BOOKLET NO. | 248

DO NOT OPEN THIS TEST BOOKLET UNTIL YOU ARE ASKED TO DO SO

TBC : AP(ASH)CHEMISTRY-TE-2018

Time Allowed : 2 Hours]   [Maximum Marks : 100

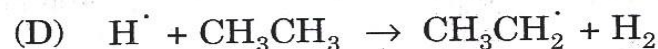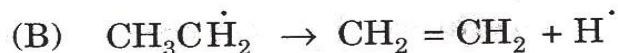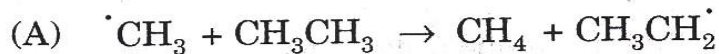### INSTRUCTIONS

1. IMMEDIATELY AFTER THE COMMENCEMENT OF THE EXAMINATION, YOU SHOULD CHECK THAT THIS 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. You have to enter your Roll Number on the Test Booklet in the Box provided alongside. **DO NOT** write **anything** else on the Test Booklet.

3. This Test Booklet contains **100** items (questions). You will select the response which you want to mark on the Answer Sheet. In case you feel that there is more than one correct response, mark the response which you consider the best. In any case, choose **ONLY ONE** response for each item.

4. You have to mark all your responses ONLY on the separate Answer Sheet provided. No erasing/correction fluid is allowed.

5. All items carry equal marks.

6. Before you proceed to mark in the Answer Sheet the response to various items in the Test Booklet, you have to fill in some particulars in the Answer Sheet as per instructions sent to you with your Admission Certificate.

7. After you have completed filling in all your responses on the Answer Sheet and the examination has concluded, you should hand over to the Invigilator *only the Answer Sheet*. You are permitted to take away with you the Test Booklet.

8. Sheets for rough work are appended in the Test Booklet at the end.

9. **Penalty for wrong answers :**
   THERE WILL BE PENALTY (NEGATIVE MARKING) FOR WRONG ANSWERS MARKED BY A CANDIDATE IN THE OBJECTIVE TYPE QUESTION PAPERS.
   (*i*) There are four alternatives for the answers to every question. For each question for which a wrong answer has been given by the candidate, **one-fourth (0.25)** of the marks assigned to that question will be deducted as penalty.
   (*ii*) If a candidate gives more than one answer, it will be treated as a **wrong answer** even if one of the given answer happen to be correct and there will be same penalty as above for that question.
   (*iii*) If a question is left blank i.e. no answer is given by the candidate, there will be **no penalty** for that question.

10. Use and carrying of Mobile Phone and Electronic Gadget is prohibited in the Examination Hall.

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1. Which one of the following species has the highest bond order, shortest bond length and maximum bond strength ?

    (A) O_2

    (B) O_2^+

    (C) O_2^-

    (D) O_2^{-2}

2. Which of the following expressions is *not* correct for the valence bond wave function for AB molecule when it is 80% covalent ?

    (A) $\psi_{covalent} = \phi_A(1)\ \phi_B(2) + \phi_A(2)\ \phi_B(1)$

    (B) $\psi_{ionic} = \phi_B(1)\ \phi_A(2)$

    (C) $\psi = c_1\psi_{covalent} + c_2\psi_{ionic}$

    (D) $\psi = 0.80[\phi_A(1)\ \phi_B(2) + \phi_A(2)\ \phi_B(1)] + 0.20[\phi_B(1)\ \phi_A(2)]$

3. Which of the following mathematical form is *not* correct for Heisenberg's uncertainty principle ?

    (A) $\Delta x \times \Delta p \geq \dfrac{\hbar}{2}$

    (B) $\Delta E \times \Delta t \geq \dfrac{\hbar}{2}$

    (C) $\Delta\theta \times \Delta l \geq \dfrac{\hbar}{2}$

    (D) $\Delta\theta \times \Delta\phi \geq \dfrac{\hbar}{2}$

4. Which of the following is a momentum operator ?

    (A) $\dfrac{\hbar}{i}\dfrac{\partial}{\partial x}$

    (B) $-\dfrac{\hbar^2}{2m}\dfrac{\partial^2}{\partial x^2}$

    (C) $i\hbar\dfrac{\partial}{\partial t}$

    (D) $-\dfrac{\hbar^2}{2m}\dfrac{\partial^2}{\partial x^2} + U$

5. Which of the following methods is used in determining the number average molar mass of a macromolecule ?

    (A) Viscosity

    (B) Osmotic pressure

    (C) Sedimentation equilibrium

    (D) Light scattering

6. Which of the following reactions is *not* a propagation step in dehydrogenation of ethane to ethene ?

   (A) $\cdot CH_3 + CH_3CH_3 \rightarrow CH_4 + CH_3\dot{C}H_2$

   (B) $CH_3\dot{C}H_2 \rightarrow CH_2 = CH_2 + \dot{H}$

   (C) $\dot{H} + CH_3\dot{C}H_2 \rightarrow CH_3CH_3$

   (D) $\dot{H} + CH_3CH_3 \rightarrow CH_3\dot{C}H_2 + H_2$

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

   (A) It is necessary to state the ionic strength when reporting the rate constant of ionic reactions.

   (B) The rate constant for a reaction between ions depends on the ionic strength of the solution. This is kinetic salt effect. The kinetic salt effect has been studied for many reactions :

   $$\log k_{eff.} = \log k^\circ_{eff.} + 2A \ Z_A \ Z_B \ I^{1/2}$$

   (The notations have their usual meaning.)

   (C) If the ions have the same sign (e.g. a reaction between cations) then increasing the ionic strength (e.g. by the addition of inert ions) increases the rate coefficient. This is because of the formation of a single, highly charged ionic complex from two less highly charged ions is favoured by a high ionic strength because new ion has a denser ionic atmosphere.
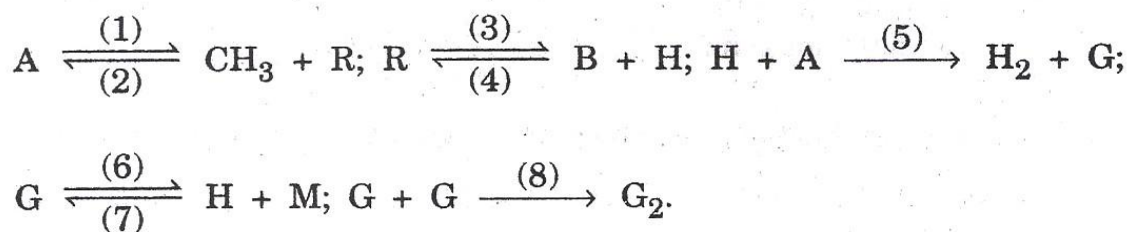
   (D) Ions of opposite charge react very fast in solution of high ionic strength. This is because the charges cancel and the complex has a much favourable interaction with its atmosphere than the separated ions.

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

   (A) The enzyme catalyst increases the activation energy of a reaction at a particular temperature like a chemical catalyst where the activation energy too increases at a given temperature. The increase of activation energy is far greater than that by a non-enzyme catalyst.

   (B) The increase in temperature results in denaturation of the enzyme protein which leads to decrease in effective concentration of the enzyme hence decrease in reaction state.

   (C) Up to 45° the reaction rate of enzyme catalysed reaction increase with rise in temperature.

   (D) At about 55° rapid denaturation completely destroys the catalytic functions of the enzyme protein.

9. A saturated hydrocarbon undergoes pyrolysis at 800 K according to the mechanism :
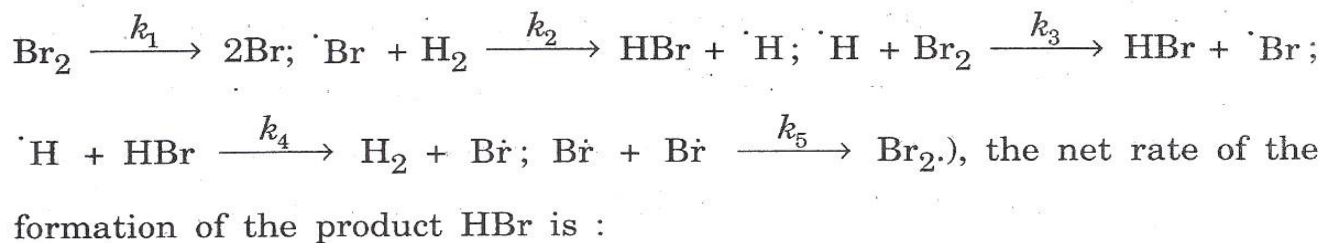
   $$A \underset{(2)}{\overset{(1)}{\rightleftharpoons}} CH_3 + R; \quad R \underset{(4)}{\overset{(3)}{\rightleftharpoons}} B + H; \quad H + A \xrightarrow{(5)} H_2 + G;$$

   $$G \underset{(7)}{\overset{(6)}{\rightleftharpoons}} H + M; \quad G + G \xrightarrow{(8)} G_2.$$

   The stable products of the reaction are B, H_2, M and G_2. The chain termination steps are :

   (A) 2 and 8   (B) 3 and 4

   (C) 5 and 6   (D) 7 and 8

   [The number indicates on the reaction arrow.]

10. In a thermal reaction between H_2 and Br_2 (chain mechanism :

$Br_2 \xrightarrow{k_1} 2Br;\ \dot{Br} + H_2 \xrightarrow{k_2} HBr + \dot{H};\ \dot{H} + Br_2 \xrightarrow{k_3} HBr + \dot{Br};$

$\dot{H} + HBr \xrightarrow{k_4} H_2 + \dot{Br};\ \dot{Br} + \dot{Br} \xrightarrow{k_5} Br_2.$), the net rate of the formation of the product HBr is :

(A) $2k_1[Br_2] - k_2[Br]\ [H_2] + k_3[H]\ [Br_2] - 2k_5[Br]^2$

(B) $2k_1[Br_2] - k_2[Br]\ [H_2] + k_3[H]\ [Br_2] + k_4[H]\ [HBr] - 2k_5[Br]^2$

(C) $k_2[Br]\ [H_2] + k_3[H]\ [Br_2] + k_4[H]\ [HBr]$

(D) $k_2[Br]\ [H_2] + k_3[H]\ [Br_2] - k_4[H]\ [HBr]$

11. Which of the following statements corresponds to third law of thermodynamics ?

(A) Nernst suggested that ΔG and ΔH approaches each other asymptotically and become equal at absolute zero.

(B) Each substance in a given state has a tendency to escape from that state. The escaping tendency is termed as fugacity.

(C) All truly perfect crystals at absolute zero temperature have zero entropy.

(D) The temperature at which μ_{JT} changes its sign is called inversion temperature.

12. Which of the following expressions is a Clausius-Clapeyron equation for the change of a pure substance involving phase transition (liquid-vapour equilibrium) under a given set of conditions (T and P) ?

(A) $\log \gamma_{\pm} = A\, z_{+}\, z_{-} \sqrt{I}$

(B) $\Gamma_2 = -\dfrac{c}{RT}\left(\dfrac{\partial r}{\partial c}\right)_T$

(C) $\left(\dfrac{\partial T}{\partial P}\right)_H = -\dfrac{1}{c_p}\left(\dfrac{\partial H}{\partial P}\right)_T$

(D) $\dfrac{d\ln P}{dT} = \dfrac{\Delta H_v}{RT^2}$

13. The phase diagram of He system is given below. Which of the following statements is *not* correct ?
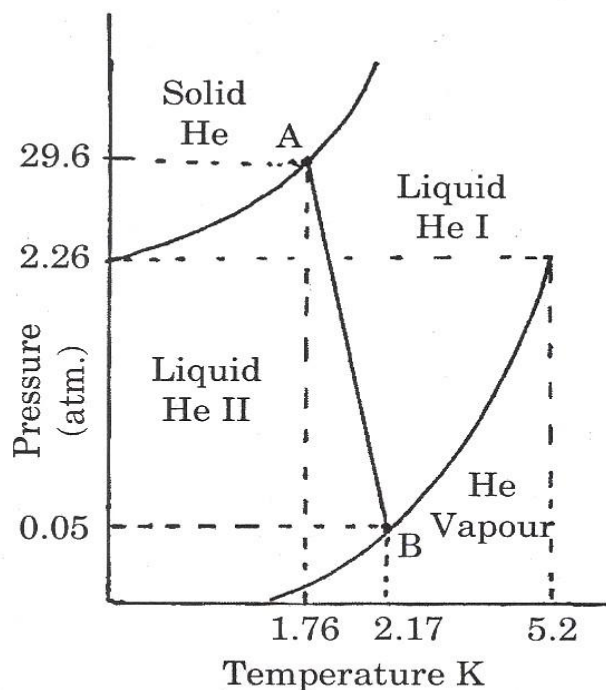
(A) The triple point B shows an equilibrium between liquid He (I) $\rightleftharpoons$ liquid He (II) $\rightleftharpoons$ He vapour at 2.17°K and 0.05 atm.

(B) The triple point A shows an equilibrium between solid He $\rightleftharpoons$ liquid He (II) $\rightleftharpoons$ He vapour at 1.76°K and 29.6 atm.

(C) The line AB called λ curve represents transition between He (I) and liquid He (II) in presence of He vapour.

(D) He is the only pure substance that exists in two different isotropic liquid phases liquid He (I) and liquid He (II). Liquid He (II) is superfluid because it has extremely low viscosity i.e. it has practically no internal friction in the vicinity of 0 K.

14. Frisch and Margrave measured ΔH°_{298} for the reaction :

$$NO(g) + CO(g) \rightarrow \frac{1}{2} N_2(g) + CO_2(g)$$
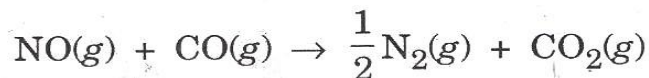
calorimetrically and found a value –373.2 kJ/mol. Given $\Delta H^\circ_f(N_2) = 0$, $\Delta H^\circ_f(CO_2) = -393.5$ kJ/mole, $\Delta H^\circ_f(CO) = -110.5$ kJ/mole, the value for $\Delta H^\circ_f(NO)$ has been calculated as :

(A) +130.8 kJ/mole   (B) +90.21 kJ/mole

(C) –656.2 kJ/mole   (D) –180.5 kJ/mole

15. Which of the following statements is *not* correct with regard to electronic partition function ?

(A) The term symbol $^{2s+1}L_J$ is a short-hand notation for all angular momenta of an atom [s = spin angular momentum, L = orbital angular momentum and J = total angular momentum].

