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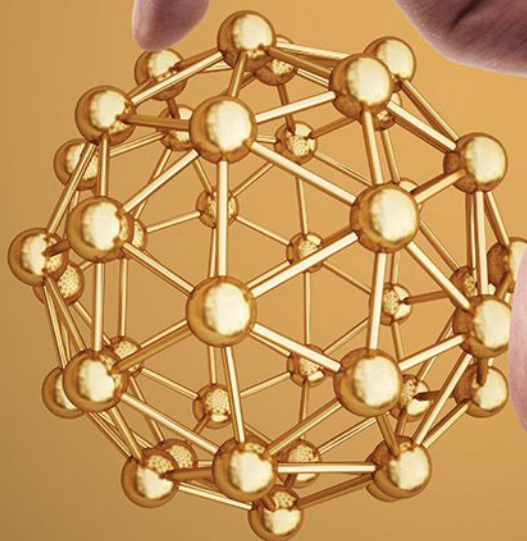
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CHEMISTRY today

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CHEMISTRY MUSING

Chemistry Musing was started from August '13 issue of Chemistry Today with the suggestion of Shri Mahabir Singh. The aim of Chemistry Musing is to augment the chances of bright students preparing for JEE (Main and Advanced) / AIPMT / AIIMS / Other PMTs & PETs with additional study material.

In every issue of Chemistry Today, 10 challenging problems are proposed in various topics of JEE (Main and Advanced) / AIPMT. The detailed solutions of these problems will be published in next issue of Chemistry Today.

The readers who have solved five or more problems may send their solutions. The names of those who send atleast five correct solutions will be published in the next issue.

We hope that our readers will enrich their problem solving skills through "Chemistry Musing" and stand in better stead while facing the competitive exams.

PROBLEM Set 28

JEE MAIN/PMTs

- Number of moles of $\text{Na}_2\text{S}_2\text{O}_3$ that will react with I_2 obtained when 1 mole of $\text{K}_2\text{Cr}_2\text{O}_7$ reacts with excess of KI in acidic medium is
(a) 2 (b) 1 (c) 4 (d) 6
- Which of the following is incorrect for extensive properties?
(a) For a single pure substance, it will depend upon the number of moles of substance.
(b) An extensive property becomes an intensive property if it is expressed in per mole.
(c) In the solution of two substances, it will depend upon two variables and number of moles.
(d) In the solution of two substances, it will depend upon one variable and number of moles.
- Which of the following statement(s) are correct?
I. Benzene, on heating with O_2 in the presence of V_2O_5 at 770 K forms maleic anhydride.
II. Iodination of benzene is done in the presence of an oxidising agent like HgO or conc. HNO_3 .
III. Acetone on condensation in presence of conc. H_2SO_4 forms mesitylene.
IV. Benzene is unsaturated hydrocarbon therefore, it decolourises bromine water.
(a) I and IV (b) II, III and IV
(c) IV only (d) I, II and III
- Of the following acids;
I. Hypophosphorus acid
II. Oxalic acid III. Glycine
(a) I and II are monobasic acids while III is dibasic and amphoteric.
(b) II is monobasic, I is dibasic and III is amphoteric.
(c) I is monobasic; II is dibasic and III is amphoteric.
(d) I and II are dibasic acids while III is amphoteric.
- Which of the following orders of acidic strength is not correct?
(a) *m*-methoxy phenol > phenol > *p*-methoxy phenol
(b) *o*-nitrobenzoic acid > *p*-nitrobenzoic acid > *m*-nitrobenzoic acid > benzoic acid
(c) acetylene > ammonia > water > hydrofluoric acid
(d) *o*-hydroxybenzoic acid > *m*-hydroxybenzoic acid > benzoic acid > *p*-hydroxybenzoic acid

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JEE ADVANCED

6. Three different compounds A, B and C are known to have the empirical formula $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$. When exposed to a dehydrating agent, A loses 2 moles of water per mole of the compound, B loses 1 mole of water and compound C loses no water at all. Which of them is the most conducting in aqueous solution?
- (a) A (b) B
(c) C
(d) All are equally conducting.

COMPREHENSION

It is best to represent the deviation from ideal behaviour in terms of the compressibility factor Z.

$$Z = \frac{PV}{(PV)_{\text{ideal}}} = \frac{PV}{nRT}$$

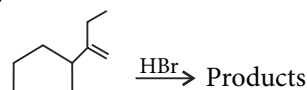
At moderately low pressure, carbon monoxide, methane and ammonia are more compressible than an ideal gas. It is observed that although carbon monoxide and methane exhibit marked deviation

from ideal behaviour only at high pressure yet ammonia exhibits large deviation even at low pressure.

7. The critical compressibility factor for a gas is
(a) 1 (b) 8/3
(c) 3/8 (d) None of these
8. For NH_3 , $Z < 1$. Therefore, the volume occupied by one mole of NH_3 at STP is
(a) 22.4 L (b) > 22.4 L
(c) < 22.4 L (d) 0

INTEGER VALUE

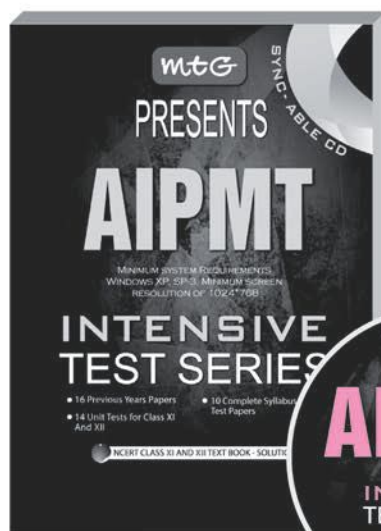
9. Total number of carbocations possible in the following reaction is



10. A mixture of water and nitrobenzene boils at 99°C . In the vapours of mixture, partial vapour pressures of water and nitrobenzene are 733 mm Hg and 27 mm Hg respectively. The $W_{\text{H}_2\text{O}}/W_{\text{C}_6\text{H}_5\text{NO}_2}$ is

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EXAMINER'S MIND

CLASS XI



The questions given in this column have been prepared strictly on the basis of NCERT Chemistry for Class XI. This year JEE (Main & Advanced)/AIPMT/AIIMS/other PMTs have drawn their papers heavily from NCERT books.

HYDROGEN | s-BLOCK ELEMENTS

SECTION - I

Only One Option Correct Type

This section contains 20 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

- The spectrum of He is similar to
 - H
 - Na
 - Li⁺
 - He⁺
- An unknown inorganic compound (X) loses its water of crystallisation on heating and its aqueous solution gives the following reactions :
 - It gives a white turbidity with dilute HCl solution.
 - It decolourises a solution of iodine in potassium iodide.
 - It gives a white precipitate with silver nitrate solution which turns black on standing.
 The compound (X) is
 - Na₂CO₃·10H₂O
 - Na₂S₂O₃·5H₂O
 - Na₂SO₄·10H₂O
 - none of these.
- The solubility of lithium halides in non-polar solvents follows the order
 - LiI > LiBr > LiCl > LiF
 - LiF > LiI > LiBr > LiCl
 - LiCl > LiF > LiI > LiBr
 - LiBr > LiCl > LiF > LiI
- Which one of the following sequences represents the increasing order of the polarising power of the cationic species, K⁺, Ca²⁺, Mg²⁺, Be²⁺
 - Ca²⁺ < Mg²⁺ < Be²⁺ < K⁺
 - Mg²⁺ < Be²⁺ < K⁺ < Ca²⁺
 - Be²⁺ < K⁺ < Ca²⁺ < Mg²⁺
 - K⁺ < Ca²⁺ < Mg²⁺ < Be²⁺
- BaSO₄ is water insoluble although it is an ionic compound because of
 - low lattice energy
 - high bond energy
 - lattice energy > solvation energy
 - solvation energy > lattice energy.
- The electron affinity of Be is similar to
 - He
 - B
 - Li
 - Na
- Read the following statements.
 - Cs⁺ is highly hydrated.
 - Li has highest melting point among Li, Na, K and Rb.
 - In alkali metals, only Li forms nitride.
 The correct statements are
 - I and II
 - II and III
 - I and III
 - I, II and III
- Oxidation state of hydrogen is zero in
 - CaH₂
 - NaH
 - PdH₂
 - NH₃
- Decomposition of H₂O₂ is retarded by
 - H₃PO₄
 - alcohol
 - acetanilide
 - all of these.
- Substance which absorbs CO₂ and violently reacts with H₂O with sound is
 - H₂SO₄
 - CaCO₃
 - ZnO
 - CaO
- Which of the following has the highest conductivity?
 - Li⁺
 - Cs⁺
 - Na⁺
 - K⁺

12. Which of the following on thermal decomposition yields a basic as well as an acidic oxide?
 (a) KClO_3 (b) CaCO_3
 (c) NH_4NO_3 (d) NaNO_3
13. The melting point of most of the solid substances increase with an increases of pressure. However, ice melts at a temperature lower than its usual melting point when pressure is increased. This is because
 (a) ice is less denser than H_2O
 (b) pressure generates heat
 (c) the chemical bonds break under pressure
 (d) ice is not a true solid.
14. A deliquescent white crystalline hydroxide X reacts with a nitrate Y to form another hydroxide which decomposes to give an insoluble brown layer of its oxide. X is a powerful cautery and breaks down the proteins of skin flesh to a pasty mass. X and Y are respectively
 (a) NaOH , AgNO_3 (b) NaOH , $\text{Zn}(\text{NO}_3)_2$
 (c) NaOH , $\text{Al}(\text{NO}_3)_3$ (d) $\text{Ca}(\text{OH})_2$, HgNO_3
15. How does H_2O_2 differ from O_3 in its chemical action?
 (a) In oxidising PbS to PbSO_4
 (b) In liberating I_2 from KI
 (c) In decolourising acidified KMnO_4
 (d) In oxidising $\text{K}_4[\text{Fe}(\text{CN})_6]$ to $\text{K}_3[\text{Fe}(\text{CN})_6]$
16. A compound which can be used in space vehicles both to absorb CO_2 and liberate O_2 is
 (a) NaOH (b) Na_2O
 (c) Na_2O_2 (d) none of these.
17. In Down's cell (for production of sodium), graphite anode is used because
 (a) graphite has no reaction with sodium
 (b) graphite has no reaction with chlorine
 (c) graphite can easily be fashioned in circular form
 (d) none of these.
18. Which of the following elements does not form hydride by direct heating with dihydrogen?
 (a) Be (b) Mg
 (c) Sr (d) Ba
19. One mole of magnesium nitride on reacting with an excess of water gives
 (a) one mole of ammonia
 (b) two moles of nitric acid
 (c) two moles of ammonia
 (d) one mole of nitric acid.
20. The molarity of a 100 mL solution containing 5.1 g of hydrogen peroxide is
 (a) 0.15 M (b) 1.5 M
 (c) 3.0 M (d) 50.0 M

SECTION - II

One or More Options Correct Type

21. The reagent(s) used for softening the temporary hardness of water is (are)
 (a) $\text{Ca}_3(\text{PO}_4)_2$ (b) $\text{Ca}(\text{OH})_2$
 (c) Na_2CO_3 (d) NaOCl
22. The hydroxides which sublime on heating are
 (a) LiOH (b) KOH
 (c) RbOH (d) $\text{Mg}(\text{OH})_2$
23. H_2 is evolved when NaOH solution reacts with
 (a) Sn (b) Fe
 (c) Zn (d) Mo
24. Identify the correct statement(s).
 (a) Elemental sodium can be prepared and isolated by electrolysing an aqueous solution of sodium chloride.
 (b) Elemental sodium is a strong oxidising agent.
 (c) Elemental sodium is insoluble in ammonia.
 (d) Elemental sodium is easily oxidised.
25. Select the correct statement(s) about lime light.
 (a) It is produced in oxy-hydrogen flame.
 (b) It is used in welding.
 (c) Temperature of lime light is sufficient to melt even platinum.
 (d) It is produced in an endothermic reaction.

SECTION - III

Paragraph Type

This section contains 2 paragraphs each describing theory, experiment, data, etc. Six questions relate to two paragraphs with three questions on each paragraph. Each question of a paragraph has only one correct answer among the four choices (a), (b), (c) and (d).

Paragraph for Questions 26 to 28

Dihydrogen, under certain reaction conditions, combines with almost all elements, except noble gases, to form binary compounds, called hydrides. If ' E ' is the symbol of an element then hydride can be expressed as EH_x (e.g., MgH_2) or E_mH_n (e.g., B_2H_6).

26. Which of the following hydrides is electron-precise hydride?
 (a) B_2H_6 (b) NH_3
 (c) H_2O (d) CH_4
27. Which of the following statements about metallic hydrides is correct?
 (a) They are also called interstitial hydrides.
 (b) They are non-stoichiometric, being deficient in hydrogen.
 (c) They are good conductors of electricity.
 (d) All of these.
28. A hydride of nitrogen which is acidic in nature is
 (a) NH_3 (b) N_2H_4
 (c) N_2H_2 (d) N_3H

Paragraph for Questions 29 to 31

The chemistry of alkaline earth metals is very much like that of the alkali metals. However, some differences arise because of reduced atomic and ionic sizes and increased cationic charges in case of alkaline earth metals. Their oxides and hydroxides are less basic than the alkali metal oxides and hydroxides. Industrially important compounds of calcium include calcium oxide (lime), calcium hydroxide (slaked lime), calcium sulphate (Plaster of Paris), calcium carbonate (limestone) and cement.

29. Setting of plaster of Paris involves
 (a) oxidation with atmospheric oxygen
 (b) combination with atmospheric CO_2
 (c) dehydration
 (d) hydration to yield another hydrate.
30. Cement containing excess amount of lime results in
 (a) weak strength
 (b) cracks during setting
 (c) slow setting
 (d) quick setting.
31. Chemical A is used for water softening to remove temporary hardness. A reacts with sodium carbonate to generate caustic soda. When CO_2 is bubbled through A, it turns cloudy. What is the chemical formula of A?
 (a) $CaCO_3$ (b) CaO
 (c) $Ca(OH)_2$ (d) $Ca(HCO_3)_2$

SECTION - IV

Matching List Type

This section contains 3 multiple choice questions. Each question has matching lists. The codes for the lists have choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

32. Match the species given in List I with their properties or applications given in List II and select the correct answer using the code given below the lists :

List I		List II	
P. H	1. Used as a germicide in the name of perhydrol.		
Q. H_2	2. Can be reduced to dihydrogen by NaH.		
R. H_2O	3. Can be used in hydroformylation of olefin.		
S. H_2O_2	4. Can be used in cutting and welding.		
P Q R S			
(a) 1 2 3 4			
(b) 4 3 2 1			
(c) 4 2 3 1			
(d) 3 4 2 1			

33. Match the compounds in List I with their specific properties in List II and select the correct answer using the code given below the lists :

List I		List II	
P. $BeCO_3$	1. Temporary hardness		
Q. $BaCl_2$	2. Permanent hardness		
R. $MgSO_4$	3. Decomposes readily		
S. $Ca(HCO_3)_2$	4. Gives green edged flame		
P Q R S			
(a) 4 3 2 1			
(b) 3 4 2 1			
(c) 2 3 1 4			
(d) 3 1 4 2			

34. Match the compounds in List I with their uses in List II and select the correct answer using the code given below the lists :

List I		List II	
P. KO_2	1. Baking		
Q. $NaHCO_3$	2. Photovoltaic cell		
R. $LiCl$	3. Submarines		
S. Cs	4. Humidity control		
P Q R S			
(a) 4 3 2 1			
(b) 3 4 2 1			
(c) 2 3 1 4			
(d) 3 1 4 2			

SECTION - V

Assertion-Reason Type

In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as :

- (a) If both assertion and reason are true and reason is the correct explanation of assertion.
 (b) If both assertion and reason are true but reason is not the correct explanation of assertion.
 (c) If assertion is true but reason is false.
 (d) If both assertion and reason are false.

35. **Assertion** : Some metals like Pt and Pd can be used as storage materials for H_2 gas.

Reason : Pt and Pd can adsorb large volumes of H_2 gas.

36. **Assertion** : K, Rb and Cs (group I elements) can also form superoxides.

Reason : The ionic radii of K, Rb and Cs show the trend, $Cs^+ < Rb^+ < K^+$.

37. **Assertion** : H_2O_2 is stored in wax-lined glass or plastic vessels.

Reason : H_2O_2 decomposes slowly on exposure to light.

38. **Assertion** : Beryllium does not impart any characteristic colour to the bunsen flame.

Reason : Due to its very high ionisation energy, beryllium requires a large amount of energy for excitation of the electrons.

39. **Assertion** : Soft water lathers with soap but hard water does not.

Reason : Hard water reacts with soap to form insoluble salts which form scum, not lather.

40. **Assertion** : Li_2CO_3 decomposes easily on heating to form Li_2O and CO_2 .

Reason : Li^+ is very small in size and applies very high polarising power on CO_3^{2-} ion leading to the decomposition of Li_2CO_3 .

SECTION - VI

Integer Value Correct Type

This section contains 10 questions. The answer to each question is a single digit integer, ranging from 0 to 9 (both inclusive).

41. To 8.4 mL H_2O_2 , excess of acidified solution of KI was added. The iodine liberated required 20 mL of 0.3 N $Na_2S_2O_3$ solution. Volume strength of H_2O_2 solution is

42. Number of moles of CO_2 evolved on heating a mixture containing 2 moles each of Li_2CO_3 and K_2CO_3 is

43. The degree of hardness of a sample of water containing 6 mg of $MgSO_4$ (molecular mass 120) per kg of water is

44. Number of molecules of water of crystallisation in sodium thiosulphate is

45. Number of moles of acidified potassium permanganate reduced by five moles of H_2O_2 is

46. Compounds X and Y are obtained by the reaction of Cl_2 with cold and dil. NaOH and compounds X and Z are formed with hot and conc. NaOH. The oxidation state of chlorine in Z is

47. Mass of H_2O_2 in grams required to oxidise 3.0 g of H_2S gas is

48. Magnesium oxide when mixed with a saturated solution of magnesium chloride sets to a hard mass like cement known as 'sorel cement'. The composition of sorel cement is $MgCl_2 \cdot nMgO \cdot xH_2O$. The value of n is

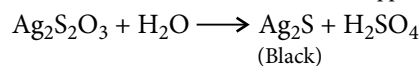
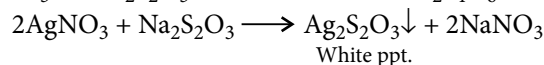
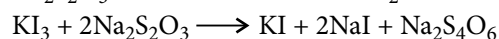
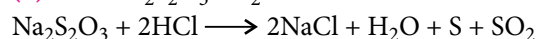
49. The number of hydrides formed by Cr is

50. The percentage of magnesium in magnalium is

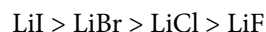
SOLUTIONS

1. (c) : Li^+ has similar spectrum to that of He as they both contain two electrons.

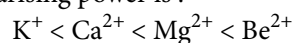
2. (b) : $X = Na_2S_2O_3 \cdot 5H_2O$



3. (a) : As the size of the anion increases from F^- to I^- , the covalent character increases and hence the solubility in non-polar solvent increases. Therefore, the order will be



4. (d) : Higher the charge/size ratio, higher is the polarising power. Hence, the increasing order of the polarising power is :

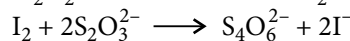
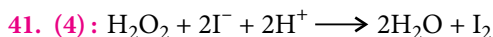
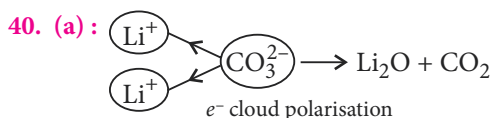
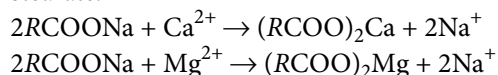


5. (c) : Lattice energy of alkaline earth metal sulphates remains almost same down the group. This is because the sulphate anion is so big that increase in size of the cation down the group does not make any difference. However, the hydration energy (solvation energy) decreases down the group. Hence, the solubility of BaSO_4 is lowest.
6. (a) : Be : $1s^2 2s^2$
He : $1s^2$
Due to stable electronic configuration, tendency to gain electron is minimum.
7. (b) : Degree of hydration decreases with the ionic size as we move from Li^+ to Cs^+ . Thus, Cs^+ is least hydrated and I is incorrect. Metallic bonding is stronger in lithium, so it has higher melting point. Thus, II is correct. Only Li forms nitride. Thus, III is correct.
8. (c) : H_2 is adsorbed on Pd-surface. Thus, it is in molecular state with oxidation number of hydrogen = 0.
9. (d) : Acetanilide, alcohol and H_3PO_4 are negative catalysts and retard decomposition of H_2O_2 .
10. (d) : $\text{CaO} + \text{CO}_2 \longrightarrow \text{CaCO}_3$
On adding water, it gives a hissing sound and forms calcium hydroxide.
 $\text{CaO} + \text{H}_2\text{O} \longrightarrow \text{Ca(OH)}_2$
11. (b) : Cs^+ , due to its very high ionic mobility has the highest conductivity.
12. (b) : $\text{CaCO}_3 \xrightarrow{\Delta} \text{CaO} + \text{CO}_2$
Basic Acidic
13. (a) : Ice occupy more volume than liquid water
Ice \rightleftharpoons Water
(More volume) (Less volume)
Increase of pressure favours forward reaction (Le-Chatelier's principle).
14. (a) : $\text{NaOH} + \text{AgNO}_3 \longrightarrow \text{AgOH} + \text{NaNO}_3$
(X) (Y) Unstable
 $2\text{AgOH} \longrightarrow \text{Ag}_2\text{O} + \text{H}_2\text{O}$
Brown
- (X) is a powerful cautery and breaks down the proteins of skin flesh to a pasty mass.
15. (c) : O_3 does not decolourise KMnO_4 .
16. (c) : $2\text{Na}_2\text{O}_2 + 2\text{CO}_2 \longrightarrow 2\text{Na}_2\text{CO}_3 + \text{O}_2$
17. (b) : Anode (of graphite) has no reaction with chlorine (liberated at anode).
18. (a) : Due to high ionisation enthalpy and small size, Be does not react with H_2 by direct heating.
19. (c) : $\text{Mg}_3\text{N}_2 + 6\text{H}_2\text{O} \longrightarrow 3\text{Mg(OH)}_2 + 2\text{NH}_3$
1 mole 2 moles
20. (b) : $M = \frac{5.1 \times 1000}{34 \times 100} = 1.5 \text{ M}$
21. (b, c, d)
22. (a, b, c, d) : For alkali metal hydroxides, the thermal stability increases on moving from Li to Cs, however, they sublime at about 400°C and the vapours mainly consist of dimer, $(\text{MOH})_2$.
23. (a, c) : $\text{Sn} + 2\text{NaOH} + \text{H}_2\text{O} \longrightarrow \text{Na}_2\text{SnO}_3 + 2\text{H}_2$
 $\text{Zn} + 2\text{NaOH} \longrightarrow \text{Na}_2\text{ZnO}_2 + \text{H}_2$
24. (d) : Elemental sodium is easily oxidised (has low *I.P.*) and acts as a reductant.
25. (a, b, c)
26. (d) : CH_4 is an electron precise hydride since there are exact number of electrons to form normal covalent bonds.
- $$\begin{array}{c} \text{H} \\ \times \\ \text{H} \times \cdot \text{C} \cdot \times \text{H} \\ \times \\ \text{H} \end{array}$$
27. (d)
28. (d) : N_3H (hydrazoic acid) is the acidic hydride of nitrogen.
29. (d) : Setting of plaster of Paris involves hydration to give another hydrate.
- $$\begin{array}{ccc} \text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O} + 1\frac{1}{2}\text{H}_2\text{O} & \xrightarrow{\text{Setting}} & \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \\ \text{Plaster of Paris} & & \text{Orthorhombic} \\ & & \downarrow \text{Hardening} \\ & & \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \\ & & \text{Monoclinic (gypsum)} \end{array}$$
30. (b) : Cement containing excess of lime cracks during setting.
31. (c) : $\text{Ca(OH)}_2 + \text{Na}_2\text{CO}_3 \rightleftharpoons \text{CaCO}_3 + 2\text{NaOH}$
(A) (Caustic soda)
 $\text{Ca(OH)}_2 + \text{CO}_2 \longrightarrow \text{CaCO}_3 + \text{H}_2\text{O}$
(A)
32. (b) 33. (b)
34. (d) 35. (a)
36. (c) : Atomic as well as ionic radii increase down the group. Hence ionic radii will show the trend : $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+$
37. (b) : H_2O_2 decomposes slowly on exposure to light.
 $2\text{H}_2\text{O}_2(l) \rightarrow 2\text{H}_2\text{O}(l) + \text{O}_2(g)$

In the presence of metal surfaces or traces of alkali (present in glass containers), the above reaction is catalysed. Hence, H_2O_2 is stored in wax-lined glass or plastic containers in dark.

38. (a)

39. (a) : Hard water contains calcium and magnesium salts which react with soap containing sodium stearate ($\text{C}_{17}\text{H}_{35}\text{COONa}$) to precipitate out Ca/Mg stearate.



$$N_1 V_1 = N_2 V_2$$

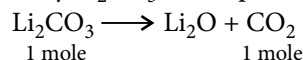
(H_2O_2) ($\text{Na}_2\text{S}_2\text{O}_3$)

$$N_1 \times 8.4 = 0.3 \times 20 \Rightarrow N_1 = 0.7143$$

Now, volume strength = normality \times 5.6

$$\Rightarrow \text{Volume strength} = 0.7143 \times 5.6 = 4$$

42. (2) : Only Li_2CO_3 decomposes and gives out CO_2 .



\therefore Two moles of Li_2CO_3 will give out 2 moles of CO_2 .

43. (5) : 6 mg of MgSO_4 present in 10^3 g of water.
 10^6 g of water will contain = 6000 mg of MgSO_4
 = 6 g of MgSO_4

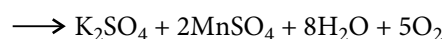
120 g of $\text{MgSO}_4 \equiv 100$ g of CaCO_3

$$\text{So, 6 g of } \text{MgSO}_4 = \frac{100}{120} \times 6 = 5 \text{ g of } \text{CaCO}_3$$

i.e., Hardness = 5 ppm

44. (5) : $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$

45. (2) : $2\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 + 5\text{H}_2\text{O}_2$
 2 moles 5 moles



46. (5) : $\text{Cl}_2 + 2\text{NaOH} \longrightarrow \text{NaCl} + \text{NaClO} + \text{H}_2\text{O}$
 (Cold and dilute) (X) (Y)

$3\text{Cl}_2 + 6\text{NaOH} \longrightarrow 5\text{NaCl} + \text{NaClO}_3 + 3\text{H}_2\text{O}$
 (Hot and conc.) (X) (Z)

In Z, *i.e.*, NaClO_3 , the oxidation state of Cl is +5.

47. (3) : $\text{H}_2\text{S} + \text{H}_2\text{O}_2 \longrightarrow 2\text{H}_2\text{O} + \text{S}$
 34 g 34 g

48. (5) : $\text{MgCl}_2 \cdot 5\text{MgO} \cdot x\text{H}_2\text{O}$

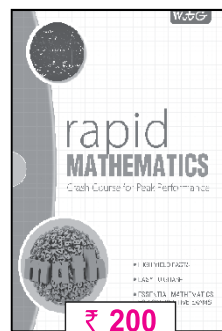
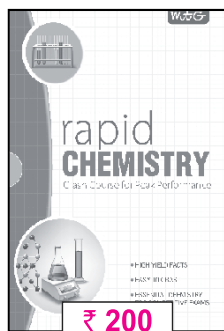
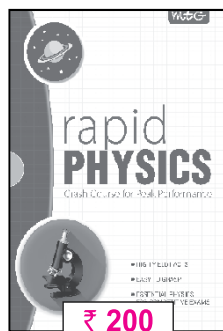
49. (2)

50. (5) : Magnalium : 95% Al + 5% Mg

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NEWS CORNER

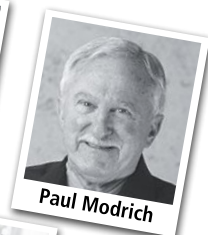
Nobel Prize 2015

The Nobel Prize in Chemistry 2015 is awarded to Tomas Lindahl, Paul Modrich and Aziz Sancar for having mapped, at a molecular level, how cells repair damaged DNA and safeguard the genetic information.

Tomas Lindahl showed that DNA, which had been thought to be a stable molecule, would decay quickly without a way to monitor and fix it. The molecular machinery he discovered is called base excision repair, which constantly counteracts the collapse of our DNA.

Aziz Sancar has mapped nucleotide excision repair, the mechanism that cells use to repair UV damage to DNA. People born with defects in this repair system will develop skin cancer if they are exposed to sunlight.

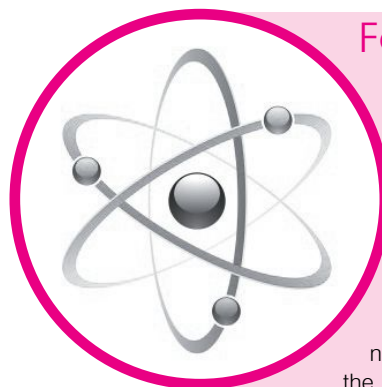
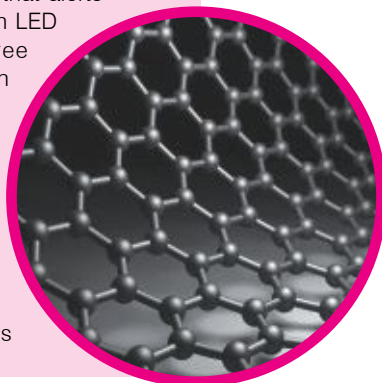
Paul Modrich has demonstrated how the cell corrects errors that occur when DNA is replicated during cell division. This mechanism called mismatch repair, reduces the error frequency during DNA replication by about a thousandfold.



Graphene- coated fabrics detect dangerous gases

Scientists of Electronics and Telecommunications Research Institute and Konkuk University in the Republic of Korea prepared a fabric by wrapping graphene oxide sheets on cotton and polyester yarn with the help of nanoglue called bovine serum albumin (BSA).

Then the graphene oxide yarns were exposed to a chemical reduction process, which involves the gaining of electrons. These reduced-graphene-oxide-coated fabrics were found to be particularly sensitive to nitrogen dioxide, a pollutant gas. Exposure of these specially treated fabrics to 0.25 ppm of nitrogen dioxide for 30 minutes led to a change in the electrical resistance of the reduced graphene oxide that alerts wearer of fabric by turning on LED light. The fabrics were three times more sensitive to nitrogen dioxide in air as compared to another reduced graphene oxide sensor previously prepared on a flat material. These materials in future may be incorporated with air-purifying filters to act as "smart filters" that can both detect and filter harmful gases from air.



Four new isotopes discovered

H M Devaraja, PhD student at MCNS from Manipal Centre of Natural Sciences (MCNS) at Manipal University in collaboration with GSI-Giessen, Germany have discovered four new atomic nuclei to be added to the chart of the nuclides. The newly discovered two isotopes of americium and one each of berkelium and neptunium have fewer neutrons and are lighter than the previously known isotopes of the respective elements. For the experiment, the scientists shot at a 300-nanometer-thick foil of curium with accelerated calcium nuclei. In the collisions studied, the atomic nuclei of the two elements touched, and formed a compound system for an extremely short time. Before the compound system could break apart again, after about a sextillionth of a second, the two nuclei involved exchanged a number of their nuclear building-blocks — protons and neutrons.

Different isotopes were formed as the end products of this exchange. According to scientific estimates, more than 4,000 additional, undiscovered isotopes should also exist and they have already started experiments to identify them.



CONCEPT BOOSTER

Dear students!! Hopefully the last article helped you in understanding the basic format of Qualitative Analysis. This article also contains useful information about this topic. Now you start practicing problems with topics I have covered and with the Group Analysis which you may find in any practical book. All the very best.

*Arunava Sarkar

Concept Corner

A few important points regarding dry heating test :

- Test tube should be perfectly dried. While drying in the test tube, keep the test tube in slanting or oblique position keeping the mouth of the test tube slightly in downward direction so that the drops of water getting condensed on the relatively cooler upper part can come out and do not fall back on the hotter bottom part. This can break the test tube.
- Never heat a test tube strongly at a particular point. This can break the test tube immediately.
- To detect a gas evolved from the mouth of the test tube any of the following two methodologies is used :
 - (i) A filter paper strip is dipped into a suitable reagent and is held near the mouth of the test tube from where the gas is evolved.
 - (ii) The suitable reagent is taken in a gas detector tube and the gas is passed through it.

Charcoal Cavity Test

Charcoal cavity test can be performed under two types of flame :

- (a) Oxidising flame (b) Reducing flame

(a) Oxidising flame

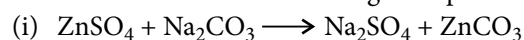
Heat a little amount of the substance in a charcoal groove under the oxidising flame. Note whether the changes are matching with the following list.

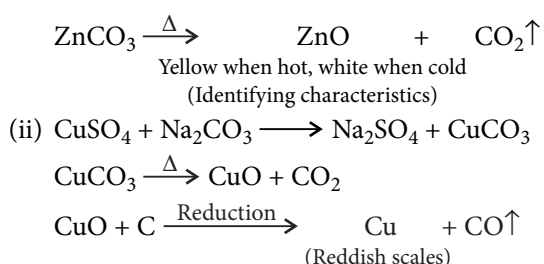
Observations		Inferences	
(i)	Substance melts and molten substance is absorbed into pores of charcoal.	(i)	Alkali metal salts specially of Na, K and possibly one or two alkaline earth metals.
(ii)	The substance catches fire on heating. <i>i.e.</i> , deflagrates	(ii)	Nitrates, nitrites, iodates
(iii)	The substance decrepitates (break up on heating with an audible sound)	(iii)	Mainly NaCl, KCl
(iv)	Residue left in the charcoal block is white and when hot it is incandescent.	(iv)	Ca, Al, Mg, Zn, Sn, Ba salts.

(b) Reducing flame

The substance and anhydrous Na_2CO_3 are taken in the ratio 1 : 2 and the mixture is placed in the groove or cavity of the charcoal block. This mixture is moistened with a drop of water and is heated under the reducing flame.

