Booklet Serial No. : 263

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TEST BOOKLET

AP (CC) CHEMISTRY—2018

Time Allowed : 2 Hours] [Maximum Marks : 100

All questions carry equal marks.

INSTRUCTIONS

1. Immediately after the commencement of the examination, you should check that test booklet does not have any unprinted or torn or missing pages or items, etc. If so, get it replaced by a complete test booklet.
2. Write your Roll Number only in the box provided alongside. Do not write anything else on the Test Booklet.
3. This Test Booklet contains **100** items (questions). Each item comprises four responses (answers). Choose only one response for each item which you consider the best.
4. After the candidate has read each item in the Test Booklet and decided which of the given responses is correct or the best, he has to mark the circle containing the letter of the selected response by blackening it completely with Black or Blue ball pen. In the following example, response "C" is so marked :

   Ⓐ Ⓑ ● Ⓓ

5. Do the encoding carefully as given in the illustrations. While encoding your particulars or marking the answers on answer sheet, you should blacken the circle corresponding to the choice in full and no part of the circle should be left unfilled. After the response has been marked in the ANSWER SHEET, no erasing/fluid is allowed.
6. You have to mark all your responses ONLY on the ANSWER SHEET separately given according to 'INSTRUCTIONS FOR CANDIDATES' already supplied to you. *Responses marked on the Test Booklet or in any paper other than the answer sheet shall not be examined.*
7. All items carry equal marks. Attempt all items. Your total marks will depend only on the number of correct responses marked by you in the Answer Sheet. There will be negative marking and 1/4 (0.25) of the marks will be deducted as penalty for wrong answers.
8. Before you proceed to mark responses in the Answer Sheet fill in the particulars in the front portion of the Answer Sheet as per the instructions sent to you.
9. If a candidate gives more than one answer, it will be treated as a wrong answer even if one of the given answers happens to be correct.
10. After you have completed the test, hand over the Answer Sheet only, to the Invigilator.

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P.T.O.

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1. Which of the following is an expression for thermodynamic equation of state ?

(A) $\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$ (B) $\Delta F = \Delta H + T\left(\frac{\partial(\Delta F)}{\partial T}\right)_P$

(C) $\Delta A = \Delta E + T\left(\frac{\partial(\Delta A)}{\partial T}\right)_V$ (D) $\mu_i - T\left(\frac{\delta\mu_i}{\partial T}\right) = \bar{H}_i$

2. Which of the following statements is *correct* for Joule's law ?

(A) For an ideal gas the change of enthalpy with pressure at constant temperature is zero

(B) Entropy of a pure and crystalline substance (this means the substance is pure with respect to both composition and orientation in the solid) should be zero at 0 K at all pressures

(C) Rate of expansion of solid with temperature should become zero at 0 K

(D) Energy content of an ideal gas is independent of volume at constant temperature

3. Which of the following mixture of fuel gases is used to have the maximum flame temperature about 4900°K ?

(A) N_2O and C_2H_2 (B) O_2 and C_2H_2

(C) O_2 and $(CN)_2$ (D) H_2 and air

4. Which of the following single cell battery has the highest potential ?

(A) Lead-acid battery (B) Lithium ion battery

(C) Nickel metal hydride battery (D) Alkaline cell battery

5. Which of the following is an example of electrolytic concentration cell without transference reversible to anion ?

(A) $Pt|H_2(g), HCl(a_1) : HCl(a_2), H_2(g)|Pt$

(B) $Pt|H_2(g)\ HCl(a_1), AgCl(s), Ag|Ag, AgCl(s), HCl(a_2), H_2(g)|Pt$

(C) $Zn|ZnSO_4(a_1), PbSO_4(s), Pb|Pb, PbSO_4(s), ZnSO_4(a_2)|Zn$

(D) $Ag|AgCl(s), HCl(a_1)\ H_2(g), Pt|Pt, H_2(g), HCl(a_2), AgCl(s)Ag$

6. Which of the following statements is *not* correct ?

(A) For a uni-univalent electrolyte (KCl) the molality of each ion is 'm' and its valency unity assuming complete ionisation the ionic strength of the solution is 'm'.

(B) For a uni-bivalent electrolyte (K_2SO_4) assuming complete ionisation the molality of a negative ion is m and its valency two, whereas the molality of a positive ion is $2m$ and its valency unity, the ionic strength of the solution is $2m$.

(C) For a bi-univalent electrolyte ($BaCl_2$) assuming complete ionisation the molality of a positive ion is m and its valency two whereas the molality of a negative ion is $2m$ and its valency unity, the ionic strength of the solution is $3m$.

(D) For a bi-bivalent electrolyte ($MgSO_4$) the molality of each ion is m and its valency two for each ion, the ionic strength of the solution is $4m$. (The electrolyte is assumed to be completely ionised)

7. Which of the following statements is *not* correct ?

(A) NMR as well as optical absorption and vibrational spectroscopy can be used to study chemical kinetics reaction occurring in microsecond and on longer time scale.

(B) Perturbation, relaxation methods are used to study the reaction kinetics where equilibrium is perturbed such that the system is no longer at equilibrium. Any technique such as pressure, pH or temperature perturbation is used to study reaction kinetics.

(C) Ultra fast reaction kinetics associated with vision, photosynthesis, atmospheric pressures and charge carrier dynamics in semiconductors can be studied by stop flow techniques on time scale as short as 10^{-3}s.

(D) Flesh photolysis technique using light pulses as short as 10 fentosecond (10^{-14} s) in the visible region of the electromagnetic spectrum are used to study reaction dynamics.

8. The effect of ionic strength on rate constants of ionic reactions has been studied. Which of the following reactions gives a zero slope (i.e. $Z_A \cdot Z_B = 0$) when $\log \frac{k}{k_0}$ is plotted with μ :

(A) $S_2O_8^{-\,-} + \bar{I} \rightarrow 2SO_4^{-2} + I_2$

(B) $[Cr(NH_2CONH_2)_6]^{+3} + 6H_2O \rightarrow [Cr(H_2O)_6]^{+3} + 6NH_2CONH_2$

(C) $[Co(NH_3)_5Br]^{+2} + O\bar{H} \rightarrow [Co(NH_3)_5(OH)]^{+2} + B\bar{r}$

(D) $NH_4^{+} + CN\bar{O} \rightarrow CO(NH_2)_2$

9. The proposed mechanism for dehydrogenation of ethane $CH_3 . CH_3 \rightarrow CH_2 = CH_2 + H_2$ is as :

$CH_3 . CH_3 \xrightarrow{k_1} 2\dot{C}H_3$; $\dot{C}H_3 + CH_3CH_3 \xrightarrow{k_2} CH_4 + \dot{C}H_2CH_3$

$\dot{C}H_2CH_3 \xrightarrow{k_3} CH_2 = CH_2 + \dot{H}$; $\dot{H} + CH_3CH_3 \xrightarrow{k_4} H_2 + \dot{C}H_2CH_3$;

$\dot{H} + \dot{C}H_2CH_3 \xrightarrow{k_5} CH_3CH_3$

The steady state approximation concept applied to get $\frac{d(\dot{C}H_2CH_3)}{dt} =$

(A) $2k_1[CH_3CH_3] - k_2[\dot{C}H_3][CH_3CH_3]$

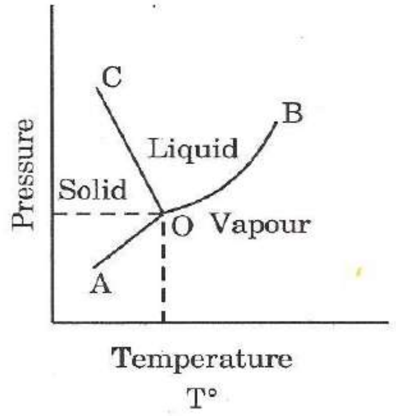
(B) $k_3[\dot{C}H_2CH_3] - k_4[\dot{H}][CH_3CH_3] - k_5[\dot{H}][\dot{C}H_2CH_3]$

(C) $k_2[\dot{C}H_3][CH_3CH_3] - k_3[\dot{C}H_2CH_3] + k_4[\dot{H}][CH_3CH_3] - k_5[\dot{H}][\dot{C}H_2CH_3]$

(D) $k_2[\dot{C}H_3][CH_3CH_3] - k_1[CH_3CH_3] + k_3[\dot{C}H_2CH_3]$

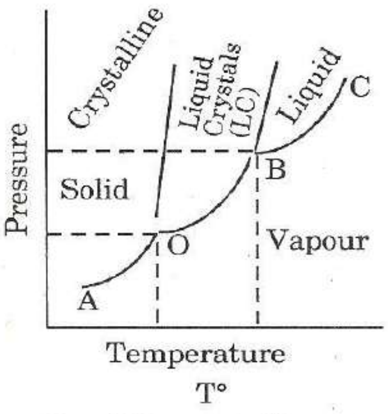
10. The schematic phase diagrams of some systems are given below. Identify the phase diagram of a substance which undergoes a mesomorphic change :

(A)



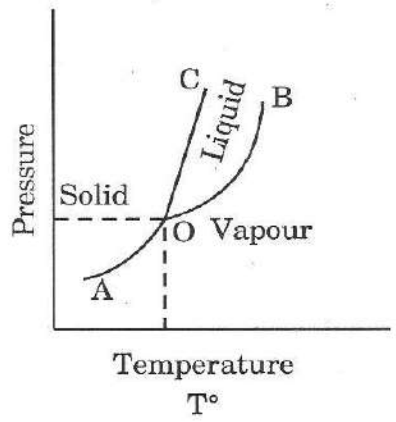
O is a triple point

(B)



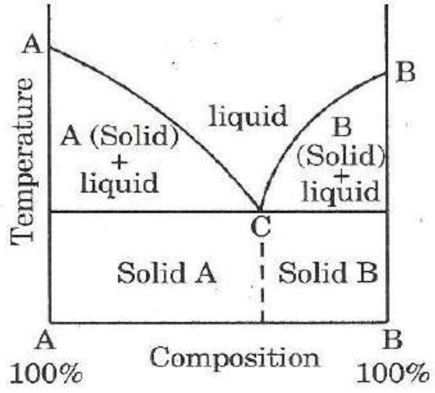
O and B are triple points
LC = liquid crystals

(C)



O is a triple point

(D)



C is a eutectic point
A and B are solids and
represent melting points

11. Which of the following is a Hamiltonian for lithium atom ?

(A) $$\hat{H} = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2 + \nabla_3^2) + \frac{1}{4\pi \in_0}\left[-\frac{3e^2}{r_1} - \frac{3e^2}{r_2} - \frac{3e^2}{r_3} + \frac{e^2}{r_{1,2}} + \frac{e^2}{r_{2,3}} + \frac{e^2}{r_{3,1}}\right]$$

(B) $$\hat{H} = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) + \frac{1}{4\pi \in_0}\left[-\frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{r_{1,2}}\right]$$

(C) $$\begin{aligned}\hat{H} = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2 + \nabla_3^2) + \frac{1}{4\pi \in_0}\Bigg[&-\frac{e^2}{r_{A_1}} - \frac{e^2}{r_{A_2}} - \frac{e^2}{r_{A_3}} - \frac{e^2}{r_{B_1}} - \frac{e^2}{r_{B_2}} - \frac{e^2}{r_{B_3}} + \\ &\frac{e^2}{r_{1,2}} + \frac{e^2}{r_{1,3}} + \frac{e^2}{r_{2,3}} + \frac{e^2}{r_{AB}}\Bigg]\end{aligned}$$

(D) $$\hat{H} = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) + \frac{1}{4\pi \in_0}\left[-\frac{e^2}{r_{A_1}} - \frac{e^2}{r_{A_2}} - \frac{e^2}{r_{B_1}} - \frac{e^2}{r_{B_2}} + \frac{e^2}{r_{1,2}} + \frac{e^2}{r_{AB}}\right]$$

12. A wave function is *not* acceptable because :

(A) it is continuous
(B) it has a continuous slope
(C) it is single valued
(D) it is infinite

13. Which of the following statements is *not* correct ?

(A) The energy corresponding to $n = 1$ i.e. $E_1 = \frac{h^2}{8\,ma^2}$ is called zero point energy of the particle in one-dimensional box of infinite height. The zero point energy is finite and not equal to zero and particle inside the box is not at rest even at 0 K. The occurrence of zero point energy implies uncertainty in position.

(B) The total energy depends upon the sum of the squares of three quantum numbers i.e. $E = E_x + E_y + E_z = \frac{(n_x^2 + n_y^2 + n_z^2)h^2}{8ma^2}$. The total energy is $E = \frac{12h^2}{8ma^2}$; the energy level is non-degenerate.

(C) The momentum operator is $P = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$.

(D) Schrödinger equation is $H\psi_n = E_n\psi_n$ where E_n are eigen values of the Hamiltonian operator H and $H = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + U$.

