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. Encode clearly the test booklet series A, B, C or D as the case may be in the appropriate place in the answer-sheet.

3. Write your Roll Number only in the box provided alongside. Do not write anything else on the Test Booklet.

4. 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.

5. 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:

   A  B  C  D

6. 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/liquid is allowed.

7. 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.

8. 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 no negative marking.

9. 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.

10. 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.

11. After you have completed the test, hand over the Answer Sheet only, to the Invigilator.

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

P.T.O.
1. The Hamiltonian for $\text{H}_2^+$ (two nucleus and one electron) is:

(A) $\hat{H} = -\frac{\hbar^2}{2m} V^2 + \frac{1}{4\pi\varepsilon_0} \left[ \frac{e^2}{r_A} + \frac{e^2}{r_B} - \frac{e^2}{r_{AB}} \right]$

(B) $\hat{H} = -\frac{\hbar^2}{2m} V_1^2 - \frac{\hbar^2}{2m} V_2^2 - \frac{2e^2}{4\pi\varepsilon_0 r_1} - \frac{2e^2}{4\pi\varepsilon_0 r_2} + \frac{e^2}{4\pi\varepsilon_0 r_{12}}$

(C) $\hat{H} = -\frac{\hbar^2}{2m} (V_1^2 + V_2^2) + \frac{1}{4\pi\varepsilon_0} \left[ -\frac{e^2}{r_{A1}} - \frac{e^2}{r_{A2}} - \frac{e^2}{r_{B1}} - \frac{e^2}{r_{B2}} + \frac{e^2}{r_{12}} + \frac{e^2}{r_{AB}} \right]$

(D) $\hat{H} = -\frac{\hbar^2}{2m} V^2 + V_{A,B}$

\[ r_1 = \text{distance of electron 1 from the nucleus, } r_2 = \text{distance of electron 2 from the nucleus, } r_A = \text{distance of the electron from the nucleus A and } r_B = \text{distance of the electron from the nucleus B, } r_{AB} = \text{distance between the nucleus and others have their usual meanings.}\]

2. The complete valence bond wave function of AB molecule (assuming that it is formed from $1s$ orbital of A and $2p_z$-orbital of B, the bond has some ionic character because of electronegativity difference between A and B is written as:

(A) $\psi = \phi_A(1) \cdot \phi_B(2) + \phi_B(1) \phi_A(2)$

(B) $\psi = \phi_B(1) + \phi_B(2)$

(C) $\psi = C_1 \psi_{\text{covalent}} + C_2 \psi_{\text{ionic}}$ with $C_1^2 + C_2^2 = 1$

(D) $\psi = \sqrt{C_1} [\phi_{A1}; \phi_{B2}] + \sqrt{C_2} [\phi_{B1}; \phi_{A2}] + \sqrt{C_1} [\psi_{B1}; \psi_{B2}]$
3. The term symbol for sodium in the ground state is:

(A) \(4 \ s_{3/2}\)  

(B) \(2 \ s_{1/2}\)  

(C) \(3 \ p_0\)  

(D) \(2 \ p_{3/2}\)  

4. The eigen value equation is of the form

\[(\text{operator}) \ (\text{function}) = (\text{numerical factor}) \ (\text{same function})\]

Which of the following is an eigen function when an operator \(\frac{d}{dx}\) operates on:

(A) \(e^{ax}\)  

(B) \(e^{ax}\)  

(C) \(\sin ax\)  

(D) \(\cos ax\)  

5. Which of the following energy levels of a particle in a three-dimensional cubical box is three-fold degenerate?

(A) \(12 \ \frac{\hbar^2}{8ma^2}\)  

(B) \(14 \ \frac{\hbar^2}{8ma^2}\)  

(C) \(6 \ \frac{\hbar^2}{8ma^2}\)  

(D) \(29 \ \frac{\hbar^2}{8ma^2}\)
6. Which of the following species gives an equally spaced three lines of equal intensity ratio (1 : 1 : 1) electron spin resonance spectrum?

(A) naphthalene negative ion

(B) methyl radical

(C) 1, 4-benzene semiquinine radical anion

(D) $(SO_3)_2NO^-$

7. Which of the following statements is not correct?

[The dipole moment of chlorobenzene is 1.70 D]

(A) The value for 1, 3-dichlorobenzene is calculated as $P_{1,3} = P_{\text{mono}} = 1.70$ D and it is in agreement with experimental value 1.68 D

(B) The value for 1, 4-dichlorobenzene is calculated as $P_{1,4} = 2.40$ D

(C) The value for 1, 2-dichlorobenzene is calculated as $P_{1,2} = 1.732 \times P_{\text{mono}} = 2.94$ D and the agreement with experimental value 2.53 D is not satisfactory

(D) The expression for calculating $P_{1,2}$ is written as:

$$P_{1,2} = (p^2 + p^2 + 2pp \cos 60)^{1/2} = \sqrt{3} P_{\text{mono}} = 1.732 P_{\text{mono}}$$

The angle between C—Cl bond vectors may be larger than 60° because of mutual repulsion of relatively negative chlorine atoms
The first order nmr spectrum of phenylethyl acetate \( \text{CH}_3\text{C}—\text{OCH}_2\text{CH}_2\text{C}_6\text{H}_5 \) has been observed as given below:

Which of the following statements is *not* correct?

(A) The signals \( \text{(ii)} \) and \( \text{(iii)} \) are symmetrically arranged about the chemical shift of the two groups at 175 cps and 257 cps. The coupling constants have been found as 7 cps. The ratio of the intensities of the signals is \( 1 : 2 : 1 \).

(B) The three protons in the methyl group are equivalent. There are no protons nearby to couple with methyl protons resulting in sharp single peak at 120 cps.

(C) The chemically but not magnetically equivalent protons gives a single sharp peak at 435 cps.

(D) The signals at \( \text{(ii)} \) corresponds \( \text{CH}_2 \) group adjacent to phenyl group and signal at \( \text{(iii)} \) corresponds to \( \text{CH}_2 \) group adjacent to oxygen of the acetate group.
A researcher synthesised a metal complex Zn(PMP)$_2$ where PMP is N-phenyl-3-mercaptobipropionamide ($\text{CH}_2(\text{SH})\text{CH}_2\text{CONH C}_6\text{H}_5$), a bidentate chelating agent. After purification and elemental analysis the researcher obtained an IR absorption spectra of PMP and its zinc complex on Perkin-Elmer Infrared spectrophotometer 577 in KBr pellets. The following results were obtained in IR spectrum of PMP.

$\nu_{\text{NH}}$ (trans): 3360, 3268, 3185 cm$^{-1}$, amide I (essentially $\nu_C = 0$): 1653 cm$^{-1}$, amide II: 1538 cm$^{-1}$, amide III: 1253 cm$^{-1}$ and $\nu_{\text{SH}} = 2545$ cm$^{-1}$.

(intensities are not given here)

In Zn(PMP)$_2$ one important absorption band was missing and a new absorption band was seen at about 400 cm$^{-1}$.

The missing absorption band was:

(A) 3360, 3280, 3180 cm$^{-1}$
(B) 1653, 1538 cm$^{-1}$
(C) 2545 cm$^{-1}$
(D) 1250 cm$^{-1}$

10. Which of the following statements is not correct?

(A) UV absorption spectrum of a polyatomic molecule in the gaseous state appears only as broad band or band envelope due to closely spaced sublevels. There occurs simultaneous transitions of vibrational rotational in addition to electronic transition

(B) The vibrational-rotational structure is lost in solution due to interaction between neighbouring molecule and by solvation

(C) The steric effects also influence the UV absorption spectral studies there is a decrease in absorption intensity and no change in wavelength, sometimes shifts to shorter wavelength and decrease in absorption intensity Non-coplanarization may cause hypso or bathochromic shifts

(D) In an electronic transition the excited molecule may return to the ground state by absorption of energy
11. Which of the following statements is not correct?

(A) The $n \rightarrow \pi^*$ transition in mesityl oxide [CH$_3$COCH = C(CH$_3$)$_2$] shows a hypsochromic shift in $\lambda_{\text{max}}$ with a change in polarity of the solvent.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>iso-octane</th>
<th>CH$_3$CN</th>
<th>CHCl$_3$</th>
<th>CH$_3$OH</th>
<th>CH$_3$OH</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda_{\text{max}}$ (nm)</td>
<td>321</td>
<td>314</td>
<td>315</td>
<td>308</td>
<td></td>
</tr>
</tbody>
</table>

(B) The $\pi - \pi^*$ in mesityl oxide shows a bathochromic shift in $\lambda_{\text{max}}$ with change in polarity of the solvent.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>iso-octane</th>
<th>CH$_3$CN</th>
<th>CHCl$_3$</th>
<th>CH$_3$OH</th>
<th>H$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda_{\text{max}}$ (nm)</td>
<td>230.6</td>
<td>234</td>
<td>238</td>
<td>237</td>
<td>242</td>
</tr>
</tbody>
</table>

(C) Compounds which do not exhibit absorption ($t = 1$) in 220-280 nm region may be aliphatic or alicyclic hydrocarbon or their simple derivatives.