If the substance is metallic carbonate then it decomposes to give corresponding oxides. Sometimes, the oxides formed can even undergo reduction to the metallic state and can produce metallic bead. Take the following examples :





The following two tables will cover up almost all types of cases :

Table-1

Residue	Metallic bead	Inferences
Yellow when hot, white when cold.	Not observed	Zn^{2+}
No such residue.	Red scales or beads	Cu^{2+}
Black	None	Only confirms that the salt is coloured.
White residue which glows or becomes incandescent when heated.	None	Ba^{2+} , Mg^{2+} , Ca^{2+}
Brown when hot, yellow when cold.	Grey bead on the paper	Pb^{2+}

Table-2

Observations		Inferences	
(i)	Metallic bead	(i)	Pb, Sb, Bi, Ag, Sn salts.
(ii)	Cluster of small beads	(ii)	Sn salts confirmed.
(iii)	Red scales	(iii)	Cu salts
(iv)	Malleable bead which marks paper	(iv)	Pb-salts
(v)	Greyish black, attracted by magnet	(v)	Fe, Co, Ni salts. Mn can also be there.
(vi)	Green	(vi)	Cr salts
(vii)	Brown residue or incrustation	(vii)	Cd-salts

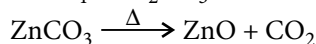
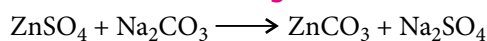
Cobalt Nitrate Test

Cobalt nitrate test is performed only when a white residue is obtained after charcoal cavity test. A drop of water is added at this time to the mass and it is heated

in the oxidising flame with a blow pipe. After this one or two more drops of cobalt nitrate solution are added and then it is again heated in the oxidising flame. Note down the change in the colour taking place.

Observations		Inferences	
(i)	Green residue	(i)	Zinc (Zn)
(ii)	Dirty green residue	(ii)	Tin (Sn)
(iii)	Pink residue	(iii)	Mg
(iv)	Blue infusible residue	(iv)	Al
(v)	Blue fusible residue	(v)	PO_4^{3-} , BO_3^{3-} , arsenites, silicates
(vi)	Grey residue	(vi)	Ca, Sr, Ba

Add to Your Knowledge



Note :

- Do not perform cobalt nitrate test for the coloured salt.
- Addition of excess cobalt nitrate turns the whole mass into black as black cobalt oxide is formed.

Flame Test

At first, clean platinum wire with concentrated HCl and keep the wire in a water glass. Hold it at the base of the non-luminous flame and wait until the flame becomes colourless.

Hold and clean platinum wire near the base of the non-luminous flame after moistening it with conc. HCl and a little bit of powdered substance is taken on the tip of the wire. Without looking through the double blue glass observe and note the colour changes carefully.

Observations		Inferences	
	With double blue glass	Without double blue glass	
1.	Colourless	Persistent vivid golden yellow	Na
2.	Crimson red	Bluish violet	K
3.	Purple	Persistent crimson	Sr

4.	Bluish green	Persistent apple green	Ba
5.	Light green	Brick red	Ca
6.	Bluish green	–	Cu
7.	Blue flame	–	H ₃ BO ₃ , BO ₂ ⁻
8.	Lambent blue	–	Pb, Sb, As, Bi, Sn
9.	Transient yellowish green flame	–	MnCl ₂

Note :

- Some metals like Pb, Sb, As, Cu and Sn, in their salt forms corrode Pt wire. This is why sometimes asbestos fibre is used for them.

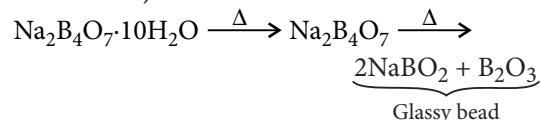
Borax Bead Test

This test is performed for coloured salts only. Take a platinum wire. Give it a loop form at the tip and heat the cleaned Pt-loop taking borax at its loop. This will give a transparent borax bead. Now, touch this with the salt particles very slowly and just take a particle of the salt on the hot bead and heat; at first with the oxidising flame and then with the reducing flame.

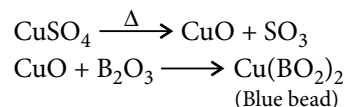
	Observations		Inferences
	Oxidising flame	Reducing flame	
1.	Deep blue both in hot and cold conditions	Deep blue both in hot and cold conditions	Co
2.	Yellow when hot, green when cold	Green in both hot and cold conditions	Cr
3.	Reddish yellow when hot, pale-yellow when cold	Bottle green when hot and cold both	Fe
4.	Violet when hot, reddish brown when cold	Opaque grey in both hot and cold conditions	Ni
5.	Green when hot, blue when cold	Colourless when hot, brown-red when cold	Cu
6.	Violet/amethyst when hot, amethyst-red when cold	Grey/colourless in both hot and cold conditions	Mn

Reactions Involved

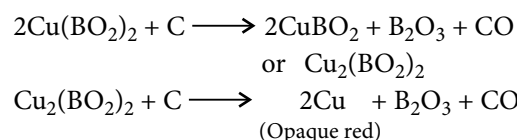
- At first, on heating borax gives a colourless glassy bead of NaBO₂ (sodium metaborate) and B₂O₃ (boron trioxide).



- When a coloured salt is heated, the glassy bead gives coloured metaborate in the oxidising flame. As an example, copper, under similar conditions give blue colour.



In the reducing flame, different colours come for different reactions.

**Special Test**

- Microcosmic bead test :**

This test is carried out instead of borax bead test. As in the borax bead test, here also a transparent bead is prepared at the loop of a cleaned Pt wire. Just touching the salt with this hot Pt wire loop, a tiny particle is taken and at first it is heated in oxidising flame and then in the reducing flame. Observe the changes carefully.

	Observations		Inferences
	Oxidising flame	Reducing flame	
1.	Brownish	Greyish	Ni
2.	Blue in both hot and cold conditions	Colourless when hot and reddish brown when cold.	Cu
3.	Green in both hot and cold conditions	Green in both hot and cold conditions	Cr
4.	Reddish violet in both hot and cold conditions	Colourless in both the conditions	Mn
5.	Green when hot, blue when cold	Blue in both the conditions	Co

○ **NaOH extract test :**

Salts which have amphoteric behaviour and mostly contain Na, K, Ca, Ba can be tested with NaOH extract test.

To perform the test, boil a small quantity of the sample with NaOH and filter. Divide the filtrate into three parts and after performing tests observe the changes carefully.

	Tests	Observations	Inferences
1.	Heat one part of the extract with solidified NH_4Cl	White gelatinous ppt.	All salts
2.	Second part is acidified with CH_3COOH	Yellow or orange ppt.	As_2S_3 , Sb_2S_3
3.	Third part is acidified with CH_3COOH and H_2S gas is passed	White ppt.	Zn salts

Concept Corner

Solubility of salts on the basis of anionic part

S.No.	Anion	Major solubility	Exception if any
1.	CO_3^{2-}	Generally insoluble in water	Ammonium and alkali metal carbonates are soluble.
2.	Cl^-	Alkali metal chlorides are fairly soluble. PbCl_2 and AgCl are sparingly soluble. Insoluble salts are Hg_2Cl_2 , BiOCl , SbOCl , CuCl , Hg_2OCl_2 . BiOCl contains BiO^+ and SbOCl contains SbO^+ . $\text{Bi}^{3+} + \text{H}_2\text{O} \rightarrow [\text{BiO}]^+$	-
3.	Br^-	Maximum bromides are water soluble. PbBr_2 is very less soluble in cold water but fairly soluble in hot water.	Cuprous, silver and mercurous bromides are insoluble in water.
4.	I^-	Alkali and alkaline earth metal iodides are fairly soluble.	Hg(I) , Hg(II) , Ag , Cu(I) , Pb^{2+} , Bi^{3+} iodides are insoluble.
5.	SO_4^{2-}	Insoluble — Ba, Sr, Pb (in water) Sparingly soluble — Ca, Hg(II)	Hg(I) , Bi and Cr sulphates are insoluble in water but dissolve in dilute HCl or HNO_3
6.	SO_3^{2-}	Alkali metal sulphites and ammonium sulphites are water soluble. Mostly other sulphites are insoluble	-
7.	PO_4^{3-}	Alkali metal phosphates and ammonium phosphates are soluble in water. Alkaline earth metal primary phosphates are fairly soluble.	Lithium phosphate is insoluble. Secondary and tertiary phosphates of alkaline earth metals are mostly insoluble. Some are sparingly soluble.
8.	$\text{NO}_2^- / \text{NO}_3^-$	Almost all nitrites and nitrates are soluble in water.	AgNO_2 is sparingly soluble. Mercury and bismuth nitrates are better soluble in dilute HNO_3 .





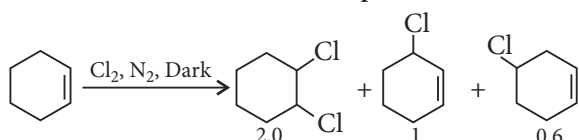
ADVANCED CHEMISTRY BLOC

(ORGANIC CHEMISTRY—BASIC REACTIONS OF ALKENES)

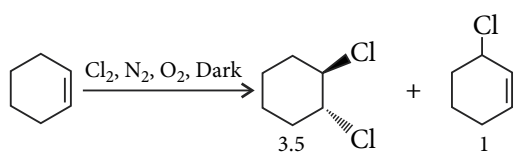
Mukul C. Ray, Odisha

Ionic and Radical Addition are Competing Reactions

The direct addition of chlorine to an alkene is strongly exothermic. The addition of chlorine *via* a radical pathway is generally preferred in non-polar medium and can be initiated by light or heat. However, even in the absence of light, energy generated by the onset of an ionic addition seems to be sufficient to initiate a subsequent radical chain reaction. Such radical addition generates even some substitution products.



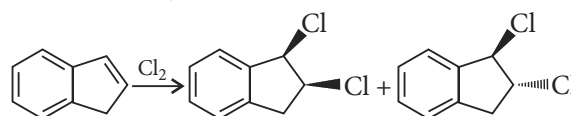
The numbers written below the products indicate the molar ratio of products formed. Again, radical additions are not normally stereospecific, except in few cases. To suppress the radical pathway, chlorination is carried out not only in dark but also in presence of oxygen that acts as radical scavenger. But these also do not eliminate the chances of substitution.



The addition product has *trans* stereochemistry indicating ionic mechanism. In ionic addition of chlorine, there is a cyclic bridged intermediate that does not undergo rearrangement. Thus, the addition is *trans* stereospecific.

But the stereochemistry of chlorine addition to alkene also has something very distinct. The cyclic chloronium cation may exist together with chloride as an ion pair and in the case of aromatic alkenes, the chloronium ring may open to form a stabilised carbenium ion,

which then adds chloride. This addition can be both *cis* and *trans*. The product distribution is therefore strongly solvent dependent. Solvents of low polarity lead to an increasing amount of *syn* facial addition, due to presence of closely associated ion pairs.



- I. In heptane solvent : 73 27
 II. In nitromethane solvent : 44 56

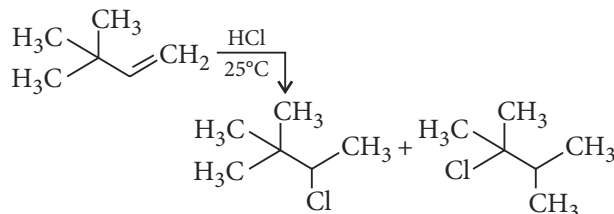
The numbers written below the products indicate their percentage yield. Nitromethane being more polar than heptane yields lower percentage of *syn* product.

HX Addition Products also Depend on the Nature of Solvent

The most useful procedure to study is to react dry HCl gas and the alkene neat or in an inert organic solvent. Alkenes yielding tertiary or benzylic alkyl chlorides react most readily. Reactants like styrene (vinyl benzene) add HCl only at -80°C without polymerisation. At more elevated temperature polymerisation prevails.

HBr adds to alkene more rapidly than does HCl in an exothermic process.

The stereochemistry of addition may be either *syn* or *anti*. Product distribution may be strongly influenced by the solvent.



- I. Neat reaction : 50 50
 II. Nitromethane solvent : 17 83

ACE

YOUR WAY CBSE XI



Series 3

CHAPTERWISE UNIT TEST : HYDROGEN | THE *s*-BLOCK ELEMENTS | THE *p*-BLOCK ELEMENTS

GENERAL INSTRUCTIONS

- (i) All questions are compulsory.
- (ii) Q. no. 1 to 5 are very short answer questions and carry 1 mark each.
- (iii) Q. no. 6 to 10 are short answer questions and carry 2 marks each.
- (iv) Q. no. 11 to 17 are also short answer questions and carry 3 marks each.
- (v) Q. no. 18 is a value based question and carries 4 marks.
- (vi) Q. no. 19 and 20 are long answer questions and carry 5 marks each.
- (vii) Use log tables if necessary, use of calculators is not allowed.

1. How is heavy water produced from ordinary water?
 2. Why can caesium be used in photoelectric cell while lithium cannot?
 3. Why is boric acid considered as a weak acid?
 4. Old lead paintings are generally washed with dilute solution of hydrogen peroxide in order to regain their colour. Why?
 5. Why is BaSO_4 insoluble in water while BeSO_4 is soluble?
 6. Give reasons for the following :
 - (i) CCl_4 is immiscible in water whereas, SiCl_4 is easily hydrolysed.
 - (ii) Carbon has a strong tendency for catenation as compared to silicon.
- OR**
- Explain the following :
- (i) Gallium has higher ionisation enthalpy than aluminium.
 - (ii) Aluminium forms $[\text{AlF}_6]^{3-}$ ion but boron does not form $[\text{BF}_6]^{3-}$ ion.
7. What is the difference between the terms 'hydrolysis' and 'hydration'?
 8. Why is the temperature maintained around 393 K during the preparation of plaster of Paris?
 9. Complete the following chemical equations :

$$\text{Z} + 3\text{LiAlH}_4 \longrightarrow \text{X} + 3\text{LiF} + 3\text{AlF}_3$$

$$\text{X} + 6\text{H}_2\text{O} \longrightarrow \text{Y} + 6\text{H}_2$$
 10. Write chemical reactions to justify that hydrogen peroxide can function as an oxidising as well as a reducing agent.
 11. How would you distinguish between
 - (i) Magnesium and calcium
 - (ii) Na_2CO_3 and NaHCO_3
 - (iii) KNO_3 and LiNO_3
 12. Explain the following :
 - (i) PbO_2 is a stronger oxidising agent than SnO_2 .
 - (ii) HNO_3 can be stored in aluminium vessel while NaOH solution cannot.
 - (iii) Anhydrous aluminium chloride is used as a catalyst.
 13. What do you understand by
 - (i) electron-deficient,
 - (ii) electron-precise and
 - (iii) electron-rich compounds of hydrogen?
 Provide justification with suitable examples.

14. What happens when
- beryllium carbide reacts with water
 - magnesium nitrate is heated
 - quick lime is heated in an electric furnace with powdered coke?
15. (i) Explain why BF_3 exists but BH_3 does not.
 (ii) Compare the B — F bond length in BF_3 and BF_4^- .
16. (i) What causes temporary and permanent hardness of water? Name two methods which can be used to remove both temporary and permanent hardness of water.
 (ii) Write one chemical reaction for the preparation of D_2O_2 .

OR

Compare the structures of H_2O and H_2O_2 .

17. Comment on each of the following observations :
- Mobilities of the alkali metal ions in aqueous solution are $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+$.
 - Lithium is the only alkali metal to form a nitride directly.
 - E° for $M_{(aq)}^{2+} + 2e^- \longrightarrow M_{(s)}$ (where $M = \text{Ca}, \text{Sr}$ or Ba) is nearly constant.
18. Aluminium cookwares are light, strong, conduct heat well and are easily affordable. Suhani, a Class XI student, suggested her mother that they should rather buy a bit expensive steel utensils especially for storing water and cooking acidic foods.
- Why aluminium vessels should not be used for storing water?
 - What values are displayed by Suhani?
 - Give composition and uses of two important alloys of aluminium.
19. (i) Explain the following terms :
 (a) syngas (b) water-gas shift reaction
 (c) fuel-cell.
 (ii) (a) How does H_2O_2 behave as a bleaching agent?
 (b) Calculate the strength of 5 volume H_2O_2 solution.

OR

- Do you expect different products in solution when aluminium(III) chloride and potassium chloride are treated separately with (i) normal water (ii) acidified water, and (iii) alkaline water? Write equations wherever necessary.
- Discuss the principle and method of softening of hard water by synthetic ion-exchange resins.

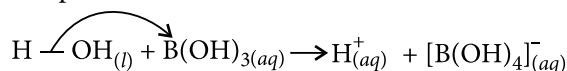
20. (i) Calcium burns in air to produce a white powder which dissolves in water to produce a gas (A) and the solution is alkaline. The solution on exposure to air produces a thin solid layer of (B) on the surface. Identify (A) and (B).
 (ii) (a) Potassium carbonate cannot be prepared by Solvay process. Why?
 (b) Draw the structure of BeCl_2 (vapour).

OR

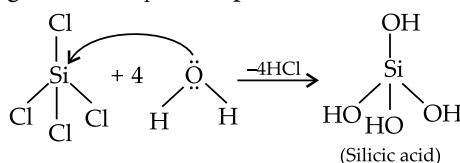
- Give reasons for the following :
 (a) A solution of Na_2CO_3 is alkaline.
 (b) Alkali metals are prepared by electrolysis of their fused chlorides.
 (c) Sodium is found to be more useful than potassium.
- Discuss the various reactions that occur in the Solvay process.

SOLUTIONS

- Heavy water is produced by continuous electrolysis of ordinary water containing alkali.
- Caesium has the lowest while lithium has the highest ionisation enthalpy hence, caesium can lose electrons very easily while lithium cannot.
- Because, it does not release H^+ ions on its own instead it accepts a OH^- ion from water molecule to complete its octet and in turn releases H^+ ions.



- Old lead paintings become black due to the formation of PbS which is oxidised to PbSO_4 (white) by H_2O_2 .
- The lattice enthalpy of BaSO_4 is much more than its hydration enthalpy hence, it is insoluble in water but hydration enthalpy of BeSO_4 is much higher than its lattice enthalpy because of small size of Be^{2+} ions therefore, it is highly soluble in water.
- (i) CCl_4 cannot be hydrolysed by water because carbon atom cannot accommodate lone pair of electrons from oxygen atom of water due to absence of d -orbital. SiCl_4 can be hydrolysed to give $\text{Si}(\text{OH})_4$ due to presence of d -orbitals.



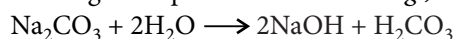
- (ii) Carbon-carbon bond dissociation energy is higher than that of silicon-silicon bond dissociation energy therefore, carbon has a strong tendency for catenation as compared to silicon.

OR

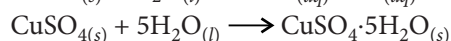
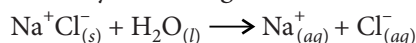
- (i) Due to ineffective shielding of valence electrons by the intervening $3d$ -electrons, the effective nuclear charge on Ga is slightly higher than that on Al and hence, the ΔH_f of gallium is slightly higher than that of Al.
- (ii) Al has vacant d -orbitals and hence can expand its coordination number from 4 to 6. Therefore, it forms octahedral $[\text{AlF}_6]^{3-}$ ion in which Al undergoes sp^3d^2 hybridisation. In contrast, B does not have d -orbitals and can have a maximum coordination number of 4. Therefore, B forms $[\text{BF}_4]^-$ but not $[\text{BF}_6]^{3-}$.

7. When H^+ and OH^- ions of H_2O interact with anion and cation of the salt respectively to give the original acid and base then the reaction is called hydrolysis.

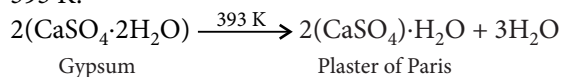
It changes the pH of the solution. *e.g.*,



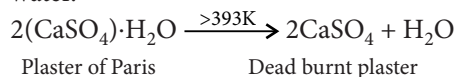
When H_2O is added to ions or molecules to give hydrated ions or compounds then the reaction is called hydration. *e.g.*,



8. Plaster of Paris is prepared by heating gypsum to 393 K.



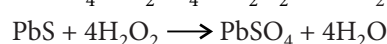
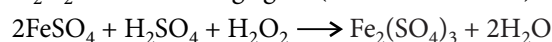
If the temperature is raised above 393 K, plaster of Paris is further dehydrated to form anhydrous calcium sulphate which is also called dead burnt plaster since it loses the properties of setting with water.



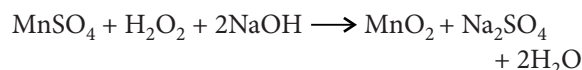
9. $4\text{BF}_3 + 3\text{LiAlH}_4 \xrightarrow{\text{Diethyl ether}} 2\text{B}_2\text{H}_6 + 3\text{LiF} + 3\text{AlF}_3$
(Z) (X)
- $\text{B}_2\text{H}_6 + 6\text{H}_2\text{O} \longrightarrow 2\text{H}_3\text{BO}_3 + 6\text{H}_2$
(X) (Y)

10. H_2O_2 acts as an oxidising and a reducing agent both in acidic as well as in basic medium.

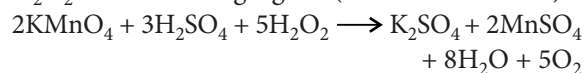
H_2O_2 as an oxidising agent (in acidic medium) :



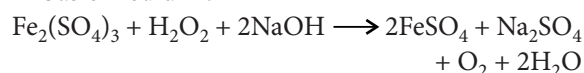
In basic medium :



H_2O_2 as a reducing agent (in acidic medium) :



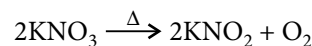
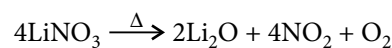
In basic medium :



11. (i) Magnesium when heated in a flame does not impart any colour to the flame whereas calcium imparts a brick red colour to the flame.

- (ii) Na_2CO_3 does not decompose, *i.e.*, stable towards heat but sodium bicarbonate decomposes to give CO_2 gas which turns lime water milky.

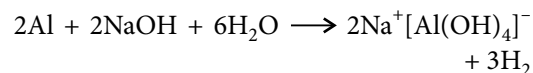
- (iii) LiNO_3 on heating gives brown fumes of NO_2 whereas KNO_3 on decomposition gives colourless O_2 gas.



12. (i) In both the oxides, the oxidation state of metals is +4. In lead, the inert pair effect is maximum hence, its +4 oxidation state is not stable and it readily gets converted to +2 oxidation state. Therefore, PbO_2 acts as a strong oxidising agent. In tin, +4 oxidation state is more stable than +2 oxidation state hence, SnO_2 is a weaker oxidising agent.

- (ii) Aluminium turns passive with HNO_3 due to the formation of protective oxide film on its surface. This film prevents the further action of conc. HNO_3 hence, HNO_3 can be stored in aluminium vessel.

Aluminium dissolves in aqueous NaOH hence, it cannot be stored in aluminium vessel.



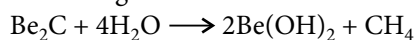
- (iii) In AlCl_3 , Al has only six electrons in its valence shell. It needs two more electrons to complete its octet therefore, it acts as a Lewis acid catalyst.

13. (i) Electron-deficient hydrides : These compounds have too few electrons to write their conventional Lewis structures. The hydrides of group 13 elements *e.g.*, B_2H_6 are electron deficient molecules and hence, they act as Lewis acids.

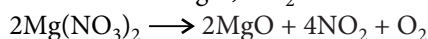
(ii) Electron-precise hydrides : These compounds have the required number of electrons to write their conventional Lewis structures. All elements of group 14 form such compounds *e.g.*, CH_4 and they have tetrahedral structure.

(iii) Electron rich compounds of hydrogen : These compounds have excess electrons which are present as lone pairs. Elements of group 15-17 form such compounds *e.g.*, NH_3 has one lone pair, H_2O has two lone pairs and HF has three lone pairs.

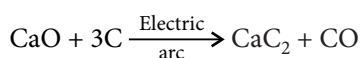
14. (i) Methane gas is evolved.



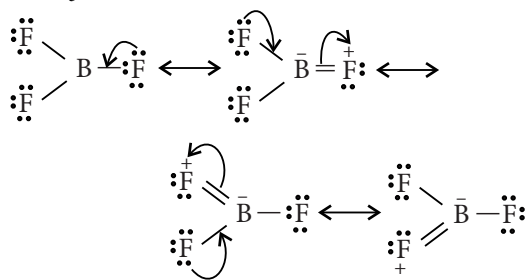
(ii) Brown coloured gas, NO_2 is evolved.



(iii) Calcium carbide is formed with evolution of carbon monoxide.



15. (i) Due to $p\pi - p\pi$ back bonding, the lone pair of electrons of F is donated to the B-atom. This delocalisation reduces the deficiency of electrons on B thereby increasing the stability of BF_3 molecule.



Due to absence of lone pair of electrons on H-atom, this compensation does not occur in BH_3 . In other words, electron deficiency of B stays and hence to reduce its electron deficiency, BH_3 dimerises to form B_2H_6 .

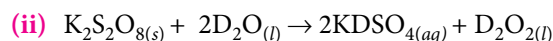
(ii) B—F bonds in BF_3 have double bond character hence, BF_3 has shorter B—F bond length than BF_4^- .

16. (i) Temporary hardness of water is due to the presence of magnesium and calcium hydrogen carbonates. It can be very easily removed by simply boiling the hard water for sometime. Permanent hardness of water is due to the presence of soluble salts of magnesium and calcium in the form of chlorides and sulphates in water. It cannot be easily removed.

Following methods are used to remove both temporary and permanent hardness of water.

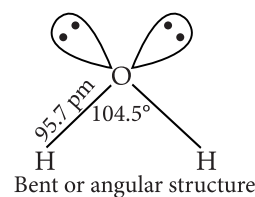
(a) Lime-soda process

(b) Ion exchange method

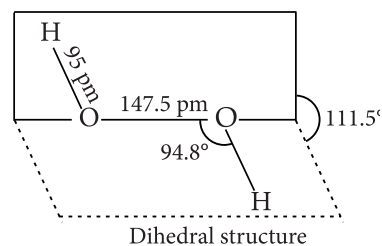


OR

In H_2O molecule, the oxygen is sp^3 -hybridised. Two half-filled sp^3 -orbitals form O—H σ -bonds, while the other two contain lone pairs of electrons. The expected $\angle HOH$ is 109.5° , but the experimental value is 104.5° . This is because $lp-lp$ repulsion $>$ $bp-lp$ repulsion.



On the other hand, H_2O_2 is a non-planar molecule. The dihedral angle between two planes is 111.5° and $\angle OOH$ is 94.8° . (Gas phase)



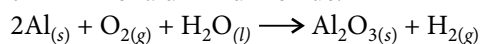
17. (i) This is attributed to the hydration of the cation in water which increases the size of the cation and thus, decreases its mobility. Due to the smallest size, Li^+ ion is hydrated to the maximum and has least mobility while Cs^+ ion due to least hydration has maximum mobility.

(ii) Lithium is a very strong reducing agent. As a result, it directly combines with nitrogen to form its nitride (Li_3N).

(iii) E° of any M^{2+}/M electrode depends upon three factors :

(a) enthalpy of vaporisation, (b) ionisation enthalpy (c) enthalpy of hydration. Since the combined effect of these factors is approximately the same for Ca, Sr and Ba, therefore, their electrode potentials are nearly constant.

18. (i) Al reacts with H_2O and dissolved O_2 to form a thin film of aluminium oxide.



A very small amount of Al_2O_3 may dissolve to give a few ppm of Al^{3+} ions in the solution. Since Al^{3+} ions are injurious to health, therefore drinking water should not be kept in aluminium vessels.

(ii) Suhani showed awareness and application of knowledge in day to day life.

(iii) Two important alloys of aluminium are :

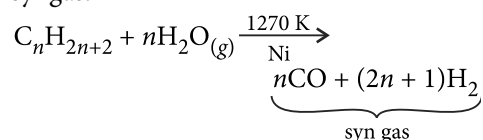
(a) Magnalium - 95% Al and 5% Mg.

It is used in the construction of airships, balances and pistons of motor engines.

(b) Duralumin - 95% Al, 4% Cu, 0.5% Mg and 0.5% Mn.

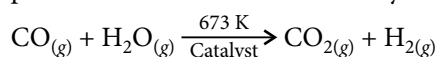
It is used for making aeroplanes and automobile parts.

19. (i) (a) Syngas : The mixture of CO and H_2 used for the synthesis of methanol and a number of hydrocarbons is called synthesis gas or syngas.



Nowadays, syngas is produced from sewage, saw dust, scrap wood, newspapers, etc.

(b) Water-gas shift reaction : The production of dihydrogen can be increased by reacting CO of syngas mixture with steam in the presence of iron chromate as catalyst.

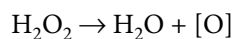


This is called water-gas shift reaction.

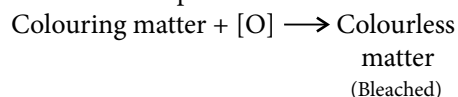
(c) Fuel cell : It is a commercial cell in which the chemical energy produced during the combustion of fuel is converted directly

into electricity, e.g., $H_2 - O_2$ fuel cell. A fuel cell is used as a source of electrical energy in the space vehicles.

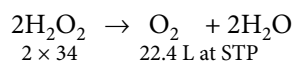
(ii) (a) H_2O_2 acts as a bleaching agent due to the release of nascent oxygen.



Thus, the bleaching action of hydrogen peroxide is permanent and is due to oxidation. It oxidises the colouring matter to a colourless product.



(b) 5 volume H_2O_2 solution means that 1 L of this H_2O_2 solution will give 5 L oxygen at STP.



$$2 \times 34 \quad 22.4 \text{ L at STP}$$

22.4 L of O_2 is produced from $H_2O_2 = 68 \text{ g}$
5 L of O_2 is produced from H_2O_2

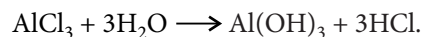
$$= \frac{68 \times 5}{22.4} = 15.18 \text{ g}$$

Hence, strength of 5 volume H_2O_2 = 15.18 g/L

OR

(i) Both the compounds are salts and they react differently with water.

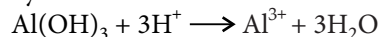
Aluminium (III) chloride or $AlCl_3$ will react with water as follows :



The reaction is known as hydrolysis.

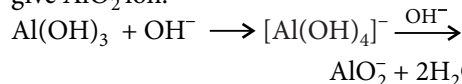
(i) In normal water, both $Al(OH)_3$ and HCl will be present.

(ii) In acidic water, $Al(OH)_3$ will be neutralised by the acid added.

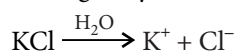


(iii) In alkaline water, HCl will be neutralised by the alkali added.

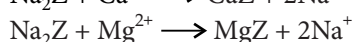
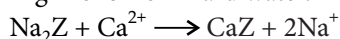
Also, $Al(OH)_3$ reacts to form $[Al(OH)_4]^-$ a soluble complex, which further reacts to give AlO_2^- ion.



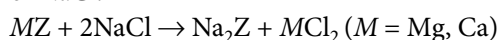
Potassium chloride is a salt of strong acid and strong base. It will remain as such under all the conditions and will not undergo any chemical reaction.



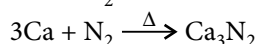
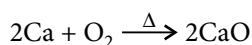
- (ii) Hard water is made soft by a very common ion exchange resin method. In this method, the hard water is allowed to pass over a zeolite bed [zeolites are sodium aluminium silicates ($\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8 \cdot x\text{H}_2\text{O}$)] during which the Na^+ ions from zeolite are replaced by Ca^{2+} and Mg^{2+} ions from hard water.



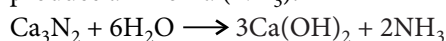
When whole of the Na^+ ions of the zeolite have been exchanged, the zeolite is regenerated by treating it with strong (or saturated) solution of NaCl .



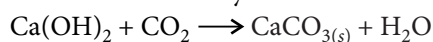
20. (i) Calcium burns in air to form calcium oxide and calcium nitride.



Calcium nitride (Ca_3N_2) reacts with water to produce ammonia (NH_3).

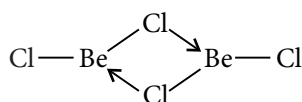


The solution is alkaline due to the formation of $\text{Ca}(\text{OH})_2$. The solution reacts with CO_2 present in air to form CaCO_3 which being insoluble forms a thin solid layer on the surface.



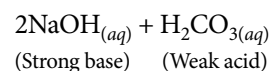
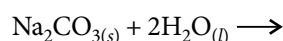
Thus, 'A' is NH_3 and 'B' is CaCO_3 .

- (ii) (a) Solvay process cannot be extended to the manufacture of K_2CO_3 because KHCO_3 is too soluble to be precipitated by the addition of ammonium hydrogen carbonate to a saturated solution of potassium chloride.
- (b) BeCl_2 exists as a dimer in vapour phase, which dissolves into the linear monomer $\text{Cl}-\text{Be}-\text{Cl}$ at 1200 K.



OR

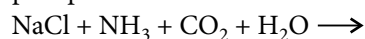
- (i) (a) Na_2CO_3 is a salt of a weak acid, carbonic acid (H_2CO_3) and a strong base, sodium hydroxide (NaOH) therefore, it undergoes hydrolysis to produce strong base NaOH and hence its aqueous solution is alkaline in nature.



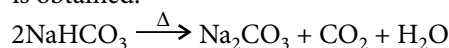
- (b) Since the discharge potential of alkali metals is much higher than that of hydrogen, therefore, when the aqueous solution of any alkali metal chloride is subjected to electrolysis, H_2 instead of the alkali metal is produced at the cathode. Therefore, to prepare alkali metals, electrolysis of their fused chlorides is carried out.

- (c) Sodium ions are found primarily in the blood plasma and in the interstitial fluid which surrounds the cells while potassium ions are primarily present within the cell fluids. Sodium ions help in the transmission of nerve signals, in regulating the flow of water across cell membranes and in the transport of sugars and amino acids into the cells. Thus, sodium is found to be more useful than potassium.

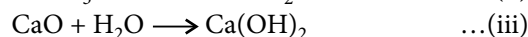
- (ii) In Solvay ammonia process, CO_2 is passed through brine, (*i.e.*, a concentrated solution of NaCl) saturated with ammonia when sodium bicarbonate being sparingly soluble gets precipitated.



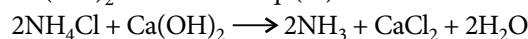
Sodium bicarbonate thus formed is filtered, dried and then heated when sodium carbonate is obtained.



CO_2 needed for the reaction shown in eq. (i) is prepared by heating calcium carbonate and the quick lime, CaO thus formed is dissolved in water to form slaked lime, $\text{Ca}(\text{OH})_2$

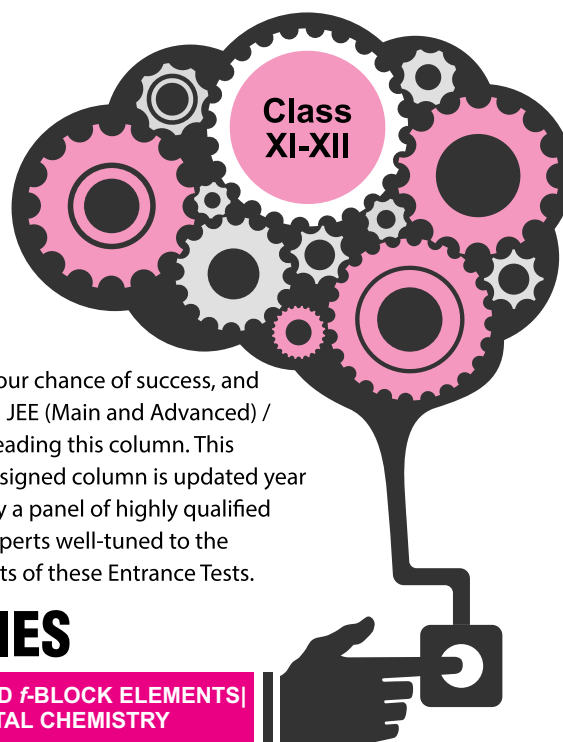


NH_3 needed for the purpose is prepared by heating NH_4Cl obtained in eq. (i) with $\text{Ca}(\text{OH})_2$ obtained in eq. (iii)



Therefore, the only byproduct of the reaction is calcium chloride, CaCl_2 .