14. The vibrational partition function with zero point energy is :

(A) $q = \frac{(2\pi mkT)^{3/2}.V}{h^3}$

(B) $q = \frac{e^{-\beta hc\bar{\upsilon}/2}}{1 - e^{\beta hc\bar{\upsilon}}}$

(C) $q = \sum_n g_n e^{-\beta hcE_n}$

(D) $q = \frac{1}{1 - e^{\beta hc\bar{\upsilon}}}$

15. Which of the following statements is *not* correct ?

(A) Helmholtz energy A(A = U − TS) and its relationship to the canonical partition function gives $A = kT \ln q$. With this knowledge and working on the system of ideal gases one could not obtain the gas law $PV = nRT$, hence the law remain empirical as given by Boyle, Charles, Gay Lussac.

(B) Gibbs energy (thermodynamic expression G = H − TS) is used to obtain statistical expression for Gibbs energy $G = nRT \ln\left(\frac{q}{N}\right)$. It provides insight into the origin of Gibbs energy. The partition function quantifies the number of states that are accessible at a given temperature.

(C) The Sackur-Tetrode equation $S = \frac{5}{2}nR + nR \ln V + \frac{3}{2}nR \ln T - nR \ln\left(\frac{n^{2/3}.N_A^{2/3}h^2}{2\pi mk}\right)$ gives first and fourth terms which are not explainable from classical thermodynamics. Their contribution is important from statistical perspective.

(D) The reason for the systematic discrepancy between calculated and experimental entropies for molecular system such as CO, is called residual entropy or entropy associated with molecular orientation in the molecular crystal at low temperature.

16. Which of the following statements is *not* correct ?

(A) In Maxwell-Boltzmann statistics the particles are assumed to be distinguishable and any number of particles may occupy the same energy level. The particles which follow Maxwell-Boltzmann statistics are called maxwellons or boltzons.

(B) In Bose-Einstein statistics the particles are indistinguishable and any number of particles may occupy a given energy level. This statistics is obeyed by particles having integral spin such as H_2, N_2, D_2, He^4 and photons. Particles obeying B–E statistics are called bosons.

(C) In Fermi-Dirac statistics the particles are indistinguishable and only one particle may occupy a given energy level. This statistics is obeyed by particles with half integral spins protons, electrons, He^3, NO. The particles which obey F – D statistics are called fermions.

(D) An ensemble is defined as a collection of identical units or replicas of a system. An ensemble in which V, T and N are constant is called grand-canonical ensemble.

17. Which of the following statements is *not* correct ?

(A) An absorption spectrum of an organic compound in its ethanolic solution does not show any absorption beyond 200 nm in UV region. This shows that the compound is not aromatic.

(B) An absorption band due to $\pi \rightarrow \pi^*$ transition in UV region generally gets shifted to longer wavelength i.e. red shift or bathochromic shift with increase in polarity of the solvent.

(C) An absorption band due to $n \rightarrow \pi^*$ transition in UV region gets shifted to shorter wavelength i.e. blue shift or hypsochromic shift with increase in polarity of the solvent.

(D) Three characteristic absorption bands of benzene due to its π-electron system are observed in UV region at about 180 nm ($\in_{max} = 47000$), 200 nm ($\in_{max} \sim 7000$) and 260 nm ($\in_{max} \sim 220$).

However the absorption band due to C_6H_6 in UV region get appreciably shifted to longer wavelength due to change in polarity of the solvent. The vibrational structure of B-band is destroyed almost completely.

18. Which of the following statements is *not* correct ?

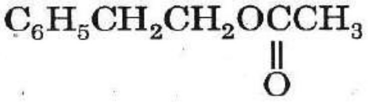
(A) In nmr spectroscopy a proton shows an absorption peak at 600 cps with reference to TMS at 60 MHz instrument. The same proton will absorb at $\frac{40}{60} \times 100$ i.e. 400 cps on 40 MHz instrument. Similarly this proton will absorb at 1000 cps with reference to TMS on 100 MHz instrument.

(B) With increase in electronegativity of a substituent the absorption signal due to proton gets shifted to the right i.e. upfield or diamagnetic shift.

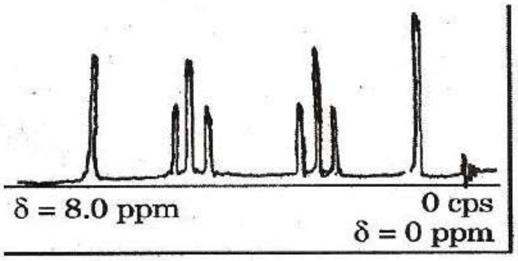
(C) The relationship of one group of nuclei to other nearby groups of nuclei is known from finer details of the absorption signal.

(D) The relative number of nuclei in each different environment is known from relative areas under the absorption curve for the various signals.

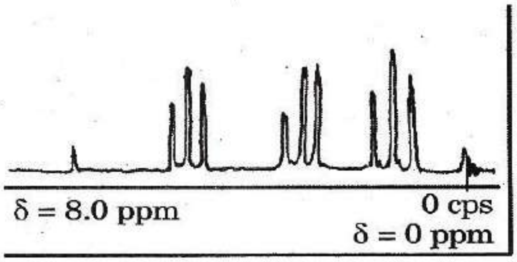
19. The nmr spectra of compounds CH_3CH_2OH; $CH_3CH_2CH_2.ON_2$; CH_3CHO and $C_6H_5CH_2CH_2O\underset{\underset{O}{\|}}{C}CH_3$ are given below. Which of the following first order spectrum matches with the expected spectrum of the compound CH_3CHO ?



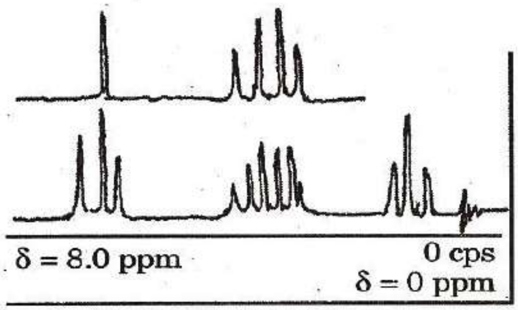
(A)



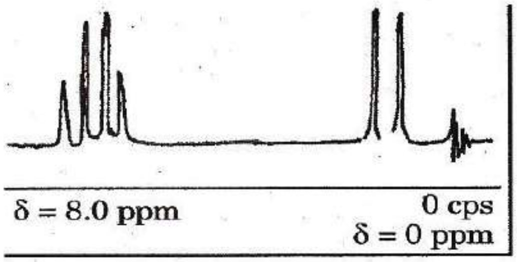
(B)



(C)

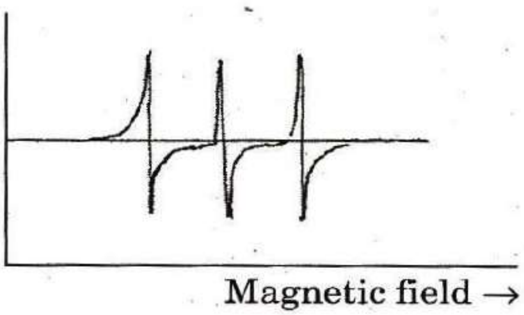


(D)

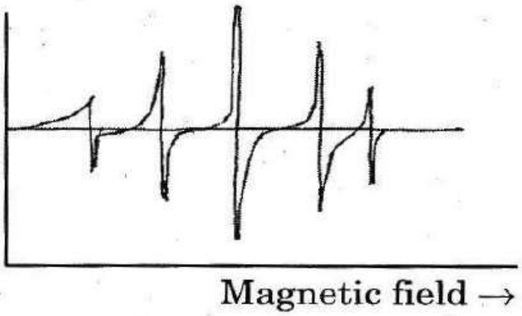


20. Which of the following is an esr spectrum matches with the expected spectrum of benzene radical anion $(C_6\bar{H}_6)$. An esr spectra of few compounds $\dot{C}H_3$ radical, $(SO_3)_2N\bar{O}$ $CH_3\dot{C}HOH$ radical and $C_6H_6^-$ are given below :

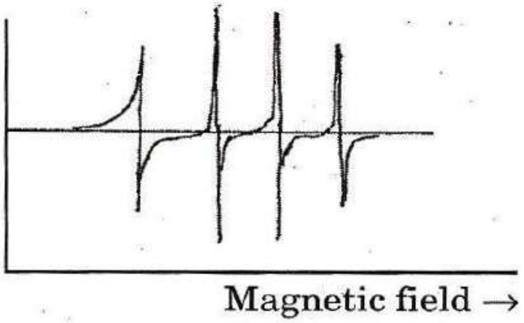
(A)



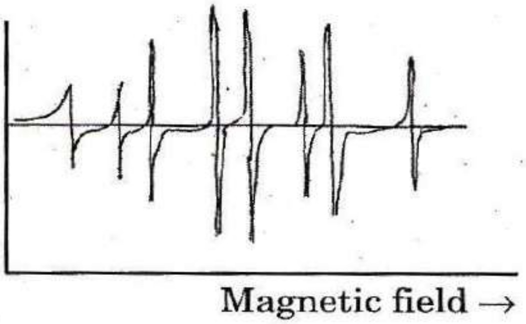
(B)



(C)



(D)



21. Which of the following statements is *not* correct ?

(A) For preliminary examination of an infrared absorption spectrum, an absorption spectrum is divided broadly in three parts (*i*) group frequency region 4000–1300 cm^{-1}, (*ii*) skeletal vibration frequency region 910-650 cm^{-1} and (*iii*) fingerprint region 1300-910 cm^{-1}.

(B) The absence of absorption in 1850-1540 cm^{-1} region excludes a structure containing a carbonyl group.

(C) The lack of a strong absorption band in 910-650 cm^{-1} region generally indicates an aromatic structure.

(D) Overtones and combination bands are characteristically weak except where Fermi resonance occurs. These bands of lower frequency frequently appear in high frequency region of the spectrum.

22. In which of the following compounds a no bonded hydroxyl absorption band is observed even in absorption spectrum of neat sample ?

(A) *o*-hydroxy acetophenone (B) *p*-hydroxy acetophenone

(C) 2, 6-di-*t*-butyl phenol (D) *n*-butyl alcohol

23. Which of the following statements is *not* correct ?

(A) Protassium oleate is added incrementally to water at 50°, it dissolves to form K^+ and oleate ions and the surface tension decreases continuously from that of pure water. When the concentration of potassium oleate is reached 0.0035 M, a break appears in the surface tension-concentration curve and thereafter surface tension levels off at an almost constant value ~ 30 dynes/cm.

(B) The discontinuity at this concentration (0.0035 M) is also observed in osmotic pressure, conductance measurements.

(C) The above observation is explained on the association of oleate ions into clusters, called micelles. The initial concentration at which micelles appear is called critical micelles concentration (CMC). Below CMC the oleate ion exists in solution as individual entities (ions).

(D) The micellisation of an association colloid occurs at definite concentration at each temperature. An increase in temperature lowers CMC. The presence of electrolyte raises the CMC. The micelles once formed cannot be destroyed even by diluting the solution.

24. Which of the following statements is *not* correct ?

(A) The number of atoms in a primitive cubic cell for example that of polonium is one. [Each atom at the corners of a cube is shared by 8 unit cells i.e. $n = 8 \times \frac{1}{8} = 1$]

(B) The body centred cubic cell contains $n = 8 \times \frac{1}{8} + 1 = 2$. [Each b.c.c. has one atom in the body and 8 corners of the cube as before].

(C) The face centred cubic cell contains $n = 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$ [Each face of a cube has one atom shared by two unit cells. There are 6 faces of a cube and eight corners as before].

(D) The diamond lattice has 8 atoms on the 8 corners, each shared by 8 unit cell. Also there are 6 atoms on the faces, each shared by two unit cells as before. There are two atoms in the unit cell. Thus, $n = 8 \times \frac{1}{8} + 6 \times \frac{1}{2} + 2 = 6$ atoms.

25. Which of the following statements (including gross mathematical values) is *not* correct ?

[Given : The dipole moments of nitrobenzene, toluene and chlorobenzene are 3.93 D, 0.46 D and 1.55 D respectively . $\cos 120 = -\frac{1}{2}$, $\cos 60 = \frac{1}{2}$]

(A) The dipole moment of 1, 2-disubstituted benzene ($C_6H_4X_2$) and 1, 3-disubstituted benzene ($C_6H_4X_2$) are 1.732 p and p respectively where p is the dipole moment of monosubstituted benzene (C_6H_5X).

(B) The dipole moment of 1, 4-chloronitrobenzene is $p = (3.93 - 1.55)\ D = 2.38\ D$.

