} \end{cases}$

Antisymmetric : $[\alpha(1)\,\beta(2) - \beta(1)\,\alpha(2)/\sqrt{2}$

Thus, $\psi^{(0)} = 1s(1)\, 1s(2) \cdot \frac{1}{\sqrt{2}}$

$[\alpha(1)\,\beta(2) - \beta(1)\,\alpha(2)]$

So, spin part $= \frac{1}{\sqrt{2}}[\alpha(1)\,\beta(2) - \beta(1)\,\alpha(2)]$

Spatial part $= 1s(1)\, 1s(2)$

119. (C) All species are in gaseous phase, Hence P = 1

number of components, C = N — E

where N = 4

E = equations = 1, *viz*,

$2NO + O_2 \rightarrow 2NO_2$

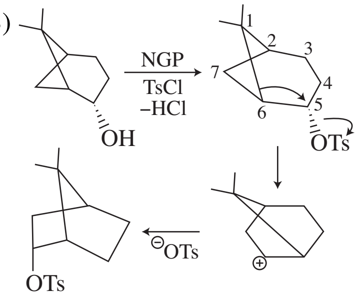
So, C = 4 – 1 = 3

degrees of freedom,

$$F = C - P + 2$$
$$= 3 - 1 + 2 = 4$$

Thus, **P = 1, C = 3, F = 4**

120. (B)




121. (A) Wave function for ground state (one-D harmonic oscillator)

$$\psi^{(0)} = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2} \text{ even function}$$

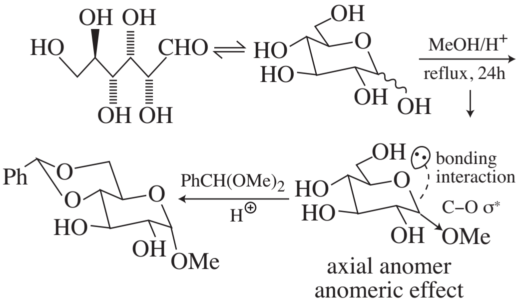
∴ First order correction to the energy

$$\Delta E = \int \psi^{(0)*}\, \hat{H}^{(1)}\, \psi^{(0)}\, dt$$
$$= \int_{-\infty}^{\infty} \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2} . \lambda x \,.\, \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}\, dx$$
$$= \lambda \left(\frac{\alpha}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} x \,.\, e^{-\alpha x^2}\, dx$$

∵ the integrand here is overall an odd function, so the integral vanishes.

$$\Delta E = 0$$

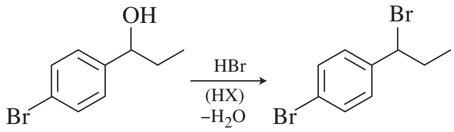
122. (B) The reaction is simply known as acetal formation of glucose which is driven by anomeric effect.




123. (C) If M, M + 2 and M + 4 in the ratio of 1 : 2 : 1, this confirms two Br group in A as

$$(a + b)^2 = a^2 + b^2 + 2ab$$
$$= 1 : 2 : 1$$

Thus,




124. (A) Quinine belongs to the quinoline group of alkaloids and is known as a cinchona alkaloid.

| **Natural product** | | **Group** |
|---|---|---|
| Ephedrine | — | Phenyl ethly amine |
| Colchicine | — | Tropolone |
| Strychnine | — | Tetrahydrooxepine |

125. (B) $E_0 = \frac{0{\cdot}125h^2}{ma^2}$

$\psi(x) = x\,(x - a), E_1$

linear combination of $x\,(x - a)$ and $x^2(x - a)^2$, $E_2$

Variational principle tells that ground state energy is always less than other higher level energies.

So, $E_0 < (E_1, E_2)$

Now, $E_2$ is obtained from even functions (two), it have high value than $E_1$

Thus, $\boxed{E_0 < E_2 < E_1}$

126. (C) $\text{pH} = 14 - \frac{1}{2}(p^{Kw}) + \frac{1}{2}p^{Ka} + (\log C) \times \frac{1}{2}$

$$p^{Ka} = -\log Ka$$
$$= -\log(2\cdot5 \times 10^{-5})$$
$$= 4\cdot60$$
$$p^{Kw} = 14$$
$$\log C = \log(0\cdot01) = -2$$
$$\therefore \quad pH = 14 - \frac{1}{2}(14) + \frac{1}{4}(4\cdot6) + (-2) \times \frac{1}{2}$$
$$= 14 - 7 + 2\cdot3 - 1$$
$$= 8\cdot3$$

127. (A) We know that for H-atom, energy, K.E. and P.E. holds following relation

$$\langle T \rangle = -\frac{1}{2}\langle V \rangle = -\langle E \rangle$$

Given that $\langle E \rangle = -13\cdot598$

$$\because \quad \langle T \rangle = -\langle E \rangle$$
$$\therefore \quad \boxed{\langle T \rangle = 13\cdot598}$$

and $\langle V \rangle = 2\langle E \rangle$

$$= 2 \times (-13\cdot598)$$
$$\boxed{\langle V \rangle = -27\cdot196}$$

128. (B) $\psi = 0\cdot8\,\varphi_A + 0\cdot4\,\varphi_B$ – normalized M.O.

$\varphi_A$ and $\varphi_B$ are also normalized

An overlap integral is a direct measure of the extent of the overlap of the orbitals centered on two different nuclei.

We know that,

$$\psi = a\varphi_A + b\varphi_B$$
$$a = 0\cdot8, b = 0\cdot4$$

Thus, overlap integral,

$$S_{AB} = \int a\varphi_A \cdot b\varphi_B \, dt$$
$$= ab = 0\cdot8 \times 0\cdot4$$
$$= 0\cdot32$$

129. (B)

$$K_1 = \frac{[Fe]^2 [CO_2]^3}{[Fe_2O_3] [CO]^3},$$
$$K_2 = \frac{[CO]^2 [O_2]}{[CO_2]^2}$$
$$K_{eq} = \frac{[Fe]^4 [O_2]^3}{[Fe_2O_3]^2},$$
$$K_1^2 = \frac{[Fe]^4 [CO_2]^6}{[Fe_2O_3]^2 [CO]^6},$$
$$K_2^3 = \frac{[CO]^6 [O_2]^3}{[CO_2]^6}$$

Now, $K_1^2 \cdot K_2^3 = \frac{[Fe]^4 [O_2]^3}{[Fe_2O_3]^2}$

Thus, $K_{eq} = K_1^2 \cdot K_2^3$

$$= (0\cdot05)^2 \cdot (2 \times 10^{-12})^3$$
$$= \frac{1}{400} \times 8 \times 10^{-36}$$
$$= 2 \times 10^{-38}$$

130. (B) In bomb calorimeter, the heat of combustion, $q_V$ at constant volume is internal energy and given by

$$q_V = C \times \theta \times \frac{M}{m}$$
$$= 2\cdot5 \text{ kJ K}^{-1} \times 4K \times \frac{50 \text{ g mol}^{-1}}{0\cdot5}$$
$$= 1000 \text{ kJ mol}^{-1}$$

Since $q_V$ always has –ve sign.

Thus, molar internal energy = – 1000 kJ

131. (B) atom + diatomic molecule → non-linear transition state
↓
product

Thus,

$$A = \left(\frac{RT}{h}\right) \frac{f_{rot}}{f_{trans} \cdot f_{rot}}$$
$$= \left(\frac{k_B T}{h}\right) \cdot N_A \frac{f}{f_{trans} \cdot f_{rot}}$$

132. (A) $(h\,K\,1) = (1\,1\,0)$

$$\therefore \quad d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$
$$= \frac{4\cdot242 \text{ Å}}{1\cdot414} = 3\text{Å}$$

133. (A) $A_xB_y$

A atoms – all corners and face centre

$$= \frac{1}{8} \times 8 + \frac{1}{2} \times 6$$
$$= 1 + 3 = 4$$

B atoms – 4 tetrahedral voids

Thus, $x = 4, y = 4$

$A_4B_4$

134. (D) $\dot{C}D_3$, For D, I = 1

Thus, no. of lines in ESR spectrum

$$= 2nI + 1$$
$$= 2 \times 3 \times 1 + 1 = 7$$

135. (B) We know,

$$I = \mu r^2$$
$$2r = 2 \times 120 \times 10^{-12} \text{ m}$$

$$\overset{2r}{\longleftrightarrow}$$
$$O = C = O$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$
$$= \frac{2{\cdot}5 \times 10^{-27} \times 2{\cdot}5 \times 10^{-27}}{(2{\cdot}5 + 2{\cdot}5) \times 10^{-27}}$$

Thus, $I = 1{\cdot}25 \times 10^{-27} \times (2{\cdot}4 \times 10^{-10})^2$

$$= 7{\cdot}2 \times 10^{-45} \text{ kg m}^2$$

Since, C atom is on axis of rotation = do not contribute to I.

136. (C) $\phi_f = \dfrac{K_f}{K_f + K_{IC} + K_{ISC}}$

fluorescence lifetime,

$$\tau_0 = \frac{\phi_f}{K_f}$$
$$\tau = \frac{1}{K_f + K_{IC} + K_{ISC}}$$
$$= \frac{10}{12 \times 10^8 \, s^{-1}}$$
$$= 8{\cdot}3 \times 10^{-9} \, s$$

Thus, $\phi_f = \dfrac{\tau}{\tau_0} = \dfrac{0{\cdot}83 \times 10^{-8} \, s}{5 \times 10^{-9} \, s}$

137. (B) We know that Debye-Huckel Screening length

$$K^{-1} = \left( \frac{\varepsilon \, k_B T}{4\pi} \frac{1}{\sum_i n_j^0 \, z_i^2 \, e_0^2} \right)^{1/2}$$

same ionic strength

$\varepsilon$ = dielectric constants

$$k^{-1} \propto (\varepsilon)^{1/2}$$

Thus, it should be 2, 5 and 9.

138. (C) Simple Huckel molecular orbital theory is—

(i) Energy of similar orbital coulomb integral.

(ii) adjacent atoms – Resonance integral

(iii) for same and different orbitals – overlap integral.

(iv) distinguishes *cis*-butadiene and cyclobutadiene.

139. (A) Nondissociative Langmuir adsorption

$$\frac{1}{\theta} = \frac{1}{K_{eq} P} + 1$$

Thus, $\dfrac{1}{\theta} - 1 = \dfrac{1}{K_{eq} P}$

$$\Rightarrow \quad \frac{1}{K_{eq}} = P \left( \frac{1}{\theta} - 1 \right)$$
$$\frac{1}{K_{eq}} = 30 \text{ bar} \left( \frac{10}{0{\cdot}6} - 1 \right)$$
$$= \left( 30 \times \frac{2}{3} \right) \text{bar}$$

Thus, $K_{eq} = \dfrac{3}{30 \times 2} = \dfrac{1}{20}$

$$= 0{\cdot}05 \text{ bar}^{-1}$$

140. (C) Variance = $\sigma^2$

$\sigma$ is standard deviation

$$\sigma = \sqrt{\text{variance}}$$
$$= \sqrt{0{\cdot}04} = 0{\cdot}20$$

coefficient of variation

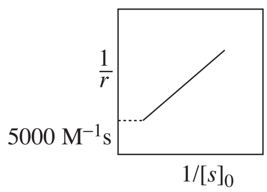
$$= \frac{\sigma}{\bar{x}} \times 100$$

($\bar{x}$ is mean of data)

$$= \frac{0{\cdot}20}{8} \times 100$$
$$= 2{\cdot}5\%$$

141. (D) $[E]_0 = 1 \times 10^{-9}$ M

$$\frac{1}{r} = \frac{Km}{r_{max}} \cdot \frac{1}{[s]_0} + \frac{1}{r_{max}}$$




$$\frac{1}{r_{max}} = 5000 \text{ M}^{-1}\text{s}$$
$$r_{max} = \frac{1}{5} \times 10^{-3} \text{ Ms}^{-1}$$

$$K_2 = \frac{\frac{1}{5} \times 10^{-3}\,\text{Ms}^{-1}}{1 \times 10^{-9}\,\text{M}}$$

$$= \frac{1}{5} \times 10^{6}\,\text{S}^{-1}$$

$$= 2 \times 10^{5}\,\text{S}^{-1}$$

$$\boxed{\text{TON} = K_2 = \frac{r_{max}}{[E]_0}}$$

142. (A)

| $D_3$ | E | $2C_3$ | $3C_2$ |
|---|---|---|---|
| $A_1$ | 1 | 1 | 1 |
| $A_2$ | 1 | 1 | – 1 |
| $E_2$ | 2 | – 1 | 0 |
| $E \otimes E$ | 4 | 1 | 0 |

Let us check with options

| | | | |
|---|---|---|---|
| (i) $A_1 + A_2 + E$ | 4 | 1 | 0 |
| (ii) $2A_1 + E$ | 4 | 1 | 1 |
| (iii) $2A_2 + E$ | 4 | 1 | – 2 |
| (iv) $2A_1 + 2A_2$ | 4 | 4 | 0 |

143. (C) There are two fold axes at right angles to one another, there must necessarily be a third at right angles to both.

$$[x_1, y_1, z_1] \xrightarrow{C_2(x)} [x_1, -y_1, -z_1] \xrightarrow{C_2(y)} [-x_1, -y_1, z_1]$$

$$[x_1, y_1, z_1] \xrightarrow{C_2(x)} [x_1, -y_1, z_1]$$

Thus, $C_2(x).C_2(y) = C_2(z)$

144. (B)

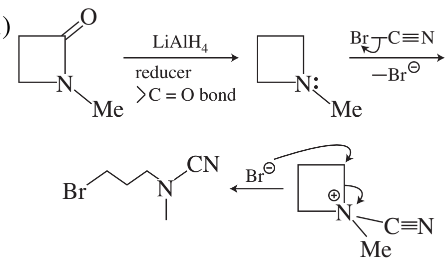
| | A | B | C |
|---|---|---|---|
| $\Delta G^\circ =$ | 1·654F | 4·98F | – 0·071F |

Cell with A and B ⇒ since less +ve value of A,

Thus, Fe will reduce

Cell with A and C ⇒ Fe oxidized

145. (A)

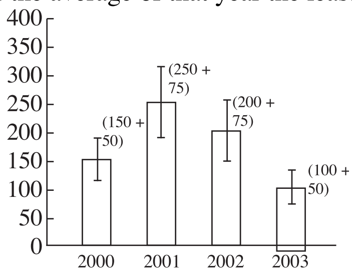


# Chemical Sciences
## CSIR-UGC NET/JRF Exam.
### (December 2014)
### Solved Paper

# December 2014
# Chemical Sciences

## PART–A

1. Average yield of a product in different years is shown in the histogram. If the vertical bars indicate variability during the year, then during which year was the per cent variability over the average of that year the least ?




(A) 2000 (B) 2001
(C) 2002 (D) 2003

2. A rectangle of length $d$ and breadth $d/2$ is revolved once completely around its length and once around its breadth. The ratio of volumes swept in the two cases is—
(A) 1 : 1 (B) 1 : 2
(C) 1 : 3 (D) 1 : 4

3. A long ribbon is wound around a spool up to a radius R. Holding the tip of the ribbon, a boy runs away from the spool with a constant speed maintaining the unwound portion of the ribbon horizontal. In 4 minutes, the radius of the wound portion becomes $\frac{R}{\sqrt{2}}$. In what further time, it will become $\frac{R}{2}$ ?

(A) $\sqrt{2}$ min (B) 2 min
(C) $2\sqrt{2}$ min (D) 4 min

4. If $n$ is a positive integer, then
$n(n + 1) (n + 2) (n + 3) (n + 4) (n + 5) (n + 6)$
is divisible by—
(A) 3 but not 7 (B) 3 and 7
(C) 7 but not 3 (D) neither 3 nor 7

5. The area (in $m^2$) of a triangular park of dimensions 50 m, 120m and 130 m is—
(A) 3000 (B) 3250
(C) 5550 (D) 7800

6. Lunch-dinner pattern of a person for $m$ days is given below. He has a choice of a VEG or a NON-VEG meal for his lunch/dinner—
(1) If he takes a NON-VEG lunch he will have only VEG for dinner.
(2) He takes NON-VEG dinner for exactly 9 days.
(3) He takes VEG lunch for exactly 15 days.
(4) He takes a total of 14 NON-VEG meals.

What is $m$ ?
(A) 18 (B) 24
(C) 20 (D) 38

7. A bank offers a scheme wherein deposits made for 1600 days are doubled in value. The interest being compounded daily. The interest accrued on a deposit of ₹ 1000 over the first 400 days would be ₹—
(A) 250 (B) 183
(C) 148 (D) 190

8. What is the next number of the following sequence ?
2, 3, 4, 7, 6, 11, 8, 15, 10 …
(A) 12 (B) 13
(C) 17 (D) 19

9. Two locomotives are running towards each other with speeds of 60 and 40 km/h. An object keeps on flying to and fro from the front tip of one locomotive to the front tip of the other with a speed of 70 km/h. After 30

minutes, the two locomotives collide and the object is crushed. What distance did the object cover before being crushed ?

(A) 50 km (B) 45 km
(C) 35 km (D) 10 km

10. Weights (in kg) of 13 persons are given below—

70, 72, 74, 76, 78, 80, 82, 84, 86, 88, 90, 92, 94.

Two new persons having weights 100 kg and 79 kg join the group. The average weight of the group increases by—

(A) 0 kg (B) 1 kg
(C) 1·6 kg (D) 1·8 kg

11. A code consists of at most two identical letters followed by at most four identical digits. The code must have at least one letter and one digit. How many distinct codes can be generated using letters A to Z and digits 1 to 9 ?

(A) 936 (B) 1148
(C) 1872 (D) 2574

12. Two solid iron spheres are heated to 100°C and then allowed to cool. One has the size of a football; the other has the size of a pea. Which sphere will attain the room temperature (constant) first ?

(A) The bigger sphere
(B) The smaller sphere
(C) Both spheres will take the same time
(D) It will depend on the room temperature

13. Find the missing letter—

| | | | |
|---|---|---|---|
| A | ? | Q | E |
| C | M | S | C |
| E | K | U | A |
| G | I | W | Y |

(A) L (B) Q
(C) N (D) O

14. The least significant bit of an 8-bit binary number is zero. A binary number whose value is 8 times the previous number has—

(A) 12 bits ending with three zeros
(B) 11 bits ending with four zeros
(C) 11 bits ending with three zeros
(D) 12 bits ending with four zeroes

15. A person sells two objects at ₹ 1035 each. On the first object he suffers a loss of 10% while on the second he gains 15%. What is his net loss/gain percentage ?

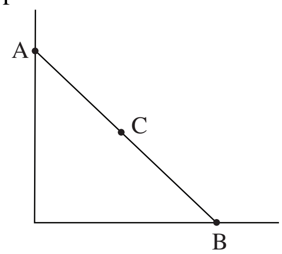
(A) 5% gain (B) < 1% gain
(C) < 1% loss (D) no loss, no gain

16. Continue the sequence

2, 5, 10, 17, 28, 41, –, –, –

(A) 58, 77, 100 (B) 64, 81, 100
(C) 43, 47, 53 (D) 55, 89, 113

17. A ladder rests against a wall as shown. The top and the bottom ends of the ladder are marked A and B. The base B slips. The central point C of the ladder falls along—




(A) a parabola (B) the arc of a circle
(C) a straight line (D) a hyperbola

18. 20% of students of a particular course get jobs within one year of passing. 20% of the remaining students get jobs by the end of second year of passing. If 16 students are still jobless, how many students had passed the course ?

(A) 32 (B) 64
(C) 25 (D) 100

19. Binomial theorem in algebra gives $(1 + x)^n = a_0 + a_1x + a_2x^2 + \ldots\ldots + a_nx^n$, where $a_0, a_1, \ldots\ldots, a_n$ are constants depending on $n$. What is the sum $a_0 + a_1 + a_2 + \ldots\ldots + a_n$ ?

(A) $2^n$ (B) $n$
(C) $n^2$ (D) $n^2 + n$

20. A sphere is made up of very thin concentric shells of increasing radii (leaving no gaps). The mass of an arbitrarily chosen shell is—

(A) equal to the mass of the preceding shell
(B) proportional to its volume
(C) proportional to its radius
(D) proportional to its surface area

## PART–B

21. The correct order of the retention of cations on a sulfonated cation exchange resin column is—
(A) $Ag^+ > K^+ > Na^+ > Li^+$
(B) $K^+ > Na^+ > Ag^+ > Li^+$
(C) $Li^+ > Na^+ > K^+ > Ag^+$
(D) $Li^+ > Na^+ > Ag^+ > K^+$

22. Among $F^-$, $Na^+$, $O^{2-}$ and $Mg^{2+}$ ions, those having the highest and the lowest ionic radii respectively are—
(A) $O^{2-}$ and $Na^+$ (B) $F^-$ and $Mg^{2+}$
(C) $O^{2-}$ and $Mg^{2+}$ (D) $Mg^{2+}$ and $O^{2-}$

23. In a polarographic measurement, (aqueous KCl solution used as supporting electrolyte) an applied potential more than + 0·4 V, results mainly in the formation of—
(A) $Hg^I$ (B) $Hg^{II}$
(C) $Cl_2$ (D) $O_2$

24. The reaction between $SbF_5$ and two equivalents of HF leads to the formation of—
(A) $H_2SbF_3 + 2F_2$ (B) $HSbF_2 + 3F_2$
(C) $SbF_3 + H_2 + 2F_2$ (D) $[SbF_6]^- [H_2F]^+$

25. The extent of π-electron conjugation in macrocyclic rings of (a) heme, (b) coenzyme $B_{12}$ and (c) chlorophyll follows the order—
(A) (a) > (c) > (b) (B) (a) > (b) > (c)
(C) (c) > (a) > (b) (D) (b) ≈ (a) > (c)

26. The point group symmetries for *trans*-$[Cr(en)_2F_2]^+$ and $[TiCl_6]^{3-}$, respectively, are—
(A) $D_{4d}$ and $D_{3d}$ (B) $D_{3d}$ and $D_{4d}$
(C) $D_{4h}$ and $D_{3h}$ (D) $D_{3h}$ and $D_{4h}$

27. The S and L values for $^{15}N$ atom respectively, are—
(A) $\frac{1}{2}$ and 1 (B) $\frac{1}{2}$ and 0
(C) 1 and 0 (D) $\frac{3}{2}$ and 0

28. The product of the reaction of propene, CO and $H_2$ in the presence of $CO_2(CO)_8$ as a catalyst is—
(A) butanoic acid (B) butanal
(C) 2-butanone (D) methylpropanoate

29. The rate of the reaction
$Ni(CO)_4 + PPh_3 \xrightarrow{hv} [Ni(CO)_3 (PPh_3)] + CO$
depends on—
(A) concentration of both the reactants
(B) concentration of $Ni(CO)_4$ only
(C) concentration of $PPh_3$ only
(D) the steric bulk of $PPh_3$

30. The hapticities '$x$' and '$y$' of the arene moieties in the diamagnetic complex $[(\eta^x - C_6H_6) Ru(\eta^y - C_6H_6)]$ respectively are—
(A) 6 and 6 (B) 4 and 4
(C) 4 and 6 (D) 6 and 2

31. The correct order of the isomeric shift in Mossbauer spectra ($^{57}Fe$ source) of iron compounds is—
(A) Fe(II) > Fe(III) > Fe(IV)
(B) Fe(III) > Fe(II) > Fe(IV)
(C) Fe(IV) > Fe(III) > Fe(II)
(D) Fe(IV) > Fe(II) > Fe(III)

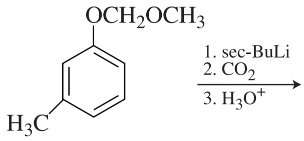
32. The δ-bond is formed via the overlap of—
(A) $d_{x^2-y^2}$ and $d_{x^2-y^2}$ orbitals
(B) $d_{xz}$ and $d_{xz}$ orbitals
(C) $d_{xy}$ and $d_{xy}$ orbitals
(D) $d_{yz}$ and $d_{yz}$ orbitals

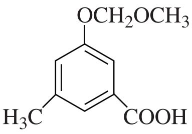
33. Reductive elimination step in hydrogenation of alkenes by Wilkinson catalyst results in (neglecting solvent in coordination sphere of Rh)
(A) T-shaped $[Rh(PPh_3)_2Cl]$
(B) Trigonal-planar $[Rh(PPh_3)_2Cl]^{2+}$
(C) T-shaped $[Rh(H)(PPh_3)Cl]^+$
(D) Trigonal-planar $[Rh(H)(PPh_3)_2]$

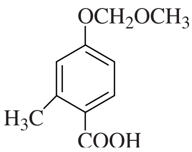
34. In the following reaction
$[PtCl_4]^{2-} + NO_2 \longrightarrow A \xrightarrow{NH_3} B$
compound B is—
(A) *trans*–$[PtCl_2(NO_2)(NH_3)]^-$
(B) *cis*–$[PtCl_2(NO_2)(NH_3)]^-$
(C) *trans*–$[PtCl_2(NH_3)_2]$
(D) *cis*–$[PtCl_2(NO_2)_2]^{2-}$

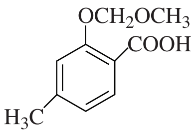
35. $Co_4(CO)_{12}$ adopts the—
(A) *closo*—structure
(B) *nido*—structure
(C) *arachno*—structure
(D) *hypho*—structure

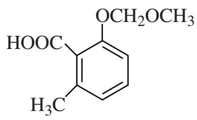
36. The major product formed in the following reaction is—



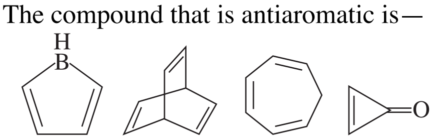

(A)


(B)



(C)


(D)


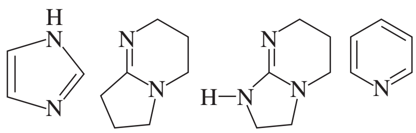

37. The compound that is antiaromatic is—




I II III IV

(A) I (B) II
(C) III (D) IV

38. The decreasing order of basicity of the following compounds is—




I II III IV

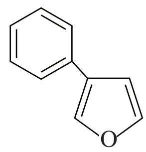
(A) III > II > III > IV (B) IV > I > II > III
(C) III > II > I > IV (D) IV > III > II > I

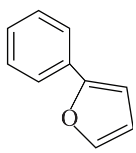
39. The configurations of carbon atoms $C_3$ and $C_4$ in D-ribose, respectively, are—
(A) R and S (B) S and R
(C) R and R (D) S and S

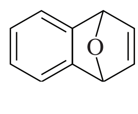
40. The number of histidine amino acid nitrogen atoms coordinated to bimetallic active site of oxyhemocyanin and oxyhemerythrin, respectively, are—
(A) 2, 3 and 3, 3 (B) 3, 3 and 2, 3
(C) 3, 3 and 2, 2 (D) 2, 4 and 3, 2

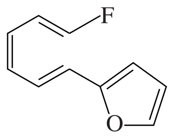
41. In the most stable conformation of neomenthol, stereochemical orientation of the three substituents on the cyclohexane ring are—
(A) OH : equatorial; *i*-Pr : equatorial and Me : equatorial
(B) OH : axial; *i*-Pr : equatorial and Me : equatorial
(C) OH : equatorial; *i*-Pr : equatorial and Me : axial
(D) OH : equatorial; *i*-Pr : axial and Me : equatorial

42. The reaction of 1-bromo-2-fluorobenzene with furan in the presence of one equivalent of Mg gives—

(A)


(B)


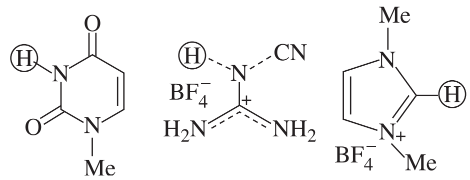

(C)


(D)



43. Identify correct statements for mercury as an environment pollutant :
1. Carbanionic biomethylation converts it to $MeHg^+$.
2. Thiol group of cysteine has strong affinity for mercury.
3. Mercury containing industrial catalyst release caused Minamata disaster.

The correct answer is—
(A) 1 and 2 (B) 1 and 3
(C) 2 and 3 (D) 1, 2 and 3

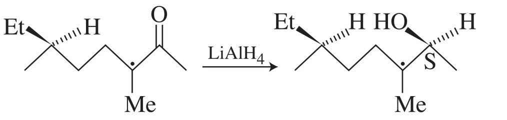
44. The increasing order of *p*K*a* value of the circled hydrogens in the following compounds is—




I II III

(A) I < II < III (B) I < III < II
(C) II < I < III (D) II < III < I

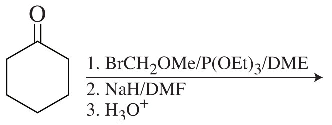
45. The absolute configurations of the chiral centres of starting ketone in the following reaction is—

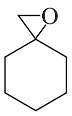


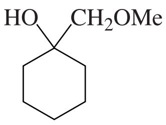

Major product

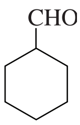
(A) 3R, 6S (B) 3S, 6S
(C) 3R, 6R (D) 3S, 6R

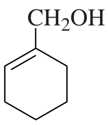
46. The product for the following sequence of reactions is—



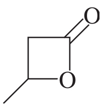

(A) 

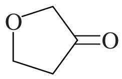

(B) 

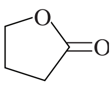

(C) 

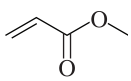

(D) 


47. A compound with molecular formula $C_4H_6O_2$ shows band at 1770 $cm^{-1}$ in IR spectrum and peaks at 178, 68, 28, and 22 ppm in $^{13}C$ NMR spectrum. The correct structure of the compound is—

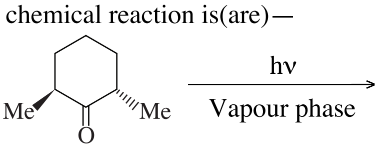
(A) 


(B) 


(C) 

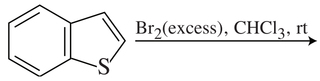

(D) 

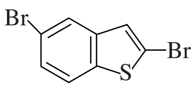

48. The cyclic product(s) of the following photochemical reaction is(are)—

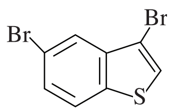


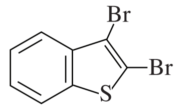

(A) only *cis*-1, 2-dimethylcyclopentane
(B) only *trans*-1, 2-dimethylcyclopentane
(C) a mixture of *cis*- and *trans*-1, 2-dimethylcyclopentanes
(D) only 2, 6-dimethylcyclohexanol

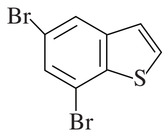
49. The major product of the following reaction is—



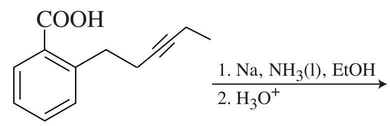

(A) 

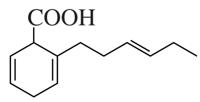

(B) 

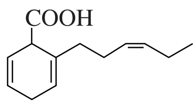

(C) 

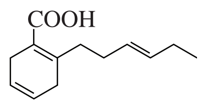

(D) 

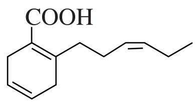

50. The major product of the following reaction is—




(A) 


(B) 


(C) 


(D) 


51. For the cell reaction,

$Sn(s) + Sn^{4+}(aq) \rightleftharpoons 2Sn^{2+}(aq)$,

separate electrode reactions could be written with the respective standard electrode potential data at 25°C as—

$Sn^{4+}(aq) + 2e \rightarrow Sn^{2+}(aq), E^0 = +0{\cdot}15$ V

$Sn^{2+}(aq) + 2e \rightarrow Sn(s), E^0 = +0{\cdot}14$ V

When RT/F is given as 25·7 mV, logarithm of the equilibrium constant (ln K) is obtained as—

(A) 22·6 (B) 226
(C) 2·26 (D) $2{\cdot}26 \times 10^{-1}$

52. For a particle of mass $m$ confined in a box of length L, assume $\Delta x = L$. Assume further that $\Delta p$ (min) $= (p^2)^{1/2}$. Use the uncertainty principle to obtain an estimate of the energy of the particle. The value will be—

(A) $\frac{h^2}{(8mL^2)}$ (B) $\frac{h^2}{(8mL^2)}$

(C) $\frac{h^2}{(32mL^2)}$ (D) $\frac{h^2}{(2mL^2)}$

53. The mass of metastable ion produced due to decomposition of $F_1^+$ in the following mass fragmentation sequence is—

$$\underset{M^+,\ 222}{\text{Diethyl phthalate}} \longrightarrow \underset{(177)}{F_1^+} \longrightarrow F_2^+ + CO$$

(A) 141·2 (B) 125·4
(C) 45·0 (D) 210·2

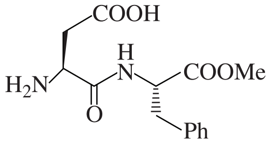
54. If the component of the orbital angular momentum along the molecular axis of a heteronuclear diatomic molecule is nonzero, the rotational-vibrational spectrum will show—
(A) P and R branches only
(B) P and Q branches only
(C) Q and R branches only
(D) all the P, Q and R branches

55. The ratio of the relative intensities of the carbon signals in the first order $^{13}C$ NMR spectrum of $CD_3Cl$ is—
(A) 1 : 4 : 6 : 4 : 1
(B) 1 : 3 : 3 : 1
(C) 1 : 6 : 15 : 20 : 15 : 6 : 1
(D) 1 : 3 : 6 : 7 : 6 : 3 : 1

56. Bond lengths of homonuclear diatomic molecules can be determined with the help of both—
(A) rotational and vibrational spectroscopy
(B) rotational and rotational Raman spectroscopy
(C) rotational Raman and electronic spectroscopy
(D) vibrational and electronic spectroscopy

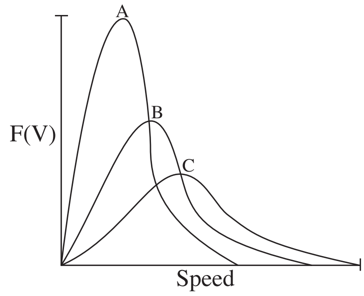
57. The biosynthetic precursor of **abietic acid** is—
(A) shikimic acid (B) mevalonic acid
(C) chorismic acid (D) cinnamic acid

58. The amino acid constituents of artificial sweetener given below are—




(A) D-Glutamic acid and L-phenylglycine
(B) L-Glutamic acid and L-phenylalanine
(C) L-Aspartic acid and L-phenylalanine
(D) L-Aspartic acid and L-tyrosine

59.