(D) The dissociation constants of weak acids or weak bases cannot be determined using UV absorption spectrophotometric technique even though the validity of Lambert and Beer's Law has been checked. The effects of substituents on $pK_a$ value, as studied by Hammett's equation

$$\log \frac{k}{k_0} = \rho \sigma,$$

does not give satisfactory results.

12. The mechanism for the photochemical reaction between hydrogen and bromine has been proposed as:

(i) $\text{Br}_2 \xrightarrow{h \nu} 2\text{Br}$

(ii) $\text{Br} + \text{H}_2 \xrightarrow{k_2} \text{HBr} + \text{H}$

(iii) $\text{H} + \text{Br}_2 \xrightarrow{k_3} \text{HBr} + \text{Br}$

(iv) $\text{H} + \text{HBr} \xrightarrow{k_4} \text{H}_2 + \text{Br}$

(v) $\text{Br} + \text{Br} \xrightarrow{k_5} \text{Br}_2$

The rate of formation of HBr is given as:

(A) $k_2[\text{H}_2][\text{Br}] + k_3[\text{H}][\text{Br}_2] - k_4[\text{H}][\text{HBr}]$

(B) $k_2[\text{H}_2][\text{Br}] - k_3[\text{H}][\text{Br}_2] - k_4[\text{H}][\text{HBr}]$

(C) $2 \text{ Iabs.} - k_2[\text{H}_2][\text{Br}] + k_3[\text{H}][\text{Br}_2] + k_4[\text{H}][\text{HBr}] - 2k_5[\text{Br}]^2$

(D) $\text{ Iabs.} + k_3[\text{H}][\text{Br}_2] - k_5[\text{Br}]^2$

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P.T.O.
Anthracene in benzene dimerises and simultaneously fluoresces when irradiated with light of a certain frequency $\nu$. The frequency of radiation emitted in fluorescence is $\nu'$ where $\nu' < \nu$. The following two mechanisms have been proposed:

**First Mechanism**

\[
A + h\nu \xrightarrow{k_1} A^* \\
A^* + A \xrightarrow{k_2} A_2 \\
A^* \xrightarrow{k_3} A + h\nu'
\]

**Second Mechanism**

\[
A + h\nu \xrightarrow{k_1} A^* \\
A^* + A \xrightarrow{k_2} A_2 \\
A^* \xrightarrow{k_3} A + h\nu'
\]

Which of the following statements is not correct?

(A) Using the first mechanism, the quantum yield for the formation of dimer $(A_2)$ is $\phi_{A(2)} = \frac{k_1 k_3 [A]}{k_2 [A] + k_3}$ i.e., $\phi_{A(2)} = \frac{k_1 [A]}{[A] + \frac{k_3}{k_2}}$ ....(i)

$\phi_{A(2)}$ is unity since maximum number of molecules $A_2$ formed for each quantum of radiation is one.

(B) If anthracene concentration $[A]$ is very low i.e., $[A] < \left(\frac{k_3}{k_2}\right)$.

From (i) in (a) $\phi_{A(2)} = \frac{k_1 k_3 [A]}{k_2}$

$\phi_{A(2)}$ increases with the increase in concentration of the monomer, $[A]$.

(C) If anthracene concentration $[A] >> \left(\frac{k_3}{k_2}\right)$.

From relation (i) in (a) $\phi_{A(2)} = k_1$

$\phi_{A(2)}$ is independent of $[A]$.

(D) Using second mechanism, the $\phi_{A(2)}$ depends upon the intensity of light absorbed which is in agreement with the experimental result.
14. Which of the following statements is not correct?

(A) The unit for $n$th order of a reaction $(dm^3)^{n-1} \text{ mol}^{1-n} \text{ s}^{-1}$

(B) The $t_{1/2}$ for $n$th order of a reaction is given as $\frac{2^{n-1} - 1}{k_n(n-1)a_0^{n-1}}$ when $n \geq 2$.

(C) In a catalytic experiment involving Haber's process, $N_2 + 3H_2 \rightarrow 2NH_3$, the rate of reaction was measured as

$$\text{rate} = \frac{\Delta(NH_3)}{\Delta t} = 2.0 \times 10^{-14} \text{ mol l}^{-1} \text{s}^{-1}$$

The rate of reaction expressed in terms of $N_2$ is

$$-\frac{\Delta(N_2)}{\Delta t} = 2 \times 2.0 \times 10^{-4} = 4.0 \times 10^{-4} \text{ mol l}^{-1} \text{s}^{-1}$$

(D) In an enzyme solution sucrose undergo fermentation if 0.1 M sucrose solution is reduced to 0.05 M in 10 hrs and to 0.025 M in 20 hrs. The reaction is found to be first order

15. Which of the following orders of a reaction for which rate constant $(k)$ has the same numerical value regardless of the unit used for expressing the concentration of the reactant or products?

(A) Zero order  (B) First order

(C) Second order  (D) Third order
16. Which of the following statements is correct?

(A) An ensemble consisting of identical closed systems in thermal contact with each other. The thermal contact ensures that they are at the same temperature, but allows them to exchange energy with each other; the total energy of the ensemble (E) is constant. The imaginary collection of replications is called grand canonical ensemble. N,V,T, is common.

(B) The canonical ensemble requires that all systems should have exactly the same energy instead of constant temperature, each system is individually isolated. N,V,E, is common.

(C) In microcanonical ensemble volume and temperature of each system is the same but they are open, this means matter can be imagined to pass between the system, the composition of each one may fluctuate but chemical potential is the same in each system μ, V, T is common.

(D) The principle of equal a priori probabilities states that all possibilities for the distribution of energy are equally probable. For example, states corresponding to a given vibrational energy are as likely to be populated as states corresponding to rotational energy.
Which of the following statements is not correct?

(A) A reflection in a plane of symmetry or a mirror plane is denoted by \( \sigma \). If reflection in a plane passing through the molecule leaves it apparently unchanged then it has a plane of symmetry. If the plane contains a principal axis, then it is called vertical and denoted by \( \sigma_v \).

(B) A rotation about an axis of symmetry is denoted by \( C_n \). If a rotation through \( \frac{360^\circ}{n} \) leaves the molecule apparently unchanged, it is said to have an \( n \)-fold axis of symmetry.

(C) The identity operation is denoted by \( E \). An \( n \)-fold improper rotation consists of an \( n \)-fold rotation followed by horizontal reflection.

(D) An inversion through a centre of symmetry denoted by \( i \). Imagine taking each point in an object, moving it to its centre and then moving it out the same distance on the other side. If the object looks unchanged it has centre of inversion.

18. Which of the following statements is not correct?

(A) Viscosity of a gas decreases with increase in temperature whereas viscosity of a liquid increases with increase in temperature.

(B) Viscosity of a gas is independent of pressure since at high pressure more molecules are available to transport momentum but they carry it less far an account of mean free path.

(C) Gases become cooler during Joule-Thomson expansion if they are below a certain temperature called inversion temperature \( T_i = \frac{2a}{Rb} \). \( \text{H}_2 \) and \( \text{He} \) have very low \( T_i \). These gases will also show a cooling effect if temperature is below their \( T_i \). At ordinary temperature \( \text{H}_2 \) and \( \text{He} \) show heating effect.

(D) Gases in states with the same value of reduced temperature and reduced pressure deviate from ideality to the same extent i.e., \( Z = \frac{PV}{RT} \) will approximately the same.
19. Which of the following thermodynamic relations forms the basis of phase rule?

(A) \( n_1d\mu_1 + n_2d\mu_2 + \ldots + n_id\mu_i + \ldots = 0 \)

(B) \( \mu_1dn_1 + \mu_2dn_2 + \ldots + \mu_idn_i + \ldots = 0 \)

(C) \( \frac{dP}{dT} = \frac{\Delta H}{T\Delta v} \)

(D) \( \Delta S_{\text{vap}} = \frac{\Delta Hv}{T_b} \approx 21 \text{ cal deg}^{-1} \text{ mol}^{-1} \)

20. Which of the following statements is not correct?

(A) The fugacity \((f)\) is a pressure like quantity that is used to treat the free energy of non-ideal gas. For ideal gas \(dP = RTd\ln P\) and for the gas which does not behave ideally i.e., real gas \(dF = RTd\ln f\).