(C) The dipole moment of 1, 3-chloronitrobenzene is

$$p = \left\{(-3.93)^2 + (-1.55)^2 + 2\,(-3.93)\,(-1.55)\cos 120°\right\}^{1/2} = 3.43$$

(D) The dipole moment of 1, 2-nitrotoluene is :

$$p = \left\{(-3.93)^2 + (0.46)^2 + 2\,(-3.93)\,(0.46)\cos 60\right\}^{1/2} = 3.72$$

26. Which of the following is *not* the characteristic of chemisorption but that of physisorption ?

(A) The adsorption is reversible in nature

(B) The adsorption is monolayer and follows Langmuir adsorption isotherm

(C) The heat of adsorption is high, 80 to 420 kJ per mol

(D) The activation energy of desorption is high and this adsorption occurs at high temperature

27. Which of the following statements is *not* correct ?

(A) The phase reaction, $NH_4Cl \rightleftharpoons NH_3 + HCl$ involves three chemical species but is a one component system since the products of dissociation of NH_4Cl are in one single-phase

(B) The system consisting of NaCl, KCl and H_2O has five phases and three components

(C) The system consisting of NaCl, KBr and H_2O has three phases and three components

(D) Increase in external pressure raises the lower critical solution temperature (CST) values and lowers the upper critical solution temperature (CST) values. At enough high pressure the two CST values merge into each other and the liquid pair will then be miscible at all temperatures

28. Which of the following is an example of solvolytic reaction in non-aqueous medium ?

(A) $HCl + NaCN \rightarrow NaCl + HCN$

(B) $AsCl_3 + 3H_2S \rightarrow As_2S_3 + 6HCl$

(C) $NH_4Cl + NaNH_2 \rightarrow NaCl + 2NH_3$

(D) $SOCl_2 + K_2SO_3 \rightarrow 2KCl + 2SO_2$

29. Which of the following statements is *not* correct ?

(A) Alkali or alkaline earth metals dissolve in liquid ammonia giving blue solution. The blue colour gets deepened on further addition of alkali metal till a bronze phase separates out.

(B) Unlike other alkali metals caesium does not give blue solution in liquid ammonia but a bronze coloured solution.

(C) The blue coloured solution is due to solvated electrons, $e(NH_3^-)$ and it is independent of the metal dissolved and it has broad maximum at 1450 nm.

(D) The dilute solutions are paramagnetic, the paramagnetism decreases with the increase in concentration of metal ion due to formation of electron pairs.

30. Which of the following steps/expressions is *not* correct ?

(A) The valence bond wave function $\psi_{VB} = \psi_{covalent} + \psi_{ionic}$. It can also be written as $\psi_{VB} = (1 - \lambda)\psi_{covalent} + \lambda\psi_{ionic}$. λ is a parameter whose value determines the polar character or ionicity of the bond.

(B) The valence bond wave function for hydrogen molecule can be written as $\psi_{VB} = \frac{1}{\sqrt{2}}[\phi_A(1)\phi_B(2) + \phi_A(2)\phi_B(1)]$ where $\frac{1}{\sqrt{2}}$ is the normalisation constant obtained by normalising ψ_{VB}.

(C) The molecular orbital wave function for hydrogen molecule $\psi_{MO} = \psi_1\psi_2$ where ψ_1 and ψ_2 are normalised wave function for MOs of hydrogen

$$\psi_1 = \frac{1}{\sqrt{2}}[\phi_A(1) + \phi_B(2)] \text{ and } \psi_2 = \frac{1}{\sqrt{2}}[\phi_A(2) + \phi_B(1)]$$

$$\psi_{MO} = \psi_1\psi_2 = \frac{1}{2}[\phi_A(1)\phi_B(2) - \phi_B(1)\phi_A(2)] + \frac{1}{2}[\phi_A(1)\phi_B(1) + \phi_B(2)\phi_A(2)]$$

(D) For hydrogen molecule the ionic structures are in which electron 1 and 2 are located on nucleus A or on B giving structures $H_A^+H_B^-$ and $H_A^-H_B^+$. Valence bond ignores and does not give any weightage to ionic structures but MO takes into account both ionic and covalent structures.

31. Which of the following pair of elements have highest possible and the maximum number of oxidation states ?

(A) Uranium and americum

(B) Curium and berkelium

(C) Mandelevium and fermium

(D) Neptunium and plutonium

32. Which of the group of elements (triad) of trivalent metal ions of inner transition elements gives pink colour due to *f-f* transitions.

(A) Yb, Cm, Ac
(B) Pm, Er, Am
(C) U, Np, Pu
(D) Dy, Sm, Tb

33. Which of the following statements is *not* correct with reference to inner transition elements ?

(A) *f*-orbitals are not well shielded from the surrounding of ions, the various states arising from the f^n configurations are split by the external field to a large extent.

(B) The *f-f* transition occur from one J-state of the f^n configuration to another J-state of this configuration, the absorption bands are extremely sharp.

(C) The absorption bands are quite unlike the broad band observed for *d-d* transitions. However they are similar to those for free atoms.

(D) All absorption bands found in the visible and near UV spectra of the lanthanide +3 ions have sharp line structure. There are also bands due to ligand-metal charge transfer with reducing ligands.

34. Which of the following statements is *not* correct ?

(A) There are three series obtained by three naturally occurring elements thorium, uranium and actinium.

(B) They decay by a series of α and β emissions and produce radioactive elements which are successively more stable until a stable isotope, the end product $^{206}_{82}Pb$, $^{207}_{82}Pb$ and $^{208}_{82}Pb$ is reached.

(C) Thorium ($4n$), uranium ($4n + 2$) and actinium ($4n + 3$) series have the numbers in bracket which indicate that the parent and all the members of a particular series have mass numbers exactly divisible by four, or divisible by four with a remainder two or three.

(D) Following the discovery of artificial post uranium elements, $^{237}_{93}Np$ the fourth natural neptunium ($4n + 1$) series has been added and as before the mass number is divisible by four with remainder one. The end product is $^{209}_{82}Pb$ by emitting in all 8α and 4β particles. There is a natural cross-linking between the four series.

35. Which of the following statements is *not* correct ?

(A) The simplest nuclear fusion reaction involves ${}_{1}^{1}\mathrm{H}$, ${}_{1}^{2}\mathrm{H}$ and ${}_{1}^{3}\mathrm{H}$ isotopes. A large amount of energy is required to overcome repulsion between positively charged nuclei to get them close enough (1 – 2 fm) to react. A sufficient high temperature is required (10^8 K).

(B) ${}_{1}^{2}\mathrm{H}$ and ${}_{1}^{3}\mathrm{H}$ on heating to a very high temperature, over a million degree produces plasma (fourth state of matter composed essentially of gaseous ion and a matrix of free electrons). Since atoms are stripped off their electrons, collisions will be between nuclei. Some collisions will result in fusion reaction, sufficient plasma density is required

$${}_{1}^{3}\mathrm{H} + {}_{1}^{2}\mathrm{H} \rightarrow {}_{2}^{4}\mathrm{He} + {}_{0}^{1}n + \text{energy}.$$

(C) Fusion reaction is a thermal reaction not very different in its kindling from an ordinary fire but requires a very high temperature. Like fission reactions it requires a critical mass.

(D) Deuterium is available from natural source but tritium is difficult to obtain and is extremely expensive. Tritium is produced in a fusion reactor by bombarding a blanket of lithium with neutrons

$${}_{0}^{1}n + {}_{3}^{6}\mathrm{Li} \rightarrow {}_{1}^{3}\mathrm{H} + {}_{2}^{4}\mathrm{He};\ {}_{0}^{1}n + {}_{3}^{7}\mathrm{Li} \rightarrow {}_{1}^{3}\mathrm{H} + {}_{2}^{4}\mathrm{He} + {}_{0}^{1}n$$

Similarly deuterium reacts only at high temperature of several million degrees. The simplest reactions are :

$${}_{1}^{2}\mathrm{H} + {}_{1}^{2}\mathrm{H} \rightarrow {}_{1}^{3}\mathrm{H} + {}_{1}^{1}\mathrm{H};\quad {}_{1}^{2}\mathrm{H} + {}_{1}^{2}\mathrm{H} \rightarrow {}_{2}^{3}\mathrm{He} + {}_{0}^{1}n$$

36. Which of the following statements is *not* correct with regard to valence bond theory as applied to metal complexes ?

(A) The original atomic orbitals of the ligand atom gets hybridised to provide a new set of equivalent bonding orbitals having definite directional properties which determines the shape and relative strength of bonds important in connection with complexes.

The central metal atom makes available a number of orbitals equal to its coordination number for the formation of covalent bonds with ligand orbitals.

(B) A covalent σ-bond arises from the overlap of a vacant metal orbital and a filled orbital of the donor group which should contain at least one lone pair of electrons.

(C) In addition to σ-bond formation there is also a possibility that a π-bond may be formed providing that suitable *d*-electrons of the metal are present in an orbital which can overlap with a vacant orbital on the donor atom. The σ-bond is thus strengthened.

(D) For $[CoF_6]^{-3}$ the *d*-orbitals used are of same principal energy level as the *s* and *p*-orbitals while $[Co(NH_3)_6]^{+3}$ uses *d*-orbitals of a lower principal energy level than the *s* and *p*-orbitals. Pauling called the former as outer orbital complex and the latter as inner orbital complex.

37. Which of the following statements is *not* correct with reference to crystal field theory (CFT) for complexes ?

(A) Crystal field theory explains satisfactorily and explicitly as delocalisation of ligand electrons and d orbitals become more important i.e. as covalent bond increases.

(B) Crystal field theory cannot properly explain the relative strength of ligands and gives little information concerning the excited states in which the electron or charge transfer occurring.

(C) CFT can explain detailed magnetic properties and absorption spectra of complexes.

(D) CFT can predict or interpret favourable coordination number, stereochemistry and explain thermodynamic properties of complexes.

38. Give the *correct* sequence of the ligands in spectrochemical series :

(A) $\overline{I} < H_2O < \text{dien} < \text{dipy} < NO_2^- < C\overline{N}$

(B) $\overline{I} < H_2O < \text{dipy} < \text{dien} < C\overline{N} < N\overline{O}_2$

(C) $\overline{I} < H_2O < \text{dipy} < C\overline{N} < \text{dien} < N\overline{O}_2$

(D) $\overline{I} < H_2O < \text{dien} < N\overline{O}_2 < \text{dipy} < C\overline{N}$

39. Which of the following statements or expressions is *not* correct ?

The paramagnetism of transition metal complex depends on factor such as :

(A) Large multiplet separation : The magnetic moment

$$\mu_{\text{effec.}} = g\sqrt{J(J+1)}\ \text{BM}$$

where

$$g = \left[1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}\right]$$

The magnetic moment, μ is independent of stereochemical environment and the magnetic dilution. This behaviour is true with rare earth ions where the incomplete level lies well shielded from the surface of the ion.

(B) Small multiplet separation : The energy level separation is very small as compared to kT. Spin orbit coupling is negligible and hence ignored. This type of magnetic behaviour is important as the limiting case as the first transition series when orbital contribution to the magnetic moment are not quenched

$$\mu_{\text{effec.}} = \sqrt{L(L+1)}\ \text{BM}$$

(C) Spin only : For many of the first transition series ions, particularly first half of the series experimental results have shown that the orbital contribution to the magnetic moment may be completely ignored. This leads to the sample expression :

$\mu_{\text{effec.}} = \sqrt{4S(S+1)}\ \text{BM} = \sqrt{n(n+2)}$ where n is the number of unpaired electrons.

The knowledge of unpaired electrons is useful in determining oxidation state of metal ion in a complex.

(D) Heavy atoms : There occurs a reduction in observed magnetic moment below the spin only value for second and particularly third transition series elements. The reduction cannot be attributed to ligand field strength.

40. Few manganese complexes are given below. Which of the following complex involve d^2sp^3 hybrid orbitals and it has magnetic moment 1.73 BM ?

(A) $K_2[MnCl_4]$ (B) $[MnPy_6]Br_2$

(C) $K_4[Mn(NCS)_6].3H_2O$ (D) $K_4[Mn(CN)_6].3H_2O$

41. Which of the following chromium complex show only two optical isomers ?

(A) $[Cr(en)_3]^{+3}$ (B) $[Cr(en)_2Cl_2]^+$

(C) $[Cr(NH_3)_4ClBr]Br$ (D) $[Cr(NH_3)_4Br_2]NO_2$

42. Which of the following statements is *not* correct ?

(A) In anion of Zeiss salt $[PtCl_3 . C_2H_4]^-$ the plane of the olefin and C=C itself are perpendicular to one of the expected bond direction from the central atom. In addition the expected line of a bond orbital from the metal strikes C=C at its mid-point.

(B) The bonding is assumed to consists of two independent components (*i*) the overlap of the π-electron density of the olefin with a σ-type acceptor orbital on the metal atom (*ii*) a back bond resulting from flow of electron density from filled metal d_{xz} or other $d_\pi - p_\pi$ hybrid orbital into antibonding orbitals on the carbon atom. The two components are synergically related.

(C) The donation of π-bond electrons to the metal σ-orbital and the introduction of electrons into the π-antibonding orbital both strengthen the π-bonding in the olefin. There is a significant shortening of olefin C—C bond except in anion of Zeiss salt. This has been found in complexes with $C_2(CN)_4$ where C—C bond is short than normal single bond.

(D) On theoretical and experimental grounds it appears that metal-olefin bond is essentially electroneutral with donation and back acceptance approximately balanced.

43. Which of the following statements is *not* correct with reference organometallic compound ?

(A) The number of carbon attached to a metal atom is specified by a prefix such as trihapto-, tetrahapto-, pentahapto-denoted as h^3-, h^4-, h^5- and so on. The compound, ferrocene is bis (pentahaptocyclopentadienyl) iron i.e. $(h^5 - C_5H_5)_2$ Fe.

(B) bis (penta haptocyclopentadienyl) iron is orange crystalline compound mp 274°C. It has two unpaired electrons. It is thermally unstable.