(B) For most molecules the excited electronic energy level lie so far above the ground state compared with kT that all the molecules may be considered to be in the ground state at ordinary temperatures. The electronic partition function is given as :

$$g_{el} = \sum_i g_{el} \cdot i e^{-\epsilon_i/kT} = g_0 e^0 + g_1 e^{-\epsilon_1/kT} + g_2 e^{-\epsilon_2/kT} + \ldots\ldots$$

$= g_0$ (the second, third and subsequent terms are negligible)

(C) The ground electronic state of free atoms are generally degenerate. For hydrogen atom with electronic configuration $1s^1$ $g_0 = 2J + 1$ i.e. $2 \times \frac{1}{2} + 1 = 2$. Similarly for helium atom the electronic configuration $1s^2$, $g_0 = 1$. Thus g_{el} for hydrogen and helium are 2 and 1 respectively.

(D) The ground electronic states of most molecules and stable ion are invariable non-degenerate i.e. are singlets so that $g_0 = 1$ and hence $g_{el} = 1$. For oxygen $g_0 = 1$ and $g_{el} = 1$. Also for NO $g_0 = 1$ and hence $g_{el} = 1$. Thus for Na and Cl $g_0 = 1$ in each case and hence $g_{el} = 1$ and 2 for Na and Cl respectively.

16. Which of the following partial miscible liquid pairs has both lower and upper critical solution temperature ?

    (A) Water and Phenol

    (B) Aniline and *n*-hexane

    (C) Glycerine and *m*-toluene

    (D) Water and diethyl aniline

17. Which of the following statements is *correct* ?

    (A) The temperature at which a real gas obeys Boyle's law is known as consolute temperature.

    (B) The temperature above which a gas cannot be liquefied, no matter how the high pressure may be is called critical temperature.

    (C) The temperature at which μ_{JT} changes its sign is called Boyle temperature.

    (D) The temperature above or below which a pair of partially miscible liquid becomes miscible in all proportion is called inversion temperature.

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

    (A) The total angular momentum that can arise for a *d*-electron with spin is 5/2, 3/2, while for a *s*-electron with spin it is 1/2.

    (B) The total orbital angular momentum quantum number for d^2 electron is 4, 3, 2, 1, 0 correspondingly G, F, D, P, S terms respectively.

    (C) The total orbital angular momentum quantum number for p^3 electrons that can arise, is :

    First coupling : minimum value $1 - 1 = 0$ ∴ L′ = 2, 1, 0

    Now couple l_3 with 2, to give L = 3, 2, 1; with 1, to give L = 2, 1, 0; and with 0 to give 1.

    The over all result is L = 3, 2, 2, 1, 1, 1, 0 i.e. F, 2D, 3P, S respectively.

    (D) The value of J for a *p*-electron is $\frac{3}{2}$, $\frac{1}{2}$. Similarly for a *f*-electron the value of J is $\frac{7}{2}$, $\frac{5}{2}$, $\frac{3}{2}$.

19. Which of the following appears to be a reason for a high quantum yield in a photochemical reaction ?

(A) A photochemical reaction has a quantum efficiency 1 and shows no temperature dependence. It suggests that the reaction involves only a primary process *i.e.* a reaction proceeds in one step with the absorption of radiation.

(B) The nature of products formed in a primary process depends on the obtained absorption spectrum. If the spectrum includes only a series of lines then the product is only an excited molecule.

(C) The secondary process may involve only one or more than one steps. Sometimes the secondary processes represent the chain reaction caused by generation of atoms and free radicals in primary process and quantum yield gets affected by the chain propagating steps.

(D) The rate of a photochemical reaction in general depends upon the intensity of the absorbed radiation.

20. Which of the following is a Schrödinger equation for a harmonic oscillator ?

(A) $-\dfrac{\hbar^2}{2m}\dfrac{\partial^2 \psi}{\partial x^2} = E_\psi$

(for a free particle)

(B) $-\dfrac{\hbar^2}{2m}\dfrac{\partial^2 \phi}{\partial x^2} + \dfrac{1}{2}kx^2\psi = E_\psi$

(C) $-\dfrac{\hbar^2}{2m}\nabla^2_\psi + V_\psi = E_\psi$

(D) $H_\psi = E_\psi$

where $V = V_{(x,\, y,\, z)}$ and $\psi = \psi_{(x,\, y,\, z)}$ and $\nabla^2 = \dfrac{\partial^2}{\partial x^2} + \dfrac{\partial^2}{\partial y^2} + \dfrac{\partial^2}{\partial z^2}$

21. Which of the following statements is *not* correct with reference to symmetry elements in PCl_5 molecule ?

(A) A three fold rotation axis C_3 that passes through two Cl axial and a central P atoms.

(B) A mirror plane σ_h that passes through the centres of the three equatorial Cl atoms. Reflection through this plane leaves the equatorial Cl atoms in their original location and exchanges the axial Cl atoms.

(C) Three mirror planes σ_v that contains two axial Cl and P and one of equatorial Cl atoms.

(D) Four C_2 axes that pass through the central P and one of the equatorial Cl atoms.

22. Which of the following statements is *not* correct with reference to molecular symmetry ?

(A) Symmetry elements are geometric entities such as axes, planes or points with respect to which operations can be carried out.

(B) Symmetry operations are actions with respect to the symmetry elements that leaves the molecule in a configuration that cannot be distinguished from the original configuration.

(C) Symmetry elements do not contribute in determination of the selection rules for transitions between states of the molecule in all forms of spectroscopy. It also does not tell us which atomic orbital contribute to a given molecular orbital.

(D) All molecules have vibrational modes. The number of vibrational modes that are infrared and Raman active and degeneracy of a given vibrational frequency depend on the molecular symmetry.

Which of the following statements is *not* correct ?

(A) The absence or presence of permanent dipole moment (μ_x) is not relevant for the absorption of infrared radiation. It is the dynamic dipolement, generated due to vibration of the molecule if satisfies the condition $\frac{d\mu_x}{dx} \neq 0$ the vibrational excitation to occur.

(B) The molecules N_2, O_2 and H_2 which have zero permanent and transient dipole moment do not absorb IR radiation emitted by the earth. Therefore all IR radiations pass through the atmosphere and escapes into the space. Greenhouses CO_2, NO_x and hydrocarbons absorb IR radiations emitted by the earth and radiate back to the earth. This increases the temperature of the earth and causes global warming.

(C) It is a permanent dipole moment that determines if a molecule will undergo rotational transition by absorbing energy in the microwave portion of the light spectrum. Homonuclear diatomic molecule have neither permanent nor dynamic dipole moment cannot take up the energy.

(D) Every spectroscopy has selection rules that govern the transitions that can occur between eigenstates of a system. For absorption by a quantum mechanical harmonic oscillator $\Delta n = +1$. In most cases only the $n = 0 \rightarrow n = 1$ transition is observed in vibrational spectroscopy.

The CO and CH_4 being linear and non-linear molecule are expected to give one and nine vibrational modes respectively. The single peak in CO spectrum is much broader than would be expected for vibrational peak and it has a deep minimum at the central frequency. Only two vibrational modes are seen at 1306 cm^{-1} and 3020 cm^{-1} due δ_{CH} bending and ν_{CH} stretching vibration respectively. Application of molecular symmetry and group theory fail to provide an answer to such large discrepancies between the expected and observed frequencies.

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

(A) Raman and infrared absorption spectroscopy are complementary and both can be used to study the vibration of molecules.

(B) Consider a molecule with a characteristic vibrational frequency in an electromagnetic field that has time dependent electric field. The electric field distorts the molecule slightly because negative valence electrons and the positive nuclei and their core electrons experience force in opposite direction. This induces time dependent dipole moment of magnitude $\mu_{induced}(t)$ in the molecule of the same frequency as the field. The dipole moment is linearly proportional to the magnitude of electric field and the proportionality constant is called polarisability.

(C) For vibrational modes to be Raman active the polarisability of the molecule must change as it vibrates. Although $\frac{d\mu_x}{dx} = 0$ for homonuclear diatomic molecule making them infrared active the stretching vibration of a homonuclear is Raman inactive.

(D) The most significant difference between these two spectroscopies is the light source needed to implement the technique. For infrared absorption the light source must have significant intensity in the infrared portion of the spectrum. Raman spectroscopy is a scattering technique the frequency of light used need not match the frequency of the transition being studied. Thus, a source in the visible part of the spectrum is generally used to study rotational and vibrational modes.

25. Which of the following statements is *not* correct with reference to NMR spectroscopy ?

(A) A methyl group attached to an electron rich atom such as Li or Al will have a negative chemical shift indicating that ^1H nucleus is more shielded than in $(CH_3)_4Si$.

(B) If a neighbouring group is more electronegative than hydrogen, it will withdraw electron density from the region around ^1H nucleus. The nucleus is less shielded and the NMR resonance frequency appears at a larger value of δ.

(C) The spin-lattice relaxation time T_1 determines the rate at which the energy absorbed from the radiofrequency field dissipated to the surroundings and if T_1 is not sufficiently small energy is not lost quickly enough to the surroundings and the population of the excited state becomes as large as that of the ground state. If the population of the excited state and ground state are equal, the net absorption at the transition frequency is zero which means no NMR.

(D) An aromatic ring has a strong magnetic anisotropy. A sizable ring current is induced when the magnetic field is perpendicular to the plane of the ring but the current is negligible when the magnetic field lies in the plane of the ring.

26. Which of the following NMR—(^{1}H) spectrum matches with the expected NMR spectrum of the compound, methyl β-cyanopropionate (nmr sketches are not to scale) ?
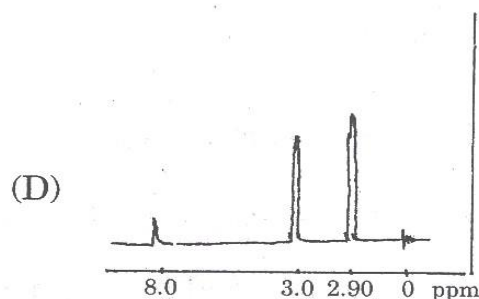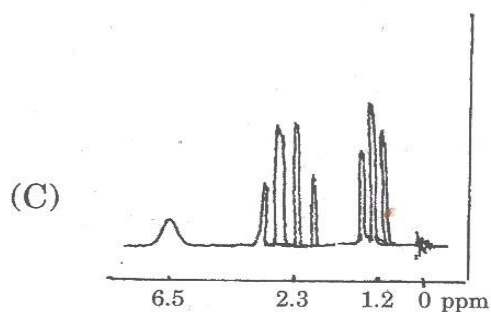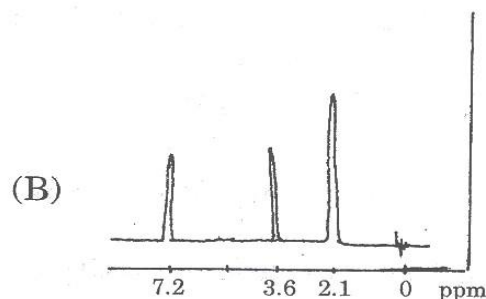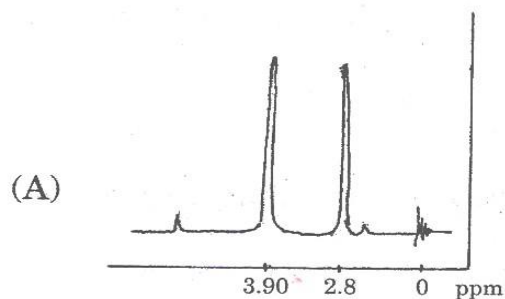

27. A research scholar obtained an IR absorption spectrum of the compound in nujol mull which he presumes as N-phenyl-2-mercaptoacetamide. What criterion he should adopt to identify the compound unambiguously by just looking at the spectrum ? [He has examined the frequencies in the following four groups.]

   (A) $\nu_{\text{N-H trans}}$: 3320-3270 cm^{-1}

   (B) $\nu_{\text{C=O (amide I)}}$: 1680-1630 cm^{-1}

   (C) $\nu_{\text{C=C}}$: 1650 and 1450 cm^{-1}

   (D) $\nu_{\text{S-H}}$: 2600-2550 cm^{-1}

28. Which of the following statements is *not* correct with reference to mass spectrum of alcohol ?

(A) A peak m/e 31 due to $CH_2 = \overset{+}{\overset{..}{O}}H$ is quite diagnostic for primary alcohol provided it is more intense than m/e 45, 59, 73.

(B) A distinct and sometimes prominent peak can usually be found at M-18 from loss of water.

(C) Elimination of H_2O together with elimination of an olifine from primary alcohol accounts for the peak at M-46
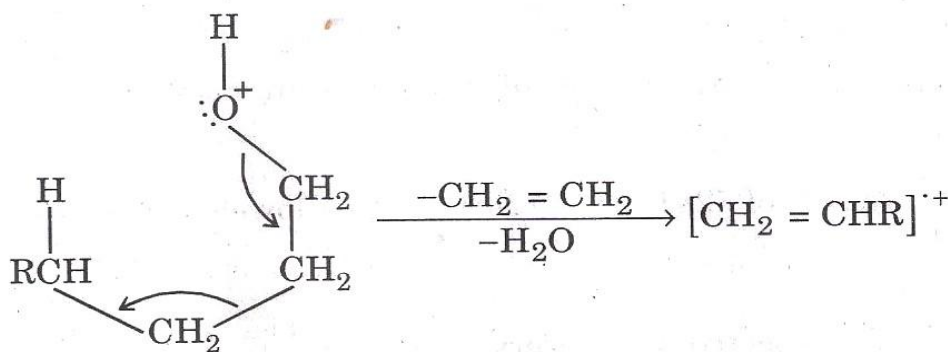
(D) The molecular ion peak due to $\underset{R}{\overset{R}{>}}C = \overset{+}{\overset{..}{O}}H$, m/e 59, 73, 87 is not very prominent in tertiary alcohol, $CH_3CH_2-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$.