(B) The molecular partition function is represented by \(Q\) i.e., \(Q = \sum_{i=0}^{\infty} g_ie^{-u_i/RT}\) where \(g_i\) is the statistical weight factor representing number of possible quantum states having the same or almost the same energy.

(C) Entropies as obtained by spectroscopic results are greater than those obtained from third law of thermodynamics.

(D) The entropy of system and surrounding together is constant for all natural and irreversible processes.
21. The Gibbs adsorption equation is:

(A) \[ \Gamma = - \frac{C}{RT} \left( \frac{d\gamma}{dc} \right)_T \]

(B) \[ \frac{P}{x/m} = \frac{1}{k_1 k_2} + \frac{P}{k_2} \]

(C) \[ \frac{P}{V_{\text{Total}} (P_0 - P)} = \frac{1}{V_{\text{mono}}} + \frac{C - 1}{V_{\text{mono}} C} \left( \frac{P}{P_0} \right) \]

(D) \[ \frac{x}{m} = kP^{1/2} \]

22. Which of the following is an example of electrolyte concentration cell reversible to cation without transference?

(A) \( \text{Pt} | H_2(g) | HCl(c_1) | HCl(c_2) | | H_2(g) | \text{Pt} \)

(B) \( \text{Pt} | H_2(g) | HCl(c_1) | \text{AgCl} | \text{Ag} | \text{Ag} | \text{AgCl} | HCl(c_2) | \text{Pt} \)

(C) \( \text{Ag} | \text{AgCl} | \text{NaCl}(aq, c_1) | \text{NaCl}(aq, c_2) | \text{AgCl} | \text{Ag} \)

(D) \( \text{Pb} - \text{Hg}(a_1) | \text{PbSO}_4(\text{solution}) | \text{Hg} - \text{Pb}(a_2) \)
Which of the following diagrams represents mono molecular layer adsorption?

- (A) adsorption of $N_2$ on charcoal at $-180^\circ C$
- (B) adsorption of $N_2$ on Fe catalyst at $-195^\circ C$
- (C) adsorption of $Br_2$ on silica gel at $80^\circ C$
- (D) adsorption of $C_6H_6$ on silical gel at $50^\circ C$

24. An ionic selective membrane can be used to form an electrochemical cell whose e.m.f. depends on the concentration of that ion. Which of the following statements is not correct?

(A) Glass electrode is sensitive to $H^+$ ions. It is made of thin walled bulb of low melting point glass of high electrical conductivity. An electrode not the cell usually consists of the arrangement $Ag \ | AgCl(s) \ HCl(C = 1) \ | glass$. The glass membrane of the glass electrode separates two different solution as does the KCl salt bridge. Unlike the salt bridge which provides for general ionic conduction across the liquid junction, the glass membrane leads to a cell whose e.m.f. is responsive to hydrogen ions.

(B) Liquid membrane electrodes are in use for developing electrodes sensitive to $Ca^{+2}$ and $Mg^{+2}$ ions. Solid state membrane are in use for e.g. fluoride ion electrode

(C) All above electrodes when supplemented with a reference electrode produce a potential which is given by the Nernst equation

$$E = \text{Constant} + \ln a_m$$

where $a_m$ is the activity of the ion to which the electrode is selective

(D) Liquid junction potential is eliminated by the use of salt bridge. Salt KCl is used because transference number of cation ($K^+$) and anion ($Cl^-$) are nearly equal or rather same.
The difference between the potential of the electrode when gas evolution is actually observed and the theoretical, i.e., reversible, value for the same evolution is called overvoltage (or bubble overvoltage).

Which of the following statements is not correct?

(A) If pure Zn is connected to Cu as in simple voltaic cell and both are dipped in dilute HCl. Zn readily dissolves and H₂ is liberated at Cu (anode). Hydrogen overvoltage is ~ 0.2 V. Similar effect has been observed if Zn rod contains Cu or any other metal as an impurity with low hydrogen voltage. This is called corrosion.

(B) The metal can be prevented from corrosion by coating the surface with an impermeable layer. Galvanising i.e., the coating of the Fe with Zn is also a form of surface coating. Corrosion of Zn is thermodynamically favoured and Fe survives. Zn gets protected by an impermeable by a layer of hydrated oxide which is kinetically inert.

(C) Corrosion can be prevented by cathodic protection. The object is connected to a metal Mg (more electronegative, standard potential – 2.36 V). Mg acts as a sacrificial anode supplying its own electrode to Fe and decaying to Mg⁺² in the process. Fe of the ship can get protected by this method which is much cheaper than ship building.

(D) In place of galvanisation of an iron object tin plating is also preferred as its oxide forms an impermeable protective layer. However, oxide formation is thermodynamically stable but kinetically unstable. The oxide forms a permeable layer over a fairly wide pH range.
26. Which of the following diagrams represents a condition for the acceptability of the wave function $\psi$:

(A) \[ \psi \]

(B) \[ \psi \]

(C) \[ \psi \]

(D) \[ \psi \]

27. Which of the following statements is not correct?

(A) He(I) behaves like a normal liquid. It has boiling point 4.22 K and critical temperature 5.20 K.

(B) Helium has a liquid I and liquid II phase transition at its $\lambda$-line

(C) He(II) is a superfluid and it flows without viscosity (i.e., zero viscosity)

(D) He (solid) can be obtained only by holding the atoms together by applying pressure. Solid He, helium (I) and helium (gas) are in equilibrium at triple point 2.17 K. It is highly unstable system.
28. Which of the following is an example of coordination position isomerism

(A) $[\text{Cr(H}_2\text{O})_5\text{(SCN)}]^+{}^2$ and $[\text{Cr(H}_2\text{O})_5\text{(NCS)}]^+{}^2$

(B) \[
\begin{array}{c}
\text{NH}_2 \\
\text{CH}_2\text{CH}-(\text{CH}_3)
\end{array}
\quad \text{and} \quad
\begin{array}{c}
\text{NH}_2 \\
\text{CH}_2\text{CH}-(\text{CH}_2)
\end{array}
\]

(C) $(\text{NH}_3)_4\text{Co}<\text{OH} <\text{Co(NH}_3)_2\text{Cl}_2$ and $\text{Cl( NH}_3)_4\text{Co}<\text{OH} <\text{Co(NH}_3)_3\text{Cl}$

(D) \[
\begin{array}{c}
\text{H}_3\text{N} \\
\text{Cl}
\end{array}
\quad \text{and} \quad
\begin{array}{c}
\text{H}_3\text{N} \\
\text{Co} \\
\text{Cl} \\
\text{NH}_3
\end{array}
\]

29. Which of the following statements is correct?

(A) Valence bond theory explains satisfactorily the spectra, excited states or kinetics of complexes.

(B) Crystal field theory does not explain distortions from regular geometries, magnetic and kinetic behaviour. CFT has no place for π-bonding in complexes.

(C) Molecular orbital theory requires much less tedious calculations as compared to calculations in CFT. Large number of approximations are involved in calculations.

(D) In actual practice the modified CFT in which allowance is made for the overlap of the metal and ligand orbitals. The theory is adjusted crystal field theory (ACFT) or ligand field theory (LFT), in which simplicity of CFT is retained with the inclusion of M–L σ and π-bond.
30. Which of the following structural affixes are used when three groups on an octahedron is such a relationship that one is cis to the two others which are themselves trans:

(A) nido (a nest like structure)

(B) octahedro (6 atoms bound into a pentagonal prism)

(C) triprismo (6 atoms bound into a triangular prism)

(D) mer. (meridional)

31. Which of the following statements is correct on the basis of VBT approach?

(A) Stereochemistry of $d^8$ system of Ni involves $sp^3$ hybrid orbitals and magnetism corresponds to two unpaired electrons, for example $[\text{Ni(NH}_3)_4 \text{Cl}_2]$ (green complex).

(B) Stereochemistry of $d^8$ system of Ni involves $dsp^2$ hybrid orbitals and magnetism corresponds to two unpaired electrons, for example $K_2 \text{Ni(CN)}_4$ (Yellow complex).

(C) Stereochemistry of $d^8$ system of Pd involves $dsp^2$ hybrid orbitals and magnetism corresponds to two unpaired electrons.

(D) Stereochemistry of $d^8$ system of Pt involves $dsp^2$ hybrid orbitals and magnetism corresponds to two unpaired electrons.