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ACCELERATED LEARNING SERIES

Unit 5 **p**-BLOCK ELEMENTS (GROUP 15 TO 18) | **d**-AND **f**-BLOCK ELEMENTS | COORDINATION COMPOUNDS | ENVIRONMENTAL CHEMISTRY

p-BLOCK ELEMENTS (GROUP 15 TO 18)

- General Trends in Physical and Chemical Properties
- Structure, Preparation, Properties and Uses of Some Important Compounds

TIPS TO REMEMBER

- Elements in which the last electron enters any one of the three *p*-orbitals of their respective outermost shell are called *p*-block elements.

Group 15 Elements (Nitrogen Family)

- Group 15 elements are collectively called *pnictogens*.

□ General characteristics :

Electronic configuration	$ns^2 np^3$
Elements	${}^7\text{N}$, ${}^{15}\text{P}$, ${}^{33}\text{As}$, ${}^{51}\text{Sb}$, ${}^{83}\text{Bi}$
Physical state and metallic character	N_2 (unreactive gas), P_4 (solid non metal), As_4 and Sb_4 (Solid metalloids), Bi (metal)
Atomic radii	Increase down the group, smaller than that of group 14 elements due to increased nuclear charge.
Melting and boiling points	M.pt. increases from N to As and then decreases whereas b pt. increases from N to Sb and decreases very slightly.

Ionisation enthalpy	Decreases regularly down the group due to increase in size.
Electronegativity	Decreases down the group.
Allotropy	Nitrogen (α and β -Nitrogen), phosphorus (white, red, scarlet, violet, α - black, β -black), arsenic (grey, yellow, black) antimony (metallic, yellow, explosive)

○ Allotropes of phosphorus :

- *White phosphorus* : It is a white translucent waxy solid, poisonous in nature, insoluble in water, soluble in CS_2 and glows in dark (chemiluminescence). It consists of discrete tetrahedral P_4 molecule and is less stable and more reactive because of angular strain in P_4 molecule.
- *Red phosphorus* : It is odourless and having iron grey lustre, non-poisonous, insoluble in water as well as in CS_2 , less reactive than white phosphorus and does not glow in the dark. It is polymeric consisting of chains of P_4 tetrahedra.

Chemical properties :

- Stability of +3 oxidation state increases and that of +5 decreases down the group due to *inert pair effect*.
- Halides** : All the elements form trihalides of the type MX_3 and except nitrogen, all form pentahalides of the type MX_5 .
 - Stability : $NF_3 > NCl_3 > NBr_3$
 - Lewis acid strength : $PCl_3 > AsCl_3 > SbCl_3$ and $PF_3 > PBr_3 > PI_3$
 - Lewis base strength : $Ni_3 > NBr_3 > NCl_3 > NF_3$
 - Bond angle : $PF_3 < PCl_3 < PBr_3 < PI_3$ (increasing *b.p.* - *b.p.* repulsions)
- Hydrides** : All the elements form hydrides of the type MH_3 which are covalent and pyramidal in shape.

General trends of hydrides :

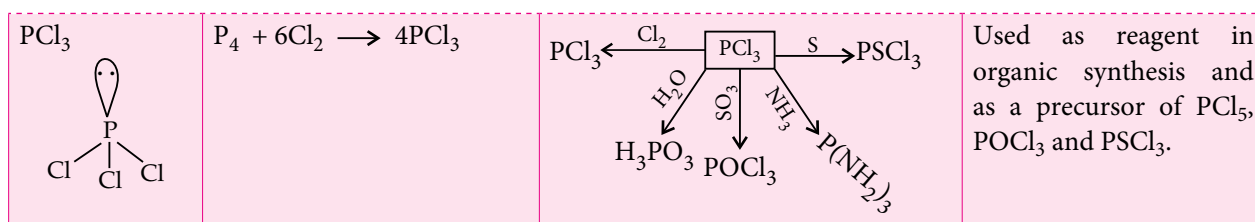
• Ease of formation	Max	• Reducing character	
• Stability	↑	• Covalent character	
• Basic character		NH ₃	
• Solubility		PH ₃	• Poisonous nature
• Bond angle		AsH ₃	• Rate of combustion
• Strength of M-H bond		SbH ₃	Max
• Dipole moment	BiH ₃		
• Decomposition temperature			

- Oxides** : All these elements form oxides of the type X_2O_3 , X_2O_4 and X_2O_5 .

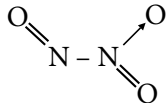
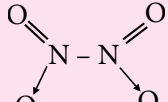
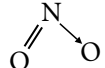
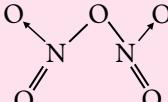
N ₂ O ₃	P ₂ O ₃	As ₂ O ₃	Sb ₂ O ₃	Bi ₂ O ₃	Acidic nature increases ↓
N ₂ O ₄	P ₂ O ₄	As ₂ O ₄	Sb ₂ O ₄	Bi ₂ O ₄	
N ₂ O ₅	P ₂ O ₅	As ₂ O ₅	Sb ₂ O ₅	Bi ₂ O ₅	
Acidic nature decreases →					

Preparation, Properties and Uses of Some Important Compounds

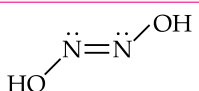
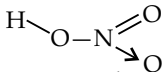
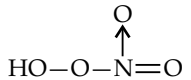
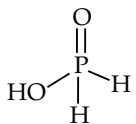
Compound	Preparation	Properties	Uses
N ₂ N≡N	$NH_4Cl + NaNO_2 \rightarrow N_2 \uparrow + 2H_2O + NaCl$ $(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 \uparrow + 4H_2O + Cr_2O_3$ $Ba(N_3)_2 \xrightarrow{\Delta} Ba + 3N_2 \uparrow$		Used in manufacture of nitric acid, ammonia, calcium cyanamide and other nitrogen compounds.
NH ₃ 	$N_{2(g)} + 3H_{2(g)} \xrightleftharpoons{773K} 2NH_3$; $\Delta H_f^\circ = -46.1 \text{ kJ/mol}$ (Haber's process)		Used in refrigerators, manufacturing of rayon, HNO ₃ , NaHCO ₃ , nitrogenous fertilizers.
PH ₃ 	$Ca_3P_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2PH_3$		Used as dehydrating agent.
HNO ₃ 	$2KNO_3 + H_2SO_4 \rightarrow 2HNO_3 + K_2SO_4$		Used as fertilizers, explosives, perfumes and dyes.
PCl ₅ 	$P_4 + 10Cl_2 \rightarrow 4PCl_5$ (white or red)		Used as chlorinating and dehydrating agent.

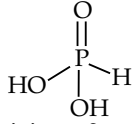
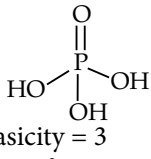
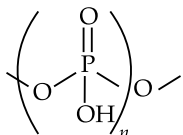
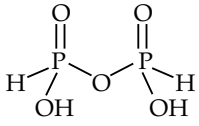
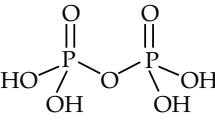
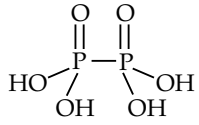


□ Oxides of nitrogen :

Oxide	Physical Appearance	Structure
N_2O Nitrous oxide	Colourless gas	$\text{N} \equiv \text{N} \rightarrow \text{O}$
NO Nitric oxide	Colourless	$\text{N} = \text{O}$
N_2O_3 Dinitrogen trioxide	Blue solid	
N_2O_4 Dinitrogen tetraoxide	Colourless liquid	
NO_2 Nitrogen dioxide	Brown gas	
N_2O_5 Dinitrogen pentoxide	Colourless gas	

□ Oxoacids of nitrogen and phosphorus :

Oxoacid	Structure	Properties
Hyponitrous acid ($\text{H}_2\text{N}_2\text{O}_2$)		Weak acid
Nitrous acid (HNO_2)	$\text{H}-\text{O}-\ddot{\text{N}}=\text{O}$	Weak and unstable acid
Nitric acid (HNO_3)		Strong and stable acid
Pernitric acid (HNO_4)		Unstable and explosive
Phosphinic acid (Hypophosphorous acid), H_3PO_2	 Basicity = 1 O.S. of P = +1	Monobasic and strong reducing agent

Phosphonic acid (Orthophosphorous acid or phosphorous acid), H_3PO_3	 Basicity = 2 O.S. of P = +3	Dibasic and reducing agent
Phosphoric acid (Orthophosphoric acid), H_3PO_4	 Basicity = 3 O.S. of P = +5	Tribasic and non reducing
Metaphosphoric acid (Glacial phosphoric acid), $(\text{HPO}_3)_n$	 Basicity = 1 O.S. of P = +5	Monobasic
Pyrophosphorous acid (diphosphorous acid), $\text{H}_4\text{P}_2\text{O}_5$	 Basicity = 2 O.S. of P = +3	Dibasic
Pyrophosphoric acid (diphosphoric acid), $\text{H}_4\text{P}_2\text{O}_7$	 Basicity = 4 O.S. of P = +5	Tetrabasic
Hypophosphoric acid, $\text{H}_4\text{P}_2\text{O}_6$	 Basicity = 4 O.S. of P = +4	Tetrabasic

KEY POINT

- Nitrogen may show +5 oxidation state but it is never pentavalent.
- Quicklime is used for drying NH_3 as it reacts with other dehydrating agents.

KEY POINT

- In liquid or solid state, NO forms a loose dimer (N_2O_2) which is diamagnetic in nature.
- Phosphine in combination with acetylene is used in preparing Holme's signals for ships to know about the position of the rocks in sea.
- H_3PO_4 is used in soft drinks.
- N_2O_5 and P_2O_5 are covalent in vapour state but ionic in solid state.

SELF CHECK

- The product formed in the reaction of $SOCl_2$ with white phosphorous is
 (a) PCl_3 (b) CO_2Cl_2
 (c) $SOCl_2$ (d) $POCl_3$
 (JEE Advanced 2014)
- Concentrated nitric acid, upon long standing, turns yellow-brown due to the formation of
 (a) NO (b) NO_2
 (c) N_2O (d) N_2O_4
 (JEE Advanced 2013)
- Extra pure N_2 can be obtained by heating
 (a) NH_3 with CuO (b) NH_4NO_3
 (c) $(NH_4)_2Cr_2O_7$ (d) $Ba(N_3)_2$
 (IIT-JEE 2011)
- Which of the following statements is wrong?
 (a) The stability of hydrides increases from NH_3 to BiH_3 in group 15 of the periodic table.
 (b) Nitrogen cannot form $d\pi-p\pi$ bond.
 (c) Single N - N bond is weaker than the single P - P bond.
 (d) N_2O_4 has two resonance structure.
 (AIEEE 2011)

Oxygen Family (Group 16)

- Group 16 elements are collectively called *chalcogens*.

General characteristics :

Electronic configuration	ns^2np^4
Elements	${}_8O, {}_{16}S, {}_{34}Se, {}_{52}Te, {}_{84}Po$
Physical state and metallic characters	O_2 , (gas) S_8 (solid non-metal) Se and Te (solid metalloid) Po (radioactive)
Atomic radii	Increase down the group
Ionisation enthalpy	Decreases down the group
Electronegativity	Decreases down the group

Electron gain enthalpy	Increases from oxygen to sulphur and then decreases.
Melting and boiling points	Increase down the group upto Te and then decreases.
Allotropy	All elements show allotropy

Allotropes of sulphur :

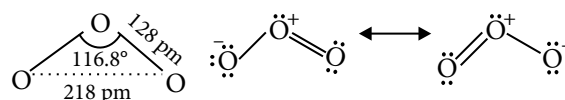
- *Rhombic sulphur* (α -sulphur) : Has S_8 molecules, yellow in colour, m.p. 385.8 K, specific gravity 2.06, insoluble in water, soluble in CS_2 .
- *Monoclinic sulphur* (β -sulphur) : Has S_8 molecules, colourless needle shaped crystals, m.p. 393 K, specific gravity 1.98, soluble in CS_2 .

Chemical properties :

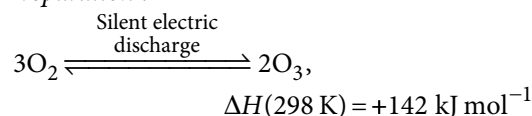
- Stability of -2 oxidation state decreases down the group, of +4 oxidation state increases and that of +6 oxidation state decreases down the group due to *inert pair effect*.
- *Hydrides* : All the elements form stable hydrides of the type H_2M .
- *General trends of hydrides* :
 - *Boiling point* : $H_2O > H_2Te > H_2Se > H_2S$
 - *Volatility* : $H_2S > H_2Se > H_2Te > H_2O$
 - *Bond angle* : $H_2O > H_2S > H_2Se > H_2Te$
 - *Acidic character* : $H_2O < H_2S < H_2Se < H_2Te$
 - *Reducing power* : $H_2Te > H_2Se > H_2S > H_2O$
- *Halides* : All elements form halides of the type EX_6, EX_4 and EX_2 .
- *Oxides* :
 - Simple oxides – MgO, Al_2O_3
 - Mixed oxides – Pb_3O_4, Fe_3O_4
 - Acidic oxides – $SO_2, Cl_2O_7, CO_2, N_2O_5$
 - Basic oxides – Na_2O, CaO, BaO
 - Amphoteric oxides – Al_2O_3
 - Neutral oxides – CO, NO, N_2O

Ozone (O_3) :

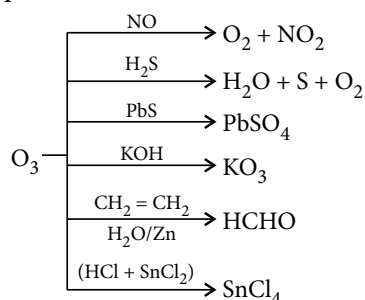
- *Structure* :



- *Preparation* :



○ **Properties :**



○ **Uses :**

- Bleaching ivory, oils, flour.
- As germicide and disinfectant for sterilising water.
- For purifying air in crowded places.
- Manufacture of KMnO_4 and artificial silk.

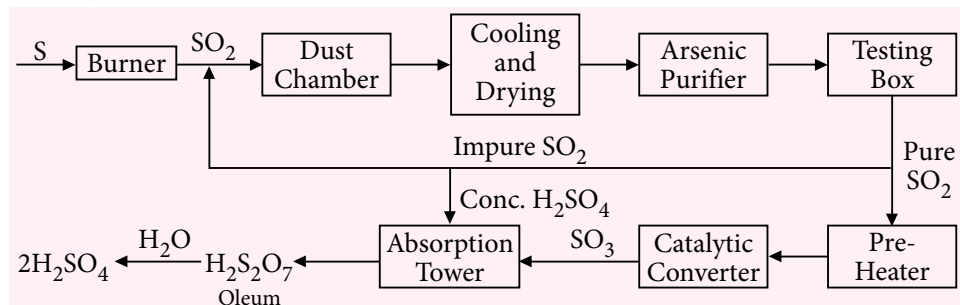
□ **Oxoacids of sulphur :**

Name	Structure	Characteristics
1. Sulphurous acid H_2SO_3		A dibasic acid, free acid does not exist, strong reducing agent.
2. Sulphuric acid H_2SO_4		A dibasic acid, stable, strong oxidising and dehydrating agent.
3. Thiosulphuric acid $\text{H}_2\text{S}_2\text{O}_3$		A dibasic acid, does not exist in free state. Salts are however quite stable e.g., $\text{Na}_2\text{S}_2\text{O}_3$, reducing agent.
4. Peroxymonosulphuric acid (Caro's acid) H_2SO_5		A dibasic acid, stable and crystalline solid, strong oxidising agent.
5. Peroxodisulphuric acid (Marshall's acid) $\text{H}_2\text{S}_2\text{O}_8$		Dibasic acid, strong oxidising agent.
6. Dithionic acid $\text{H}_2\text{S}_2\text{O}_6$		Dibasic acid, does not exist freely but its salts are quite stable.
7. Disulphuric acid or Pyrosulphuric acid $\text{H}_2\text{S}_2\text{O}_7$		A sulphuric acid analogue of acetic anhydride. It is strong enough to protonate sulphuric acid.
8. Polythionic acid $\text{H}_2\text{S}_n\text{O}_6 (n > 2)$		Stable only in aqueous solutions and rapidly destroyed at higher concentrations.
9. Hyposulphurous acid $\text{H}_2\text{S}_2\text{O}_4$		Unstable in pure form but stable as salts.

Sulphuric Acid (H₂SO₄)

Preparation :

- Contact process :



Structure	Properties	Uses
<p>Sulphuric acid</p> <p>Sulphate ion</p>	$\text{H}_2\text{SO}_4 \begin{cases} \xrightarrow{\text{NaOH}} \text{NaHSO}_4 + \text{H}_2\text{O} \\ \xrightarrow{2\text{NaOH}} \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O} \\ \xrightarrow{\text{Zn}} \text{ZnSO}_4 + \text{H}_2 \\ \xrightarrow{\text{C}_{12}\text{H}_{22}\text{O}_{11}} 12\text{C} + 11\text{H}_2\text{O} \\ \xrightarrow{\text{S}_8} \text{SO}_2 + \text{H}_2\text{O} \\ \xrightarrow{\text{Na}_2\text{S}} \text{Na}_2\text{SO}_4 + \text{H}_2\text{S} \\ \xrightarrow{\text{BaCl}_2} \text{BaSO}_4 + \text{HCl} \\ \xrightarrow{\text{K}_4[\text{Fe}(\text{CN})_6]} \text{K}_2\text{SO}_4 + \text{FeSO}_4 + (\text{NH}_4)_2\text{SO}_4 + \text{CO}\uparrow \end{cases}$	<p>It is used as oxidising agent, dehydrating agent and for the preparation of dyes, drugs, explosives, volatile acids, etc.</p>

KEY POINT

- Se is a photo-conductor, having poor electrical conductance when in dark but its conductance increases by a factor 1,000 when exposed to light.
- Hexahalides of Cl, Br and I are not formed because of larger size of these halogens.

SELF CHECK

5. Which of the following statements regarding sulphur is incorrect?
- S₂ molecule is paramagnetic.
 - The vapour at 200°C consists mostly of S₈ rings.
 - At 600°C the gas mainly consists of S₂ molecules.
 - The oxidation state of sulphur is never less than +4 in its compounds.

(AIEEE 2011)

Halogen Family (Group 17)

- Group 17 elements are collectively called *halogens*.

General characteristics :

Electronic configuration	ns^2np^5
Elements	${}_{9}\text{F}$, ${}_{17}\text{Cl}$, ${}_{35}\text{Br}$, ${}_{85}\text{At}$
Colour and physical state	F ₂ (pale yellow gas), Cl ₂ (greenish yellow gas), Br ₂ (reddish brown liquid), I ₂ (purple solid)
Atomic radii	Increase down the group
Ionisation enthalpy	Very high and decreases down the group.
Electronegativity	Decreases down the group.
Electron gain enthalpy	Cl > F > Br > I
Melting and boiling points	Increase down the group
Bond energy	Cl ₂ > Br ₂ > F ₂ > I ₂
Heat of hydration	F ⁻ > Cl ⁻ > Br ⁻ > I ⁻

Chemical properties :

- F shows only -1 oxidation state while other elements show -1, +1, +3, +5 and +7 oxidation states also.
- General trends of hydrogen halides :
 - The order of reactivity : $F_2 > Cl_2 > Br_2 > I_2$
 - Boiling points : $HF > HI > HBr > HCl$
 - Melting points : $HI > HF > HBr > HCl$
 - Bond lengths : $HI > HBr > HCl > HF$
 - Bond dissociation enthalpy : $HF > HCl > HBr > HI$
 - Acidic strength : $HI > HBr > HCl > HF$
 - Thermal stability : $HF > HCl > HBr > HI$
 - Reducing power : $HI > HBr > HCl > HF$

Oxides : OF_2, O_2F_2

Cl_2O, ClO_2, Cl_2O_6 and Cl_2O_7

Br_2O, BrO_2, BrO_3

I_2O_4, I_4O_9

○ All are covalent and powerful oxidising agents.

○ Oxidising power : $Cl_2O > ClO_2 > Cl_2O_6 > Cl_2O_7$

○ Stability : $Cl_2O < ClO_2 < Cl_2O_6 < Cl_2O_7$

○ Solid Cl_2O_6 is ionic and exists as ClO_2^+ and ClO_4^- ions.

Oxo-acids :

Hypohalous acid : HXO , Halous acid : HXO_2 , Halic acid : HXO_3 , Perhalic acid : HXO_4

Hydrochloric Acid

Preparation	Properties	Uses
$NaCl + H_2SO_4 \xrightarrow{420K} NaHSO_4 + HCl;$ $NaHSO_4 + NaCl \xrightarrow{823K} Na_2SO_4 + HCl$	Colourless and pungent smelling gas, easily liquifiable, extremely soluble in water. $Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2;$ $Na_2SO_3 + 2HCl \longrightarrow 2NaCl + H_2O + SO_2$	3 parts of conc. HCl and 1 part of conc. HNO_3 is used for dissolving noble metals e.g., gold, platinum $Au + 4H^+ + NO_3^- + 4Cl^- \longrightarrow AuCl_4^- + NO + 2H_2O;$ $3Pt + 16H^+ + 4NO_3^- + 18Cl^- \longrightarrow 3PtCl_6^{2-} + 4NO + 8H_2O$

Interhalogen Compounds

Type	Hybridisation	Shape	Structure
AX	sp^3	Linear	
AX_3	sp^3d	T-shaped	
AX_5	sp^3d^2	Square pyramidal	
AX_7	sp^3d^3	Pentagonal bipyramidal	

KEY POINT

- Many of the oxoacids of halogens are found to exist in solution state or isolated only in the form of their salts.
- The oxoanions of halogens are strong oxidising agents especially in acidic solution.
- Fluorine containing interhalogens are typical Lewis acids and strong oxidising agents.
- Iodine also forms I^+ and I^{3+} cations due to less ionisation energy as $(CH_3COO)_3I$, $I(ClO_4)_3$ and IPO_4 have been isolated.
- Because of the tendency to form hydrogen bond, metal fluorides are solvated by HF giving species of the type HF_2^- etc. KHF_2 ($KF \cdot HF$), KH_2F_3 ($KF \cdot 2HF$) and KH_3F_4 ($KF \cdot 3HF$) are known examples.

SELF CHECK

6. Which among the following is the most reactive ?
(a) I_2 (b) ICl (c) Cl_2 (d) Br_2
(JEE Main 2015)
7. Among the following oxoacids, the correct decreasing order of acid strength is
(a) $HClO_2 > HClO_4 > HClO_3 > HOCl$
(b) $HOCl > HClO_2 > HClO_3 > HClO_4$
(c) $HClO_4 > HOCl > HClO_2 > HClO_3$
(d) $HClO_4 > HClO_3 > HClO_2 > HOCl$
(JEE Main 2014)

Noble Gases (Group 18)

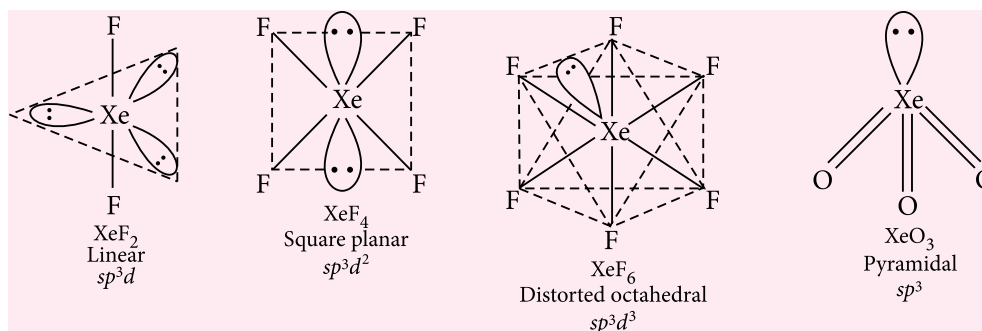
General characteristics :

Electronic configuration	$ns^2 np^6$
Elements	${}^2\text{He}, {}^{10}\text{Ne}, {}^{18}\text{Ar}, {}^{36}\text{Kr}, {}^{54}\text{Xe}, {}^{86}\text{Rn}$
Physical state	All are monoatomic gases
Atomic radii	Increase down the group.
Electron gain enthalpy	Positive
Melting and boiling points	Very low due to weak dispersion forces

Uses :

Helium	Neon	Argon	Krypton	Xenon
To lift weather balloons and air ships	For advertising	To create an inert atmosphere	For runway and approach lights in airports	In electric flash bulbs for high speed photography
As breathing mixture	For filling sodium vapour lamps	In geiger counters		
For inflating the tyres of aeroplanes	In beacon lights	To date the age of rocks		

Compounds of Xenon

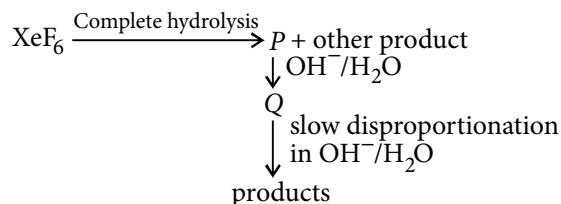


KEY POINT

- Noble gases have high ionisation enthalpies and almost zero electron affinity values.
- Noble gases (especially Xe and Kr) form noble gas compounds with oxygen and fluorine.
- Ar, Kr and Xe form clathrate compounds but He and Ne do not.
- Only He forms interstitial compounds with metals.
- XeO_3 explodes violently when dry and its explosion power is 22 times more than TNT.

SELF CHECK

8. Under ambient conditions, the total number of gases released as products in the final step of the reaction scheme shown below is



- (a) 0
(b) 1
(c) 2
(d) 3

(JEE Advanced 2014)

d-AND f-BLOCK ELEMENTS

- Introduction
- Properties
- Some Important Compounds

TIPS TO REMEMBER**Transition Elements**

- Elements in which the last electron enters any one of the five *d*-orbitals of their respective penultimate shell are known as *transition elements*.
- Their general electronic configuration is $(n-1)d^{1-10}ns^{0-2}$ where *n* is the outermost shell. When electrons are filled, *ns*-orbital is filled first then $(n-1)d$ -orbital and during oxidation, *ns* electrons are lost first then $(n-1)d$ -electrons.
- The presence of unpaired and unfilled *d*-orbitals favours *covalent bonding*.

□ **General characteristics :**

Melting and boiling points	High due to strong metallic bonding
Enthalpies of atomisation	High due to strong interatomic interactions
Ionisation enthalpies	Generally increases from left to right in a series

Some Important Compounds

Compounds	Preparation	Properties	Uses
Potassium dichromate ($K_2Cr_2O_7$)	From sodium dichromate (obtained from chromite ore) $Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$	Orange red, crystalline solid, oxidising agent having melting point $398^\circ C$. Oxidising agent in acidic medium : $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ Oxidises : I^- to I_2 , H_2S to S , Sn^{2+} to Sn^{4+} , Fe^{2+} to Fe^{3+}	In dyeing, photography and leather industry.
Potassium permanganate ($KMnO_4$)	From potassium manganate (obtained from pyrolusite) $2K_2MnO_4 + Cl_2 \rightarrow 2KMnO_4 + 2KCl$	Deep purple, crystalline solid, oxidising agent, having melting point $240^\circ C$. Oxidising agent in acidic medium : $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ Oxidises : I^- to I_2 , Fe^{2+} to Fe^{3+} , $C_2O_4^{2-}$ to CO_2 , S^{2-} to S , SO_3^{2-} to SO_4^{2-} , NO_2^- to NO_3^- Oxidising agent in alkaline or neutral medium : $MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$ Oxidises : I^- to IO_3^- , $S_2O_3^{2-}$ to SO_4^{2-} , Mn^{2+} to MnO_2	As a disinfectant, germicide, and Baeyer's reagent (alkaline $KMnO_4$).

Oxidation states	Variable due to participation of <i>ns</i> and $(n-1)d$ electrons
Atomic radii	Decrease from left to right but become constant when pairing of electrons takes place
Coloured compounds	Form coloured compounds due to <i>d-d</i> transitions
Catalytic behaviour	Due to variable oxidation states and ability to form complexes
Interstitial compounds	Due to empty spaces in their lattices, small atoms can be easily accommodated
Alloy formation	Due to similar atomic sizes

Magnetic properties

- Transition metal ions and their compounds are paramagnetic due to presence of unpaired electrons in the $(n-1)d$ -orbitals and it is calculated by using the formula, $\mu = \sqrt{n(n+2)}$ where *n* is the no. of unpaired electrons.

Formation of complex compounds

- Transition metals form a large number of complexes due to high nuclear charge and small size and availability of empty *d*-orbitals to accept lone pair of electrons donated by ligands.

Inner Transition Elements

□ **Lanthanoids** : The elements with atomic numbers 58 to 71 *i.e.*, cerium to lutetium (which come immediately after lanthanum, $Z = 57$) are called lanthanoids.

□ **Actinoids** : The elements with atomic number 90 to 103 *i.e.*, thorium to lawrencium (which come immediately after actinium, $Z = 89$) are called actinoids.

□ They are called *f-block elements* because last electron enters into *f*-orbital.

□ **General electronic configuration :**

$$(n-2)f^{1-14}(n-1)d^{0-1}ns^2$$

□ **General characteristics of lanthanoids :**

○ **Oxidation states** : Common oxidation state is +3. Eu^{2+} ($4f^7$), Yb^{2+} ($4f^{14}$), Ce^{4+} ($4f^0$) and Tb^{4+} ($4f^7$) are also quite stable.

○ **Reducing properties** : Ions with +2 oxidation state are reducing in nature.

○ **Oxidising properties** : Ions with +4 oxidation state are oxidising in nature.

○ **Paramagnetism** : Most of the metals and ions are paramagnetic due to the presence of unpaired electrons.

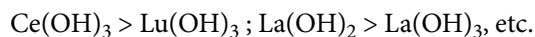
○ **Colour** : All metals are silvery white.

○ **Lanthanoid contraction** : The contraction of size of lanthanoids and trivalent ions with increase in atomic number is called lanthanoid contraction. This is due to increase in nuclear charge and negligible screening (shielding) of $4f$ electrons.

□ **Effect of lanthanoid contraction :**

○ Because of small difference in size of lanthanoids, their separation is possible by ion exchange method.

○ Basic strength of hydroxides is more for larger cation.



○ Radii of elements in same group from 4th to 12th groups in $4d$ and $5d$ series are very close and these elements in each group are called *chemical twins*. *e.g.*, Zr and Hf, Nb and Ta, etc.

○ The properties of complex formation increase from La to Lu because of decrease in size and increase in "charge : size" ratio.

○ There is very slight increase in electronegativity from La to Lu.

□ **General characteristics of actinoids :**

○ They show higher oxidation states of +4, +5, +6 and +7 besides +3.

○ Along the series atomic radius continuously decreases, though in many cases radii are not known because of radioactive nature.

○ Oxides and hydroxides are more basic than that of lanthanoids. Ions having unpaired electrons are coloured (except f^0 and f^7) and are paramagnetic.

KEY POINT

- All transition elements belong to *d*-block. Zn, Cd and Hg are not transition elements and are called non-typical transition elements or pseudo transition elements.
- Anhydrous FeSO_4 and CuSO_4 are white because of absence of crystal field splitting, though they have unpaired electrons.
- Cu^{2+} ($3d^9$, $E^\circ_{\text{Cu}^{2+}/\text{Cu}} = 0.34\text{V}$) is more stable than Cu^+ ($3d^{10}$, $E^\circ_{\text{Cu}^+/\text{Cu}} = 0.54\text{V}$) except for the cases of large anions, *e.g.*, CuI is more stable than CuI_2 , CuCN is more stable than $\text{Cu}(\text{CN})_2$.
- Among *d*-block elements tungsten (W, At. No. = 74) has highest m.pt. (3410°C) while mercury (Hg, At. No. = 80) has lowest m.pt. (-38.9°C).
- ${}_{43}\text{Tc}$ was the first artificial element and was named technetium which means artificial.

SELF CHECK

9. Match the catalysts to the correct processes.

Catalyst	Process
(A) TiCl_4	(i) Wacker process
(B) PdCl_2	(ii) Ziegler-Natta polymerisation
(C) CuCl_2	(iii) Contact process
(D) V_2O_5	(iv) Deacon's process
(a) (A) - (ii), (B) - (iii), (C) - (iv), (D) - (i)	
(b) (A) - (iii), (B) - (i), (C) - (ii), (D) - (iv)	
(c) (A) - (iii), (B) - (ii), (C) - (iv), (D) - (i)	
(d) (A) - (ii), (B) - (i), (C) - (iv), (D) - (iii)	

(JEE Main 2015)

10. The colour of KMnO_4 is due to

- (a) $L \rightarrow M$ charge transfer transition
 (b) $\sigma \rightarrow \sigma^*$ transition
 (c) $M \rightarrow L$ charge transfer transition
 (d) $d-d$ transition. (JEE Main 2015)

11. The colour of light absorbed by an aqueous solution of CuSO_4 is
 (a) orange-red (b) blue-green
 (c) yellow (d) violet.
 (JEE Advanced 2012)
12. The equation which is balanced and represents the correct product(s) is
 (a) $\text{CuSO}_4 + 4\text{KCN} \rightarrow \text{K}_2[\text{Cu}(\text{CN})_4] + \text{K}_2\text{SO}_4$
 (b) $\text{Li}_2\text{O} + 2\text{KCl} \rightarrow 2\text{LiCl} + \text{K}_2\text{O}$
 (c) $[\text{CoCl}(\text{NH}_3)_5]^+ + 5\text{H}^+ \rightarrow \text{Co}^{2+} + 5\text{NH}_4^+ + \text{Cl}^-$
 (d) $[\text{Mg}(\text{H}_2\text{O})_6]^{2+} + (\text{EDTA})^{4-} \xrightarrow{\text{excess NaOH}} [\text{Mg}(\text{EDTA})]^{2-} + 6\text{H}_2\text{O}$
 (JEE Main 2014)
13. Which of the following arrangements does not represent the correct order of the property stated against it?
 (a) $\text{Sc} < \text{Ti} < \text{Cr} < \text{Mn}$: number of oxidation states
 (b) $\text{V}^{2+} < \text{Cr}^{2+} < \text{Mn}^{2+} < \text{Fe}^{2+}$: paramagnetic behaviour
 (c) $\text{Ni}^{2+} < \text{Co}^{2+} < \text{Fe}^{2+} < \text{Mn}^{2+}$: ionic size
 (d) $\text{Co}^{3+} < \text{Fe}^{3+} < \text{Cr}^{3+} < \text{Sc}^{3+}$: stability in aqueous solution.
 (JEE Main 2013)

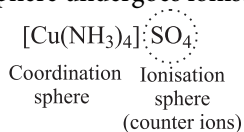
COORDINATION COMPOUNDS

- Introduction
- IUPAC Formulation and Nomenclature
- Isomerism
- Bonding - Valence Bond Approach
- Stability of Coordination Compounds
- Organometallic Compounds

TIPS TO REMEMBER

- The coordination compounds are different from double salts. Double salts are addition or molecular compounds which are stable and break up into constituents when dissolved in water.

$$\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \xrightarrow{\text{Water}} \text{Fe}_{(aq)}^{2+} + 2\text{NH}_{4(aq)}^+ + 2\text{SO}_{4(aq)}^{2-}$$
- The addition compounds in which some of the constituent ions or molecules lose their identity and when dissolved in water, they do not break up completely into individual ions, are called coordination compounds.
- For a complex compound, the species which is in ionisation sphere undergoes ionisation.