Identify the speed distribution functions of Ne, Ar, and Kr with the curves in the figure above.
(A) Ne-A, Ar-B, Kr-C
(B) Ne-B, Ar-C, Kr-A
(C) Ne-C, Ar-B, Kr-A
(D) Ne-C, Ar-A, Kr-B

60. For a process in a closed system, temperature is equal to—

(A) $\left(\frac{\partial H}{\partial P}\right)_S$ (B) $-\left(\frac{\partial A}{\partial V}\right)_T$

(C) $\left(\frac{\partial G}{\partial P}\right)_T$ (D) $\left(\frac{\partial H}{\partial S}\right)_P$

61. A reaction A + B + C $\rightarrow$ D follows the mechanism—

$$A + B \rightleftharpoons AB$$
$$AB + C \rightarrow D$$

in which first step remains essentially in equilibrium. If $\Delta H$ is the enthalpy change for the first reaction and $E_0$ is the activation energy for the second reaction, the activation energy of the overall reaction will be given by—
(A) $E_0$ (B) $E_0 - \Delta H$
(C) $E_0 + \Delta H$ (D) $E_0 + 2\Delta H$

62. Hydrogen is adsorbed on many metal surfaces by dissociation (S represents a surface site)—

$$H_2 + -\overset{|}{S}-\overset{|}{S}- \rightleftharpoons -\overset{\overset{H}{|}}{S}-\overset{\overset{H}{|}}{S}-$$

If the pressure of $H_2$ ($p$) is small, the fraction of the surface covered by hydrogen is proportional to—
(A) $p$ (B) $p^2$
(C) $p^{1/2}$ (D) $p^{3/2}$

63. The exact differential $df$ of a state function $f(x, y)$, among the following, is—

(A) $xdy$ (B) $dx - \frac{x}{y} dy$

(C) $ydx - xdy$ (D) $\frac{1}{y} dx - \frac{x}{y^2} dy$

64. The angular momentum operator $L_z = -ih \frac{\partial}{\partial \phi}$ has eigenfunctions of the form exp $[iA\phi]$. The condition that a full rotation leaves such an eigenfuction unchanged is satisfied for all the values of A—

(A) $0, \pm\frac{1}{3}, \pm\frac{2}{3}, \pm 1, \pm\frac{4}{3}, \ldots$

(B) $0, \pm 1, \pm 2, \pm 3, \ldots$

(C) $0, \pm\frac{1}{2}, \pm 1, \pm\frac{3}{2}, \ldots$

(D) $0, \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots$

65. X-ray diffraction does **not** give any structural information for—

(A) metallic solids (B) ionic solids

(C) molecular solids (D) amorphous solids

66. For an enzyme-substrate reaction, a plot between $\frac{1}{v}$ and $\frac{1}{[s]_0}$ yields a slope of 40*s*. If the enzyme concentration is 2·5 $\mu$M, then the catalytic efficiency of the enzyme is—

(A) 40 $Lmol^{-1} s^{-1}$ (B) $10^{-4}$ $Lmol^{-1} s^{-1}$

(C) $10^7$ $Lmol^{-1} s^{-1}$ (D) $10^4$ $Lmol^{-1} s^{-1}$

67. 10 ml of 0·02 M NaOH is added to 10 ml of 0·02 M acetic acid ($pK_a$ = 4·75). The pH of the solution will be closest to—

(A) 7·0 (B) 8·4

(C) 5·6 (D) 9·6

68. For a polydispersed macromolecular colloid, osmometry gives—

(A) weight–average molecular weight

(B) number–average molecular weight

(C) both weight–average and number average molecular weight

(D) viscosity–average molecular weight

69. A sample experiment revealed that PVC formed in the medium has ($M_n$) = 13, and ($M_w$) = 16, where ($M_n$) stands for the number average molar mass and ($M_w$) for the weight average molar mass. The variance of $M_n$ will then be—

(A) 39 (B) 3

(C) 1 (D) 87

70. Wavelength ($\lambda$ in nm) of the Lyman series for an one-electron ion is in the range $24 \le \lambda \le 30$. The ionization energy of the ion will be closest to $\left(1J = \frac{10^{19}}{1\cdot 6} eV\right)$—

(A) 32 eV (B) 42 eV

(C) 52 eV (D) 62 eV

## PART–C

71. $^1H$ NMR spectrum of free benzene shows a peak at ~ 7·2 ppm. The expected chemical shift (in ppm) of $C_6H_6$ ligand in $^1H$ NMR spectrum of $[(\eta^6–C_6H_6)Cr(CO)_3]$ and the reason for it, if any, is/are—

(A) 4·5; disruption of ring current

(B) 9·0; inductive effect

(C) 7·2

(D) 2·5; combination of inductive effect and disruption of ring current

72. Match the metalloproteins in column **A** with their function in column **B**—

| **Column A** | **Column B** |
|---|---|
| (a) Oxyhemocyanin | 1. hydrolysis of C-terminal peptide bond |
| (b) Carbonic anhydrase | 2. methylation |
| (c) Cytochrome $P_{450}$ | 3. conversion of $CO_2$ to $H_2CO_3$ |
| (d) Carboxypeptidase A | 4. oxidation of alkene |
| | 5. oxygen storage |
| | 6. oxygen transport |

**Codes :**

| | (a) | (b) | (c) | (d) |
|---|---|---|---|---|
| (A) | 6 | 3 | 4 | 1 |
| (B) | 5 | 3 | 1 | 6 |
| (C) | 6 | 2 | 3 | 1 |
| (D) | 5 | 4 | 3 | 1 |

73. The geometric cross-section (in barn) of a nucleus A = 125, $r_0 = 1{\cdot}4 \times 10^{-15}$ m approximately is—
(A) 1·05 (B) 1·54
(C) 2·05 (D) 2·54

74. Na[($\eta^5$–$C_5H_5$) Fe($CO_2$)] reacts with $Br_2$ to give **A**. Reaction of **A** with $LiAlH_4$ results in **B**. The proton NMR spectrum of **B** consists of two singlets of relative intensity 5 : 1. Compounds **A** and **B**, respectively, are—
(A) ($\eta^5$–$C_5H_5$) Fe$(CO)_2$Br and ($\eta^5$–$C_5H_5$) Fe$(CO)_2$H
(B) ($\eta^4$–$C_5H_5$) Fe$(CO)_2Br_2$ and ($\eta^4$–$C_5H_5$) Fe$(CO)_2$HBr
(C) ($\eta^5$–$C_5H_5$) Fe$(CO)_2$Br and ($\eta^4$–$C_5H_5$) Fe$(CO)_2(H)_2$
(D) ($\eta^5$–$C_5H_5$)Fe$(CO)_2$Br and ($\eta^5$–$C_5H_5$) Fe$(CO)_2$HBr

75. Which of the following will result in deviation from Beer's law ?
1. Change in refractive index or medium.
2. Dissociation of analyte on dilution.
3. Polychromatic light.
4. Path length of cuvette.
(A) 1, 2 and 3 (B) 2, 3 and 4
(C) 1, 3 and 4 (D) 1, 2 and 4

76. The number of stereoisomers of *trans*—[$CoCl_2$(triethylenetetramine)]Br is—
(A) One (B) Two
(C) Three (D) Four

77. The gas commonly used in generating plasma in Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP—AES) is—
(A) argon (B) carbon dioxide
(C) nitrous oxide (D) hydrogen

78. Under physiological condition, oxygen is binding to deoxyhemoglobin and deoxymyoglobin, the binding curve and its pH dependence, respectively, are—
(A) Sigmoidal and pH dependent; hyperbolic and pH independent.
(B) Hyperbolic and pH independent; sigmoidal and pH dependent.
(C) Sigmoidal and pH independent; hyperbolic and pH dependent.
(D) Hyperbolic and pH dependent; sigmoidal and pH independent.

79. The compound that undergoes oxidative addition reaction in presence of $H_2$ is—
(A) $[Mn(CO)_5]^-$
(B) [($\eta^5$–$C_5H_5$) Mo$(CO)_3]^-$
(C) [IrCl(CO) $(PPh_3)_2$]
(D) [$\eta^5$–$C_5H_5)_2$ ReH]

80. The spin-only magnetic moment and the spectroscopic ground state term symbol of manganese centre in $[MnF_6]^{3-}$ ion respectively, are—
(A) 4·9 BM and $^5$D (B) 4·9 BM and $^4$F
(C) 3·9 BM and $^3$D (D) 4·9 BM and $^3$F

81. The main products of the reaction of equimolar quantities of $XeF_6$ with $NaNO_3^-$ are—
(A) $XeOF_4$, NaF and $NO_2F$
(B) $XeO_2F_2$, NaF, NOF and $F_2$
(C) $XeOF_4$, $NaNO_2$ and $F_2$
(D) $XeF_4$, $NaNO_2$ and $F_2O$

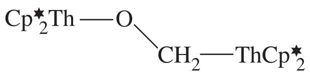
82. A borane **(X)** is reacted with ammonia to give a salt of borohydride **(Y)**. The $^{11}$B NMR spectrum of **Y** consists of a triplet and a quintet. The borane **X** is—
(A) $B_2H_6$ (B) $B_3H_9$
(C) $B_4H_8$ (D) $B_5H_9$

83. Base hydrolysis of $[CoCl(NH_3)_5]^{2+}$ is an overall second order reaction, whereas that of $[Co(CN)_6]^{3-}$ is of first order. The rates depend in both cases solely on the concentrations of the cobalt complex. This may be due to :
1. Presence of ionizable proton in $[CoCl(NH_3)_5]^{2+}$ but not in $[Co(CN)_6]^{3-}$
2. $S_{N^1CB}$ mechanism in the case of $[CoCl(NH_3)_5]^{2+}$ only
3. $S_{N^1CB}$ mechanism in the case of $[Co(CN)_6]^{3-}$ only
4. $S_{N^1CB}$ mechanism in both the complexes

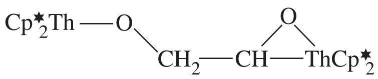
Correct explanation(s) is/are—
(A) 1 and 2 (B) 1 and 3
(C) 2 only (D) 1 and 4

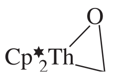
84. Hindered β—diketonates like dpmH (dpmH = dipivaloylmethane) are used for the separation of lanthanides because complexes formed with dpmH can be separated by—
(A) Gel permeation chromatography
(B) Gas chromatography
(C) Gel filtration chromatography
(D) Ion exchange chromatography

85. The final product in the reaction of $[Cp^*{}_2ThH]$ with CO in an equimolar ratio is—

(A) 


(B) 


(C) 


(D) 


86. An aqueous solution of $[Mn(H_2O)_6]^{2+}$ complex is pale pink in color. The probable reasons for it are—
1. presence of $^6A_{1g}$ ground state.
2. disallowed transition by spin selection rule.
3. presence of $^2T_{2g}$ ground state.
4. charge transfer transition.

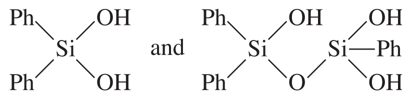
The correct answer is—

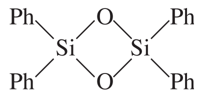
(A) 1 and 2 (B) 1 and 3
(C) 2 and 3 (D) 3 and 4

87. According to Wade's rule, anion $C_2B_9H_{12}$ adopts—
(A) *closo*—structure
(B) *nido*—structure
(C) *arachno*—structure
(D) *hypho*—structure

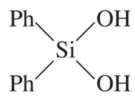
88. The reaction of phosphorus trichloride with phenyllithium in 1 : 3 molar ratio yields product 'A', which on further treatment with methyl iodide produces 'B'. The reaction of B with $^n$BuLi gives product 'C'. The products A, B and C, respectively, are—
(A) $[PPh_4]Cl$, $[Ph_2P{=}CH_2]I$, $Ph_2P(^nBu)$
(B) $PPh_3$, $[Ph_3PI]Me$, $Ph_2P(^nBu)_3$
(C) $PPh_3$, $[Ph_3PMe]I$, $Ph_3P{=}CH_2$
(D) $[PPh_4]Cl$, $[Ph_3P{=}CH_2]I$, $Ph_3P(^nBu)]Li$

89. The reaction between diphenyldichlorosilane and water in 1 : 2 molar ratio gives product A which on heating above 100°C yields a cyclic or polymeric product B. The products A and B respectively, are—

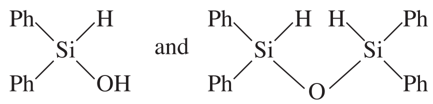
(A) 


(B) 


and $(Ph_2SiO)_n$ ($n = 3, 4$, or $\infty$)

(C) 


and $(Ph_2SiO)_n$ ($n = 3, 4$, or $\infty$)

(D) 


90. The spin-only ($\mu_S$) and spin plus orbital ($\mu_{S+L}$) magnetic moments of $[CrCl_6]^{3-}$ are—
(A) 3·87 BM and 5·20 BM
(B) 2·84 BM and 5·20 BM
(C) 3·87 BM and 6·34 BM
(D) 2·84 BM and 6·34 BM

91. The three dimensional structure of compound $[Co(Co(NH_3)_4(OH)_2)_3]Br_6$ has—
(A) twelve Co—O and twelve Co—N bonds
(B) ten Co—O and ten Co—N bonds
(C) fourteen Co—O and ten Co—N bonds
(D) twelve Co—O and ten Co—N bonds

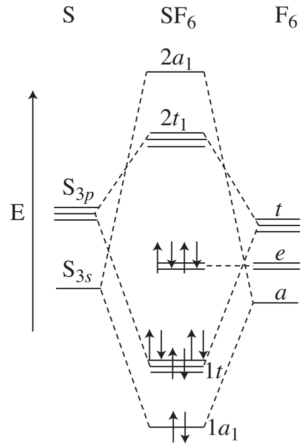
92. 12-Crown-4 binds with the alkali metal ions in the following order :
$Li^+ >> Na^+ > K^+ > Cs^+$. It is due to the—
(A) right size of cation
(B) change in entropy being positive
(C) conformational flexibility of crown ether
(D) hydrophobicity of crown ether

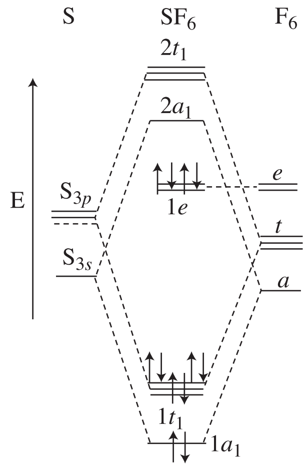
93. Complexes $HM(CO)_5$ and $[(\eta^5\text{–}C_5H_5)M'(CO)_3]_2$ obey the 18-electron rule. Identify M and M′ and their $^1H$ NMR chemical shifts relative to TMS—
(A) M = Mn, – 7·5; M′ = Cr, 4·10
(B) M = Cr, – 4·10; M′ = Mn, – 7·5
(C) M = V, – 7·5; M′ = Cr, 4·10
(D) M = Mn, – 10·22; M′ = Fe, 2·80

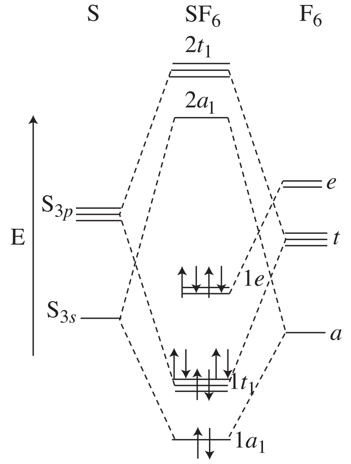
94. Gel permeation chromatography can be used to separate which of the following ?
1. Lanthanides
2. Alkaline earths
3. Fatty acids
4. Low molecular weight peptides

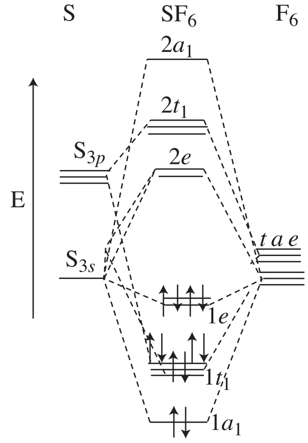
The correct answer is—
(A) 1 and 2 (B) 2 and 3
(C) 3 and 4 (D) 1 and 4

95. The correct schematic molecular energy diagram for $SF_6$ molecule is—

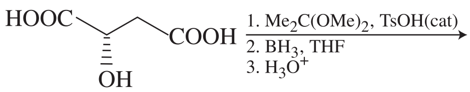
(A)


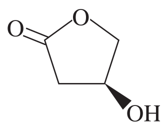

(B)


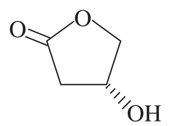

(C)


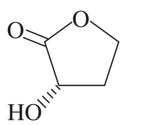

(D)


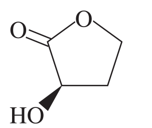

96. The major product formed in the following reaction is—



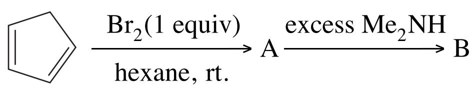

(A)


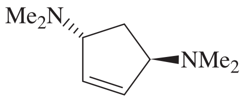

(B)


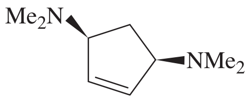

(C)


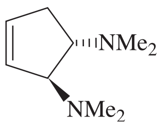

(D)


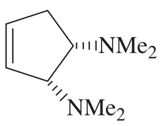

97. The product **B** in the following reaction sequence is—



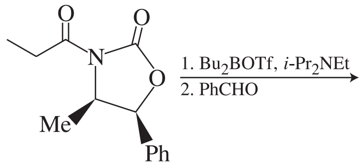
(A) 

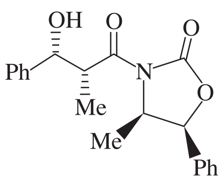
(B) 

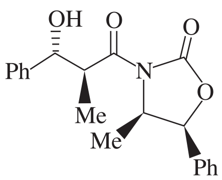
(C) 

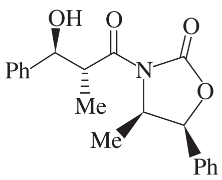
(D) 

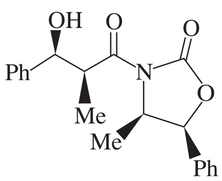
98. The major product formed in the following transformation is—



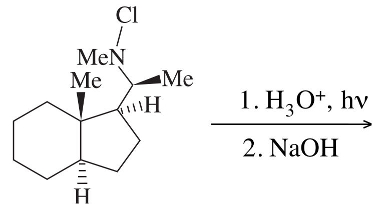
(A) 

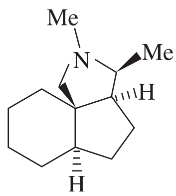
(B) 

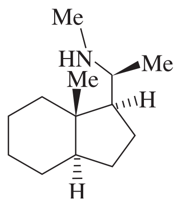
(C) 

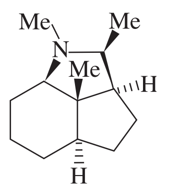
(D) 

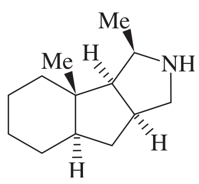
99. The major product of the following reaction is—



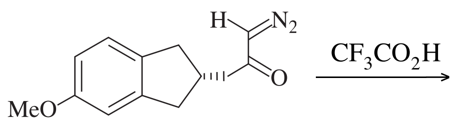
(A) 

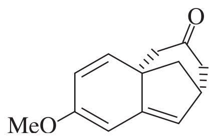
(B) 

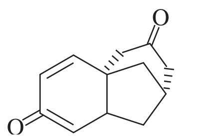
(C) 

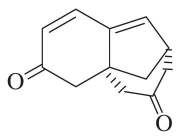
(D) 

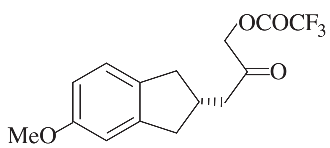
100. The major product of the following reaction is—



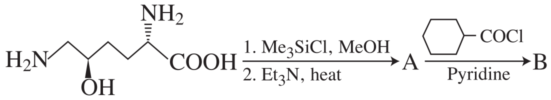
(A) 

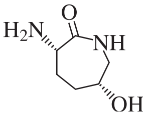
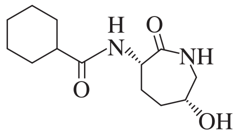
(B) 

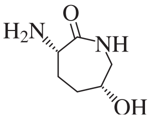
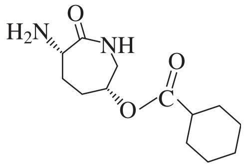
(C) 

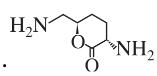
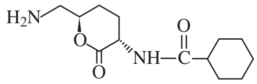
(D) 

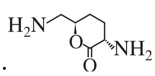
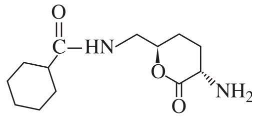
101. The products **A** and **B** in the following reaction sequence are—



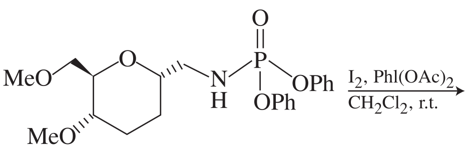

(A) 1.  2. 

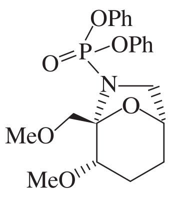
(B) 1.  2. 

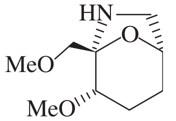
(C) 1.  2. 

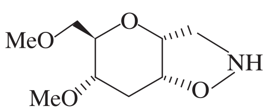
(D) 1.  2. 

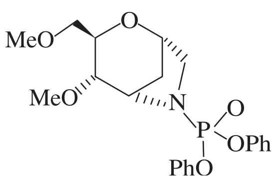
102. The major product for the following reaction is—



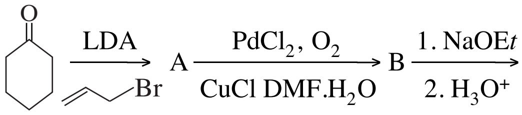

(A) 

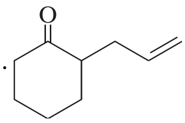
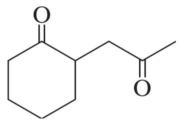
(B) 

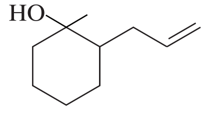
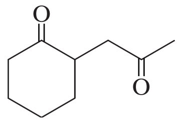
(C) 

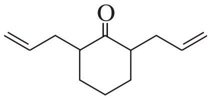
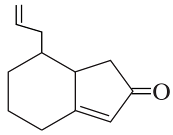
(D) 

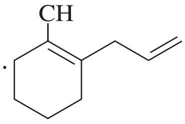
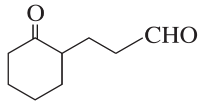
103. The products **A** and **B** in the following reaction sequence are—



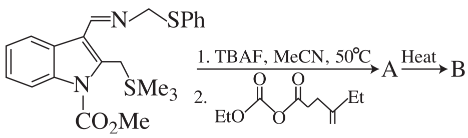

(A) 1.  2. 

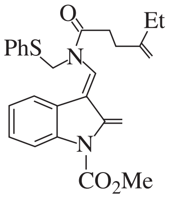
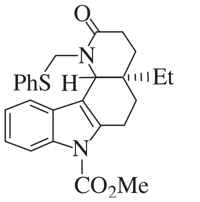
(B) 1.  2. 

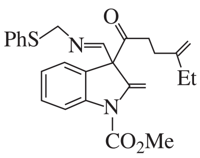
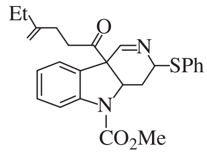
(C) 1.  2. 

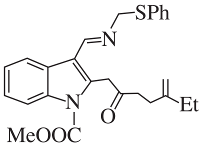
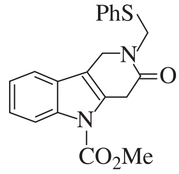
(D) 1.  2. 

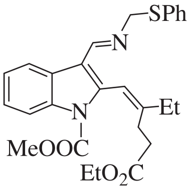
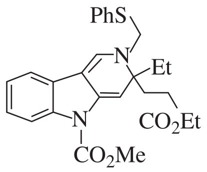
104. The products **A** and **B** in the following reaction sequence are—



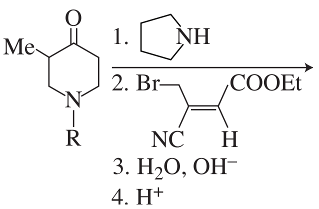

(A) 1.  2. 

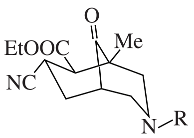
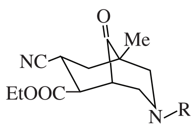
(B) 1.  2. 

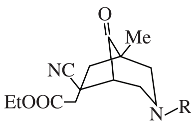
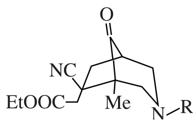
(C) 1.  2. 

(D) 1.  2. 

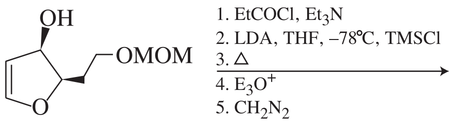
105. The major product of the following reaction—

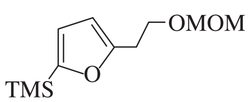


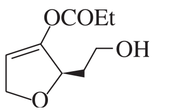
(A)  (B) 

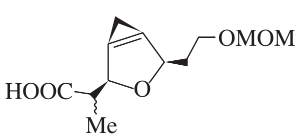
(C)  (D) 

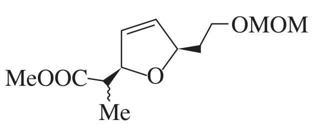
106. The major product formed in the following reaction sequence is—



(A) 

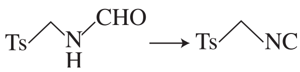
(B) 

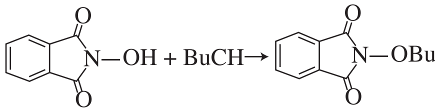
(C) 

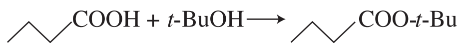
(D) 

107. The correct combinations of the reactions and the reagents are—

**Reactions**

(A) 

(B) 

(C) 

**Reagents**

(P) $PPh_3$ and $EtO_2CN{=}NCO_2Et$

(Q) $POCl_3.Et_yN$

(R) $H_2SO_4$

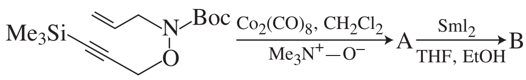
(A) A—P, B—Q, C—R

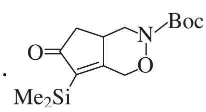
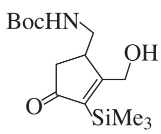
(B) A—Q, B—R, C—P

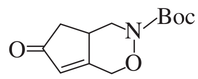
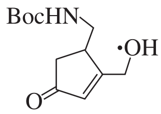
(C) A—P, B—R, C—Q

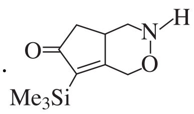
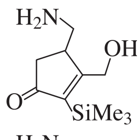
(D) A—Q, B—P, C—R

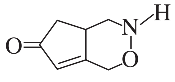
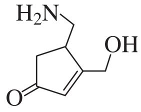
108. The products **A** and **B** in the following reaction sequence are—



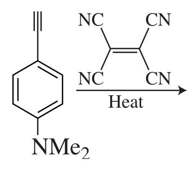
(A) 1.  2. 

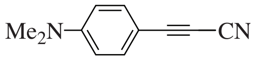
(B) 1.  2. 

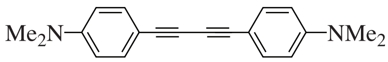
(C) 1.  2. 

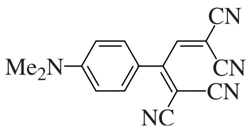
(D) 1.  2. 

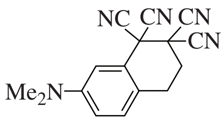
109. The major product of the following reaction is—



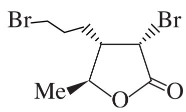
(A) 

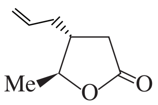
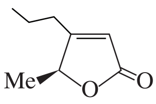
(B) 

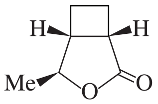
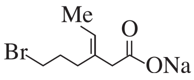
(C) 

(D) 

110. The major product of the following reaction is—



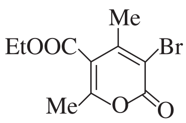

(A) 
(B) 

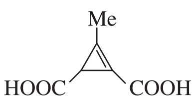
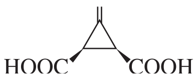
(C) 
(D) 

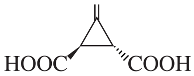
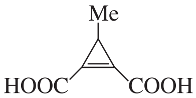
111. The following reaction gives a product (racemic) which exhibits the following NMR data—

$^1$H NMR : δ 2·67 (2H, *s*), 5·60 (2H, *s*) ppm;
$^{13}$C NMR : δ 170·3, 129·0, 105·0, 25·4 ppm.

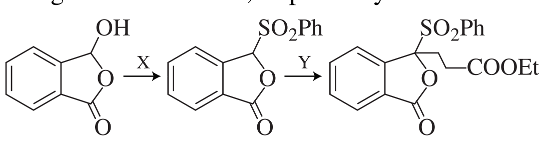
The structure of the product (racemic) is—




(A) 
(B) 

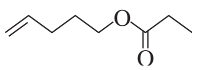
(C) 
(D) 

112. In the following reaction sequence, the reagents **X** and **Y** are, respectively—



(A) X = $PhSO_2H$, $BF_3OEt_2$ and Y = $CH_2$=CHCOOEt, $BF_3$ $OEt_2$
(B) X = 1. PhSH, PTSA; 2. *m*-CPBA and Y = $CH_2$=CHCOOEt, $BF_3$ $OEt_2$
(C) X = $PhSO_3H$, $BF_3$ $OEt_2$ and Y = LDA, $CH_2$=CHCOOEt
(D) X = 1. PhSH, PTSA; 2. *m*-CPBA and Y = LDA, $CH_2$=CHCOOEt

113. The reactive intermediate and the product formed in the following reaction are—



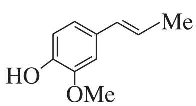
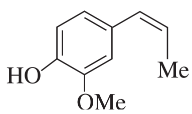

(A) Free radical and 4-iodomethyloxepan-2 one
(B) Free radical and 5-iodooxacan-2-one
(C) Carbene and 3-oxabicyclo [5.1.0] octane 2-one
(D) Carbene and (E)-5-iodopent-3-en-1-yl acetate

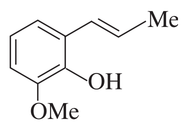
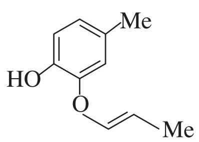
114. An organic compound having molecular formula $C_{10}H_{12}O_2$ exhibits the following spectral data—

IR : 3400 (br), 1600 cm$^{-1}$.

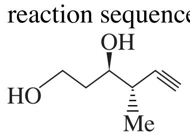
$^1$H NMR : δ 1·85 (3H, *d*, J = 6Hz), 3·8 (3H, *s*), 5·0 (1H, *s*, $D_2O$ exchangeable), 6·0 (1H, dq, J = 18, 6 Hz), 6·28 (1H, *d*, J = 18 Hz), 6·75 (1H, *d*, J = 8 Hz), 6·8 (1H, *s*), 6·90 (1H, *d*, J = 8 Hz) ppm; $^{13}$C NMR : δ 146·5, 144·0, 131·0, 130·5, 123·0, 119·0, 114·0, 108·0, 55·0, 18·0 ppm.