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

(A) The energies required to effect a transition are very much different in NMR and ESR. The ESR transition occur at frequencies in the microwave region compared to frequencies in the radiofrequency region for NMR.

(B) The selection rule for esr transition is $\Delta m_I = \pm 1$ and $\Delta m_S = 0$ while for nmr transition it is, $\Delta m_I = 0$ and $\Delta m_S = \pm 1$.

(C) The interaction of an unpaired electron with a set of n equivalent nuclei of spin I_i and another set of m equivalent nuclei of spin I_j leads to the observation of $(2nI_i + 1)(2mI_j + 1)$ allowed transition.

A six line spectrum is observed from a radical containing a single $^{14}_{7}N$ nucleus (I = 1) and a single proton (I = $\frac{1}{2}$).

(D) A radical containing a $^{17}_{8}O$ nucleus (I = $\frac{5}{2}$), a $^{19}_{9}F$ nucleus (I = $\frac{1}{2}$) and a $^{1}_{1}H$ nucleus (I = $\frac{1}{2}$) gives a 24 line spectrum.

30. Which of the following electrodes is used in strongly alkaline solution ?

(A) Mercury — mercuric oxide electrode

(B) Mercury — mercurous sulphate electrode

(C) Mercury — mercurous chloride electrode

(D) Silver — silver chloride electrode

31. Which of the following is an example of electrode concentration cell ?

(A) $Hg—Zn(c_1)$, $ZnSO_4(aq.)$, $Hg—Zn(c_2)$

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

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

(D) $Ag|AgCl(s)$, $HCl(a_1)$: $HCl(a_2)$,, $AgCl(s)|Ag$

32. Which of the following solutions has the highest ionic strength at a particular temperature assuming 100% ionisation of the electrolyte ?

(A) 0.15 KCl solution

(B) 0.25 M K_2SO_4 solution

(C) 0.20 $BaCl_2$ solution

(D) a solution which is 0.1 M in KCl and 0.2 M in K_2SO_4

33. Out of the five major bases :

(i) Adenine (A),

(ii) Cytosine (C),
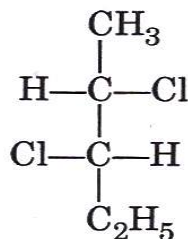
(iii) Guanine (G),

(iv) Thymine (T) and

(v) Uracil (U)

the common bases which are present in RNA and DNA are :

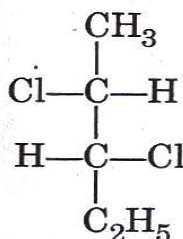(A) A and G   (B) C and T

(C) T and U   (D) A and U

34. Which of the following fat soluble vitamins functions like hormone ?

(A) Vitamin K exists in different forms — K_1, K_2 and K_3. It is essential for coagulation. It functions as co-enzyme.

(B) Vitamin E is a group of tocopherols and tocotrienols. It is essential for the membrane structure and integrity of the cell. It is least toxic.

(C) Vitamin A relates to many structurally and biologically active molecules. It acts in the process of vision.

(D) Vitamin D resembles sterols in structure : cholecalciferol (Vitamin D_3) and Ergocalciferol (Vitamin D_2). Vitamin D_3 is synthesised in the skin by UV radiation of sun. The biologically active form of vitamin D calcitriol is produced in kidney.
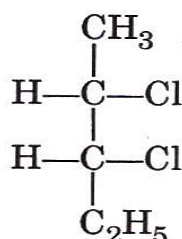
35. 2, 3-dichloropentane has two chiral centres : $CH_3-CH_2-\overset{.}{C}H-\overset{.}{C}H-CH_3$ i.e.

with Cl and Cl on the two central carbons.

$$
\begin{array}{cccc}
CH_3 & CH_3 & CH_3 & CH_3 \\
H-\overset{|}{C}-Cl & Cl-\overset{|}{C}-H & H-\overset{|}{C}-Cl & Cl-\overset{|}{C}-H \\
Cl-\overset{|}{C}-H & H-\overset{|}{C}-Cl & H-\overset{|}{C}-Cl & Cl-\overset{|}{C}-H \\
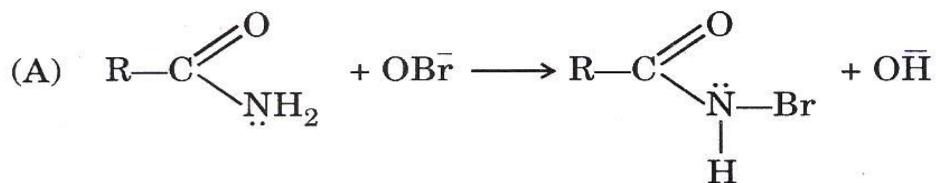C_2H_5 & C_2H_5 & C_2H_5 & C_2H_5 \\
(I) & (II) & (III) & (IV)
\end{array}
$$
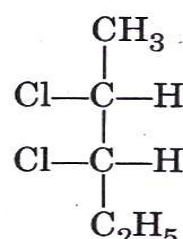
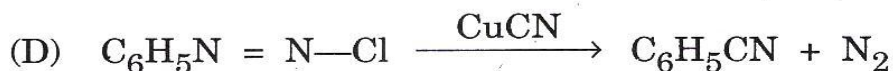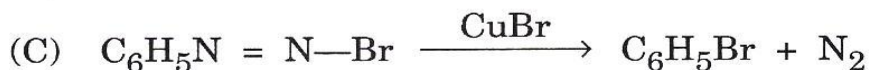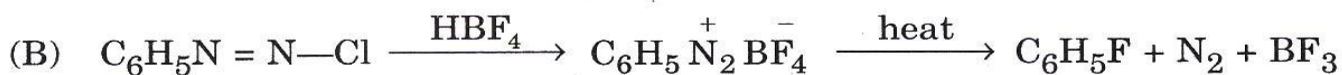Which of the following specification to structure is *not* correct with reference to R, S-configuration ?
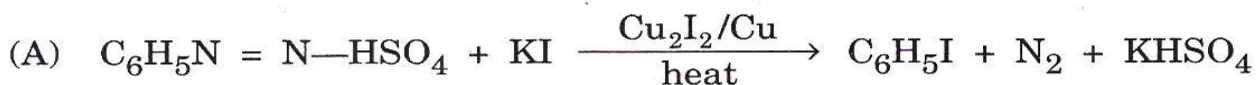
(A) Stereoisomer I is (2S, 3S)-2, 3-dichloropentane and stereoisomer II is (2R, 3R)-2, 3-dichloropentane. I and II are enantiomers.

(B) Stereoisomer III is (2S, 3R)-2, 3-dichloropentane and stereoisomer IV is (2R, 3S)-2, 3-dichloropentane. III and IV are enantiomers.

(C) Enantiomers I and II have opposite — i.e. mirror-image configuration about both chiral centres : (2S, 3S) and (2R, 3R).

(D) As diastereomers I and III have opposite configurations about one chiral centre and the same configuration about the other : (2R, 3S) and (2S, 3R).
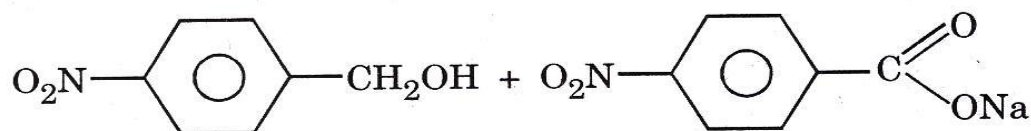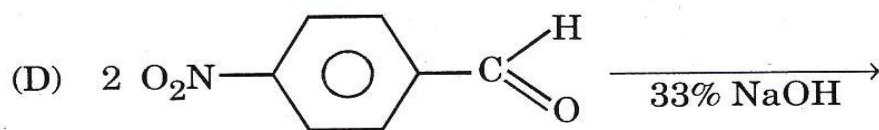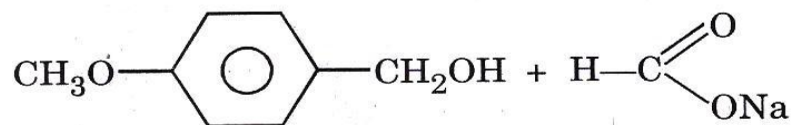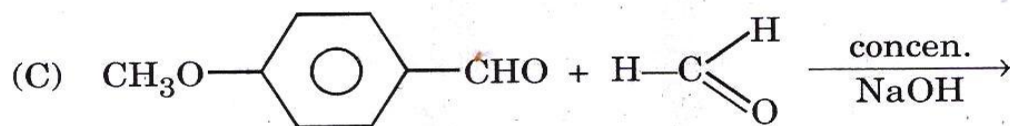
36. In which of the following steps the Hofmann rearrangement actually occurs in the degradation of amides ?

(A) $R-C\overset{O}{\underset{\underset{\cdot\cdot}{NH_2}}{\big<}}$ + $O\bar{Br}$ $\longrightarrow$ $R-C\overset{O}{\underset{\underset{H}{\overset{\cdot}{N}-Br}}{\big<}}$ + $O\bar{H}$

(B) $R-C\overset{O}{\underset{\underset{H}{\overset{\cdot}{N}-Br}}{\big<}}$ + $O\bar{H}$ $\longrightarrow$ $R-C\overset{O}{\underset{\underset{\ominus}{\overset{\cdot}{N}-Br}}{\big<}}$

(C) $R-C\overset{O}{\underset{\underset{\ominus}{\overset{\cdot\cdot}{N}-Br}}{\big<}}$ $\longrightarrow$ $R-C\overset{O}{\underset{\overset{\cdot\cdot}{N}}{\big<}}$ + $\bar{Br}$ ⎫

$R-C\overset{O}{\underset{\overset{\cdot\cdot}{N}}{\big<}}$ $\longrightarrow$ $R-\overset{\cdot\cdot}{N}=C=O$ ⎬ simultaneous

(D) $R-\overset{\cdot\cdot}{N}=C=O$ + $2O\bar{H}$ $\xrightarrow{H_2O}$ $R-\overset{\cdot\cdot}{N}H_2$ + CO_3^{-2}
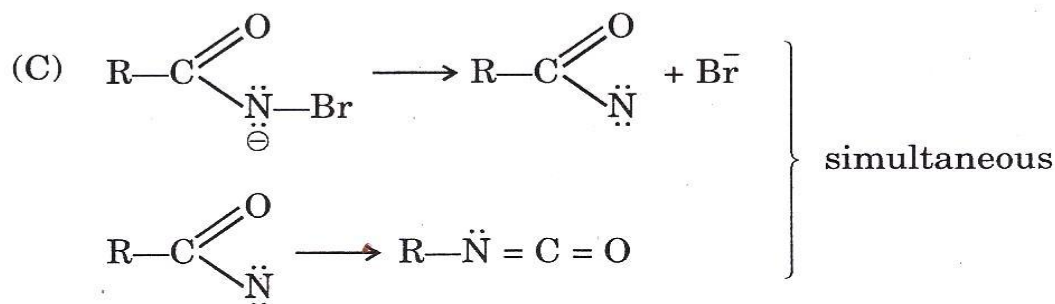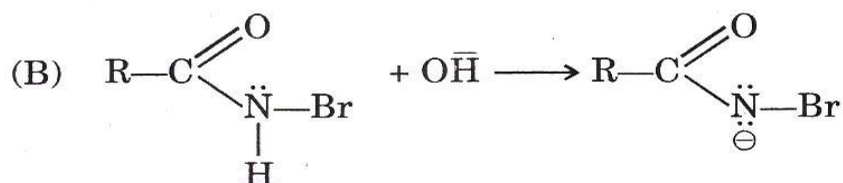
37. Which of the following reactions involves superfluous reactant (i.e., not required) in the preparation of the compound ?