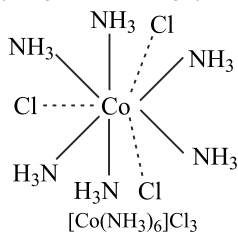
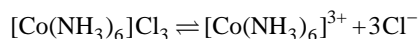


- The neutral molecules, anions or cations which are directly linked with the central metal atom or ion are called ligands. The ligands are attached to the central metal ion or atom through *coordinate bonds* or *dative linkage*.
- The number of ligating (linking) atoms present in a ligand is called denticity of ligands e.g., CN^- has denticity 1, $\begin{matrix} \text{COO}^- \\ | \\ \text{COO}^- \end{matrix}$ has denticity 2, $[\text{EDTA}]^{4-}$ has denticity 6.
- Ligands can be classified as
 - *Mono or unidentate ligands* : Ligands with one donor site e.g., F^- , Cl^- , Br^- , H_2O , CN^- , NO_2^- , OH^- , CO , etc.
 - *Bidentate ligands* : Ligands which have two donor atoms at two positions. e.g., Ethylenediamine, oxalate, glycine, etc.
 - *Polydentate ligands* : The ligands having several donor atoms are called polydentate ligands. e.g., Diethylenetriamine having 3 donor atoms is tridentate, EDTA with 6 donor atoms is hexadentate.
 - When coordination of more than one sigma electron pair donor group from the ligand takes place to the same central metal atom or ion, it is called chelation. The resulting complex has ring structure and such ligand is called chelating ligand.
 - Chelating ligands form more stable complexes than similar ordinary complexes, in which the ligands act as monodentate.
- **Effective atomic number (EAN)** : It is the resultant number of electrons with the metal atom or ion after gaining electrons from the donor atoms of the ligands. $\text{EAN} = \text{Atomic number of metal} - \text{Number of electrons lost in ion formation} + \text{Number of electrons gained from the donor atoms of the ligands}$.

Werner's Coordination Theory

- It explains the nature of bonding in complexes. Metals show two different kinds of valencies.
 - *Primary valency* : Non directional and ionisable. It is equal to the oxidation state of the central metal ion.
 - *Secondary valency* : Directional and non-ionisable. It is equal to the coordination number of the metal. It is commonly satisfied by neutral and negatively charged or some times by positively charged ligands.

- The ionisation of the coordination compound is written as :



Representation of $\text{CoCl}_3 \cdot 6\text{NH}_3$ complex according to Werner's theory

IUPAC Nomenclature

- **Rules for naming coordination compounds :**

- The cation is named first then the anion.
- In naming coordination sphere, ligands are named first in alphabetical order followed by metal atom and then oxidation state of metal by a roman numeral in parentheses.
- Name of coordination compounds is started with a small letter and the complex part is written as one word.
- Name of anionic ligands end in *-o*. e.g., Cl^- : Chlorido
- Neutral ligands (with a few exceptions) retain their names e.g., NH_3 : Ammine
- Name of cationic ligands end in *-ium*. e.g., NO_2^+ : Nitronium
- Certain ligands are represented by abbreviations in parentheses instead of their complex structural formulae. e.g., ethylenediamine (*en*).
- Ambidentate ligands are named by using different names of ligands or by placing the symbol of donor atom.
- e.g., $-\text{SCN}^-$ (Thiocyanato-S or Thiocyanato), $-\text{NCS}^-$ (Thiocyanato-N or Isothiocyanato), $-\text{ONO}^-$ (Nitrito-O or Nitrito), $-\text{NO}_2^-$ (Nitrito-N or Nitro)
- The prefixes *di-*, *tri-*, *tetra-*, *penta-* and *hexa-* are used to indicate the number of each ligand. If the ligand name includes such a prefix, the ligand name should be placed in parentheses and preceded by *bis-*(2), *tris-*(3), *tetrakis-*(4), *pentakis-*(5) and *hexakis-*(6).
- When the coordination sphere is anionic, name of central metal ends in *-ate*.

- **Some examples :**

$\text{K}_3[\text{Fe}(\text{CN})_5\text{NO}]$: Potassium pentacyanonitrosyl ferrate(II).

$[\text{CoCl}_2(\text{NO}_2)(\text{NH}_3)_3]$: Triamminedichloronitro cobalt(III).

$[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$: Tetraammineplatinum(II) tetrachloroplatinate(II).

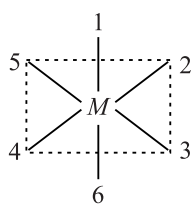
ISOMERISM

- **Structural isomerism :** It is displayed by compounds that have different ligands within their coordination sphere.

- *Ionisation isomerism* : Isomers that give different ions in solution.
e.g., $[(\text{Co}(\text{NH}_3)_5\text{Br})\text{Cl}]$; $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Br}$.
- *Hydrate isomerism* : Isomers having different number of H_2O as a ligand and as water of hydration.
e.g., $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$; $[\text{CrCl}(\text{H}_2\text{O})_5]\text{Cl}_2 \cdot \text{H}_2\text{O}$
 $[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot \text{H}_2\text{O}$
- *Coordination isomerism* : The ligands are interchanged in both the cationic and anionic ions.
e.g., $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$; $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$
- *Linkage isomerism* : This type of isomerism exists when ambidentate ligand is coordinated with its different donor atoms.
e.g., $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$; $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$.

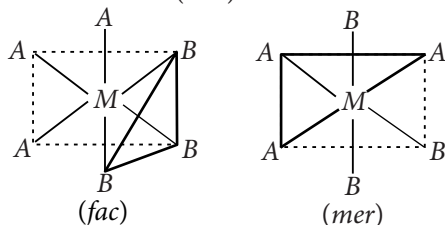
- **Stereoisomerism :** It is displayed by compounds which contain the same ligands in their coordination sphere but differ in the spatial arrangements of ligands around the central atom.

- *Geometrical isomerism* : It arises due to different possible geometric arrangement of the ligands.
 - When ligands occupy adjacent positions, these are referred to as *cis*-positions. When ligands occupy opposite position, these are referred to as *trans*-positions. This type of isomerism is called *cis-trans isomerism*.
 - The complexes having coordination number 4 adopt tetrahedral or square planar geometry. Geometrical isomerism is not possible in tetrahedral complexes.
 - Square planar complexes of the type MA_2X_2 , MA_2XY , MABX_2 , MABXY can exist as geometrical isomers.
 - In octahedral complexes,



Position 1-6, 2-4 and 3-5 are *trans* while positions 1-2, 1-3, 1-4, 1-5, 2-3, 2-5, 6-3, 6-4, etc. are *cis* to each other.

- Octahedral complexes of the type MA_6 or MA_5B would not show geometrical isomerism as expected.
- In octahedral complexes of type $[MA_3B_3]$ if 3 same ligands occupy adjacent positions at the corner of an octahedral face then it is *facial (fac) isomer* and when positions are around the meridian of the octahedron then it is *meridional (mer) isomer*.



- *Optical isomerism*: It is shown by the isomers which rotate the plane of polarised light equally but in opposite directions. These isomers are called *enantiomers*. The optical isomers possess the property of chirality.

- The essential condition for a substance to show optical activity is that the substance should not have an element of symmetry in its structure.

- Complexes of the type $M(AA)_3$ (where AA is symmetrical bidentate ligand) such as $[Co(en)_3]^{3+}$ and $[Cr(ox)_3]^{3-}$ exist as optical isomers.

Complexes of the type *cis* $[M(AA)_2X_2]$ or $[M(AA)_2XY]$ also exhibit optical activity. *Trans* form of these type complexes does not show optical isomerism *i.e.*, it can not be resolved into optical isomers.

Bonding in Coordination Compounds

□ **Valence bond theory**: It was developed by Pauling.

- A suitable number of vacant orbitals must be present in the central metal atom or ion for the formation of coordinate bonds with the ligands.
- Central metal ion can use appropriate number of s , p or d -orbitals for hybridisation depending upon the total number of ligands.
- The outer orbital (high spin) or inner orbital (low spin) complexes are formed depending upon whether outer d -orbitals or inner d -orbitals are used.

Formula	At. No. of central metal atom	Outer electronic configuration of metal atom	Hybridisation	Shape	Magnetic behaviour	EAN
1. $[Cr(NH_3)_6]^{3+}$	24	$4s^1 3d^5$	$d^2 sp^3$	Octahedral	Paramagnetic	$24 - 3 + 12 = 33$
2. $[Ni(NH_3)_6]^{2+}$	28	$4s^2 3d^8$	$sp^3 d^2$	Octahedral	Paramagnetic	$28 - 2 + 12 = 38$
3. $[Fe(CN)_6]^{4-}$	26	$4s^2 3d^6$	$d^2 sp^3$	Octahedral	Diamagnetic	$26 - 2 + 12 = 36$
4. $[Fe(CN)_6]^{3-}$	26	$4s^2 3d^6$	$d^2 sp^3$	Octahedral	Paramagnetic	$26 - 3 + 12 = 35$
5. $[Co(NH_3)_6]^{3+}$	27	$4s^2 3d^7$	$d^2 sp^3$	Octahedral	Diamagnetic	$27 - 3 + 12 = 36$
6. $[CoF_6]^{3+}$	27	$4s^2 3d^7$	$sp^3 d^2$	Octahedral	Paramagnetic	$27 - 3 + 12 = 36$
7. $[Ni(H_2O)_6]^{2+}$	28	$4s^2 3d^8$	$d^2 sp^3$	Octahedral	Paramagnetic	$28 - 2 + 12 = 38$
8. $[Ni(CO)_4]$	28	$4s^2 3d^8$	sp^3	Tetrahedral	Diamagnetic	$28 - 0 + 8 = 36$
9. $[Ni(CN)_4]^{2-}$	28	$4s^2 3d^8$	dsp^2	Square planar	Diamagnetic	$28 - 2 + 8 = 34$
10. $[MnCl_4]^{2-}$	25	$4s^2 3d^5$	sp^3	Tetrahedral	Paramagnetic	$25 - 2 + 8 = 31$

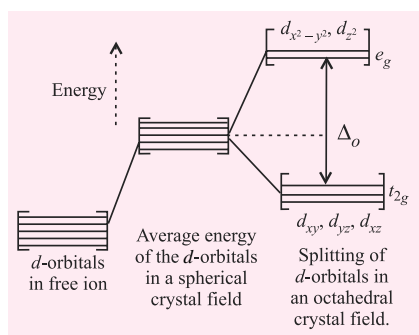
11. $[\text{NiCl}_4]^{2-}$	28	$4s^2 3d^8$	sp^3	Tetrahedral	Paramagnetic	$28 - 2 + 8 = 34$
12. $[\text{Co}(\text{CO})_4]^-$	27	$4s^2 3d^7$	sp^3	Tetrahedral	Diamagnetic	$27 + 1 + 8 = 36$
13. $[\text{Cu}(\text{NH}_3)_4]^{2+}$	29	$4s^1 3d^{10}$	$sp^2 d$	Square planar	Paramagnetic	$29 - 2 + 8 = 35$
14. $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$	78	$6s^1 5d^9$	dsp^2	Square planar	Diamagnetic	$78 - 2 + 8 = 84$
15. $[\text{Fe}(\text{CO})_5]$	26	$4s^2 3d^6$	dsp^3	Trigonal bipyramidal	Diamagnetic	$26 - 0 + 10 = 36$
16. $[\text{Ag}(\text{NH}_3)_2]^+$	47	$5s^1 4d^{10}$	sp	Linear	Diamagnetic	$47 - 1 + 4 = 50$
17. $[\text{Cr}(\text{CO})_6]$	24	$4s^1 3d^5$	$d^2 sp^3$	Octahedral	Diamagnetic	$24 + 0 = 24$
18. $[\text{Zn}(\text{NH}_3)_4]^{2+}$	30	$4s^2 3d^{10}$	sp^3	Tetrahedral	Diamagnetic	$30 - 2 + 8 = 36$
19. $[\text{Co}(\text{en})_3]^{3+}$	27	$4s^2 3d^7$	$d^2 sp^3$	Octahedral	Diamagnetic	$27 - 3 + 12 = 36$
20. $[\text{Co}(\text{NH}_3)_5\text{ONO}]^{2+}$	27	$4s^2 3d^7$	$d^2 sp^3$	Octahedral	Diamagnetic	$27 - 3 + 12 = 36$
21. $[\text{Cr}(\text{EDTA})]^-$	24	$4s^1 3d^5$	$d^2 sp^3$	Octahedral	Paramagnetic	$24 - 3 + 12 = 33$
22. $\text{K}_3[\text{Co}(\text{C}_2\text{O}_4)_3]$	27	$4s^2 3d^7$	$d^2 sp^3$	Octahedral	Diamagnetic	$27 - 3 + 12 = 36$

- The magnetic moment (μ) of the complexes depend upon number of unpaired electrons as :

$\mu = \sqrt{n(n+2)}$, where n is the number of unpaired electrons.

- **Crystal field theory** : It assumes the ligands to be point charges and there is electrostatic force of attraction between ligands and metal atom or ion. When ligands approach the central metal ion, then the five degenerate orbitals do not possess equal energy any more and results in splitting, which depends upon nature of ligand field strength.

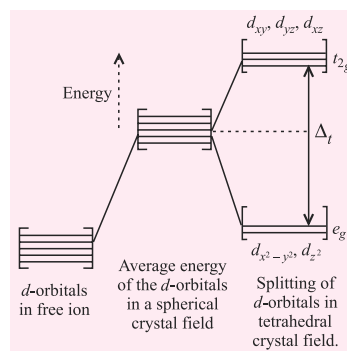
- The greater the ease with which the ligand can approach the metal ion, the greater will be the crystal field splitting caused by it.
- Crystal field splitting in octahedral coordination complexes can be shown as :



- If $\Delta_o < P$ (where 'P' is energy required for forced pairing of electrons) then the electrons will

remain unpaired and a high spin complex is formed.

- If $\Delta_o > P$, then pairing of electrons takes place and a low spin complex is formed.
- Crystal field splitting in tetrahedral complexes can be shown as :



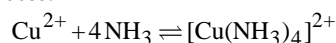
Difference in energy between e_g and t_{2g} level is less.

$$\Delta_t = \frac{4}{9} \Delta_o.$$

- **Spectrochemical Series** : Arrangement of ligands in the order of increasing field strength.

$\text{I}^- < \text{Br}^- < \text{S}^{2-} < \text{SCN}^- < \text{NO}_3^- < \text{F}^- < \text{OH}^- < \text{ox}^{2-}$ and $< \text{O}^{2-} < \text{H}_2\text{O} < \text{NCS}^- < \text{py} \approx \text{NH}_3 < \text{en} < \text{dipy} < \text{O} - \text{phen} < \text{NO}_2^- < \text{CN}^- < \text{CO}$.

- **Stability of complexes** : The formation of the complex in a solution is a reversible and exothermic process.

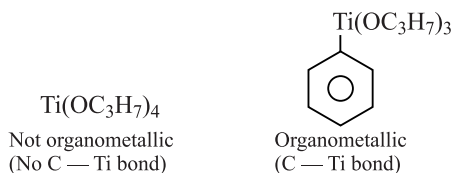


$$K = \frac{[\text{Cu}(\text{NH}_3)_4]^{2+}}{[\text{Cu}^{2+}][\text{NH}_3]^4} \text{ where, } K = \text{stability constant}$$

- Higher the value of stability constant (K), higher will be the stability of complex.
- Higher the polarising power of metal ion and basicity of ligand, higher will be the stability of complex.

Organometallic Compounds

- Organometallic compounds are those compounds which contain one or more metal-carbon bonds *e.g.*,



- **σ -bonded organometallics** : The compounds containing metal carbon sigma bonds are called σ -bonded organometallic compounds.
e.g., $R - \text{Mg} - X$, $(\text{CH}_3)_3\text{Al}$, $[\text{Si}(\text{CH}_3)_4]$
- **π -bonded organometallics** : The compounds containing metal carbon double bond are called π -bonded organometallics.
e.g., $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]$ or $\text{K}[\text{PtCl}_3(\eta^2 - \text{C}_2\text{H}_4)]$
 $\text{Fe}(\eta^5 - \text{C}_5\text{H}_5)_2$, $\text{Cr}(\eta^6 - \text{C}_6\text{H}_6)_2$

Applications of Coordination Compounds

- Coordination compounds are of great importance in biological system, *e.g.*, chlorophyll, haemoglobin, myoglobin, etc. are coordinate compounds of Mg, Fe and Co respectively.
- In qualitative analysis, basic radicals are confirmed by converting them into suitable coordinate complex with characteristic colour.
- Coordination compounds are used for quantitative analysis.
- Hardness of water can be estimated by complex formation using EDTA.
- Complex *cis*- $[\text{PtCl}_2(\text{NH}_3)_2]$ known as *cis*-platin is used in cancer treatment.
- EDTA is often used for treatment of lead poisoning.
- Coordination compound formation technique is also used in metal extraction. *e.g.*, silver and gold are extracted through formation of their cyanide complexes.
- Coordination compounds are also used in electroplating, photography, dyes, etc.
- Coordination compounds are used as catalyst, *e.g.*, Wilkinson's catalyst, $(\text{Ph}_3\text{P})_3\text{RhCl}$ is used for dehydrogenation of alkenes, Ziegler-Natta catalyst, $[\text{TiCl}_4 + (\text{C}_2\text{H}_5)_3\text{Al}]$ is used for polymerisation of ethene.

KEY POINT

- A polydentate ligand has flexidentate character *i.e.*, its all donor atoms may or may not form coordinate bonds with central metal atom.
- In chemistry of complexes, the magnetic moment of complex gives an idea about the number of unpaired electrons present in it and then electronic arrangement is written which has the same number of unpaired electrons.
- Most stable carbonyls are formed by *d*-block metals kept at the central part of *d*-block.
- Mononuclear carbonyls are colourless or light coloured while polynuclear carbonyls are deeply coloured.
- Some complexes like CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$, MnO_4^- etc have d^0 configuration of metal ion but have intense colour due to charge transfer spectra and not due to *d-d* transition.

SELF CHECK

- Which of the following compounds is not yellow coloured?
(a) $(\text{NH}_4)_3[\text{As}(\text{Mo}_3\text{O}_{10})_4]$
(b) BaCrO_4
(c) $\text{Zn}_2[\text{Fe}(\text{CN})_6]$
(d) $\text{K}_3[\text{Co}(\text{NO}_2)_6]$ (JEE Main 2015)
- The number of geometric isomers that can exist for square planar $[\text{Pt}(\text{Cl})(\text{py})(\text{NH}_3)(\text{NH}_2\text{OH})]^+$ is (*py* = pyridine)
(a) 4 (b) 6
(c) 2 (d) 3 (JEE Main 2015)
- Consider the following complex ions, *P*, *Q* and *R*.
 $P = [\text{FeF}_6]^{3-}$, $Q = [\text{V}(\text{H}_2\text{O})_6]^{2+}$ and $R = [\text{Fe}(\text{H}_2\text{O})_6]^{2+}$.
The correct order of the complex ions, according to their spin-only magnetic moment values (in B.M.) is
(a) $R < Q < P$ (b) $Q < R < P$
(c) $R < P < Q$ (d) $Q < P < R$
(JEE Advanced 2013)
- $\text{NiCl}_2\{\text{P}(\text{C}_2\text{H}_5)_2(\text{C}_6\text{H}_5)\}_2$ exhibits temperature dependent magnetic behaviour (paramagnetic/diamagnetic). The coordination geometries of Ni^{2+} in the paramagnetic and diamagnetic states are respectively
(a) tetrahedral and tetrahedral
(b) square planar and square planar

- (c) tetrahedral and square planar
(d) square planar and tetrahedral.

(JEE Advanced 2012)

18. The octahedral complex of a metal ion M^{3+} with four monodentate ligands L_1, L_2, L_3 and L_4 absorbs wavelengths in the region of red, green, yellow and blue, respectively. The increasing order of ligand strength of the four ligands is

- (a) $L_1 < L_2 < L_4 < L_3$ (b) $L_4 < L_3 < L_2 < L_1$
(c) $L_1 < L_3 < L_2 < L_4$ (d) $L_3 < L_2 < L_4 < L_1$

(JEE Main 2014)

19. Which of the following complex species is not expected to exhibit optical isomerism?

- (a) $[\text{Co}(\text{en})(\text{NH}_3)_2\text{Cl}_2]^+$
(b) $[\text{Co}(\text{en})_3]^{3+}$
(c) $[\text{Co}(\text{en})_2\text{Cl}_2]^+$
(d) $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$

(JEE Main 2013)

20. Which among the following will be named as dibromidobis(ethylenediamine) chromium(III) bromide?

- (a) $[\text{Cr}(\text{en})_2\text{Br}_2]\text{Br}$ (b) $[\text{Cr}(\text{en})\text{Br}_4]^-$
(c) $[\text{Cr}(\text{en})\text{Br}_2]\text{Br}$ (d) $[\text{Cr}(\text{en})_3]\text{Br}_3$

(JEE Main 2012)

ENVIRONMENTAL CHEMISTRY

- Introduction
- Environmental Pollution and Pollutants
- Types of Pollutants
- Types of Pollution : Air, Water and Soil Pollution

TIPS TO REMEMBER

- Environmental chemistry is the branch of chemistry that deals with the study of various chemical processes taking place in various segments of the environment.

Components of Environment :

- **Atmosphere** : Cover of gases upto the height of 1600 km from the surface of earth.

Regions of atmosphere

Region	Altitude from earth's surface	Temperature range	Gases/Species present
Troposphere	0-10 km	Decreases from 15 to -56°C	$\text{N}_2, \text{O}_2, \text{CO}_2, \text{H}_2\text{O}$ vapours
Stratosphere or (ozonosphere)	10-50 km	Increases from -56 to -2°C	$\text{N}_2, \text{O}_2, \text{O}_3$ O-atoms
Mesosphere	50-85 km	Decreases from -2 to -92°C	$\text{N}_2, \text{O}_2, \text{O}_2^+, \text{NO}^+$
Thermosphere	85-500 km	Increases from -92 to 1200°C	$\text{O}_2^+, \text{O}^+, \text{NO}^+, e^-$.

- **Hydrosphere** : Water bodies (sea, oceans, rivers, lakes, etc.) covers about 75% of earth's surface.
- **Lithosphere** : Solid part consisting of soil, rocks, mountains, etc.
- **Biosphere** : Part where living organisms interact with lithosphere, hydrosphere and atmosphere.
- **Abiotic components (non-living)** : Lithosphere, hydrosphere, atmosphere.
- **Biotic components (living)** : plants, animals and human beings.

Types of Pollutants

- **Primary pollutants and secondary pollutants** : Primary air pollutants are chemicals that are released into the air (e.g., NO) before they undergo further reactions to become secondary air pollutants (smog and acid rain).
- **Biodegradable and non-biodegradable pollutants** :
- *Biodegradable pollutants* : They are easily decomposed by micro-organisms either naturally or by suitable treatment. e.g., cow-dung, domestic sewage, etc.
 - *Non-biodegradable pollutants* : They are either decomposed slowly or not decomposed at all. e.g., Hg, DDT, PCBs, etc.

Types of Pollution

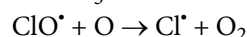
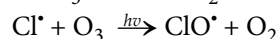
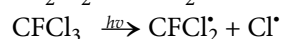
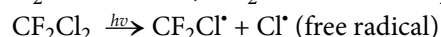
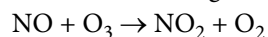
- **Air Pollution** : It is the addition of undesirable materials into the atmosphere either due to natural phenomena or due to human activity on the earth which adversely affect the quality of the air and hence affects the life on the earth.

Pollutants	Major Sources	Effects
CO	Incomplete combustion of carbonaceous matter in automobile engines and defective furnaces, incomplete combustion of agricultural and slash matter, volcanic eruptions, forest fires.	Carbon monoxide is toxic. It binds with haemoglobin in red blood cells and prevents them from combining with oxygen. Low levels of CO cause headaches and dizziness. Concentrations of ~1% causes death in minutes.
NO _x	Combustion of fuel, natural-forest fires, anthro-stationary combustion sources (factories and power plants), transportation.	Toxic to living tissues, harmful to paints, textiles and metals.
SO _x	Anthro-stationary combustion sources, industries, volcanic eruptions and also found in metal ores, coal and decay products.	They are respiratory tract irritants, low concentration causes throat and eye-irritation, causes breathlessness, affect larynx.
Hydrocarbons	Combustion of fuel in automobiles, refineries, anaerobic bacterial decomposition of organic matter, natural gas.	At concentration greater than 500–1000 ppm, they have carcinogenic effect in lungs. They react with O ₂ and NO _x to form photochemical smog which have a strong damaging effect on human beings as well as plants.
CFC's	CFC's were used primarily as refrigerants, in aerosol sprays and in the plastics industry. Freons are stable (lasts for over 80 years), inflammable and inert (in the lower atmosphere).	React with stratospheric ozone. When CFC's are broken down, chlorine free radicals are produced These can react with more than 100,00 molecules of ozone thus, depleting the ozone layer.
Particulates	Volcanic eruptions, fly ash, smelting and mining operations, smoke from incomplete combustion, dust from crushers and grinders.	Inhalation of metallic particles leads to respiratory disorders like asthma, bronchitis, lung cancer, etc.

Ozone Depletion

- ❑ A thin layer of ozone gas (O₃) encircles the earth and prevents about 99% of the ultraviolet radiations of sun from reaching the earth.
- ❑ UV light strikes O₃ molecules, which split apart. The products reunite, giving off heat and reforming ozone. The ozone layer continues renewing itself while converting UV light into heat (infrared radiations).
- ❑ $O_3 + \text{UV light} \rightarrow O + O_2$
 $O + O_2 \rightarrow O_3 + \text{Infrared radiations(heat)}$.
- ❑ The ozone layer has been degraded by chemicals that have been released into the atmosphere on industrial scales.
- ❑ The primary culprits are CFC's (chlorofluoro carbons) and NO₂. The C—Cl bond can be broken by the UV light in the upper atmosphere to form a chlorine radical. NO₂ can also produce an oxygen radical. These radicals can catalytically break ozone into oxygen.

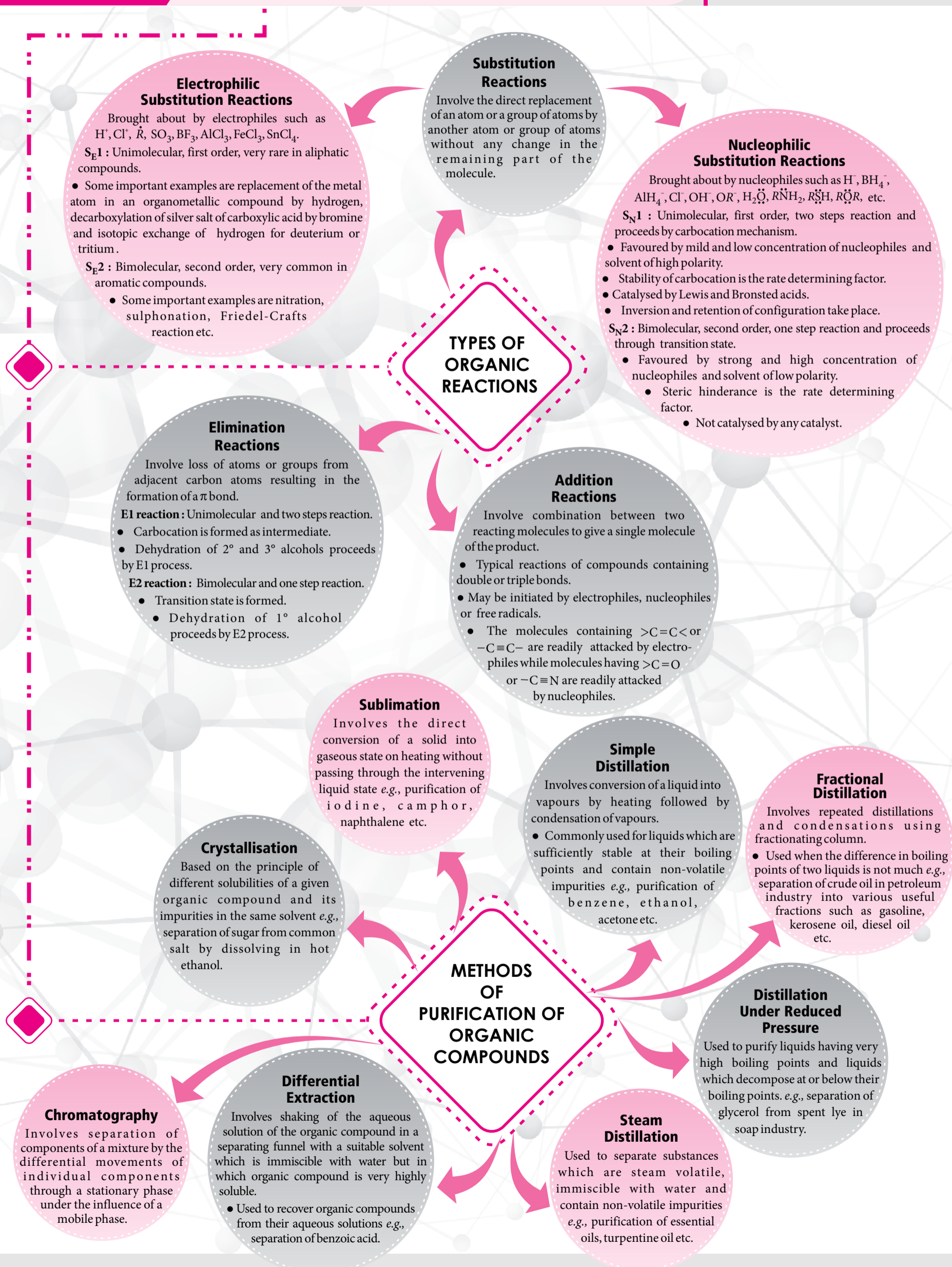
- ❑ Reactions showing ozone depletion are :



- *Environmental effects of ozone depletion* : Ozone depletion increases the amount of UV light that strikes the earth's surface. An excess of this type of light causes damage to living organisms as :
 - *Eyes* : cataracts-blurred vision or blindness.
 - *Skin* : severe burns/cancer.
 - *Immune system* : weaker immune response *i.e.*, more susceptible to diseases.
 - *Crops* : interference with photosynthesis *i.e.*, lower crop yield.
 - *Marine ecosystem* : planktons near the surface die which disrupts the food chain.

GENERAL ORGANIC CHEMISTRY (TYPES OF ORGANIC REACTIONS AND METHODS OF PURIFICATION OF ORGANIC COMPOUNDS)

Reaction mechanism explains the pathway through which an organic reaction takes place and the various methods of purification of organic compounds are based on their physical and chemical properties.



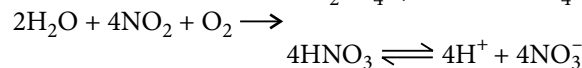
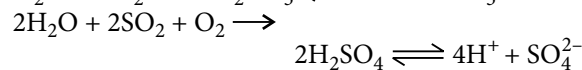
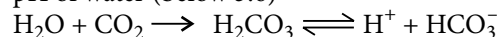
Greenhouse Effect and Global Warming

- The energy trapping phenomenon by infrared active gaseous molecules and vapours called *greenhouse gases* such as carbon dioxide, methane, ozone, chlorofluorocarbon compounds (CFC's) and water vapours present in the atmosphere is termed as *greenhouse effect*.
- The greenhouse gases (infrared absorbers) are increasing in the atmosphere to such an extent that less re-radiated energy is able to escape from the atmosphere. The greater quantities of greenhouse gases absorb this long-wave radiation effectively. The energy is then re-radiated into the lower atmosphere. The gases may be said to be acting like a blanket, absorbing more and more radiations in the atmosphere. This could lead to a progressive increase in temperature (global warming) and eventually to climatic change.
- The degree that a gas contributes to the greenhouse effect depends on its effectiveness as an IR- absorber, and its prevalence in the atmosphere.
- Particulate in the atmosphere have the opposite effect. They block light before it reaches the earth. This decrease in radiation coming to the earth decreases the temperature.
- **Effects of global warming :**
 - Oceans will absorb more heat energy, making hurricanes and typhoons more common.
 - Ocean current patterns and the world's weather patterns will be altered significantly which will lead to flooding in some areas and droughts in others.
 - *Melting of polar ice caps and glaciers* : This would raise the sea level, flooding up to 20% of the world's land mass.
 - Increase in the global temperature increases the incidence of infectious diseases like dengue, malaria, yellow fever, sleeping sickness etc.
- **Control and prevention :**
 - Fossil fuels combustion should be avoided.
 - Industries should purify smoke to certain extent before releasing it into air.
 - Planting more and more trees is also a method to maintain the O₂-CO₂ balance.
 - *Catalytic converters* : Devices attached to a vehicle's exhaust system to convert CO and hydrocarbons into water and carbon dioxide.
 - *Scrubbers* : Pollutant-laden air is passed through a mixture of water and lime which traps particulates and sulphur oxide gases.

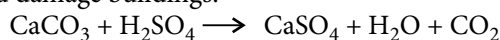
- HCFC's and HFC's are used in place of CFC's because they are largely destroyed in the lower region of the atmosphere.

Acid Rain

- The oxides of C, N and S present in the atmosphere, dissolve in water and produce acids and lower the pH of water (below 5.6)



The acids are toxic to vegetation, react with marble and damage buildings.



Acids corrode water pipes and produce salts with heavy metal ions *viz.*, Cu, Pb, Hg and Al which are toxic in nature.

Smog

- The word smog has its origin from smoke and fog. It is a major air pollutant.