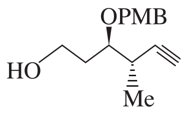
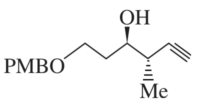
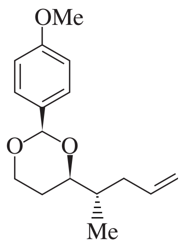
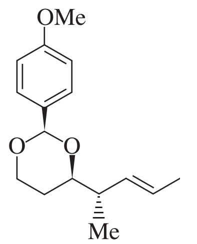
The structure of the compound is—

(A) 
(B) 

(C) 
(D) 

115. The major product formed in the following reaction sequence is—



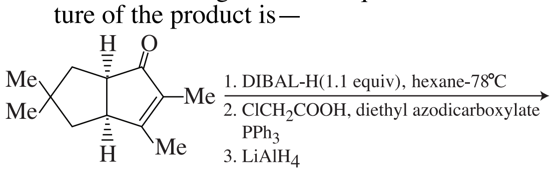
(A) 
(B) 
(C) 
(D) 

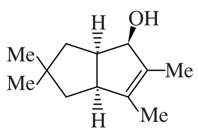
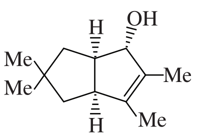
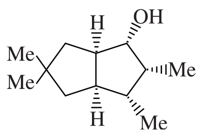
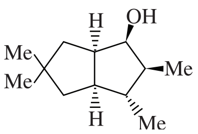
116. The correct combination of the following reactions and their ρ values is—

| Entry | Reaction | Entry | ρ value |
|---|---|---|---|
| A | $ArNH_2$ + PhCOCl in benzene | P | + 2·01 |
| B | ArO + EtI in EtOH | Q | – 0·99 |
| C | $ArCO_2Et$ + aq NaOH in EtOH | R | – 2·69 |
| | | S | + 0·78 |

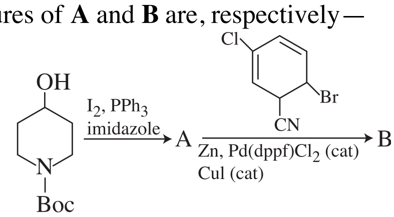
(A) A—P; B—R; C—P
(B) A—R; B—Q; C—P
(C) A—R; B—P; C—Q
(D) A—Q; B—R; C—S

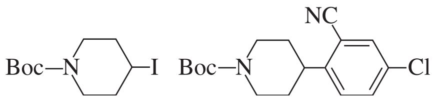
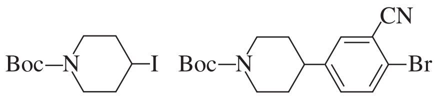
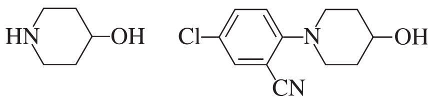
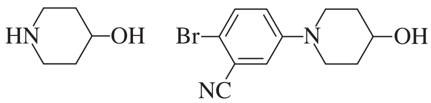
117. In the following reaction sequence, the structure of the product is—



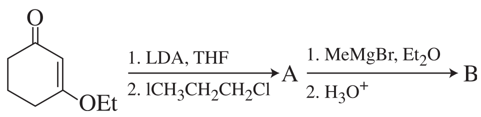
(A) 
(B) 
(C) 
(D) 

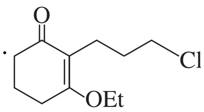
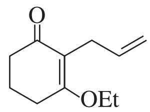
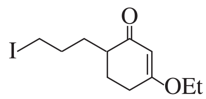
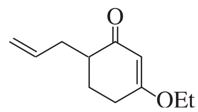
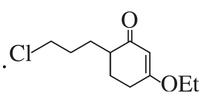
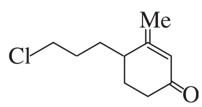
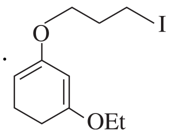
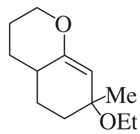
118. In the following reaction sequence, the structures of **A** and **B** are, respectively—



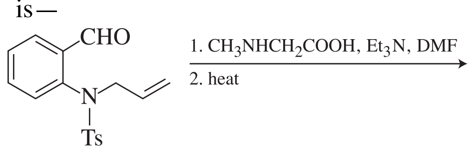
(A) 
(B) 
(C) 
(D) 

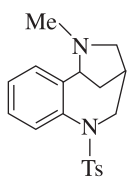
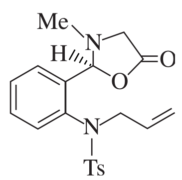
119. The major products A and B formed in the following reaction sequence are—

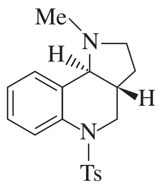


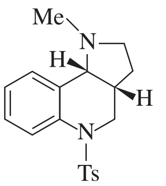
(A) 1.  2. 
(B) 1.  2. 
(C) 1.  2. 
(D) 1.  2. 

120. The major product of the following reaction is—



(A) 
(B) 

(C)


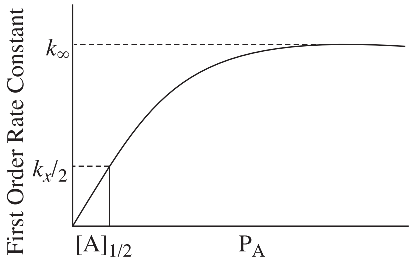

(D)



121. Species A undergoes a unimolecular reaction as follows—

$$A + A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^* + A$$

$$A^* \xrightarrow{k_2} P$$

For this reaction, the first order rate constant at high pressure is $k_\infty$. The first order rate constant becomes $\frac{k_\infty}{2}$ when pressure of A is $[A]_{1/2}$.




The value of $k_1$ will be—

(A) $\frac{k_\infty}{[A]_{1/2}}$ (B) $k_\infty[A]_{1/2}$

(C) $k_\infty - [A]_{1/2}$ (D) $\frac{[A]_{1/2}}{k_\infty}$

122. The low and high temperature limits of vibrational partition function are ($\theta = h\nu/k$).

(A) $e^{-\theta/T}$ and $\frac{T}{\theta} e^{-\theta/T}$ (B) $e^{-\theta/2T}$ and $\frac{T}{\theta} e^{-\theta/2T}$

(C) $e^{-\theta/2T}$ and $\frac{T}{\theta} e^{-\theta/T}$ (D) $e^{-\theta/2T}$ and $\frac{\theta}{T} e^{-\theta/2T}$

123. A particle in a 1-dimentional box of length L is perturbed by a delta function potential, $\delta\left(x - \frac{L}{2}\right)$, in the middle of the box. The first order energy correction to the ground state will be—

(A) 0 (B) 1

(C) $\frac{L}{2}$ (D) $\frac{2}{L}$

[Hint : $\int_{+\infty}^{-\infty} f(x)\,\delta(x-a)dx = f(a)$]

124. For a gaseous reaction, $2NO(g) + Cl_2(g) \rightarrow$ Non-linear T.S. $\rightarrow$ 2NOCl, the pre-exponential factor in the rate constant is proportional to—

(A) $T^{1/2}$ (B) $T^{-1/2}$

(C) $T^{-5/2}$ (D) $T^{-7/2}$

125. The probability of finding the harmonic oscillator in the energy level $n = 1$ is (neglect zero point energy and assume $h\nu = k_BT$).

(A) $e$ (B) $e^2$

(C) $1 - e^{-2}$ (D) $e^{-2}(e - 1)$

126. At high pressure, the fugacity coefficient of a real gas is greater than one, because—

(A) attractive term overweighs the repulsive term

(B) repulsive term overweighs the attractive term

(C) repulsive term is equal to the attractive term

(D) the system is independent of both the attractive and repulsive terms

127. If the bond length of a heteronuclear diatomic molecule is greater in the upper vibrational state, the gap between the successive absorption lines of P-branch—

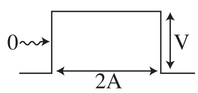
(A) increases non-linearly

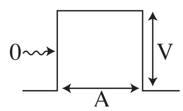
(B) decreases non-linearly

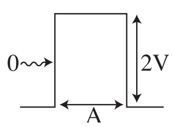
(C) increases linearly

(D) decreases linearly

128. A quantum particle with fixed initial energy $E_0 < V$ is allowed to strike the following four barriers separately. The transmission probability is maximum in—

(A)



(B)



(C)
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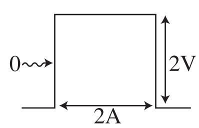


129. EPR spectrum of a free radical containing nuclei with nonzero nuclear spin is obtained if the following selection rules are observed—
(A) $\Delta m_s = 0$, $\Delta m_1 = 0$
(B) $\Delta m_s = \pm 1$, $\Delta m_1 = 0$
(C) $\Delta m_s = \pm 1$, $\Delta m_1 = \pm 1$
(D) $\Delta m_s = 0$, $\Delta m_1 = \pm 1$

130. Given the following two relations,
$$x_1 d\mu_1 + x_2 d\mu_2 = 0 \quad \ldots(1)$$
and $$x_1 d\bar{V}_1 + x_2 d\bar{V}_2 = 0, \quad \ldots(2)$$
for a binary liquid mixture at constant temperature and pressure, the true statement is that,
(A) both the relations are correct.
(B) relation A is correct, but B is not.
(C) relation B is correct, but A is not.
(D) both the relations are incorrect except for very dilute solution.

131. The operators $S_\pm$ are defined by—
$S_\pm = S_x \pm iS_y$,
where $S_x$ and $S_y$ are components of the spin angular momentum operator. The commutator $[S_z, S_+]$ is—
(A) $\hbar S_+$ (B) $\hbar S_-$
(C) $-\hbar S_+$ (D) $-\hbar S_-$

132. The configuration [Ne] $2p^1\ 3p^1$ has a $^3D$ term. Its levels are—
(A) $^3D_{3/2}$, $^3D_{1/2}$
(B) $^3D_{5/2}$, $^3D_{3/2}$, $^3D_{1/2}$
(C) $^3D_3$, $^3D_2$, $^3D_1$
(D) $^3D_3$, $^3D_2$, $^3D_1$, $^3D_0$

133. The fraction of groups condensed at time $t$ in any stepwise condensation polymerization (overall second order) reaction is—
(A) $1 + kt[A]_0$ (B) $\frac{1}{1 + kt[A]_0}$
(C) $\frac{kt[A]_0}{1 + kt[A]_0}$ (D) $\frac{1 + kt[A]_0}{kt[A]_0}$

134. If $D_0(A)$ and $I(A)$ refer respectively to the dissociation energy and ionization potential of A (where A is either H, $H_2$, or $H_2^+$ species), the correct relation among the following is—
(A) $D_0(H_2) = D_0(H_2^+) + I(H) - I(H_2)$
(B) $D_0(H_2) = D_0(H_2^+) - I(H) + I(H_2)$
(C) $D_0(H_2^+) = D_0(H_2) + I(H) + I(H_2)$
(D) $D_0(H_2^+) = D_0(H_2) - I(H) - I(H_2)$

135. Fuel cells provide clean electrical energy to a variety of applications including automobiles and stationary power sources. Normally hydrogen combines with oxygen to give electrical energy and water. If we use butane instead of hydrogen at 1·0 bar and 298 K, the following reaction occurs—
$$C_4H_{10}(g) + \frac{13}{2} O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l)$$
If the change in the Gibbs free energy of this reaction is—
2746·06 kJ mol$^{-1}$, involving 26 electrons, its open circuit voltage is—
(A) 1·55 V (B) 1·09 V
(C) 3·15 V (D) 2·06 V

136. A solid consisting of only X atoms has a close-packed structure with X-X distance of 160 pm. Assuming it to be a closed-packed structure of hard spheres with radius equal to half of the X-X bond length, the number of atoms in 1 cm$^3$ would be—
(A) $6·023 \times 10^{27}$ (B) $3·45 \times 10^{23}$
(C) $6·02 \times 10^{21}$ (D) $3·8 \times 10^{21}$

137. The character table of $C_{2v}$ point group is given below. In *cis*-butadiene molecule the vibrational modes belonging to $A_2$ irreducible representation are IR inactive. The remaining IR active modes are—

| $C_{2v}$ | E | $C_2$ | $\sigma_v$ | $\sigma'_y$ | |
|---|---|---|---|---|---|
| $A_1$ | 1 | 1 | 1 | 1 | $z, x^2, y^2, z$ |
| $A_2$ | 1 | 1 | – 1 | – 1 | $R_z, xy$ |
| $B_1$ | 1 | – 1 | 1 | – 1 | $x, R_y, xz$ |
| $B_2$ | 1 | – 1 | – 1 | 1 | $y, R_x, yz$ |

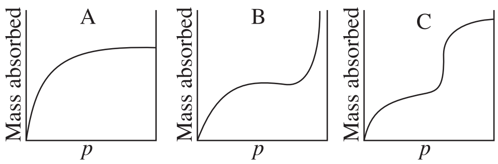
(A) $7A_1 + 5B_1 + 8B_2$
(B) $9A_1 + 4B_1 + 7B_2$
(C) $7A_1 + 3B_1 + 7B_2$
(D) $9A_1 + 3B_1 + 8B_2$

138. The product $\sigma^{xy}.S_4^z$ ($S_4^z$ is the four fold improper axis of rotation around the $z$ axis, and $\sigma^{xy}$ is the reflection in the $xy$ plane) is—

(A) $C_4^z$ (B) $C_4^z.i$

(C) $C_4^y$ (D) $C_2^z$

139. Among the following figures,




the variations of mass adsorbed with pressure for a monolayer and a multilayer are represented by—

(A) A and C respectively

(B) A and B respectively

(C) C and A respectively

(D) B and A respectively

140. According to Huckel theory, the $\pi$ electron charge on the central carbon atom in propenyl cation $(CH_2CHCH_2)^+$ is (in units of electronic charge).

(A) $\frac{1}{2}$ (B) $\frac{1}{\sqrt{2}}$

(C) 1 (D) 2

141. For some one-electron system with $l = 0$ and $m = 0$, the functions $N_0\, e^{-\sigma}$ and $N_1(2 - \sigma)e^{-\sigma/2}$ refer respectively to the ground ($E_0$) and first excited ($E_1$) energy levels. If a variational wave function $N_2(3 - \sigma)e^{-\sigma}$ yields and average energy $\overline{E}$, it will satisfy—

(A) $\overline{E} \geq 0$ (B) $0 \leq \overline{E} \leq E_0$

(C) $\overline{E} \geq E_1$ (D) $E_0 \leq \overline{E} \leq E_1$

142. A Slater determinant corresponding to the ionic part of the ground state valence bond wave function of $H_2$ molecule is ($1s_a\alpha$, $1s_a\beta$, $1s_b\alpha$, $1s_b\beta$ are atomic spin orbitals of hydrogen atoms $a$ and $b$ of the hydrogen molecule)

(A) $\begin{vmatrix} 1s_a\alpha(1) & 1s_a\beta(1) \\ 1s_a\alpha(2) & 1s_a\beta(2) \end{vmatrix}$

(B) $\begin{vmatrix} 1s_a\alpha(1) & 1s_b\beta(1) \\ 1s_a\alpha(2) & 1s_b\beta(2) \end{vmatrix}$

(C) $\begin{vmatrix} 1s_a\alpha(1) & 1s_b\alpha(1) \\ 1s_a\alpha(2) & 1s_b\alpha(2) \end{vmatrix}$

(D) $\begin{vmatrix} 1s_a\alpha(1) & 1s_b\beta(1) \\ 1s_a\alpha(1) & 1s_b\beta(2) \end{vmatrix}$

143. The number of microstates that are possible, when two particles are distributed in four states such that the resulting wave functions are antisymmetric with respect to exchange of the particles, is—

(A) 16 (B) 12

(C) 8 (D) 6

144. When $T \rightarrow \infty$, value of the single-particle partition function will be (given : degeneracy of level $j = g_j$).

(A) 1 (B) $g_0$

(C) $\sum_j g_j$ (D) $\frac{1}{\sum_j g_j}$

145. The rate constant for a reaction

$$A^{1+} + B^{n+} \longrightarrow P$$

is measured in two different aqueous solutions of ionic strengths 0·01 M and 0·04 M. If $\log \frac{k_{0\cdot04}}{k_{0\cdot01}} = 0\cdot3$, the charge $n$ on B is closest to—

(A) 1 (B) 2

(C) 3 (D) 6

## Answers with Hints

1. (B) In 2001,

$$\frac{(250 + 75) + (250 - 75)}{2} = 250$$

and $$\frac{75}{250} \times 100 = 30\%$$

(least per cent variability)

Other years it is 33%, 37·5% and 50%

2. (B) When a rectangle is revolved around any axis, its create cylinder with height according to that axis.

Thus, Volume $V_1 = lwh$

$= \text{length} \times \text{width} \times \text{height}$

$= d \times \frac{d}{2} \times \frac{d}{2} = \frac{d^3}{4}$

and $V_2 = d \times \frac{d}{2} \times d = \frac{d^3}{2}$

Thus, ratio $\frac{V_1}{V_2} = \frac{d^3}{4} \cdot \frac{2}{d^3} = \frac{1}{2}$

$\Rightarrow$ $\boxed{V_1 : V_2 :: 1 : 2}$

3. (B) Its very common that in 4 minutes the wound portion becomes $\frac{R}{\sqrt{2}} = \frac{R}{1{\cdot}41}$. Then in further app. 2 minutes, it will become $= \frac{R}{2}$.

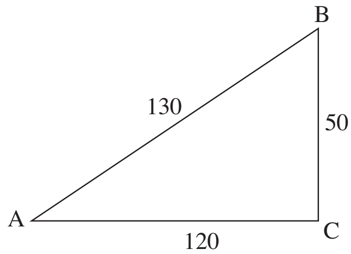
$$\left(\frac{1{\cdot}41}{2} = 0{\cdot}70\right)$$

4. (B) A number is divisible by 3 if the sum of its digits is divisible by 3.

   A number is divisible by 7 if after doubling last digit and subtracting it from remaining leading truncated number is divisible by 7.

   Thus, given combination is divisible by 3 and 7.

5. (A)




Area of Δ ABC $= \frac{1}{2} \times \text{base} \times \text{height}$

$= \frac{1}{2} \times 120 \times 50$

$= 3000 \text{ m}^2$

6. (C) According to given statements, it is clear that the value of $m$ is 20 then he takes 14 non-veg meals.

7. (D) Don't use formula, just think, how ?

   Amount doubled in 1600 days (4·4 years)

   Then in 1·1 years (400 days) interest of ₹ 1000 should be around 200. Thus right option is 190.

8. (D) Series is increasing and decreasing and option is 19.

9. (C) Since locomotives are running towards each other and collide and object has crushed. Then only speed of object which matters.

   Thus, distance = speed × time

   $= 70 \text{ km/h} \times \frac{1}{2} \text{ hour}$

   $= 35 \text{ km}$

10. (B) Average

$$= \frac{70 + 72 + 74 + 76 + 78 + 80 + 82 + 84 + 86 + 88 + 90 + 92 + 94}{13}$$

= 82 kg

Two new persons average weight

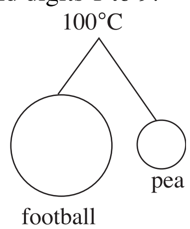
$$= \frac{100 + 79}{2} = 89{\cdot}5 \text{ kg}$$

Thus, total average $= \frac{1066 + 179}{15} = 83$ kg

Thus, increase in average = 1 kg

11. (C) 1872 codes can be generated using letters A to Z and digits 1 to 9.

12. (B)




Cooling is much faster in smaller sphere, so attain room temperature first.

13. (D) From below, we find the gap of 1 letter in English alphabet, so, I J K L M N O

14. (B)

15. (B) $1035 \times \frac{10}{100} = 103{\cdot}5 \Rightarrow 1138{\cdot}50$

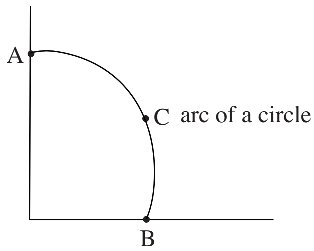
$1035 \times \frac{15}{100} = 155{\cdot}25 \Rightarrow \frac{+\,879{\cdot}75}{2018{\cdot}25}$

Thus, % gain $= \frac{2018{\cdot}25}{2070} \times 100 \approx < 1\%$

16. (A) 2 + 3 = 5 + 5 = 10 + 7 = 17 + 11 = 28 + 13 = 41 + 17 = 58 + 19 = 77 + 23 = 100

addition of prime numbers in increasing order.

17. (B)




18. (C) $25 \times \frac{20}{100} = 5$ students get job within 1 year of passing

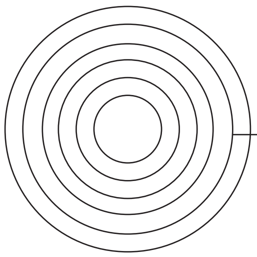
$20 \times \frac{20}{100} = 4$ students get job by end of 2nd year of passing remaining students = 16

So, correct option is 25, (we have to check options)

19. (A) $(1 + x)^n = a_0 + a_1x + a_2x^2 + \ldots\ldots a_nx^n$

Then, $a_0 + a_1 + a_2 + a_3 + \ldots\ldots a_n = 2^n$

20. (D)




Surface area of sphere = $4\pi r^2$

$r$ is radius,

mass depends upon surface area

Thus, the mass is proportional to its surface area.

21. (A) Cation exchange resin–exchanges cations and depends on bigger size which is attached till last time. Thus, the correct order of retention of cations is (distribution constant, $k$) $Ag^+ > k^+ > Na^+ > Li^+$

22. (C) All have 10 $e^-$s but ionic radius is greater in case of highest – ve charge which gives increased radius (ionic). Thus, $O^{2-}$ has highest and $Mg^{+2}$ has lowest ionic radii.

23. (A) In a polarographic measurement, (aq. KCl sol. used as supporting electrolyte) an applied potential more than + 4V, results the formation of $Hg^+$.

DME worked at potential + 0·4V to – 0·2V

24. (D) $SbF_5 + 2HF \longrightarrow [SbF_6]^- [H_2F]^+$

strongest acid in the system, is $10^{16}$ times stronger than 100% $H_2SO_4$.

25. (A) Heme – porphyrin ring (11 π)

Coenzyme $B_{12}$ — Corrin ring

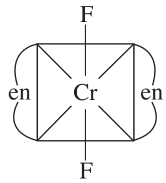
Chlorophyll — Chlorin ring (10 π)

Thus, π – $e^-$ extent of conjugation is

Heme > Chlorophyll > Coenzyme $B_{12}$

(a) > (c) > (b)

26. (*)



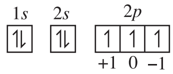

$TiCl_6]^{3-}$

$D_4h : C_4 + 4C_2 + 4\sigma_v + \sigma_n$

$D_2h : C_2 + 2C_2 + 2\sigma_v + \sigma_n$

None of the given alternative are correct.

27. (D) $^{14}N$ or $^{15}N$




no. of protons same

$$S = \frac{n}{2} = \frac{3}{2}$$

$$L = +1 \times 1 + 0 \times 1 + -1 \times 1 = 0$$

Thus, $\boxed{S = \frac{3}{2}, L = 0}$

28. (B) Hydroformylation (Oxo synthesis)

$$CH_3{-}CH{=}CH_2 \xrightarrow[CO_2(CO)_8]{CO + H_2} CH_3CH_2CH_2CHO$$

(normal) butanol

+ $(CH_3)_2CHCHO$

isobutyraldehyde

29. (B) $Ni(CO)_4 + PPh_3 \xrightarrow{h\nu} [Ni(CO)_3PPh_3] + CO$

18 $e^-$s complex.

For substitution, it must follow dissociative mechanism ($SN^1$). Hence, it depends only on $Ni(CO)_4$ concentration.

30. (C) $[(\eta^x - C_6H_6)Ru\ (\eta^y - C_6H_6)]$ – diamagnetic

Ru – 8 $e^-$ in valence shell, want 10 more $e^-$ for $18e^-$ system, so hepticity will be 4 and 6.

$x = 4, y = 6$.

31. (A) Isomeric shift is given by—

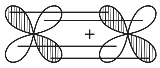
$$\delta = k(R_e^2 - R_g^2) \quad \{[\psi_s^2(0)]_b - [\psi_s^2(0)]_a\}$$

| oxidised ferric ions ($Fe^{+3}$) have lower isomeric effect than $Fe^{+2}$ | $e^-$ density difference on nucleus ($a$ = source, $b$ = sample) |
|---|---|

because $s - e^-$ density at nucleus of $Fe^{+3}$ is greater due to a weaker screening effect by delectrons.

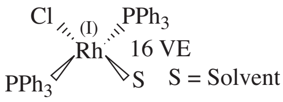
So, δ : Fe(II) > Fe(III) > Fe(IV)

32. (C) *dxy* and *dxy* orbitals $(Re_2Cl_8)^{2-}$
Two nodal planes which contain the internuclear axis and go through both axis.



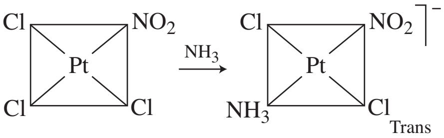
= delta bond formation $2dxy$ or $2dx^2-y^2$ orbitals interacting.

33. (A) after reductive climination step




⇒ neglecting solvent, $[PPh_3-Rh-PPh_3]$ with Cl on Rh

34. (A) $[P + Cl_4]^{-2} + NO_2^- \rightarrow$

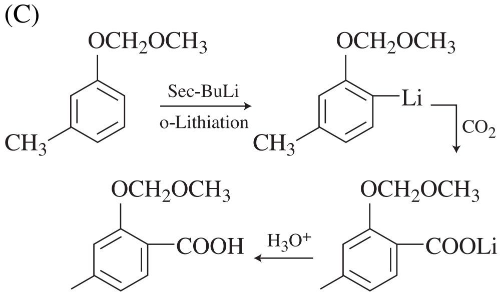



trans effect of $NO_2^- > Cl$

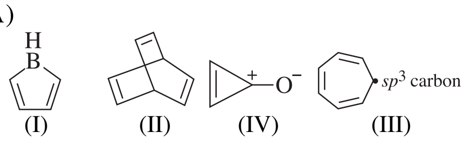
35. (B) $CO_4(CO)_{12}$
Total Valence electron = 4 × 9 + 12 × 2 = 60
Putting $n = 4$ in $14n + 4$ Wade's Rule

| | | |
|---|---|---|
| | $14n + 2$ ⇒ | Closo |
| We have | $14n + 4$ = | 60 |
| ⇒ Nido structure | $14n + 6$ ⇒ | arachno |

36. (C)




37. (A)



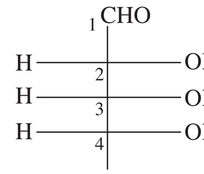

(I) 4$n\pi$ system, Huckel rule antiaromatic; (II) (IV) aromatic; (III) non-aromatic

38. (C) Availability of lone pairs on N-atom decides basicity in these cases. Clearly, pyridine is least basic due to N- is part of aromatic ring ($sp^2$ system).

Greater $e^-$ density leads to greater basic character. Thus,

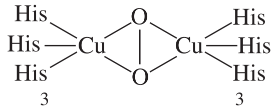
III > II > I > IV

39. (C) R and R

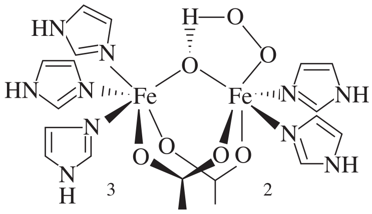



D-ribose

40. (B)

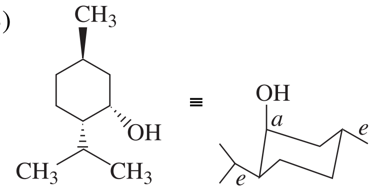



Oxyhemocyanin



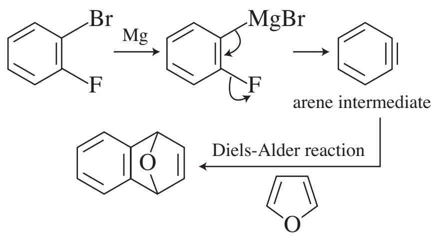

Oxyhemerythrin

41. (B)




OH : axial, *i*-Pr : equatorial, Me : equatorial

42. (C)




43. (D) Biomethylation is a process whereby living organisms produce a direct linkage of a methyl group to a metal or metalloid, thus forming metal-carbon bonds found in soil extensively.

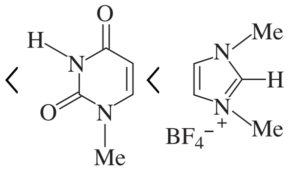
Thus, all statements are common and correct.

44. (C) $p^{ka} = -\log ka$, greater *ka* leads to lower value of $p^{ka}$.

Electron withdrawing group ⇒ greater *ka* ⇒ lower $p^{ka}$.

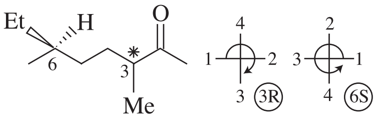
Electron releasing group ⇒ lowers acidity (ka) ⇒ greater $p^{ka}$.

Thus,

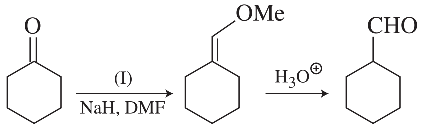
2-cyano guanidine < 

II < I < III

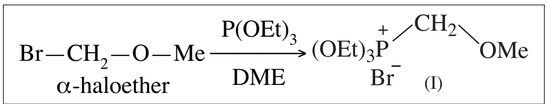
45. (A) Crams Rule, smaller nucleophile, trans aldol product



46. (C)



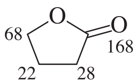
Ketone — Cyclohexane carboxaldehyde




wittig reagents

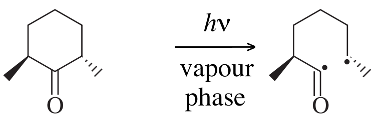
47. (C) $C_4H_6O_2$

IR : 1770 cm$^{-1}$ implier γ-lactone

hence, 

$^{13}$C NMR : 178, 68, 28, 22

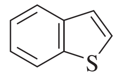
48. (C)



2,6-dimethyl cyclohexanone — α-cleavage

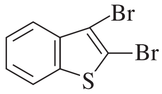
$\xrightarrow[\text{of C—C bond}]{\text{free rotation}}$ Mixture of cis & trans-1, 2-dimethyl cyclopentanes

49. (C)



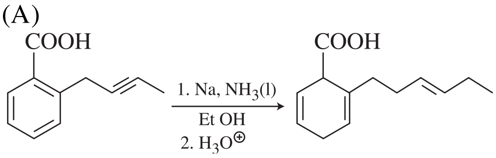
Benzothiophene

$\xrightarrow[\text{CHCl}_3,\ r^+]{\text{Br}_2\text{(excess)}}$



Bromination at 2,3-position

50. (A)



**Birch reduction** $e^-$ withdrawing gp, reduction at ipso and 4-position and alkynes into alkenes with trans-geometry

51. (A)

$$S_{n(s)} \rightarrow S_n^{+2}(aq) + 2e^-, \quad E_1^\circ = +0{\cdot}14\text{V}$$

$$S_n^{+4}(aq) + 2e^- \rightarrow S_n^{+2}(aq), \quad E_2^\circ = +0{\cdot}15\text{V}$$

$$S_{n(s)} + S_n^{+4}(aq) \rightarrow 2S_n^{+2}(aq)$$

$$-nFE_3^\circ = -nFE_1^\circ - nFE_2^\circ$$

$$4E_3^\circ = 2E_1^\circ + 2E_2^\circ$$

$$E_3^\circ = \frac{0{\cdot}29}{2} = 0{\cdot}145$$

Thus $\ln k = \frac{nFE_3^\circ}{RT} = \frac{4 \times 0{\cdot}145}{25{\cdot}7 \times 10^{-3}\text{V}}$

$$= 22{\cdot}56 \approx 22{\cdot}6$$

52. (B) We know that

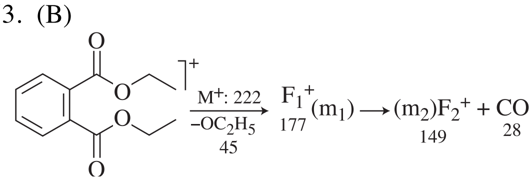
$$\Delta p\, \Delta x \geq \frac{\hbar}{2}$$

$$\Rightarrow \quad \Delta p = \frac{\hbar}{2L}$$

Energy of the particle

$$= \frac{(\Delta p)^2}{2m} = \left(\frac{\hbar}{2L}\right)^2 \frac{1}{2m} = \frac{\hbar^2}{8mL^2}$$

53. (B)




metastable ion peak,

$$m^* = \frac{m_2^2}{m_1}$$

$$= \frac{(149)^2}{177} \simeq 125{\cdot}429$$

54. (D) The selection rule have two consequences—

(1) Both vibrational and rotational quantum numbers must change. The transition—

ΔV = ± 1, ΔJ = 0 (Q-branch) is forbidden.

(2) The energy change of rotation can be either subtracted from or added to the energy change of vibration, giving the *p*- & R-branches of the spectrum respectively.

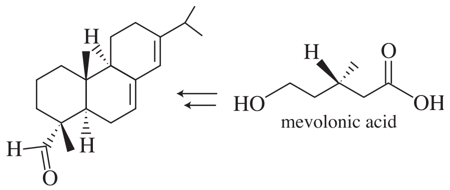
55. (D) $CD_3Cl$; $n = 3, I = 1$

$$2nI + 1 = 7 \text{ non-pascal triangle}$$

so, intensity ratio : : 1 : 3 : 6 : 7 : 6 : 3 : 1

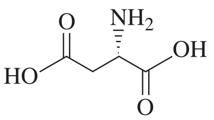
56. (C) Since homonuclear diatomic molecules are both rotational & IR inactive (absence of dipole moment). So rotational Raman and electronic spectroscopy can be used for determination of bond-lengths.

57. (B)

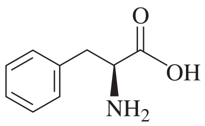



abietic acid

58. (C)




L-aspartic acid




L-phenylalanine

59. (C) $\nu_{mp} = \sqrt{\dfrac{2kT}{M}}$, thus, greater the mass, lesser will be the $\nu_{mp}$.

Thus, Ne – C, Ar – B, Kr – A.

60. (D) We know that

$$dH = TdS + VdP$$

Thus, $\left(\dfrac{\partial H}{\partial S}\right)_P = T \qquad (dP = 0)$

61. (C) The difference between the activation energy for forward & backward reaction is $\Delta H$. Since given that $E_0$ is activation energy for second reaction. The activation energy of overall reaction will be $E_0 + \Delta H$.

62. (C) Fractional coverage ($\theta$) for diatomic molecule on metal surface,

$$\theta = \frac{(KP)^{1/2}}{1 + (KP)^{1/2}}$$

since P is small, $1 > (KP)^{1/2}$.

$$\theta = K^{1/2}P^{1/2}$$

$$\Rightarrow \quad \theta \propto P^{1/2}$$

63. (D) $N = \dfrac{1}{Y}$

$$\Rightarrow \quad \left(\frac{\partial N}{\partial y}\right)_x = -\frac{1}{y^2}$$

$$M = -\frac{x}{y^2}$$

$$\Rightarrow \quad \left(\frac{\partial M}{\partial x}\right)_y = -\frac{1}{y^2}$$

$$\because \quad \left(\frac{\partial N}{\partial y}\right)_x = \left(\frac{\partial M}{\partial x}\right)_y$$

$\therefore$ equation is exact.

64. (B) $L_Z = -i\hbar \dfrac{\partial}{\partial \phi}$

The eigen function equation is

$$L_Z Y_l^m = -i\hbar \frac{\partial}{\partial \phi} Y_l^m$$

$$Y_l^m = f_{(0)}.e^{iA\phi}$$

$f$ is arbitrary function $\phi$ must be periodic for Y is to be unchanged with period $2\pi$.

Thus, value of A should be $A = 0, \pm 1, \pm 2, \ldots$

65. (D) X-Ray Diffraction method is used for crystal structure identification and study.

Amorphous solids don't show XRD.