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32. The crystal field theory is unable to explain satisfactorily:

(A) detailed magnetic properties

(B) relative strength of ligands

(C) absorption spectra of complexes

(D) thermodynamic properties

33. Which of the following statements is not correct?

(A) The magnetic moment of \([\text{Mn Br}_4]^{-2}\) corresponds to five unpaired electrons. Mn is in +2 oxidation state and forms 4-coordinate complex. It is tetrahedral.

(B) The magnetic moment of \([\text{Mn(CN)}_6]^{-3}\) corresponds to two unpaired electrons. Mn is in +3 oxidation state. It is octahedral complex involving inner 3d-orbitals i.e., \(d^2sp^3\) hybridisation.

(C) The brown ring nitrate test in laboratory is due to the formation of \([\text{Fe(H}_2\text{O)}_5(\text{NO})]^{+2}\). The magnetic moment corresponds to three unpaired electrons. It forms an octahedral complex involving outer 4d orbitals i.e., \(sp^3d^2\) hybridisation.

(D) Ni(II) forms an octahedral complex and uses inner d-orbitals i.e., \(d^2sp^3\) hybridisation irrespective of the fact that ligand is weak or strong field.
34. Which of the following statements is not correct?

(A) (i) The sequence of ligands in spectrochemical series in order of increasing $\Delta$ is as:

$$\text{Cl} < \text{I} < \text{Br} < \text{OH} < \text{H}_2\text{O} < \text{NO}_3^- < \text{NH}_3 < \text{en} < \text{dipy} < \text{CN}$$

(ii) The natural order of stability of complexes of divalent metal ions is as:

$$\text{Mn} < \text{Fe} > \text{Co} < \text{Ni} > \text{Cu} < \text{Zn}$$

(B) The magnitude of CF splitting increases as the charge on metal increases.
The CF splitting for complexes of metal ion in the first transition series (3$d$) and having same oxidation state increases approximately by 40% on going to the elements of second transition series and almost by the same amount on going to the elements of third transition series.

(C) Each electron occupying the $t_{2g}$ orbital stabilised the complex by $-0.4 \Delta_0$ (i.e., $-4Dq$) and each electron occupying the higher energy, eg, orbital destabilised the complex by $0.6 \Delta_0$ ($6D_q$). The gain in energy achieved by preferential filling of lower energy $t_{2g}$ orbital is called crystal field stabilisation energy (CFSE).

(D) In a low spin state since pairing of electron takes place the energy of the system will be raised by P where P is the pairing energy.
35. Which of the following statements is not correct?

While studying the cis- and trans- equilibria in square planar complexes it has been observed that:

(A) Concentration of trans-isomer is usually more than in cis-form

(B) Bonding energy favours cis-form due to π-bonding effects

(C) Increasing steric hindrance favours the cis-compounds

(D) Entropy changes favour trans-complexes by Ca 40 JK⁻¹ mol⁻¹ to the release of solvent molecules from the trans-complexes since polar bond in the cis-form is changed to non-polar bond in trans-form

36. In which of the following reactions sulphuric acid acts as a base in sulphuric acid solvent?

(A) \( \text{NH}_2\text{CONH}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{NH}_2\text{CONH}_3^+ + \text{HSO}_4^- \)

(B) \( \text{H}_3\text{BO}_3 + 6\text{H}_2\text{SO}_4 \rightarrow [\text{B(HSO}_4^-)_4]^- + 3\text{H}_2\text{O} + 2\text{HSO}_4^- \)

(C) \( \text{HNO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{NO}_2^- + 2\text{HSO}_4^- + \text{H}_2\text{O} \)

(D) \( \text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{SO}_4 \rightarrow \text{C}_2\text{H}_5\text{OH}_2^- + \text{HSO}_4^- \)

37. Which of the following reactions is not an example of acid-base neutralisation reaction in non-aqueous medium?

(A) \( \text{SOCl}_2 + [\text{(CH}_3^-)_4\text{N}]_2\text{SO}_3 \rightarrow 2\text{(CH}_3^-)_4\text{NCl} + 2\text{SO}_2 \)

(B) \( \text{NH}_4\text{Cl} + \text{NaNH}_2 \rightarrow \text{NaCl} + 2\text{NH}_3 \)

(C) \( \text{Cl}_2 + 2\text{NH}_3 \rightarrow \text{NH}_2\text{Cl} + \text{NH}_4\text{Cl} \)

(D) \( \text{HCl} + \text{NaCN} \rightarrow \text{NaCl} + \text{HCN} \)
38. Which of the following reactions takes place by inner sphere mechanism?
(A) \([\text{Co}(\text{NH}_3)_5\text{Cl}]^2+ + \text{Cr}^{3+} + 5\text{H}^+ \rightarrow [\text{Cr(H}_2\text{O})_3\text{Cl}]^2+ + \text{CO}^{4+} + 5\text{NH}_4^+\]
(B) \([\text{Fe}^4(\text{CN})_6]^{3-} + [\text{Fe}(\text{CN})_6]^3 \rightarrow [\text{Fe}^4(\text{CN})_6]^{4-} + [\text{Fe}(\text{CN})_6]^4\]
(C) \([\text{Co}^6(\text{NH}_3)_6]^{3+} + [\text{Co}(\text{NH}_3)_6]^2 \rightarrow [\text{Co}^6(\text{NH}_3)_6]^{4+} + [\text{Co}(\text{NH}_3)_6]^3\]
(D) \([\text{Os}^6(\text{bipy})_6]^{3+} + [\text{Os}(\text{bipy})]^2 \rightarrow [\text{Os}^6(\text{bipy})_6]^{4+} + [\text{Os}(\text{bipy})]^3\]

39. Which of the following diagrams represents an interstitial alloy?

- [Image of diagrams]

(A) Pure metal lattice  (B) Alloy  (C) Alloy  (D) Alloy

40. Which of the following statements is not correct?

(A) The BN group is isoelectronic with C\(_2\) group. Boron nitride has an ordered layer structure closely resembling that of graphite but with layers superimposed so that B and N atom lie vertically above one another.

(B) The B—N distance within layers is 1.45 Å appreciable shorter than in the tetrahedrally bonded compound H\(_3\)N—BH\(_3\)(1.56 Å) and indicative of \(\pi\)-bonding involving lone pair of electron on the nitrogen and the empty boron \(p\)-orbitals.

(C) Like graphite BN is not a good lubricant. There exists van der Waals interaction between hexagonal layers, 3.30Å apart. Further like graphite it is white and in an insulator.

(D) When boron nitride is heated at 1500°–2000°C and 50,000 atm. pressure in the presence of Li or Mg nitride as catalyst it forms another form of boron nitride like that of diamond with alternate atoms replaced by B and N. It is hard like diamond.
41. Which of the following statements in not correct with regard to cyanogen chemistry?

(A) The CN⁻ ion is isoelectronic with CO and NO⁺. The CN⁻ is pseudo halogen and its chemistry is like that of halogen.

(B) C₂N₂ and HCN are thermodynamically unstable with respect to decomposition into their elements, hydrolysis by H₂O and oxidation by atmospheric oxygen.

(C) These are also kinetically unstable and their transition metal cyano complexes have not been studied extensively so as to throw more light into the development of theories of chemical bonding in transition metal chemistry.

(D) (CN)₂ is a poisonous colourless gas which when pure remain unchanged over long period at ordinary temperature. (CN)₂ is one of the most endothermic compounds known with ΔH° = 297 kJ/ mole.

42. Which of the following acids of phosphorus is monobasic and is reducing agent?

(A) H₄P₂O₆

(B) H₃PO₂

(C) H₃PO₃

(D) H₃PO₄
43. Which of the following statements is not correct?

The compounds (CH₃)₃N and (SiH₃)₃N have similar formula but have totally different structures:

(A) (CH₃)₃N: has tetrahedral arrangement. The methyl groups and a lone pair of electrons are at the apex of the tetrahedron. There is sp³ hybridisation.

(B) (SiH₃)₃N: has three sp² hybrid orbitals, that are used for σ-bonding giving a triangular planar structure. The lone pair of electrons occupy a p-orbital at right angle to the triangular plane.

(C) This overlaps with empty d-orbitals on each three silicon atoms and results in π-bonding i.e., pₚ - dₚ bonding. It is from a full p-orbital to a vacant d-orbital. N – Si bond length is shortened. N has no donor properties.

(D) Similar pₚ - dₚ bonding is also possible in (CH₃)₃N: molecule. C has also d-orbital like Si. The molecule is pyramidal.

44. Which of the following statements is not correct?

(A) With germanium +4 oxidation state is most stable but with lead +2 oxidation state is stable. PbI₄ does not exist because oxidising power of Pb(IV) and reducing power of I⁻ results in PbI₂ always being formed.