Classical smog	Photochemical smog
Also called as <i>London smog</i> .	Also called as <i>Los Angeles smog</i> .
Formed due to oxides of sulphur.	Formed due to oxides of nitrogen.
Contains primary pollutants.	Contains secondary pollutants.
Causes bronchitis and problems in lungs.	Causes irritation in eyes.

- **Water pollution** : Water pollution is defined as the contamination of water by foreign substances which makes it harmful for health of animals or plants or aquatic life and makes it unfit for domestic, industrial and agricultural use.

Pollutants	Major sources
Natural wastes	Leaching of minerals, silt from soil erosion, falling of organic matter from river banks, etc.
Organic chemicals	Pesticides, surfactants, detergents, industrial wastes.
Metals (Hg, As, Pb, Cd, etc.)	Nuclear power plants, mining, metal plating industries.

Man-made wastes	Sewage, domestic waste, soaps and detergents, waste from animal sheds and slaughter houses, run off from agricultural fields, industrial wastes, oil pollution.
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- *Effects of water pollution :*
 - High concentrations of fluoride are poisonous and are harmful to bones and teeth at levels over 10 ppm.
 - Excess nitrate in drinking water can lead to 'blue baby' syndrome.
 - Excess sulphate (> 500 ppm) causes laxative effect.
- Remedial measures :
 - Degradation of organic content of waste water by microbial oxidation.
 - Removal of phosphates, coagulation, filtration, and disinfection using chlorine for improving the quality of waste water.
 - Sewage treatment should be improved.
 - Settlement of the filtered waste water to remove suspended solids, oily and greasy material which floats on the surface can be skimmed off.
- **Biological oxygen demand (BOD) :** It is a measure of the oxygen required to biologically decompose any organic material in a sample of water. It is usually measured over a period of five days in a sealed container. The oxygen content of the water is measured after this time to find what is left.
 - "Pure Water" has a BOD < 1 ppm. Water with BOD over 5 ppm is considered polluted.
 - High BOD can remove all the oxygen from a water sample. A river can re-oxygenate itself through mechanical action, but a lake or ocean may remain de-oxygenated for a long period of time.
 - High levels of nitrates (fertilizers runoff) can cause large algae blooms. As these die, their decomposition can consume all the available oxygen. Further decomposition occurs anaerobically which produces toxic and foul smelling products.
 - Living things that enter this area die, decompose and consume any oxygen left. This will create a dead zone for living organisms in the water body. This process is called *eutrophication*.
- Another important factor in oxygen solubility is the temperature. Dissolved oxygen requires a stable, hydrogen bonded sphere. Higher temperature do not favour stable hydrogen bonds thus warm water will have a lower oxygen solubility.
- Thermal pollution can damage bodies. Additionally, a warm layer of water can form a low-solubility blanket over a colder body of water that limits the transfer of oxygen to the colder water below.
- **Chemical oxygen demand (COD) :** In COD determination, a known quantity of water sample is oxidised by acidified $K_2Cr_2O_7$. The unused amount of dichromate is determined by back titration. The amount of oxygen used in oxidation is calculated from consumed concentration of $K_2Cr_2O_7$. COD for pure water = 4 ppm.
- **Soil pollution :** It is defined as the build-up of persistent toxic compounds, chemicals, salts, radioactive materials or disease causing agents in soils which have adverse effects on plants growth and animals health.
 - *Causes of soil pollution :*
 - Deforestation is a major cause for soil erosion, where soil particles are dislodged and carried away by water or wind. As a result, the soil loses important nutrients found in it.
 - Polluted water discharged from factories.
 - Oil and petroleum leaked from vehicles is washed off the road by the rain into the surroundings.
 - Acid rain (fumes from factories mixing with rain).
 - Over application of pesticides and fertilizers which runoff from farms and crops.
 - Septic tank seepage, lagoon seepage, sanitary/hazardous landfill seepage.
 - *Effects of soil pollution :*
 - Polluted soil runoff into rivers and kills the fishes, plants and other aquatic life.
 - Crops and fodder grown on polluted soil may pass on the pollutants to the consumers.
 - Soil structure is damaged (clay ionic structure impaired).
 - May release vapours and hydrocarbons into buildings and cellars and cause corrosion of foundations and pipelines.

- Contaminated soil decreases soil fertility and hence there is decrease in the crop yield.
- When soil pollution modifies the soil structure, death of many beneficial soil organisms (e.g., earthworms) in the soil may take place.
- People living near polluted land tend to have higher incidences of migraines, nausea, fatigue, skin disorders and even miscarriages.

❑ **Prevention of Soil Pollution :**

- Reuse and recycle unwanted items.
- Make use of organic fertilizers and organic pesticides, because they are usually made of natural substances so are biodegradable.
- Insist on buying natural and organic food, because chemical pesticides and fertilizers are not used in their growing process.
- Cut down the usage of paper or use recycled paper.

KEY POINT

- Environmental pollution can be controlled by *green chemistry*. It is a way of thinking and is about utilising the existing knowledge and principles of chemistry and other sciences to reduce the adverse impact on environment.
- COD is always higher than BOD for the same sample of water.

SELF CHECK

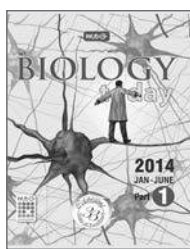
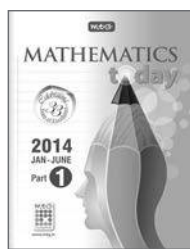
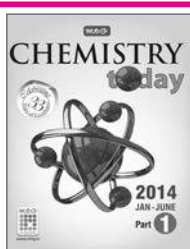
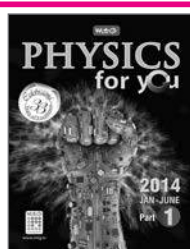
- The gas leaked from a storage tank of the Union Carbide plant in Bhopal gas tragedy was
 - phosgene
 - methylisocyanate
 - methylamine
 - ammonia.
 (JEE Main 2013)
- Photochemical smog consists of excessive amount of X, in addition to aldehydes, ketones, peroxyacetyl nitrates (PAN) and so forth, X is
 - CH₄
 - CO
 - CO₂
 - O₃
 (JEE Main 2015)
- Addition of phosphate fertilizers to water bodies causes
 - enhanced growth of algae
 - increase in amount of dissolved oxygen in water
 - deposition of calcium phosphate
 - increase in fish population.
 (JEE Main 2015)

ANSWER KEYS (SELF CHECK)

1. (a) 2. (b) 3. (d) 4. (a) 5. (d)
 6. (b) 7. (d) 8. (c) 9. (d) 10. (a)
 11. (a) 12. (c) 13. (b) 14. (c) 15. (d)
 16. (b) 17. (c) 18. (c) 19. (d) 20. (a)
 21. (b) 22. (d) 23. (a)



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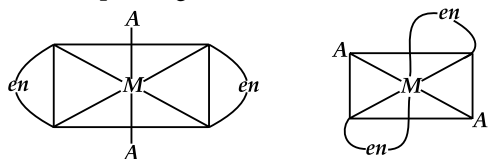
Exam Café

QUESTIONS FOR PRACTICE

- Red phosphorus is chemically unreactive because
 - it does not contain P – P bonds
 - it does not contain tetrahedral P_4 molecules
 - it does not catch fire in air even upto 400°C
 - it has a polymeric structure.
- Which of the following species is basic and reducing?
 - SO_3^{2-}
 - SO_4^{2-}
 - $\text{S}_2\text{O}_4^{2-}$
 - HSO_4^-
- The set with correct order of acidity is
 - $\text{HClO} < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}_4$
 - $\text{HClO}_4 < \text{HClO}_3 < \text{HClO}_2 < \text{HClO}$
 - $\text{HClO}_4 < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}$
 - $\text{HClO}_4 < \text{HClO} < \text{HClO}_2 < \text{HClO}_3$.
- Which of the following statements is incorrect?
 - XeF_2 is a powerful reducing agent.
 - XeF_2 is obtained by the direct reaction between F_2 and Xe at high pressure.
 - XeF_2 undergoes alkaline hydrolysis to give O_2 and Xe.
 - XeF_2 contains two bond pairs and three lone pairs.
- When K_2CrO_4 is added to CuSO_4 solution, there is formation of CuCrO_4 as well as CuCr_2O_7 . Formation of CuCr_2O_7 is due to
 - basic nature of CuSO_4 solution which converts CrO_4^{2-} to $\text{Cr}_2\text{O}_7^{2-}$
 - acidic nature of CuSO_4 solution which converts CrO_4^{2-} to $\text{Cr}_2\text{O}_7^{2-}$
 - CuSO_4 has the typical property of converting CuCrO_4 formed to CuCr_2O_7
 - no CuCr_2O_7 is formed.
- The electronic configuration of actinoids cannot be assigned with degree of certainty because of
 - small energy difference between $5f$ and $6d$ levels
 - overlapping of inner orbitals
 - free movement of electrons over all the orbitals
 - none of the above.
- Which of the following is not a proper method to dispose sludge?
 - Incineration
 - Dumping
 - Anaerobic digestion by microbes
 - Filtration
- Which of the following has phosphorus in +3 oxidation state?
 - Phosphinic acid
 - Metaphosphoric acid
 - Phosphonic acid
 - Pyrophosphoric acid
- The reason for the stability of Gd^{3+} ion is
 - half filled $4f$ subshell
 - completely filled $4f$ subshell
 - possesses the general electronic configuration of noble gases
 - empty $4f$ subshell.
- In solid state, the colour of oxygen has been observed as pale blue. This pale colour of oxygen is due to electronic transitions from
 - the triplet ground state to the excited singlet state
 - the triplet ground state to antibonding $\sigma 2p_z$ molecular orbital
 - the antibonding π -molecular orbitals to the bonding $\sigma 2p_z$ molecular orbital
 - the singlet ground state to the excited triplet state.
- Of the interhalogen AX_3 compounds, ClF_3 is most reactive but BrF_3 has higher conductance in liquid state. This is because
 - BrF_3 has higher molecular mass
 - ClF_3 is more volatile
 - BrF_3 dissociates into BrF_2^+ and BrF_4^- most easily
 - electrical conductance does not depend on concentration.
- The most polarisable noble gas is
 - Kr
 - Ne
 - Xe
 - Ar
- If KMnO_4 is reduced by oxalic acid in an acidic medium, then oxidation number of Mn changes from
 - 4 to 2
 - 6 to 4
 - 7 to 2
 - 7 to 4

14. Knowing that the chemistry of lanthanoids (Ln) is dominated by its +3 oxidation state, which of the following statements is incorrect ?
- Because of the large size of the Ln(III) ions the bonding in its compounds is predominantly ionic in character.
 - The ionic sizes of Ln(III) decrease in general with increasing atomic number.
 - Ln(III) compounds are generally colourless.
 - Ln(III) hydroxides are mainly basic in character.

15. The two complexes given below are



- geometrical isomers
 - position isomers
 - optical isomers
 - identical.
16. N_2O resembles O_2 in that
- it is involved in production of photochemical smog.
 - it is estimated quantitatively in organic compounds by Duma's method.
 - it supports combustion.
 - it is used to prevent growth of botulism bacteria in food.
17. Most stable tetrachloride formed by group 16 elements is
- SCl_4
 - $SeCl_4$
 - $TeCl_4$
 - OCl_4
18. Chlorine cannot displace
- iodine from NaI
 - bromine from NaBr
 - fluorine from NaF
 - none of these.
19. When same amount of zinc is treated separately with excess of sulphuric acid and excess of sodium hydroxide solution the ratio of volumes of hydrogen evolved is
- 1 : 1
 - 1 : 2
 - 2 : 1
 - 9 : 4
20. The IUPAC name for $[Co(NH_3)_6][Cr(CN)_6]$ is
- hexaamminecobalt(III) hexacyano chromium (VI)
 - hexaamminecobalt(III) hexacyano chromate (III)
 - hexacyanochromium(III)hexaamminecobalt(III)
 - hexacyanochromiumcobalthexaammine(VI).

21. Presence of high concentration of ozone and smog in atmospheric air causes
- embrittlement and decreases of folding resistance of paper
 - cracking of rubber products
 - fading of dye on textiles
 - damage of electrical insulator on high tension power line.

22. For which pair of complexes is the order of values of Δ_o correct?

- $[Rh(NH_3)_6]^{3+} > [Co(NH_3)_6]^{3+}$
- $[Fe(CN)_6]^{4-} > [Fe(CN)_6]^{3-}$
- $[Cr(H_2O)_6]^{2+} > [Cr(H_2O)_6]^{3+}$
- $[CrF_6]^{3-} > [Cr(CN)_6]^{3-}$

23. Which of the following is not tetrahedral?

- SCl_4
- SO_4^{2-}
- $Ni(CO)_4$
- $NiCl_4^{2-}$

24. Which of the following sequences represents the correct increasing order of bond angles in the given molecules ?

- $H_2O < OF_2 < OCl_2 < ClO_2$
- $OCl_2 < ClO_2 < H_2O < OF_2$
- $OF_2 < H_2O < OCl_2 < ClO_2$
- $ClO_2 < OF_2 < OCl_2 < H_2O$

25. $HgCl_2$ and $SnCl_2$ cannot coexist in a solution due to

- common ion effect
- solubility product
- redox change
- all of these.

26. Match the lists I and II and pick the correct matching from the codes given below :

List I **List II**

- | | |
|--|--------------------------------|
| (A) $[Ag(CN)_2]^-$ | 1. Square planar and 1.73 B.M. |
| (B) $[Cu(CN)_4]^{3-}$ | 2. Linear and zero |
| (C) $[Cu(CN)_6]^{4-}$ | 3. Octahedral and zero |
| (D) $[Cu(NH_3)_4]^{2+}$ | 4. Tetrahedral and zero |
| (E) $[Fe(CN)_6]^{4-}$ | 5. Octahedral and 1.73 B.M. |
| (a) A - 2, B - 4, C - 5, D - 1, E - 3 | |
| (b) A - 5, B - 4, C - 1, D - 3, E - 2 | |
| (c) A - 1, B - 3, C - 4, D - 2, E - 5 | |
| (d) A - 4, B - 5, C - 2, D - 1, E - 3. | |

27. N_2 can be obtained by

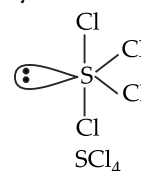
- passing NH_3 over red-hot copper (II) oxide
- heating $(NH_4)_2Cr_2O_7$
- passing NH_3 into suspension of bleaching powder
- all of these.

28. There is no S – S bond in
 (a) $S_2O_4^{2-}$ (b) $S_4O_6^{2-}$
 (c) $S_2O_3^{2-}$ (d) $S_2O_7^{2-}$.
29. Paramagnetic oxide of chlorine is
 (a) ClO_3 (b) Cl_2O_6
 (c) Cl_2O (d) None of these.
30. The oxide which is also called as chromic acid is
 (a) CrO_2 (b) Cr_2O_3
 (c) CrO_3 (d) CrO

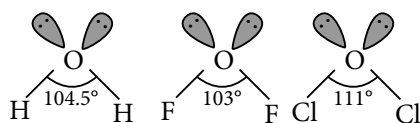
SOLUTIONS

1. (d): In red phosphorus, one of the P_4 bonds is broken, and one additional bond is formed with a neighbouring tetrahedron resulting in a more chain-like structure.
 It is formed by heating white phosphorus to 523K, it becomes an amorphous network of atoms that reduces strain and gives greater stability thereby renders it unreactive.
2. (a): All the given species are basic but only SO_3^{2-} is reducing in nature. It reduces halogens to haloacids.
 $H_2SO_3 + H_2O + X_2 \longrightarrow H_2SO_4 + 2HX$
3. (a): The larger the number of oxygen atoms attached to the chlorine, the larger is the acidity.
4. (a): XeF_2 is a strong oxidising agent. It oxidises Cl^- to Cl_2 .
 $XeF_2 + 2HCl \longrightarrow Xe + 2HF + Cl_2$
5. (b)
6. (a): For the first four actinide elements, Th, Pa, U and Np, the difference in energy between $5f$ and $6d$ -orbitals is small. Thus, in these elements (and their ions) electrons may occupy the $5f$ or the $6d$ levels or sometimes both. Later in the actinide series the $5f$ -orbitals do become appreciably lower in energy. Thus, from Pu onwards the $5f$ -shell fills in a regular way and the elements become very similar.
7. (d)
8. (c): Phosphinic acid (H_3PO_2): +1
 Metaphosphoric acid (HPO_3): +5
 Phosphonic acid (H_3PO_3): +3
 Pyrophosphoric acid ($H_4P_2O_7$): +5
9. (a): $Gd (Z = 64) \longrightarrow [Xe]4f^7 5d^1 6s^2$
 $\therefore Gd^{3+} \longrightarrow [Xe]4f^7$
 Gd^{3+} is highly stable due to stable half-filled configuration.
10. (a): The colour of solid oxygen is due to electronic transition from the triplet ground state (i.e., $\pi^*2p_x^1 \pi^*2p_y^1$) to the excited singlet state (i.e., $\pi^*2p_x^2$ or $\pi^*2p_y^2$).
11. (c): In liquid state BrF_3 dissociates into BrF_2^+ and BrF_4^- ions most easily.
12. (c): Xe has largest atomic radius and thus valence shell electrons are less effectively pulled towards nucleus, hence Xe is easily polarisable.
13. (c): In acidic medium

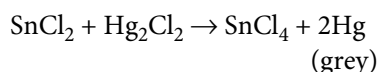
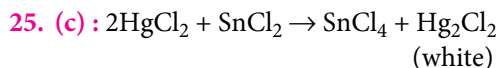
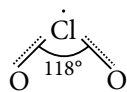
$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$
 $(Mn = +7)$
 $(Mn = +2)$
14. (c): Ln^{3+} compounds are generally coloured in the solid state as well as in aqueous solution. Colour appears due to presence of unpaired f -electrons which undergo $f-f$ transition.
15. (d): Both represent only one molecule and no isomerism is seen.
16. (c): It does so because it decomposes to molecular nitrogen and oxygen when heated.
 $2N_2O \longrightarrow 2N_2 + O_2$
17. (c): SCl_4 exists as a monomer (liquid) whereas $SeCl_4$ and $TeCl_4$ exist as tetramers (solids). As the size of the element increases from S to Te, the van der Waal's forces of attraction between the molecules increase and the stability increases. Hence $TeCl_4$ is most stable. OCl_4 is not formed.
18. (c): Because fluorine is more electronegative than chlorine.
19. (a): $Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$
 $Zn + 2NaOH \rightarrow Na_2ZnO_2 + H_2$
 \therefore Ratio of volumes of H_2 evolved is 1 : 1.
20. (b): Hexaamminecobalt(III) hexacyanochromate (III).
21. (b)
22. (a): The magnitude of Δ_o increases in going down a group.
23. (a): SCl_4 is sp^3d hybridised and see-saw in shape.



24. (c): Bond angle of OCl_2 is more than H_2O due to larger size of Cl-atom than H-atom.



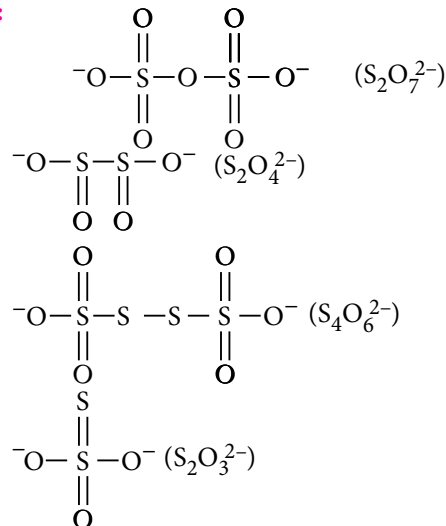
Due to partial π -bond character in one of the two Cl - O bonds, the O - Cl - O bond angle increases to 118° . Therefore, correct order of increasing bond angle is : $\text{OF}_2 < \text{OH}_2 < \text{OCl}_2 < \text{ClO}_2$.



26. (a) : $[\text{Ag}(\text{CN})_2]^-$ is linear (sp) with no unpaired electron hence, magnetic moment = 0
 $[\text{Cu}(\text{CN})_4]^{3-}$ is tetrahedral (sp^3) with no unpaired electron hence, magnetic moment = 0
 $[\text{Cu}(\text{CN})_6]^{4-}$ is octahedral ($sp^3 d^2$) with one unpaired electron hence, magnetic moment = 1.73 BM.
 $[\text{Cu}(\text{NH}_3)_4]^{2+}$ is square planar (dsp^2) with one unpaired electron hence, magnetic moment = 1.73 BM.
 $[\text{Fe}(\text{CN})_6]^{4-}$ is octahedral ($d^2 sp^3$) with no unpaired electron hence, magnetic moment = 0.

27. (d) : (a) $3\text{CuO} + 2\text{NH}_3 \rightarrow 3\text{Cu} + \text{N}_2 + 3\text{H}_2\text{O}$
 (b) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7 \rightarrow \text{N}_2 + 4\text{H}_2\text{O} + \text{Cr}_2\text{O}_3$
 (c) $3\text{CaOCl}_2 + 2\text{NH}_3 \rightarrow 3\text{CaCl}_2 + 3\text{H}_2\text{O} + \text{N}_2$

28. (d) :



29. (a) : ClO_3 has 41 electrons and thus at least one electron should be unpaired.

30. (c)



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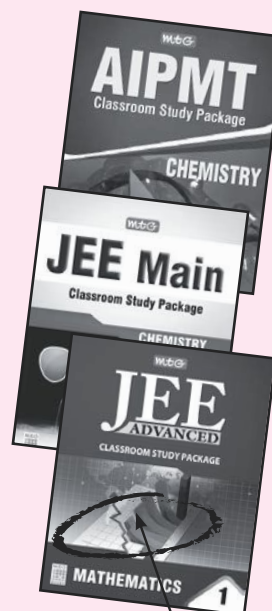
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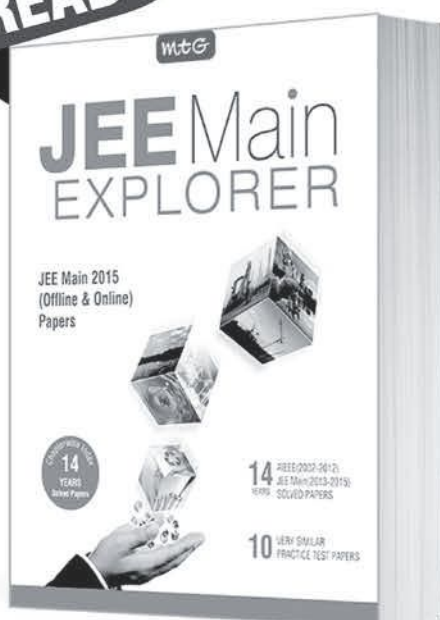
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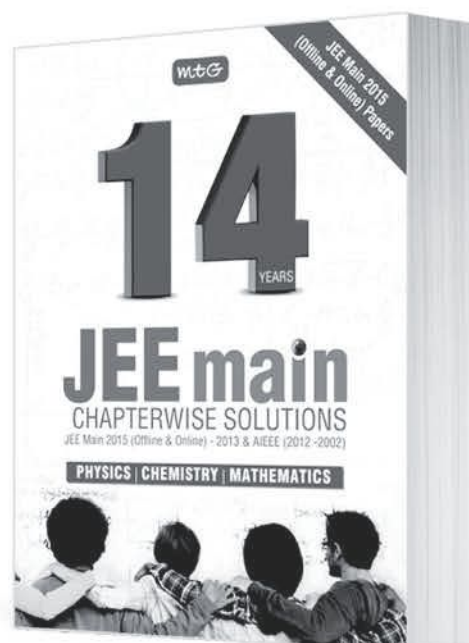
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CHAPTERWISE PRACTICE PAPER : HALOALKANES AND HALOARENES | ALCOHOLS, PHENOLS AND ETHERS

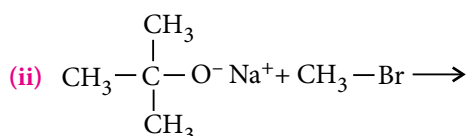
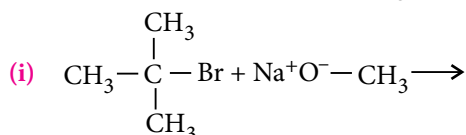
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Maximum Marks : 70

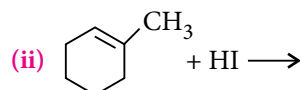
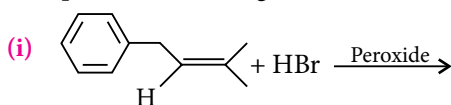
GENERAL INSTRUCTIONS

- All questions are compulsory.
- Q. no. 1 to 5 are very short answer questions and carry 1 mark each.
- Q. no. 6 to 10 are short answer questions and carry 2 marks each.
- Q. no. 11 to 22 are also short answer questions and carry 3 marks each.
- Q. no. 23 is a value based question and carries 4 marks.
- Q. no. 24 to 26 are long answer questions and carry 5 marks each.
- Use log tables if necessary, use of calculators is not allowed.

- What are allylic alcohols?
- Predict the product of the following reactions :



- Out of *ortho* and *para* isomers of aryl halides which one has higher melting point?
- Arrange the following alkyl halides in the order of increasing dipole moment.
 $\text{CH}_3 - \text{F}$, $\text{CH}_3 - \text{Cl}$, $\text{CH}_3 - \text{Br}$, $\text{CH}_3 - \text{I}$
- What happens when phenol is oxidised by $\text{Na}_2\text{Cr}_2\text{O}_7$ and H_2SO_4 ?
- Complete the following reactions :



- o*-Nitrophenol is steam volatile while *p*-nitrophenol is not. Why?

OR

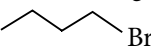

Compare carbon — oxygen bond lengths in phenol and methanol.

- Write the structure of 4-*tert*-butyl-3-iodoheptane.
 - In the following pairs of halogen compounds, which compound undergoes $\text{S}_{\text{N}}1$ reaction faster?
 $\text{C}(\text{CH}_3)_3\text{Cl}$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$
- Give two methods for the synthesis of anisole.
 - Draw structures of all the isomers of anisole.
- Suggest a reagent for conversion of
 - ethanol to ethanal
 - ethanol to ethanoic acid.

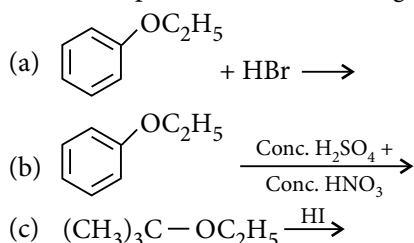
11. (i) Why are haloalkanes insoluble in water?
 (ii) In the preparation of Grignard reagent, all the starting materials must be dry. Why?
 (iii) Electrophilic substitution reactions in haloarenes occur slowly and require more drastic conditions. Why?
12. (i) Is it desirable to synthesise alcohols in a copper vessel?
 (ii) Draw the structures of all the isomeric alcohols of molecular formula $C_5H_{12}O$, give their IUPAC names. Classify them as 1°, 2° and 3° alcohols.
13. Compound (A) with molecular formula C_4H_9Br is treated with aqueous KOH solution. The rate of this reaction depends upon the concentration of the compound 'A' only. When another optically active isomer 'B' of this compound was treated with aqueous KOH solution, the rate of reaction was found to be dependent on concentration of compound and KOH both.
 (i) Write down the structural formula of both compounds 'A' and 'B'.
 (ii) Out of these two compounds, which one will be converted to the product with inverted configuration.
14. (i) Which bond is cleaved in alkyl phenyl ether on reaction with HI?
 (ii) What happens when anisole is treated with Br_2 in CH_3COOH ?
15. (i) Identify the products of mononitration of 3-methylphenol.
 (ii) Explain the terms
 (a) denatured spirit
 (b) rectified spirit.
- OR**
- (i) What happens when phenol is treated with bromine water?
 (ii) Give an example of each of the following :
 (a) Kolbe's reaction
 (b) Reimer—Tiemann reaction
16. (i) Why is $SOCl_2$ (thionyl chloride) preferred for the preparation of alkyl chloride from alkyl alcohol?
 (ii) Explain Finkelstein reaction. Give example.
17. Alcohol A (C_3H_8O) on heating with Cu gives B which shows following reactions :
- (I) B gives iodoform test.
 (II) B forms oxime with NH_2OH .
 (III) B does not reduce Tollens' reagent.
 Identify (A).
18. (i) Write the mechanism of the reaction of HI with methoxymethane.
 (ii) What is the order of reactivity of hydrogen halides (HX) with a particular dialkyl ether?
19. (i) Alcohols are more soluble in water than the hydrocarbons of comparable molecular masses.
 (ii) Explain the order of reactivity for electrophilic substitution of benzene (I), phenol (II) and nitrobenzene (III) is $III < I < II$.
20. (i) Arrange the following in the increasing reactivity for S_N1 and S_N2 reactions.
 $C_6H_5CH_2Br$, $C_6H_5CH(C_6H_5)Br$, $C_6H_5CH(CH_3)Br$, $C_6H_5C(CH_3)_2Br$
 (ii) What is Sandmeyer's reaction?
21. What happens when
 (i) Ethyl alcohol reacts with red P and Br_2 ?
 (ii) Ethanol is heated with conc. H_2SO_4 at 443 K?
 (iii) 3° alcohol is treated with $KMnO_4$ at high temperature?
22. A sweet smelling organic compound 'A' is slowly oxidised by air in the presence of light to a highly poisonous gas. On warming with silver powder it forms a gaseous substance 'B' which is also produced by the action of calcium carbide on water. Identify 'A' and 'B' and write the equations of the reactions involved.
23. To refrain people from drinking alcohol the production of alcohol is Government controlled and a heavy excise duty is levied on the sale of alcoholic beverages. However to supply cheaper alcohol to industries where it is used in large quantities, it is denatured.
 (i) What are the values displayed by the Government?
 (ii) Should production of alcohol be completely banned? Give two reasons.
 (iii) Why alcohol is denatured?
 (iv) How can we spread awareness to stop addiction to alcohol?

24. (i) Write chemical equations and reaction conditions for the conversion of
 (a) Chlorobenzene to phenol
 (b) Propene to 1-bromopropane
 (c) Chlorobenzene to toluene.
- (ii) Predict all the alkenes that would be formed by dehydrohalogenation of the following halides with sodium ethoxide in ethanol and identify the major alkene.
 (a) 1-Bromo-1-methylcyclohexane
 (b) 2-Chloro-2-methylbutane

OR

- (i) How is chloroform prepared? Write its uses.
 (ii) Which alkyl halide from the following pair is chiral and undergoes S_N2 reaction faster?
 (a)  Br
 (b)  Br
- (iii) Give reasons for the following :
 (a) (\pm) -Butan-2-ol is optically inactive.
 (b) Ethyl iodide undergoes S_N2 reaction faster than ethyl bromide.

25. (i) Predict the products of the following reactions :



- (ii) Illustrate with examples the limitations of Williamson synthesis for the preparation of certain types of ethers.

OR

- (i) How would you account for the following :
 (a) Ethers possess a dipole moment even if the alkyl radicals in the molecule are identical.
 (b) Carboxylic acids have higher boiling points than alcohols of comparable molecular masses.
- (ii) Describe the following processes with an example in each case :
 (a) Protonation
 (b) Acetylation

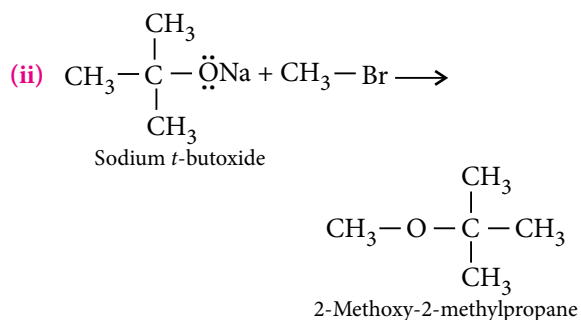
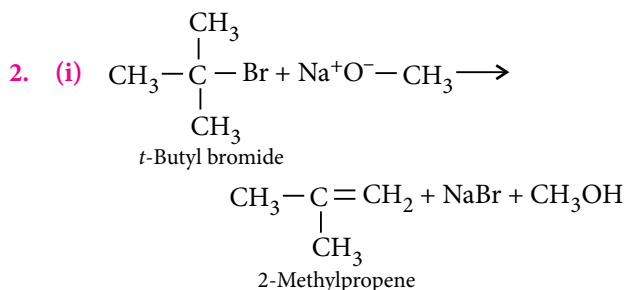
26. (i) Describe a chemical test each to distinguish between the following pairs :
 (a) ethanol and phenol.
 (b) 1-propanol and 2-propanol.
- (ii) A compound 'A' ($\text{C}_2\text{H}_6\text{O}$) on oxidation by PCC gave 'B', which on treatment with aqueous alkali and subsequent heating furnished 'C'. 'B' on oxidation by KMnO_4 forms a monobasic acid with molar mass 60 g mol^{-1} .

OR

- (i) Why does phenol give tribromophenol on bromination with bromine water?
 (ii) Phenol is acidic while hexanol is neutral towards a solution of NaOH. Why?
 (iii) *m*-Aminophenol is stronger acid than *o*-aminophenol.

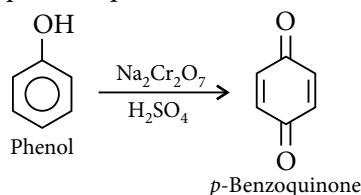
SOLUTIONS

1. Alcohols in which $-\text{OH}$ group is attached to sp^3 hybridised carbon next to the carbon-carbon double bond are called allylic alcohols. *e.g.*, $\text{CH}_2=\text{CH}-\text{CH}_2-\text{OH}$ (Allyl alcohol).

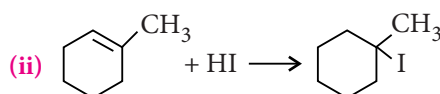
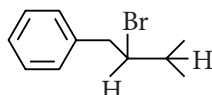


3. *p*-Isomer has higher melting point due to symmetry.
 4. Increasing order of dipole moment :
 $\text{CH}_3-\text{I} < \text{CH}_3-\text{Br} < \text{CH}_3-\text{F} < \text{CH}_3-\text{Cl}$

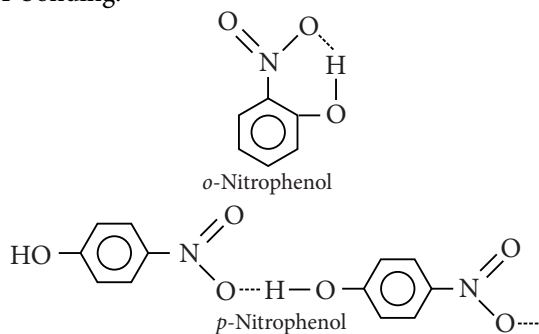
5. *p*-Benzoquinone is formed.



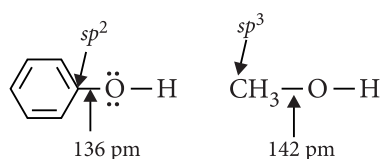
6. (i)



7. *o*-Nitrophenol is steam volatile due to intramolecular H-bonding while *p*-nitrophenol has high boiling point due to the presence of intermolecular H-bonding.