(A) $C_6H_5N = N-HSO_4$ + KI $\xrightarrow[\text{heat}]{Cu_2I_2/Cu}$ C_6H_5I + N_2 + $KHSO_4$

(B) $C_6H_5N = N-Cl$ $\xrightarrow{HBF_4}$ $C_6H_5 \overset{+}{N_2} \bar{BF_4}$ $\xrightarrow{\text{heat}}$ C_6H_5F + N_2 + BF_3

(C) $C_6H_5N = N-Br$ $\xrightarrow{CuBr}$ C_6H_5Br + N_2

(D) $C_6H_5N = N-Cl$ $\xrightarrow{CuCN}$ C_6H_5CN + N_2

38. Which of the following reactions *does not* take place ?
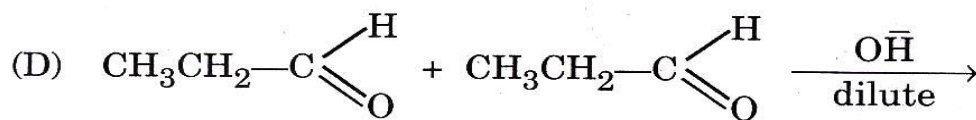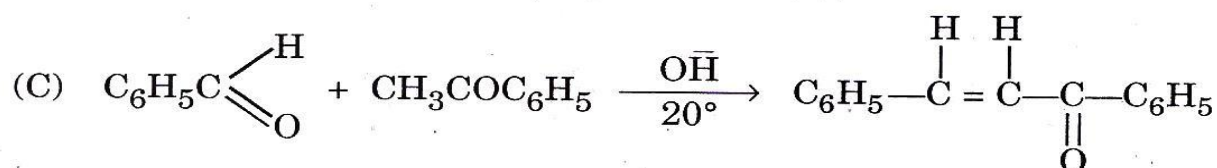
(A) $(CH_3)_3C-\overset{\displaystyle H}{\underset{\displaystyle O}{C}}$ + $H-\overset{\displaystyle H}{\underset{\displaystyle O}{C}}$ $\xrightarrow[\text{NaOH}]{\text{concen.}}$ $(CH_3)_3CCH_2OH$

$+ \ H-\overset{\displaystyle O}{\underset{\displaystyle ONa}{C}}$

(B) $(CH_3)_3C-\overset{\displaystyle H}{\underset{\displaystyle O}{C}}$ + $H-\overset{\displaystyle H}{\underset{\displaystyle O}{C}}$ $\xrightarrow[\text{NaOH}]{\text{dilute}}$ $(CH_3)_3C-\overset{\displaystyle H}{\underset{\displaystyle OH}{C}}-\overset{\displaystyle H}{\underset{\displaystyle O}{C}}$

(C) CH_3O-⟨O⟩$-CHO$ + $H-\overset{\displaystyle H}{\underset{\displaystyle O}{C}}$ $\xrightarrow[\text{NaOH}]{\text{concen.}}$

CH_3O-⟨O⟩$-CH_2OH$ + $H-\overset{\displaystyle O}{\underset{\displaystyle ONa}{C}}$

(D) $2 \ O_2N-$⟨O⟩$-\overset{\displaystyle H}{\underset{\displaystyle O}{C}}$ $\xrightarrow{33\% \text{ NaOH}}$

O_2N-⟨O⟩$-CH_2OH$ + O_2N-⟨O⟩$-\overset{\displaystyle O}{\underset{\displaystyle ONa}{C}}$
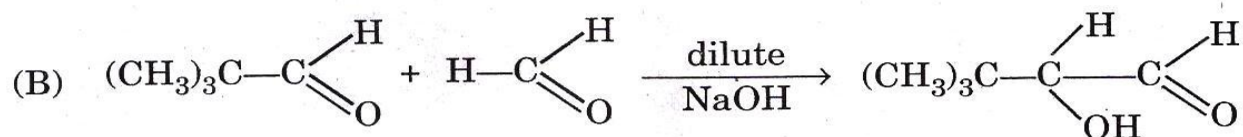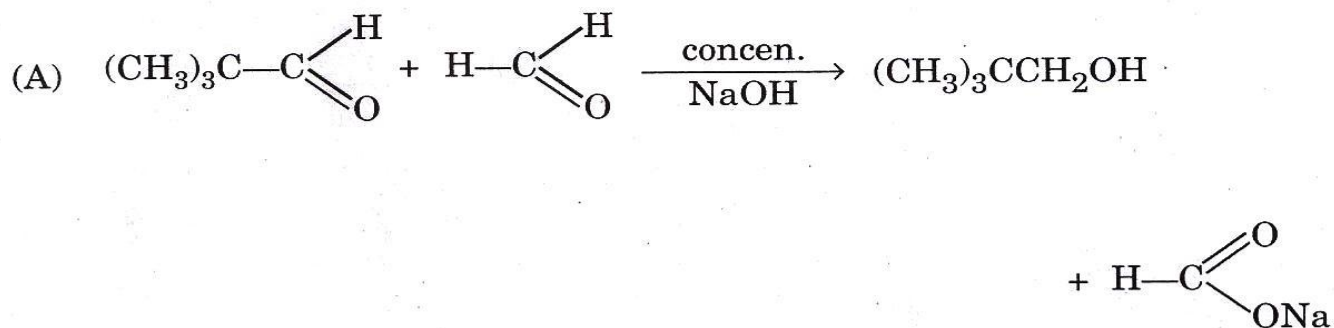
39. Which of the following is an example of aldol condensation reaction ?

(A) $C_6H_5C\begin{smallmatrix} H \\ O \end{smallmatrix}$ + $\begin{smallmatrix} CH_3CO \\ CH_3CO \end{smallmatrix}O$ $\xrightarrow{CH_3COONa}$ $C_6H_5CH = CHCOOH$

$+ CH_3COOH$

(B) $C_6H_5C\begin{smallmatrix} H \\ O \end{smallmatrix}$ + CH_3COCH_3 $\xrightarrow[100°]{\overline{O}H}$ $C_6H_5-\overset{H}{\underset{}{C}} = \overset{H}{\underset{}{C}}-\overset{O}{\underset{||}{C}}-CH_3$

(C) $C_6H_5C\begin{smallmatrix} H \\ O \end{smallmatrix}$ + $CH_3COC_6H_5$ $\xrightarrow[20°]{\overline{O}H}$ $C_6H_5-\overset{H}{\underset{}{C}} = \overset{H}{\underset{}{C}}-\overset{O}{\underset{||}{C}}-C_6H_5$

(D) $CH_3CH_2-C\begin{smallmatrix} H \\ O \end{smallmatrix}$ + $CH_3CH_2-C\begin{smallmatrix} H \\ O \end{smallmatrix}$ $\xrightarrow[dilute]{\overline{O}H}$

$CH_3CH_2-\overset{H}{\underset{OH}{C}}-\overset{CH_3}{\underset{H}{C}}-C\begin{smallmatrix} H \\ O \end{smallmatrix}$

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

(A) Methylene is obtained by the photolysis of either diazomethane or ketene.

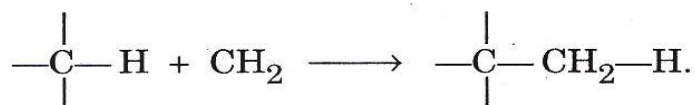$$CH_2 = N = N \xrightarrow[\text{Photolysis}]{\text{UV}} CH_2 + N_2$$

$$CH_2 = C = O \xrightarrow[\text{Photolysis}]{\text{UV}} CH_2 + CO.$$
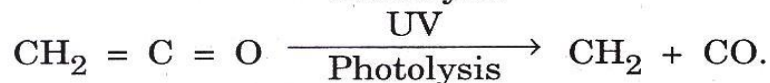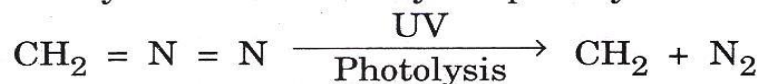
(B) Methylene in which the unshared electrons are paired $CH_2:$, $H:\ddot{C}:H$ called singlet methylene.

Methylene in which the unshared electrons are not paired $\cdot CH_2\cdot$, $H:\dot{C}:H$ called triplet methylene.
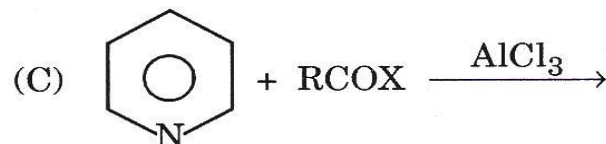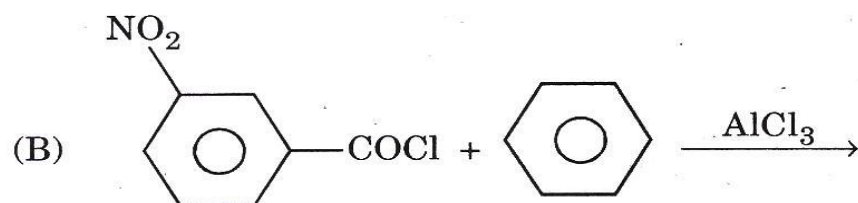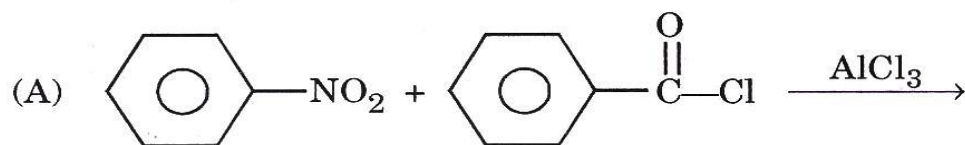
(C) The photolysis of diazomethane in liquid cis-2-butene gives trans-1, 2-dimethyl cyclopropane but if photolysis of diazomethane is done in liquid trans-2-butene, cis-1, 2-dimethyl cyclopropane is obtained.

$$CH_3CH = CHCH_3 + CH_2N_2 \xrightarrow[\text{Photolysis}]{\text{UV}} CH_3—CH—CH—CH_3 + N_2.$$
$$\overset{\displaystyle CH_2}{}$$
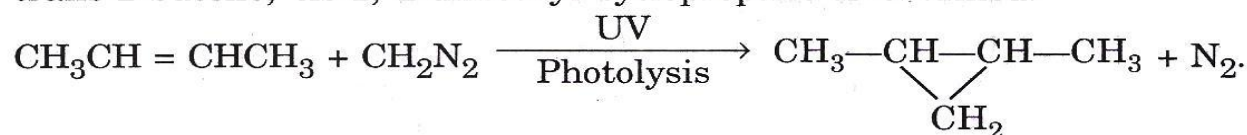
(D) Methylene undergoes insertion reaction

$$—\overset{|}{\underset{|}{C}}—H + CH_2 \longrightarrow —\overset{|}{\underset{|}{C}}—CH_2—H.$$

41. Which of the following Friedel-Craft reactions will take place ?

(A) ⟨benzene⟩—NO_2 + ⟨benzene⟩—$\overset{O}{\overset{||}{C}}$—Cl $\xrightarrow{AlCl_3}$

(B) ⟨benzene, NO_2⟩—COCl + ⟨benzene⟩ $\xrightarrow{AlCl_3}$

(C) ⟨pyridine, N⟩ + RCOX $\xrightarrow{AlCl_3}$

(D) ⟨benzene, NH_2⟩ + RCOCl $\xrightarrow{AlCl_3}$
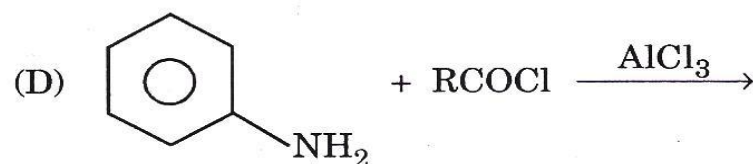
42. Which of the following statements is *not* correct with regard to stereochemistry of 1, 2-dimethyl cyclohexane (chair conformation) ?

(A) trans-1, 2-dimethyl cyclohexane can exist in two conformations. In one both CH_3 groups are in equatorial position and in the other both CH_3 groups are in axial position. Two CH_3 groups because of lesser crowding between CH_3 groups and axial hydrogens of the ring are in equatorial position (a more stable conformation is diequatorial one).

(B) cis-1, 2-dimethyl cyclohexane can also exist in two conformations, only one CH_3 group can occupy an equatorial position.

(C) In the most stable conformation (diequatorial) of the trans-isomer, the CH_3 groups are exactly the same distance apart as they are in either conformation of the cis-isomer. It is the repulsion between the CH_3 groups that causes the difference in stability between cis- and trans-isomer, as can be inferred from planar representation.

(D) It has been concluded that a total of 2.7 kcal of van der Waal strain for the cis-1, 2-dimethyl cyclohexane. In trans-1, 2-dimethyl cyclohexane has 0.9 kcal van der Waal strain on the molecule. The trans-isomer should be more stable than the cis-isomer by 1.8 kcal. This is found to be true with the measured value 1.87 kcal.

Chair conformations of trans-1, 2-dimethyl cyclohexane I and II :

| Diequatorial | Diaxial |
| (I) | (II) |
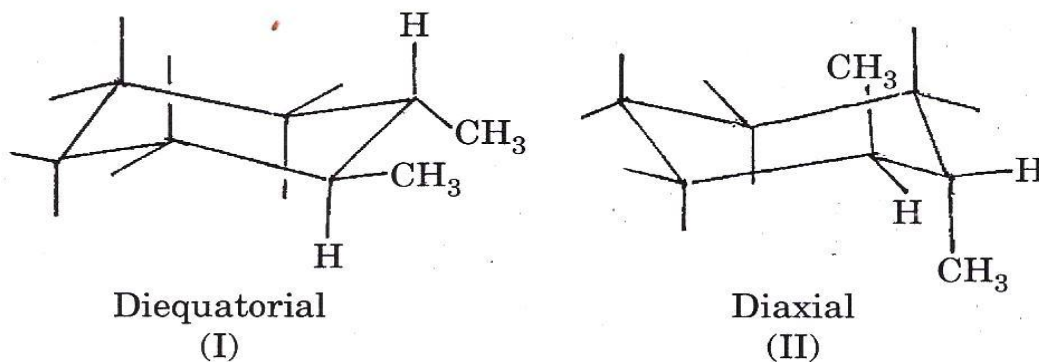
Chair conformations of cis-1, 2-dimethyl cyclohexane III and IV :