(B) Colour is associated with electrons being promoted from one energy level to another and absorbing or emitting the energy difference between the two levels. This is very common in transition elements allowing promotion from one d-level to the other.

(C) In main groups the s and p electron sub-shells are filled when a compound is formed, so promotion within the same sub-shell is possible. Promotion from one shell to another for eg. 2p to 3p level involves so much energy that absorption lines would appear in visible region.

(D) SnI₄ is orange is colour. It absorbs blue colour and reflected light contains a higher proportion of red and orange. The energy absorbed causes the transfer of an electron from I to Sn [Temporary reduction of Sn(IV) to Sn(III)]. Since transferring an electron to another atom is transferring a charge, such spectra are called charge transfer spectra.
45. Which of the following statements is not correct?

(A) Actinides are f-block elements and have an incomplete 5f-subshells. Cm\(^{+3}\), the analogue of Gd\(^{+3}\), has half filled subshell \(f^7\) and Lr has completely filled 5f-subshell. 5f subshell is progressively filled until we reach lawrentium.

Energies of 5f, 6d, 7s and 7p-orbitals are comparable over a range of U – Am. Since the orbitals also overlap spatially, bonding can involve any or all of them.

(B) Sm\(^{+3}\), Eu\(^{+3}\) and Yb\(^{+3}\) can be reduced to dipositive state in aqueous solution. Sm\(^{+3}\) and Yb\(^{+3}\) require alkali metal amalgam for reduction. Eu\(^{+3}\) can be reduced by Zn or Mg. All the three can be obtained by electrolytic reduction. Sm(II) and Yb(II) are unstable with respect to oxidation even by \(\text{H}_2\text{O}\). They are oxidised.

(C) Am, Cf, Es, Fm, Md and No have stable +2 oxidation state. Md\(^{+2}\) is even more stable than Eu\(^{+2}\) and Yb\(^{+2}\). Md\(^+\) can be reduced by Zn|Hg amalgam. The reduction potential of \(E_{\text{Md}^{+2}/\text{Md}^{0}} = -0.15\) V.

(D) Actinides have much less tendency to form complexes than lanthanides. The dominant oxidation in actinides is +4 as in lanthanides throughout the series. La has only +4 oxidation state as it acquires inert gas configuration.
46. Which of the following triads of trivalent ions do not show absorption due to \( f - f \) transition in visible region?

(A) \( \text{Eu}^{3+}, \text{Tb}^{3+}, \text{Am}^{3+} \)

(B) \( \text{Gd}^{3+}, \text{Cm}^{3+}, \text{Yb}^{3+} \)

(C) \( \text{Dy}^{3+}, \text{Np}^{3+}, \text{Pu}^{3+} \)

(D) \( \text{Sm}^{3+}, \text{Ho}^{3+}, \text{Pm}^{3+} \)

47. Silicones form polymer through condensation with silicon bonds. The starting material for producing silicon rubber is:

(A) Trimethyl monochlorosilane

(B) Methyl trichlorosilane

(C) Dimethyl dichlorosilane

(D) Orthosilicic acid
Which of the following statements in not correct?

(A) Compounds of the type KCl, PtCl₂, C₂H₄, H₂O or K[PtCl₃, C₂H₄]. H₂O in which olefines function as coordinating group are known. Such compound can also be obtained by the action of ethylene on PtCl₂ dissolved in alcoholic HCl other olefines such as styrene, cyclohexene can replace C₂H₄ in the anion of Zeise salt or in [PtCl₂.C₂H₄]₂.

(B) Ethylene and olefinic ligands exercise a strong trans-effect in substitution reaction so that mixed complexes in almost all cases are cis-isomers. Corresponding trans-complexes have been obtained by the introduction of olefines into ammine complex.

(C) The olefine complexes shows a suggestive resemblance to the carbonyl complexes, the double bond is the point of attachment of the ligand. It acts as a monodentate ligand and resemble the π-bonding type. It differs from the carbonyl group and from all other monodentate ligands, in that there is no lone pair of electrons to form a σ-type L → M bond.

(D) From the crystal structure of Zeise salt and analogous Pd compound it appears that the double bond is perpendicular to, and symmetrically placed with respect to the coordination plane. Overlap of the π-bonding orbital of the olefine with a vacant σ-type orbital of Pt(dsp²) furnishes as L → M bond of essentially σ-type. To this is added a π-type of bond originating from the overlap of a (5dₓᵧ, 6pₓ) filled orbital of Pt atom with the π-antibonding orbital of the double bond.
49. Which of the following radioactive elements belongs to *d*-block elements?

(A) Astatin  (B) Technetium

(C) Franciscium  (D) Polonium

50. Which of the following compounds is the only pure nitrosyl compound?

(A) Co(NO)_3  (B) Fe(NO)_4

(C) Cr(NO)_4  (D) Ru(NO)_4

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

CO and dinitrogen are isoelectronic:

(A) [Ru(NH₃)₅N₂]Cl₂ is the first reported dinitrogen complex. [Ru(NH₃)₅N₂]^2⁺ cation can be obtained by the reaction [Ru(NH₃)₅-H₂O]^3+ with dinitrogen at 100 atm pressure. There is no way of reductively transforming the coordinating dinitrogen to ammonia.

(B) The bonding in M - N₂ group is qualitatively similar to M - CO group. The same two basic components M ← N₂ σ donation and M → N₂ π-acceptance are involved.

(C) N = N bond weakening results from both σ-donation and π-back acceptance in dinitrogen complex. For CO complexes weakening of the CO bond is due entirely to back donation from metal dπ orbitals to CO π*-orbitals, with the σ-donation slightly cancelling some of this effect.

(D) CO is weaker than N₂ in both its σ-donor and π-acceptor functions which means poor stability of CO complexes.
Which of the following statements is related to unsatisfactory oxidation number?

(A) In $[\text{Fe(CN)}_5\text{NO}]^{-2}$ nitroprusside ion metal is assigned an oxidation number +2 which implies it has $d^6$ configuration. This is plausible value, Mössbauer and other physical evidence indicates that effective oxidation number is actually close to +3.

No first transfers its $\pi^*$ electron to Fe in order to become NO$^+$ and this cation serves as electron donor and finally $d_\pi$ electron density is transferred back to very $\pi^*$-orbital from which an electron was initially removed.

(B) The oxidation number of Fe in Fe(NO)$_2$ (CO)$_2$ and Co in Co(NO)$_3$ are -2 and -3 respectively.

(C) In $[\text{Co en}_2\text{Cl} (\text{NO})]^{+1}$ and $[\text{Co(NH}_3)_5 (\text{NO})]^{+2}$ if NO is treated as NO$^-$ ion the presence of Co(II) is then implied. This seems consistent with the large number cobalt (III) ammine complexes.

(D) In linear MNO groups the basic interaction is by donation of a $\sigma$ pair from N along with a covalent $N\pi^* - d\pi$ bond, often with some additional bonding due to $d_\pi \rightarrow N\pi^*$ interaction.

In bent MNO group the interaction is basically a single covalent bond formed by a $\sigma$ electron on the metal and a $\sigma$ electron in an $sp^2$ orbital on N with a range of bond polarity possible.
The decay by a series of α and β emissions and produce radioactive elements which are successively more stable and finally a stable isotope is reached. Which of the following series gives the end product $^{209}_{83}\text{Bi}$?

(A) $4n$ series

(B) $4n + 1$ series

(C) $4n + 2$ series

(D) $4n + 3$ series

Which of the following statements is not correct?

(A) A nucleophilic reagent at the β-carbon to form an ion in which the negative charge is partly accommodated by electronegative oxygen atom. An electrophilic reagent attacks the oxygen to form the carbocation in which positive charge is accommodated by carbon

$$\begin{align*}
\text{C} &= \text{C} - \text{C} = \text{O} \\
\text{H} &= \text{Z} \\
\text{C} &= \text{C} = \text{C} = \text{O} \\
\text{H}^+ &= \text{Z} \\
\text{C} &= \text{C} - \text{C} - \text{C} - \text{OH}
\end{align*}$$

(B) The intermediate ion has a negative charge in nucleophilic addition whereas the ion carries a positive charge in electrophilic addition.

(C) An electron withdrawing group deactivates a C = C towards nucleophilic addition while it activates towards electrophilic addition.

(D) An electron withdrawing group stabilises the transition state leading to the formation of the intermediate anion in nucleophilic addition by helping to disperse the developing negative charge.
55. Which form of cyclohexane is most stable?