(C) Cyclopentadiene is weakly acidic ($pK_a \sim 20$). It gives sandwich compounds. The ion has aromatic sextet of π-electrons. Because of intrinsic stability of $C_5\bar{H}_5$, cyclopentadienyl metal compounds are taken as they contain $C_5\bar{H}_5$ anions and metal cations like metal halides.

(D) Some of the ionic $M(C_5H_5)_2$ compounds have sandwich structures like that of ferrocene. The beryllium compound, $Be(C_5H_5)_2$ has unsymmetrical sandwich structure in which Be atom oscillates between two position since beryllium radius is very small that even at the closest distance of approach it cannot make good bonds to the two C_5H_5 rings simultaneously.

44. Which of the following statements is *not* correct for complexes of π-acceptor ligands ?

(A) The metal atom are in low positive, zero or negative formal oxidation states. The ligands stabilise low oxidation states.

(B) The ligand form bonds to the metal by using σ-orbitals and exercise their π-acidity by using π-orbitals whose nodal planes include the axis of the π-bond. The ability of ligands to accept electron density into low lying empty π-orbitals is called π-acidity.

(C) The ligand possess vacant π-orbitals in addition to lone pair. These vacant orbitals accept electron density from filled metal orbits to form a type of π-bonding that supplements the σ-bonding arising from lone pair donation.

(D) The metal atom lies out of the molecular plane of the ligand in these complexes of π-acceptor ligands.

45. CO and N_2 (dinitrogen) are isoelectronic has led to speculation as to the possible existence of M-NN bonds analogous to M-CO bond. Which of the following reaction of ruthenium to prepare $[Ru(NH_3)_5N_2]^{+2}$ appears to be of utmost importance and of practical utility.

$[Ru(NH_3)_5N_2]^{+2}$ can be obtained in a number of ways by the reaction of :

(A) N_2H_4 with aqueous $RuCl_3$

(B) NaN_3 with $[Ru(NH_3)_5(H_2O)]^{+3}$

(C) N_2(100 atm) with $[Ru(NH_3)_5(H_2O)]^{+3}$

(D) $RuCl_3$ with Zn in NH_3 (aq.)

46. Which of the following statements is *not* correct ?

(A) C_2 molecule : The molecule would contain a total of 12 electrons and are arranged in MO_s as : $\sigma 1s^2 \sigma^* 1s^2$, $\sigma 2s^2 \sigma^* 2s^2$, $\pi 2p_x^2 \pi 2p_y^2$. The molecule is stable since two π $2p$ bonding orbitals provide 4λ stabilisation energy giving two bonds.

(B) H_2^+ and He_2^+ : The H_2^+ has one electron in σ 1s bonding orbital. The energy of this ion is lower than that of constituent atom by an amount λ. There is some stabilisation. H_2^+ exists and H_2 is much more stable. In He_2^+ ion there are three electrons which are arranged in MO_s as, $\sigma 1s^2 \sigma^* 1s^1$, thus, there is $(2\lambda - \lambda) = \lambda$ stabilisation. These species have been detected spectroscopically.

(C) Be_2 molecule : The molecule has 8 electrons in its MO_s giving a configuration $\sigma 1s^2 \sigma^* 1s^2, \sigma 2s^2 \sigma^* 2s^2$, i.e. $KK\sigma 2s^2 \sigma^* 2s^2$. There is no stabilisation energy. The molecule Be_2 does not exist.

(D) The superoxide ion $\bar{O}_2$ in KO_2 has 17 electrons and it has the configuration $\sigma 1s^2 \sigma^* 1s^2, \sigma 2s^2 \sigma^* 2s^2, \sigma 2p_x^2\ \pi 2p_y^2\ \pi 2p_z^2\ \pi^* 2p_y \pi^* 2p_z^1$. The orbital $\sigma 2p_x^2$ and $\pi 2p_z^2$ has 4λ stabilisation while $\pi^* 2p_z^1$ has λ stabilisation. The ion has 5λ stabilisation. The ion is diamagnetic.

47. Which of the following statements is *not* correct ?

(A) CO molecule has 14 electrons. The electronic configuration, assuming the order of energy levels to be the same as for light atoms like C, is as : $\sigma 1s^2\ \sigma^* 1s^2, \sigma 2s^2 \sigma^* 2s^2,\ \pi 2p_y^2\, \pi 2p_z^2\, \sigma 2p_x^2$. It has one σ and two π-bonds and thus a bond order 3. In CO^+ species the bond order is reduced to 2.5. The bond length in CO and CO^+ species are experimentally found as 1.128 and 1.115 Å respectively.

(B) Higher bond orders are associated with shorter bond length and higher bond strengths.

The electronic configuration of NO molecule is as :

KK, $\sigma 2s^2\ \sigma^* 2s^2, \sigma 2p_z^2\ \pi 2p_x^2\ \pi 2p_y^2\ \pi^* 2p_x^1$

Out of the following four species NO, NO^+, NO^{+2} and $N\bar{O}$, the species NO^+ has the highest bond order and shortest bond length.

(C) CN has electronic configuration KK, $\sigma 2s^2\ \sigma^* 2s^2, \pi 2p_x^2\ \pi 2p_y^2\ \sigma 2p_z^1$ and $C\bar{N}$ has the electronic configuration KK, $\sigma 2s^2\ \sigma^* 2s^2, \pi 2p_x^2\ \pi 2p_y^2\ \sigma 2p_z^2$ CN has higher bond order, it has larger bond energy and smaller bond length than $C\bar{N}$. The $C\bar{N}$ is paramagnetic while CN is diamagnetic.

(D) F_2 molecule has the electronic configuration $\sigma 1s^2 \sigma^* 1s^2, \sigma 2s^2\ \sigma^* 2s^2$, $\sigma 2p_x^2, \pi 2p_y^2\ \pi 2p_z^2\ \pi^* 2p_y^2\ \pi^* 2p_z^2$. The bond order is 1. The F – F bond is weak and this is attributed to small size of fluorine atoms and repulsion between lone pair of electrons in adjacent atoms.

48. Which of the following description relates to interstitial alloy ?

(A) Two metals are completely miscible with each other, they can form continuous range of solid solutions. For such solution (*i*) the two metal must be similar in size (*ii*) both the metals have the same crystal structure (*iii*) chemical properties of the metal atoms should be similar. They form an alloy.

(B) The two metals have widely different electronegativities and forms an alloy.

(C) The two metals have widely different sizes and metals remain insoluble in each other so they solidify in separate crystallites.

(D) Structure of many metals is a closely packed lattice of spherical atoms or ions. There are many tetrahedral or octahedral holes. If the element has small atoms they can be accommodated in these holes without altering the structure of the metal. The invading atom occupy interstitial position in the metal lattice. An alloy is obtained.

49. The crown ethers are complexing agents.

Which of the following statements is *not* correct ?

(A) The organic part of the molecule is puckered to give the crown arrangement and the oxygen atom with their lone pairs are nearly planar about the metal ion at the centre of the ring. These oxygen atoms may complex with a metal ion even large ions for eg. alkali metal ion. dibenzo-18 crown-6 is one such example.

(B) Crown-4, acyclic polyether with four oxygens is selective for K^+ ion-Li^+ ion prefers crown-5 while Na^+ prefers crown-6.

(C) The bonding of the metal ion to the polyether is largely electrostatic and a close fit between the size of the metal ion and the size of the hole in the centre of the polyether is essential.

(D) Crown ethers are added to organic solvents to make them dissolve inorganic salts which being ionic, would not normally dissolve. Polyethers of this type act as ion carriers inside living cell to transport ion across cell membrane and thus maintains the balance between Na^+ and K^+ inside and outside cell.

50. Which of the following statements is *not* correct ?

(A) The cryptates are three-dimensional equivalent of crown ether but contains nitrogen atom which provide branching and act as extra donor sites in adidtion to oxygen atoms to bond to the metal ion.

(B) The ligand completely wrap round and hide the cation. This is called cryptates. One such cryptate is $N[CH_2CH_2OCH_2CH_2OCH_2CH_2]_3N$ called cryptand-222 and forms a complex [Rb(crypt)] CNS . H_2O in which Rb has coordination number 8.

(C) Such complexes are used in solvent extraction, stabilising uncommon oxidation states and promoting otherwise improbable reaction.

(D) Some unusual compound $[Na(cryptand)]^- Na^+$, $[K (cryptand)]^- K^+$ are formed Na^- and K^- are completely shielded by cryptand. With excess of cryptand $[Cs^+(cryptand)]$ $[cryptand . \bar{e}]$ are formed.

51. The electron transfer reaction involves (*a*) no net chemical change, and **(*b*)** chemical change (usual oxidation-reduction reaction). The former are called electron exchange processes.

Which of the following electron transfer reaction takes place through outer-sphere mechanism ?

(A) $\text{cis-}[Cr(H_2O)_4(N_3)_2]^+ + {}^*Cr^{+2} \rightarrow \text{cis-}[Cr^*(H_2O)_4(N_3)_2]^+ + Cr^{+2}$

(B) $\text{cis-}[Co(NH_3)_4(OOCR)_2]^+ + Cr^{+2} \rightarrow \text{cis-}[Cr(H_2O)_4(OOCR)_2]^+ + Co^{+2}$

(C) $Co[EDTA]^- + Cr^{+2} \rightarrow Cr(H_2O)_3(EDTA)]^- + Co^{+2}$

(D) $[Fe(CN)_6]^{-4} + (Mo(CN)_6]^{-3} \rightarrow [Fe(CN)_6]^{-3} + [Mo(CN)_6]^{-4}$

52. Some spectral transitions are allowed and some are forbidden. The statements of which transitions are allowed, are the selection rules. The selection rule for esr transitions are :

(A) $\Delta m_I = 0, \Delta m_s = \pm 1$

(B) $\Delta m_I = \pm 1, \Delta m_s = 0$

(C) Δn = any integer, $\Delta l = \pm 1$

(D) $\Delta m_I = \pm 2, \Delta m_s = \pm 1$

53. Which of the following statements is *not* correct ?

(A) The term symbol is written as ${}^{2s\,+\,1}L_J$ where s is the total spin, L the total orbital quantum number and J is the total angular quantum number.

The left hand superscript $2s + 1$ is the multiplicity, thus, when all electrons are paired, there is no net spin *i.e.* $s = 0$ this gives a singlet term. When there are two unpaired electrons, the total spin $s = \frac{1}{2} + \frac{1}{2} = 1$, the multiplicity $2s + 1$ becomes 3 giving a triplet.

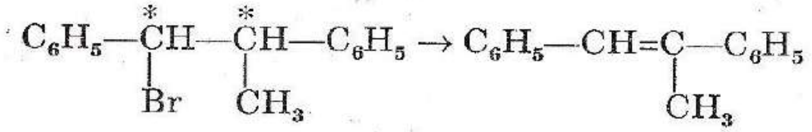
(B) L is the total orbital quantum number which is obtained by coupling the individual orbital angular momenta. For two electrons the possible L values are $L = (l_1 + l_2), (l_1 + l_2 - 1), \ldots\ldots\ (l_1 - l_2)$ so that two p-electrons ($l_1 = l_2 = 1$) L = 2, 1, 0 i.e. D, P, S respectively. An appropriate letter for L is used.

The right subscript on the term symbol is the value of J total angular momentum quantum number. The orbital angular momenta of all the electrons couple to give some total L, all spins are similarly coupled to give some total s and then these couple through spin-orbit interaction to give a total J. $J = (L + S), (L + S - 1) \ldots\ldots\ (L - S)$.

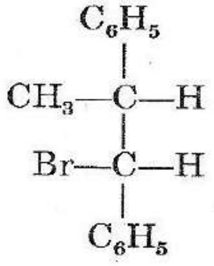
(C) The term symbol for the ground configuration of fluorine $K2s^22p^5$ which can be treated as $KL2p^{-1}$. Thus $L = l = 1$ and $S = s = \frac{1}{2}$. Two values of J are 3/2 and 1/2. The term symbol for the two levels are $2p_{3/2}$ and $2p_{1/2}$.

(D) For sodium the configuration is $KL3s^1$. Consider a single $3s$ electron. Since $L = l = 0$ and $S = s = \frac{1}{2}$. It is possible for $J = J = S = \frac{1}{2}$. The term of symbol of Na is ${}^1S_0$. The transition giving rise to the sodium doublet are ${}^2P_{5/2} \rightarrow {}^2P_{3/2}$ and ${}^2P_{3/2} \rightarrow {}^1S_0$.

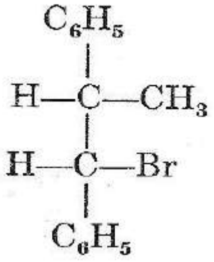
54. 1-Bromo-1, 2-diphenyl propane has two chiral centres :



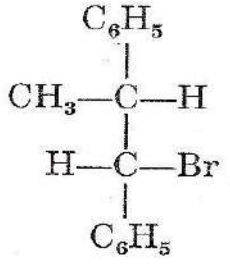
$$C_6H_5-\underset{Br}{\overset{*}{C}H}-\underset{CH_3}{\overset{*}{C}H}-C_6H_5 \rightarrow C_6H_5-CH=\underset{CH_3}{C}-C_6H_5$$



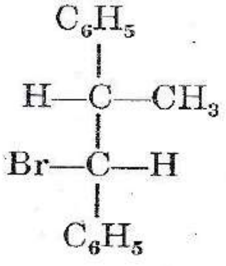
(I)



(II)



(III)



(IV)

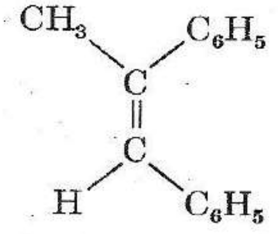
Which of the following statements is *not* correct ?