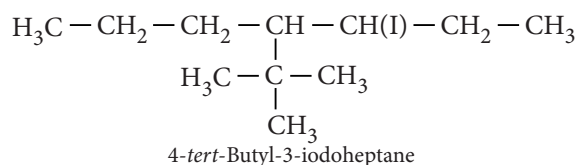
OR



C — O bond length in phenol is shorter than that in methanol due to

- (a) lone pairs of oxygen atom in phenol are in conjugation with aromatic ring. Thus, there is some double bond character with shorter bond length than in methanol in which there is no conjugation.
(b) C-atom in phenol with sp^2 hybridisation is more electronegative than the C-atom in methanol with sp^3 hybridisation. Thus, bond length decreases.

8. (i)

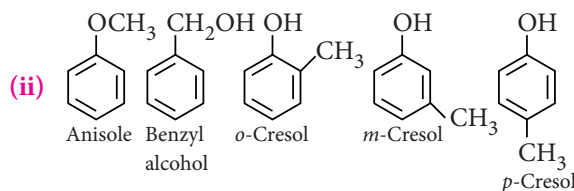
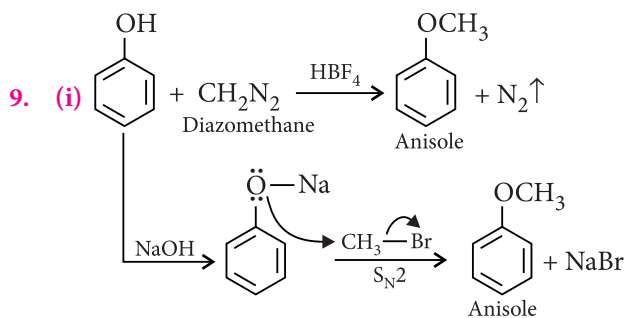


- (ii) S_N1 reaction proceeds via the formation of a carbocation intermediate. This intermediate is formed by the cleavage of the C — X bond. More stable the resultant carbocation, faster is the S_N1 reaction.

Order of stability of carbocations is

3° carbocation > 2° carbocation > 1° carbocation

will react faster as the 3° carbocation is more stable.



10. (i) To convert ethanol to ethanal, PCC is used. It stops the reaction at this stage only and prevents its further oxidation to carboxylic acid.

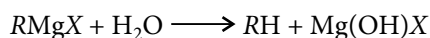
- (ii) Acidified KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$ or any strong oxidising agent converts ethanol to ethanoic acid.



11. (i) Although haloalkanes are polar in nature, yet they are insoluble in water because they are not able to form hydrogen bonding with water molecules.

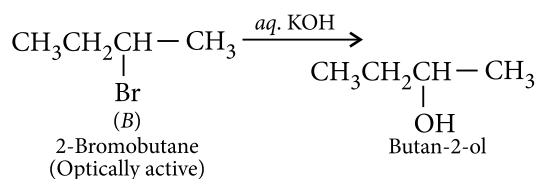
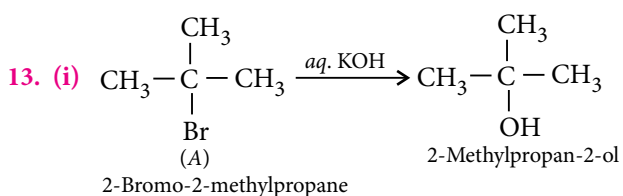
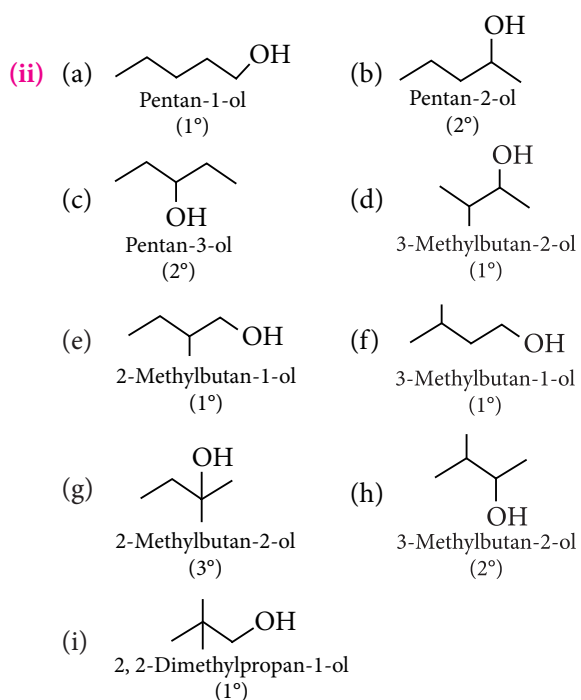
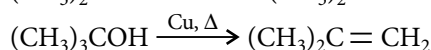
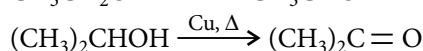
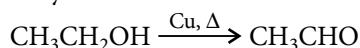
- (ii) Grignard reagents are highly reactive and react with any source of proton to give hydrocarbon.

Therefore, if any starting material contains moisture then Grignard reagent is converted into alkane.

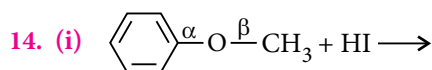


(iii) Due to $-I$ effect, halogen withdraws electron density towards it and overall deactivation of the ring takes place. Therefore, for better yield drastic conditions are required.

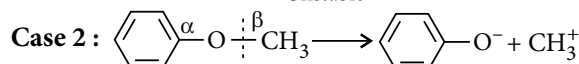
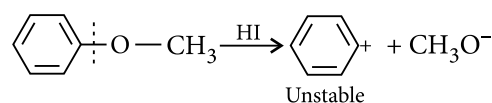
12. (i) It is not desirable to synthesise alcohols in copper vessel as it can undergo oxidation or dehydration.



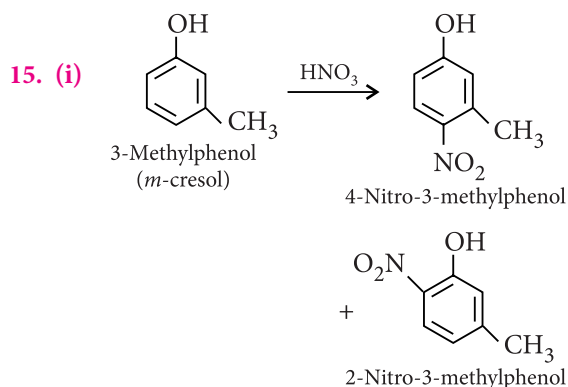
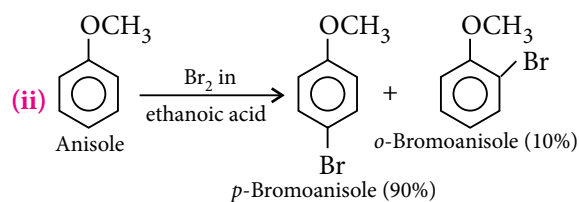
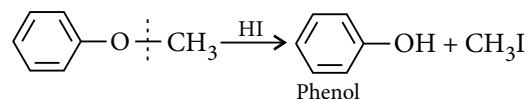
(ii) Compound (B) will be converted to product with inverted configuration as it undergoes $\text{S}_{\text{N}}2$ nucleophilic substitution in which the nucleophile attaches itself on the side opposite to the one where the halogen atom is present. Compound (A) being a tertiary halide, undergoes $\text{S}_{\text{N}}1$ substitution which is accompanied by racemisation.



Case 1 : If (C – O) α bond breaks, phenyl carbocation is formed which is least stable.



If (C – O) β -bond breaks, phenoxide ion is formed which is stabilised by resonance. Thus, alkyl – O bond breaks.

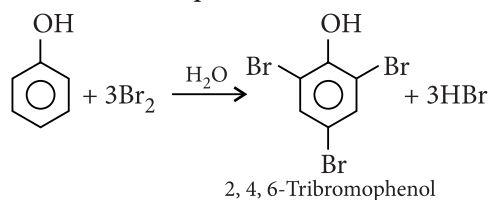


(ii) (a) Denatured spirit : Commercial ethanol made unfit for drinking by mixing pyridine (a foul smelling liquid) and CuSO_4 (to give blue colour for identification) is called denatured spirit and the process is called denaturation of alcohol.

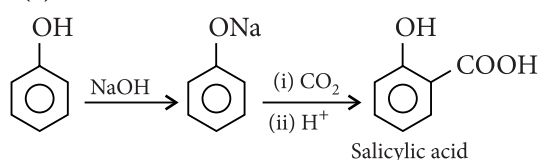
(b) Rectified spirit : 95.5% ethanol + 4.5% water mixture obtained by fermentation of sucrose is called rectified spirit. This mixture boils at 351.15 K and pure ethanol also boils at 351.3 K. Thus, rectified spirit cannot be separated into components by simple fractional distillation.

OR

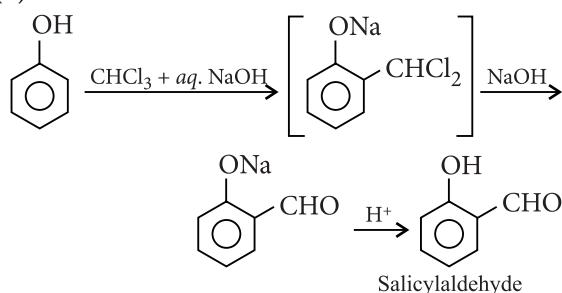
(i) 2, 4, 6-Tribromophenol is formed.



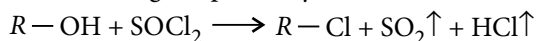
(ii) (a) Kolbe's reaction :



(b) Reimer—Tiemann reaction :



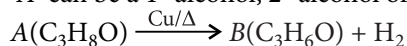
16. (i) Thionyl chloride is preferred because other two products formed are escapable gases. Hence, the reaction gives pure alkyl halide.



(ii) Alkyl iodide is often prepared by the reaction of alkyl chloride/bromide with NaI in dry acetone. This is called Finkelstein reaction.



17. 'A' can be a 1° alcohol, 2° alcohol or an ether.

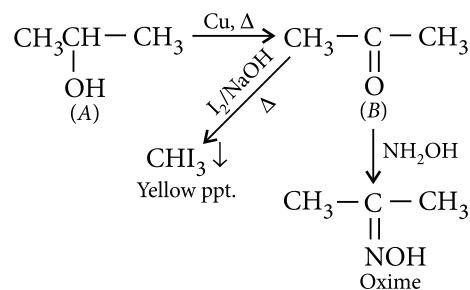


'B' gives iodoform test thus, $\left(CH_3-C(=O)- \right)$ group must be present in (B).

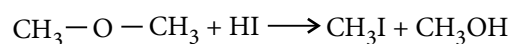
'B' forms oxime thus, $>C=O$ group must be present in (B).

'B' does not reduce Tollens' reagent thus, $\begin{matrix} H \\ \diagdown \\ C=O \end{matrix}$ group is absent.

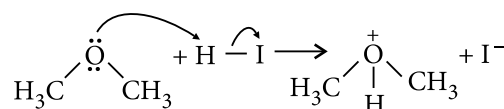
Thus, (A) is $(CH_3)_2CHOH$



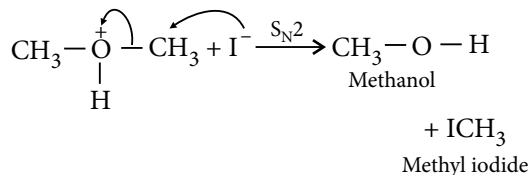
18. (i) The reaction between methoxymethane and HI is



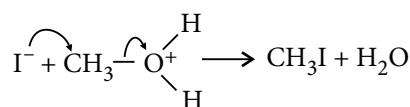
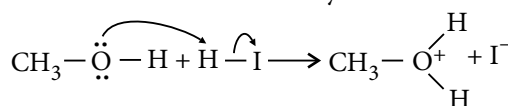
Step 1 : Generation of oxonium ion (Protonation of ether molecule)



Step 2 : Nucleophilic attack on oxonium ion

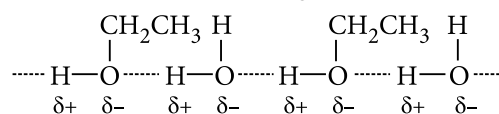


If excess of HI is used, methanol formed above reacts with HI to form methyl iodide.



(ii) Reactivity order of hydrogen halides :
HI > HBr > HCl

19. (i) CH_3CH_2OH (molar mass 46) is a polar compound and is soluble in water due to intermolecular H-bonding

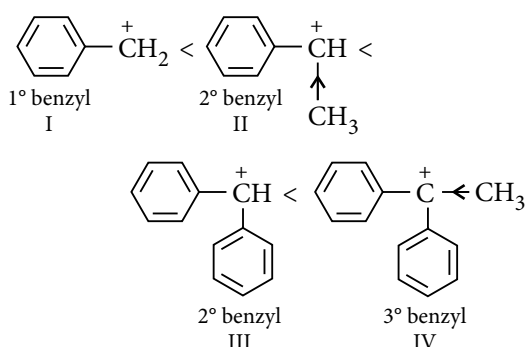


$\text{CH}_3\text{CH}_2\text{CH}_3$ (molar mass 44) is insoluble in water as it lacks polarity and force of attraction between water and propane is very weak.

- (ii) $-\text{NO}_2$ group is deactivating and *m*-directing as it decreases electron density for electrophilic attack. $-\text{OH}$ group is activating and *o*, *p*-directing as it increases electron density for electrophilic attack.

Thus, reactivity order for electrophilic substitution reaction is $\text{III} < \text{I} < \text{II}$.

20. (i) For $\text{S}_{\text{N}}1$, carbocation formed is resonance stabilised which is in the order :

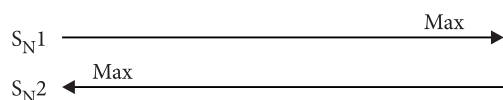
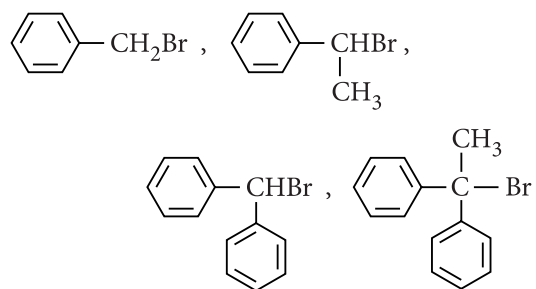


II is more stable than I since $-\text{CH}_3$ group is electron donating group.

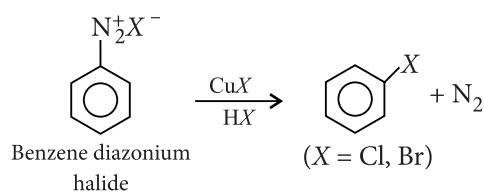
III (2° benzyl) is more stable than II due to delocalisation of +ve charge on two aromatic rings.

IV (3° benzyl) is more stable than III.

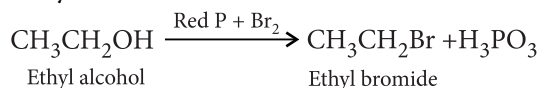
Thus, the reactivity order for $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ is



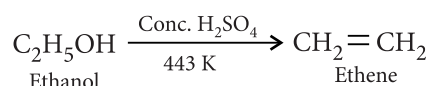
- (ii) A reaction in which diazonium salt is used for the preparation of aryl halides (chloride, bromide) is called Sandmeyer's reaction.



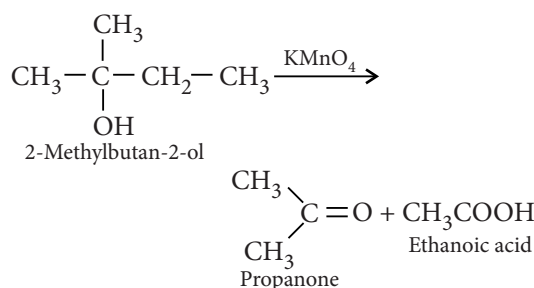
21. (i) Ethyl bromide is formed.



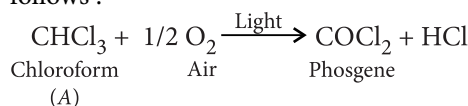
- (ii) Ethene is formed.



- (iii) 3° alcohol reacts with KMnO_4 at high temperature to give carboxylic acid having lesser number of carbon atoms.

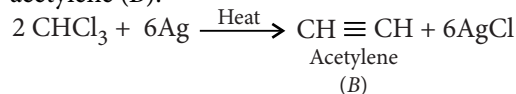


22. The sweet smelling organic compound 'A' is chloroform (CHCl_3). Its chemical reactions are as follows :

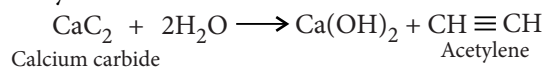


Phosgene is a highly poisonous gas.

The action of chloroform with silver powder gives acetylene (B).



Calcium carbide when reacted with water also gives acetylene.



23. (i) The Government is concerned about the well being of people and takes responsibility for the same.

- (ii) No, production of alcohol should not be banned as :

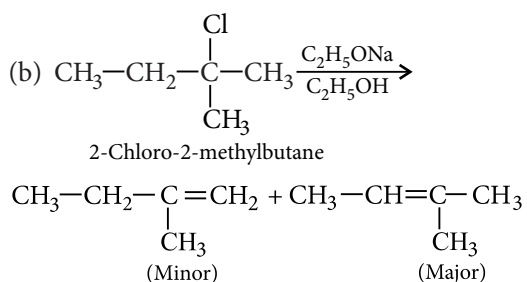
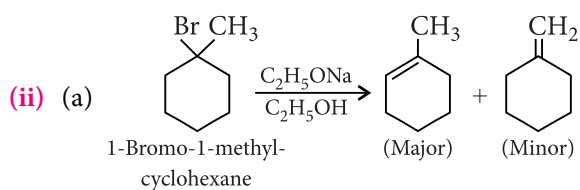
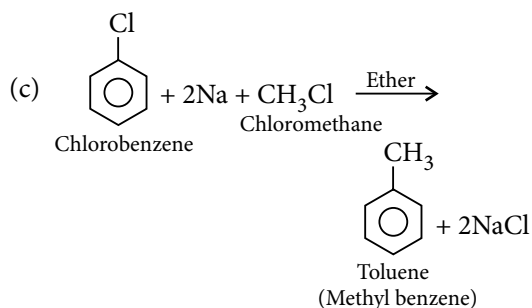
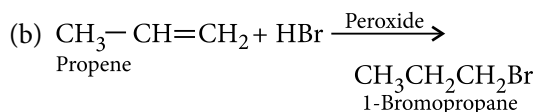
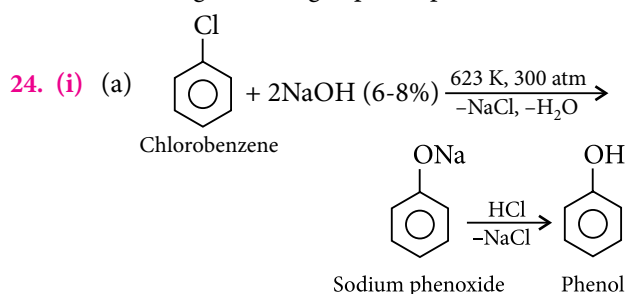
(a) It is an important solvent for paints, lacquers, dyes, perfumes etc.

(b) It is used as an antiseptic and disinfectant and can also be used in the manufacture of important chemicals such as ether, chloroform etc.

(iii) Industrial alcohol is cheaper and to prevent workers from drinking this alcohol, it is denatured and hence rendered unfit for drinking.

(iv) We can spread awareness by

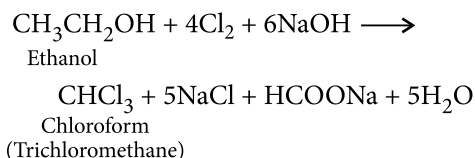
- (a) showing programmes like skits, dramas, plays etc. to alcoholics, which will highlight the bad effects of alcohol.
 (b) slogan writing at public places.



OR

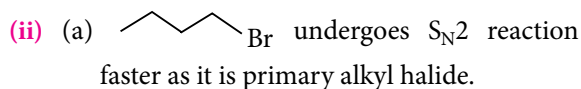
(i) Preparation of chloroform (CHCl₃) :

It can be prepared by the action of sodium hypochlorite (Cl₂ + NaOH) on ethanol.

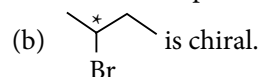


Uses: Chloroform is used

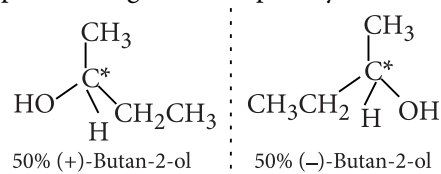
- as a solvent for fats, waxes, resins etc.
- as a laboratory reagent.
- as a preservative for anatomical specimens.
- in medicines.

(ii) (a) 

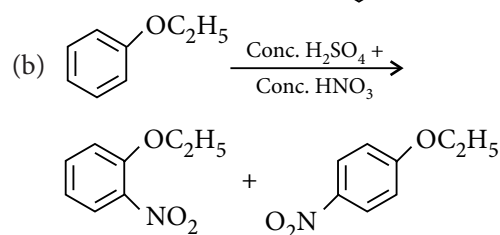
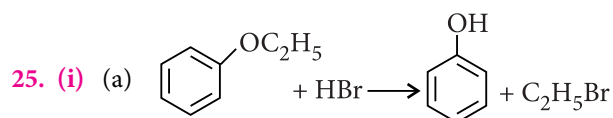
1-Bromobutane undergoes S_N2 reaction faster as it is primary alkyl halide.

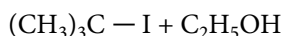
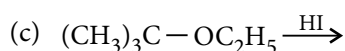
(b)  is chiral.

(iii) (a) (±)-Butan-2-ol is optically inactive because it exists in two enantiomeric forms which are non-superimposable mirror images of each other. Both the isomers are present in equal amounts therefore, it does not rotate the plane of polarized light and is optically inactive.

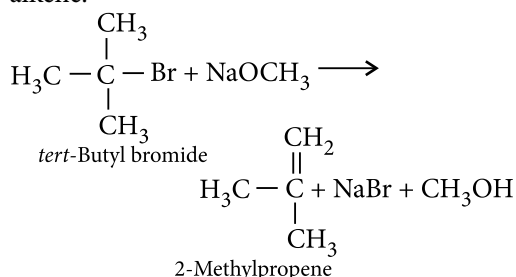


(b) Since I⁻ ion is a better leaving group than Br⁻ ion therefore, CH₃CH₂I reacts faster than CH₃CH₂Br in S_N2 reaction with OH⁻ ion.





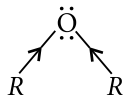
- (ii) The main limitation of Williamson ether synthesis lies in its unemployability for preparation of unsymmetrical ethers where the compound contains secondary or tertiary alkyl groups. e.g., reaction between *tert*-butyl bromide and sodium methoxide yields an alkene.



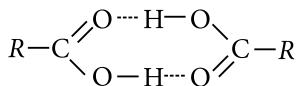
This is because the competing elimination reaction predominates over S_N2 and alkene is formed.

OR

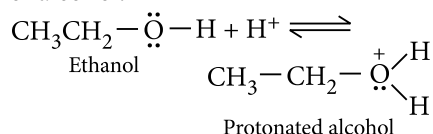
- (i) (a) Due to the bent structure of ethers and polarity of C—O bond, all ethers have a net dipole moment.



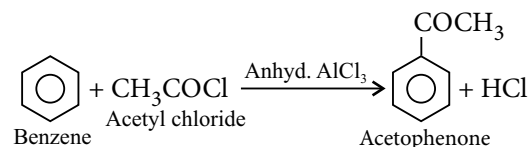
- (b) Carboxylic acids form dimeric structures due to intermolecular hydrogen bonding. The effective mass of the acid becomes double of the actual mass. Hence, carboxylic acids have higher boiling points than alcohols of comparable molecular masses.



- (ii) (a) Protonation : In the presence of a strong mineral acid an alcohol molecule combines with proton (H^+ ion) to form oxonium salt. This is called protonation of alcohol.

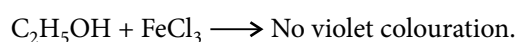
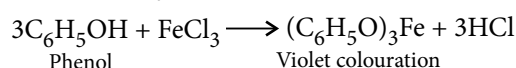


- (b) Acetylation : Introduction of acetyl group into an aromatic compound in the presence of a Lewis acid like anhydrous $AlCl_3$ is called acetylation.



26. (i) (a) Distinction between ethanol and phenol :

$FeCl_3$ test : Phenol gives a violet colouration with neutral $FeCl_3$ solution while ethanol does not.



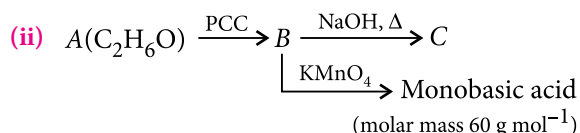
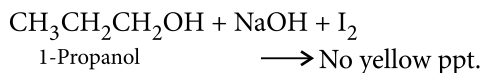
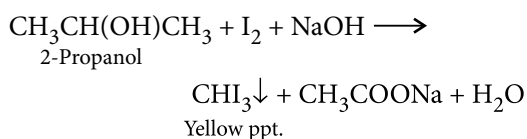
- (b) Distinction between 1-propanol and 2-propanol :

Iodoform test : When 2-propanol is warmed with sodium hypoiodite, it gives yellow precipitate of iodoform while 1-propanol does not respond to iodoform test.

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General formula of monocarboxylic acid is

$$\text{C}_n\text{H}_{2n}\text{O}_2 = 60 \text{ molar mass (given)}$$

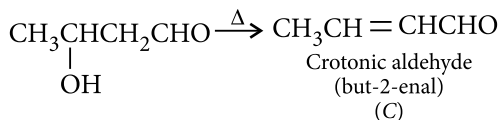
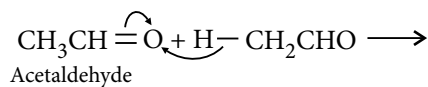
$$12n + 2n + 32 = 60$$

$$14n = 28 \Rightarrow n = 2$$

Thus, acid is $\text{C}_2\text{H}_4\text{O}_2$ i.e., CH_3COOH .

CH_3COOH is obtained by oxidation of 'B' with KMnO_4 . Thus, 'B' is CH_3CHO (acetaldehyde). 'B' is obtained by PCC oxidation of 'A' hence, 'A' is $\text{CH}_3\text{CH}_2\text{OH}$ (ethyl alcohol).

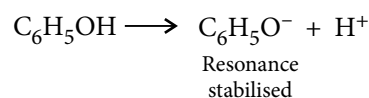
'B' with NaOH undergoes aldol condensation.



OR

(i) The solvents like CS_2 and CHCl_3 are of low polarity which make the medium inert and only monobromophenol is formed. When it is treated with bromine water it gives tribromophenol because the high polarity of water molecule ionises phenol to phenoxide ion which increases electron density on benzene ring.

(ii) The phenoxide ion formed after loss of proton from phenol is resonance stabilised and thus, phenol loses H^+ ion to show acidic character.



On the other hand, alkoxide ion formed from hexanol shows no such resonance stabilisation and is unstable.

(iii) In substituted phenols, the presence of electron releasing group decreases the acidic strength of phenol. This effect is more pronounced when such a group is present at *ortho* and *para*-positions. It is due to the increased negative charge in phenoxide ion. Thus *m*-aminophenol is stronger acid than *o*-aminophenol.

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EXAMINER'S MIND CLASS XII



The questions given in this column have been prepared strictly on the basis of NCERT Chemistry for Class XII. This year JEE (Main & Advanced)/AIPMT/AIIMS/other PMTs have drawn their papers heavily from NCERT books.

COORDINATION COMPOUNDS | HALOALKANES AND HALOARENES

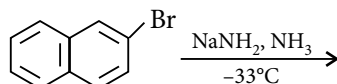
SECTION - I

Only One Option Correct Type

This section contains 20 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

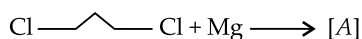
1. When 0.1 mol of $\text{CoCl}_3(\text{NH}_3)_5$ is treated with excess of AgNO_3 , 0.2 mol of AgCl is obtained. The conductivity of solution will correspond to
 (a) 1 : 3 electrolyte (b) 1 : 2 electrolyte
 (c) 1 : 1 electrolyte (d) 3 : 1 electrolyte.

2. How many isomeric naphthylamines are expected in the following reaction?



- (a) Two (b) One
 (c) Four (d) Three
3. How many EDTA (ethylenediaminetetraacetic acid) molecules are required to make an octahedral complex with Ca^{2+} ion?
 (a) Six (b) Three
 (c) One (d) Two

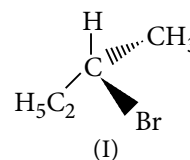
4. What is the product [A] in the following reaction?



- (a) (b) $\text{Cl}-\text{Mg}-\text{C}_6\text{H}_5-\text{Mg}-\text{Cl}$
 (c) Both (a) and (b) (d) None of these
5. Aqueous solution of nickel sulphate on treating with pyridine and then adding a solution of sodium nitrate gives dark blue crystals of

- (a) $[\text{Ni}(\text{py})_4]\text{SO}_4$
 (b) $[\text{Ni}(\text{py})_2(\text{NO}_2)_2]$
 (c) $[\text{Ni}(\text{py})_4](\text{NO}_2)_2$
 (d) $[\text{Ni}(\text{py})_3(\text{NO}_2)_2]\text{SO}_4$

6. Which of the following structures is enantiomeric with the molecule (I) given below :

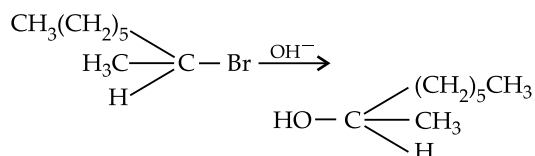


- (a) (b)
 (c) (d)

7. The stability constants of the complexes formed by a metal ion (M^{2+}) with NH_3 , CN^- , H_2O and *en* are of the order 10^{11} , 10^{27} , 10^{15} , and 10^8 respectively. This shows
 (a) *en* is the strongest ligand
 (b) CN^- is the strongest ligand
 (c) H_2O is the strongest ligand
 (d) all the ligands are equally strong.
8. Although hexafluoroethane (C_2F_6 , b.pt. -79°C) and ethane (C_2H_6 , b.pt. -89°C) differ very much in their molecular weights, their boiling points differ only by 10°C . This is due to
 (a) low polarizability of F
 (b) nearly similar size of F and H
 (c) high polarizability of F
 (d) both (a) and (b)

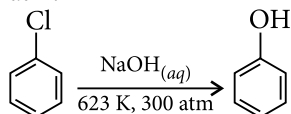
9. Which is not true about the metal-ligand complex?
- Larger the ligand, more stable is the metal-ligand complex.
 - Highly charged ligand forms stronger bonds.
 - Larger the permanent dipole moment of the ligand, more stable is the bond.
 - Greater the ionisation potential of central metal, stronger is the bond.

10. The reaction described below is

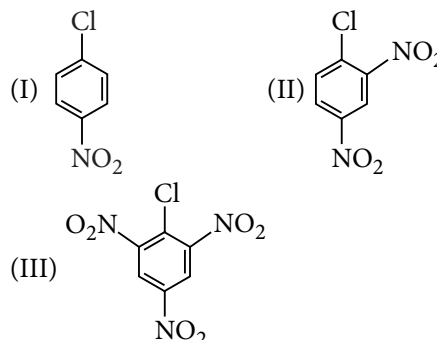


- $\text{S}_{\text{E}}1$
 - $\text{S}_{\text{N}}2$
 - $\text{S}_{\text{N}}1$
 - $\text{S}_{\text{E}}2$
11. Which of the following statements is not correct?
- Pt^{2+} compounds are more stable than Ni^{2+} .
 - Pt^{4+} compounds are more stable than Ni^{4+} .
 - K_2PtCl_6 is known compound but K_2NiCl_6 is not known
 - None of these.
12. Bottles containing $\text{C}_6\text{H}_5\text{I}$ and $\text{C}_6\text{H}_5\text{CH}_2\text{I}$ lost their original labels. They were labelled A and B for testing. A and B were separately taken in test tubes and boiled with NaOH solution. The end solution in each tube was made acidic with dilute HNO_3 and some AgNO_3 solution was added. Solution B gave yellow precipitate. Which one of the following statements is true for the experiment?
- Addition of HNO_3 was unnecessary
 - A was $\text{C}_6\text{H}_5\text{I}$
 - A was $\text{C}_6\text{H}_5\text{CH}_2\text{I}$
 - B was $\text{C}_6\text{H}_5\text{I}$
13. In solid $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ copper is coordinated to
- 4 water molecules
 - 5 water molecules
 - 1 sulphate molecule
 - 1 water molecule.

14. Chlorobenzene can be converted into phenol by heating in aqueous sodium hydroxide solution at a temperature of 623 K and a pressure of 300 atm.



What will be the order of reactivity of following compounds towards the above substitution reaction?



- (III) > (II) > (I)
- (II) > (III) > (I)
- (I) > (II) > (III)
- (I) > (III) > (II)

15. The correct IUPAC name of the compound $[\text{Cr}(\text{NH}_3)_5(\text{NCS})][\text{ZnCl}_4]$, is

- pentaammineisothiocyanatochromium(III) tetrachloridozincate(II)
- pentaammineisothiocyanatozinc chloridochromate(III)
- pentaammineisothiocyanatochromate(II)
- isothiocyanatopentaamminechromium(II) zincchlorido(IV).

16. Predict the major products, P_1 and P_2 in the following two reactions.

- $\text{Me}_2\text{CHBr} \xrightarrow{\text{CH}_3\text{COO}^-} P_1$
 - $\text{CH}_3(\text{CH}_2)_{15}\text{CH}_2\text{CH}_2\text{Br} \xrightarrow{(\text{CH}_3)_3\text{CO}^-} P_2$
- P_1 is $\text{Me}_2\text{CHOCOCH}_3$, P_2 is $\text{CH}_3(\text{CH}_2)_{15}\text{CH}_2\text{CH}_2\text{OCMe}_3$
 - P_1 is $\text{Me}_2\text{CHOCOCH}_3$, P_2 is $\text{CH}_3(\text{CH}_2)_{15}\text{CH}=\text{CH}_2$
 - P_1 is $\text{CH}_3\text{CH}=\text{CH}_2$, P_2 is $\text{CH}_3(\text{CH}_2)_{15}\text{CH}_2\text{CH}_2\text{OCMe}_3$
 - P_1 is $\text{CH}_3\text{CH}=\text{CH}_2$, P_2 is $\text{CH}_3(\text{CH}_2)_{15}\text{CH}=\text{CH}_2$

17. The EAN of metal atoms in $\text{Fe}(\text{NO})_2(\text{CO})_2$ and $\text{Co}_2(\text{CO})_8$ respectively are

- 34, 35
- 34, 36
- 36, 36
- 36, 35

18. Which set of reagents will produce CCl_2F_2 ?

- $\text{C} + \text{F}_2 + \text{Cl}_2 \longrightarrow$
- $\text{CH}_3\text{Cl} + \text{F}_2 \longrightarrow$
- $\text{CCl}_4 + \text{SbF}_3 \xrightarrow{\text{SbCl}_5}$
- $\text{CCl}_4 + \text{F}_2 \longrightarrow$

19. $[\text{Ni}(\text{NH}_3)_2]^{2+} \xrightarrow{\text{Conc. HCl}} \text{'A'} + \text{'B'}$
The molecular formula of both 'A' and 'B' is same. 'A' can be converted to 'B' by boiling in dil. HCl. 'A' on reaction with oxalic acid yields a complex having the formula $\text{Ni}(\text{NH}_3)_2(\text{C}_2\text{O}_4)$ but 'B' does not.