66. (D) The Lineweaver burk equation is given by—

$$\frac{1}{V} = \frac{1}{V_{max}} + \frac{k_m}{V_{max}} \cdot \frac{1}{[s]_0}$$

Given $\dfrac{k_m}{V_{max}} = 40s$, $[E] = 2{\cdot}5 \times 10^{-6}$ M

We know that at maximum velocity,

$$[ES] = [E]$$

$$\therefore \quad V_{max} = k_2[E]$$

Thus, Efficiency $= \dfrac{k_2}{k_m} = \dfrac{V_{max}}{[E]_x V_{max} \times 40s}$

$$= 10^4 \text{ Lmol}^{-1} s^{-1}$$

67. (B) $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

| | | | | |
|---|---|---|---|---|
| I | 0·01 | | 0 | 0 |
| C | $-x$ | | $+x$ | $+x$ |
| E | $+0{\cdot}01 - x$ | | $+x$ | $+x$ |

$$[CH_3COO^-] = 10 \times \frac{0{\cdot}2}{10 + 10} = 0{\cdot}01$$

$$p^{ka} = 4{\cdot}75$$

$$\Rightarrow \quad k_a = 1{\cdot}8 \times 10^{-8}$$

Thus, $k_b = 5{\cdot}6 \times 10^{-10}$

$$= \frac{x^2}{0{\cdot}01}$$

$$x = [\overline{O}H] = 2{\cdot}36 \times 10^{-6}$$

$$p^{OH} = 5{\cdot}62$$

Hence, $p^H = 14 - p^{OH} = 8{\cdot}38 \simeq 8{\cdot}4$.

68. (B) $f_{00}$ polydispersed macromolecular colloid; $\overline{M}_w > \overline{M}_n$ osmometry gives number average molecular weight, $\overline{M}_n$.

69. (A) $\langle M_n \rangle = 13,$

$\langle M_w \rangle = 16,$

The variance, $\sigma^2$ for molecular weight determination

$$\sigma^2 = \overline{M}_n^2 \left(\frac{\overline{M}_w}{\overline{M}_n} - 1\right)$$

$$= (13)^2 \left(\frac{16}{13} - 1\right)$$

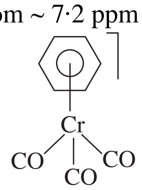
$$= 169 \times \frac{3}{13} = 39$$

70. (C) $\text{I.E.} = \frac{hc}{\lambda} = \frac{6{\cdot}626 \times 10^{-34} \times 3 \times 10^8 \times 10^{19}}{24 \times 10^{-9} \times 1{\cdot}6}$

$= 52$ eV

Ionization energy is the energy required to remove an electron from outermost orbital of gaseous system.

71. (A) All the given options are incorrect except (1). There is **ring current disruption** after formation of complex in $[\eta^6 - (C_6H_6)Cr(CO)_3]$. The shift in $\delta$ is also attributed to this reason from ~ 7·2 ppm to 4·4 (almost).




72. (A) Oxyhemocyanin—oxygen transport specifically in invertebrates.

Carbonic anhydrase—In Red Blood Cells, $CO_2$ to $HCO_3$.

Cytochrome $P_{450}$—Oxydation of alkene, monooxygenose, green catalyst.

Carboxypeptidase A—Hydrolysis of C-terminal peptide bond.

73. (B) Geometric cross-section = $\pi r^2$

and $r = r_0(A)^{1/3}$

Thus, $r = 1{\cdot}4 \times 10^{-15}\text{ m} \times (125)^{1/3}$

$= 0{\cdot}7 \times 10^{-14}$ m

Hence, GC-S $= 3{\cdot}14 \times (0{\cdot}7 \times 10^{-14})^2 m^2$

$\simeq 1{\cdot}54 \times 10^{-28}\text{ m}^2$

(1 barn = $10^{-28}$ m$^2$)

$\simeq 1{\cdot}54$ barn

74. (A) $Na[(\eta^5\text{-}C_5H_5)\,Fe(CO)_2] \xrightarrow{Br_2}$
17e$^-$ system

$[(\eta^5\text{-}C_5H_5)\,Fe(CO)_2\,Br] \xrightarrow[18e^-]{LiAlH_4}$ system

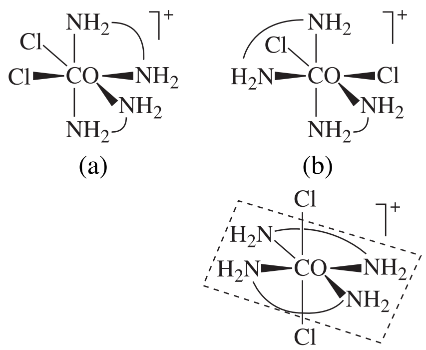
substitution of Br with H.

$[(\eta^5\text{-}C_5H_5)\,Fe(CO)_2H]$

$^1$H NMR appears for 5H of Cp and 1H in ration 5 : 1.

75. (A) Path length of curvetle is not responsible for deviation from ideal behaviour. All the remaining statement, A, B and C will result in deviation form.

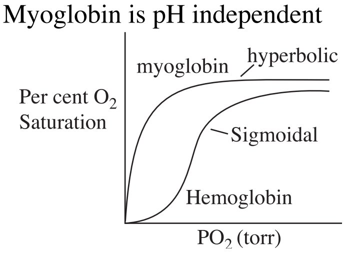
76. (C) Three isomers shown as—




(c) mirror plane

77. (A) Also known as inductively coupled plasma optical emission spectroscopy (ICP-OES) is an analytical technique used for the detection of trace metals. Argon gas is typically used to create the **plasma.**

78. (A) Myoglobin is pH independent




Lungs (gills) $Hb + 4O_2 \rightarrow Hb(O_2)_4$

Tissues $Hb(O_2)_4 + 4\,Mb \rightarrow 4\,Mb(O_2) + Hb$

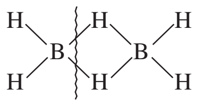
pH dependence shown by hemoglobin is known as Bohr effect (binds one $H^+$ for every dioxygen molecules).

79. (C) Iridium complex is 16 e$^-$ system and favourable for oxidative addition reaction in presence of $H_2$, commonly known as Vaska's complex. Rest are 18 e$^-$ stable complex compound.

80. (A) $M_n^{+3}$ : | 1 | 1 | 1 | 1 |

$2S + 1 = 5$, $L = 2(D)$, $\mu = \sqrt{n(n+2)}$
no. of unpaired electrons = 4
So, $\mu_{S.O.} = 4{\cdot}9$ BM.

81. (A) $XeF_6 + NaNO_3 \rightarrow XeOF_4 + NaF + NO_2F$
Nitrodes react with $XeF_6$ to form $XeOF_4$. This safe & convenient route involves reaction of $XeF_6$ with a stoichiometric deficiency of $NaNO_3$.

82. (A)  $\xrightarrow[\text{Unsymmetric Cleavage}]{2NH_3}$

$[(BH_2)(NH_3)_2][BH_4]$
2H → triplet
4H → quinlet

Other product is Borohydride salt $[BH_2(NH_3)_2][BH_4]$ which gives triplet and quinlet in $^{11}B$. NMR spectrum due to 2H and ⱪ H respectively.

83. (A) $[CoCl(NH_3)_5]^{2+} \xrightarrow[-H_2O]{^-OH}$
$S_N1CB$

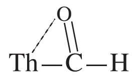
$[CoCl(NH_2)(NH_3)_4]^+$
$-Cl^{\ominus}$ ↓ Slow

$[CO(OH)(NH_3)_5]^{2+} \xleftarrow[\text{fast}]{H_2O}$ $[Co(NH_2)(NH_3)_4]^{2+}$

In $[Co(CN)_6]^{3-}$, no ionizable proton.
Thus, statements A & B are correct.

84. (B) By gas chromatography.

85. (D)



$(\eta^5\ CP_2)$ TH—H + CO → $(\eta^5\ (CP_2)$
CO insertion occurs in case of Thorium hydride A driving force for this reaction is the strong interaction of oxygen of inserted CO with thorium atom.

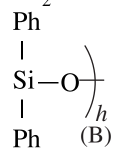
86. (A) $M_n^{+2}$ : | 1 | 1 | 1 | 1 | 1 |

$2s + 1 = 6$, $L = 0$ (s)
Spin selection rule, $\Delta s = 0$
$6s \longrightarrow 6A_{1g}$ ground state
Violated and disallowed transition charge transfer impossible and $^2T_{2g}$ is not ground state.
Hence, A & B are correct.

87. (B) $C_2B_9H_{12}$, According to Wade's rule
$= (CH) \times 2 + (BH) \times 9 + 1 + 1$
$= 3 \times 2 + 2 \times 9 + 1 + 1 = 26$ or 13 $e^-$ pair
$= (m + 2)$ $e^-$ pair ⇒ Nido structure.

88. (C) $PCl_3 + 3PhCl \xrightarrow{6Na} PPh_3 + 6NaCl$
(A) ↓ MeI
$Ph_3P{=}CH_2 \xleftarrow[-BuH,\ -Li^{\oplus}]{BuLi} [Ph_3PMe]^+ I^-$
ylides (C) (B)

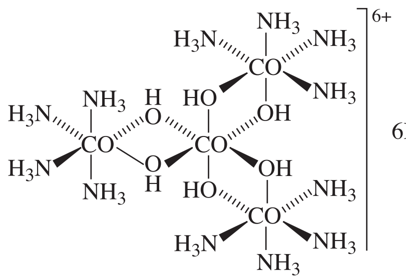
89. (C) $Ph_2SiCl_2 \xrightarrow[-2HCl]{2H_2O} Ph_2Si(OH)_2$
(A) Δ ↓ 100°C – $H_2O$

Polymeric structure 

90. (A) $Cr^{+3}$ : | 1 | 1 | 1 | | |

$\mu_{S.O.} = \sqrt{n(n+2)}$
$= \sqrt{3(3+2)} = 3{\cdot}87$ B.M.
and $\mu_{S+L} = \sqrt{n(n+2) + L(L+1)}$
$= \sqrt{15 + 12} = \sqrt{27} = 5{\cdot}20$ BM

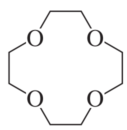
91. (A)



6Br⁻

**Inorganic optically active complex—**
12Co—O and 12 Co—N bonds

92. (A) The size of the cavity is responsible for binding with alkali metals. So, crown ether binds different metals. Thus, right size of cation is important factor.



12-crown-4

93. (A) $HMn(CO)_5$ and $[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2$
δ : – 7·5 4·10

94. (C) Type of size exclusion chromatography (SEC), that separates analytes on the basis of size. Analysis of polymers is done by this technique. Thus, from given options, fatty acids low molecular weight peptides can be separated by this method.

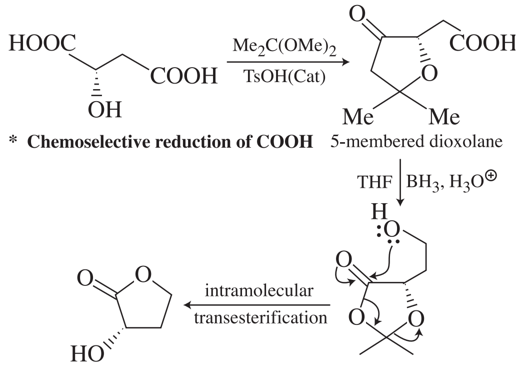
95. (A) $SF_6$ : 6 S-F bonds, 12 $e^{-}s$ involved
hypervalent

4-orbitals ($1a_1$, $1t_1$) : bonding

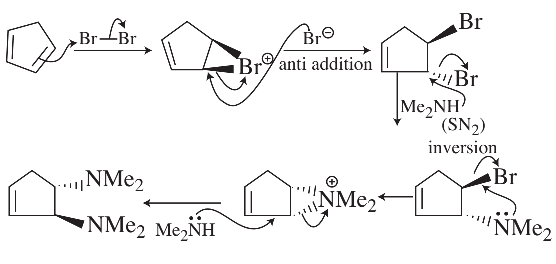
4-orbitals ($2t_1$, $2a_1$) : anti-bonding

2-orbitals (1e) : non-bonding

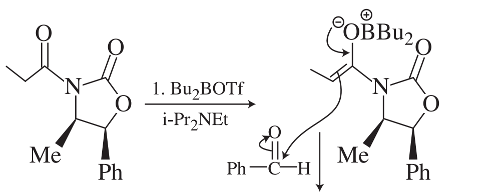
96. (C)



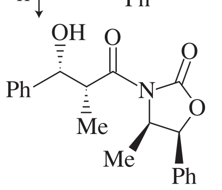
97. (C)



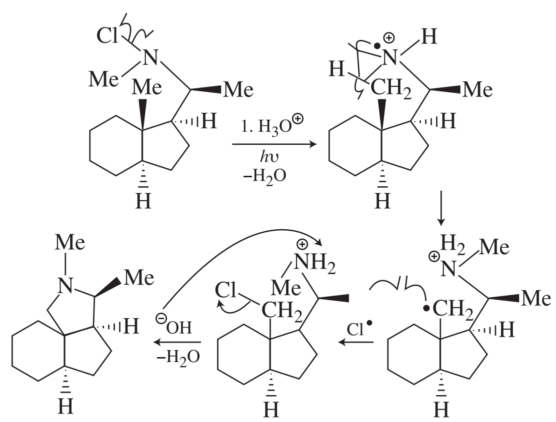
98. (A) Diastereoselective proplem-formation of cis enolode thus cis-aldol product.



small ligand (Bu), good leaving gp (OTf) and hindered amine ($i$-$Pr_2NEt$) facilitates the reaction.



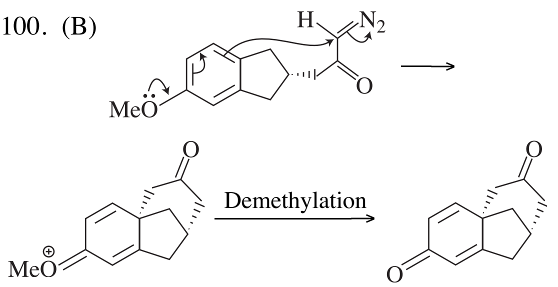
99. (A)



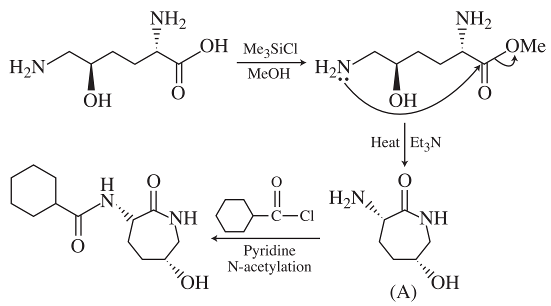
Hoffmann—Loffler—Fretyag reaction

⇒ Free radical mechanism

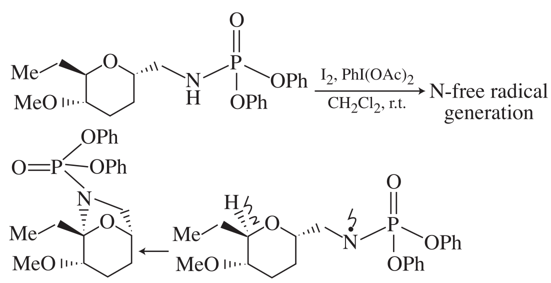
100. (B)



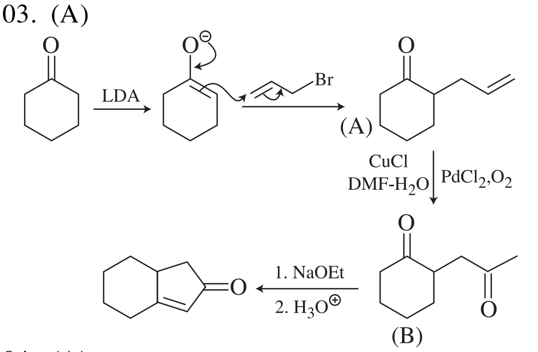
101. (A)



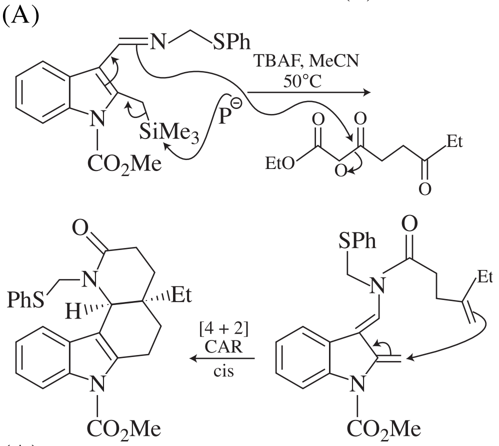
102. (A)



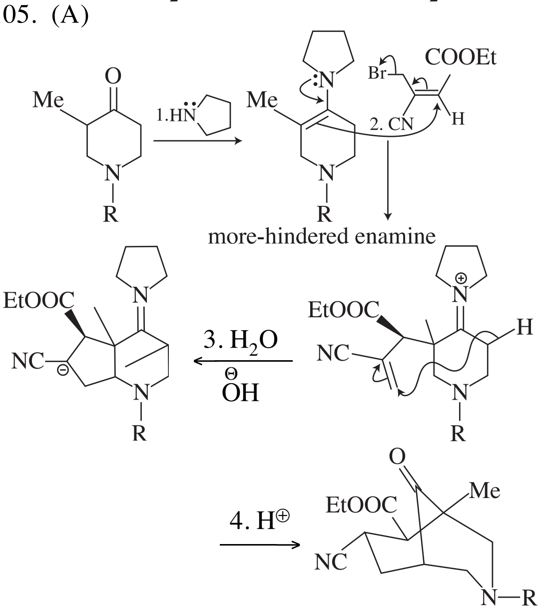
103. (A)




104. (A)

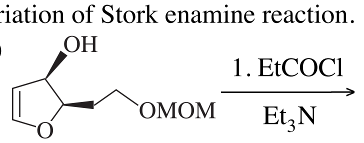


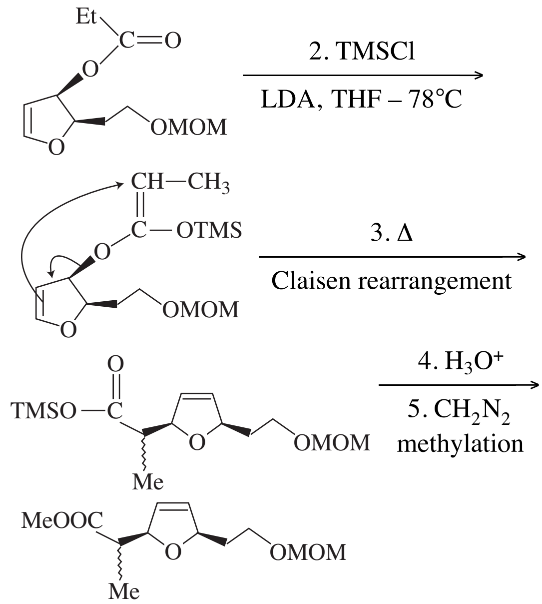

105. (A)




Variation of Stork enamine reaction.

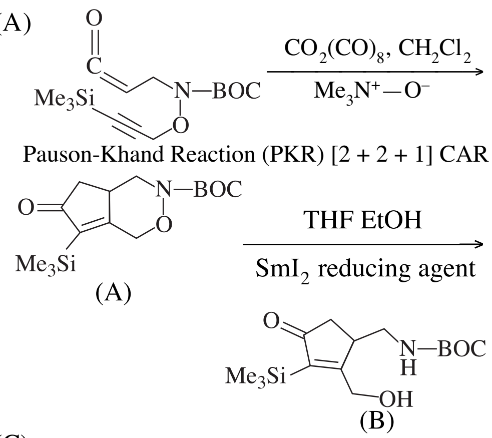
106. (D)



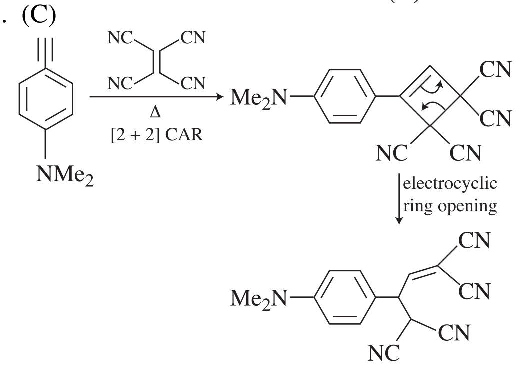




107. (D) A is dehydration reaction using $POCl_3$, $Et_3N$. B is esterification using …… $PPh_3$ and $EtO_2CN{=}NCO_2Et$. C is butylation using $H_2SO_4$.

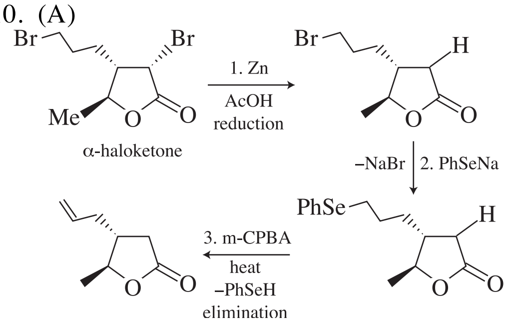
108. (A)




109. (C)

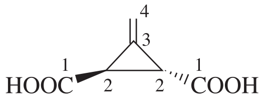


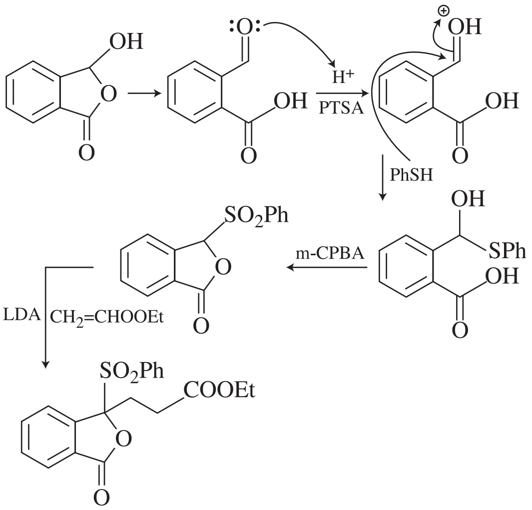
110. (A)



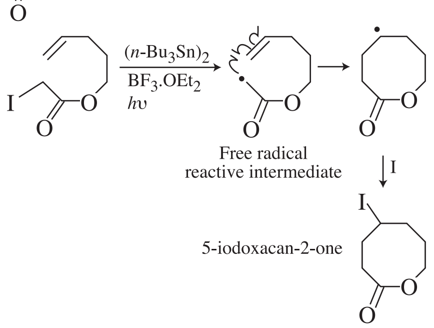

111. (C) δ 2·67 (2H, S) indicates $^{13}$C NMR shows 4 signals. Thus structure may be (2) or (3). >= entity

112. (D)

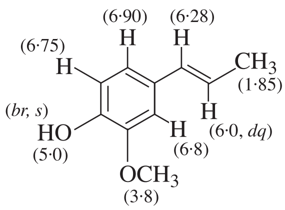



113. (B)

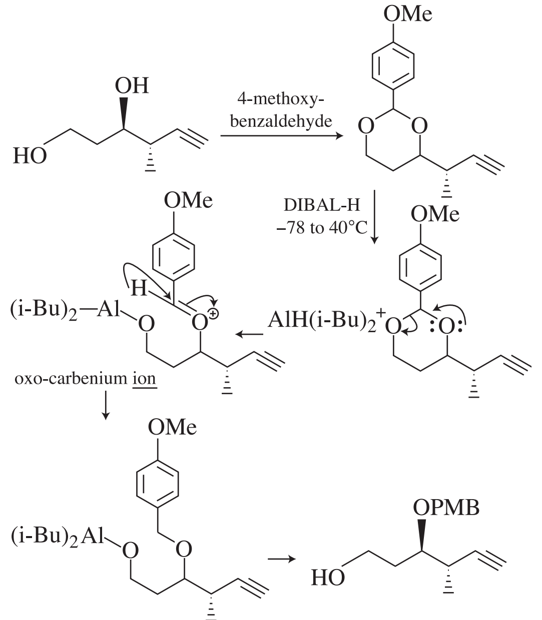



114. (A) $C_{10}H_{12}O_2$




⇒ δ 6·28 & J = 18 Hz indicates trans-geometry of double bond.

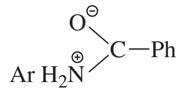
115. (A)




116. (B) δ = reaction constant

$$\text{(A) } Ar\ddot{N}H_2 + Cl-\overset{\overset{\displaystyle O}{\|}}{C}-Ph \xrightarrow[\text{rds}]{\text{benzene}}$$

moderate negativeδ value (– 2·69) R




positive charge near ring

$$\text{(B) } ArO^- + EtI \xrightarrow[\text{rds}]{\text{EtOH}} ArOEt$$

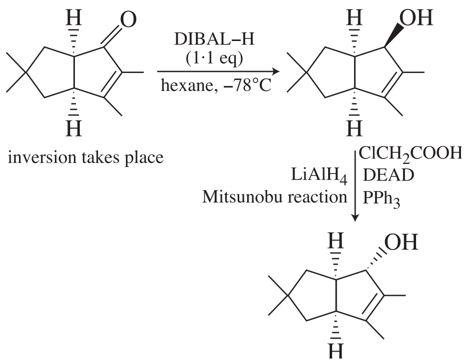
no electron change small δ value (– 0·99) Q.

$$\text{(C) } Ar-\overset{\overset{\displaystyle O}{\|}}{C}-OEt + \text{aq. NaOH} \xrightarrow[\text{rds}]{\text{EtOH}}$$

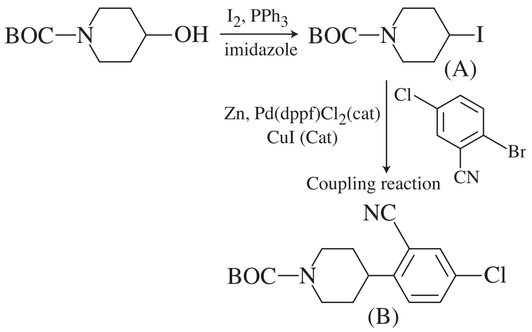
$$Ar-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

Moderate positive δ value (+ 2·01) P/e$^-$*s* flow into transition state.

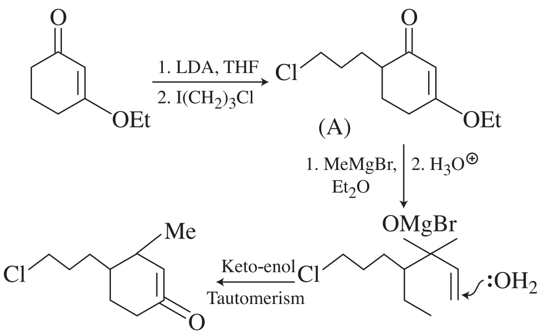
117. (B)



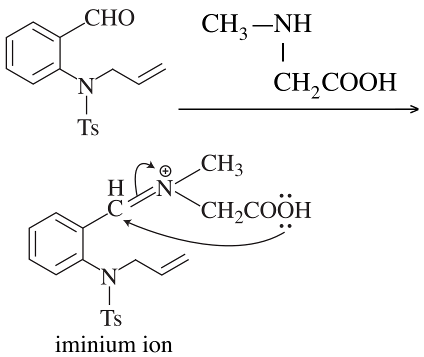

118. (A)

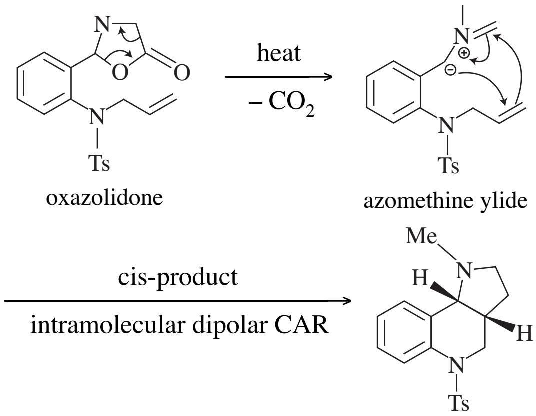



119. (C)




120. (D)




121. (A) We know that for unimolecular reaction first order rate constant

$$k_{uni} = \frac{k_1 k_2 [A]}{k_{-1}[A] + k_2}$$

When $k_{-1}[A] = k_2$,

then $k_{uni} = \frac{k_\infty}{2}$ and $[A] = [A]_{1/2}$

$$k_{uni} = \frac{k_1[A]}{2}$$

$$\Rightarrow \quad \frac{k_{00}}{2} = \frac{k_1[A]_{1/2}}{2}$$

$$\Rightarrow \quad k_1 = \frac{k_\infty}{[A]_{1/2}}$$

122. (B) Vibrational partition function is given by—

$$q_{vib} = \frac{e^{-\theta/2T}}{1 - e^{-\theta/T}},$$

where $\theta = \frac{h\nu}{k}$

(1) At low T, $\theta/T >> 1$, so $e^{-\theta/T}$ is negligible

Thus, $q_{vib} = e^{-\theta/2T}$

(2) At high T, $\theta/T << 1$

Then, $e^{-\theta/T} = 1 - \theta/T + \ldots\ldots$

Hence, $q_{vib} = \frac{e^{-\theta/2T}}{1-(1-\theta/T)}$

$$\Rightarrow \quad q_{vib} = \frac{T}{\theta} e^{-\theta/2T}$$

123. (D) First order energy correction is—

$$E_n^{(1)} = \langle \psi_n^{(0)} | \overset{n}{H} | \psi_n^{(0)*} \rangle$$

$$\psi_n^{(0)} = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$$

Thus, $$E_n^{(1)} = \frac{2}{L}\int_{-L}^{L} \sin^2\left(\frac{n\pi x}{L}\right) \delta\left(x - \frac{L}{2}\right) dx$$

for ground state $n = 1$

$$E_n^{(1)} = \frac{2}{L}\int_{-L}^{L} \sin^2\left(\frac{\pi x}{L}\right) \delta\left(x - \frac{L}{2}\right) dx$$

$$\because \int_{-\infty}^{\infty} \delta(x-a)dx = 1$$

Thus, $$\boxed{E_n^{(1)} = \frac{2}{L}}$$

124. (D) Rate constant $k_{(T)} = \frac{k_B T}{n} \frac{q_{t.s.}}{q_{NO}\, q_{Cl_2}} e^{\frac{-\Delta E_0}{RT}}$

Since $$q_{trans} = \left(\frac{2m\pi\, k_B T}{h^2}\right)^{3/2}$$

$$k_{(T)} \propto \frac{T.T^{3/2}.T.}{T^{3/2}.T.T.T^{3/2}.T.T.} \propto \frac{1}{T^{7/2}}$$

$$\boxed{k_{(T)} = T^{-7/2}}$$

125. (D) $$E_n = \left(n + \frac{1}{2}\right) h\nu$$

Probability, $$P_{(E)} = \frac{e^{-E/k_BT}}{\sum_i e^{-E/k_BT}}$$

$$= \frac{e^{-3/2}}{e^{-1/2} + e^{-3/2}} = \frac{e^{-1}}{(1 + e^{-1})}$$

$$= \frac{e^{-1}.e}{e+1} \times \frac{(e-1)}{(e-1)} = \frac{e-1}{e^2-1}$$

$$e^2 >> 1$$

$$= \frac{e-1}{e^2}$$

$$\Rightarrow \boxed{p_{(E)} = e^{-2}(e-1)}$$

126. (B) Fugacity coefficient is given by—

$$\ln r = \int_0^P \frac{(Z-1)}{P} dP$$

$$\because Z = \frac{PV}{RT}$$

At high pressure, $z >> 1$

Thus $r > 1$

Thus, repulsive term overweighs the attractive term.

127. (A) Rotational-vibrational spectrum

$$\Delta\tilde{E} = 2mB + \tilde{\nu}_e(1 - 2\tilde{x}_e)$$

In upper vibrational state

$$B_1 < B_0$$

$$B = \frac{h}{8\pi^2(\mu r^2)C} \text{cm}^{-1}$$

$r$ = bond length

Thus, the gap between the successive absorption lines of $p$-branch increases non-linearly.

128. (B) Transmission probability is inversely proportional to barrier width and height.

129. (B) Selection rule of EPR spectrum for a free radical containing nuclei with non-zero nuclear spin

$$\Delta m_s = \pm 1,$$
$$\Delta m_I = 0$$

130. (A) Relation (A) is true and it is Gibbs-Duhem equation.

We know that

$$\sum_{i=1}^{i} N i d u_i = -SdT + Vdp$$

At constant T and P, relation (B) is also true.

131. (A) $$[S_z, S_+] = [S_z, S_x] + i[S_z, S_y]$$
$$= i\hbar S_y + i(-i\hbar S_x)$$
$$= \hbar(S_x + iS_y) = \hbar S_+$$

132. (C) [Ne]

| 1 | | |
|---|---|---|

2P

| 1 | | |
|---|---|---|

3P

Term = $^3D$

$$S = \frac{n}{2} = 1,$$
$$L = 2(D)$$
$$J = (L-S) \text{ to } (L+S)$$
$$= 1, 2, 3$$

Thus, $^3D_3, {}^3D_2, {}^3D_1$

133. (C) Stepwise condensation polymerization, overall rate law is given as

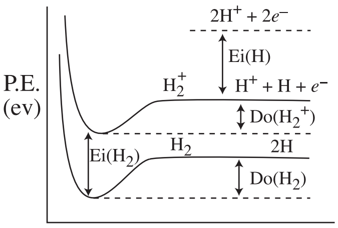
$$\frac{d[A]}{dt} = -k[A]^2$$

$$\therefore [A] = \frac{[A]_0}{1 + kt[A]_0}$$

Fraction of groups condensed at time $t$.

$$f = \frac{[A]_0 - [A]}{[A]_0} = \frac{k + [A]_0}{1 + k + [A]_0}$$

134. (B)




Thus, $\boxed{D_0(H_2) = D_0(H_2^+) - I(H) + I(H_2)}$

$r$ (internuclear distance).