(A) I and II are enantiomers, III and IV are enantiomers. Each pair is diastereomeric with other pair.

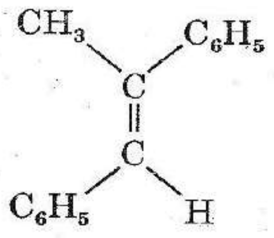
(B) I and II are called erythro isomers, III and IV are threo isomer.

(C) The product also exists as stereoisomer, a pair of geometric isomers Z and E.

(D) Erythro isomer I and II yields E-alkene, threo isomer yields Z-alkene



Z-alkene



E-alkene

55. Which of the following statements/chemical equations is *correct* with regard to non-stereospecific addition of CH_2 ?

(A) CH_2 is formed by the photolysis of diazomethane or ketene

$$CH_2=\overset{+}{N}=\bar{N}\xrightarrow[\text{Radiation}]{\text{UV}}CH_2+N_2;\ CH_2=C=O$$

$$\xrightarrow[\text{Radiation}]{\text{UV}}CH_2+CO$$

methylene exists in two different spin states.

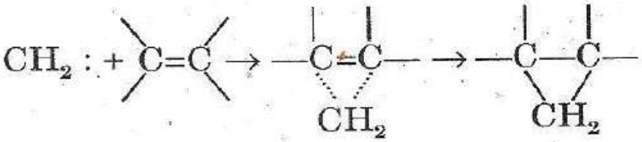
singlet methylene : CH_2 i.e. 

$H:\overset{\textstyle H}{\ddot{C}}:$

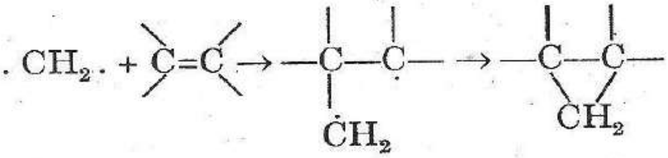
triplet methylene : $.CH_2.$ i.e. $H:\dot{\underset{\cdot}{C}}:H$

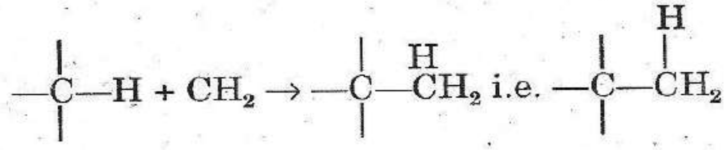
(B) CH_2N_2 + cis-2-butene → cis-1, 2-dimethyl cyclopropane

CH_2N_2 + trans-2-butene → trans-1, 2-dimethyl cyclopropane



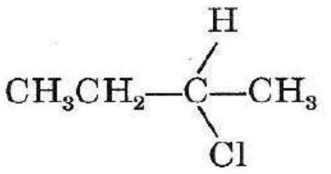
(C) CH_2N_2 + 2-butene → cis- and trans- 1, 2-dimethyl cyclopropane
cis- or trans-

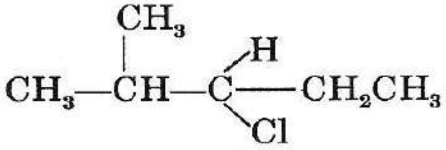


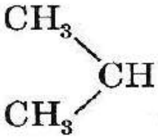
(D) CH_2 goes insertion reaction 

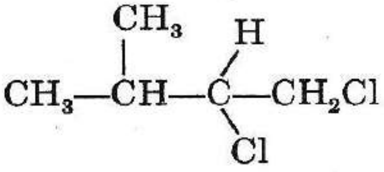
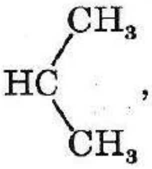
$-\overset{|}{\underset{|}{C}}-H+CH_2\rightarrow-\overset{|}{\underset{|}{C}}-\overset{H}{CH_2}$ i.e. $-\overset{|}{\underset{|}{C}}-\overset{\overset{\textstyle H}{|}}{CH_2}$

56. Which of the following has a *correct* sequence of priority for R, S-configuration ?

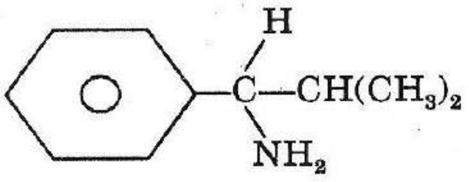
(A)  : Priority sequence is Cl, CH_3, C_2H_5 and H

(B)  : Priority sequence is Cl, C_2H_5,

 and H

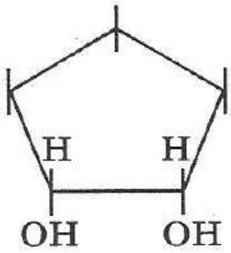
(C)  : Priority sequence is Cl,  ,

CH_2Cl and H

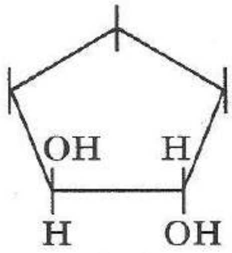
(D)  : Priority sequence is NH_2, C_6H_5,

C_3H_7 (iso), H

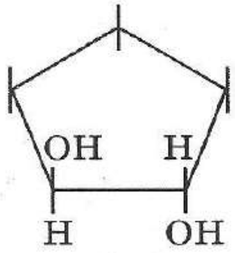
57. 1, 2-cyclopentane diol has two chiral centres. Which of the statements is *not* correct ?



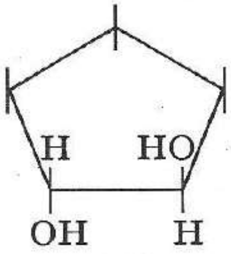
(I)



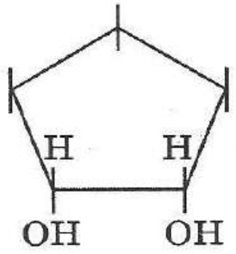
(II)



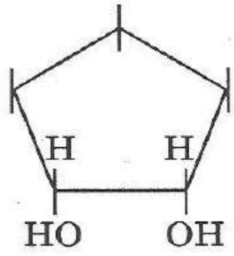
(III)



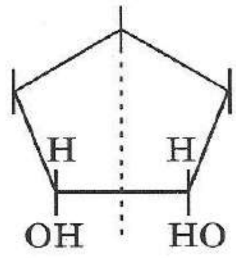
(IV)



(V)



(VI)



(VII)

(A) Structures I and II are not superimposable, hence these are stereoisomers. These are not interconvertible, these are not conformational isomers. These are not mirror images, hence these are diastereomers. They have different physical properties. These are configurational isomers. Structure I is cis-configuration whereas structure II is trans-configuration.

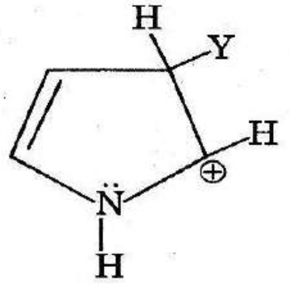
(B) Cis-1, 2-cyclopentane diol is not chiral inspite of two chiral centres whereas trans-1, 2-cyclopentane diol is chiral. Structures III and IV are not superimposable. These are enantiomers and are optically active.

(C) Cis-1, 2-cyclopentane diol has structures V and VI. These are superimposable. It cannot exist in two enantiomeric forms and it is optically inactive. It is a meso compound. One half of the molecule is the mirror image of the other half structure VII.

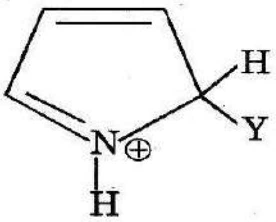
(D) Meso-cis-1, 2-cyclopentane diol are enantiomers of trans-diol and not diastereomers.

58. Which of the following structures contributes more relatively to the hybrid structure of pyrrole on electrophilic attack at position 2 ?

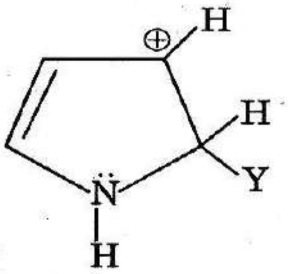
(A)



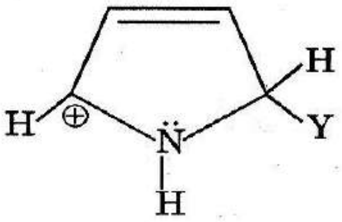
(B)



(C)



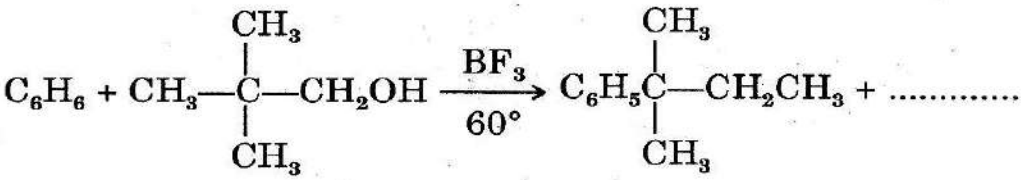
(D)



59. Which of the following Friedel-Crafts alkylation reaction gives one more additional (organic) product ?

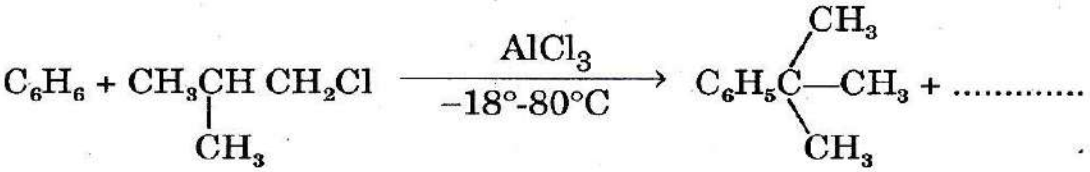
(A) $C_6H_6 + CH_3CH_2CH_2Cl \xrightarrow[-18^\circ\text{-}80^\circ C]{AlCl_3} C_6H_5CH_2CH_2CH_3 + \ldots\ldots\ldots\ldots$

(B)



$$C_6H_6 + CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_2OH \xrightarrow[60^\circ]{BF_3} C_6H_5\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_2CH_3 + \ldots\ldots\ldots\ldots$$

(C)

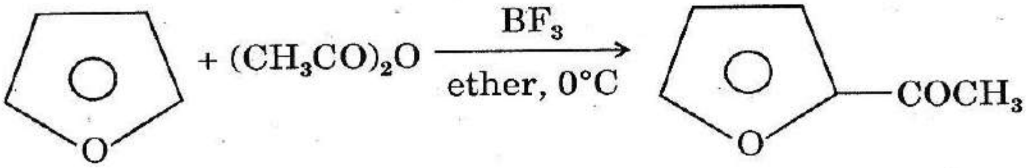


$$C_6H_6 + CH_3\underset{CH_3}{\underset{|}{CH}}\,CH_2Cl \xrightarrow[-18^\circ\text{-}80^\circ C]{AlCl_3} C_6H_5\underset{CH_3}{\overset{CH_3}{C}}-CH_3 + \ldots\ldots\ldots\ldots$$

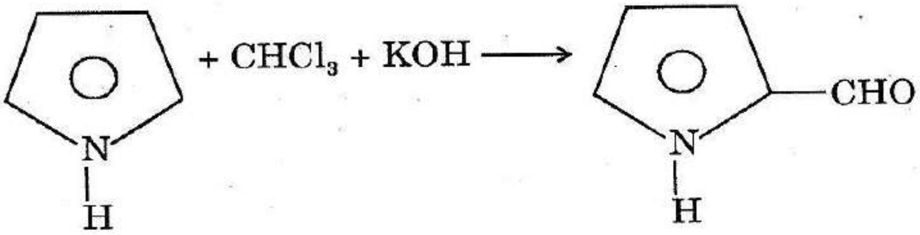
(D) $C_6H_6 + ClCH_2CH_2Cl \xrightarrow{AlCl_3} C_6H_5CH_2CH_2C_6H_5 + \ldots\ldots\ldots\ldots$

60. Which of the following is an example of Friedel-Crafts acylation reaction ?

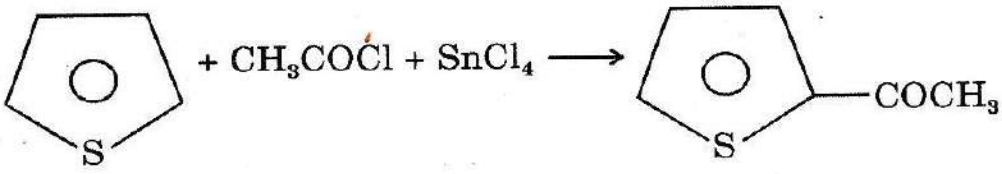
(A)