(A)  

(B)  

(C)  

(D)  

56. Which of the following compounds on reaction with Grignard reagent gives primary alcohol?

(A) \( \text{CH}_3\text{C} = \text{CH}_3 \)

(B) \( \text{CH}_3\text{C} = \text{O} \)

(C) \( \text{CH}_3\text{C} \equiv \text{NH}_2 \)

(D) \( \text{CH}_2\text{CH}_2\text{O} \)

57. Which of the following reactions does not take place as desired?

(A) \[ \text{R-Cl} + 2\text{CH}_3\text{MgI} \rightarrow \text{R-C-CH}_3 \text{OH} \]

(B) \[ \text{RX} \xrightarrow{\text{Li}} \text{RLi} \xrightarrow{\text{CuX}} \text{R}_2\text{CuLi} \]

(C) \[ \text{O}_2\text{N-C-Cl} + \text{CH}_3\text{MgI} \rightarrow \text{O}_2\text{N-C-CH}_3 \]

(D) \[ 2\text{O}_2\text{N-C-Cl} + (\text{CH}_3)_2\text{CuLi} \rightarrow 2\text{O}_2\text{N-C-CH}_3 \]
58. Which of the following compounds is not prepared from \( \text{C}_6\text{H}_5\text{N} = \text{N} - \text{Cl} \) using Sandmeyer's reaction?

(A) \( \text{C}_6\text{H}_5\text{I} \)  
(B) \( \text{C}_6\text{H}_5\text{Br} \)  
(C) \( \text{C}_6\text{H}_5\text{Cl} \)  
(D) \( \text{C}_6\text{H}_5\text{CN} \)

59. Which of the following is not a limitation of Friedel-Crafts' alkylation reaction?

(A) aromatic compounds containing \( \text{NH}_2, \text{NHR}, \text{NR}_2 \) group in the ring

(B) an aromatic ring less reactive than that of halobenzenes

(C) the possible rearrangement of alkyl group

(D) an aryl halide can take the place of an alkyl halide

60. Which of the following is not a correct step in the mechanism of Friedel-Crafts acylation reaction?

(A) \( \text{R-C} + \text{AlCl}_3 \rightarrow \text{R-C} = \overline{\text{O}} + \text{AlCl}_4 \)

(B) \( \text{ArH} + \text{R-C} = \overline{\text{O}} \rightarrow \text{Ar}^+ \overline{\text{H}} \rightarrow \text{Ar}^+ \text{C=R} + \text{HCl} + \text{AlCl}_3 \)

(C) \( \text{Ar}^+ \text{H} \rightarrow \text{Ar}^+ \text{C=R} + \text{HCl} + \text{AlCl}_3 \)

(D) \( \text{Cl-Al-Cl-R} + \text{C}_6\text{H}_5 \rightarrow \left[ \text{C}_6\text{H}_5^+ \right] \rightarrow \text{C}_6\text{H}_3^+ \text{H} + \text{AlCl}_4^- \)
61. \( o \)-tetralone is subjected to Clemensen reduction tetralin is formed. Clemensen reduction involves the reductant:

(A) Zn (Hg) and HCl  \hspace{1cm} (B) \ H_2 \text{ in the presence of Ni}

(C) \( \text{N}_2\text{H}_4 \), base (OH) \hspace{1cm} (D) Zn and NH\(_4\)Cl

62. In which of the following reactions \( \beta \)-substituted product is obtained?

(A) \[ \text{HNO}_3, \text{H}_2\text{SO}_4 \text{, } 50-60^\circ \text{C} \]

(B) \[ \text{Br}_2, \text{CCl}_4 \text{, reflux} \]

(C) \[ \text{CH}_3\text{COCl, AlCl}_3 \text{, Solvent: } \text{C}_6\text{H}_5\text{NO}_2 \]

(D) \[ \text{Concen. H}_2\text{SO}_4 \text{, 80}^\circ \text{C} \]
63. Which of the following statements is not correct?

In terms of valence bond naphthalene is considered to be a resonance hybrid of the three structures

(A) All C – C bonds in naphthalene are the same like in C₆H₆

(B) The C₁ – C₂ bond is shorter than C₂ – C₃ bond. The C₁ – C₂ bond is double in two structures

(C) The C₂ – C₃ bond is single in two structures and double in one only

(D) The C₁ – C₂ bond has more double bond character than single whereas the C₂ – C₃ bond has more single bond character than double bond

64. Which of the following reagents will react with anthracene to produce 9, 10-dinitro-9, 10-dihydroanthracene?

(A) nitric acid and acetic acid

(B) nitric acid and acetic anhydride

(C) excess nitric acid

(D) nitric acid and ethyl alcohol
65. Which of the following reactions gives niacin (vitamin)?

(A) \[
\begin{array}{c}
\text{CH}_3 \\
\text{N}
\end{array}
\xrightarrow{\text{KMnO}_4}
\]

(B) \[
\begin{array}{c}
\text{N} \\
\text{300°}
\end{array}
\xrightarrow{\text{KNO}_3, \text{H}_2\text{SO}_4}
\]

(C) \[
\begin{array}{c}
\text{CH}_3 \\
\text{N}
\end{array}
\xrightarrow{\text{KMnO}_4}
\]

(D) \[
\begin{array}{c}
\text{N} \\
\text{pyrrole}
\end{array}
\xrightarrow{+ \text{C}_6\text{H}_5\text{N}=\text{N}--\text{Cl}}
\]

66. Which of the following is not correct?

In base protonated bromination of acetone

\[
\text{CH}_3\text{COCH}_3 + \text{Br}_2 + :\text{B} \rightarrow \text{CH}_3\text{COCH}_2\text{Br} + \text{B}^- + \text{H}:\text{B}
\]

(A) rate of reaction depends on the concentration of acetone and base

(B) rate determining step of the reaction is the formation of enol

(C) rate of reaction is independent of the concentration of bromine

(D) rate determining step of the reaction is the formation of carbanion
67. Which of the following is a slow step reaction in acid (HB) catalysed bromination of acetone?

(A) \( \text{CH}_3\text{C}=\text{CH}_3 + \text{H} : \text{B} \xrightarrow{\text{C}}} \text{CH}_3\text{C}=\text{CH}_3 + \text{H} : \text{B} \\
\text{OH}\text{ OH}^\dagger \\

(B) \text{CH}_3\text{C}-\text{CH}_3 + :\text{B} \rightarrow \text{CH}_3\text{C}=\text{CH}_2 + \text{H} : \text{B} \\
\text{OH}^\dagger \text{ OH} \\

(C) \text{CH}_3\text{C}=\text{CH}_2 + \text{X}_2 \rightarrow \text{CH}_3\text{C}-\text{CH}_2\text{X} + \text{X} \\
\text{OH} \text{ OH} \\

(D) \text{CH}_3\text{C}=\text{CH}_2\text{X} + :\text{B} \xrightarrow{\text{C}}} \text{CH}_3\text{C}-\text{CH}_2\text{X} + \text{H} : \text{B} \\
\text{OH} \text{ OH} \\
[X_2 \text{ stands for Br}_2] \\

68. Which of the following isomeric acids *cannot* obtained from malonic ester (diethyl malonate)?

(A) \text{n-valeric acid} \\

(B) \text{isovaleric acid} \\

(C) \text{trimethyl acetic acid} \\

(D) \text{\(\alpha\)-methyl butyric acid}
69. Some of the aldol condensation or crossed aldol condensation reactions are given below. Which of the condensation reactions does not take place?

(A) \[ \text{C}_6\text{H}_5\text{CHO} + \text{CH}_3\text{CHO} \xrightarrow{\text{dil OH} / 20^\circ} \text{C}_6\text{H}_5\text{C}=\text{C} - \text{C}=\text{O} \]

(B) \[ \text{C}_6\text{H}_5\text{CHO} + \text{C}_6\text{H}_5\text{CHO} \xrightarrow{\text{dil OH}} \text{C}_6\text{H}_5\text{C} - \text{C} - \text{C}_6\text{H}_5 \]

(C) \[ \text{CH}_3\text{C}=\text{C} - \text{CH}_3 + \text{C}=\text{O} \xrightarrow{\text{dil OH}} \text{CH}_3\text{C} - \text{C} - \text{C} - \text{C} = \text{O} \]

(D) \[ \text{CH}_3\text{CH}_2\text{C} - \text{O} + \text{CH}_3\text{CH}_2\text{C} - \text{O} \xrightarrow{\text{dil OH}} \text{CH}_3\text{CH}_2\text{C} - \text{C} - \text{C} - \text{C} = \text{O} \]

70. The acid strength increases in the order beginning with weakest acid:

(A) acetic acid < propionic acid < formic acid < acrylic acid < propiolic acid

(B) acrylic acid < propionic acid < propiolic acid < acetic acid < formic acid

(C) propiolic acid < acrylic acid < propionic acid < acetic acid < formic acid

(D) propionic acid < acetic acid < acrylic acid < formic acid < propiolic acid

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71. Which of the following reactions takes place with the formation of carbocation?