From the above information we can say that

- (a) 'A' is square planar but 'B' is tetrahedral
(b) 'A' and 'B' both are tetrahedral, 'A' is optically active compound whereas 'B' is optically inactive
(c) both 'A' and 'B' are square planar, 'A' is *trans*-isomer and 'B' is *cis*-isomer
(d) both 'A' and 'B' are square planar, 'A' is *cis*-isomer and 'B' is *trans*-isomer.
20. Which of the following order is not correct?
(a) $\text{MeBr} > \text{Me}_2\text{CHBr} > \text{Me}_3\text{CBr} > \text{Et}_3\text{CBr}(\text{S}_{\text{N}}2)$
(b) $\text{Me}_3\text{CBr} > \text{Me}_2\text{CHBr} > \text{Me}_2\text{CHCH}_2\text{Br} > \text{MeCH}_2\text{CH}_2\text{CH}_2\text{Br}(\text{E}_2)$
(c) $\text{PhCH}_2\text{Br} > \text{PhCHBrMe} > \text{PhCBrMe}_2 > \text{PhCBrMePh}(\text{S}_{\text{N}}1)$
(d) $\text{MeI} > \text{MeBr} > \text{MeCl} > \text{MeF}(\text{S}_{\text{N}}2)$

SECTION - II

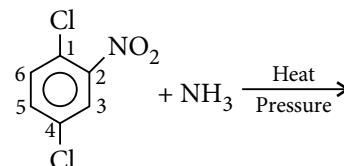
One or More Options Correct Type

This section contains 5 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which ONE or MORE are correct.

21. In which of the following cases, the complex ion formed will migrate towards the anode under the electric field?
(a) Excess of aqueous KCN added to CdSO_4
(b) Aqueous solution of CuSO_4 containing excess of NH_3
(c) AgBr added to hypo solution in excess
(d) A solution of AgNO_3 in aqueous KCN
22. Which reagent will be used for the following reaction?
 $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \longrightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl} + \text{CH}_3\text{CH}_2\text{CHClCH}_3$
(a) $\text{Cl}_2/\text{UV light}$
(b) $\text{NaCl} + \text{H}_2\text{SO}_4$
(c) Cl_2 gas in dark
(d) Cl_2 gas in the presence of iron in dark.
23. Which of the following statements is/are correct?
(a) The complex CuCl_4^{2-} exists, but CuI_4^{2-} does not.

- (b) A bidentate chelating ligand replaces two monodentate ligands located in *cis* positions of square planar complex.
(c) A singly bidentate chelating ligand replaces two monodentate ligands located in *trans* positions of square planar complex.
(d) $[\text{Fe}(\text{CN})_6]^{3-}$ is more stable than $[\text{Fe}(\text{CN})_6]^{4-}$

24. Which of the following statement is false regarding following reaction?



- (a) No reaction is possible because $-\text{Cl}$ is present on benzene ring.
(b) A nucleophilic substitution will take place in which both $-\text{Cl}$ will be replaced by two $-\text{NH}_2$ groups.
(c) A nucleophilic substitution will take place in which only $-\text{Cl}$ attached on C1 will be replaced by $-\text{NH}_2$.
(d) A nucleophilic substitution will take place in which only $-\text{Cl}$ attached on C₄ will be replaced by $-\text{NH}_2$.

25. Mn^{2+} forms different complexes with Br^- ions having magnetic moment value 5.92 BM. The correct formula and geometry of the complex, is

- (a) $[\text{MnBr}_4]^{2-}$; tetrahedral
(b) $[\text{MnBr}_4]^{2-}$; square planar
(c) $[\text{MnBr}_6]^{4-}$; octahedral
(d) $[\text{MnBr}_5]^{3-}$; trigonal planar.

SECTION - III

Paragraph Type

This section contains 2 paragraphs each describing theory, experiment, data, etc. Six questions relate to two paragraphs with three questions on each paragraph. Each question of a paragraph has only one correct answer among the four choices (a), (b), (c) and (d).

Paragraph for Questions 26 to 28

The splitting of the degenerate *d*-orbitals levels due to the presence of ligands in a definite geometry is termed as crystal field splitting and the energy separation is denoted by Δ_o . The crystal field splitting depends upon the field produced by the ligand and charge on the metal ion.

26. Given the following data about the absorption maxima of several complex ions, what is the order of Δ_o for these ions?

Compound	λ_{\max}
$[\text{CrCl}_6]^{3-}$	758
$[\text{Cr}(\text{NH}_3)_6]^{3+}$	465
$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$	694

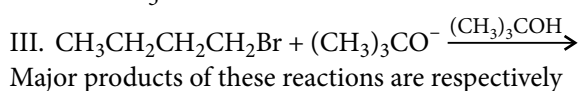
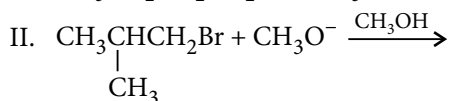
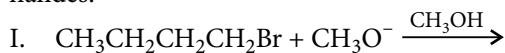
- (a) $\Delta_o[\text{CrCl}_6]^{3-} < \Delta_o[\text{Cr}(\text{NH}_3)_6]^{3+} < \Delta_o[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$
 (b) $\Delta_o[\text{Cr}(\text{NH}_3)_6]^{3+} < \Delta_o[\text{Cr}(\text{H}_2\text{O})_6]^{3+} < \Delta_o[\text{CrCl}_6]^{3-}$
 (c) $\Delta_o[\text{CrCl}_6]^{3-} < \Delta_o[\text{Cr}(\text{H}_2\text{O})_6]^{3+} < \Delta_o[\text{Cr}(\text{NH}_3)_6]^{3+}$
 (d) $\Delta_o[\text{Cr}(\text{H}_2\text{O})_6]^{3+} < \Delta_o[\text{Cr}(\text{NH}_3)_6]^{3+} < \Delta_o[\text{CrCl}_6]^{3-}$
27. Predict the order of Δ_o for the following compounds:
 I. $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$
 II. $[\text{Fe}(\text{CN})_2(\text{H}_2\text{O})_4]$
 III. $[\text{Fe}(\text{CN})_4(\text{H}_2\text{O})_2]^{2-}$
 (a) $\Delta_o(\text{I}) < \Delta_o(\text{II}) < \Delta_o(\text{III})$
 (b) $\Delta_o(\text{II}) < \Delta_o(\text{I}) < \Delta_o(\text{III})$
 (c) $\Delta_o(\text{III}) < \Delta_o(\text{II}) < \Delta_o(\text{I})$
 (d) $\Delta_o(\text{II}) < \Delta_o(\text{III}) < \Delta_o(\text{I})$

28. What is the most likely configuration of the cobalt d -electrons for the species CoCl_6^{3-} and $\text{Co}(\text{NO}_2)_6^{3-}$?
 (a) CoCl_6^{3-} : low spin ; $\text{Co}(\text{NO}_2)_6^{3-}$: low spin
 (b) CoCl_6^{3-} : high spin ; $\text{Co}(\text{NO}_2)_6^{3-}$: low spin
 (c) CoCl_6^{3-} : low spin ; $\text{Co}(\text{NO}_2)_6^{3-}$: high spin
 (d) CoCl_6^{3-} : high spin ; $\text{Co}(\text{NO}_2)_6^{3-}$: high spin

Paragraph for Questions 29 to 31

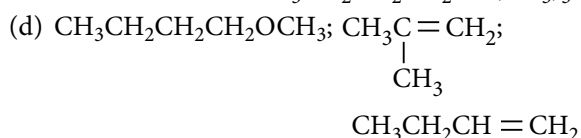
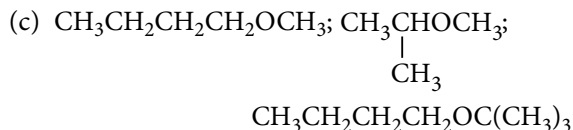
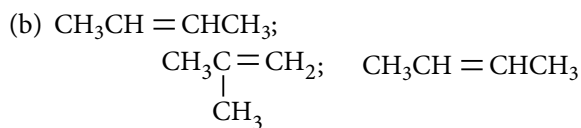
An alkyl halide with α -hydrogen atoms when reacted with a base or a nucleophile has two competing routes substitution ($\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$) and elimination. Which route will be taken up depends upon the nature of alkyl halide, strength and size of base/nucleophile and reaction conditions.

29. Consider the following reactions of primary alkyl halides.

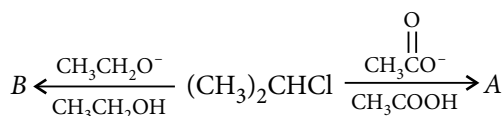


Major products of these reactions are respectively

- (a) $\text{CH}_3\text{CH}_2\text{CH} = \text{CH}_2$;
 $\text{CH}_3\underset{\text{CH}_3}{\text{C}} = \text{CH}_2$; $\text{CH}_3\text{CH}_2\text{CH} = \text{CH}_2$

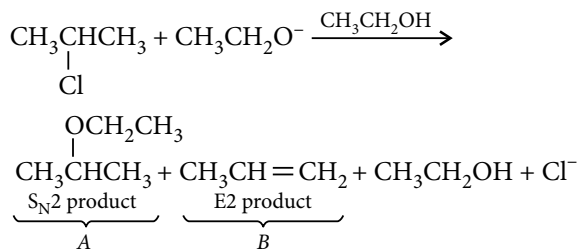


30. Consider the following $\text{S}_{\text{N}}2/\text{E}2$ reactions on 2-chloropropane.

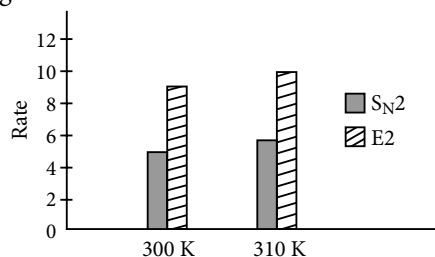


Select the correct alternate(s).

- (a) Major products A and B are the substitution products.
 (b) Major products A and B are the elimination products.
 (c) Major product A is the substitution product and major product B is the elimination product.
 (d) Major product A is the elimination product and major product B is the substitution product.
31. Consider the following reaction,



The reaction is studied at 300 K and 310 K. Rates of the formation of A and B have been given below in the figure.



- I. Rate of formation of S_N2 product as well as of E_2 product increases with increase in temperature.
 II. E_2 reaction is more favoured than S_N2 reaction on increasing temperature.
 III. Temperature coefficient of the elimination reaction in the given temperature range is about 1.05.
 IV. Rate constant is independent of temperature.

Select the correct statement(s) based on the above figure.

- (a) I and II (b) II and III
 (c) I, II and III (d) IV only

SECTION - IV

Matching List Type

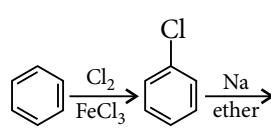
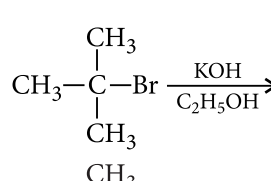
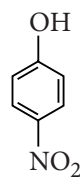
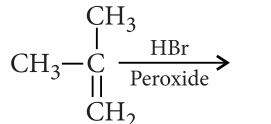
This section contains 3 multiple choice questions. Each question has matching lists. The codes for the lists have choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

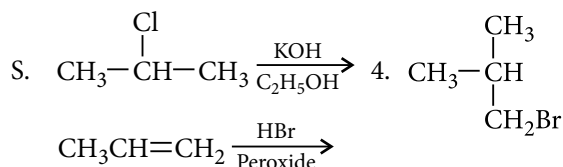
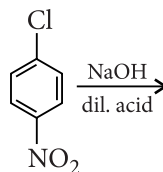
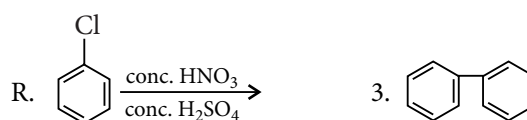
32. Match the ions in List I with their geometries and magnetic moments in List II and select the correct answer using the code given below the lists :

List I		List II	
P. $[\text{Ag}(\text{CN})_2]^-$		1. Square planar and 1.73 BM	
Q. $[\text{Cu}(\text{CN})_4]^{3-}$		2. Linear and zero	
R. $[\text{Cu}(\text{NH}_3)_4]^{2+}$		3. Octahedral and zero	
S. $[\text{Fe}(\text{CN})_6]^{4-}$		4. Tetrahedral and zero	

P	Q	R	S
(a) 1	2	3	4
(b) 2	4	1	3
(c) 4	2	3	1
(d) 3	4	2	1

33. Match the List I with List II and select the correct answer using the code given below the lists :

List I		List II	
P. 		1. $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$	
Q. 		2. 	
			



	P	Q	R	S
(a)	4	2	1	3
(b)	3	4	2	1
(c)	2	1	3	4
(d)	1	3	4	2

34. Match List-I with List-II and select the correct answer using the code given below the lists :

List I		List II	
(Metal ion configuration in strong field ligand)		(CFSE, Δ_o value)	
P. d^4		1. -1.6	
Q. d^5		2. -1.8	
R. d^6		3. -2.0	
S. d^7		4. -2.4	

P	Q	R	S
(a) 1	2	3	4
(b) 4	3	1	2
(c) 1	3	4	2
(d) 1	4	3	1

SECTION - V

Assertion Reason Type

In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as :

- (a) If both assertion and reason are true and reason is the correct explanation of assertion.
 (b) If both assertion and reason are true but reason is not the correct explanation of assertion.
 (c) If assertion is true but reason is false.
 (d) If both assertion and reason are false.

35. **Assertion:** S_N2 reaction proceeds with racemisation while S_N1 reaction proceeds with complete stereochemical inversion.

Reason: S_N2 is two steps reaction while S_N1 is one step reaction.

36. **Assertion:** Tetrahedral complexes having two different types of unidentate ligands coordinated with central metal ion will show geometrical isomerism.

Reason: Geometrical isomerism arises in homoleptic complexes due to different possible geometric arrangements of the ligands.

37. **Assertion:** An optically active aryl halide does not undergo S_N2 reaction with an aqueous solution of KOH.

Reason: S_N2 reactions always proceed with inversion of configuration.

38. **Assertion:** The ligands nitro and nitrito are called ambidentate ligands.

Reason: These ligands give linkage isomers.

39. **Assertion:** Chlorination of ethylbenzene with Cl, in presence of heat and light mainly yields 1-chloro-1-phenylethane.

Reason: The reaction occurs through intermediate formation of the radical, $C_6H_5\dot{C}HCH_3$.

40. **Assertion:** Toxic metal ions are removed by the chelating ligands.

Reason: Chelate complexes tend to be more stable.

SECTION - VI

Integer Value Correct Type

This section contains 10 questions. The answer to each question is a single digit integer, ranging from 0 to 9 (both inclusive).

41. A hydrocarbon (X) having molecular weight 70 gives a single monochloride but three dichlorides on chlorination in the presence of ultraviolet light. The number of C-atoms in hydrocarbon (X) are

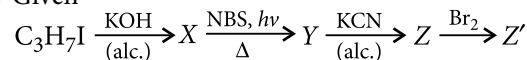
42. The number of chloride ion(s) produced by complex tetraamminedichloroplatinum(IV) chloride in an aqueous solution is/are

43. From the following compounds the number of alkenes which on addition of HBr would give the same product in the presence or absence of peroxide is

Propene, 1-butene, 2-butene, 2-methylpropene, 3-methyl-1-butene, 2,3-dimethyl-1-butene, 2-pentene, 1-pentene, 4-methyl-2-pentene.

44. If chloride ions satisfy all the primary valencies of cobalt then, the total number of ions formed due to ionisation of the compound $CoCl_3 \cdot 6H_2O$ is

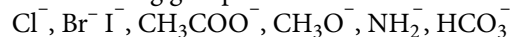
45. Given



No. of carbon atoms in the product Z' is

46. In the coordination compound, $K_4[Ni(CN)_4]$, the oxidation state of nickel is

47. From the following number of anions which act as better leaving groups than OH^- is



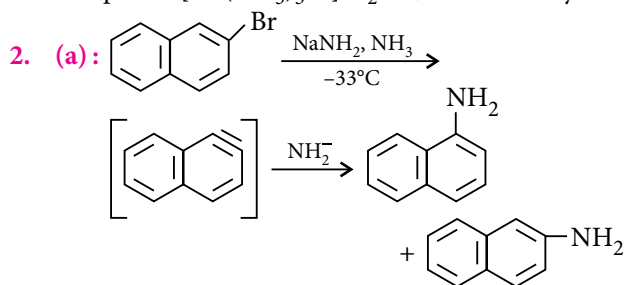
48. Among the following, number of reagents required to distinguish chlorobenzene from chlorocyclohexane is $AgNO_3/C_2H_5OH$, Br_2/CCl_4 , $[Ag(NH_3)_2]OH$, $AgCN/HNO_3$, Na fusion/ $AgNO_3$

49. 9.65 C of electric current is passed through fused anhydrous magnesium chloride. The magnesium metal thus obtained is completely converted into a Grignard reagent. The $x \times 10^{-5}$ mol of the Grignard reagent were obtained. Here value of x is

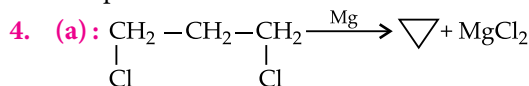
50. The total isomers formed by $[Co(en)_2Cl_2]Br$ are

SOLUTIONS

1. (b): 0.2 mol of AgCl is obtained when 0.1 mol of $CoCl_3(NH_3)_5$ is treated with excess of $AgNO_3$ which shows that one molecule of the complex gives two Cl^- ions in solution. Thus, the formula of the complex is $[Co(NH_3)_5Cl]Cl_2$ i.e., 1 : 2 electrolyte.



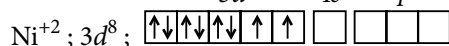
3. (c): EDTA being hexadentate ligand, only one molecule is sufficient to make an octahedral complex with Ca^{2+} ion.



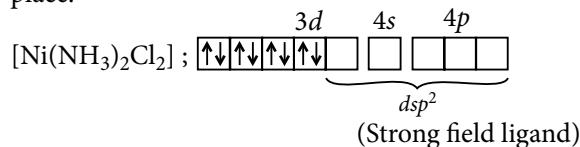
α and γ -dihalogen derivatives of an alkane on treatment with Mg give cycloalkanes.

5. (c): $\text{NiSO}_4 + 4\text{py} + 2\text{NaNO}_3 \longrightarrow \text{Na}_2\text{SO}_4 + [\text{Ni}(\text{py})_4](\text{NO}_2)_2$
Blue
6. (a): Compound (a) is enantiomer of compound (I) because the configuration of two groups, *i.e.*, CH_3 and C_2H_5 in them is reversed at the chiral carbon.
7. (b): Higher the value of stability constant, stronger will be the ligand. Thus CN^- is the strongest ligand as the value of stability constant of the complex formed by M^{2+} with CN^- is 10^{27} .
8. (d): Small difference in boiling points of C_2F_6 and C_2H_6 is due to the fact that
(i) the F atom is only slightly larger than H, and
(ii) F has low polarizability.
9. (a): Larger the ligand, lesser is the stability of metal ligand complex.
10. (b): In case of optically active alkyl halides, the product formed as a result of $\text{S}_{\text{N}}2$ mechanism has the inverted configuration as compared to the reactant.
11. (a): $IE_1 + IE_2$ for Ni = $2.49 \times 10^3 \text{ kJ mol}^{-1}$;
 $IE_1 + IE_2 + IE_3 + IE_4$ for Ni = $11.29 \times 10^3 \text{ kJ mol}^{-1}$;
 $IE_1 + IE_2$ for Pt = $2.66 \times 10^3 \text{ kJ mol}^{-1}$;
 $IE_1 + IE_2 + IE_3 + IE_4$ for Pt = $9.36 \times 10^3 \text{ kJ mol}^{-1}$
12. (b): Aliphatic halides respond to the given reaction.
13. (a): Four water molecules are coordinated to copper.
- $$\left[\begin{array}{c} \text{H}_2\text{O} \quad \text{OH}_2 \\ \diagdown \quad \diagup \\ \text{Cu} \\ \diagup \quad \diagdown \\ \text{H}_2\text{O} \quad \text{OH}_2 \end{array} \right]^{2+} \left[\begin{array}{c} \text{H} \cdots \text{O} \\ \diagdown \quad \diagup \\ \text{S} \\ \diagup \quad \diagdown \\ \text{H} \cdots \text{O} \end{array} \right]^{2-}$$
14. (a): The presence of an electron withdrawing group ($-\text{NO}_2$) at *ortho* and *para*-positions increases the reactivity of haloarenes towards nucleophilic substitution reaction.
15. (a): Pentaammineisothiocyanatochromium(III) tetrachloridozincate(II).
16. (b): (i) Weak bases like CH_3COO^- , Cl^- etc. favours substitution rather than elimination.
(ii) Sterically hindered base favours elimination reaction, no matter the alkyl halide is primary.
17. (c): $[\text{Fe}(\text{NO})_2(\text{CO})_2]$: 26 electrons of Fe + 6 electrons from 2NO molecules and 4 electrons from 2CO molecules = 36
 $\text{Co}_2(\text{CO})_8$: 27 electrons of Co + 1 electron shared from another Co atom + 8 electrons from 4 CO molecules = 36

18. (c): $3\text{CCl}_4 + 2\text{SbF}_3 \xrightarrow{\text{SbCl}_5} 3\text{CCl}_2\text{F}_2 + 2\text{SbCl}_3$
Freon-12
19. (d): $[\text{Ni}(\text{NH}_3)_2]^{2+} \xrightarrow{\text{Conc. HCl}} [\text{Ni}(\text{NH}_3)_2\text{Cl}_2] + [\text{Ni}(\text{NH}_3)_2\text{Cl}_2]$
In this complex the oxidation state of Ni is +2.

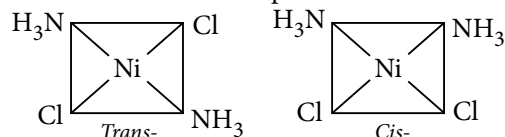


In complex $[\text{Ni}(\text{NH}_3)_2\text{Cl}_2]$, dsp^2 hybridisation takes place.



Thus the complex is square planar.

The two isomers of this complex are



The *cis*-isomer can easily form a chelate ring with oxalate group.

The *cis*-isomers can be converted to *trans*-isomer on boiling with dil. HCl.

Hence 'A' is *cis*-isomer and 'B' is *trans*-isomer.

20. (c): More the stability of intermediate carbonium ion, more is the chance of $\text{S}_{\text{N}}1$ mechanism. The intermediates obtained will be $\text{Ph}\overset{+}{\text{C}}\text{H}_2$ (i), $\text{Ph}\overset{+}{\text{C}}\text{H}-\text{Me}$ (ii), $\text{Ph}\overset{+}{\text{C}}-\text{Me}_2$ (iii), $\text{Ph}\overset{+}{\text{C}}\text{MePh}$ (iv). The stability is of the order $\text{iv} > \text{iii} > \text{ii} > \text{i}$.

21. (a, c, d):

- (a) $\text{CdSO}_4 + 4\text{KCN} \longrightarrow \text{K}_2[\text{Cd}(\text{CN})_4] + \text{K}_2\text{SO}_4$;
Complex ion: $[\text{Cd}(\text{CN})_4]^{2-}$
- (b) $\text{CuSO}_4 + 4\text{NH}_3 \longrightarrow [\text{Cu}(\text{NH}_3)_4]\text{SO}_4$;
Complex ion: $[\text{Cu}(\text{NH}_3)_4]^{2+}$
- (c) $\text{AgBr} + 2\text{Na}_2\text{S}_2\text{O}_3 \longrightarrow \text{Na}_3[\text{Ag}(\text{S}_2\text{O}_3)_2] + \text{NaBr}$;
Complex ion: $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$
- (d) $\text{AgNO}_3 + 2\text{KCN} \longrightarrow \text{K}[\text{Ag}(\text{CN})_2] + \text{KNO}_3$;
Complex ion: $[\text{Ag}(\text{CN})_2]^-$

22. (a)

23. (a, b, d):

- (a) Cu^{2+} is reduced to Cu^+ by I^- but not by Cl^- .
 $\text{Cu}^{2+} + \text{I}^- \longrightarrow \text{CuI}$; $\text{CuI} + 3\text{I}^- \longrightarrow [\text{CuI}_4]^{3-}$
- (c) The *trans* positions are too distant for a bidentate ligand to span.
- (d) Fe (III) in $[\text{Fe}(\text{CN})_6]^{3-}$ has greater charge density than Fe(II) in $[\text{Fe}(\text{CN})_6]^{4-}$ hence the former has greater stability than the latter.

24. (a, b, d): The $-\text{Cl}$ group present in the *o*- and *p*-positions to the electron-withdrawing group is activated towards nucleophilic substitution, hence, only $-\text{Cl}$ present on the *o*- and/or *p*-position to the $-\text{NO}_2$ group will be replaced.

25. (a, c)

26. (c): The value of splitting factor, Δ_o , is inversely related to the wavelength of maximum absorption,

$$\lambda_{\text{max}} \left(E = h\nu = \frac{hc}{\lambda} \right)$$

27. (a): The value of Δ_o for mixed ligands depends on the additive contribution of the ligand strengths. Since CN^- has greater ligand strength than H_2O , the strength increases as the number of CN^- ions increases.

28. (b): Weak field ligands (like Cl^-) giving low value of Δ_o form high spin octahedral complexes whereas strong field ligands (like NO_2^-) give rise to low spin (spin paired) complexes.

29. (d) 30. (c) 31. (c)

32. (b) 33. (b) 34. (c)

35. (d): $\text{S}_{\text{N}}2$ reaction proceeds with complete stereochemical inversion while $\text{S}_{\text{N}}1$ reaction proceeds with racemisation. $\text{S}_{\text{N}}2$ reaction is one step in which incoming nucleophile attacks from the side opposite to that of outgoing leaving group and hence inversion of configuration occurs.

36. (d): Tetrahedral complexes do not show geometrical isomerism because relative positions of the unidentate ligands attached to the central metal atom are same with respect to each other. This type of isomerism arises in heteroleptic complexes.

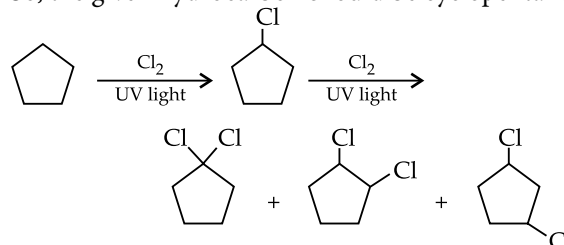
37. (b): Aryl halides do not undergo nucleophilic substitution under ordinary conditions. This is due to resonance, because of which the carbon-chlorine bond acquires partial double bond character, hence it becomes shorter and stronger and thus cannot be replaced by nucleophiles.

38. (b): When a monodentate ligand has two possible donor atoms and can attach in two different ways to the central metal atom, it is called ambidentate ligand.

39. (a): Chlorination of ethylbenzene with Cl_2 in presence of heat and light gives 1-chloro-1-phenylethane due to formation of more stable $\text{C}_6\text{H}_5\dot{\text{C}}\text{HCH}_3$ (2°) radical.

40. (a)

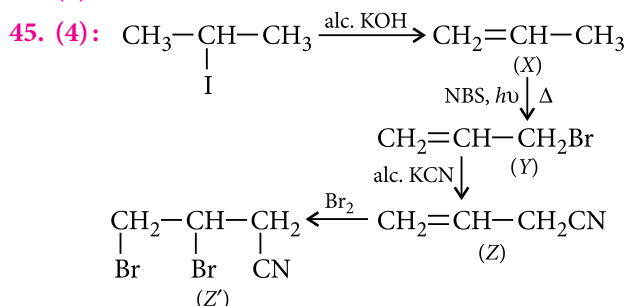
41. (5): Since the hydrocarbon (X) gives only a single monochloride, it implies that all the C—H bonds must be of the same type. So, the given hydrocarbon should be cyclopentane.



42. (2): The complex is $[\text{PtCl}_2(\text{NH}_3)_4]\text{Cl}_2$
Ions formed = $[\text{PtCl}_2(\text{NH}_3)_4]^{2+} + 2\text{Cl}^-$

43. (1): Only 2-butene is symmetrical and hence gives the same product in presence or absence of peroxide.

44. (4)

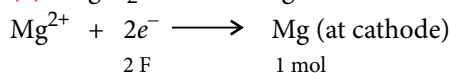


46. (0): $4(+1) + x + (-1) \times 4 = 0 \Rightarrow 4 + x - 4 = 0, x = 0$

47. (5)

48. (1): Only $\text{AgNO}_3/\text{C}_2\text{H}_5\text{OH}$ is used to distinguish chlorobenzene from chlorocyclohexane.

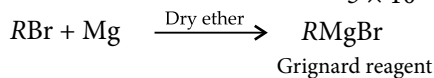
49. (5): $\text{MgCl}_2 \longrightarrow \text{Mg}^{2+} + 2\text{Cl}^-$



$\therefore 2 \text{ F}(2 \times 96500 \text{ C}) \text{ charge deposit} = 1 \text{ mol of Mg}$

$\therefore 9.65 \text{ C charge will deposit} = \frac{1 \times 9.65}{2 \times 96500}$

$= 5 \times 10^{-5} \text{ mol of Mg}$



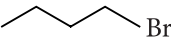
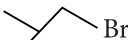

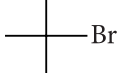
In order to prepare Grignard reagent, one mole of Mg is used per mole of reagent obtained. Thus, by $5 \times 10^{-5} \text{ mol of Mg}$, $5 \times 10^{-5} \text{ mol of Grignard reagent}$ are obtained.

50. (4): The complex $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Br}$ forms total four isomers—one is its ionisation isomer $[\text{Co}(\text{en})_2\text{ClBr}]\text{Cl}$, *cis* isomer (which exists in two optical isomers, dextro and laevo) and *trans* isomer.



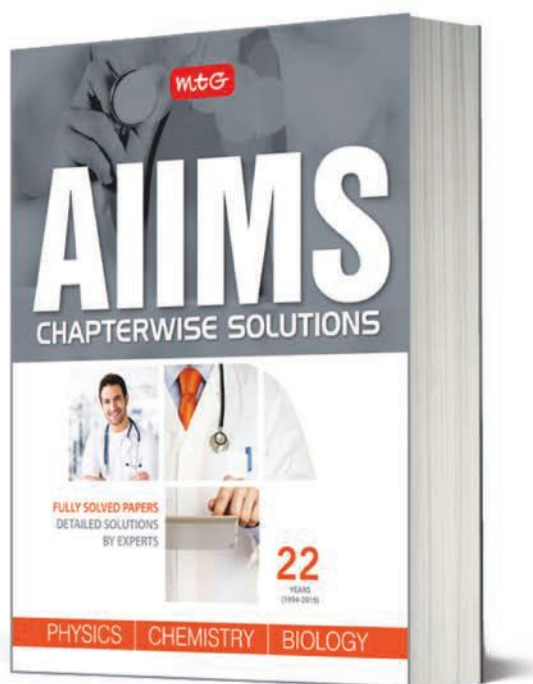
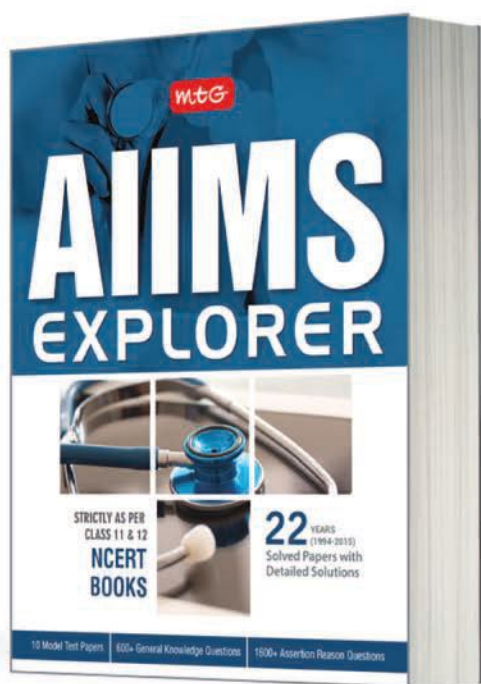
OLYMPIAD PROBLEMS



- When the value of the azimuthal quantum number is 3, the maximum and the minimum values of spin multiplicities are
 (a) 4, 3 (b) 8, 1
 (c) 1, 3 (d) 8, 2
- A sample contains 9.81 g Zn (at. mass 65), 1.8×10^{23} atoms of Cr and 0.6 g atoms of O_2 . The simple formula of this compound is
 (a) $ZnCrO_4$ (b) $ZnCr_2O_4$
 (c) Zn_2CrO_4 (d) $ZnCrO_3$
- The enthalpy of neutralisation of oxalic acid ($H_2C_2O_4$) by a strong base is $-25.4 \text{ kcal mol}^{-1}$. The enthalpy of neutralisation of the reaction between a strong acid and strong base is $-13.7 \text{ kcal equiv}^{-1}$. The enthalpy of dissociation of $H_2C_2O_4 \rightleftharpoons 2H^+ + C_2O_4^{2-}$ is
 (a) $1.0 \text{ kcal mol}^{-1}$ (b) $2.0 \text{ kcal mol}^{-1}$
 (c) $18.55 \text{ kcal mol}^{-1}$ (d) $11.7 \text{ kcal mol}^{-1}$
- Four moles of Cl_2 undergo disproportionation involving in all six moles of electrons. The number of moles of Cl_2 losing and gaining electrons are respectively
 (a) 1 and 3 (b) 3 and 1
 (c) 2 and 2 (d) none of these.
- Gadolinium (^{153}Gd), which has a half-life of 242 days, is used to detect osteoporosis. The percentage of ^{153}Gd left in a patient's system after 2 years will be
 (a) 33.0 (b) 25.0
 (c) 12.5 (d) 6.25
- In which of the following pairs both the species have similarity in bond angles between adjacent chlorine atoms?
 (a) PCl_3, PCl_4^+ (b) PCl_4^+, PCl_5
 (c) PCl_5, PCl_6^- (d) PCl_4^+, PCl_6^-
- Formation of free radical takes place with absorption of minimum energy in
 (a)  Br (b)  Br
 (c)  Br (d)  Br
- For $[Ni(CN)_4]^{2-}$ and $[Ni(CN)_4]^{4-}$, which of the following statements is incorrect?
 (a) They differ in hybridisation but magnetic properties are same.
 (b) Magnetic properties, hybridisation are different and both the complexes do not show optical isomerism.
 (c) They differ in shape, EAN value and both the complexes do not show geometrical isomerism.
 (d) They differ in number of atoms in a given plane and have same dipole moment.
- An element has atomic weight 39. Its electronic configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$. Choose the correct statement for this element.
 (a) It has large *I.E.*
 (b) It is a transition element.
 (c) It is isotonic with $^{36}_{18}Ar$.
 (d) Its stable oxide is M_2O .
- $CH_3-C(=O)-H$ and $Ph-C(=O)-H$ can be differentiated by
 (a) Tollens' reagent (b) Fehling's solution
 (c) Lucas reagent (d) Victor Meyer's test.