135. (B) $\Delta G = 2746{\cdot}06 \text{ kJ mol}^{-1}$

We know, $\Delta G = n\text{FE}$

So, $E = \dfrac{\Delta G}{nF} = \dfrac{2746{\cdot}06 \times 10^3 \text{ J mol}^{-1}}{26 \times 96500}$

$= 1{\cdot}0944 \text{ V} \simeq 1{\cdot}09\text{V}$

136. (B) *ccp* means *fcc* structure

$r = 160 \text{ pm}$

$\because \quad a\sqrt{2} = 4r$

$a = \dfrac{4r}{\sqrt{2}}$

no. of atoms in *fcc* = 4

So, no. of atoms in 1 cm$^3$ (one atom)

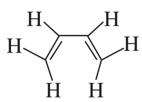
$= \dfrac{4}{a^3} = \dfrac{4(\sqrt{2})^2}{(4r)^3}$

$= \dfrac{4 \times (\sqrt{2})^3}{4 \times 4 \times 4 \times (160)^3 \times (10^{-10})^3}$

$= 3{\cdot}45 \times 10^{23}$

137. (D)

| 1 | E | $C_2$ | $\sigma_V$ | $\sigma_V{}^1$ |
|---|---|---|---|---|
| no. of unshifted atoms | 10 | 0 | 0 | 10 |
| Character per atom | 3 | – 1 | 1 | 1 |
| | 30 | 0 | 0 | 10 |



order of group, $h = 4$

$A_1 = 10, A_2 = 5, B_1 = 5, B_2 = 10$

$l_{trans} = B_1 + B_2 + A_1, \; l_{rot} = B_2 + B_1 + A_2$

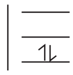
Thus, IR active model = $9A_1 + 3B_1 + 8B_2$

138. (A) $\sigma^{xy}.S_4^z = C_4^z$ (rotation axis)

139. (B) A represents Langmuir adsorption isotherm for monolayer adsorption.

B represents BET curve for multilayer adsorption C also represents multilayer adsorption for benzene on $Fe_2O_3$ at 50°C.

140. (C) Wave function for central carbon in propenyl cation



$\psi_2 = \dfrac{1}{\sqrt{2}}\phi_1 - \dfrac{1}{\sqrt{2}}\phi_3$

$\pi$-electron charge

$q_r = \sum \eta_i c_{ir}^2$

So, $q_2 = 2 \times \left(\dfrac{1}{\sqrt{2}}\right)^2 + 0 + 0$

$= 1$

141. (C)

142. (A) $\begin{vmatrix} 1S_a\,\alpha(1) & 1S_a\,\beta(1) \\ 1S_a\,\alpha(2) & 1S_a\,\beta(2) \end{vmatrix}$

$= 1S_a\,\alpha(1)\,1S_a\,\beta(2) - 1S_a\,\beta(1)\,1S_a\,\alpha(2)$

$\alpha$ and $\beta$ are spin up and down

According to Pauli's principle, 2 electrons in '*a*' atomic orbital with spin up and down.

143. (D) No. of microstates

$= \dfrac{\lfloor 4}{\lfloor 2\ \lfloor 4-2}$

$= \dfrac{4 \times 3 \times \lfloor 2}{\lfloor 2 \times 2 \times 1} = 6$

144. (C) Partition function

$f = \sum_j g_j\, e^{-\varepsilon_i/kT}$

When $T \to \infty$, $e^{-\varepsilon_i/kT} \to 1$

Thus, $f = \sum_j g_j$

145. (C) We know that

$\log k = \log k_0 + 1{\cdot}018\, |Z_A Z_B|\, \sqrt{I}$

$\dfrac{\log k_{0{\cdot}04}}{\log k_{0{\cdot}01}} = 1{\cdot}018\,(1{\cdot}x)\,[(0{\cdot}04)^{1/2} - (0{\cdot}01)^{1/2}]$

$0{\cdot}3 = 1{\cdot}018 \times x[0{\cdot}2 - 0{\cdot}1]$

$x = \dfrac{0{\cdot}30}{0{\cdot}1080} = 2{\cdot}77 \approx 3$

# Chemical Sciences

## CSIR-UGC-NET/JRF Exam.

**(June 2015)**

**Solved Paper**

# June 2015
# Chemical Sciences

**PART A**

1. Each of the following pairs of words hides a number, based on which you can arrange them in ascending order. Pick the correct answer :

   I. Cloth reel

   J. Silent wonder

   K. Good tone

   L. Bronze rod

   (A) L, K, J, I (B) I, J, K, L

   (C) K, L, J, I (D) K, J, I, L

2. Which of the following values is same as $2^{2^{2^2}}$ ?

   (A) $2^6$ (B) $2^8$

   (C) $2^{16}$ (D) $2^{222}$

3. A 12 m × 4 m rectangular roof is resting on four 4 m tall thin poles. Sunlight falls on the roof at an angle of 45° from the east, creating a shadow on the ground. What will be the area of the shadow ?

   (A) 24 $m^2$ (B) 36 $m^2$

   (C) 48 $m^2$ (D) 60 $m^2$

4. If

$$\begin{array}{r} 2\,a \\ \times\, b\,2 \\ \hline c\,6 \\ 8\,4\phantom{0} \\ \hline 8\,d\,6 \\ \hline \end{array}$$

   Here $a$, $b$, $c$ and $d$ are digits.

   Then $a + b$ =

   (A) 4 (B) 9

   (C) 11 (D) 16

5. The maximum number of points formed by intersection of all pairs of diagonals of convex octagon is—

   (A) 70 (B) 400

   (C) 120 (D) 190

6. Find the height of a box of base area 24 cm × 48 cm, in which the longest stick that can be kept is 56 cm long—

   (A) 8 cm (B) 32 cm

   (C) 37·5 cm (D) 16 cm

7. The product of the perimeter of a triangle, the radius of its in-circle, and a number gives the area of the triangle. The number is—

   (A) 1/4 (B) 1/3

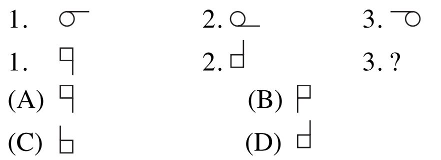
   (C) 1/2 (D) 1

8. An infinite row of boxes is arranged. Each box has half the volume of the previous box. If the largest box has a volume of 20 cc, what is the total volume of all the boxes ?

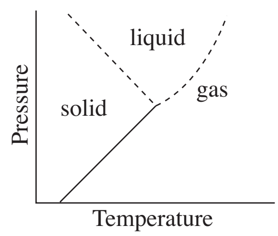
   (A) Infinite (B) 400 cc

   (C) 40 cc (D) 80 cc

9. Find the missing element based on the given pattern—




10. By reading the accompanying graph, determine the INCORRECT statement out of the following—




   (A) Melting point increases with pressure

   (B) Melting point decreases with pressure

   (C) Boiling point increases with pressure

   (D) Solid, liquid and gas can co-exist at the same pressure and temperature

11. If you change only one observation from a set of 10 observations, which of the following will definitely change ?
(A) Mean (B) Median
(C) Mode (D) Standard deviation

12. A man starts his journey at 0100 Hrs. local time to reach another country at 0900 Hrs local time on the same date. He starts a return journey on the same night at 2100 Hrs. local time to his original place, taking the same time to travel back. If the time zone of his country of visit lags by 10 hours, the duration for which the man was away from his place is—
(A) 48 hours (B) 20 hours
(C) 25 hours (D) 36 hours

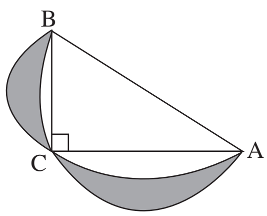
13. Let $r$ be a positive number satisfying

$$r^{(1/1234)} + r^{(-1/1234)} = 2$$

Then $r^{4321} + r^{-4321} = ?$
(A) 2 (B) $2^{(4321/1234)}$
(C) $2^{3087}$ (D) $2^{1234}$

14. A float is drifting in a river, 10 m downstream of a boat that can be rowed at a speed of 10 m/minute in still water. If the boat is rowed downstream, the time taken to catch up with the float—
(A) will be 1 minute
(B) will be more than 1 min
(C) will be less than 1 min
(D) can be determined only if the speed of the river is known

15. ABC is a right angled triangle inscribed in a semicircle. Smaller semicircles are drawn on sides BC and AC. If the area of the triangle is $a$, what is the total area of the shaded lumes ?




(A) $a$ (B) $\pi a$
(C) $a/\pi$ (D) $a/2\pi$

16. An ant can lift another ant of its size whereas an elephant cannot lift another elephant of its size, because—
(A) ant muscle fibres are stronger than elephant muscle fibres
(B) ant has proportionately thicker legs than elephant
(C) strength scales as the square of the size while weight scales as cube of the size
(D) ants work cooperatively, whereas elephants work as individuals

17. Consider a series of letters placed in the following way :

U…G…C…C…S…I…R

Each letter moves one step to its right and the extreme right letter takes the first position, completing one operation. After which of the following numbers of operations do the Cs not sit side by side ?
(A) 3 (B) 10
(C) 19 (D) 25

18. An inclined plane rests against a horizontal cylinder of radius R. If the plane makes an angle of 30° with the ground, the point of contact of the plane with the cylinder is at a height of—
(A) 1·500 R (B) 1·866 R
(C) 1·414 R (D) 1·000 R

19. What is the maximum number of parallel, non-overlapping cricket pitches (length 24 m, width 3 m) that can be laid in a field of diameter 140 m, if the boundary is required to be at least 60 m from the centre of any pitch ?
(A) 6 (B) 7
(C) 12 (D) 4

20. In a fast moving car with open windows, the driver feels a continuous incoming breeze. The pressure inside the car, however, does not keep increasing because—
(A) air coming in from the front window goes out from the rear
(B) air comes in as well as goes out through every window but the driver only feels the incoming one
(C) no air actually comes in and the feeling of breeze is an illusion
(D) cool air reduces the temperature therefore the pressure does not increase

## PART B

21. The biological functions of carbonic anhydrase and carboxypeptidase A, respectively, are—
(A) interconversion of $CO_2$ and carbonates and hydrolysis of peptide bond
(B) gene regulation and interconversion of $CO_2$ and carbonates
(C) gene regulation and hydrolysis of peptide bond
(D) interconversion of $CO_2$ and carbonates and gene regulation

22. $Fe–N_{porphyrin}$ bond distances in the deoxy- and oxy-haemoglobin, respectively are—
(A) ~ 2·1 and 2·0 Å (B) ~2·0 and 2·0 Å
(C) ~2·2 and 2·3 Å (D) ~2·3 and 2·5 Å

23. The binding modes of NO in 18 electron compounds $[Co(CO)_3(NO)]$ and $[Ni(\eta^5 – Cp)(NO)]$, respectively are—
(A) linear and bent
(B) bent and linear
(C) linear and linear
(D) bent and bent

24. The role of copper salt as co-catalyst in Wacker process is—
(A) oxidation of Pd(0) by Cu(II)
(B) oxidation of Pd(0) by Cu(I)
(C) oxidation of Pd(II) by Cu(I)
(D) oxidation of Pd(II) by Cu(II)

25. For typical Fischer and Schrock carbenes, consider the following statements—
1. Oxidation state of metal is low in Fischer carbene and high in Schrock carbene.
2. Auxiliary ligands are π-acceptor in Fischer carbene and non-π-acceptor in Schrock carbene.
3. Substituents on carbene carbon are non-π-donor in Fischer carbene and π-donor in Schrock carbene.
4. Carbene carbon is electrophilic in Fischer carbene and nucleophilic in Schrock carbene.

The correct statements are—
(A) 1, 2 and 3 (B) 1, 2 and 4
(C) 2, 3 and 4 (D) 1, 3 and 4

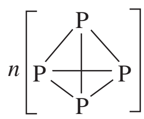
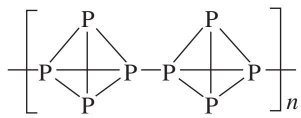
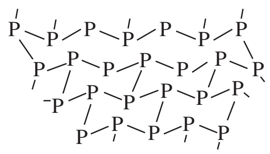
26. The species having he strongest gas phase proton affinity among the following—
(A) $N^{3-}$ (B) $NF_3$
(C) $NH_3$ (D) $N(CH_3)_3$

27. Consider the following statements regarding the diffusion current at dropping mercury electrode.
1. It does not depend on mercury flow rate.
2. It depends on drop time.
3. It depends on temperature.

Correct statement(s) is/are—
(A) 1 only (B) 2 only
(C) 1 and 2 (D) 2 and 3

28. Q value for the reaction $^{13}N(n, p)^{13}C$ is 3·236 MeV. The threshold energy (in MeV) for the reaction $^{13}C(p, n)^{13}N$ is—
(A) – 3·236 (B) – 3·485
(C) 3·485 (D) 3·845

29. The $^{119}Sn$ NMR chemical shift (approximately in ppm) corresponding to $(\eta^5\text{-}Cp)_2Sn$ (relative to $Me_4Sn$) is—
(A) – 4 (B) + 137
(C) + 346 (D) – 2200

30. All forms of phosphorus upon melting, exist as—
(A)

(B)

(C) $n$ (P ≡ P)
(D)


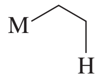
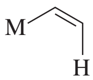
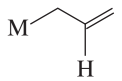
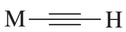
31. For the oxidation state(s) of sulphur atoms in $S_2O$, consider the following—
1. – 2 and + 4
2. 0 and + 2
3. + 4 and 0

The correct answer(s) is/are—
(A) 1 and 2 (B) 1 and 3
(C) 2 and 3 (D) 3 only

32. The correct set of pseudohalide anions is—
    (A) $CN^-$, $ClO_4^-$, $BF_4^-$, $PF_6^-$
    (B) $N_3^-$, $NO_3^-$, $HSO_4^-$, $AsF_6^-$
    (C) $SCN^-$, $PO_4^{3-}$, $H_2PO_4^-$, $N_3^-$
    (D) $CN^-$, $N_3^-$, $SCN^-$, $NCN^{2-}$

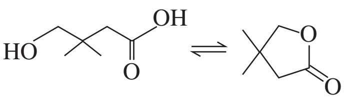
33. In transition metal phoshine (M—$PR_3$) complexes, the back-bonding involves donation of electrons from—
    (A) $M(t_{2g}) \rightarrow PR_3(\sigma^*)$
    (B) $M(t_{2g}) \rightarrow PR_3(\pi^*)$
    (C) $M(e_g) \rightarrow P(d)$
    (D) $PR_3(\pi) \rightarrow M(t_{2g})$

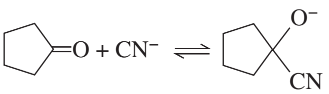
34. The refluxing of $RhCl_3.3H_2O$ with an excess of $PPh_3$ in ethanol gives a complex **A**.
    Complex **A** and the valence electron count on rhodium are, respectively—
    (A) $[RhCl(PPh_3)_3]$, 16
    (B) $[RhCl(PPh_3)_5]$, 16
    (C) $[RhCl(PPh_3)_3]$, 18
    (D) $[RhCl(PPh_3)_5]$, 18

35. The β-hydrogen elimination will be facile in—
    (A) 
    (B) 
    (C) 
    (D) 

36. The reaction $[Co(CN)_5H_2O]^{2-} + X^- \rightarrow [Co(CN)_5X]^{2-} + H_2O$ follows a/an—
    (A) Interchange dissociative ($I_d$) mechanism
    (B) Dissociative (D) mechanism
    (C) Associative (A) mechanism
    (D) Interchange Associative ($I_a$) mechanism

37. Correct statement on the effect of addition of aq. HCl on the equilibrium is—


… Eq. A

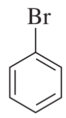
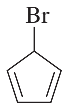
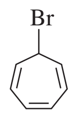
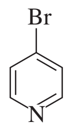

… Eq. B

    (A) Equilibrium will shift towards right in case of both A and B
    (B) Equilibrium will shift towards left in case of both A and B
    (C) Equilibrium will shift towards right in A and left in case of B
    (D) Equilibrium will shift towards right in B and left in case of A

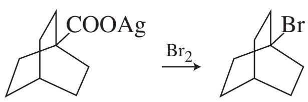
38. The compound that exhibits sharp bands at 3300 and 2150 $cm^{-1}$ in the IR spectrum is—
    (A) 1-butyne (B) 2-butyne
    (C) butyronitrile (D) butylamine

39. The $^1H$ NMR spectrum of a dilute solution of a mixture of acetone and dichloromethane in $CDCl_3$ exhibits two singlets of 1 : 1 intensity. Molar ratio of acetone to dichloromethane in the solution is—
    (A) 3 : 1 (B) 1 : 3
    (C) 1 : 1 (D) 1 : 2

40. Intense band generally observed for a carbonyl group in the IR specturm is due to—
    (A) The force constant of CO bond is large
    (B) The force constant of CO bond is small
    (C) There is no change in dipole moment for CO bond stretching
    (D) The dipole moment change due to CO bond stretching is large

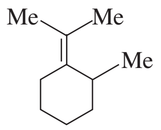
41. The compound that gives precipitate on warming with aqueous $AgNO_3$ is—
    (A) 
    (B) 
    (C) 
    (D) 

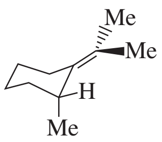
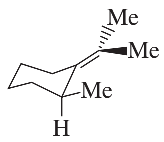
42. Following reaction goes through—

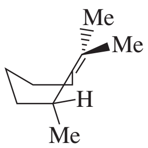
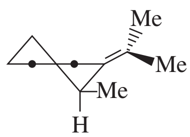



    (A) Free radical intermediate
    (B) carbanion intermediate
    (C) carbocation intermediate
    (D) carbene intermediate

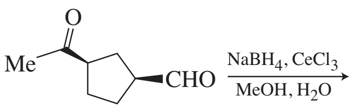
43. The most stable conformation for the following compound is—

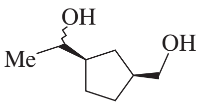


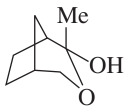
(A)  (B) 

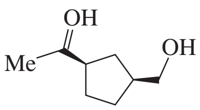
(C)  (D) 

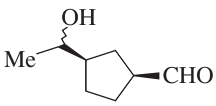
44. The major product formed in the following reaction is—



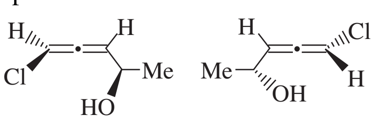
(A) 

(B) 

(C) 

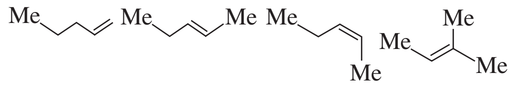
(D) 

45. The correct relation between the following compounds is—



(A) enantiomers
(B) diastereomers
(C) homomers (identical)
(D) constitutional isomers

46. The correct order of heat of hydrogenation for the following compounds is—



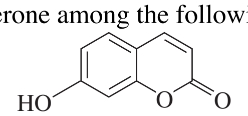
I II III IV

(A) I > II > III > IV (B) I > III > II > IV
(C) IV > I > III > II (D) IV > II > I > III

47. Among the following, the correct statement (s) about ribose is (are)—
1. On reduction with $NaBH_4$ it gives optically inactive product.
2. On reaction with methanolic HCl it gives a furanoside.
3. On reaction with $Br_2$–$CaCO_3$–water it gives optically inactive product.
4. It gives positive Tollen's test.

(A) 1, 2 and 4 (B) 1, 2 and 3
(C) 2 and 3 (D) 4 only

48. Biogenetic precursors for the natural product umbelliferone among the following are—



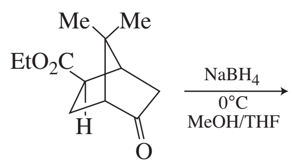
umbelliferone

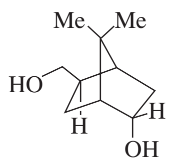
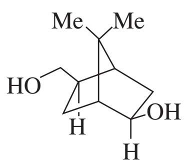
1. L-tryptophan 2. cinnamic acid
3. L-methionine 4. L-phenylalanine

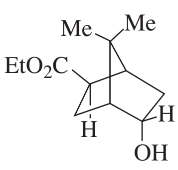
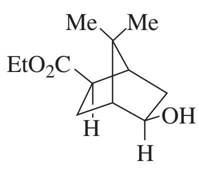
(A) 1 and 2 (B) 2 and 4
(C) 2 and 3 (D) 3 and 4

49. Number of signals in the $^{13}C\{H\}$ NMR spectrum of (R)–4-methylpentan-2-ol are—
(A) 3 (B) 4
(C) 5 (D) 6

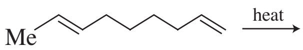
50. The major product formed in the following reaction is—

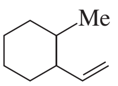
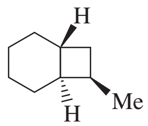


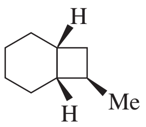
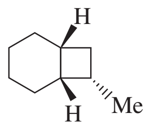
(A)  (B) 

(C)  (D) 

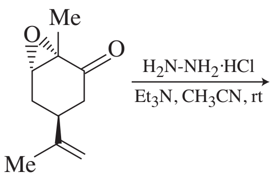
51. The major product formed in the following reaction is—

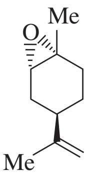
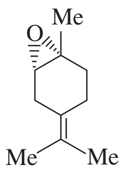


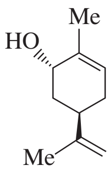
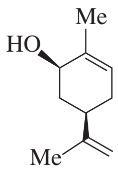
(A)  (B) 

(C)  (D) 

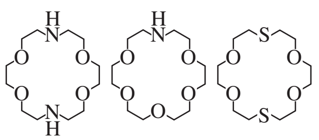
52. The major product formed in the following reaction is—




(A)  (B) 

(C)  (D) 

53. The magnitude of the stability constants for $K^+$ ion complexes of the following supramolecular hosts follows the order—



A B C

(A) B > A > C (B) C > A > B
(C) A > B > C (D) C > B > A

54. Antitubercular drug(s) among the following is (are)—

1. Salbutamol 2. Ethambutanol
3. Isoniazid 4. Diazepam

(A) 1 and 2 (B) 2 and 3
(C) 3 and 4 (D) 4 alone

55. A particle is in a one-dimensional box with a potential $V_0$ inside the box and infinite outside. An energy state corresponding to $n = 0$ ($n$ : quantum number) is not allowed because—

(A) the total energy becomes zero
(B) the average momentum becomes zero
(C) the wave function becomes zero every where
(D) the potential $V_0 \neq 0$

56. An eigenstate of energy satisfies $H\Psi_n = E_n \Psi_n$. In the presence of an extra constant potential $V_0$—

(A) both $E_n$ and $\Psi_n$ will change
(B) both $E_n$ and the average kinetic energy will change
(C) only $E_n$ will change, but not $\Psi_n$
(D) only $\Psi_n$ will change, but not $E_n$

57. The intensity of a light beam decreases by 50% when it passes through a sample of 1·0 cm path length. The percentage of transmission of the light passing through the same sample, but of 3·0 cm path length, would be—

(A) 50·0 (B) 25·0
(C) 16·67 (D) 12·5

58. The electric-dipole allowed transition among the following is—

(A) $^3S \rightarrow {}^3D$ (B) $^3S \rightarrow {}^3P$
(C) $^3S \rightarrow {}^1D$ (D) $^3S \rightarrow {}^1F$

59. The product $C_2^x \sigma_{xy}$ ($C_2^x$ is the two-fold rotation axis around the $x$-axis and $\sigma_{xy}$ is the $xy$ mirror plane) is—

(A) $\sigma_{xz}$ (B) $\sigma_{yz}$
(C) $C_2^y$ (D) $C_2^z$

60. The simplest ground-state VB wave function of a diatomic molecule like HCl is written as $\Psi = \Psi_H (1s, 1)\, \Psi_{Cl} (3p_z, 2) + B$ where B stands for—

(A) $\Psi_H (3p_z, 2)\, \Psi_{Cl} (1s, 1)$
(B) $\Psi_H (1s, 2)\, \Psi_{Cl} (3p_z, 1)$
(C) $\Psi_{Cl} (1s, 2)\, \Psi_{Cl} (3p_z, 1)$
(D) $\Psi_{Cl} (1s, 2)\, \Psi_H (3p_z, 1)$

61. Heat capacity of a species is independent of temperature if it is—

(A) tetratomic (B) triatomic
(C) diatomic (D) monatomic

62. In a chemical reaction : $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$, xenon gas is added at constant volume. The equilibrium—
(A) will shift towards the reactant
(B) will shift towards the products
(C) will not change the amount of reactant and products
(D) will increase both reactant and products

63. The temperature-dependence of a reaction is give by
$k = AT^2 \exp(-E_0/RT)$.
The activation energy ($E_a$) of the reaction is give by—
(A) $E_0 + \frac{1}{2}RT$ (B) $E_0$
(C) $E_0 + 2RT$ (D) $2E_0 + RT$

64. For a reaction, $2A + B \rightarrow 3Z$, if the rate of consumption of A is $2 \times 10^{-4}$ mol dm$^{-3}$ $s^{-1}$, the rate of formation of Z (in mol dm$^{-3}$ $s^{-1}$) will be—
(A) $3 \times 10^{-4}$ (B) $2 \times 10^{-4}$
(C) $\frac{4}{3} \times 10^{-4}$ (D) $4 \times 10^{-4}$

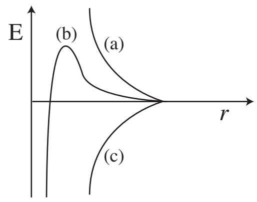
65. Dominant contribution to the escaping tendency of a charged particle with uniform concentration in a phase, depends on—
(A) chemical potential of that phase
(B) electric potential of the phase
(C) thermal energy of that phase
(D) gravitational potential of that phase

66. The intrinsic viscosity depends on the molar mass as $[\eta] = KM^a$.
The empirical constants K and $a$ are dependent on—
(A) solvent only
(B) polymer only
(C) polymer-solvent pair
(D) polymer-polymer interaction

67. The correct ΔG for the cell reaction involving steps
$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ is—
(A) $\Delta G° - RT \ln \frac{a_{Zn^{2+}}}{a_{Cu^{2+}}}$
(B) $\Delta G° + RT \ln \frac{a_{Zn^{2+}}}{a_{Cu(s)}}$
(C) $\Delta G° - RT \ln \frac{a_{Zn(s)}}{a_{Cu^{2+}}}$
(D) $\Delta G° + RT \ln \frac{a_{Zn^{2+}}}{a_{Cu^{2+}}}$

68. The lowest energy-state of an atom with electronic configuration $ns^1\ np^1$ has the term symbol—
(A) $^3p_1$ (B) $^1p_1$
(C) $^3p_2$ (D) $^3p_0$

69. Energy of interaction of colloidal particles as a function of distance of separation can be identified as (1) van der Waals, (2) double layer, (3) van der Waals and double layer. The correct order of interactions in the figure corresponding to curves (a), (b) and (c) respectively, is—




(A) 1, 2, 3 (B) 2, 3, 1
(C) 3, 1, 2 (D) 1, 3, 2

70. The packing factor (PF) and number of atomic sites per unit cell (N) of an FCC crystal system are—
(A) PF = 0·52 and N = 3
(B) PF = 0·74 and N = 3
(C) PF = 0·52 and N = 4
(D) PF = 0·74 and N = 4

## PART C

71. Differential pulse polarography (DPP) is more sensitive than D.C. Polarography (DCP). Consider following reasons for it—
1. Non-faradic current is less in DPP in comparison to DCP.
2. Non-faradic current is more in DPP in comparison to DCP.
3. Polarogram of DPP is of different shape than that of DCP.

Correct reasons(s) is/are—
(A) 1 and 3 (B) 2 and 3
(C) 2 only (D) 1 only

72. Considering the following parameters with reference to the fluorescence of a solution :
    1. Molar absorptivity of fluorescent molecule.
    2. Intensity of light source used for excitation.
    3. Dissolved oxygen

    The correct answer for the enhancement of fluorescence with the increase in these parameters is/are—
    (A) 1 and 2 (B) 2 and 3
    (C) 1 and 3 (D) 3 only

73. The geometric cross section of $^{125}Sn$ (in barn) is nearly—
    (A) 1·33 (B) 1·53
    (C) 1·73 (D) 1·93

74. Match column A (coupling reactions) with column B (reagents)—

| | Column A | | Column B |
|---|---|---|---|
| a. | Suzuki coupling | i. | $CH_2=CHCO_2CH_3$ |
| b. | Heck coupling | ii. | $RB(OH)_2$ |
| c. | Sonogashira coupling | iii. | $PhCO(CH_2)_3ZnI$ |
| d. | Negeshi coupling | iv. | $HC{\equiv}CR$ |
| | | v. | $SnR_4$ |

The correct match is—

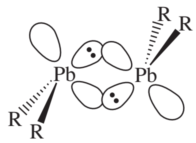
| | (a) | (b) | (c) | (d) |
|---|---|---|---|---|
| (A) | ii | i | iv | iii |
| (B) | i | v | iii | iv |
| (C) | iv | iii | ii | i |
| (D) | ii | iii | iv | v |

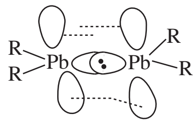
75. The oxoacid of phosphorus having P atoms in + 4, + 3 and + 4 oxidation states respectively, is—
    (A) $H_5P_3O_{10}$ (B) $H_5P_3O_7$
    (C) $H_5P_3O_8$ (D) $H_5P_3O_9$

76. The geometries of $[Br_3]^+$ and $[I_5]^+$ respectively, are—
    (A) trigonal and tetrahedral
    (B) tetrahedral and trigonal bipyramidal
    (C) tetrahedral and tetrahedral
    (D) linear and trigonal pyramidal

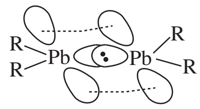
77. According to Wade's theory the anion $[B_{12}H_{12}]^{2-}$ adopts—
    (A) *closo* - structure (B) *arachno* - structure
    (C) *hypo* - structure (D) *nido* - structure

78. Considering the intert pair effect on lead, the most probable structure of $PbR_2$ [R = 2, 6–$C_6H_3$ (2, 6—$Pr_2C_6H_3)_2$] is—

(A) 

(B) 


(C) 

(D) 


79. The reaction of $SbCl_3$ with 3 equivalents of EtMgBr yields compound **X**. Two equivalents of $SbI_3$ react with one equivalent of **X** to give Y. In the solid state, **Y** has a 1D-polymeric structure in which each Sb is in a square pyramidal environment. Compounds **X** and **Y** respectively, are—
    (A) $SbEt_3$ and $[Sb(Et)I_2]_n$
    (B) $Sb(Et_2)Cl$ and $[Sb(Et_2)Cl]_n$
    (C) $SbEt_3$ and $[SbEt_2Br_2]_n$
    (D) $Sb(Et)Br_2$ and $[SbEt(I)(Br)]_n$

80. Match the complexes given in column I with the electronic transitions (mainly responsible for their colours) listed in column II

| | I | | II |
|---|---|---|---|
| a. | Fe(II)-protoporphyrin IX | 1. | $\pi \to \pi^*$ |
| b. | $[Mn(H_2O)_6]Cl_2$ | 2. | spin allowed $d \to d$ |
| c. | $[Co(H_2O)_6]Cl_2$ | 3. | spin forbidden $d \to d$ |
| | | 4. | M → L charge transfer |

The correct answer is—

| | (a) | (b) | (c) |
|---|---|---|---|
| (A) | 1 | 3 | 2 |
| (B) | 4 | 2 | 3 |
| (C) | 1 | 3 | 4 |
| (D) | 1 | 2 | 3 |

81. The following statements are given regarding the agostic interaction C—H···Ir observed in $[Ir(Ph_3P)_3Cl]$.
    1. Upfield shift of C—H proton in $^1H$ NMR spectrum.
    2. Increased acid character of C—H.
    3. $\nu_{C-H}$ in IR spectrum shifts to higher wavenumber.

    The correct answer is/are—
    (A) 1 and 3 (B) 2 and 3
    (C) 1 and 2 (D) 3 only

82. Amongst the following :
1. $[Mn(\eta^5 - Cp)(CO)_3]$,
2. $[Os(\eta^5\text{–}Cp)_2]$,
3. $[Ru(\eta^5\text{–}Cp)_2]$ and
4. $[Fe(\eta^5\text{–}Cp)_2]$,

the compounds with most shielded and deshielded Cp protons respectively, are—

(A) 4 and 1 (B) 4 and 2
(C) 3 and 1 (D) 3 and 2

83. Total number of vertices in metal clusters $[Ru_6(C)(CO)_{17}]$, $[Os_5(C)(CO)_{15}]$ and $[Ru_5(C)(CO)_{16}]$ are 6, 5 and 5 respectively. The predicted structures of these complexes, respectively, are—

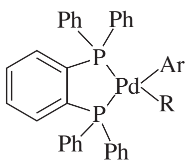
(A) *closo, nido* and *nido*
(B) *closo, nido* and *arachno*
(C) *arachno, closo* and *nido*
(D) *arachno*, *nido* and *closo*

84. Among the complexes,
1. $K_4[Cr(CN)_6]$
2. $K_4[Fe(CN)_6]$
3. $K_3[Co(CN)_6]$
4. $K_4[Mn(CN)_6]$

Jahn-Teller distortion is expected in—

(A) 1, 2 and 3 (B) 2, 3 and 4
(C) 1 and 4 (D) 2 and 3

85. The reductive elimination of Ar—R (coupled product) from A is facile when—

A 

(A) $R = CH_3$ (B) $R = CH_2Ph$
(C) $R = CH_2COPh$ (D) $R = CH_2CF_3$

86. The total number of metal ions and the number of coordinated imidazole units of histidine in the active site of oxy-hemocyanin, respectively, are—

(A) $2Cu^{2+}$ and 6 (B) $2Fe^{2+}$ and 5
(C) $2C^{u+}$ and 6 (D) $Fe^{2+}$ and 3

87. Match the action of $H_2O_2$ in aqueous medium given in column A with the oxidation/ reduction listed in column B :

| A : action of $H_2O_2$ | B : type of reaction |
|---|---|
| a. Oxidation in acid | 1. $[Fe(CN)_6]^{3-} \rightarrow [Fe(CN)_6]^{4-}$ |
| b. Oxidation in base | 2. $[Fe(CN)_6]^{4-} \rightarrow [Fe(CN)_6]^{3-}$ |
| c. Reduction in acid | 3. $MnO_4^- \rightarrow Mn^{2+}$ |
| d. Reduction in base | 4. $Mn^{2+} \rightarrow Mn^{4+}$ |

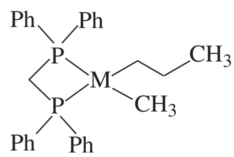
The correct answer is—

| | (a) | (b) | (c) | (d) |
|---|---|---|---|---|
| (A) | 1 | 2 | 3 | 4 |
| (B) | 2 | 4 | 3 | 1 |
| (C) | 3 | 4 | 2 | 1 |
| (D) | 4 | 1 | 3 | 2 |

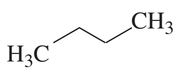
88. The reduced form of a metal ion M in a complex is NMR active. On oxidation, the complex gives an EPR signal with $g_{\parallel} \approx 2{\cdot}2$ and $g_{\perp} \approx 2{\cdot}0$. Mössbauer spectroscopy cannot characterise the metal complex. The M is—

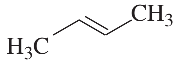
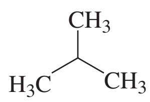
(A) Zn (B) Sn
(C) Cu (D) Fe

89. The least probable product from A on reductive elimination is—



A

(A)  (B) $CH_4$

(C)  (D) 

90. Water plays different roles in the following reactions—
1. $2H_2O + Ca \rightarrow Ca^{2+} + 2OH^- + H_2$
2. $nH_2O + Cl \rightarrow [Cl(H_2O)_n]^-$
3. $6H_2O + Mg^{2+} \rightarrow [Mg(H_2O)_6]^{2+}$
4. $2H_2O + 2F_2 \rightarrow 4HF + O_2$

The correct role of water in each reaction is—

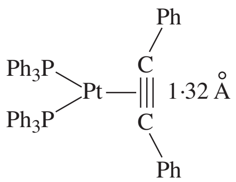
(A) (1) oxidant, (2) acid, (3) base and (4) reductant

(B) (1) oxidant, (2) base, (3) acid and (4) reductant

(C) (1) acid, (2) oxidant, (3) reductant and (4) base

(D) (1) base, (2) reductant, (3) oxidant and (4) base

91. With respect to σ and π bonding in Pt—||| in the structure given below, which of the following represent the correct bonding ?