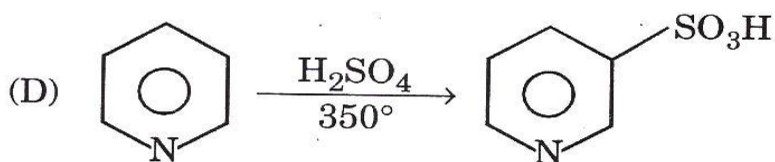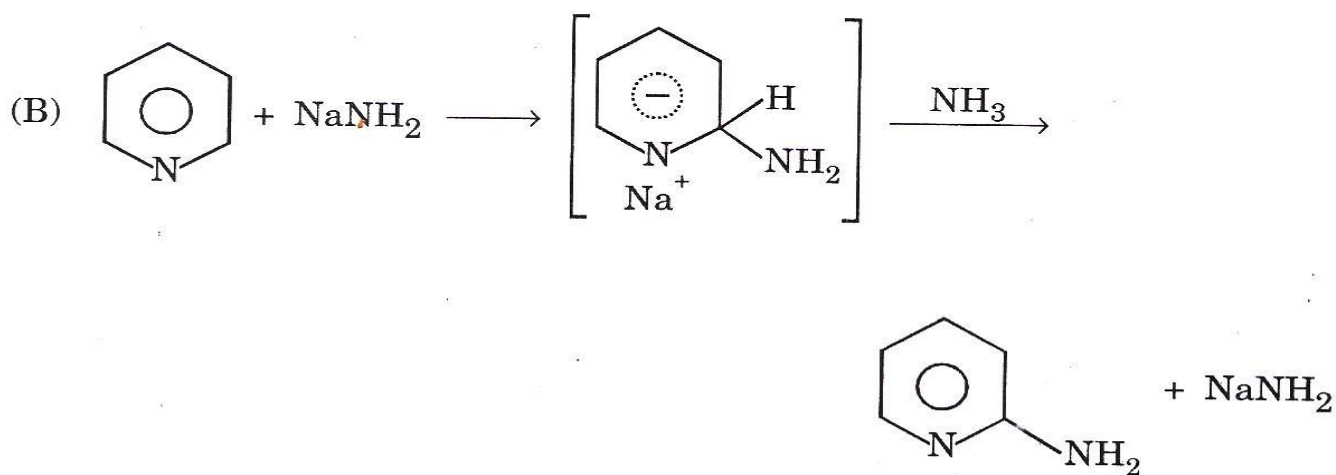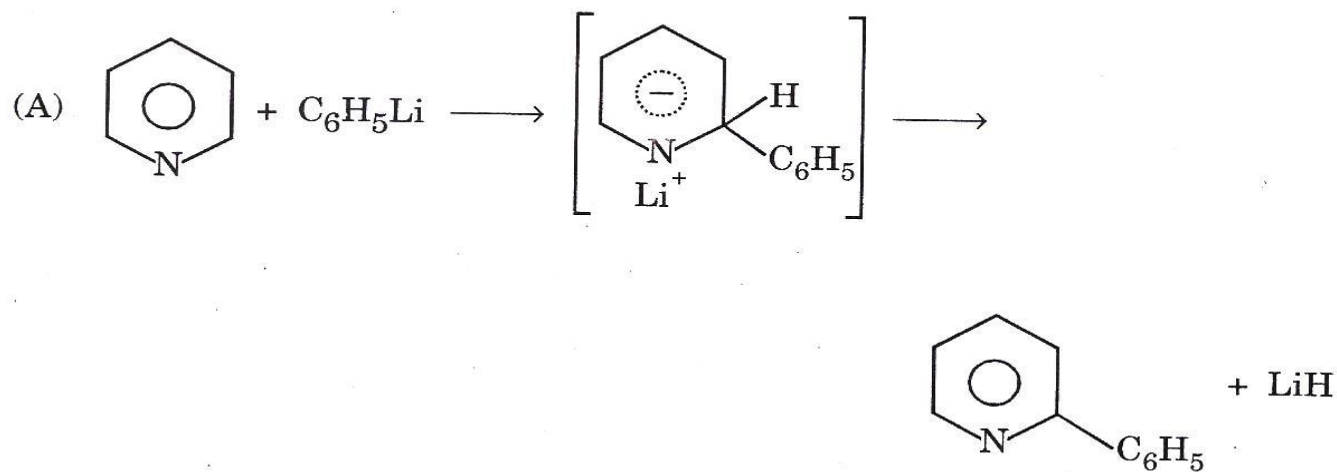
| Equatorial-axial | Axial-equatorial |
| (III) | (IV) |
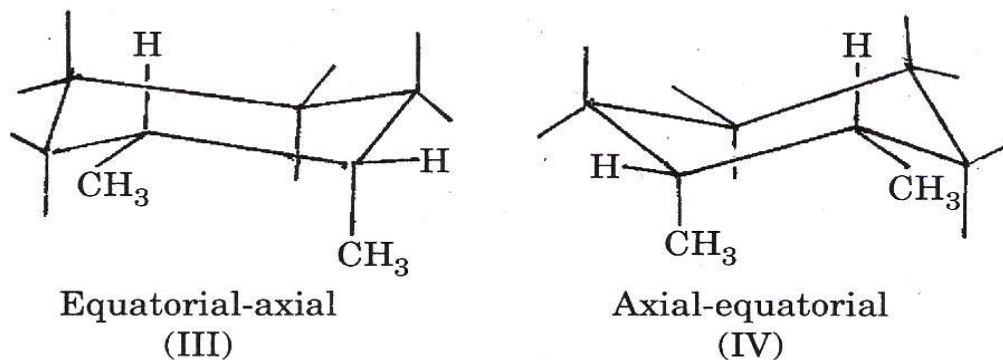
43. The product, 9-nitroanthracene is obtained from anthracene by the action of :

(A) Nitric acid and acetic anhydride

(B) Nitric acid and ethyl alcohol

(C) Nitric acid and acetic acid

(D) Nitric acid in excess

44. In pyrrole attack at position 2 is faster because in the process a more stable cation is formed which is a hybrid of :
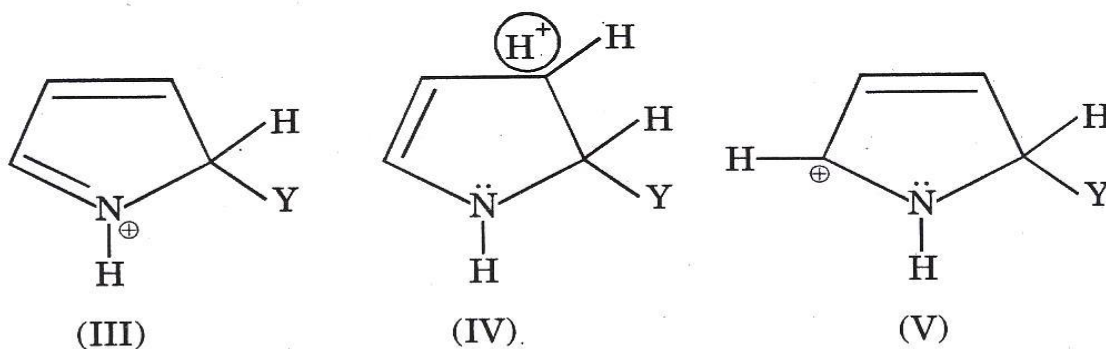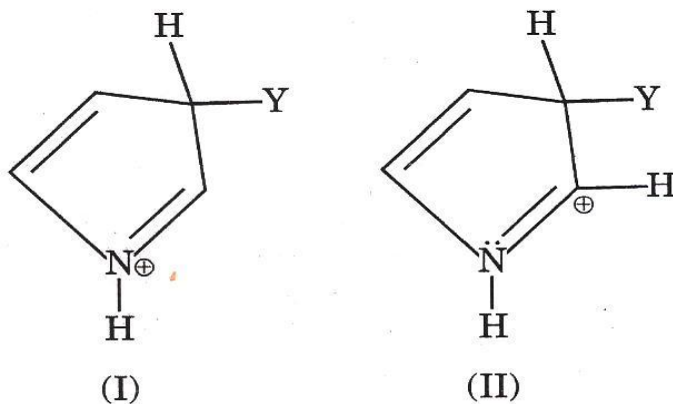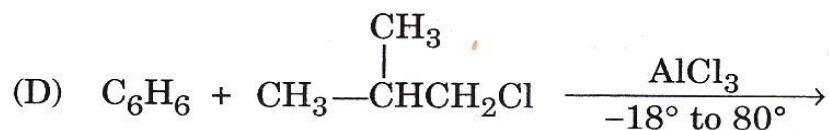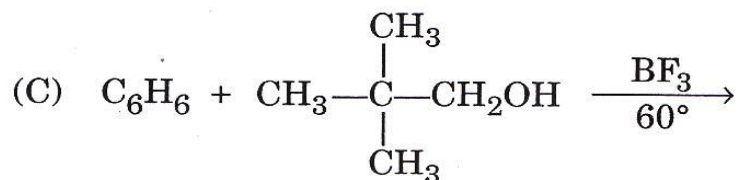

(A) Structure I, II and IV

(B) Structure III and IV

(C) Structure III, IV and V

(D) Structure I, II and III

45. Which of the following is *not* an example of nucleophilic substitution reaction ?

(A) [pyridine] + C_6H_5Li ⟶ [pyridine anion with N^- Li^+, H, C_6H_5] ⟶

[2-phenylpyridine] + LiH

(B) [pyridine] + $NaNH_2$ ⟶ [pyridine anion with N^- Na^+, H, NH_2] $\xrightarrow{NH_3}$

[2-aminopyridine] + $NaNH_2$

(C) $CH_2 = CH—CH_2OH \xrightarrow{HBr} CH_2 = CH—CH_2Br$

(D) [pyridine] $\xrightarrow[350°]{H_2SO_4}$ [pyridine-SO_3H]

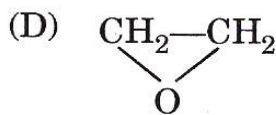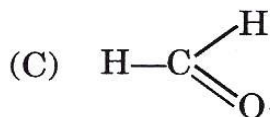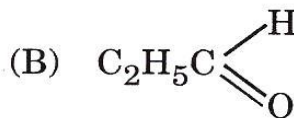46. Which of the following reactions gives an additional product, isopropyl benzene also (yield about 65%) ?

(A) $C_6H_6 + CH_3CH_2CH_2CH_2Cl \xrightarrow[0°]{AlCl_3}$

(B) $C_6H_6 + CH_3CH_2CH_2Cl \xrightarrow[-18° \text{ to } 80°]{AlCl_3}$

(C) $C_6H_6 + CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2OH \xrightarrow[60°]{BF_3}$

(D) $C_6H_6 + CH_3-\underset{\underset{CH_3}{|}}{CH}CH_2Cl \xrightarrow[-18° \text{ to } 80°]{AlCl_3}$
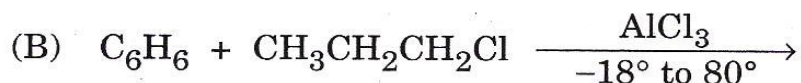
47. Which of the following compounds reacts with Grignard reagent, C_2H_5MgBr, to obtain n-butanol ?

(A) $C_2H_5-\overset{\overset{O}{\|}}{C}-OC_2H_5$

(B) $C_2H_5C\overset{\diagup H}{\diagdown_O}$

(C) $H-C\overset{\diagup H}{\diagdown_O}$

(D) $\overset{CH_2-CH_2}{\underset{O}{\diagdown \diagup}}$
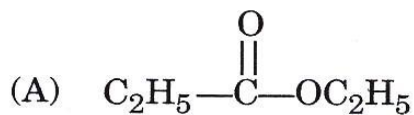
48. Which of the following statements is *correct* ?

(A) Lithium organocuprate reacts readily with acid chloride $\left(R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl\right)$ to yield tertiary alcohol.

(B) Organocopper are less reactive than Grignard reagent toward alkyl halides.

(C) Organocopper reagents do not react with many of the functional groups with which Grignard reagents and organolithium do react, for example —NO$_2$, —CN, —CO—, —COOR.

$2\ O_2N-\langle\bigcirc\rangle-C\overset{\nearrow O}{\searrow_{Cl}}\ +\ (CH_3)_2CuLi\ \longrightarrow$

$2\ O_2N-\langle\bigcirc\rangle-\overset{\overset{\displaystyle}{}}{\underset{\underset{\displaystyle O}{\|}}{C}}-CH_3$
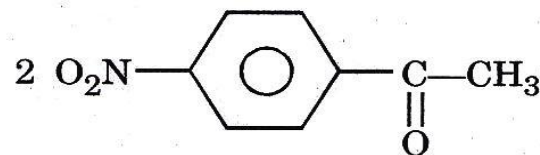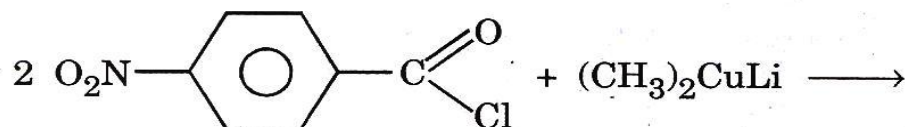
(D) Grignard reagents or organolithiums react readily with acid chloride to give ketones.

49. Which of the following statements is *not* correct regarding carbohydrates ?

(A) D-(+)-glucose has cyclic structure and it has one more chiral centre than Fischer's original open chain structure.

(B) D-(+)-glucose exists in two isomeric forms which do not undergo muta-rotation. α-D-(+)-glucose and β-D-(+)-glucose are diastereomers differing in configuration about C-1. Such a pair of diastereomers are called epimers.

(C) D-(+)-glucose form two isomeric methyl-D-glucosides. Two mono methyl derivatives of D-(+)-glucose are known one with m.p. 165° and specific rotation +158° and the other with m.p. 107° and specific rotation –33°C. The isomer with high +ve rotation is called methyl α-D-glucoside and the other is methyl-β-D-glucoside. These do not undergo mutarotation and do not reduce Tollens and Fehling's reagent.

(D) D-(+)-glucose undergo typical reactions of aldehyde-osazone formation reduction of Tollens and Fehling's reagent are presumably due to small amount of open chain compound. The concentration is too low for positive Schiff's test and bisulphite addition.

50. Which of the following statements is *not* correct with regard to carbohydrates ?

(A) Maltose, a disaccharide, reduces Tollens and Fehling's reagent. Maltose exists in α- and β-forms which undergo mutarotation. It yields osazone with phenyl hydrazine. Maltose is made up of two D-(+)-glucose units. An enzyme maltase converts maltose completely into glucose units joined by α-glucoside linkage. It is an α-anomer.

(B) Cellobiose is a disaccharides. It exists in α- and β-forms which undergo mutarotation. Cellobiose is hydrolysed by an enzyme emulsion and not by maltase. D-glucose units are joined by β-linkage. It is β-anomer.

(C) Lactose exists in α- and β-forms which undergo mutarotation. Emulsion splits β-linkage only. It converts into equal amount of D-(+)-glucose and D-(+)-galactose. It is a galactoside and not glucoside. It is β-anomer.

(D) Sucrose on hydrolysis with an enzyme invertase (from yeast) gives D-(+)-glucose and D-(−)-fructose. It must be both a glucoside and D-fructoside. Two hexoses are joined by glycoside linkage between C-1 of glucose and C-2 of fructose. The single link effectively block both carbonyl functions.