(A) The neopentyl chloride \( \text{Me-} \overset{\text{Me}}{\text{C-}}\text{CH}_{2}\text{Cl} \) on hydrolysis does not give \( \text{Me-} \overset{\text{Me}}{\text{C-}}\text{CH}_{2}\text{OH} \) but \( \text{Me-} \overset{\text{Me}}{\text{C-}}\text{CH}_{2}\text{Me} \) (t-arryl alcohol)

(B) \( \text{C}_6\text{H}_5\text{CHO} + (\text{CH}_3\text{CO})_2\text{O} \xrightarrow{\text{CH}_3\text{COONa}} \text{C}_6\text{H}_5\text{CH}==\text{CHCOOH} \)

acetic anhydride

acetic acid

(C) \( 2\text{CH}_3\text{COOC}_2\text{H}_5 + \text{C}_2\text{H}_5\text{ONa} \xrightarrow{\text{C}_2\text{H}_5\text{OH}} \text{CH}_3\text{COCHCOOC}_2\text{H}_5^+ \)

\[ \downarrow \text{H}^+ \]

\( \text{CH}_3\text{COCH}_2\text{COOC}_2\text{H}_5 \)

(D)

\( \text{C}_6\text{H}_5\text{CH}==\text{CH}-\overset{\text{COOC}_2\text{H}_5}{\text{C}}\text{C}_6\text{H}_5 + \text{CH}_2\text{COOC}_2\text{H}_5 \xrightarrow{\text{piperidine}} \text{C}_6\text{H}_5\text{C}-\overset{\text{H}}{\text{C}}\text{H}-\overset{\text{COC}_2\text{H}_5}{\text{C}}\text{C}_6\text{H}_5 \)

\( \text{CH} (\text{COOC}_2\text{H}_5)_2 \)
Which of the following statements is not correct?

(A) Many alkene additions are affected by small amount of peroxides reactions occurring in under such conditions are free radical chain reactions. For example \( CH_2=CH_2 + HBr \xrightarrow{\text{Peroxide}} CH_3CH_2CH_2Br \). The reaction is abnormal in the sense that it does not follow Markownikoff's rule.

(B) Hydrogen iodide does not undergo abnormal addition to olefines under normal circumstances. This is because hydrogen-iodide is too strong to be broken readily in the atom abstraction reaction.

(C) The chain initiation takes place:

\[
\begin{align*}
\text{C}_6\text{H}_5\text{C}=\text{O} \quad \text{UV} \quad 2\text{C}_6\text{H}_5\text{CO}_2
\\
\text{C}_6\text{H}_5\text{CO}_2 + HBr \rightarrow \text{C}_6\text{H}_5\text{COOH} + Br^-
\end{align*}
\]

The chain propagates as: \( Br^- + CH_3CH=CH_2 \rightarrow CH_3CHCH_2Br^- \)

\( CH_3CHCH_2Br^- + HBr \rightarrow CH_3CH_2CH_2Br + Br^- \)

The chain terminates as: \( 2Br^- \rightarrow Br_2 \) etc.

(D) The abnormal addition of HBr is useful in preparation of primary bromides from terminal olefines:

\[
\text{HBr} + \text{CH}_2 = \text{CH} - \text{CH}_2\text{Br} \xrightarrow{\text{peroxide}} \text{BrCH}_2\text{CH}_2\text{CH}_2\text{Br}
\]
Which of the following statements is not correct?

(A) Methylene exists in two different spin states (or different forms). Singlet methylene in which unshared electrons are not paired \( \cdot \text{CH}_2 \): \textit{i.e.}, \( \cdot \text{H:C:H} \), and triplet methylene in which unshared electrons are paired \( \text{CH}_2 \): \textit{i.e.}, \( \text{H:C:H} \)

(B) Methylene is formed by the photolysis of diazomethane or ketene

\[(i) \quad \text{CH}_2 = \text{N} = \text{N} \xrightarrow{\text{UV}} : \text{CH}_2 + \text{N}_2 \]

\[(ii) \quad \text{CH}_2 = \text{C} = \text{O} \xrightarrow{\text{UV}} : \text{CH}_2 + \text{CO} \]

The starting material, diazomethane and ketene and the products, \( \text{N}_2 \) and \( \text{CO} \), are isoelectronic pairs.

(C) \( \text{CH}_4\text{CH=CHCH}_3 + \text{CH}_2\text{N}_2 \xrightarrow{\text{generated in situ}} \text{CH}_4\text{CH} - \text{CH}_2 - \text{CH}_3 + \text{N}_2 \)

1, 2-dimethyl cyclopropane

Addition to carbon-carbon double bond forms a ring. This is called cycloaddition.

Photolysis of diazomethane in liquid \textit{cis} 2-butene gives only \textit{cis}-1, 2-dimethyl cyclopropane whereas in liquid \textit{trans}-2-butene it forms \textit{trans}-1, 2-dimethyl cyclopropane. Addition is stereospecific

(D) Triplet methylene undergoes non-stereospecific addition. It is diradical (I)

\[
\text{CH}_2 + \text{C=C} \rightarrow \text{C--C} \rightarrow \text{C=C} \quad \text{CH}_2 \text{I}
\]

It adds by a free radical two step mechanism. The diradical (I) lasts long enough for rotation to occur about the central C—C bond and both \textit{cis}- and \textit{trans}-products are formed
74. Which of the following statements is not correct?

The evidence for $E_2$ mechanism for elimination reaction which follows second order kinetics are:

(A) absence of rearrangement,

(B) large hydrogen isotope effect

(C) absence of hydrogen exchange

(D) Bond breaking and bond making are taking place one after the other

(i) \[
\begin{array}{c}
\text{C} \quad \text{C} \\
\text{H} & \quad \text{X} \\
\end{array}
\rightarrow \text{slow} \quad \begin{array}{c}
\text{X} \\
\text{C} \quad \text{C} \\
\text{H} \\
\end{array}
\]

(ii) \[
\begin{array}{c}
\text{C} \quad \text{C} \\
\text{H} & \quad \text{X} \\
\end{array}
\rightarrow \text{fast} \quad \begin{array}{c}
\text{C} \quad \text{C} \\
\text{H} \\
\text{B} \\
\end{array}
\]

75. Which of the following compounds does not give an iodoform test?

(A) \[
\begin{array}{c}
\text{C}_6\text{H}_5\text{C} \quad \text{H} \\
\text{H} \\
\end{array}
\]

(B) \[
\begin{array}{c}
\text{CH}_3 \quad \text{C} \quad \text{OH} \\
\text{H} \\
\end{array}
\]

(C) \[
\begin{array}{c}
\text{C}_6\text{H}_5 \quad \text{C} \quad \text{CH}_3 \\
\text{OH} \\
\end{array}
\]

(D) \[
\begin{array}{c}
\text{CH}_3\text{CH}_2\text{CH}_2\text{C} \quad \text{CH}_3 \\
\text{OH} \\
\end{array}
\]
Molecules that are not superimposable on their images are chiral and can exist as enantiomers. Which of the following statements is not correct?

(A) A molecule and its mirror image are superimposable. This means that if the image is brought from behind the mirror where it seems to be it could be made to coincide all its part with the molecule. The non-superimposability of mirror-image gives their optical activity.

(B) 1-bromo-1, 2-diphenyl propane has two chiral centres. It has two pairs of enantiomers.

\[
\begin{align*}
&\text{CH}_3\text{-C-H} & &\text{H-C-CH}_3 & &\text{CH}_3\text{-C-H} & &\text{H-C-Br} \\
&\text{Br-C-H} & &\text{H-C-Br} & &\text{H-C-Br} & &\text{Br-C-H} \\
&\text{C}_6\text{H}_5 & &\text{C}_6\text{H}_5 & &\text{C}_6\text{H}_5 & &\text{C}_6\text{H}_5 \\
\end{align*}
\]

\(\text{I} \quad \text{erythro} \quad \text{II} \quad \text{threo} \quad \text{IV} \)

(C) 1-bromo-1, 2-diphenyl propane on dehydrohalogenation gives the stereoisomeric products—geometrical isomers V and VI.

\[
\begin{align*}
&\text{CH}_3 & &\text{CH}_3 \\
&\text{H} & &\text{C} \\
&\text{C} & &\text{C} \\
&\text{C}_6\text{H}_5 & &\text{C}_6\text{H}_5
\end{align*}
\]

\(\text{V (Z)} \quad \text{VI (E)}\)

Erythro halide (I and II) yields only Z-alkene (1,2-diphenyl-1-propene). It is stereospecific. The threo halides yields only E-alkene (1,2-diphenyl-1-propene).