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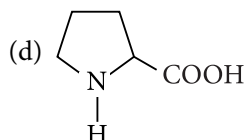
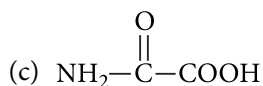
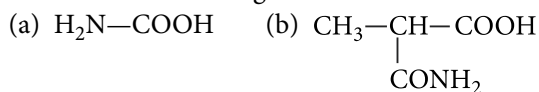
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11. Which of the following is an amino acid?



12. Which of the following order is incorrect for the indicated property?

- (a) $\text{BeO} < \text{MgO}$ - Basic strength
 (b) $\text{BeF}_2 < \text{MgF}_2 < \text{CaF}_2$ - Solubility
 $< \text{SrF}_2 < \text{BaF}_2$
 (c) $\text{SO}_2 > \text{SeO}_2 > \text{TeO}_2$ - Acidic strength
 (d) $\text{NaCl} > \text{KCl} > \text{RbCl}$ - Melting point
 $> \text{CsCl}$

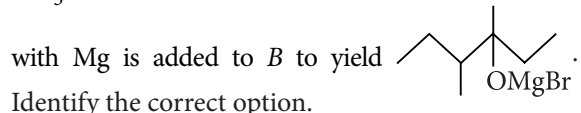
13. The pH of 0.1 M CH_3COOH (dissociation constant of acetic acid is 1.80×10^{-5} at 25°C) will be

- (a) 5 (b) 2.873
 (c) 1 (d) 0.18

14. In which of the following pairs of structures both, tetrahedral as well as octahedral holes are found?

- (a) *bcc* and *fcc* (b) *hcp* and simple cubic
 (c) *hcp* and *ccp* (d) *bcc* and *hcp*

15. Compound A is an optically active alcohol. Treatment with oxidising agent converts it to a ketone B. In a separate reaction A is treated with PBr_3 which converts it to C. C after reaction



Identify the correct option.

- I. A is 2-butanol
 II. A is 1-butanol
 III. C is 2-bromobutane
 IV. C is 1-bromobutane
 (a) I and IV (b) II and III
 (c) II and IV (d) I and III

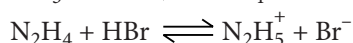
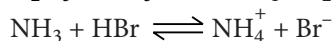
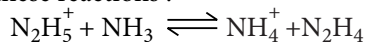
16. At CMC, the surfactant molecules do not undergo

- (a) dissociation (b) aggregation
 (c) micelle formation (d) all of these.

17. An inorganic solid (X) when heated gives out a gas which produces turbidity in lime water. Same gas is also produced when X reacts with dil. HCl. Compound (X) is

- (a) Na_2CO_3 (b) $\text{Ca}(\text{HCO}_3)_2$
 (c) NaHCO_3 (d) Na_2S

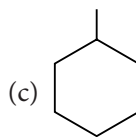
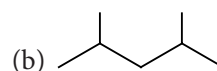
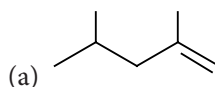
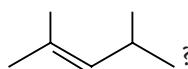
18. The position of equilibrium lies to the right in each of these reactions :



Based on this information, what is the order of acid strength?

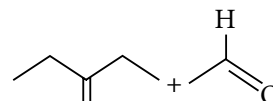
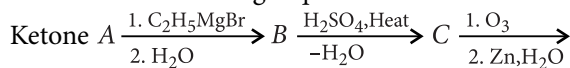
- (a) $\text{HBr} > \text{N}_2\text{H}_5^+ > \text{NH}_4^+$
 (b) $\text{N}_2\text{H}_5^+ > \text{N}_2\text{H}_4 > \text{NH}_4^+$
 (c) $\text{NH}_3 > \text{N}_2\text{H}_4 > \text{Br}^-$
 (d) $\text{N}_2\text{H}_5^+ > \text{HBr} > \text{NH}_4^+$

19. Which is the constitutional isomer of the compound

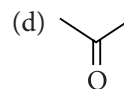
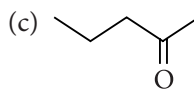
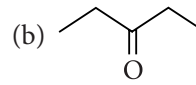
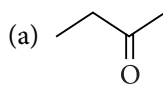


(d) Both (a) and (c)

20. Consider the following sequence of reactions :



The ketone (A) is



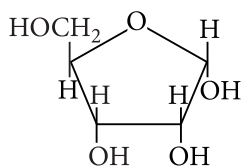
21. When Mg burns in air, it produces

- (a) MgO , MgO_2 (b) MgO , Mg_3N_2 , MgO_2
 (c) Mg_3N_2 only (d) Mg_3N_2 and MgO

22. Oxygen and hydrogen gases are produced at the anode and cathode respectively during electrolysis of dilute aqueous solution of

- (a) Na_2SO_4 (b) AgNO_3
 (c) HCl (d) CuSO_4

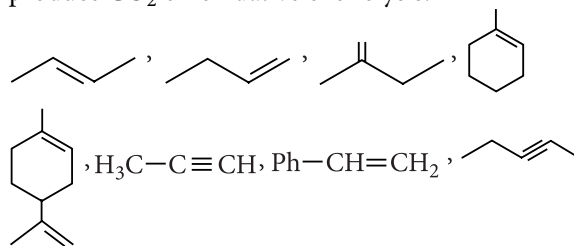
23. Two reactions with different activation energies have the same rate at room temperature. Which statement correctly describes the rates of these two reactions at the same higher temperature?
- (a) The reaction with higher activation energy will be faster.
 (b) The reaction with lower activation energy will be faster.
 (c) Both reactions will have the same rate.
 (d) None of these.
24. Which of the following represents the anomer of the compound shown?



- (a)
- (b)
- (c)
- (d) All of these.

25. Select the incorrect statement.
- (a) O_3 and O_2^- both are diamagnetic.
 (b) Out of O_2 , O_2^+ , O_3 , least O—O bond length is in O_2^+ .
 (c) Out of O_2 , O_2^+ , O_2^- , only O_2 is paramagnetic.
 (d) Out of O_2 , O_2^+ , O_2^- , maximum spin magnetic moment is of O_2 .
26. Which of the following is a chiral molecule?
- (a) 2, 4-dimethyl-1, 3-hexadiene
 (b) 2, 4-octadiene
 (c) 2, 3-octadiene
 (d) None of these.

27. A flask of gaseous CCl_4 was weighed at measured temperature and pressure. The flask was then flushed and filled with O_2 at same temperature and pressure. The weight of the CCl_4 vapour will be
- (a) five times as heavy as O_2
 (b) one fifth heavy as compared to O_2
 (c) same as that of O_2
 (d) twice as heavy as O_2 .
28. Examine the structural formulae of following compounds and find how many compounds will produce CO_2 on oxidative ozonolysis.



- (a) 3
 (b) 6
 (c) 5
 (d) All of these
29. Which of the following pairs of reactions is not related to autoreduction process?
- (a) $2HgS + 3O_2 \longrightarrow 2HgO + 2SO_2$
 $2HgO + HgS \longrightarrow 3Hg + SO_2$
 (b) $2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$
 $2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2$
 (c) $2PbS + 3O_2 \longrightarrow 2PbO + 2SO_2$
 $2PbO + C \longrightarrow 2Pb + CO_2$
 (d) $PbS + \frac{3}{2}O_2 \longrightarrow PbO + SO_2$
 $2PbO + PbS \longrightarrow 3Pb + SO_2$
30. Which of the following is paramagnetic complex?
- (a) Tetracyanonickelate(II)ion
 (b) Tetraamminezinc(II) ion
 (c) Hexaamminechromium(III) ion
 (d) Diamminesilver(I) ion

ANSWER KEYS

1. (d) 2. (b) 3. (b) 4. (a) 5. (c)
 6. (c) 7. (d) 8. (b) 9. (d) 10. (b)
 11. (d) 12. (b) 13. (b) 14. (c) 15. (d)
 16. (a) 17. (c) 18. (a) 19. (d) 20. (b)
 21. (d) 22. (a) 23. (a) 24. (b) 25. (c)
 26. (c) 27. (a) 28. (c) 29. (c) 30. (c)



LEARN FAST

Nomenclature of Organic Compounds

- **Trivial or common system** : Naming done after the source from which the compounds were first isolated.

The IUPAC System of Nomenclature

- A systematic name of an organic compound is generally derived by identifying the parent hydrocarbon and the functional group(s) attached to it.
 - By further using prefixes and suffixes, the parent name can be modified to obtain the actual name.
 - Compounds containing carbon and hydrogen only are called hydrocarbons.
 - A hydrocarbon is termed saturated if it contains only carbon-carbon single bonds. The IUPAC name for a homologous series of such compounds is alkane. Paraffin (Latin : little affinity) was the earlier name given to these compounds.
 - Unsaturated hydrocarbons are those, which contain at least one carbon-carbon double bond (alkenes) or triple bond (alkynes).

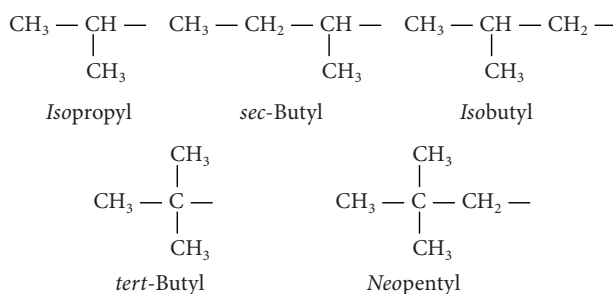
IUPAC Nomenclature of Alkanes

- **Straight chain hydrocarbons** : The names of such compounds are based on their chain structure and end with suffix '-ane' and carry a prefix indicating the number of carbon atoms present in the chain (except from CH₄ to C₄H₁₀, where the prefixes are derived from trivial names).
- The alkanes in the following table differ from each other by merely the number of -CH₂ groups in the chain. They are homologues of alkane series.

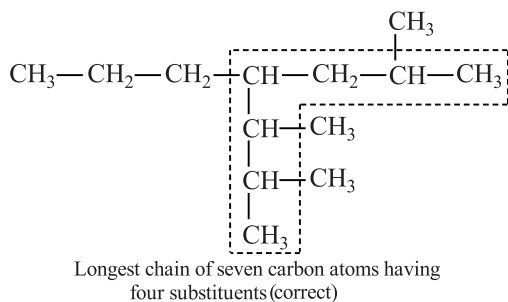
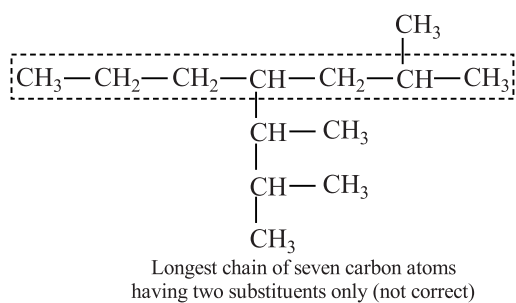
Name	Root	Formula	Name	Root	Formula
methane	meth	CH ₄	undecane	undec	C ₁₁ H ₂₄
ethane	eth	C ₂ H ₆			
propane	prop	C ₃ H ₈	dodecane	dodec	C ₁₂ H ₂₆
butane	but	C ₄ H ₁₀	tridecane	tridec	C ₁₃ H ₂₈

pentane	pent	C ₅ H ₁₂	tetradecane	tetradec	C ₁₄ H ₃₀
hexane	hex	C ₆ H ₁₄	pentadecane	pentadec	C ₁₅ H ₃₂
heptane	hept	C ₇ H ₁₆	icosane	icos	C ₂₀ H ₄₂
octane	oct	C ₈ H ₁₈	heneicosane	heneicos	C ₂₁ H ₄₄
nonane	non	C ₉ H ₂₀	docosane	docos	C ₂₂ H ₄₆
decane	dec	C ₁₀ H ₂₂	triacontane	triacont	C ₃₀ H ₆₂

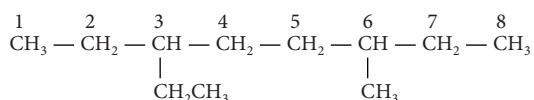
- **Branched chain hydrocarbons** : In a branched chain compound small chains of carbon atoms are attached at one or more carbon atoms of the parent chain. The small carbon chains (branches) are called alkyl groups.
 - In order to name such compounds, the names of alkyl groups are prefixed to the name of the parent alkane.
 - The name of an unbranched alkyl substituent is derived by replacing **ane** by **yl**.
 - alkane - ane + yl → alkyl
 - CH₃ methane + yl → methyl
 - CH₂CH₃ ethane + yl → ethyl
 - CH₂CH₂CH₃ propane + yl → propyl
 - The alkyl groups can be branched also.



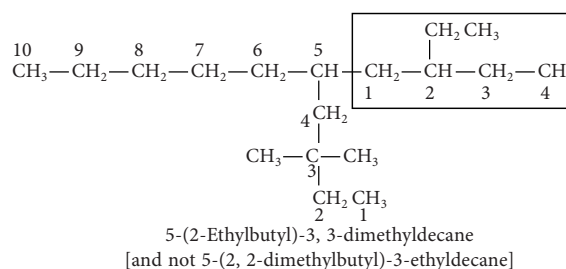
- **Longest chain rule** : The longest carbon chain in the molecule is identified.
- If there happens to be two chains of equal size, then that chain is selected which contains more number of side chains.



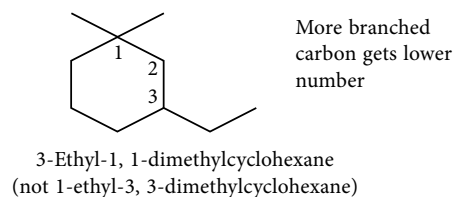
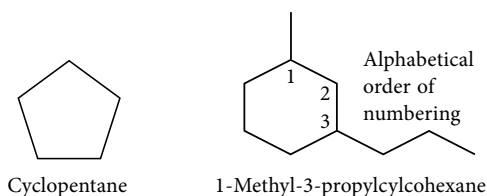
- **Lowest number rule** : The longest carbon chain is numbered as 1, 2, 3, 4, etc. starting from that end which gives the smallest possible number to the substituent.
- **Lowest set of locants rule** : When two or more substituents are present, the lowest set of locants rule is applied. According to this rule, when two or more different sets of locants containing the same number of terms is possible, then that set of locants is the lowest which when compared term by term with other sets, each in order of increasing magnitude, has the lowest term at the first point of difference.
- If there are different alkyl substituents attached to the parent chain, their names are written in the alphabetical order.
- If a substituent is present two or more times, then it is indicated by the prefix *di-*, *tri-*, *tetra-*, etc.
- If the two substituents are found in equivalent positions, the lower number is given to the one coming first in the alphabetical listing. *e.g.*,



- The carbon atom of the branch that is attached to the root alkane is numbered 1 as exemplified below. The name of such branched chain alkyl group is placed in parenthesis while naming the compound. *e.g.*,

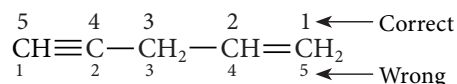


- The use of *iso* and related common prefixes for naming alkyl groups is also allowed by the IUPAC nomenclature as long as these are not further substituted.
- **Cyclic compounds** : A saturated monocyclic compound is named by prefixing 'cyclo' to the corresponding straight chain alkane. If side chains are present, then the rules given above are applied. *e.g.*,



Nomenclature of Unsaturated Hydrocarbons

- **Longest chain rule** : The longest chain is so selected as to include maximum number of double or triple bonds, even if it is not the actual longest chain of carbon atoms.
- **Lowest number rule** : Lowest number is assigned to the first unsaturated carbon according to the lowest set of locants rule.
- If double and triple bonds are at the same position from either ends, lowest number is assigned to the double bond. *e.g.*,

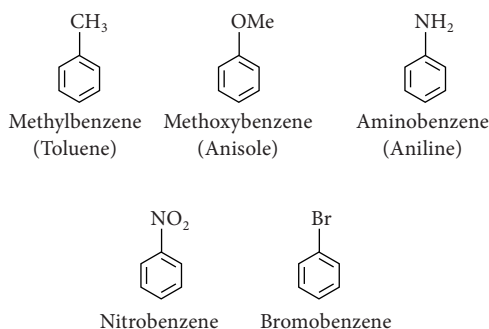


- Organic compound containing multiple bond, side chain or substituents follow the order of preference as :

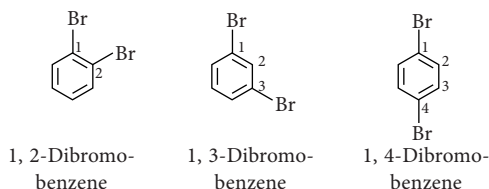
- **Longest chain rule** : Longest chain of carbon atoms containing the functional group is identified.
- **Lowest number rule** : Lowest number is assigned to the carbon atom containing the functional group.
- In IUPAC system, one of the functional groups is chosen as the principal functional group and the remaining functional groups are treated as substituents and indicated by prefixes. Order of preference is :
 - COOH > - SO₃H > - COOR > - COX >
 - CONH₂ > - CN > - NC > - CHO > >C=O
 - > - OH > - SH > - NH₂ > - OR > >C=C<
 - > - C≡C
- The parent chain is so selected that it includes the maximum number of functional groups including the principal group.

Nomenclature of Substituted Benzene Compounds

- For IUPAC nomenclature of substituted benzene compounds, the substituent is placed as prefix to the word benzene as shown in the following examples.

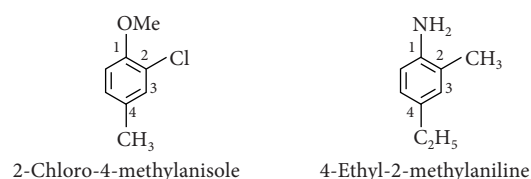
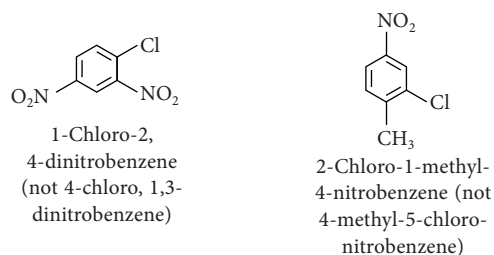


- If benzene ring is disubstituted, the position of substituents is defined by numbering the carbon atoms of the ring such that the substituents are located at the lowest numbers possible.

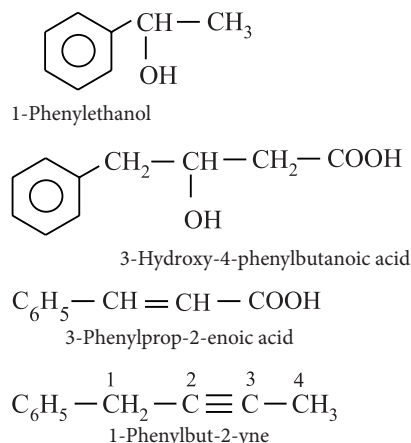


- In the trivial system of nomenclature, the terms *ortho* (*o*), *meta* (*m*) and *para* (*p*) are used as prefixes to indicate the relative positions 1, 2-; 1, 3- and 1, 4- respectively.

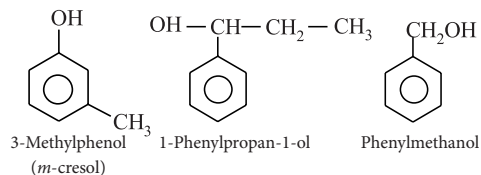
- For tri- or higher substituted benzene derivatives, these prefixes cannot be used and the compounds are named by identifying substituent positions on the ring by following the lowest locant rule. In some cases, common name of benzene derivatives is taken as the base compound. *e.g.*,



- If side chain contains a functional group, then these are said to be phenyl derivatives of the corresponding aliphatic compounds.



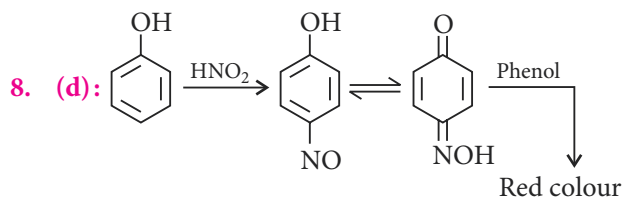
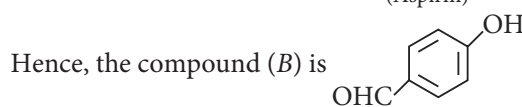
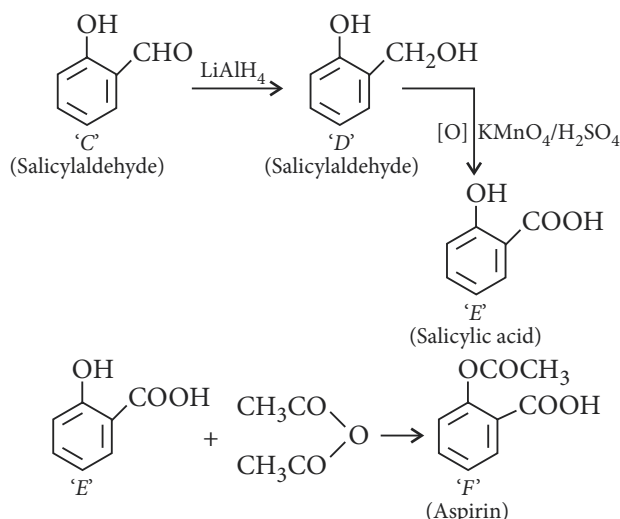
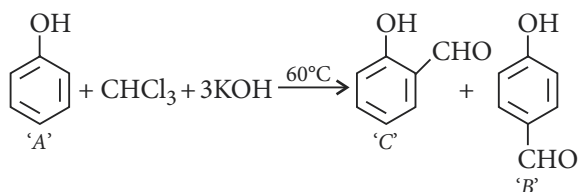
- Aryl group is a radical obtained by removal of one or more hydrogen atoms of the aromatic hydrocarbons either from side chain or from nucleus.
- The nuclear hydroxy derivatives are called phenols while the side chain substituted hydroxy derivatives are called aromatic alcohols.



CHEMISTRY MUSING

SOLUTION SET 27

- (c): O_2 has higher molecular weight than H_2 thus, it has more surface area and therefore, has more van der Waals' forces of attraction. Hence O_2 has higher T_c (critical temperature) and higher T_i (inversion temperature).
- (a): Triethylamine is insoluble in NaOH but triethylammoniumhydrogen sulphate is soluble in NaOH.
- (b): LiOH formed for a very small time is responsible for the red line in the flame.
- (b): When solid $CaCl_2$ is added to liquid water the temperature rises because $\Delta H_{\text{solution}}$ for $CaCl_2$ is $-ve$ (exothermic). When solid $CaCl_2$ is added to ice at $0^\circ C$, some of the ice will melt and the temperature will fall because $CaCl_2$ lowers the freezing point of ice/water mixture.
- (a): $NaOH + HNO_3 \longrightarrow NaNO_3 + H_2O$
 $2NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O$
 Number of milliequivalents of NaOH = $20 \times 0.1 = 2$
 Number of milliequivalents of SO_4^{2-} = $0.001 \times 1000 \times 2 = 2$
 Number of milliequivalents of NO_3^- = $0.001 \times 1000 = 1$
 2 milliequivalents of NaOH will react with 2 milliequivalents of SO_4^{2-} .
 \therefore Formula of the complex will be $[Cr(NH_3)_5NO_3]SO_4$
- (c): The bond angle between equatorial positions is 120° and bromine is bigger than chlorine so, bromine atoms will be present at equatorial positions to minimise the repulsive forces.
- (a):



9. (9): NH_4Cl is a salt of weak base and strong acid.

$$pH = -\log[H^+] = -\log \sqrt{\frac{K_w}{K_b} \times C}$$

$$pH = \frac{1}{2}[pK_w - pK_b - \log C]$$

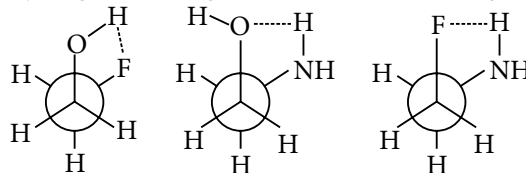
$$pH = \frac{1}{2}[pK_w - pK_b] - \log \sqrt{C}$$

$$\therefore \frac{1}{2}[pK_w - pK_b] = 2.5$$

$$pK_w - pK_b = 5$$

$$pK_b = 14 - 5 = 9$$

10. (3): Gauche form is more stable than anti when hydrogen bonding is possible between the groups.

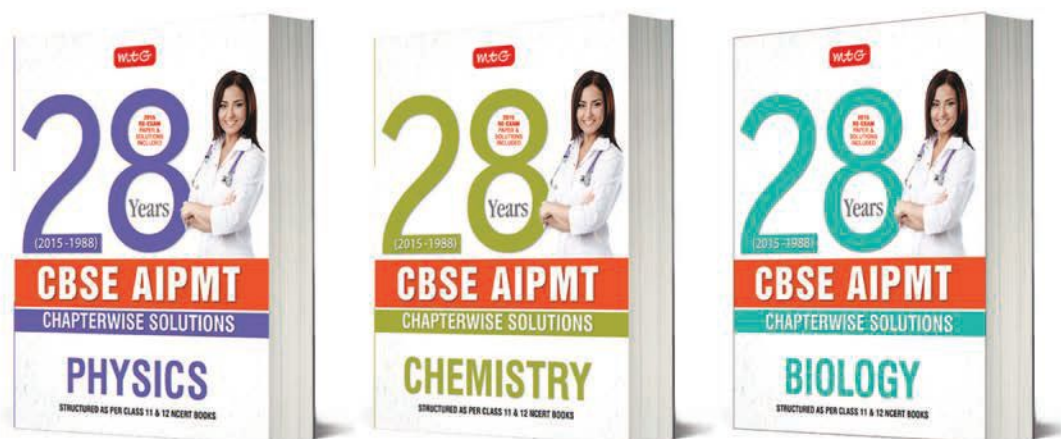


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SET 27

- Anubhav Jana (WB)
- Arunesh Varde

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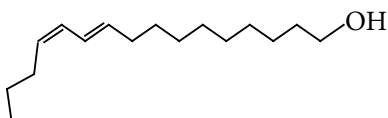
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The best questions and their solutions will be printed in this column each month.

Q1. A biologically active compound, Bombykol is obtained from a natural source. Explain the chemical reactions involved in this process.

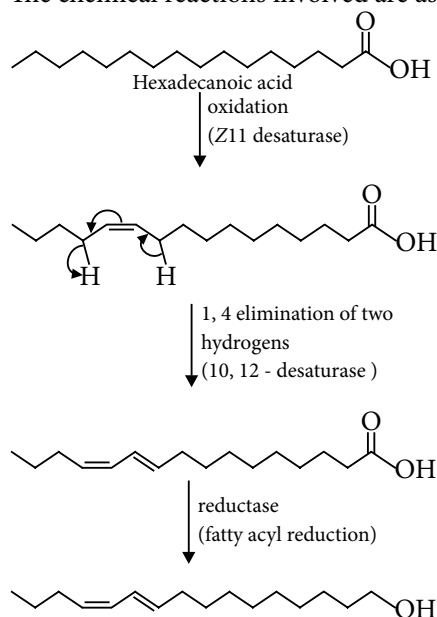
(Umesh Rastogi, Bengaluru)

Ans. Bombykol having chemical formula, $C_{16}H_{30}O$ is the sex pheromone of the silk moth. The "bomb" bit comes from the name of the silk moth, *Bombyx mori*.



IUPAC name : (10*E*, 12*Z*) - Hexadeca - 10, 12-dien - 1 - ol
The female moth makes it from hexadecanoic acid by the usual method of carboxylic acid synthesis, using acetyl coenzyme A.

The chemical reactions involved are as follows :

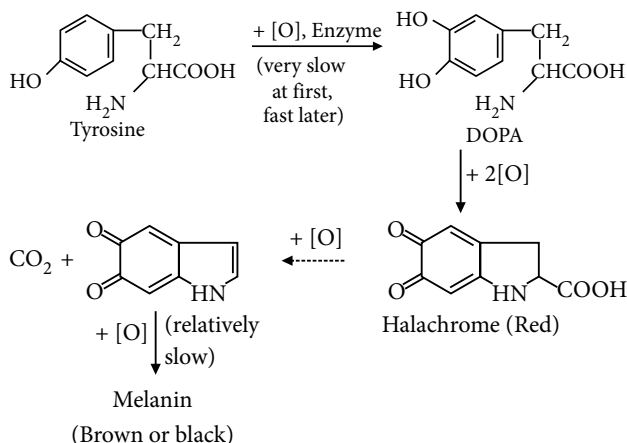


The saturated acid first undergoes oxidation catalysed by a Z11 desaturase enzyme, to generate the first double bond. The second step is more unusual, involving 1,4-elimination of two hydrogens to afford a conjugated diene, catalysed by a 10, 12- desaturase enzyme. Finally a reductase enzyme converts the carboxylic acid group into a primary alcohol (fatty acyl reduction).

Q2. Why does a chopped apple acquire a reddish tinge?

(Kavya Mishra, Ghaziabad)

Ans. The darkening of apples is due to the production of melanin. This is done by an enzyme called tyrosinase, which is present in all living tissues. When we cut apple, live tissues of the apple get exposed to oxygen. Oxygen and tyrosine combine to form melanin as shown :



In more detailed chemistry, polyphenols present in fruits are colourless, and they are recognizable by their tendency to rapidly become brown. A chopped apple turns brown at the site of a cut because the polyphenols become oxidised and the colour of the oxidised polyphenols is brown, at least on the surface.

This discolouration can be prevented by coating the cut surface with another antioxidant, such as vitamin C. Lemon juice, which is high in vitamin C is perfect for this.



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CROSSWORD



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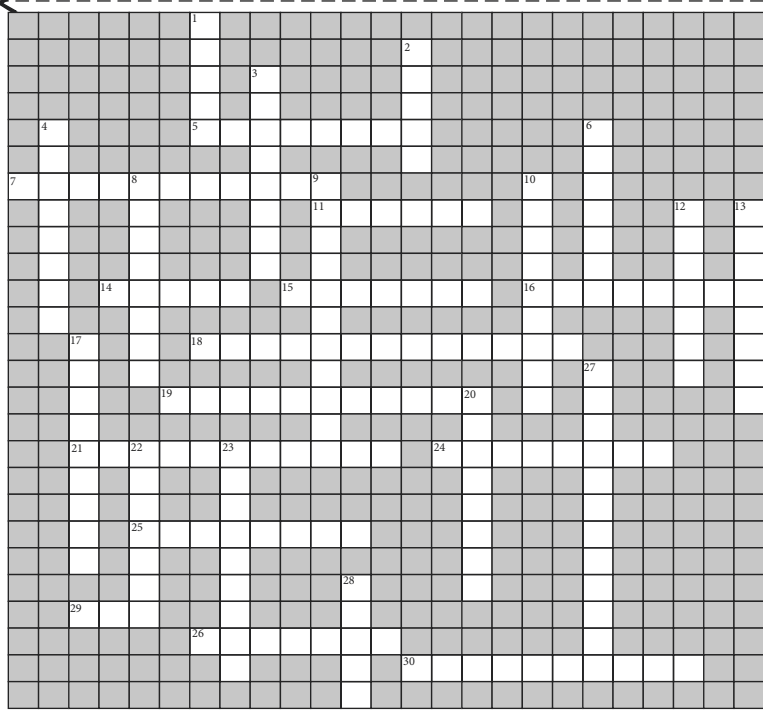
ACROSS

5. A colourless, highly poisonous flammable gas. (8)
7. The property of a crystal of having a different colour depending upon the direction of transmitted light through it. (11)
11. Solvent used to separate the components of a mixture in column chromatography. (6)
14. A sub-atomic particle that obeys Bose-Einstein statistics but not the Pauli exclusion principle. (5)
15. Polymer used in the manufacture of paints and varnishes. (7)
16. Another name of vitamin B₁. (8)
18. Production of cracking sound on heating certain crystals. (13)
19. A eutectic mixture of ice and certain salts obtained by freezing a solution. (11)
21. Species which have same number of each isotope but differ in their positions. (11)
24. Selective dissolution of the desired mineral in a suitable reagent leaving behind the impurities. (8)
25. A fuel for supersonic rockets. (8)
26. A nucleoside containing one uracil molecule linked to a ribose sugar molecule. (7)
29. Abbreviation used for the amino acid isoleucine. (3)
30. Scientist who mapped nucleotide excision repair and won the Nobel prize in chemistry in 2015. (10)

DOWN

1. Crystal system having nine planes and thirteen axes of symmetry. (5)
2. The product of condensation of hydrazine with ketones and aldehydes. (5)
3. The most ductile metal. (8)
4. Silicon compound used as a lubricant. (8)
6. Optically inactive amino acid. (7)

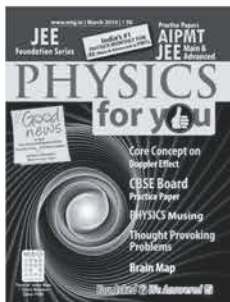
Cut Here



8. Hardest known amorphous substance. (8)
9. A polymer of acetaldehyde used as a fuel for emergency stoves. (11)
10. Trichloro derivative of sucrose. (9)
12. An important impure source of nitrate. (7)
13. Distance travelled by molecules between two successive collisions. (8)
17. Antiseptic chemical used in soaps. (9)
20. Naturally occurring alloy of gold and silver. (8)
22. IUPAC name of H₂O. (7)
23. Studies carried out at very high temperature. (9)
27. The process of conversion of household, chemical and biological waste into CO₂ and H₂O in presence of oxygen at high temperature. (12)
28. The selective reduction of *m*-dinitrobenzene to *m*-nitroaniline by aqueous ammonium sulphide. (5)



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