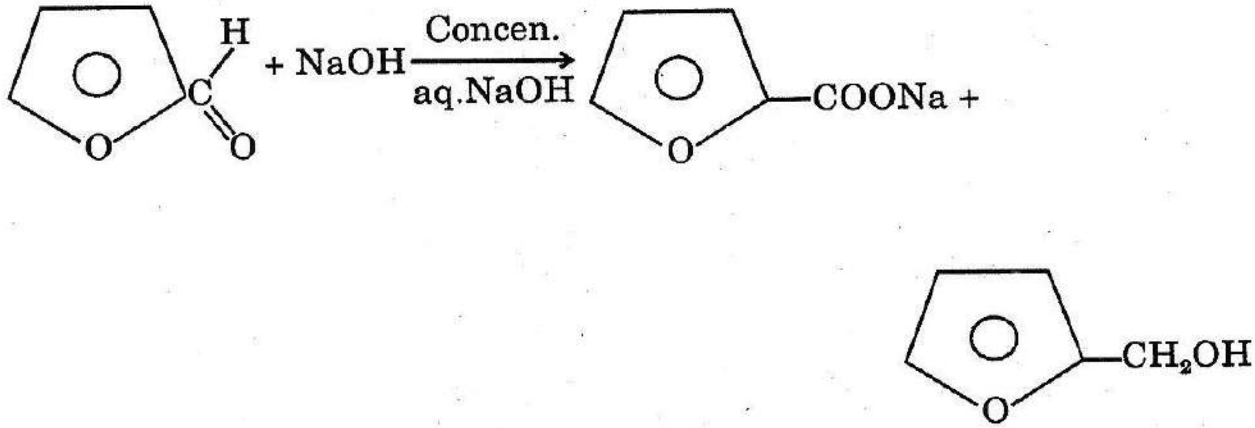
(B)



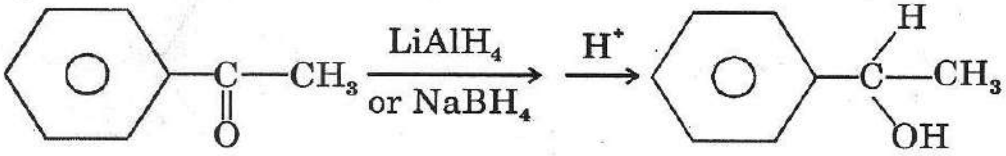
(C)

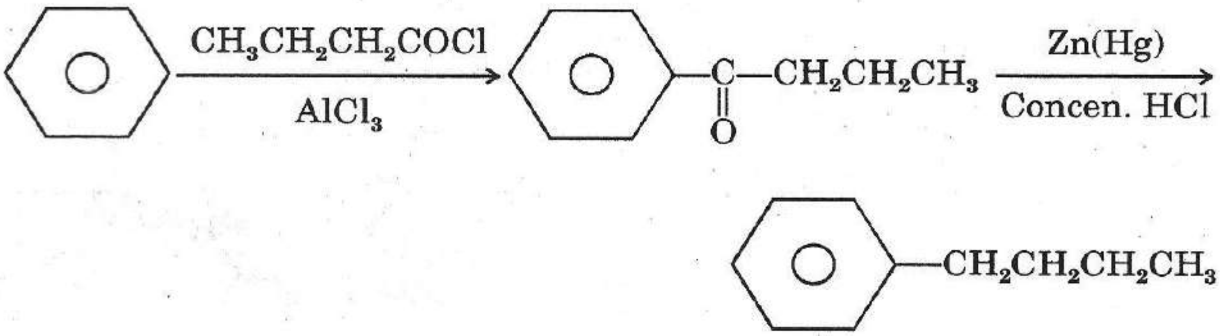


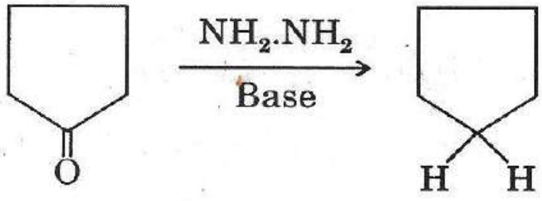
(D)



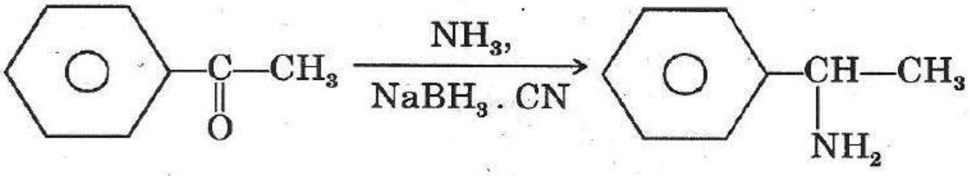
61. Which of the following reduction processes is performed by using Wolf Kishner reduction method ?

(A) 

(B) 

(C) 

Cyclopentanone Cyclopentane

(D) 

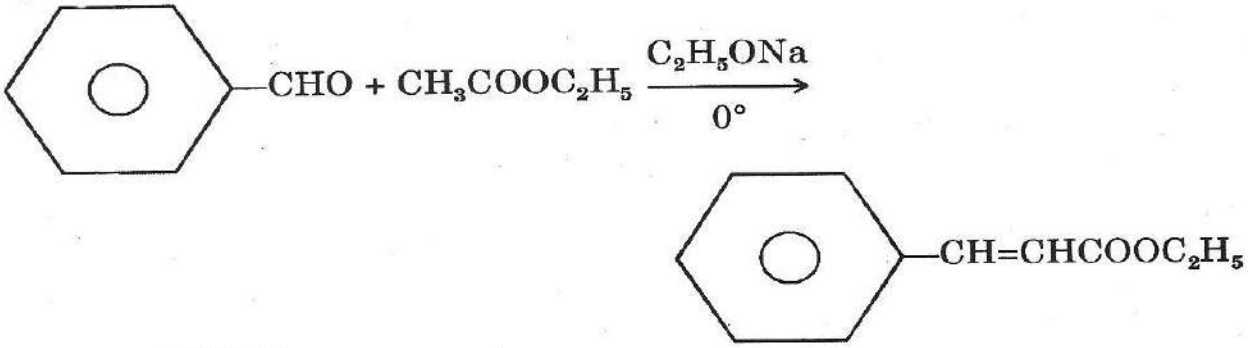
62. Which of the following two molecules of the same compound do *not* condense to give aldol type of products under the influence of dilute NaOH ?

(A) Acetaldehyde (B) Acetone

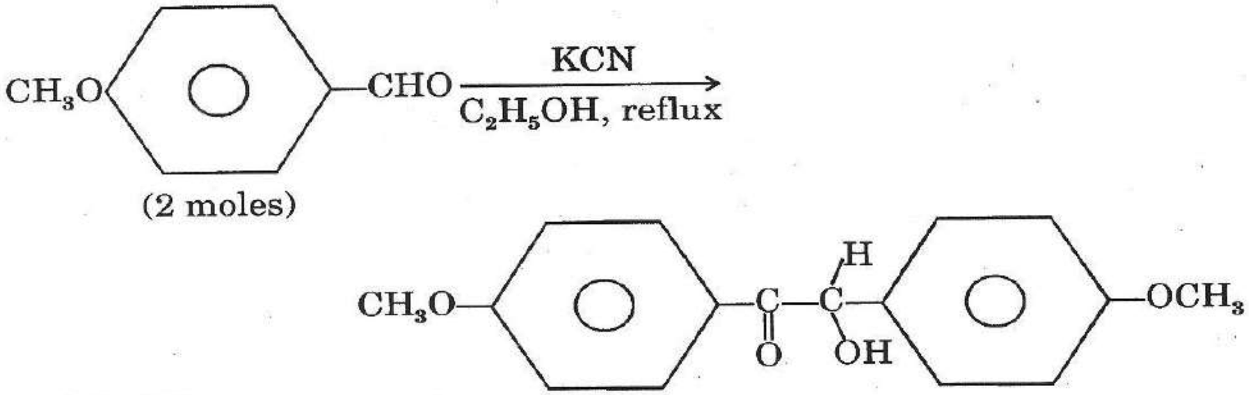
(C) Propionaldehyde (D) Trimethyl acetaldehyde

63. Identify the benzoin condensation from the following reactions ?

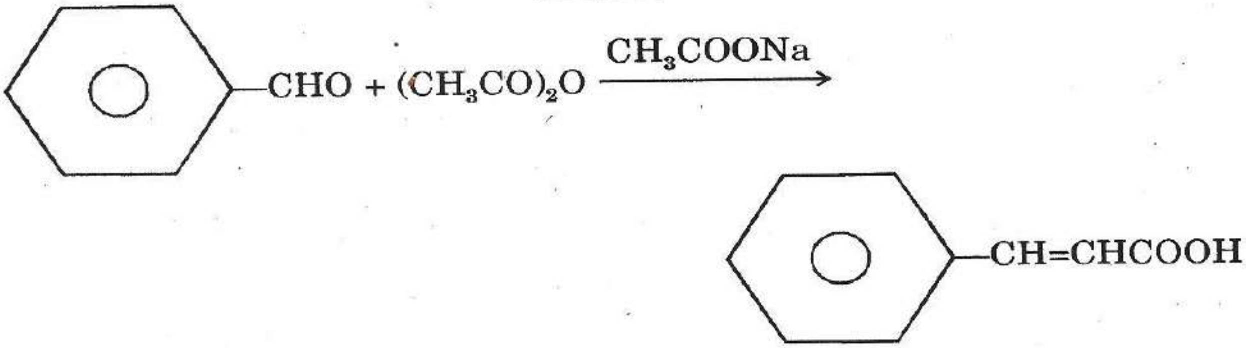
(A)



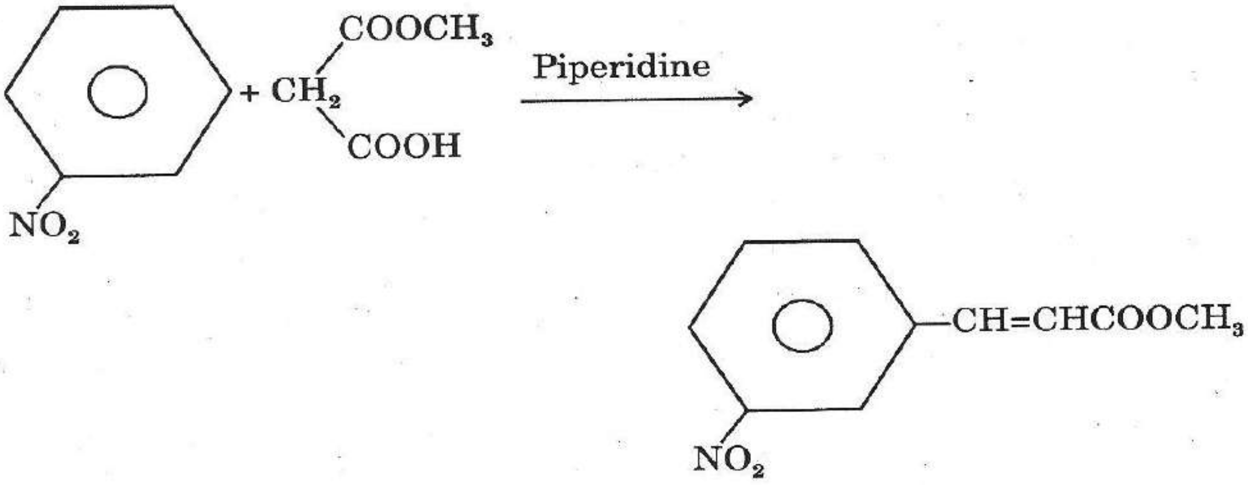
(B)



(C)



(D)

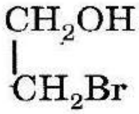
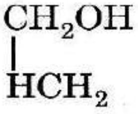


64. Which of the following statements is *not* correct ?

(A) Groups such as-R, -An, -OR, Cl if present in halide molecule do not cause any difficulty in preparing Aryl magnesium halide (eg. C_6H_5MgBr) Grignard reagent.

(B) Aromatic compounds containing substituents —NO_2, —NH_2 or C_6H_5CO do not cause any difficulty to prepare Grignard reagent (aryl magnesium halide). Compounds containing above groups may react with ArMgBr (Grignard reagent) without any difficulty.

(C) Carboxyl, hydroxyl, amino, sulphonic acid groups attached to oxygen and nitrogen are so acidic that they will decompose Grignard reagent.