(D) To describe the kind of stereospecificity that may be seen in elimination reaction, the concept of syn- and anti-eliminations are used. They indicate that the eliminated groups are lost from the same face (anti) or opposite faces (syn) of the double bond.

\[
\begin{align*}
&\text{Y} & &\text{Z} \\
&\text{C} & &\text{C} \\
&\text{Z} & &\text{C} \\
&\text{C} & &\text{C} \\
\end{align*}
\]

\((-Y-Z-) \quad \rightarrow \quad \text{syn-elimination} \quad \text{anti-elimination} \quad \rightarrow \quad (-Y-Z-) \)
77. Which of the following statements is *not* correct?

(A) All amino acids are β-aminocarboxylic acids. All are optically active. All amino acids have R-configuration.

(B) There are two non-essential amino acids in which the amino group forms a pyrrolidine ring, the acids are proline and hydroxyproline. There are ten essential amino acids out of 23 amino acids.

(C) The hydrogen ion concentration of the solution in which a particular amino acid does not migrate under the influence of electric field is called isoelectric point of that amino acid. At this point there is highest concentration of dipolar ion.

(D) The acidic group of simple amino acid is NH$_3^+$ and not COOH and the basic group is COO$^-$ and not NH$_2$ group. All peptides are amides with —CONH— linkage. In polypeptides the N-terminal amino acid residue is written on the left and the C-terminal amino acid residue at the right end.
Which of the following statements is not correct?

(A) Hofmann degradation of amides has the feature of decreasing the length of a carbon chain by one carbon atom.

\[
\text{CH}_3(\text{CH}_2)_4\text{CONH}_2 \xrightarrow{\text{NaOBr}} \text{CH}_3(\text{CH}_2)_4\text{NH}_2
\]

(B) Reduction of nitril has a special feature of keeping the number of carbon atoms same

\[
\text{CH}_3(\text{CH}_2)_4\text{C} = \text{N} \xrightarrow{} \text{CH}_3(\text{CH}_2)_4\text{NH}_2
\]

(C) Hofmann’s rearrangement can be looked upon as simultaneously occurring reaction

\[
\text{R-C-Br} \xrightarrow{} \text{R-C} \xrightarrow{\text{Br}} \text{R-C} \xrightarrow{\text{OH}} \text{R-N=C=O}
\]

(D) Ammonolysis of halides:

Displacement of halogens by NH\textsubscript{3} gives the amine salt from which free amine is obtained by treatment with OH\textsuperscript{-}.

\[
\text{RX} + \text{NH}_3 \rightarrow \text{RNH}_2\text{X}; \text{R-NH}_2\text{X} + \text{OH}^{-} \rightarrow \text{RNH}_2 + \text{H}_2\text{O} + \text{X}^{-}
\]

Alkyl halides is attacked by NH\textsubscript{3} as:

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br} \xrightarrow{\text{NH}_3} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2\text{Br}^{-}
\] (substitution)

\[
\text{Br}
\]

\[
\text{CH}_3\text{CH}_3\text{CH}_3
\]

\[
\text{CH}_3
\]

\[
\text{NH}_3
\]

\[
\text{CH}_3\text{CH}_3
\]

\[
\text{C}=\text{CH}_2 + \text{NH}_4\text{Br} \quad \text{(elimination)}
\]
79. Which of the following statements is not correct?

(A) D-(+)-glucose has two isomeric forms because of its having one more chiral centre in cyclic structure than Fischer's original open chain structure. These are two diastereomers differing in configuration about C1, α-D-(+)-glucose and β-D-(+)-glucose

(B) The typical aldehyde reactions of D-(+)-glucose for e.g. osazone formation, reduction of Tollens and Fehling's reagent bisulphite addition, Schiff's test, can easily accounted for in assuming cyclic structure of glucose

(C) Glucose yields an osazone with phenyl hydrazine. The osazone is identical with the osazone prepared from mannose. This means glucose and mannose differ only in configuration about C2. The pair of diastereomeric aldoses that differ in configuration about C2 are called epimers.

(D) Glucose and Fructose again yield the identical osazone which means that configurations about C3, C4 and C5 are identical in the two compounds

80. Given below are the some properties of oxidising agents. Taking care of these, select the most suitable oxidising agent to obtain aldonic acid from aldoses.

(A) Periodic acid (HIO₄) : Compounds that contain two or more —OH groups or =O groups on adjacent carbon atom. Carbohydrate undergoes oxidative cleavage.

(B) Tollens's reagent, Fehling solution (or Benedict's solution) : These do not differentiate aldoses and ketoses. These are oxidizing agents in alkaline medium. These can cause extensive isomerisation

(C) Nitric acid : It can cause oxidation of —CHO group along with CH₂OH group giving dicarboxylic acid

(D) Bromine water : It does not oxidise ketoses. It is an acidic reagent. It does not cause isomerisation
81. In which region of H.P. is Sareul sar lake?

(A) Jalori in Kullu  (B) Karsog in Mandi

(C) Pangi in Chamba  (D) Kotgarh in Shimla

82. From where does Pabbar river originate?

(A) Choordhar in Sirmaur  (B) Chanshal Peak in Rohru

(C) Kalpa in Kinnaur  (D) Kharapathar in Jubbal

83. According to legend who was the earliest king of Kinners?

(A) Divodas  (B) Sudasa

(C) Pradumna  (D) Krishna

84. Who is the author of *Himalayan Dreamland Journey to Kinnerlok*?

(A) K. Maitra

(B) Bansi Ram Sharma

(C) S.S. Negi

(D) M.S. Randhawa
85. Who founded the Chamba princely state?

(A) Aditya Varman       (B) Bala Varman

(C) Ajia Varman         (D) Maru

86. In which year did Sir Henry Lawrence and his wife Honoria found the Lawrence School at Sanawar?

(A) 1847 AD       (B) 1857 AD

(C) 1867 AD       (D) 1877 AD

87. At which place in Solan District of H.P. is Ambuja run cement plant?

(A) Bhararighat     (B) Danoghat

(C) Darlaghat       (D) Kandaghat

88. When was Himachal Pradesh Religious and Charitable Endowment Act passed?

(A) 1984       (B) 1988

(C) 1992       (D) 1994
89. Which Sood trader of Garli established the Bal Bharat Sabha at Shimla whose agenda was radical/revolutionary?

(A) Prithvi Chand Sood  
(B) Dina Nath Andhi

(C) Hem Chand Sood  
(D) Kishori Lal Sood

90. How many towns have been nominated in H.P. under Pradhan Mantri Awas Yojana?

(A) 9  
(B) 13

(C) 16  
(D) 19

91. With which sport is Dipa Karmakar associated?

(A) Archery  
(B) Gymnastics

(C) Wrestling  
(D) Weightlifting

92. How many districts fall in Kashmir valley of Jammu and Kashmir?

(A) 9  
(B) 10

(C) 11  
(D) 12
93. Which day is observed as Quit India Day?

(A) January 26  (B) August 4

(C) August 9  (D) October 2

94. Which Mughal warrior built the Babri Masjid at Ayodhaya?

(A) Babur  (B) Mir Baqi

(C) Jahangir  (D) None of these

95. Which airport in India is named after tribal revolutionary Birsa Munda?

(A) Bagdogra  (B) Patna

(C) Ranchi  (D) Dibrugarh

96. What is the capital of Cambodia?

(A) Kampong Chan  (B) Phnom Penh

(C) Battambang  (D) Angkor Wat

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97. To which country does Mireia Lalaguna, who was crowned Miss World 2015, belong?

(A) Spain           (B) Russia
(C) Lebanon         (D) Indonesia

98. Before declaring independence in 1991 Macedonia was a part of:

(A) Albania         (B) Yugoslavia
(C) Serbia          (D) Croatia

99. Which city of China was the venue of G-20 summit held in September 2016?

(A) Hangzhou        (B) Beijing
(C) Shanghai        (D) Canton

100. Which Jamaat-e-Islami leader of Bangladesh was hanged in early September 2016 for war crimes committed during 1971 liberation war?

(A) Motiur Rehman   (B) Mir Quasem Ali
(C) Abdullah-al-Mamun (D) None of these