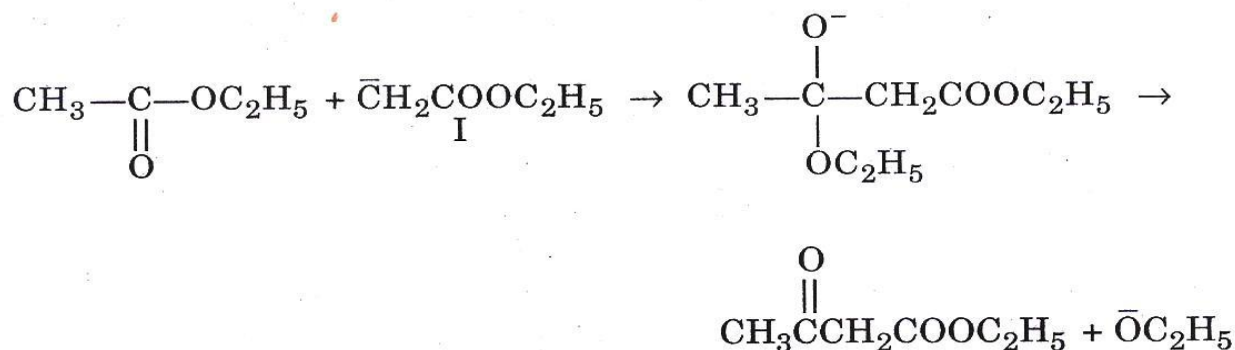It reduces Tollens and Fehling's reagent. Sucrose forms osazone. It undergoes mutarotation. It exists as α-anomer.

51. Which of the following statements/chemical reactions is *not* correct ?

The preparation of ethyl acetoacetate explains Claisen condensation.

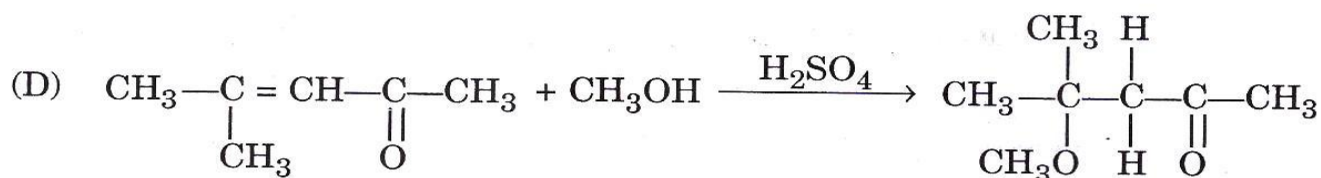(A) Ethoxide ion abstracts a hydrogen ion from the α-carbon of the ester to form carbanion I

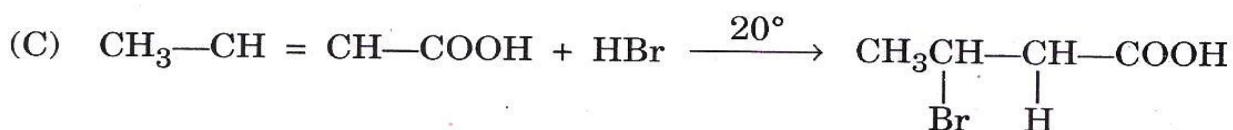$$CH_3COOC_2H_5 + OC_2\bar{H}_5 \longrightarrow C_2H_5OH + \bar{C}H_2COOC_2H_5$$
$$I$$

(B) The nucleophilic carbanion I attacks the carbonyl carbon of a second molecule of ester

$$CH_3-\underset{\underset{O}{\|}}{C}-OC_2H_5 + \bar{C}H_2COOC_2H_5 \rightarrow CH_3-\underset{\underset{OC_2H_5}{|}}{\overset{\overset{O^-}{|}}{C}}-CH_2COOC_2H_5 \rightarrow$$
$$\qquad\qquad\qquad\qquad I$$

$$CH_3\overset{O}{\overset{\|}{C}}CH_2COOC_2H_5 + \bar{O}C_2H_5$$

(C) $$CH_3\overset{O}{\overset{\|}{C}}CH_2COOC_2H_5 + OC_2\bar{H}_5 \longrightarrow CH_3CO\bar{C}HCOOC_2H_5 + C_2H_5OH$$

(D) The Claisen condensation reaction involves nucleophilic attack, leads to addition as in aldol condensation.

52. Which of the following is an example of nucleophilic addition reaction ?

(A) $C_6H_5-\overset{H}{\underset{}{C}}=\overset{H}{\underset{}{C}}-COOH + NH_2OH \longrightarrow C_6H_5-\overset{}{\underset{NHOH}{C}}-\overset{}{\underset{H}{C}}-COOH$

(B) $CH_2 = CH-COOH + H_2O \xrightarrow[100°]{H_2SO_4} CH_2-CH-COOH$ with OH and H substituents

(C) $CH_3-CH = CH-COOH + HBr \xrightarrow{20°} CH_3CH-CH-COOH$ with Br and H substituents

(D) $CH_3-\overset{}{\underset{CH_3}{C}}=CH-\overset{O}{\underset{\|}{C}}-CH_3 + CH_3OH \xrightarrow{H_2SO_4} CH_3-\overset{CH_3}{\underset{CH_3O}{C}}-\overset{H}{\underset{H}{C}}-\overset{O}{\underset{\|}{C}}-CH_3$
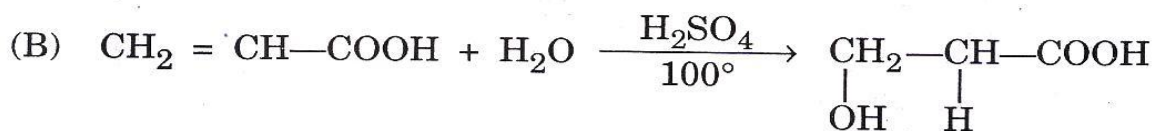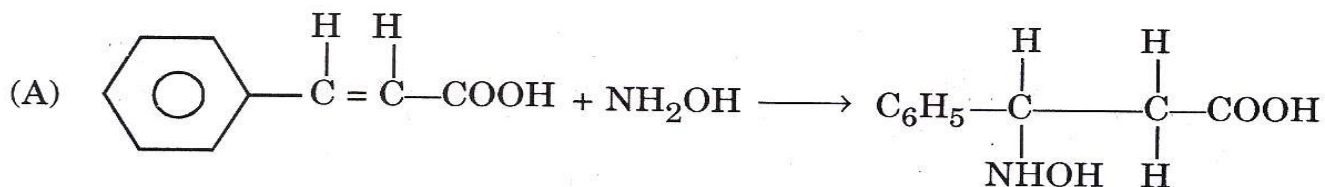
53. The carbonium can undergo three main type of reactions (a) combination with a nucleophile, (b) elimination of a proton, and (c) rearrangement of structure.

$$MeCH_2CH_2NH_2 \xrightarrow[(NaNO_2 + HCl)]{HNO_2} MeCH_2CH_2\overset{+}{N_2} \longrightarrow N_2 + MeCH_2\overset{\oplus}{CH_2}$$
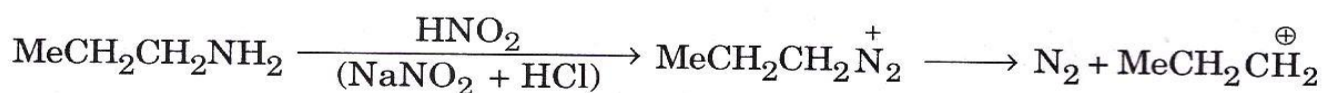
n-propyl cation I.

Which of the following statements is *not* correct ?

(A) The reaction of the n-propyl cation (I) with water as nucleophile i.e. (a) yields n-propanol.

(B) The elimination of a proton from the adjacent carbon atom in n-propyl cation (I) i.e. (b) yield propylene.

(C) The rearrangement (c) in this case migration of hydrogen yields the isopropyl cation.

(D) The isopropyl cation can then undergo elimination of a proton to yield isopropanol.

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

(A) Phenol has pKa 9.90. The presence of an electron withdrawing group in the nucleus increases acidity. In case of —NO_2 group the inductive effect will fall off with distance as we go $o\text{-} \rightarrow m\text{-} \rightarrow p$-nitrophenol.

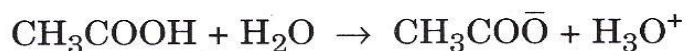The pKa of (*o*) NO_2—⟨◯⟩ (with OH), (*m*) O_2N—⟨◯⟩ (with OH) and
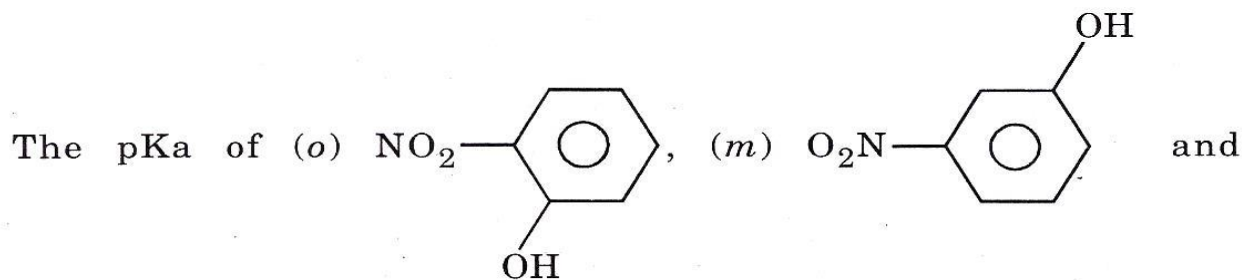
(*p*) O_2N—⟨◯⟩—OH are 7.20, 8.35 and 7.14. The result appears to be anomalous.

(B) There is an electron withdrawing mesomeric effect where —NO_2 is in o- and p- but not in m-position. This too will provide ionisation by stabilising the resultant anion. Thus o- and p-nitrophenols are expected to be more acidic than m-compound.

(C) The inductive and mesomeric effects play their role and influences the dissociation of the phenolic group as cited above in (*a*) and (*b*). 2, 4-$(O_2N)_2C_6H_4OH$ has pKa 4.01. This is in accordance with the expectation. 2, 4, 6-$(O_2N)_3C_6H_3OH$ has pKa 1.02. The compound is strongly acidic. The mesomeric effect is more predominant than inductive effect.

(D) The effect of introducing electron donating alkyl group is also appreciative. The resultant substituted phenols are weakly acidic indicating the effect of such substituents in stabilising the carboxylate ion by disturbing the interaction of its positive charge with the delocalised π-orbitals of the aromatic nucleus.

55. Which of the following kinds of spectroscopy can provide information on the energy difference between the initial and final states rather the energy levels involved in the transition ?

(A) UV absorption spectroscopy

(B) UV photoelectron spectroscopy

(C) Infrared absorption spectroscopy

(D) Rotational spectroscopy

56. The concept of resonance was introduced by Heisenberg through quantum mechanics and generalised by Pauling. Which of the following statements is *not* correct with regard to Resonance (some guiding principles are given below) :

(A) Resonating structures have the same number of unpaired electrons. The more covalent bonds there are in a valence bond structure, the greater is its stability.

(B) Structures involving formal charges are the most stable when the negative charge resides on the most electronegative and positive charge on the least electronegative atom.

(C) Dipolar valence bond structures in general are more stable than non-polar structures.

(D) Resonance can occur only between structures that correspond to very nearly the same relative positions of all atomic nuclei.

57. Which of the following statements is *not* correct with regard to non-aqueous solvent, ammonia ?

(A) The differentiating pH range of a solvent is governed by autoionisation of the solvent. It is 0 to 14 for water, 0 to 3 for sulphuric acid and 0 to 27 units for NH_3. The pH scale in ammonia is 0 (1M NH_4^+), 13.5 {neutral where $[NH_4^+] = [NH_2^-]$}, 27 (1M NH_2^-).

(B) The autoionisation of NH_3 is as, $2NH_3 \rightarrow NH_4^+ + NH_2^-$. All acids stronger than the characteristic anion of the solvent behaves as strong acids and are leveled to the solvent anion. All bases stronger than the characteristic of cation of the solvent are strong bases and are leveled to the solvent cation.

(C) Acetic acid is a strong acid in NH_3, a weak acid in water but a base in H_2SO_4.

$CH_3COOH + NH_3 \rightarrow CH_3CO\bar{O} + NH_4^+$

$CH_3COOH + H_2O \rightarrow CH_3CO\bar{O} + H_3O^+$

$CH_3COOH + H_2SO_4 \rightarrow CH_3CO\overset{+}{O}H_2 + HSO_4^-$

(D) In NH_3 strong oxidising agent do not exist. However the reducing agent shows enhanced reactivity.

58. Which of the following statements is *not* correct with regard to HCN as non-aqueous solvent ?

   (A) HCN has very high b.p. (299 K), high dielectric constant (106.8), high dipole-moment (2.93) and extensive hydrogen bonding. It is nice solvent as good as water for ionic compounds and dissolves to some extent covalent compounds also.

   (B) Solvolysis reaction : $Ag_2SO_4 + 2HCN \rightarrow 2AgCN + H_2SO_4$.

   (C) HCN autoionises as : $2HCN \rightarrow H_2\overset{+}{CN} + \overset{-}{CN}$

   Protonic acids (HCl, HNO_3, H_2SO_4 etc.) act as acids and can be neutralised against alkali cyanide solution which acts as a base.