(D) Grignard reagent cannot be prepared from a compound  $\begin{array}{l}CH_2OH\\ |\\ CH_2Br\end{array}$, since as soon as Grignard reagent is formed, the —OH group of the other molecule readily react to form  $\begin{array}{l}CH_2OH\\ |\\ HCH_2\end{array}$

65. Which of the following reactions gives phenol ?

(A) $C_6H_5N{=}N{-}Cl + C_2H_5OH \rightarrow$

(B) $C_6H_5N{=}N{-}Cl + 2H \xrightarrow[\text{stannite}]{\text{Sodium}}$

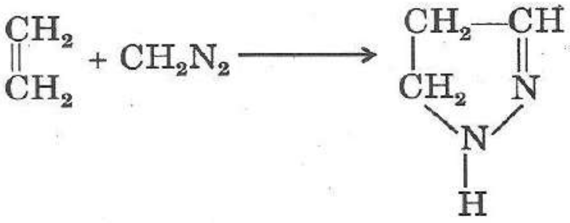
(C) $C_6H_5N{=}N{-}Cl + H_2O \xrightarrow{\text{Boil}}$

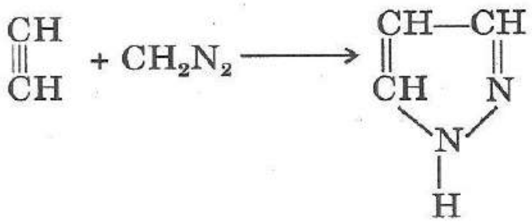
(D) $C_6H_5N{=}N{-}Cl + H_3PO_2 + H_2O \longrightarrow$

66. Which of the following reaction of diazomethane (CH_2N_2) is used for ascending the series (Arndt-Eistert reaction) ?

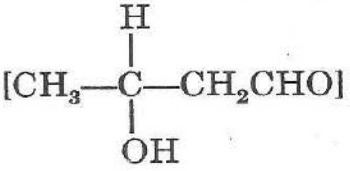
(A) $C_2H_5CHO + CH_2N_2 \rightarrow C_2H_5COCH_3 + N_2$

(B) $CH_3CH_2COCl + CH_2N_2 \rightarrow CH_3CH_2COCHN_2 \xrightarrow{H_2O} CH_3CH_2CH_2COOH + N_2$

(C) 

(D) 

67. Which of the following statements is *not* correct ?

(A) In aldol condensation $O\bar{H}$ abstracts hydrogen ion from the α-carbon of the aldehyde (for eg. CH_3CHO) to form carbanion which attacks the carbonyl carbon of the other molecule to form other carbanion, this carbanion abstracts hydrogen ion from water to form β-hydroxy aldehyde 

$[CH_3-\underset{OH}{\overset{H}{C}}-CH_2CHO]$

(B) In Claisen condensation ethoxide ion ($OC_2H_5^-$) abstracts a hydrogen ion from the α-carbon of the ester ($CH_3COOC_2H_5$) to form carbanion which attacks the carbonyl carbon of a second molecule of the ester to displace ethoxide ion and yields keto-ester ($CH_3COCH_2COOC_2H_5$).

(C) Acetoacetic ester is much weaker acid than ordinary esters or other compounds containing a single carbonyl group.

(D) In aldol condensation nucleophilic attack leads to addition, the typical reaction of aldehyde/ketone; in Claisen condensation nucleophilic attack leads to substitution, the typical reaction of acyl compound.

68. Which of the following statements is *not* correct ?

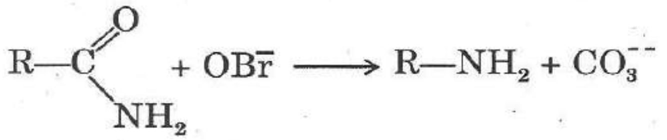
(A) Preparative nitration is almost frequently carried out with a mixture of concen. HNO_3 and concen. H_2SO_4. Sulphuric acid absorbs water formed during the reaction and so prevents the reverse reaction $C_6H_6 + HNO_3 \rightarrow C_6H_5NO_2 + H_2O$.

(B) Concen. H_2SO_4 is a medium necessary for the release of NO_2^+ from HNO_3 . $HClO_4$ also promote nitration, $(NO_2^+ClO_4^-)$ has been isolated. HF and BF_3 are also effective. Poor performance of nitration by HNO_3 by HNO_3 itself is due to small amount of available NO_2^+.

(C) Halogenation takes place in the presence of Lewis acid $ZnCl_2$, $FeBr_3$, $AlBr_3$. The Lewis acid induces some amount of polarisation in halogen molecule thereby increasing its electrophilic character. The positive end attacks the π-electron cloud of benzene. Interhalogen compounds $Br^{+\delta}$—$Cl^{-\delta}$ and $I^{+\delta}$—$Br^{-\delta}$ lead to bromination and iodination respectively.

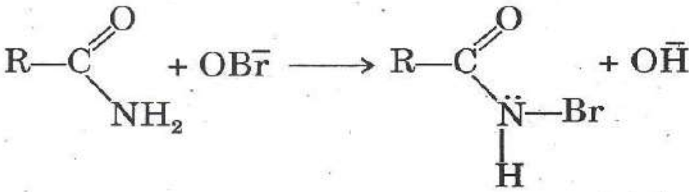
(D) In sulphonation whether the effective electrophilic agent is bisulphonium ion SO_3H^- or free SO_3. The sulphur atom in SO_3 molecule is highly electron deficient and thus sulphur of SO_3 becomes bonded to ring carbon atom. The sulphonation reaction is reversible and it is slowed down when the hydrogen atom of an aromatic nuclei are replaced by the heavier atom.

69. In Hofmann degradation of amide takes place as :



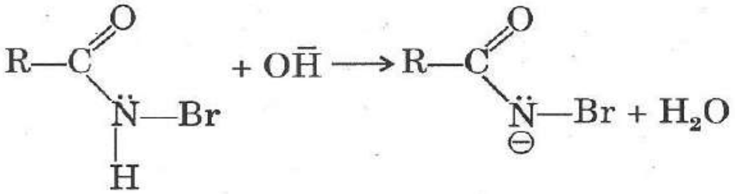
in which rearrangement occurs since the group joined to carbonyl carbon in the amide is found to join to nitrogen in the product. The steps are :

(A)



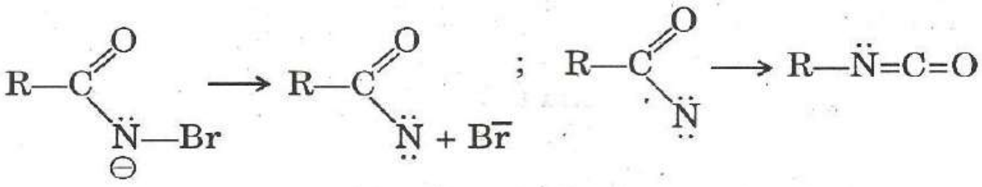
The product N-haloamide has been isolated in the absence of $\bar{OH}$

(B)



It involves abstraction of a hydrogen ion by hydroxide ion

(C) The rearrangement occurs as :



The two steps take place simutlaneously.

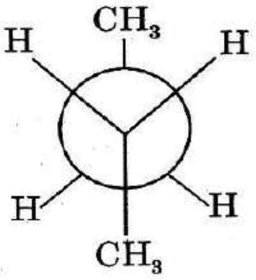
The isocyanate gets hydrolysed to form amine and CO_3^{--} ion

$R-\ddot{N}=C=O + 2\bar{O}H \rightarrow R-NH_2 + CO_3^{--}$

(D) Hofmann rearrangement is intermolecular. The chiral carbon breaks away from the carbonyl carbon and starts attaching itself to nitrogen. The migrating group does not move steps from atom to atom but takes jump. There is some loss of configuration.

70. Which of the following conformational form of n-butane is least stable ?

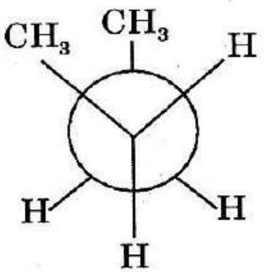
(A)



(I)

CH_3 groups are far apart. Dihedral angle 180° anti

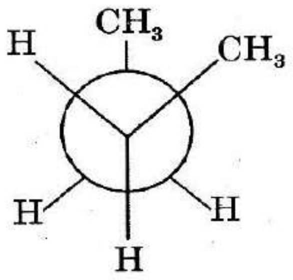
(B)



(II)

CH_3 groups are only 60° apart gauch

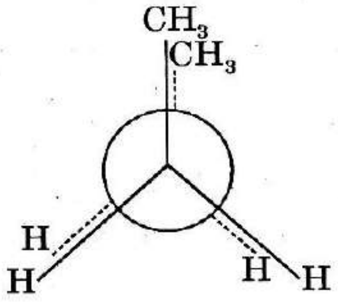
(C)



(III)

Mirror-image of II gauch

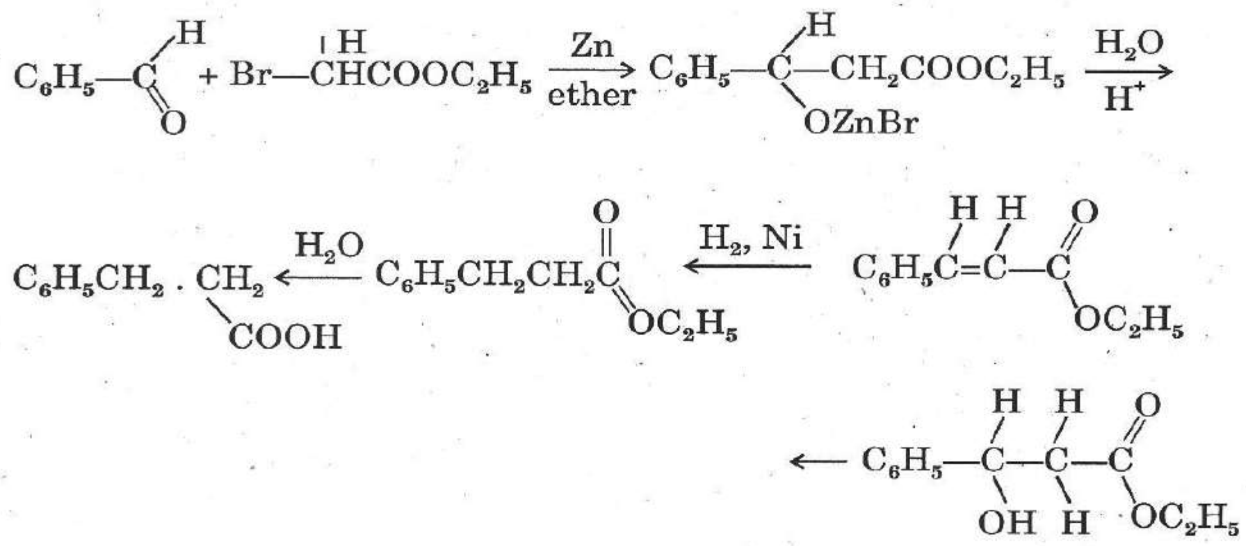
(D)

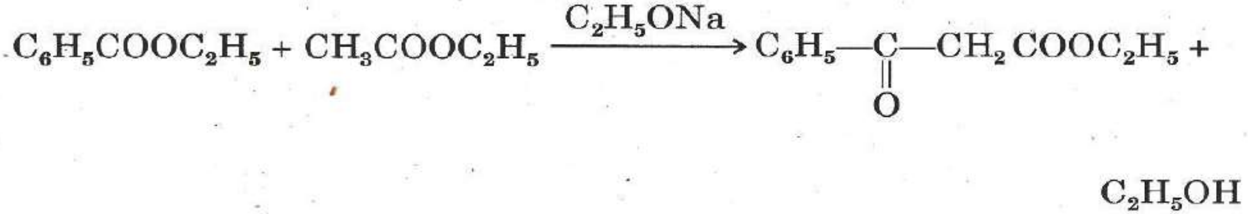


(IV)

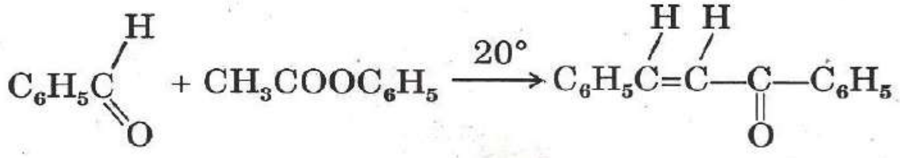
van der Waal strain Two CH_3 groups are closer than the sum of their van der Waal radii

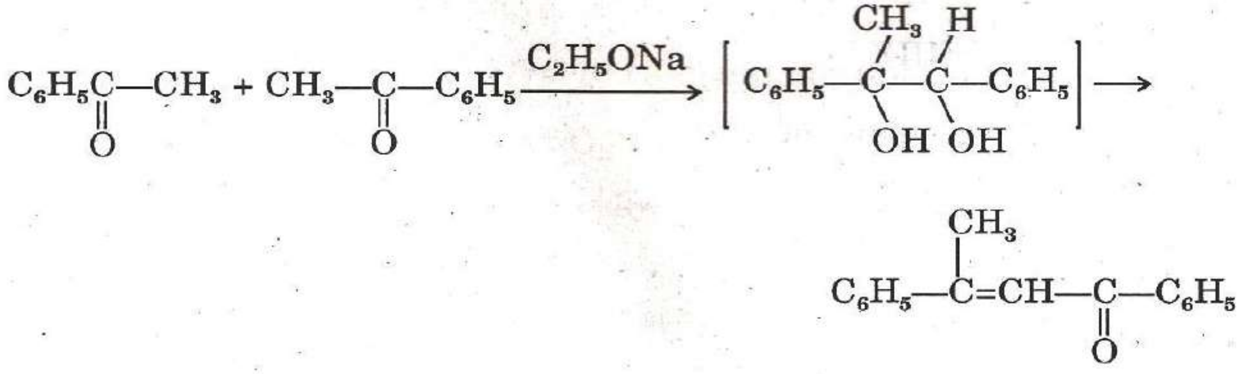
71. Which of the following is an example of the use of Reformatsky reaction for synthesis ?