(A) M(σ) → L(σ) and M(π) → L(π*)

(B) L(σ) → M(π) and L(π) → M(π)

(C) L(π) → M(π) and L(σ) → M(π)

(D) L(π) → M(σ) and M(π) → L(π*)

92. The complex $[Fe(phen)_2(NCS)_2]$ (phen = 1, 10-phenanthroline) shows spin cross-over behaviour. CFSE and $\mu_{eff}$ at 250 and 150 K respectively, are—

(A) 0·4 Δ., 4·90 BM and 2·4 Δ., 0·00 BM

(B) 2·4 Δ., 2·90 BM and 0·4 Δ., 1·77 BM

(C) 2·4 Δ., 0·00 BM and 0·4 Δ., 4·90 BM

(D) 1·2 Δ., 4·90 BM and 2·4 Δ., 0·00 BM

93. Consider the following statements with respect to uranium

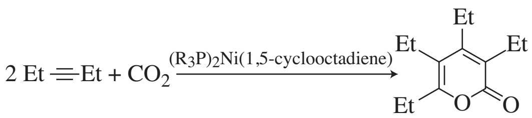
1. $UO_2^{2+}$ disproportionates more easily than $UO_2^{2+}$
2. $U_3O_8$ is its most stable oxide of U
3. Coordination number of U in $[UO_2(NO_3)_2(H_2O)_2].4H_2O$ is six
4. $UO_2^{2+}$ is linear

The correct set of statements is—

(A) 1, 2 and 4 (B) 1, 3 and 4

(C) 2, 3 and 4 (D) 1, 2 and 3

94.




For the above conversion, which of the following statements are correct ?

1. $CO_2$ combines with $Ni(PR_3)_2$ (1, 5-cyclo-octadiene)
2. Insertion of $CO_2$ occurs
3. Insertion of Et—≡—Et takes place

The correct answer is—

(A) 1 and 2 (B) 2 and 3

(C) 3 and 1 (D) 1, 2 and 3

95. Consider the following statements for $(NH_4)_2[Ce(NO_3)_6]$ (**Z**)

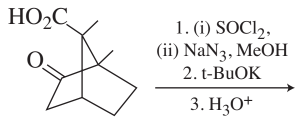
1. Coordination number of Ce is 12
2. **Z** is paramagnetic
3. **Z** is an oxidising agent
4. Reaction of $Ph_3PO$ with **Z** gives a complex having coordination number 10 for Ce.

The correct statements are—

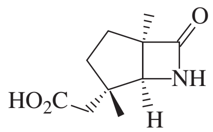
(A) 1, 2 and 3 (B) 2, 1 and 4

(C) 2, 3 and 4 (D) 1, 3 and 4

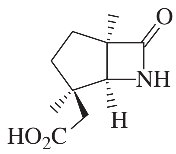
96. The major product formed in the following reaction sequence is—



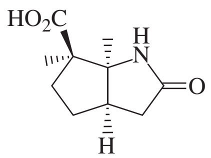

(A)



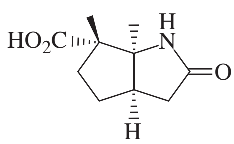

(B)



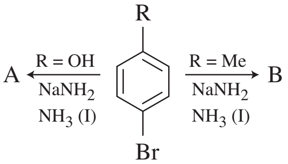

(C)

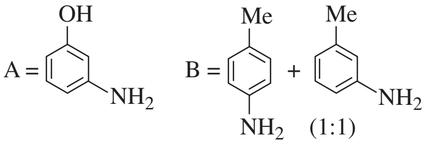


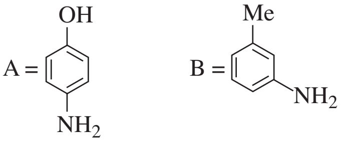

(D)

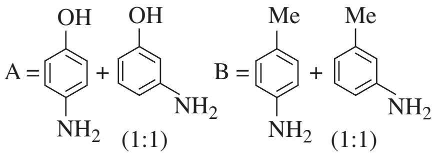


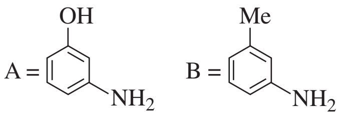
97. The major products **A** and **B** in the following reaction sequence are—



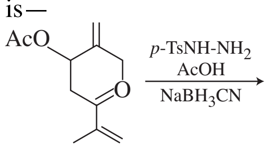
(A) 

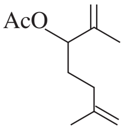
(B) 

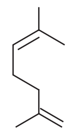
(C) 

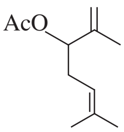
(D) 

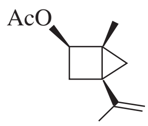
98. The major product formed in the following reaction is—



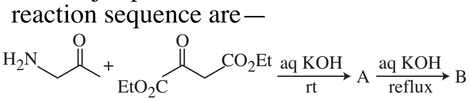
(A) 

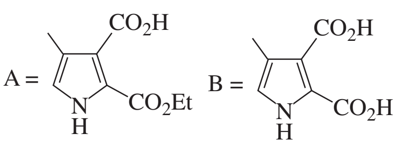
(B) 

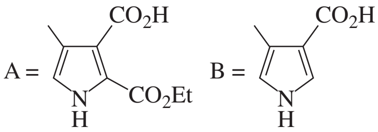
(C) 

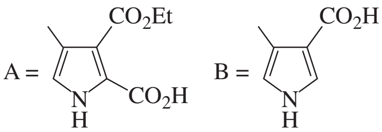
(D) 

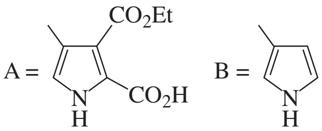
99. The major products **A** and **B** in the following reaction sequence are—



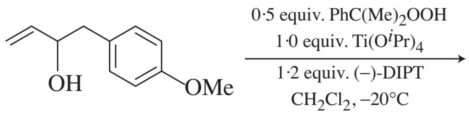
(A) 

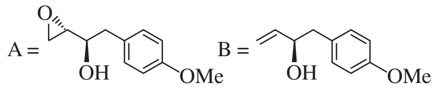
(B) 

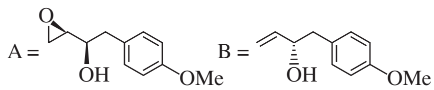
(C) 

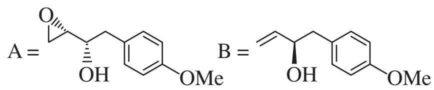
(D) 

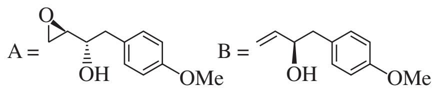
100. The major products formed in the following reaction are—



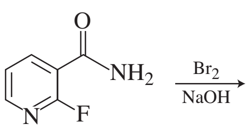
(A) 

(B) 

(C) 

(D) 

101. The correct statement about the following reaction is—



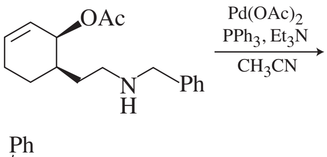
(A) The product is 2-fluoropyridin-3-amine and reaction involves nitrene intermediate

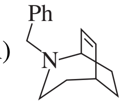
(B) The product is 2-fluoropyridin-3-amine and reaction involves radical intermediate

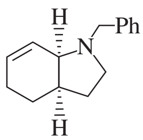
(C) The product is 2-hydroxynicotinamide and reaction involves benzyne-like intermediate

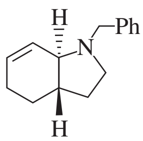
(D) The product is 2-hydroxynicotinamide and reaction involves addition-elimination mechanism

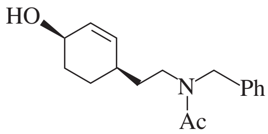
102. The major product formed in the following reaction is—



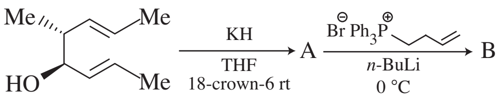
(A) 

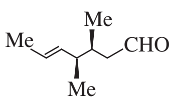
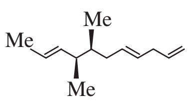
(B) 

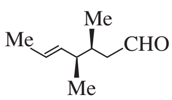
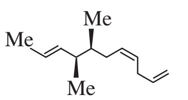
(C) 

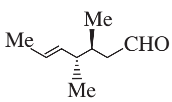
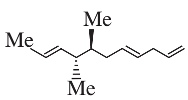
(D) 

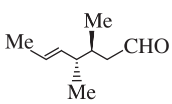
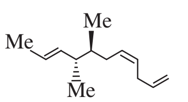
103. The major products A and B formed in the following reactions are—



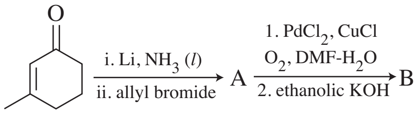
(A) A =  B = 

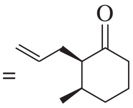
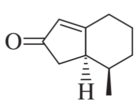
(B) A =  B = 

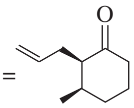
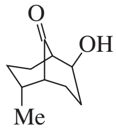
(C) A =  B = 

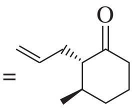
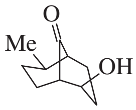
(D) A =  B = 

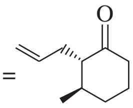
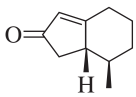
104. The major products A and B formed in the following reactions are—



(A) A =  B = 

(B) A =  B = 

(C) A =  B = 

(D) A =  B = 

105. An organic compound shows following spectral data :

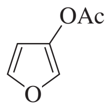
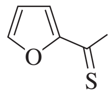
IR ($cm^{-1}$) : 1680

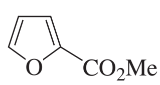
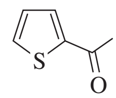
$^1H$ NMR ($CDCl_3$) : δ 7·66 (m, 1H), 7·60 (m, 1H), 7·10 (m, 1H), 2·25 (s, 3H)

$^{13}C$ NMR ($CDCl_3$) : δ 190, 144, 134, 132, 128, 28

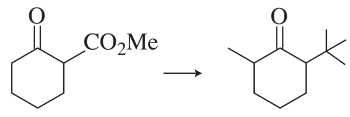
m/z (EI) : 126 ($M^+$, 100%), 128 ($M^+ + 2$, 4·9%)

The structure of the compound is—

(A)  (B) 

(C)  (D) 

106. The correct set of reagents to effect the following transformation is—



(A) (i) (a) NaOMe, MeI; (b) NaCl, wet DMSO, 160°C;

(ii) (a) LDA, – 78°C, TMSCl; (b) *t*-BuCl, $TiCl_4$, 50°C

(B) (i) (a) NaOMe, MeI; (b) aq. NaOH then HCl, heat

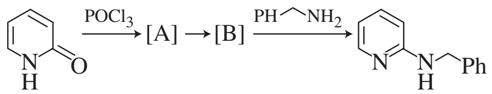
(ii) (a) $Et_3N$, TMSCl, rt; (b) *t*-BuCl, $TiCl_4$, 50°C

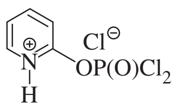
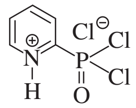
(C) (i) LDA, *t*-BuCl; (ii) LDA, MeI; (iii) aq. NaOH then HCl, heat

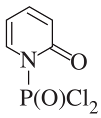
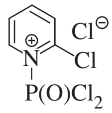
(D) (i) (a) NaCl, wet DMSO, 160°C; (b) NaH, *t*-BuCl

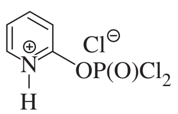
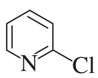
(ii) (a) morpholine, $H^+$; (b) MeI then $H_3O^+$

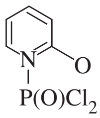
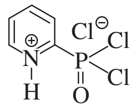
107. The correct structures of the intermediates [A] and [B] in the following reaction are—



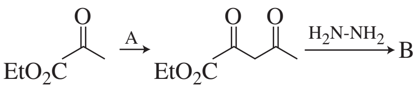

(A) A =  B = 

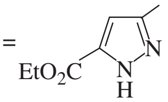
(B) A =  B = 

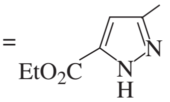
(C) A =  B = 

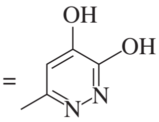
(D) A =  B = 

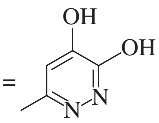
108. The correct reagent combination A and the major product B in the following reaction sequence are—



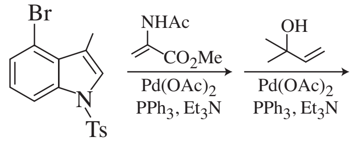

(A) A : LiHMDS, AcCl B = 

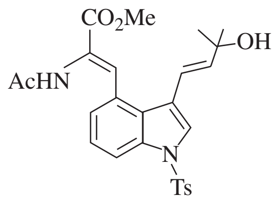
(B) A : *n*-BuLi, AcCl B = 

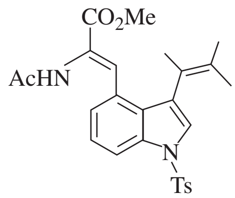
(C) A : LiHMDS, AcOEt B = 

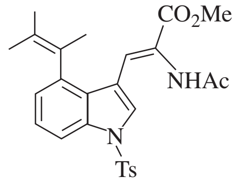
(D) A : *n*-BuLi, AcOEt B = 

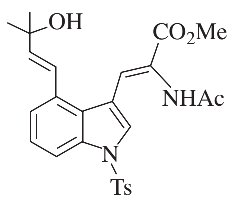
109. The major product of the following reaction sequence is—



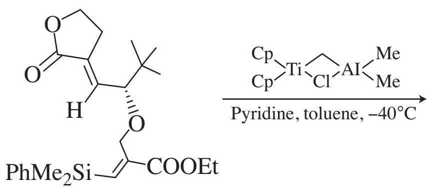

(A) 

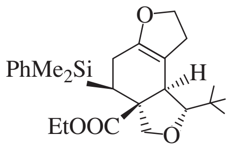
(B) 

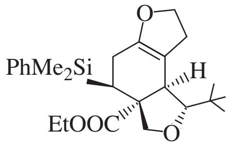
(C) 

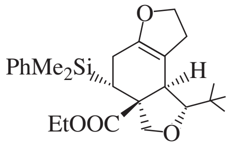
(D) 

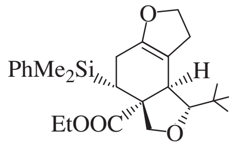
110. The major product formed in the following reaction is—



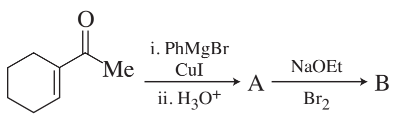
(A) 

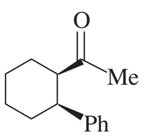
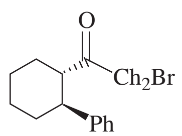
(B) 

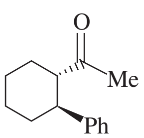
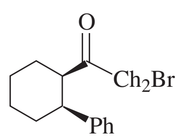
(C) 

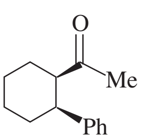
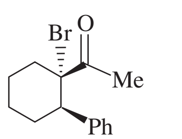
(D) 

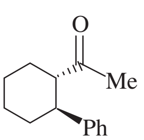
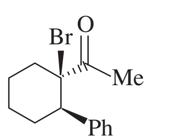
111. The major products **A** and **B** in the following synthetic sequence are—



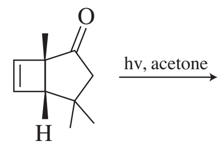
(A) A =  B = 

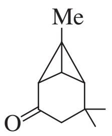
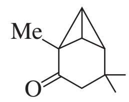
(B) A =  B = 

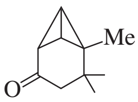
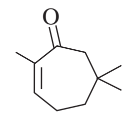
(C) A =  B = 

(D) A =  B = 

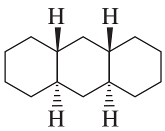
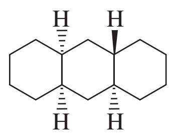
112. The major product formed in the following reaction is—

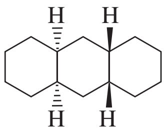
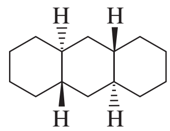


(A)  (B) 

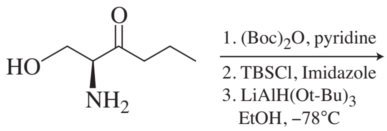
(C)  (D) 

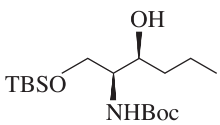
113. The hydrocarbon among the following having conformationally locked chair-boat-chair form is—

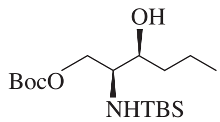
(A)  (B) 

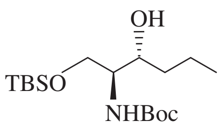
(C)  (D) 

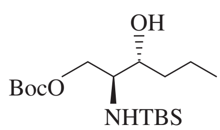
114. The major product formed in the following reaction sequence is—



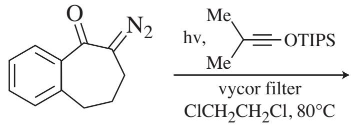
(A) 

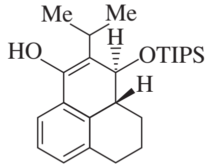
(B) 

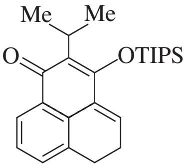
(C) 

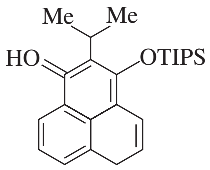
(D) 

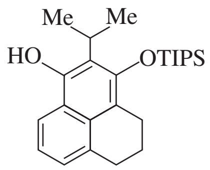
115. The major product in the following reaction sequence is—



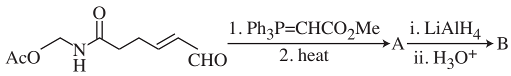

(A) 

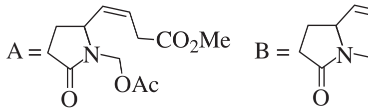
(B) 

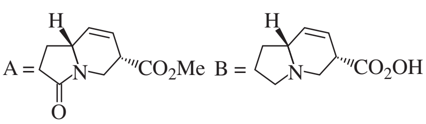
(C) 

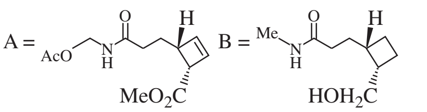
(D) 

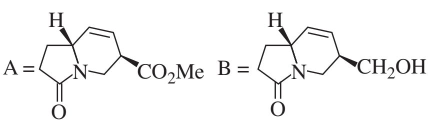
116. Structures of **A** and **B** in the following synthetic sequence are—



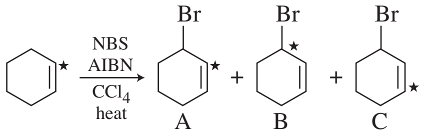

(A) 

(B) 

(C) 

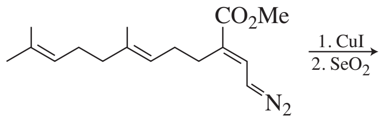
(D) 

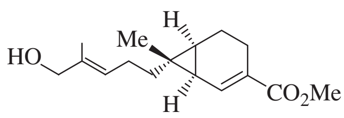
117. IN the following reaction, the ratio of **A:B:C** is (* indicates labelled carbon)

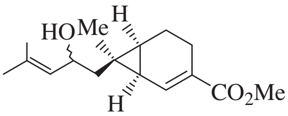


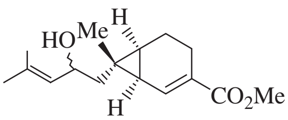

(A) 1 : 1 : 1 (B) 1 : 2 : 1
(C) 2 : 1 : 1 (D) 3 : 2 : 1

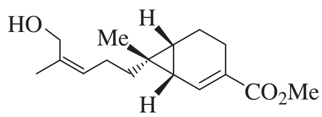
118. Structure of the major product in the following synthetic sequence is—



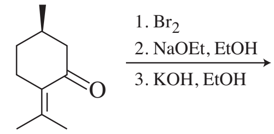

(A) 

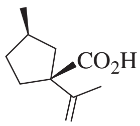
(B) 

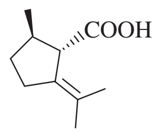
(C) 

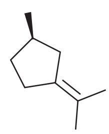
(D) 

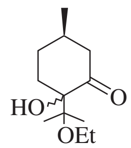
119. Major product formed in the following synthetic sequence on the monoterpene pulegone is—



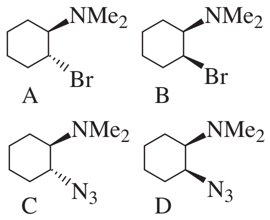

(A) 

(B) 

(C) 

(D) 

120. Optically pure isomers **A** and **B** were heated with $NaN_3$ in DMF. The correct statement from the following is—




(A) **A** gives optically pure **D** and **B** gives optically pure **C**

(B) **A** gives racemic mixture of **C** and **B** gives optically pure **C**

(C) **A** gives optically pure **C** and **B** gives racemic **C**

(D) **A** gives optically pure **D** and **B** gives racemic **D**

121. A molecular orbital of a diatomic molecule changes sign when it is rotated by 180° around the molecular axis. This orbital is—

(A) $\sigma$ (B) $\pi$

(C) $\delta$ (D) $\varphi$

122. IR active normal modes of methane belong to the irreducible representation—

| $T_d$ | E | $8C_3$ | $3C_2$ | $6S_4$ | $6\sigma_d$ | |
|---|---|---|---|---|---|---|
| $A_1$ | 1 | 1 | 1 | 1 | 1 | $x^2 + y^2 + z^2$ |
| $A_2$ | 1 | 1 | 1 | – 1 | – 1 | |
| E | 2 | – 1 | 2 | 0 | 0 | $2z^2 - x^2 - y^2$, $x^2 - y^2$ |
| $T_1$ | 3 | 0 | – 1 | 1 | – 1 | $R_x, R_y, R_z$ |
| $T_2$ | 3 | 0 | – 1 | – 1 | 1 | $x, y, z, xy, yz, zx$ |

(A) $E + A_1$ (B) $E + A_2$

(C) $T_1$ (D) $T_2$

123. The symmetric rotor among the following is—

(A) $CH_4$ (B) $CH_3Cl$

(C) $CH_2Cl_2$ (D) $CCl_4$

124. The nuclear *g*-factors of $^1H$ and $^{14}N$ are 5·6 and 0·40 respectively. If the magnetic field in an NMR spectrometer is set such that the proton resonates at 700 MHz, the $^{14}N$ nucleus would resonate at—

(A) 1750 MHz (B) 700 MHz

(C) 125 MHz (D) 50 MHz

125. The spectroscopic technique, by which the ground state dissociation energies of diatomic molecules can be estimated is—

(A) microwave spectroscopy

(B) infrared spectroscopy

(C) UV-visible absorption spectroscopy

(D) X-ray spectroscopy

126. The term symbol for the first excited state of Be with the electronic configuration $1s^2\ 2s^1\ 3s^1$ is—

(A) $^3S_1$ (B) $^3S_0$

(C) $^1S_0$ (D) $^2S_{1/2}$

127. Which of the following statements is INCORRECT ?

(A) A Slater determinant is an antisymmetrized wavefunction

(B) Electronic wavefunction should be represented by Slater determinants

(C) A Slater determinant always corresponds to a particular spin state

(D) A Slater determinant obeys the Pauli exclusion principle

128. Compare the difference of energies of the first excited and ground states of a particle confined in (i) a 1-d box ($\Delta_1$), (ii) a 2-d square box ($\Delta_2$) and (iii) a 3-d cubic box ($\Delta_3$). Assume the length of each of the boxes is the same. The correct relation between the energy differences $\Delta_1$, $\Delta_2$ and $\Delta_3$ for the three cases is—

(A) $\Delta_1 > \Delta_2 > \Delta_3$ (B) $\Delta_1 = \Delta_2 = \Delta_3$

(C) $\Delta_3 > \Delta_2 > \Delta_1$ (D) $\Delta_3 > \Delta_1 > \Delta_2$

129. The correct statement about both the average value of position ($\langle x \rangle$) and momentum ($\langle p \rangle$) of a 1-*d* harmonic oscillator wavefunction is—

(A) $\langle x \rangle \neq 0$ and $\langle p \rangle \neq 0$

(B) $\langle x \rangle = 0$ but $\langle p \rangle \neq 0$

(C) $\langle x \rangle = 0$ and $\langle p \rangle = 0$

(D) $\langle x \rangle \neq 0$ but $\langle p \rangle = 0$

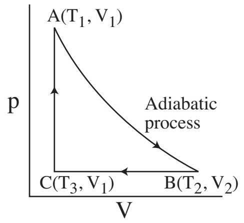
130. The value of the commutator $[x, [x, p_x]]$ is—

(A) $i\hbar x$ (B) $-i\hbar$

(C) $i\hbar$ (D) 0

131. The equilibrium constants for the reactions $CH_4(g) + 2H_2O(g) \rightleftharpoons CO_2(g) + 4H_2(g)$ and $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$ are $K_1$ and $K_2$, respectively. The equilibrium constant for the reaction
$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$ is—
(A) $K_1 \cdot K_2$ (B) $K_1 - K_2$
(C) $K_1/K_2$ (D) $K_2 - K_1$

132. Consider the progress of a system along the path shown in the figure. $\Delta S$ (B → C) for one mole of an ideal gas is then given by—



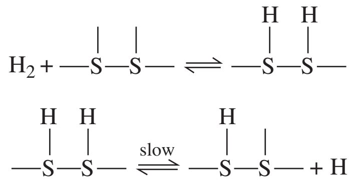

(A) $R \ln \frac{T_1}{T_3}$ (B) $R \ln \frac{T_3}{T_1}$
(C) $R \ln \frac{V_2}{V_1}$ (D) $R \ln \frac{V_1}{V_2}$

133. A thermodynamic equation that relates the chemical potential to the composition of a mixture is known as—
(A) Gibbs-Helmholtz equation
(B) Gibbs-Duhem equation
(C) Joule-Thomson equation
(D) Debye-Hückel equation

134. According to transition state theory, the temperature-dependence of pre-exponential factor (A) for a reaction between a linear and a non-linear molecule, that forms products through a non-linear transition state, is given by—
(A) T (B) $T^2$
(C) $T^{-2}$ (D) $T^{-1 \cdot 5}$

135. For a given ionic strength, (I) rate of reaction is given by
$\log \frac{k}{k_0} = -4 \times 0{\cdot}51\ (I)^{1/2}$. Which of the following reactions follows the above equation ?
(A) $S_2O_8^{2-} + I^-$
(B) $Co(NH_3)_5Br^{2+} + OH^-$
(C) $CH_3COOC_2H_5 + OH^-$
(D) $H^+ + Br + H_2O_2$

136. For a reaction on a surface




At low pressure of $H_2$, the rate is proportional to—
(A) $[H_2]$ (B) $1/[H_2]$
(C) $[H_2]^{1/2}$ (D) $1/[H_2]^{1/2}$

137. The temperature-dependence of an electrochemical cell potential is—
(A) $\frac{\Delta G}{nFT}$ (B) $\frac{\Delta H}{nF}$
(C) $\frac{\Delta S}{nF}$ (D) $\frac{\Delta S}{nFT}$

138. The single-particle partition function ($f$) for a certain system has the form $f = AVe^{BT}$. The average energy per particle will then be ($k$ is the Boltzman constant)—
(A) $BkT$ (B) $BkT^2$
(C) $kT/B$ (D) $kT/B^2$

139. The indistinguishability correction in the Boltzmann formulation is incorporated in the following way : (N = total number of particles; $f$ = single-particle partition function)
(A) Replace $f$ by $f/N!$
(B) Replace $f^N$ by $f^N/N!$
(C) Replace $f$ by $f/\ln(N!)$
(D) Replace $f^N$ by $f^N/\ln(N!)$

140. In a photochemical reaction, radicals are formed according to the equation—

$$C_4H_{10} + h\nu \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2C_2H_5$$

$$C_2H_5 + C_2H_5 \xrightarrow{k_2} C_2H_6 + C_2H_4$$

If I is the intensity of light absorbed, the rate of the overall reaction is proportional to—
(A) I (B) $I^{1/2}$
(C) $I\,[C_4H_{10}]$ (D) $I^{1/2}\,[C_4H_{10}]^{1/2}$

141. Conductometric titration of a strong acid with a strong alkali (MOH) shows linear fall of conductance up to neutralization point because of—

(A) formation of water

(B) increase in alkali concentration

(C) faster moving $H^+$ being replaced by slower moving $M^+$

(D) neutralization of acid

142. Find the probability of the link in polymers where average values of links are (1) 10, (2) 50 and (3) 100—

(A) (1) 0·99, (2) 0·98, (3) 0·90

(B) (1) 0·98, (2) 0·90, (3) 0·99

(C) (1) 0·90, (2) 0·98, (3) 0·99

(D) (1) 0·90, (2) 0·99, (3) 0·98

143. The stability of a lyophobic colloid is the consequence of—

(A) van der Waals attraction among the solute-solvent adducts

(B) Brownian motion of the colloidal particles

(C) insolubility of colloidal particles in solvent

(D) electrostatic repulsion among double-layered colloidal particles

144. In a conductometric experiment for estimation of acid dissociation constant of acetic acid, the following values were obtained in four sets of measurements :

$1{\cdot}71 \times 10^{-5}$, $1{\cdot}77 \times 10^{-5}$, $1{\cdot}79 \times 10^{-5}$ and $1{\cdot}73 \times 10^{-5}$.

The standard deviation of the data would be in the range of—

(A) $0{\cdot}010 \times 10^{-5} - 0{\cdot}019 \times 10^{-5}$

(B) $0{\cdot}020 \times 10^{-5} - 0{\cdot}029 \times 10^{-5}$

(C) $0{\cdot}030 \times 10^{-5} - 0{\cdot}039 \times 10^{-5}$

(D) $0{\cdot}040 \times 10^{-5} - 0{\cdot}049 \times 10^{-5}$

145. Silver crystallizes in face-centered cubic structure. The 2nd order diffraction angle of a beam of X-ray ($\lambda$ = 1Å) of (111) plane of the crystal is 30°. Therefore, the unit cell length of the crystal would be—

(A) $a$ = 3·151 Å (B) $a$ = 3·273 Å

(C) $a$ = 3·034 Å (D) $a$ = 3·464 Å

# Answers with Hints

1. (A) I. Cloth reel → three

J. Silent wonder → two

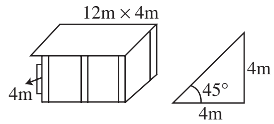
K. Good tone → one

L. Bronze rod → zero

Ascending order L, K, J, I.

2. (C) $2^{2^{2^2}} = 2^{4^2} = 2^{16}$

3. (C)




Area = 12 × 4 = 48 m$^2$

4. (C)

| | 20 | $a$ | |
|---|---|---|---|
| $10b$ | $200b$ | $10ab$ | = 840 |
| 2 | 40 | $2a$ | = $c6$ |

and 2 × $a$ gives 6 at unit place

$2 \times 3 = 6$

or $2 \times 8 = 16$

So, $a$ can be 3 or 8.

According to question,

$840 + c6 = 8d6$

which gives $c + 4 = d$

as digit at hundred place is 8, so $c$ will be between 0 and 5.

So, from table we have

$40 + 2a = c6$

$c$ should be 4 or 5

$40 + 2 \times 3 = 46$ …(I)

and $40 + 2 \times 5 = 50$ → (not possible)

So, $a = 3$, $c = 4$

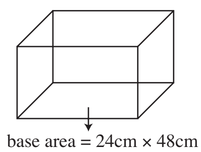
Now check from option

We obtain $a + b = 11$.

5. (A) We use combination ${}^nC_4$ point of intersection. For octagon $n = 8$.

$$^8C_4 = \frac{8!}{4! \times 4!} = \frac{8 \times 7 \times 6 \times 5 \times 4}{4! \times 4!} = 70$$

6. (D)

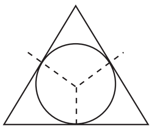



Longest stick can be kept inside the body diagonally.

So, $(24)^2 + (48)^2 + h^2 = 56^2$

after solving we get, $h$ = 16 cm.

7. (C)



Area of triangle = N.

Radius of incircle × P of triangle.