   (D) Complex formation : $Fe(CN)_3 + 3(C_2H_5)_3NHCN \rightarrow [(C_2H_5)_3NH]_3 \cdot Fe(CN)_6$

59. Which of the following substance behaves as acid in sulphuric acid medium ?

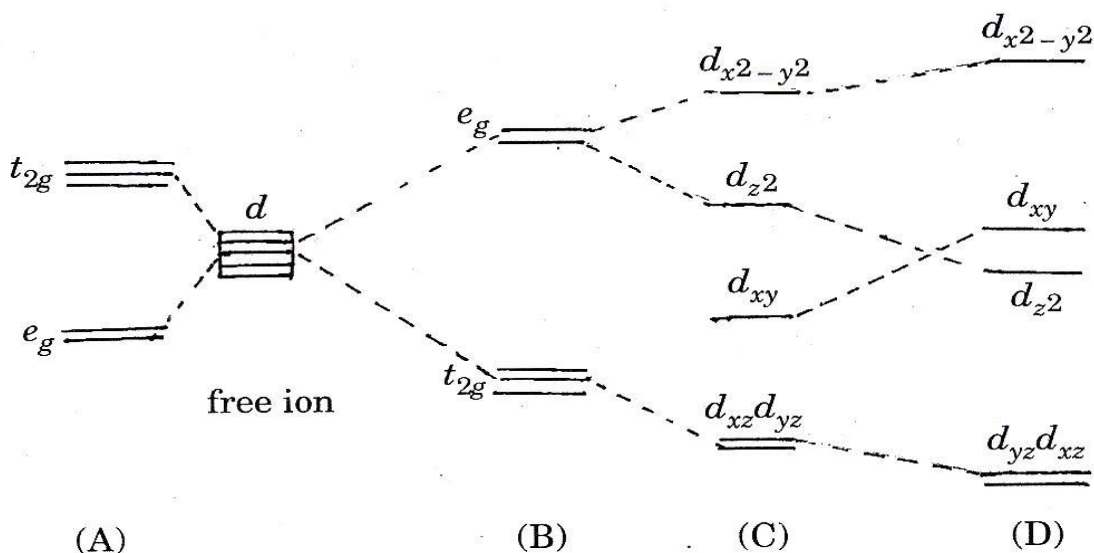   (A) $H_2NCONH_2 + H_2SO_4 \rightarrow H_2NCONH_3^+ + HSO_4^-$

   (B) $H_3BO_3 + 6H_2SO_4 \rightarrow B(HSO_4)_4^- + 3H_3^+O + 2HSO_4^-$

   (C) $HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + 2HSO_4^- + H_3O^+$

   (D) $NH_3 + H_2SO_4 \rightarrow HSO_4^- + NH_4^+$

60. Below are given some splitting pattern of d-orbitals in ligand field. Identify the splitting pattern in tetrahedral complexes :

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

61. It has been found by experimental studies of the spectra of a large number of complexes containing various metal ions in common oxidation states and various ligands. The ligands may be arranged in a series according to their capacity to cause d-orbital splitting. The d-orbital splitting increases in the following order :

(A) $F^- < Cl^- < NH_3 < H_2O <$ phen. $<$ en $< CN^-$

(B) $H_2O < F^- < Cl^- < NH_3 <$ en $< CN^- <$ phen.

(C) $Cl^- < F^- < H_2O < NH_3 <$ en $<$ phen. $< CN^-$

(D) $H_2O < F^- < NH_3 < Cl^- < CN^- <$ en $<$ phen.

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

   (A) $Cr(NH_3)_3Cl_3$ gives geometrical isomers, mer isomer (because Cl^- ions are located on the meridian of the complex) and face isomer (the three Cl^- ions are found on a face of the octahedron).

   (B) Four coordinate tetrahedral complex do not form cis- and trans-isomers because it is not possible for two ligands to be across the molecule from one another. All ligands are adjacent since all possible angles are 109° in a tetrahedron.

   (C) $[Pt(NH_3)Cl_3]^-$ do not form cis- and trans-isomers but $[Pt(NH_3)_2Cl(NO_2)]$ forms cis- and trans-isomers.

   (D) $[Ru(Phen.)_3]^{+2}$ and $[Co(en)_3]^{+3}$ do not show optical isomerism. The mirror-images are superimposable.

63. For a given ligand corresponding stability constants of complexes of bivalent ions of the first transition series are usually in the natural order, also called Irving-Williams order :

   (A) Mn < Co < Fe < Ni < Cu < Zn

   (B) Mn < Co < Ni < Fe > Cu < Zn

   (C) Mn < Fe < Co < Ni < Cu > Zn

   (D) Mn < Co > Ni < Fe > Cu < Zn
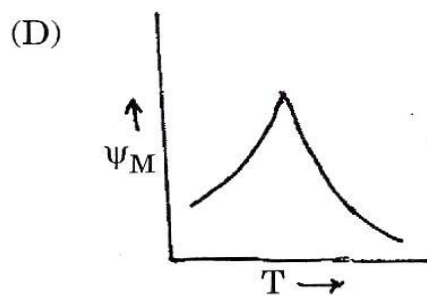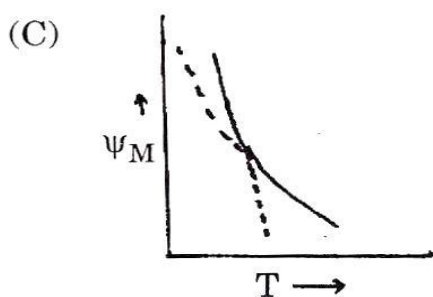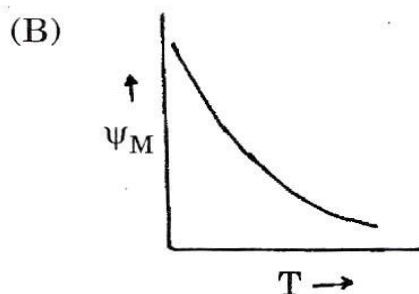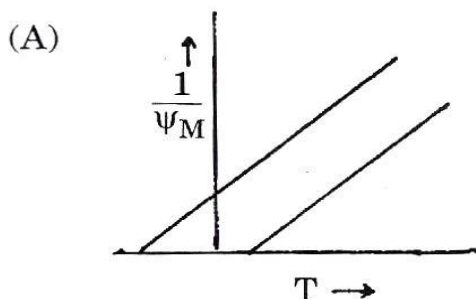
64. Which of the following statements is *not* correct ?

(A) Crystal Field Theory (CFT) treats the interaction between the metal ion and the ligand as a purely electrostatic problem in which ligand atoms are represented as point charges.

The metal-ligand interaction can be described in terms of molecular orbital (MO) formed by overlap of ligand-metal orbitals. These two approaches are very different in their algebraic formulations.

Both make use of explicit and rigorous use of symmetry properties of the complex.

(B) CFT treatment takes no account of the partly covalent nature of the metal-ligand bond and therefore whatever effects and phenomenon stem directly from covalence are entirely inexplicable in simple CFT.

(C) MOT provides a very simple and easy way of treating numerically many aspects of the electronic structure of complex. CFT does not provide numerical results in such an easy way.

(D) A modified CFT has been devised in which certain parameters are empirically adjusted to allow for the effects of covalence without explicitly introducing covalence into CFT formalism. The modified CFT is called ligand field theory (LFT). The LFT is the general name for which gradation of theories from electrostatic CFT to MO formalism.

65. Which of the following diagrams represents antiferromagnetism behaviour of a substance when ψ_M is plotted *Vs.* **T** ?

(A)

(B)

(C)

(D)

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

(A) In many of the complexes the ligand can stabilise metal in low positive, zero or negative formal oxidation states. High electron density on the metal atom in low oxidation state can be delocalised on to the ligands.

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

The ability of the ligand to accept the electron density into low lying empty π-orbitals is called π-acidity.

(C) The ligands form bonds to the metal by using σ-orbitals and exercise their π-acidity by using π-orbitals whose nodal plane include the axis of the σ-bond.

(D) The metal atom lies out of the molecular plane of the ligand.

67. Which of the following statements is of great practical value, if possible in solving food problem ?

(A) CO and N_2 are isoelectronic and led to speculation that bond M-NN may exist like M-CO bond. The compound $[Ru(NH_3)_5N_2]Cl_2$ was found. The cation $[Ru(NH_3)_5N_2]^{+2}$ can be obtained by displacing H_2O by N_2 at 100 atm from $[Ru(NH_3)_5(H_2O)_3]^{+3}$ but no way of reductively transforming the coordinated N_2 to NH_3 has been reported.

(B) The bonding in M-N_2 group is similar to M-CO groups; $M \leftarrow N_2$ σ-donation and M-N_2 π-acceptance are involved.

(C) The lower stability of N_2 complexes appear to arise from smaller differences in the energies of the MO's of CO and N_2. For CO the σ-donor orbital is weakly antibonding whereas the corresponding orbital for N_2 is of bonding character. N_2 is significantly poorer σ-donor than is CO. Weakening of CO bond is due entirely to back donation from d_π-orbital to CO π^*-orbital with σ-donation slightly cancelling some of this effect.

(D) For N_2-complexes N = N weakening results from both σ-donation and π-back acceptance. This accounts for poor stability of N_2 complexes in general.

68. Which of the following lanthanide complexes has coordination number 10 and metal ion has +4 oxidation state ?

(A) $[Ce(NO_3)_5]^{-2}$

(B) $(NH_4)_2[Ce(NO_3)_6]$

(C) $Ce(NO_3)_4(OPPh_3)_2$

(D) Cs_2CeCl_6

69. Which of the following trivalent lanthanide/actinide (*f*-block elements) do not impart any colour to the flame ?

(A) U^{+3}, Np^{+3}, Pm^{+3}

(B) Ce^{+3}, Gd^{+3}, Cm^{+3}

(C) Sm^{+3}, Dy^{+3}, Ho^{+3}

(D) Pu^{+3}, Am^{+3}, Eu^{+3}

70. Which of the following group of *f*-block elements have the highest oxidation states ?

(A) Ce, Pr, Gd, Tb

(B) Nd, Pm, Sm, Eu

(C) U, Np, Pu, Am

(D) Cf, Es, Fm, Md

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

(A) Copper is essential and is bound to proteins in the body either as metalloproteins or enzymes (for e.g. Tryrosinase in melanin pigments). Copper is important in dopamine hydroxylase, galactose oxidase, cytochrome oxidase.

(B) Haemocyanin is a copper containing protein and it is a oxygen carrier in some lower animals. It is a haem protein. The molecule is diamagnetic even though Cu^{+2} has d^9 configuration. The oxygenated haemocyanins are red coloured like human blood. Deoxygenated haemocyanins is also red but contains Cu^{+1}.

(C) There are many proteins which contain copper. They act as electron transfer agents by means of a Cu^{+2}/Cu^{+1} couple.

(D) Haemocyanin is found in many lower animals for example in the blood of carbs, snails, scorpion. The oxygenated haemocyanins have one dioxygen molecule attached to two copper atoms.

72. Which of the following statements provides impetus to research work ?

(A) A superconductor has zero or almost zero electrical resistance. It can carry an electric current without losing energy and in principle the current can flow forever. There is a critical temperature T_C at which resistance drops sharply and superconduction begins.

(B) Some superconductors do not permit a magnetic field to penetrate their bulk. This is called Meissner effect. A superconductor also expels all intermagnetic field (arising from unpaired electrons) superconductors are diamagnetic.

(C) Superconducting alloy of Nb and Ti which has T_C about 4K. Nb_3Sn and Nb_3Ge alloys have critical temperature (T_C) values 22K and 24K respectively. Low temperature superconductors have low value of T_C. This requires the use of liquid helium which is very expensive. The alloy $Bi_{1.7} Pb_{0.2} Sb_{0.1} Sr_2 Ca_2 Cu_{2.8} O_Y$ has a T_C 164K.

(D) Much pioneering work was carried out earlier on linear motors and a prototype of a train which floats on a magnetic field has been built in Japan. Much work and improvement is necessary to have a fast mode of travel in India. The prospect of making superconductors which work at room temperature continues to attract attention as power losses to be minimum on transmission of power.
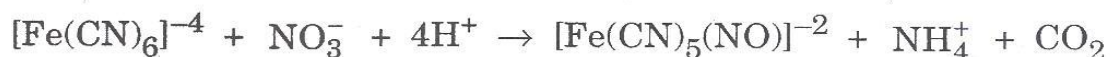
73. Which of the following statements is *not* correct ?

(A) Living organisms require at least 27 elements of which 15 are metals. The metals required in major quantities are K, Mg, Na and Ca. Minor quantities of Mn, Fe, Co, Cu, Zn and Mo and trace amounts of V, Cr, Sn, Ni and Al are required by some organisms.

(B) Bulk quantities of K, Mg, Na, Ca are required mainly to balance the electrical charge associated negatively charged organic macromolecules in the cell and also to maintain the osmotic pressure inside the cell to keep it turgid and prevent its collapse.

(C) There is a close similarity in chemial properties between alkali metals Na and K, yet their biological functions are very different. K^+ ions are actively expelled from cells whereas Na^+ are not. The ion transport involves both the active expulsion of K^+ and active take up Na^+ ion. The transport of ions requires the energy and this is obtained by hydrolysis of ATP molecule to ADP and provides enough energy to move $3K^+$ ions out of the cell and two Na^+ and one H^+ back into the cell.

(D) The different ratio of Na^+ and K^+ inside and outside cells produces electric potential across the cell membrane which is essential for the functioning of nerve and muscle cells.

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

(A) Sodium nitroprusside $Na_2[Fe(CN)_5(NO)]$, $2H_2O$ has NO^+ ligand and is obtained as brown red crystals by reacting hexacyanoferrate (II) with either 30% HNO_3 or with a nitrite

$$[Fe(CN)_6]^{-4} + NO_3^- + 4H^+ \rightarrow [Fe(CN)_5(NO)]^{-2} + NH_4^+ + CO_2$$

$$Na_4[Fe(CN)_6] + NO_2^- + H_2O \rightarrow Na_2[Fe(CN)_5(NO)] + 2NaOH + C\bar{N}$$

(B) Sodium nitroprusside reacts with sulphide ion to form purple complex

$$2[Fe(CN)_5(NO)]^{-2} + S^{-2} \rightarrow 2[Fe(CN)_5(NOS)]^{-4}$$
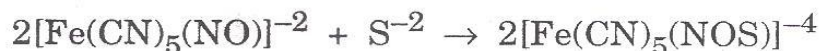
(C) $[Fe^{II}(Phen.)_3]^{+2}$ is bright red and it is used for colourimetric determination of Fe and also as redox indicator 'ferroin' in titration. It is easier to oxidise $[Fe(H_2O)_6]^{+2}$ to $[Fe(H_2O)_6]^{+3}$ than $[Fe(Phen.)_3]^{+2}$ to $[Fe(Phen.)_3]^{+3}$. The colour change is red to blue.