(A) 

(B) 

$C_6H_5COOC_2H_5 + CH_3COOC_2H_5 \xrightarrow{C_2H_5ONa} C_6H_5-\underset{\underset{O}{\|}}{C}-CH_2COOC_2H_5 + C_2H_5OH$

(C) 

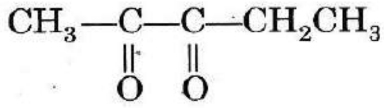
(D) 

72. Which of the following compound does *not* react with per iodic acid ?

(A) $CH_2OH.(CHOH)_4.CHO$

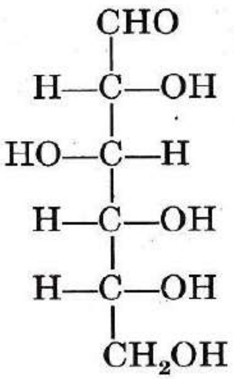
(B) $CH_2OH.CH(OCH_3).CH_2OH$

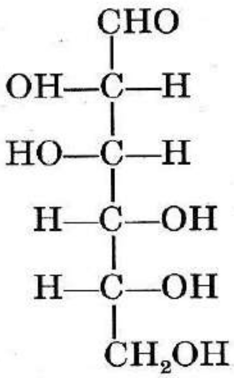
(C) $CH_2OH.(CHOH)_2.CH_2OCH_3$

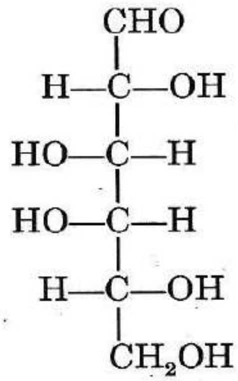
(D) 

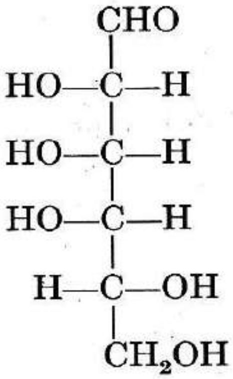
$CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-CH_2CH_3$

73. Few monosaccharides are given below. These on oxidation with nitric acid gives aldaric acid. Which one of the following configuration gives a meso compound ?

(A) 

(B) 

(C) 

(D) 

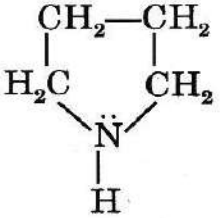
74. Which of the following does *not* exist in anomeric forms ?

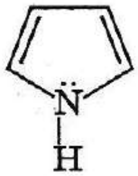
(A) sucrose (B) maltose

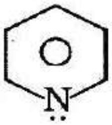
(C) lactose (D) cellobiose

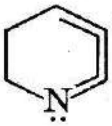
75. The correct increasing order of basicity (beginning from least basic) of the following compounds ?

(*i*) Pyrrolidine (*ii*) Pyrrole (*iii*) Pyridine (*iv*) Quinuclidine (*v*) Triethyl amine









$(C_2H_5)_3N$:

is as :

(A) (*ii*) < (*iii*) < (*iv*) < (*v*) < (*i*) (B) (*iii*) < (*ii*) < (*v*) < (*iv*) < (*i*)

(C) (*ii*) < (*iv*) < (*iii*) < (*i*) < (*v*) (D) (*iv*) < (*i*) < (*v*) < (*ii*) < (*iii*)

76. Which of the following essential amino acids contains one amino and one carboxyl group ?

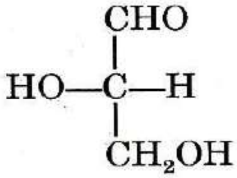
(A) Arginine (B) Lysine

(C) Histidine (D) Phenylalanine

77. Which of the following statements is *not* correct ?

(A) All essential amino acids except glycine possess asymmetric centres and are optically active.

(B) The configuration of amino acids obtained from protein hydrolysates are all similar to one another and belong to the same configurational family as L–(–) glyceraldehyde



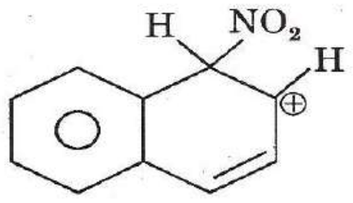
$$\begin{array}{c} \mathrm{CHO} \\ | \\ \mathrm{HO{-}C{-}H} \\ | \\ \mathrm{CH_2OH} \end{array}$$

(C) The lowest solubility of neutral amino acid in water occurs at the acidity level that provides the highest concentration of inner salt. This pH is called isoelectric point. The hydrogen ion concentration of the solution in which a particular amino acid does not migrate under the influence of electrical field is isoelectric point of that acid.

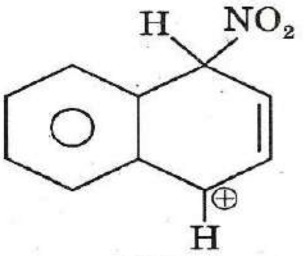
(D) Above the isoelectric point amino acids are converted to cations, below this critical pH they lose protons and form anions.

78. Which of the following statements is *not* correct with reference to orientation of electrophilic substitution in naphthalene ?

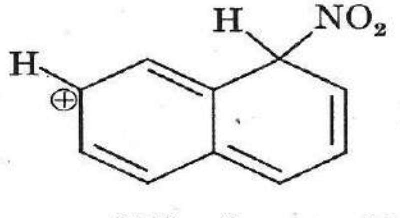
(A) The nitronium ion attaks at the α-position of $C_{10}H_8$ resulting in formation of an intermediate carbocation (hybrid structure of I and II where aromatic sextet is preserved and positive charge is accommodated by the ring under attack



(I)



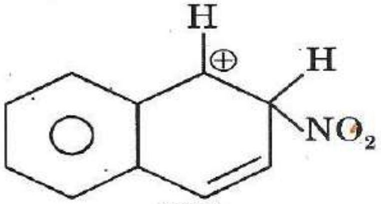
(II)



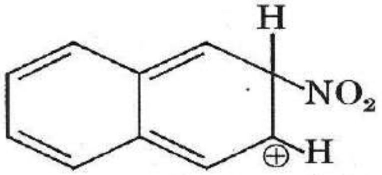
(III) (less stable)

In structure III aromatic sextet is disrupted and positive charge is accommodated by the ring not under attack.

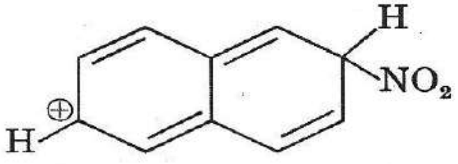
(B) The attack at the β-position of $C_{10}H_8$ yields an intermediate carbocation



(IV)



(V)



(VI)

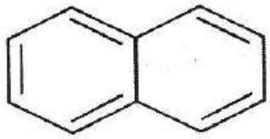
Structures IV and V positive charge is accommodated by the ring under attack. In structures V and VI aromatic sextet is disrupted in both rings and are less stable as compared to IV.

(C) In attack at β-position there are two stable structures I and II whereas in attack at α-position there is only one contributing structure IV. Nitration is favoured at β-position and occurs rapidly.

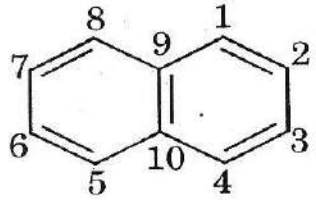
(D) In structures III, V and VI aromatic sextet is disrupted in both rings with a large sacrifice of resonance stabilisation energy. The orientation is understandable on the basis of large number of structures contributing to the intermediate carbocation, the important ones are those that requires smallest sacrifice of rsonance stabilisation. Electrophilic substitution is based on this principle.

79. Which of the following statements is *not* correct ?

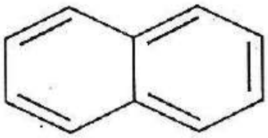
Naphthalene is considered to be a resonance hybrid of the structures I, II and III :



(I)



(II)



(III)

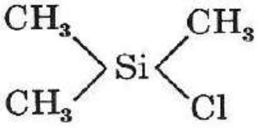
(A) All C—C bonds in naphthalene are almost the same as in benzene.

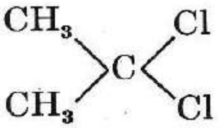
(B) The C_1—C_2 bond (1.365 Å) is shorter than C_2—C_3 bond (1.404Å).

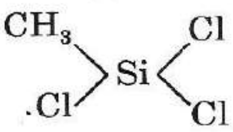
(C) The C_1—C_2 bond is double in two structures I and II and single only in one structure. The C_1—C_2 bond is expected to have more double bond character than single bond character.

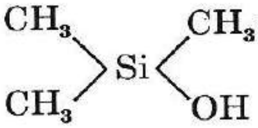
(D) The C_2—C_3 bond is single in two structures and double only in one structure. The C_2—C_3 bond has more single bond character than double bond character

80. The monomer unit of silicone is :

(A) 

(B) 

(C) 

(D) 

81. Three districts of lowest Scheduled Tribe population to total population of the districts accounting to 2011 census listwise are :

(A) Chamba, Bilaspur, Solan (B) Hamirpur, Shimla, Mandi

(C) Kangra, Kinnaur, Kullu (D) L & S, Sirmaur, Solan

82. In which year Territorial Council of H.P. was converted to Vidhan Sabha and how many legislative members are there in H.P. Vidhan Sabha ?

(A) 1st July, 1968; No. of Legislative Members 68

(B) 1st July, 1963; No. of Legislative Members 68

(C) 1st Nov., 1966; No. of Legislative Members 41

(D) 25th Jan., 1971; No. of Legislative Members 68

83. Who is author of "Kangra Valley Paintings" ?

(A) Shanta Kumar (B) Lal Chand Prarthi

(C) M.S. Randhawa (D) Harish Chand Gulari

84. What is the increase in the forest area of the state as per state of Forest Report, 2015 of Forest Survey of India ?

(A) 13 sq. km

(B) 14 sq. km

(C) 15 sq. km

(D) None of the above

85. What is the Infant Mortality Rate (IMR) in the state of H.P. as per Sample Registration Survey Report, 2016 ?

(A) 35 per thousand live births (B) 20 per thousand live births

(C) 28 per thousand live births (D) 25 per thousand live births

86. How many members are there in Rajya Sabha and Lok Sabha from the state of H.P. ?

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

(C) 5 and 4 (D) 3 and 5

87. First Chief Justice of H.P. :

(A) Justice J.N. Banerjee (B) Justice T.U. Mehta

(C) Justice R.S. Pathak (D) Justice M.H. Beg

88. Which agency executed Kol Dam Hydro Project ?

(A) National Thermal Power Corporation (NTPC)

(B) National Hydro Power Corporation (NHPC)

(C) Himachal Power Corporation (HPC)

(D) Himachal Pradesh State Electricity Board (HPSEB)

89. When was the first passenger train run on Kalka-Shimla railway line ?

(A) 2nd August, 1903
(B) 9th Nov. 1903
(C) 1st Oct., 1903
(D) 1st Jan., 1903

90. What was the earlier name of Advanced Study Institute Shimla ?

(A) Kennedy Cottage
(B) Barner Court
(C) Butler Building
(D) Vice Regal Lodge

91. Who is Chief Justice of Supreme Court of India ?

(A) Justice Dipak Mishra
(B) Justice Kehar Singh
(C) Justice Deepak Gupta
(D) Justice Ashok Bhan

92. Where is "Balakaram National Park" ?

(A) Assam
(B) Kerala
(C) Meghalaya
(D) Arunachal Pradesh

93. Who is winner of "Dadasaheb Phalke Award" for 2016 ?

(A) Gulzar
(B) Pran
(C) Kasinathuni Viswanath
(D) Dalip Kumar

94. Who gave slogan "Jai Hind" ?

(A) Mahatma Gandhi
(B) Bhagat Singh
(C) Jawahar Lal Nehru
(D) Subhash Chandra Bose

95. Which states of Indian Union touch China boarder ?

(A) Arunachal Pradesh, Uttrakhand, Sikkim, Nagaland, Assam

(B) Uttranchal, Himachal Pradesh, Mizoram, Bihar, Sikkim

(C) J & K, Uttar Pradesh, Meghalaya, West Bengal, Tripura

(D) Uttrakhand, Himachal Pradesh, J & K, Sikkim, Arunachal Pradesh

96. The capital of Mynamar (Burma) is :

(A) Beijing
(B) Naipyeda
(C) Rangoon (Yangan)
(D) Thimpu

97. Who established the "Gadar Party" ?

(A) Lala Lajpat Rai (B) Jawahar Lal Nehru

(C) Subhash Chandra Bose (D) Lala Hardayal

98. Darjiling is in which state of India ?

(A) Maharashtra (B) Tamil Nadu

(C) West Bengal (D) Assam

99. Find the odd one out :

(A) Room (B) Nest

(C) Den (D) Burrow

100. Who is the best male actor in (IIFA) Awards, 2017 ?

(A) Salman Khan (B) Karan Johar

(C) Amitabh Bachchan (D) Sahid Kapoor