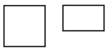
$$N = ?$$

We know incircle touches the triangle at mid point.

$$\text{Area of triangle} = \frac{1}{2}\text{base} \times \text{height}$$

$$= \frac{1}{2} \times \text{radius} \times \text{perimeter}$$

$$N = \frac{1}{2}$$

8. (C) 

Let volume be $x$

Series : $x, \frac{x}{2}, \frac{x}{4}, \ldots, \frac{x}{2^n}$ –

$$x = 20 \text{ cc}$$

$$\text{Common ratio} = \frac{1}{2}$$

Sum of the series (as series is in G.P.)

$$= \frac{x}{1-r} = \frac{20\text{cc}}{1-\frac{1}{2}}$$

$$= 40 \text{ cc}$$

9. (B) 1.  2.  3. 

1.  2.  3. 

Ratation of 180° clockwise.

10. (A) Melting point decreases with pressure, boiling point increases and also solid, liquid and gas can co-exist at the same pressure and temp.

11. (A) $\text{Mean} = \frac{\text{Sum of observation}}{\text{No. of observation}}$

If sum of observation change then mean will also change.

12. (A) Journey start

0100 Hrs local time — 0900 Hrs.

So, elapsed time = (9 – 1) hrs + lag time

= 8 hrs + 10 = 18 hrs.

Elapse time for staying

= (21 – 9)

= 12 hrs

So, duration of Man

= Elapse time including time lag

+ Return time + staying time

= 18 hrs + 18 hrs + 12 hrs

= 48 hours.

13. (A) Let $\frac{1}{1234} = x$

$$r^x + r^{-x} = 2$$

$$r^x + \frac{1}{r^x} = 2$$

$$\frac{r^{2x}+1}{r^x} = 2$$

$$r^{2x} - 2^{r^x} + 1 = 0$$

$$(r^x - 1)^2 = 0$$

or $r^x = 1$

and $r^{-x} = 1$

So, $r^{4321} + r^{-4321} = 2$

14. (A) $\text{Time taken} = \frac{\text{Distance}}{\text{Speed in still water}}$

$$= \frac{10 \text{ m}}{10\text{m/min.}}$$

$$= 1 \text{ min.}$$

15. (A) 16. (C)

17. (D) U … G … C … C … S … I … R

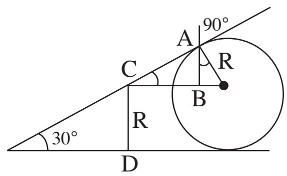
No. of letters = 7

Position of first C = 3

Second C = 4

Permutation 3 × 7 × 4 = 25

18. (B)




Height = AB + CD

AB = R cos 30°

Height = R + R cos 30°

$$= R + \frac{\sqrt{3}}{2}R$$

19. (B) Length = 24 m

Width = 3 m

Boundary is required to be at least 60 m

first pitch is at 60 m from boundary = 0

Diameter of field = 140 m

Next pitch at 63, 66, 69, 72, 75, 78, 81

60 + 81 = 141

So, leave 81

So, total possible pitches at 60, 63, 66, 69, 70, 75, 78 m position

Total = 7

20. (B)

21. (A) $CO_2 + H_2O \underset{\text{Anhydrase}}{\overset{\text{carbonic}}{\rightleftharpoons}} H_2CO_3$

Hydration occur in blood at high pH value.

Dehydration occur in lung at low pH value.

Carboxypeptidase A is pancreatic exopeptidase that hydrolise peptide bond of C terminal.

22. (A)

| **Deoxy. Hb.** | **Oxy. Hb.** |
|---|---|
| $Fe^{+2}$ HS | $Fe^{+2}$ LS |
| $t_2g^4\ eg^2$ | $t_2g^6eg^0$ |
| Fe is above the plane which tends to increase the Fe—N distance | Fe is fitted well inside the plane thus reducing Fe—N bond distance. |

23. (C) When NO is linear it donate $3e^-$

Since both complex follow $18e^-$ rule.

So $[Co(CO)_3NO] \Rightarrow$ Total valence electron

Co = 9 ($d^7s^2$)

CO = 3 × 2 = 6

NO = 3

$[Ni(\eta^5 - Cp)NO]$ = 18 $e^-$

Total Valence Electron

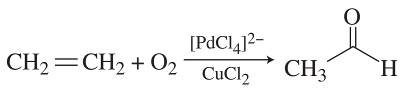
Ni = 10 ($d^8s^2$)

$\eta^5$Cp = 5

NO = 3

TVE = 18 $e^-$

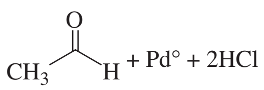
24. (A) **Wacker process—**




*i.e.*, formation of carbonyl compound by Reaction of Alkene and $O_2$ in presence of $Pd^{+2}$.

**Mechanism—**

$CH_2{=}CH_2 + [PdCl_4]^{2-} + H_2O \longrightarrow$




**Regeneration of Wacker catalyst**,

$Pd^\circ + 2\overset{II}{Cu}Cl_2 + 2Cl^- \rightarrow [PdCl_4]^{2-} + 2CuCl$

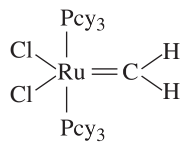
25. (B) [reference → Inorganic chemistry + Atkins]

In Fischer Carbene Oxidation State of metal is low and ligand is π acceptor and nature of Fischer carbene is electrophilic

**Ex.** : $(CO)_5\,Cr{=}C(OH)(CH_3)$ (Fischer Carbene)

While in Schrock carbene metal are in high positive oxidation state, ligand are non-π acceptor and nature of Schrock carbene is nucleophilic.

**Ex. :** Grubb Catalyst




26. (A) [Inorganic Chemistry – By Greenwood]

Proton affinity of an anion or a neutral atom or molecule is a measure of its gas phase basicity. Higher the proton affinity stronger the base and weaker the conjugate acid in gas phase.

So $N_3^-$ is strongest base.

27. (D) [Ref. → Analytical Chemistry – S.M. Kopkar]

ilkovic equation $id = 607\, nD^{1/2}\, m^{2/3}\, t^{1/6}\, c$

From this eq. $id \propto t^{1/6}$

*i.e.*, depends upon drop time ($t$ = drop time) and its value also depend upon temperature the value of $id$ (diffusion Current) increases at a rate of 1 – 2% per °C.

28. (C) The threshold energy is the minimum projectile energy necessary to satisfy mass energy and momentum conservation in a Nuclear reaction to form product in their ground state.

$$\text{T.E.} = -Q\left(\frac{m_p + m_c}{m_c}\right)$$

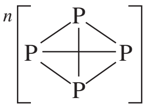
$$= -(-3{\cdot}23)\left(\frac{1+13}{13}\right)$$

$$= 3{\cdot}485$$

$^{13}N(n, p)^{13}C$ Q = 3·236

So $^{13}C(p, n)^{13}N$ = – 3·236

29. (D) ⇒ – 2200 ppm
Reference → Tin Chemistry—Fundamental Frontiers and Application By – Marcel Gielen.

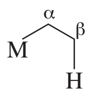
30. (A) At high temperature or at melting form phosphorous exist as symmetrical $P_4$ type structure
*i.e.*,


31. (A) $S_2O$ exist as $\overset{-2}{S}—\overset{+4}{S}—O^-$

32. (D) Pseudohalogen are polyatomic analogous of Halogen whose chemistry resemble with true Halogen common example. These anions contain nitrogen atoms.
$CN^-$, $N_3^-$, $SCN^-$, $NCN^{2-}$, OCN, $Co(CO)_4$ etc.

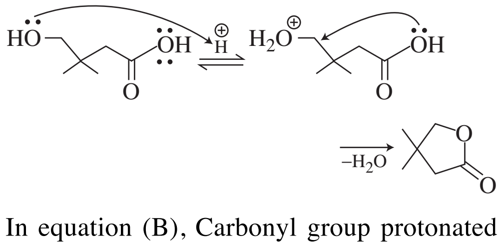
33. (A) M ($t_{2g}$) → $PR_3$ ($\sigma^*$)
Phosphines ($PR_3$) primarily function as Lewis base, interacting with metal as σ donar Ligand. $PR_3$ can accept electron density from metal into P—C ($\sigma^*$) Antibonding orbital having π symmetry.

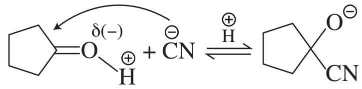
34. (A)
$RhCl_3 \cdot 3H_2O + PPh_3 \xrightarrow{\text{Ethanol}} [RhCl(PPh_3)_3]$
$RhCl(PPh_3)_3$ is Wilkinson catalyst and common method for preparation of $RhCl(PPh_3)_3$ is Refluxing of $RhCl_3 \cdot 3H_2O$ with $PPh_3$. Moreover, on counting the total valence electrons,
$[Rh(PPh_3)_2Cl] = 9 + 3 \times 2 + 1 = 16e^-$
{Cl atom cannot be bridging ∴ its contribution is 1}. Wilkinson catalyst is $16e^-$ species.

35. (A) In M—≡—H, the unit is anti-periplanar and thus β-H elimination not possible.


For β hydride elimination reaction β hydrogen should be closer to metal in other 3 option all hydrogen atoms are far so elimination not possible ($sp^2$ carbon)

36. (A) The reaction follows SN, CB mechanism in which M—Y bond is fully broken before M—X bond begins to form.
Thus, **Id mechanism** is the most evidential mechanism.
**Reference**—Principles of Structure and Reactivity. INORGANIC CHEMISTRY by James E. Huheey IV edition Ch-13, page 552.

37. (A) **Explanation**—After addition of HCl in equation (A) Primary OH group protonated and $H_2O$ removed early. *i.e.*,


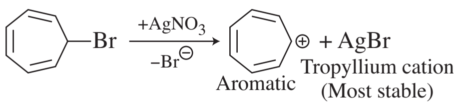
In equation (B), Carbonyl group protonated and Electrophilic charactor of C = O group increases so, $\overset{\ominus}{CN}$ ion attacks easily,


Therefore, equilibrium will shift towards right in case of both A and B.

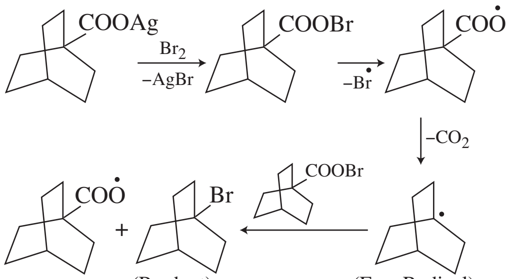
38. (A) **Explanation**—
3300 $cm^{-1}$ peak is for ≡ C—H stretch.
2150 $cm^{-1}$ is for C ≡ C—H stretch.
Thus, $CH_3$—C ≡ C—H

39. (B) **Explanation**—Acetone have 6H and Dichloromethane have 2H, when concentration is same then intensity ratio is 3 : 1. in $^1$H–NM R spectra.
But intensity ratio obtained is 1 : 1. So, concentration of Acetone and Dichloromethane must be in ratio of 1 : 3.

40. (D) **Explanation**—The intensity of IR-spectrum bands is dependent mainly on the magnitude of dipole.
More the polar charactor of a bond, the greater the intensity of IR-band. So, In case of CO the intense band observed in IR-spectrum due to large dipole moment change of CO due to bond stretching.

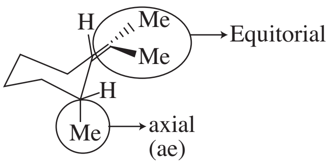
41. (C) **Explanation**—Bromo-Heptatriene give Bromide ion easily and becomes aromatic, so $AgNO_3$ give precipitate of AgBr.


42. (A) It is Hunsdiecker reaction. This reaction follows a free radical mechanism.

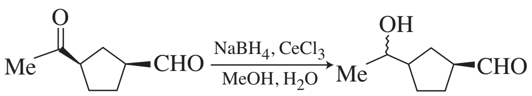



(Product) (Free Radical)

43. (A) **Explanation**—In general, 1, 2 Hetero substitution, ee is the most stable form but due to repulsion between the Methyl groups, ae form here is most stable.

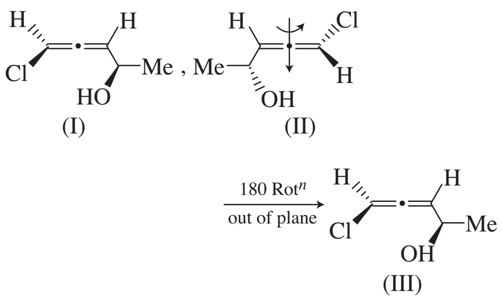



44. (D)



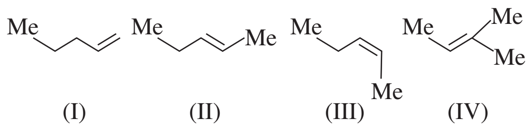

$NaBH_4$ give chemoselective reduction of ketone in presence of CHO group, when $CeCl_3$ is mixed with $NaBH_4$.

45. (C) **Explanation**—Both structures are identical; because both are super-imposable to each other, when one structure is rotated out of plane as shown below :—




I and III are Homomers. So, both structures are Homomers.

46. (B) The correct order of heat of hydrogenation of the following compounds are—




(I) (II) (III) (IV)

order, I > III > II > IV

because heat of hydrogenation of alkene

$$\propto \frac{1}{\text{Stability of Alkene}}$$

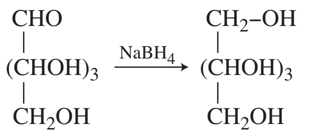
*i.e.*, more the stable Alkene less will be heat of hydrogenation.

Hence order of stability of Alkene →

I < III < II < IV

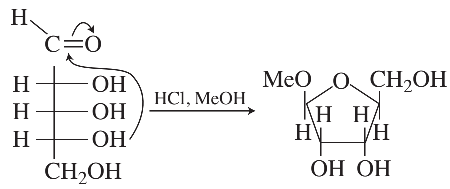
47. (A) **Explanation**—The correct statement(s) for ribose is—

(A) On reduction with $NaBH_4$ it give optically inactive product



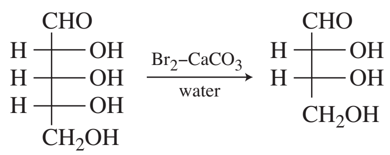

(Optical inactive)

(B) On reaction with methanolic HCl it gives a furanoside.



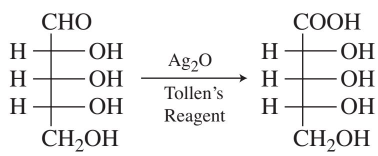

(furanoside)

(C) On reaction with $Br_2$-$CaCO_3$–water its gives following compounds—



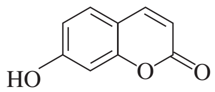

which is optical active.

(D) It gives positive follen's test.

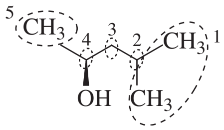



So, statement A, B and D is correct.

48. (B) Cinnamic acid is biogenatic precursors for the natural product umbelliferone




49. (C) (R)-4-methylpentane-2-ol give 5; $^{13}C$-NMR signal.




1 signal → 2 Methyl group

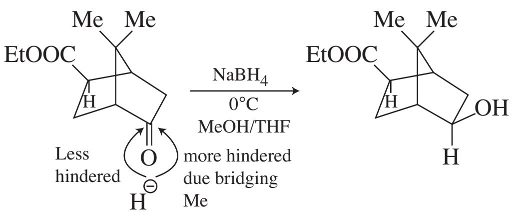
1 signal → CH

1 signal → $CH_2$

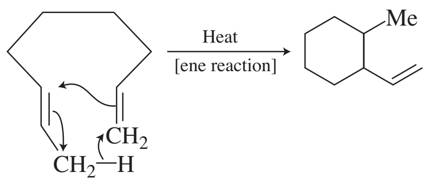
1 signal → CH (attached to OH)

1 signal → $CH_3$

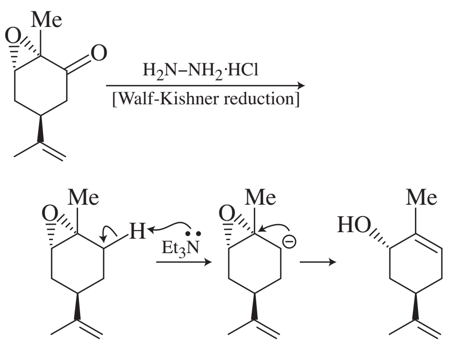
50. (D) $NaBH_4$ is chemoselective reducing agent for carbonyl group in presence of ester. In presence of steric hindrence it give hydride ion from less hindered side. So, product (D) is major product




51. (A)




52. (C)



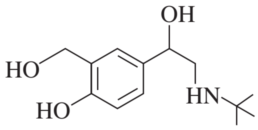

[Product]

53. (A) **Explanation**—Magnitude of stability constant for $K^+$ ion complexes of the supra molecular hosts is directly proportional to ionic interaction and size of cavity.

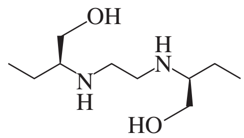
So, more the ionic interaction of hetero atom with $K^+$ ion more will be stability. So, stability order is B > A > C.

54. (B) **Explanation**—Antitubercular drug(s) among the given compounds are—

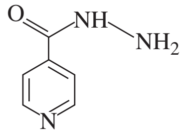
(A) **Salbutamol**—It is used for relief of bronchospasm in conditions such as 'asthma' and 'chronic abstructive'.



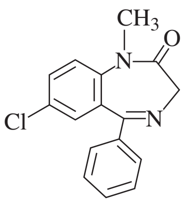

(B) Ethambutanol




(C) Isoniazid




(D) **Diazepam**—It is used treatment of 'anxiety', alcohol withdrawal syndrome, muscle spams, trouble sleeping and restless legs syndrome.




55. (C) We know that

$$\Psi = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) \text{ if } n = 0$$

then $\Psi = 0$ (*i.e.*, wavefunction become zero) and it is not possible. In I-D box for ground state $n = 1$. $n = 0$ exists only for Simple Harmonic Oscillator.

56. (C) When we add potential in the Hamaltonian the energy eigen value will shift but the eigen function will not change.

57. (D) $\frac{A_1}{A_2} = \frac{E.C.L_1}{E.C.L_2}$

$\Rightarrow \frac{\log\left(\frac{I_0}{It}\right)}{A_2} = \frac{L_1}{L_2}$

$\Rightarrow \frac{\log\frac{100}{50}}{A_2} = \frac{1}{3}$

$\frac{\log 2}{A_2} = \frac{1}{3}$

$A_2 = 3\log 2 = 3 \times 0{\cdot}3010$

$A_2 = 0{\cdot}9030$

We know that $A = \log\frac{1}{T}$

$\frac{1}{T} = \text{Antilog of } A_2$

$\Rightarrow \frac{1}{T} = \text{Antilog } 0{\cdot}903$

$\frac{1}{T} = 8$

$T = \frac{1}{8}\% = \frac{1}{8} \times 100 = 12{\cdot}5$

58. (B) For allowed transition

$\Delta S = 0$

$\Delta L = \pm 1$

$3S \rightarrow 3P$

$\Delta S = 3 - 3 = 0$

$\Delta L = (1 - 0) = \pm 1$

(For P, L = 1 for S, L = 0)

59. (A) $\begin{vmatrix} x \\ y \\ z \end{vmatrix} \xrightarrow{\sigma_{xy}} \begin{vmatrix} x \\ -y \\ z \end{vmatrix}$ ...(1)

$C_2{}^x.\sigma_{xy} = \begin{vmatrix} x \\ y \\ z \end{vmatrix} \xrightarrow{C_2(x)} \begin{vmatrix} x \\ -y \\ -z \end{vmatrix} \xrightarrow{\sigma_{xy}} \begin{vmatrix} x \\ -y \\ z \end{vmatrix}$

From eqn. (i) and (ii)

$C_2{}^x.\sigma_{xy} = \sigma_{xz}.$

60. (B) HCl is a covalent molecule. Thus, both the electrons cannot reside only in Cl atom. Thus, option (C) is wrong. In option (A) and (D) for H-atom, $3p$ orbital is not present (H → $1s$; Cl = $3s^2 3p^5$).

61. (D) For monoatomic gas it only posses translational degree of freedom so variation of heat capacity with temperature is ignored.

62. (C) At constant volume addition of inert gas does not cause any effect on equilibrium because upon addition of inert gas at constant volume, the total pressure will increase. But the concentration of the product and reactant (*i.e.*, ratio of their moles to the volume of container) will not change.

63. (C) $k = AT^n \exp.\frac{-E_0}{RT}$

is the modified form of Arrhenius Eqn.

$k = AT^2 \exp.\frac{-E_0}{RT}$ (given)

Comparing eqn. (i) and (ii) we get

$E_a = 2RT + E_0$

64. (A) $2A + B \rightarrow 3Z$

$-\frac{1}{2}\frac{D[A]}{Dt} = \frac{D[B]}{Dt} = \frac{1}{3}\frac{D[Z]}{Dt}$ ...(i)

$-\frac{D[A]}{Dt} = 2 \times 10^{-4}$ (given)

from eqn. (i)

$-\frac{1}{2}\frac{D[A]}{Dt} = \frac{1}{3}\frac{D[Z]}{Dt}$

$\frac{D[Z]}{Dt} = 3 \times \frac{1}{2} \times 2 \times 10^{-4}$

$= 3 \times 10^{-4}\ \text{mol dm}^{-3}\text{s}^{-1}$

65. (B) The escaping tendency of a charged particle from a phase can be affected by the charge state of the phase and the variable used to describe the differences is escaping tendency of electrostatic potential $\phi$ and the electrostatic potential at a point (a) is defined as the work per unit charge required to bring a positive test change reversible from infinity to the point

$$\phi_{(a)} = \frac{\delta\omega_{\infty \rightarrow a}}{d\theta}$$

**Reference**—'Principle of thermodynamics' by 'Myron Kaufam'.

66. (C) $\eta = KM^a$ (given)

It is Mark-Hauwink equation where K, $a$ is constant for polymer solvent pair.

67. (D) We know that,

$\Delta G = \Delta G° + RT \ln Q$

$Q$ = Reaction quotient,

$Q = \frac{[\text{Product}]}{[\text{Reactant}]}$

$\Delta G = \Delta G° + RT \ln \frac{[Zn^{+2}][Cu]}{[Zn][Cu^{+2}]}$

Since activity of Cu and Zn is unity

So, $\boxed{\Delta G = \Delta G° + RT \ln \frac{a_{Zn^{+2}}}{a_{Cu^{+2}}}}$

where $a$ = activity.

68. (D) Term symbol = $^{2S+1}L_J$

$$S = 1, L = 0 + 1 = 1 = P$$
$$2S + 1 = 3$$
$$J = |L + S| \ldots\ldots\ldots |L - S|$$
$$= |1 + 1| \ldots\ldots\ldots |1 - 1|$$
$$= 2, 1, 0$$

As this is half filled orbital [1] [1][ ][ ]

∴ Lower value of J will be considered.

∴ $^3P_0$.

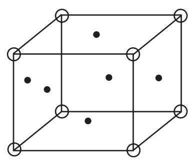
69. (B) Double layer interaction is determined by Gany–Chapmann potential ($\Psi_0\ e^{-kr}$)

$a$ = represents double layer

$b$ = represents vander Wall's and double layer.

$c$ = Van der Wall's.

70. (D) In FCC, Packing fraction is 74% and No. of atoms per unit cell is '4'.



No. of atom per unit cell

$$= 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$$

Packing fraction (ϕ)

$$= \frac{\text{Volume occupied by the particle}}{\text{Volume of unit cell}} \times 100$$

$$= \frac{4 \times \frac{4}{3}\pi r^3}{a^3} \times 100 = 74\%$$

71. (D) Differential pulse polarography (DPP) is more sensitive then (DCP) from analytical point of view because Non-foradic current is less in DPP then DCP.

72. (A) Fluorescence is directly proportional to the amount of absorbed radiation where F = KP∈$bc$.

The fluorescence signal can be increased if the radiat power of the incident beam is increased, therefore always use more intense sources.

Dissolved oxygen largely limits fluorescence since it promoters intersystem crossing because it is paramagnetic.

73. (B) We know that, According to Fermi model

$$r = r_0\,(A)^{1/3}$$
$$A = \text{mass number.}$$

$^{125}Sn \Rightarrow A = 125$

$$r = 1{\cdot}2 \times 10^{-15}\ \text{m}$$
$$(A)^{1/3} = (125)^{1/3} = 5$$
$$r = 1{\cdot}2 \times 10^{-15} \times 5$$
$$= 6 \times 10^{-15}\ \text{m}$$

Geometrical cross section = $\pi r^2$

$$1\ \text{barn} = 10^{-28}\ \text{m}^2$$

Cross section Area

$$= \frac{22}{7} \times (6 \times 10^{-15}\ \text{m})^2 \approx 1{\cdot}53$$

74. (A)

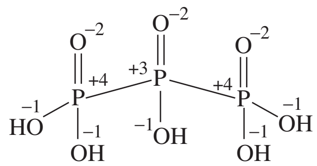
**Suzuki coupling**—Palladium catalyzed cross coupling between organoboranic acid and halides.

**Heck coupling**—Palladium catalyzed C—C coupling between aryl halides or vinyl halides and activated alkenes in the presence of a base.

**Sonogashira coupling**—This coupling terminal alkynes with aryl or vinyl halides is performed with a palladium catalyst, Cu(I) cocatalyst and amine base.

**Negeshi coupling**—This reaction is the organic reaction of an organohalide with an organic-zinc compound Pd and Ni catalyst.

75. (C) $H_5P_3O_8$




76. (B)

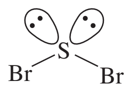
$[Br_3]^+$ Hybridisation = $sp^3$

Geometry = Td

Shape = Bent shap

$[Br_3]^+ \approx Br_2\,Br^+$

S ⇒ $SBr_2$




$[I_5]^+$ Hybridisation = $sp^3d$

Geometry = TBP

77. (A) Wade's theory,

$$F = 3b + 4c + h + x - 2n$$

$b$ = No. of boron atoms

$c$ = No. of carbon atoms

$h$ = No. of hydrogen atoms

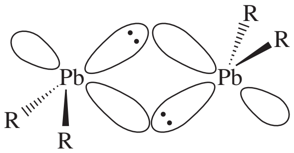
$x$ = Amount of negative ions

$n$ = No. of vertices = $b + c$

$$F = 3 \times 12 + 4 \times 0 + 12 + 2 - 2(12 + 0)$$
$$= 26$$
$$F = 2n + 2 \text{ for Closo.}$$
$$26 = 2 \times 12 + 2$$
$$= 24 + 2 = 26.$$

Hence, closo.

78. (A)




Pb show the inert pair effect.

Due to inert pair effect Pb(II) is more stable forming banana bond in which structure is only correct one.

79. (A) $SbCl_3 + 3EtMgBr \rightarrow SbEt_3 + 3MgBrCl$

$SbEt_3 + 2SbI_3 \rightarrow [Sb(Et)I_2]_n$

Polymeric structure

80. (A) Fe–porphyrin complex – colour show is due to $\pi - \pi^*$ transition.

$[Mn(H_2O)_6]Cl_2$ :

$Mn^{+2} \Rightarrow d^5$ configuration which is both spin and Laporte forbidden

$[Co(H_2O)_6]Cl_2$ :

Co(II) $\Rightarrow d^7$ configuration which is spin allowed but laporte forbidden.

81. (C) Agostic interaction can be detected by the presence of a $^1H$ NMR peak.

Agostic interaction most commonly refers to a C—H bond on a ligand that undergoes an interaction with the metal complex.

82. (A) Cp proton of complex (A) is highly deshielded because of CO ligand. CO is very good $\pi$-acceptor ligand.

Complex (D) will be highly shielded because Fe is small in size. It is more closed to nucleus.

83. (B) (M + 1) = closo, (M + 2) = nido, (M + 3) = Aracho, (M + 4) = Hypo = (M = no. of metal atom)

$$\text{Weadge Rule} = \frac{1}{2}[\text{TVE} - 12 \times \text{No. of metal}]$$

$Ru_6(C)(CO)_{17}$

$$= \frac{1}{2}[8 \times 6 + 4 + 17 \times 2 - 12 \times 6]$$
$$= \frac{1}{2}[86 - 72]$$
$$= \frac{1}{2}[14] = 7$$

(M ± 1) = closo

$[Os_5(C)(CO)_{15}]$

$$= \frac{1}{2}[74 - 12 \times 5]$$
$$= \frac{1}{2}[14] = 7 \text{ (M + 2)} \Rightarrow \text{nido}$$

$[Ru_5(C)(CO)_{16}]$

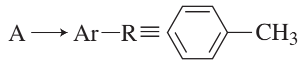
$$= \frac{1}{2}[76 - 60]$$
$$= \frac{1}{2}[16] = 8 \text{ (M + 3) Aracho.}$$

84. (C) J. T. distortion occurs where there is unsymmetrical filling of electrons in $t_{2g}$ or $eg$ orbital.

| | | | |
|---|---|---|---|
| $K_4[Cr(CN)_6]$ | | | |
| Cr = + 2 O.S. | low spin complex | | |
| Cr(II) = $d^4$ | $t_{2g}^4\ eg^0$ | (unsym) | |
| $K_4[Fe(CN)_6]$ | low spin complex | | |
| Fe(II) = $d^6$ | $t_{2g}^6\ eg^0$ | (symmetrical) | |
| $K_3[Co(CN)_6]$ | low spin complex | | |
| Co(III) $\Rightarrow d^6$ | $t_{2g}^6\ eg^0$ | (symmetrical) | |
| $K_4[Mn(CN)_6]$ | low spin complex | | |
| Mn(II) $\Rightarrow d^5$ | $t_{2g}^5\ eg^0$ | (unsym) | |

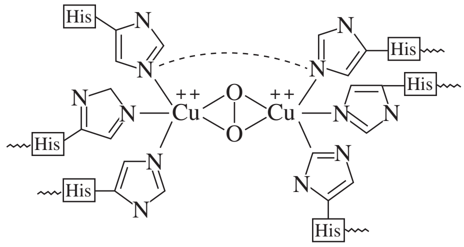
Hence only A and D is having unsymmetrical filling, hence undergo distortion.

85. (A) The reductive elimination of (A) gives toluene




So, R = $CH_3$ option A is correct.

86. (A) Structure of oxy-haemocyanin.




| | | |
|---|---|---|
| Blue colour | O.S. Cu | = II |
| | B.O. of $O_2$ | = I |

87. (B) In strong acidic condition

$$KMnO_4 \xrightarrow{H^+} Mn^{+2}$$
$$Mn^{+2} \xrightarrow{\text{Base}} Mn^{+4}$$

So, option (B) is correct., Acidified $Mn^{+2}$ is not oxidised by $H_2O_2$ but Alkaline

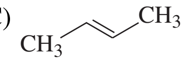
$$Mn(OH)_2 + H_2O_2 \rightarrow Mn_2O_3$$

88. (C) Oxidation of Zn to $Zn^{+2}$ will be diamagnetic hence EPR inactive.

Fe and Sn – Inactive.

EPR spectroscopy generally used for the species have one or more unpaired electron.

Cu(II) are EPR active because non-paired electron.

89. (C) 


Alkene does not undergo reductive elemination reaction easily as compared to Alkane.

90. (A) Reaction (i)

Water acting as an oxidant oxidizing Ca to $Ca^{2+}$ getting itself reduced to $H_2$.

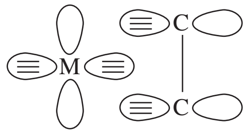
Reaction (ii) Water act as Lewis acid accepting elecron from $Cl^-$ which act as a ligand.

Reaction (iii) Water act as Lewis base donating electron to $Mg^{2+}$ which act as a.

Reaction (iv) Water acting as an reductant reducing F to $F^-$.

91. (D) Alkyne can act as 2 or 4 electron doner.

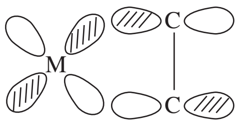
**L(π) → M(σ)** :




(Empty metal d-orbital) (Filled acetylene π-orbitals)

σ-Type donation

and **L(π) → M(σ) :**




(Metal filled *d*-orbital) (Empty acetylene π* orbitals)

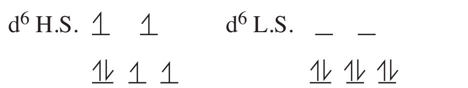
π-type donation

92. (A) $Fe(phen)_2 (NCS)_2$

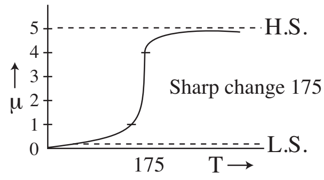
O.S. of Fe = + 2

Fe(II) = $d^6$

High spin – low spin equilibria or spin cross over




No. of unpaired electron $\mu = 4{\cdot}9$ BM | No. of unpaired $e^- = 0$ $\mu = 0{\cdot}0$ BM




$$\text{CFSE } \Delta = (-0{\cdot}4p + 0{\cdot}6q)$$

where $p$ = No. of $e^-$s in $t_{2g}$ orbital

$q$ = No. of $e^-$s in $e_g$ orbital

⇒ ***d*⁶H.S.** $\Delta = (-0{\cdot}4 \times 4 + 0{\cdot}6 \times 2)$

$= -1{\cdot}6 + 1{\cdot}2 = \mathbf{-0{\cdot}4\ \Delta}$

⇒ ***d*⁶ L.S.** $\Delta = -0{\cdot}4 \times 6 = \mathbf{-2{\cdot}4\ \Delta.}$

(–) ve sign is used for CFSE.

93. (A) $UO_2^+$ disproportionates more easily than $UO_2^{+2}$ and $U_3O_8$ is most stable oxide of U.

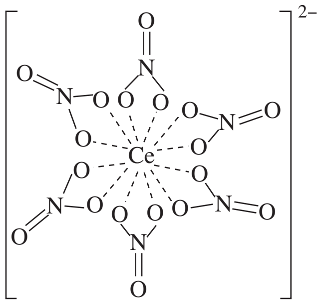
But coordination No. of U in

$[UO_2 (NO_3)_2{\cdot}(H_2O)_2]_4H_2O$ is eight.