(D) The brown ring test for NO_3^- ion depends on the forming a complex $[Fe(H_2O)_5(NO_2)]^{+2}$. H_2SO_4 reacts with NO_3^- forming NO_2 which combines with Fe^{+2} ion to form the complex $[Fe(H_2O)_5(NO_2)]^{+2}$ at the interface between two liquids.

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

(A) A pair of metals having similar sized atoms, the same number of valence electrons, and the same type of lattice when pure will form a substitution alloy. The elements Ni and Cu are so nearly alike in size that they exhibit complete solubility. Both have face centred cubic lattice. Copper-nickel alloy forms a good example of substitution alloy.

(B) A pair of metals of vastly different electronegativities with atoms of widely different sizes will form a compound alloy. $MgCu_2$ is an example of compound alloy.

(C) A pair of metals having atoms widely different in size but similar in electronegativities. The widely different sizes tend to make the metals relatively insoluble in each other, so they solidify in separate crystallites. Tin and lead form a eutectic alloy.

(D) A pair of elements one of which is a small non-metal. The non-metal atoms occupy the interstics of the larger metal atom. Iron and carbon do not form an alloy but a simple mixture.

76. Which of the following statements is *not* correct with reference to organometallic compounds (cyclopentadiene) ?

(A) Cyclopentadiene is weakly acidic (pKa = 20) dissociating as H^+ and $C_5H_5^-$ ions and it forms cyclopentadienides for e.g. $M(C_5H_5)_2$, $M(C_5H_5)$, $M(C_5H_5)_3$ where M is alkaline earth, alkali and lanthanide and actinide respectively.

(B) $Mn(C_5H_5)_2$ seems to be ionic since the Mn(II) therein retains its spin sextuplet d^5 configuration. The compound is diamagnetic like other MnX_2 compounds.

(C) Cyclopentadienides are very reactive toward air and water and react readily with $FeCl_2$ in tetrahydrofurane to give ferrocene.

(D) It is possible to have covalent $(h^5\text{-}C_5H_5)$ M groups even when the metal atom has no valence-shell d-orbitals provided it is p-orbitals of suitable energy and size. A pair of p_x and p_y orbitals can overlap with the e_1 π-orbitals of C_5H_5 in much in the same way do d_{xz} and d_{yz} orbitals. C_5H_5In and C_5H_5Tl are most suitable examples.

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

(A) Dibenzene chromium (dark brown crystals) is much more stable in air than ferrocene, with which it is isoelectronic. It undergoes aromatic substitution. X-ray and electron diffraction studies show that C-C bond lengths are not equal.

(B) Cyclooctatetraene molecule is not itself aromatic and it forms a number of complexes in which it retains polyolefin nature.

(C) Cyclooctatetraene acts a planar aromatic ligand where it is considered as $C_8H_8^{-2}$ ion (aromatic, 10-electron system) bound to a metal atom large enough to overlap effectively with such a large ring. $(C_8H_8)_2U$ and $(C_8H_8)_2Th$ are suitable examples in which 5*f*-orbitals participate in metal to ring bonding.

(D) The only example of symmetrical C_8H_8-M bonding for a *d*-block metal is found in $(C_8H_8)_3Ti_2$.

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

(A) Ce^{+3} and Yb^{+3} show exceptionally strong absorption in UV region because of transition from $4f$ to $5d$. Since $\Delta l = +1$ is an allowed transition and so gives stronger absorption than forbidden *f-f* transition. *f-d* peaks are broad in contrast to *f-f* peaks.

Charge transfer spectra are possible due to transfer of an electron from ligand to the metal. This is more probable if the metal is in high oxidation state or ligand has reducing properties.

(B) All but one of the Ln^{+3} show absorption in the visible or near UV region of the spectrum. The strong yellow colour of Ce^{+4} solution and the blood red colour of Sm^{+2} is also due to forbidden *f-f* transition.

(C) The lanthanides form no complexes with π-bonding ligands and lack of π-bonding is attributed to the non-availability of *f*-orbitals for bonding.

(D) In the spectra of transition metal ions crystal field splitting is of major importance. However in lanthanide spin-orbit coupling is more important than crystal field splitting.

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

(A) La^{+3} and Lu^{+3} have no unpaired electrons, hence are diamagnetic. All other lanthanides (Ln^{+3}) are paramagnetic.

(B) The magnetic moment of transition elements may be calculated using relation (i)

$$\mu_{S+L} = \sqrt{4S(S+1) + L(L+1)} \quad \text{......... } (i)$$

For the first row transition elements ($3d$ series) the orbital contribution is wholly (or partially) quenched by interaction with electrical field of ligands in its environment. The relation (i) becomes

$$\mu_S = \sqrt{4S(S+1)} = \sqrt{n(n+2)}$$

where 'n' is the number of unpaired electrons ...... (ii)

The experimental results are in agreement with the results obtained by using spin only formula [relation (ii)].

For Mn^{+2} has 5 unpaired electrons; $\mu = 5.92$ BM and for Gd^{+3} has 7 unpaired electrons; $\mu = 7.9$ BM.

(C) For other lanthanides ($4f$ elements), second and third row transition elements ($4d$ and $5d$ series) the simple relation (ii) does not hold good. The magnetic effect due to orbital motion of the electron has to be into account. In lanthanides the spin contribution 'S' and orbital contribution 'L' couple together to give a total quantum number J

$$\mu = g\sqrt{J(J+1)} \quad \text{where} \quad g = 1\frac{1}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)} \quad \text{......... } (iii)$$

The value of g for a free electron $= 2.0023$.

The calculated value of magnetic moment using Russel-Saunders coupling are somewhat higher than the experimental values.

(D) Like $4f$-orbitals, $5f$-orbitals do not participant in bond formation in complexes, consequently negligible ligand effects if any, inadequacy of Russell-Saunders coupling, anomalous behaviour for Sm^{+3} and Eu^{+3} also seen in Pu^{+3} and Am^{+3}, multiplet levels comparable to kT so many constraints, yet it is easier to follow.

80. Which of the following is an example of polymerisation isomerism ?

(A)

and

(B) $\left[(NH_3)_3Co \overset{OH}{\underset{OH}{-OH-}} Co(NH_3)_3 \right]^{-3}$ and $\left[Co \left\{ \overset{OH}{\underset{OH}{}} Co(NH_3)_4 \right\}_3 \right]^{-6}$

(C) $\left[\begin{array}{c} NH_3 \\ H_3N \quad ONO \\ Co \\ NH_3 \quad NH_3 \\ NH_3 \end{array} \right]^{+2}$ and $\left[\begin{array}{c} NH_3 \\ H_3N \quad NO_2 \\ Co \\ NH_3 \quad NH_3 \\ NH_3 \end{array} \right]^{+2}$

(D) $\left[Cl(NH_3)_3Co \overset{NH_2}{\underset{O_2}{}} Co(NH_3)_3Cl \right] Cl_2$ and

$\left[(NH_3)_4Co \overset{NH_2}{\underset{O_2}{}} Co(NH_3)_2Cl_2 \right] Cl_2$
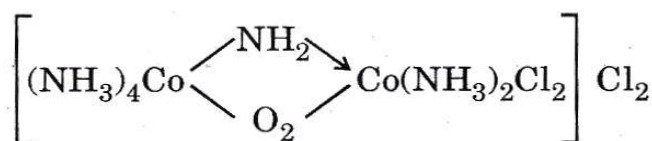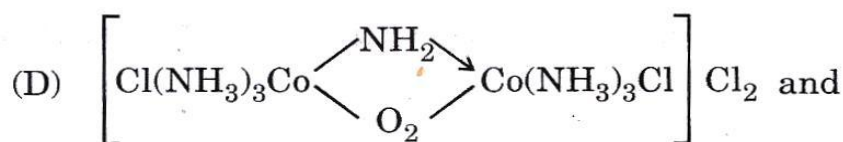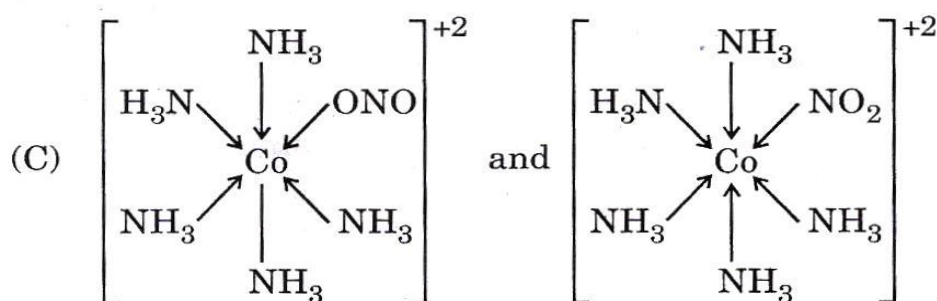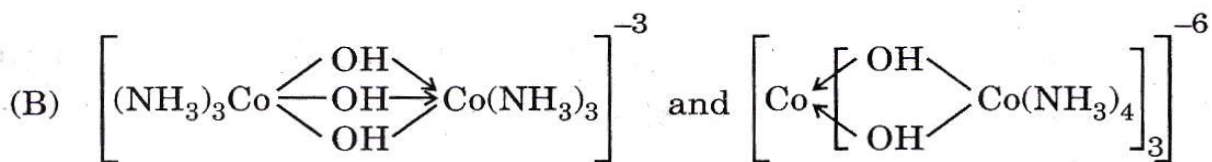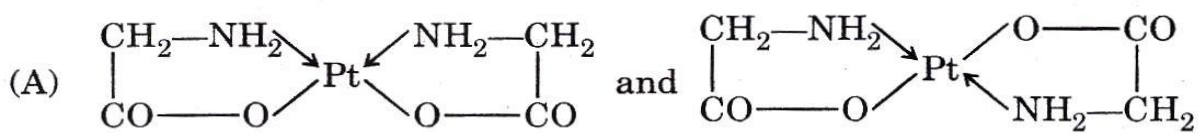
81. Which of the following lordships was a part Twelve Thakurais of Shimla Hills ?

   (A) Khaneti   (B) Kuthar

   (C) Koti   (D) Baghat

82. Which mountain pass joins Kinnaur and Tibet ?

   (A) Hamta   (B) Kangla

   (C) Shipki   (D) Jalsu

83. Which of the following lakes is located between Dodra-Kawar and Sangla ?

   (A) Bradonsar   (B) Karali

   (C) Chadra Nahan   (D) Nako

84. Which raja of Chamba princely state refused to obey the orders of Aurangzeb to demolish all the Hindu temples in his state ?

   (A) Udai Singh   (B) Umed Singh

   (C) Charhat Singh   (D) Chattar Singh

85. On which day does Manimahesh Chhari Yatra terminate ?

   (A) Radha Ashtami   (B) Durga Ashtami

   (C) Kal Bhairav Ashtami   (D) Ahoi Ashtami

86. When was the first popular ministry headed by Dr. Y.S. Parmar sworn in H.P. ?

   (A) 15th April, 1948   (B) 10th September, 1951

   (C) 24th March, 1952   (D) 2nd October, 1952

87. Which of the following painters belonged to Mandi princely state ?

   (A) Banwari   (B) Mangu

   (C) Guler Baksh   (D) Ghali

88. Which constituency Shri Brij Behari Lal Butail former Speaker of H.P. Vidhan Sabha represented ?

   (A) Jawalamukhi   (B) Nagrota

   (C) Kangra   (D) Palampur

89. Which one of the following items is *not* supplied by the H.P. State Civil Supplies Corporation ?

    (A) School Uniforms to the Education Department

    (B) Text-books to the Education Department

    (C) Ayurvedic medicines to the H.P. Hospitals

    (D) Cement to H.P. Govt. Departments

90. What is the capacity of Gyspa Hydro Electric Power Project ?

    (A) 300 MW   (B) 450 MW

    (C) 525 MW   (D) 550 MW

91. What is the name of the Medical College at Gorakhpur where several infants died in August, 2017 ?

    (A) Baba Seechewal Medical College

    (B) Baba Ram Dev Medical College

    (C) Baba Ram Das (Raghav Das) Medical College

    (D) Baba Ram Pal Medical College

92. Who is Trivendra Singh Rawat (August 2017) ?

    (A) Chief of Army Staff

    (B) Chief Election Commissioner of India

    (C) Chief Minister of Uttarakhand

    (D) Chairman of Censor Board

93. In which state of India is Lord Ayyappa temple where the entry of women is/has been an issue ?

    (A) Kerala   (B) Karnataka

    (C) Tamil Nadu   (D) Telangana

94. Approximately by what margin (of votes) did Ram Nath Kovind defeat Meira Kumar in the Presidential elections ?

(A) 2.74 Lakh (B) 2.90 Lakh

(C) 3.13 Lakh (D) 3.34 Lakh

95. What are the followers of Gurmeet Ram Rahim Singh's Dera Sacha Sauda usually called ?

(A) Chelas (B) Premis

(C) Bhaktas (D) Sadhaks

96. Against which team did Harmanpreet Kaur make 171 runs at the 2017 Women Cricket World Cup semi-final ?

(A) England (B) Australia

(C) South Africa (D) New Zealand

97. What name has been given to the hurricane that rose from the Gulf of Mexico and swept through Texas in August 2017 ?

(A) Katrina (B) Harris

(C) Harvey (D) Horrer

98. To which country does the Rohingya ethnic minority community mainly belong ?

(A) Pakistan (B) Bangladesh

(C) Nepal (D) Myanmar

99. Which day is observed as Hiroshima Day ?

(A) August 06 (B) August 09

(C) August 20 (D) September 16

100. In which city of Spain the driver of a van ploughed it into crowd killing about 13 persons on August 17, 2017 ?

(A) Barcelona (B) Madrid

(C) Seville (D) Repoll