Structure of $UO_2^{2(+)}$ is linear (Reffrac. = J.D. Lee)

94. (B) $CO_2$ does not combines with $[Ni(PR_3)_2$ (1,5 – cyclooctadiene]. Only insertion of $CO_2$ occurs and Et – ≡ – Et is inserted to complex and formed compound.

95. (D) $(NH_4)_2[Ce(NO_3)_6]$ complex $NO_3$ is bidented ligand and structure is Icosahedran *i.e.*, coordination number of Ce is 12.




In $Ce^{+4}$ more stable

$$Ce = 4f^1\ 5d^1\ 6s^2$$

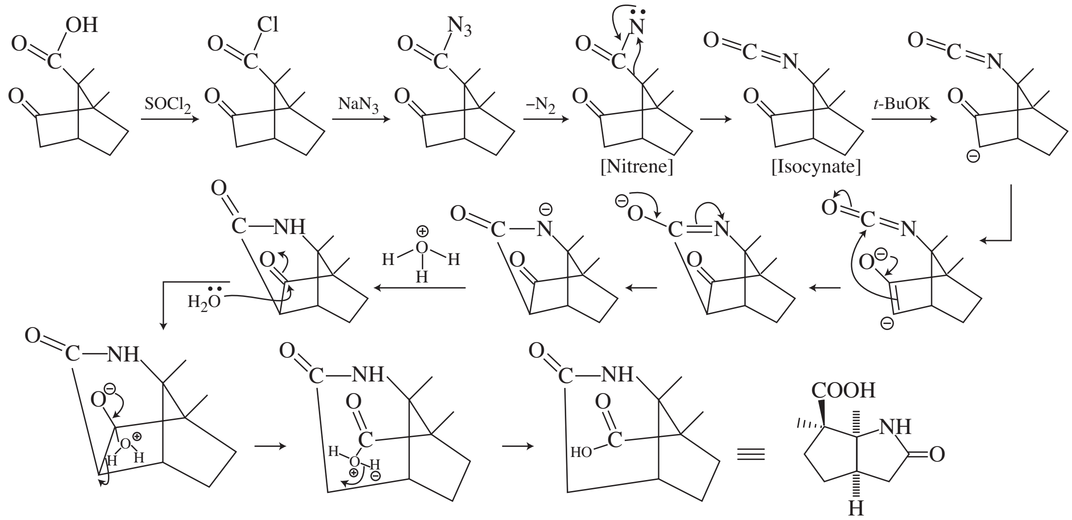
$$Ce\,(IV) = 4f^0\ 5d^1\ 6s^0$$

*i.e.*, Z is diamagnetic

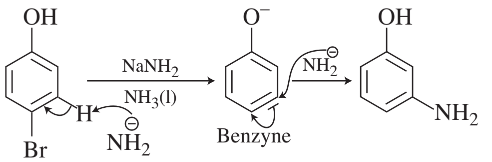
$Ce^{+4}$ is a strong one electron oxidizing agent.

$Ce^{+4}$ used in redox process.

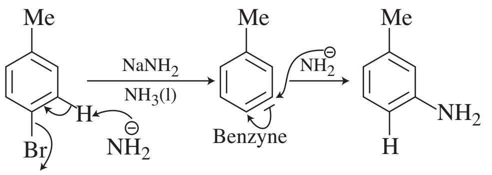
96. (C)



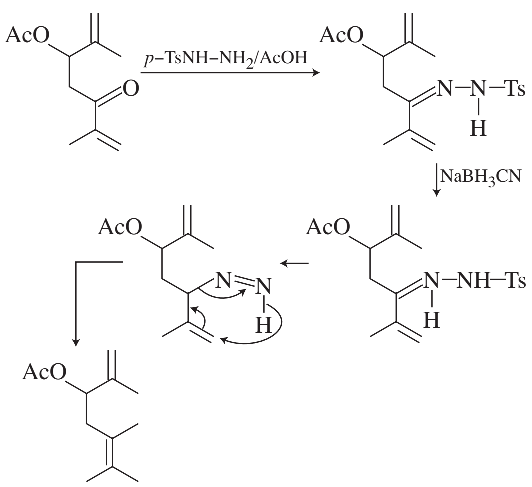
97. (D)



(OH at para position shows ($e^-$ releasing)

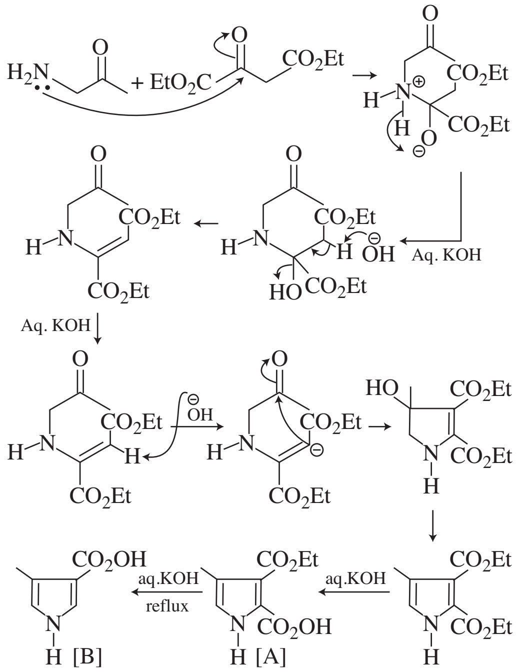


98. (C)

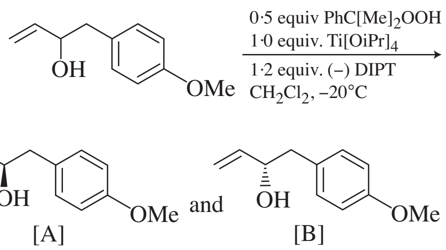


(Product)

99. (C)

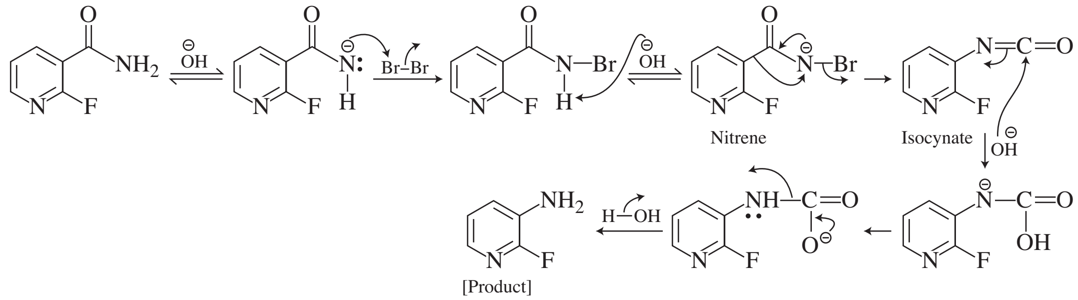


100. (A)

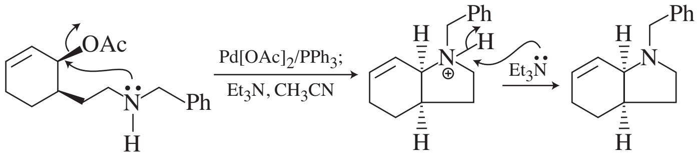


The asymetric synthesis of chiral secondary allylic alcohol or their corresponding epoxide.

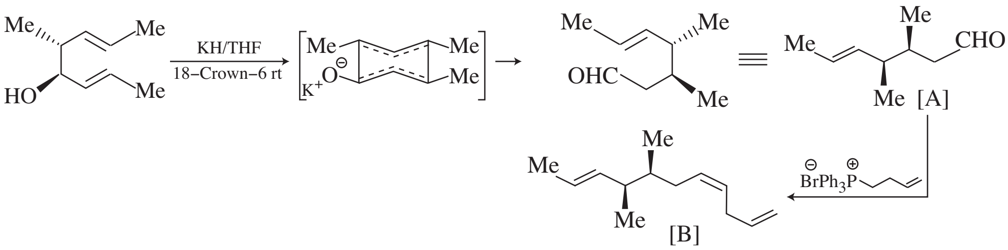
101. (A)



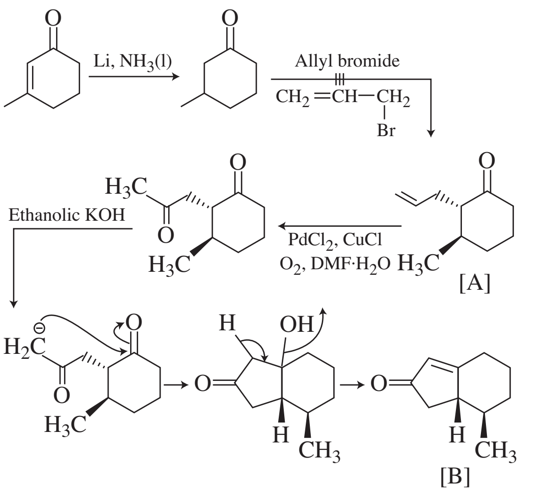

102. (B)



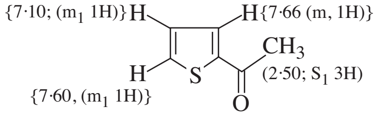

103. (B)




104. (D)




105. (D)



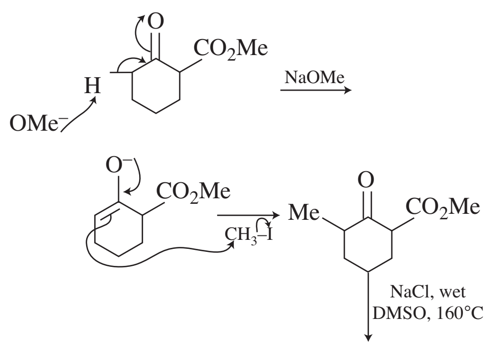

IR → 1680 → –C(=O)– (Carbonyl group)

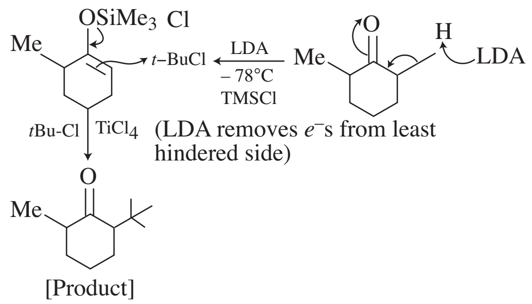
$^1H_{-NMR}$ → δ 7·66 (M, 1H), 7·60 (M, 1H) 7·10 (M, 1H), 2·50 (S, 3H)

$^{13}C_{-NMR}$ → δ·190, 144, 134, 132, 128, 28

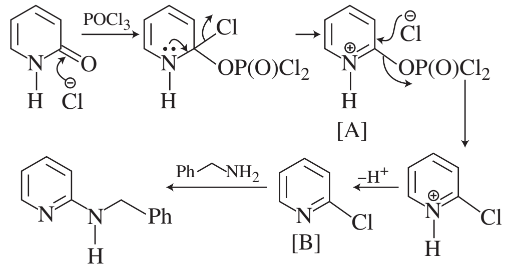
M/Z → 126 [M$^+$, 100%], 128 [M$^+$ + 2, 4·9%]

106. (A)

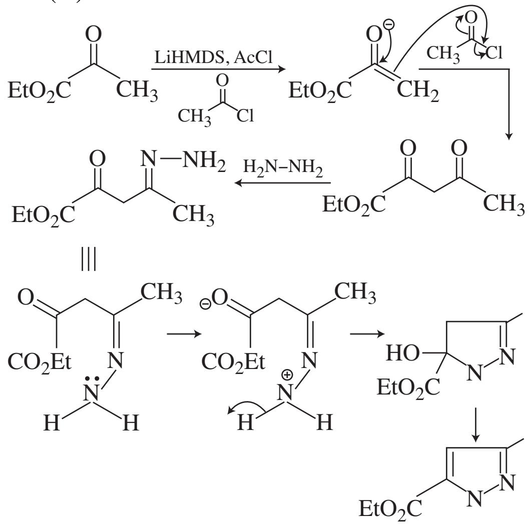




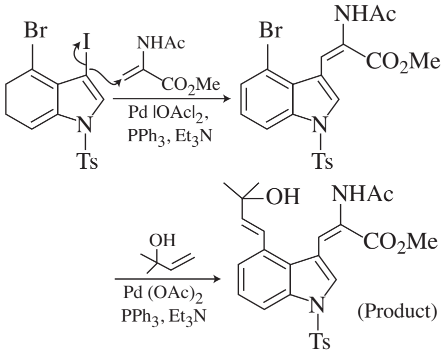

107. (C)



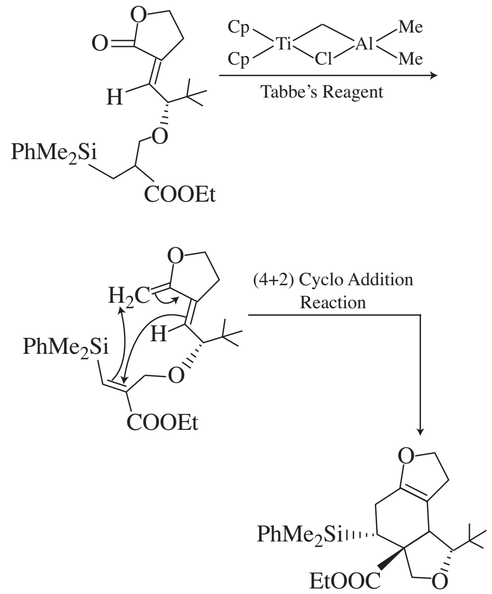
108. (A)



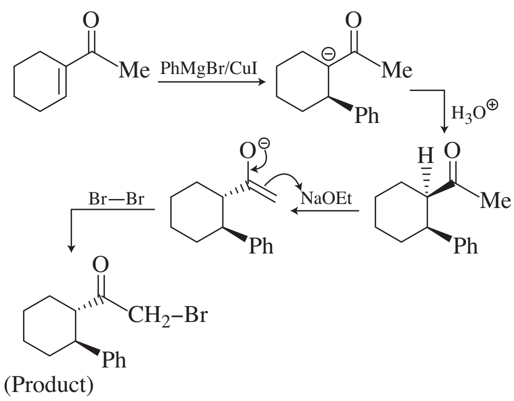
109. (D)



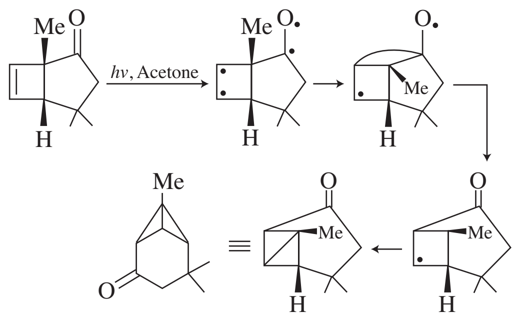

110. (C)



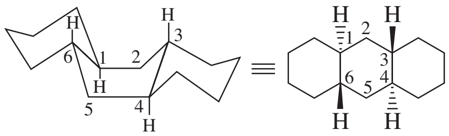

111. (A)




112. (A)

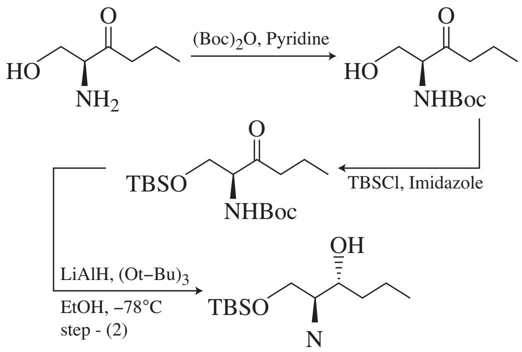


113. (D)



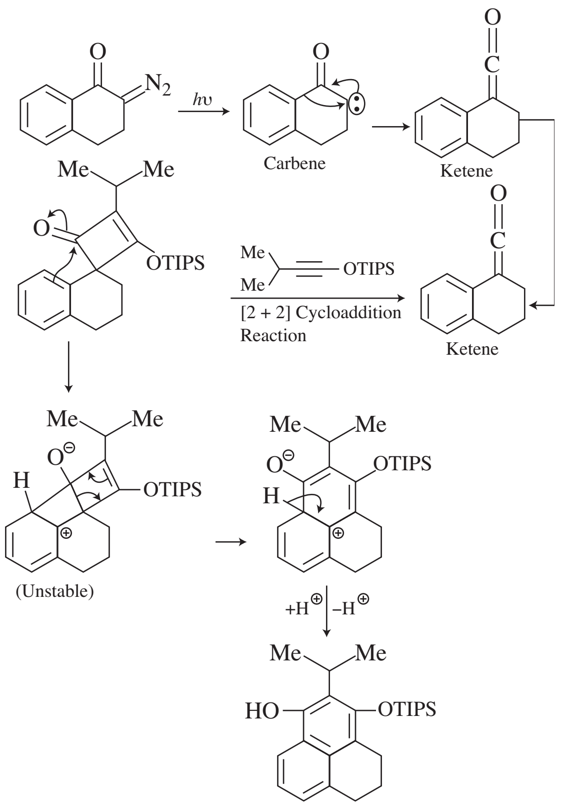
(Chair-Boat-Chair Conformation)

114. (C)

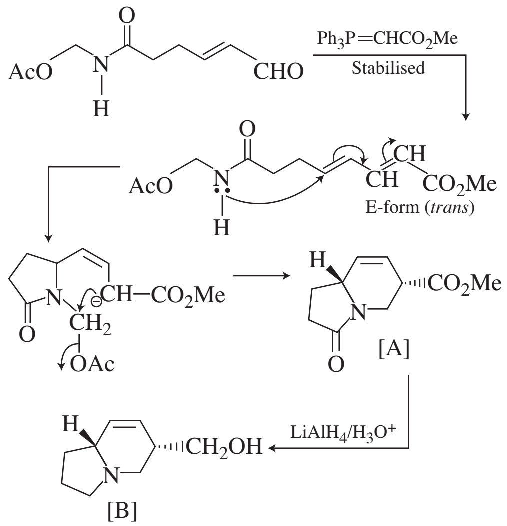



Step 2 : Chelation-controlled reduction of the ketone produces the anti-alcohol diastereo selectivity.

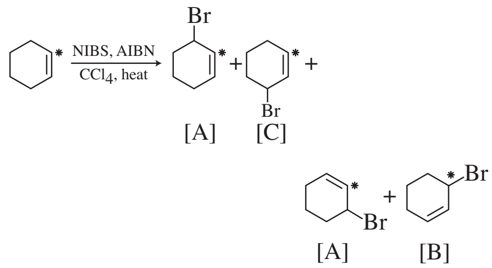
115. (D)




116. (B)

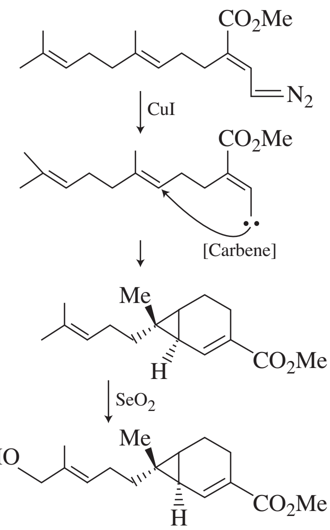



117. (C) NIBS gives bromination at allylic position. In this reaction the ratio of A : B : C = 2 : 1 : 1.

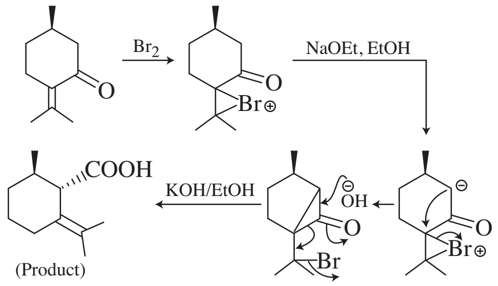



Ratio of A : B : C = 2 : 1 : 1.

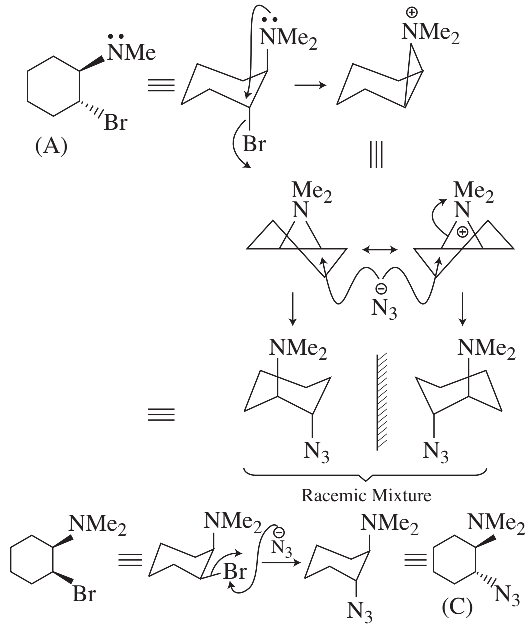
118. (A)



119. (B)




120. (B) A gives Racemic mixture of 'C' and 'B' gives optically pure 'C'.

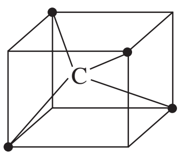



121. (B) In diatomic molecule only σ and π-bond is possible

$\sigma_{(gerade)}$ spherical $\xrightarrow{180°}$ No change occur.

$\pi_{(ungerade)}$ $\xrightarrow{180°}$ change in sign occur.

122. (D)




| order = 24 | E | $8C_3$ | $3C_2$ | $6S_4$ | $6\sigma_d$ |
|---|---|---|---|---|---|
| No. of unshifted atom | 5 | 2 | 1 | 1 | 3 |
| Contribution per atom | 3 | 0 | – 1 | – 1 | 1 |
| Reducible representation | 15 | 0 | – 1 | – 1 | 3 |

$$nA_1 = \frac{1}{24}[15 \times 1 \times 1 + 0 \times 1 \times 8 + (-1) \times 1 \times 3 + (-1) \times (+1) + 6 + 3 \times 1 \times 6] = 1$$

$$nA_2 = \frac{1}{24}[15 \times 1 \times 1 + 0 \times 1 \times 8 + (-1) \times 1 \times 3 + (-1) \times 1 \times 6 + 3 \times (-1) \times 6] = 0$$

$$nE = \frac{1}{24}[15 \times 1 \times 1 + 0 \times (-1) \times 8 + (1) \times 2 \times 3 + (-1) \times (0) \times 6 + 3 \times 0 \times 6] = 1$$

$$nT_1 = \frac{1}{24}[15 \times 1 \times 1 + 0 \times 0 \times 8 + (-1) \times (-1) \times 3 + (-1) \times 1 \times 6 + 3 \times (-1) \times 6] = 1$$

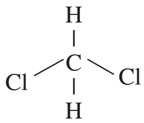
$$nT_2 = \frac{1}{24}[15 \times 1 \times 1 + 0 \times 0 \times 8 + (-1) \times (-1) \times 3 + (-1) \times (-1) \times 6 + 3 \times 1 \times 6] = 3$$

So reducible representation.

$A_1 + E + T_1 + 3T_2$

Since IR activity is count by $x, y, z$ co-ordinate so $T_2$ mode is IR active by using character table.

123. (B) Explanation $CH_4$, $CCl_4$ → Spherical mols. (All Td mols are spherical).

**$CH_2Cl_2$** ⇒  has $C_2V$ point group and thus is assymmetric top rotor.


Remaining $CHCl_3$ is symmetric top rotor.

Source–Molecular spectroscopy by Banwell.

124. (D) We know that

$$\upsilon = \frac{\gamma\beta_0}{2\pi}$$

and $g \propto \upsilon$

or $$\frac{g_H}{g_N} = \frac{\upsilon_H}{\upsilon_N}$$

$$= \frac{5{\cdot}6}{0{\cdot}4} \times \frac{700}{x} = 50 \text{ MHz}$$

125. (B) The dissociation energy $g$ a diatomic molecule is calculated from vibration spectroscopy (IR)

$$\overline{De} = \frac{\omega e\,(1 - x_e^2)}{4\,x_e}$$

126. (A) Term Symbol = $^{2S+1}LJ$

For orbital $l = 0$   0

$\boxed{1}$ $\boxed{1}$
2s   3s

$$L = 0 \rightarrow S, S = \frac{1}{2} + \frac{1}{2} = 1$$

$$2S + 1 = 2 \times 1 \times 1 = 3$$
$$J = L + S$$
$$= 0 + 1 = 1$$

Term symbol = $^3S_1$

127. (C) A slater determinent always corresponds to a particular spin state.

* Slater determinate changes by changing sign upon exchange of 2 electron.

128. (B) Energy $(\Delta_1) = \frac{\eta_x^2 h^2}{8m\, l_x^2}$ for 1 - D Box

Similarly, $\Delta_2 = \frac{h^2}{8m}\left[\frac{\eta_x^2}{L_x^2} + \frac{\eta_y^2}{L_y^2}\right]$

$$\Delta_3 = \frac{h^2}{8m}\left[\frac{\eta_x^2}{L_x^2} + \frac{\eta_y^2}{L_y^2} + \frac{\eta_z^2}{L_z^2}\right]$$

So, **1D BOX** **2D BOX** **3D BOX**

$$\Delta = \frac{n_x^2 h^2}{8m\, l_x^2} \quad \frac{h^2}{8m}\left[\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2}\right] \quad \frac{h^2}{8m}\left[\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right]$$

| | | | |
|---|---|---|---|
| Ground state | $n = 1$ | $n_x = 1, n_y = 1$ | $n_x = 1, n_y = 1, n_z = 1$ |
| Ist excited state | $n = 2$ | $n_x = 2, n_y = 1$ | $n_x = 2, n_y = 1, n_z = 1$ |

Energy difference

$$= \frac{3h^2}{8mL^2} \quad \frac{3h^2}{8mL^2} \quad \frac{3h^2}{8mL^2}$$

So, $\Delta_1 = \Delta_2 = \Delta_3$

129. (C) $\langle x \rangle = 0$

and $\langle p \rangle = 0$

Reference ⇒ Physical chemistry by 'Alkins'.

130. (D) $x.(x, P_x) = x.i\hbar = 0$

Since = $[x.P_x] = i\hbar$

When position vector commulate with constant term, it is always zero.

131. (C)

$CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2; K_1$ ...(1)

$CO + H_2O \rightleftharpoons CO_2 + H_2; K_2$ ...(2)

$CH_4 + H_2O \rightleftharpoons CO + 3H_2; K_3 = ?$ ...(3)

Substracting equation (1) and (2), we get Eqn. (3) and According to equilibrium

$$\boxed{K_3 = \frac{K_1}{K_2}}$$

132. (D) $\Delta S = C_v \ln\frac{T_2}{T_1} + R\ln\frac{V_2}{V_1}$

In this case, for process B → C,

$$\frac{T_2}{T_1} = \frac{T_3}{T_2}$$

and $\frac{V_2}{V_1} = \frac{V_1}{V_2}$

$$\therefore \quad \Delta S = C_v \ln\frac{T_3}{T_2} + R\ln\frac{V_1}{V_2}$$

$$\Delta S = \int_{T_2}^{T_3}\frac{dV}{T} + \int_{T_2}^{T_3}\frac{PdV}{T}$$

If $C_v \ln\left(\frac{T_3}{T_2}\right) = 0$

then, $(\Delta S)_{B\rightarrow C} = R\ln\frac{V_1}{V_2}$

133. (B) Gibbs-Duhem equation gives relationship between chemical potential and component of a thermodynamic system

$$\sum_{i=1}^{I} n_i\, d\mu_i = -SdT + VdP$$

134. (D) According to Transition state theory

$q_{Translational} \propto T^{3/2}$

$q_{V/b} \propto T^{\circ}$

$q_{rotational} \propto T$ (linear)

$q_{rotational} \propto T^{3/2}$ (Non-linear)

Linear + Non-linear ⇌ Non-linear T.S.

Pre exponential factor

$$A = \frac{k_b T}{h} \times \frac{Q^{\#}}{Q_a . Q_b}$$

or $A = \frac{T^1 \cdot T^{3/2} \times T^{3/2} \cdot T^0}{T^1 \cdot T^{3/2} \cdot T^{3/2}\, T^{3/2}}$

$$= T^{-1\cdot 5}$$

135. (B) **Explanation** : Primary salt effect

$$\log\frac{k}{k_0} = 2A\,|Z_+ Z_-|\sqrt{I}$$

where A = 0·51

$$\log\frac{k}{k_0} = 2 \times 0{\cdot}51\, Z_+ Z_- \sqrt{I}$$

$$= -4 \times 0{\cdot}51\sqrt{I}$$

$$Z_+ Z_- = -2$$

For option (B); + 2 × – 1 = – 2

136. (C) From Longmuir Chemisorption isotherm dissociation isotherm

$$\theta = \frac{k \cdot [P]^{1/n}}{1 + k\,[P]^{1/n}}$$

For Diatomic molecule $n = 2$

$$\theta = \frac{k \cdot [H_2]^{1/2}}{1 + k\,[H_2]^{1/2}}$$

So, at low pressure

$$\boxed{\theta = k\,[H_2]^{1/2}}$$

or $\boxed{\theta \propto [H_2]^{1/2}}$

137. (C) We know that,

$$\Delta S = nf\left(\frac{\partial \in}{\partial T}\right)_P$$

or $\boxed{\left(\frac{\partial \in}{\partial T}\right)_P = \frac{\Delta S}{nf}}$

Temperature dependence of Electrochemical cell.

138. (B) F = Partition function

$$= AVe^{BT}$$

where, A.V. = Constant.

Average Energy ($\overline{E}$)

$$= -\frac{\partial}{\partial \beta} mf \qquad \ldots(1)$$

But $\beta = \frac{1}{k_B T}$

$$\frac{\partial \beta}{\partial T} = -\frac{1}{k_B T^2}$$

$$\partial \beta = -\frac{\partial T}{k_B T^2}$$

then $\overline{E} = k_B T^2 \cdot \frac{\partial}{\partial T} mf$

$$= k_B T^2 \cdot \frac{\partial}{\partial T} \cdot m\,(Ave^{BT})$$

$$= k_B T^2 \frac{\partial}{\partial T}[mA + mU + BT]$$

$$\overline{E} = k_B T^2 \frac{\partial}{\partial T}[BT]$$

$$\boxed{\overline{E} = k_B T^2 B}$$

139. (B) For indistinguisable particles, the canonical partition function over-counts the number of microstates by the total number of possible swaps among the particle identities 'N' correcting this

$$Q = \frac{q^N}{N!}$$

140. (A) $\frac{\partial P}{\partial t} = k\,[C_2H_5]^2 \qquad \ldots(1)$

Applying steady state Approximation on $C_2H_5$

$$\frac{\partial [C_2H_5]}{\partial t} = 2k_1 I_a - 2k_{-1}[C_2H_5]^2 - 2k_2[C_2H_5]^2$$

$$2k_1 I_a = 2k_{-1}[C_2H_5]^2 + 2k_2[C_2H_5]^2$$

$$[C_2H_5]^2 = \frac{2k_1 I_a}{2(k_{-1} + k_2)}$$

Substituting above value in eq. (1)

$$\frac{\partial P}{\partial t} = \frac{kk_1 I_a}{k_{-1} + k_2} \text{ or } \boxed{\frac{\partial P}{\partial t} \propto I}$$

141. (C) Basic principle of conductometric titration; when faster moving ion is replace by slower moving ion the conductance decreases linearly.

142. (C) Since $\overline{N} = \frac{1}{1 - P}$

P = Probability of polymer link

$\overline{N}$ = Average size

(a) $10 = \frac{1}{1 - P} \Rightarrow P = 0{\cdot}9$

(b) $50 = \frac{1}{1 - P} \Rightarrow P = 0{\cdot}98$

(c) $100 = \frac{1}{1 - P} \Rightarrow P = 0{\cdot}99$

143. (D) Electrostatic repulsion among double-layered colloidal particle

**Reference :** Physical chemistry by Puri, Sharma and Pathania.

144. (C) The mean

$$\overline{x} = \frac{[1{\cdot}71 \times 10^{-5} + 1{\cdot}77 \times 10^{-5} + 1{\cdot}79 \times 10^{-5} + 1{\cdot}73 \times 10^{-5}}{4}$$

$$= \frac{[1{\cdot}71 \times 1{\cdot}77 + 1{\cdot}79 + 1{\cdot}73] \times 10^{-5}}{4}$$

$$= \frac{7{\cdot}0 \times 10^{-5}}{4} = 1{\cdot}75 \times 10^{-5}$$

Standard Deviation ($s$)

$$= \sqrt{\frac{(1{\cdot}71 - 1{\cdot}75)^2 \times 10^{-10} + (1{\cdot}77 - 1{\cdot}75) \times 10^{-10} + (1{\cdot}79 - 1{\cdot}75)^2 \times 10^{-10} + (1{\cdot}73 - 1{\cdot}75)^2 \times 10^{-10}}{(4 - 1)}}$$

$$= \sqrt{\frac{(0{\cdot}04)^2 + (0{\cdot}03)^2 + (0{\cdot}04)^2 + (0{\cdot}02)^2 \times 10^{-10}}{3}}$$

$$= \left[\sqrt{\frac{{\cdot}0016 + 0{\cdot}0009 + 0{\cdot}0016 + 0{\cdot}0004}{3}}\right] \times 10^{-5}$$

$$= \sqrt{\frac{0{\cdot}0045}{3}} \times 10^{-5}$$

$$(s) = \sqrt{0{\cdot}0015} \times 10^{-5}$$

On solving, we get standard deviation data of Range = $0{\cdot}030 \times 10^{-5} - 0{\cdot}039 \times 10^{-5}$

145. (D) From Bragg's Equation

$$n\lambda = 2d \sin \theta \qquad \ldots(1)$$

and
$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{a^2} + \frac{l^2}{a^2}$$

or
$$d^2 = \frac{a^2}{h^2 + k^2 + l^2}$$

$$d^2 = \frac{a^2}{1^2 + 1^2 + 1^2}$$

$$d^2 = \frac{a^2}{3}$$

$$\boxed{d = \frac{a}{\sqrt{3}}}$$

Putting the value of '*d*' in equation (1)

$$2 \times 1 = 2 \times \frac{a}{\sqrt{3}} \sin 30°$$

$$2 = 2 \times \frac{a}{\sqrt{3}} \cdot \frac{1}{2}$$

$$a = 2\sqrt{3}$$

$$= 2 \times 1{\cdot}732$$

$$\boxed{a = 3{\cdot}464 \text{ Å}}$$

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