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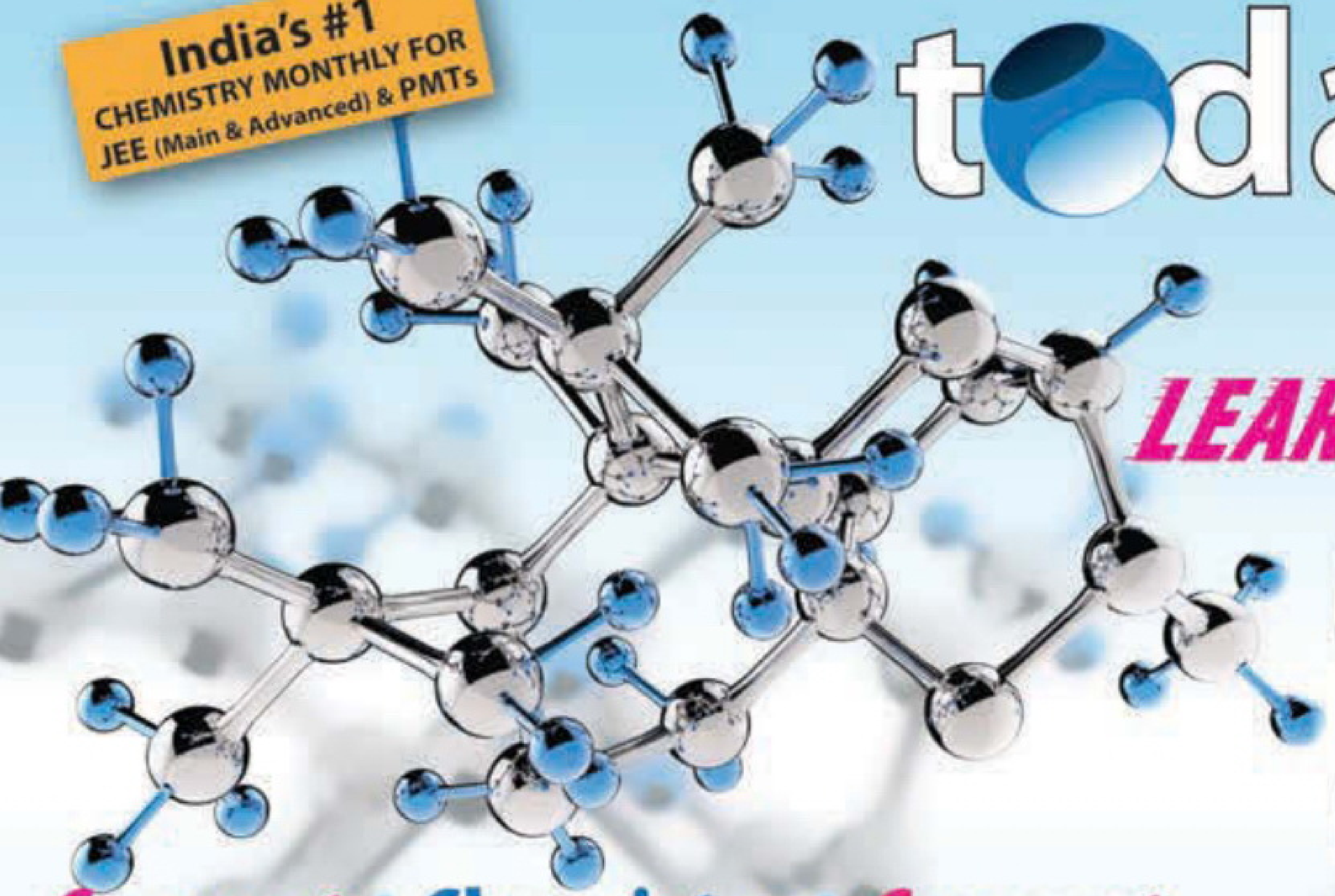

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Contents

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Editor : Anil Ahlawat

editorial

The Best Medicines need not be Bitter

This is good news for children as well as grown-ups. Here we have a sample of this by taking two examples. But once there is taste we can go for others.

A natural compound found in pomegranate cures or at least slows down Alzheimer's disease and some of its symptoms. A painful inflammation which accompanies illnesses such as Rheumatoid arthritis and Parkinson's disease could also be reduced by the use of the compound found in pomegranate. A daily dose of pomegranate juice is the best way of prevention of many diseases. Dr. Olumayokun Olajide of the University of Huddersfield and his group are pursuing this problem very actively. Drugs developed from this fruit will be immensely helpful for people who have symptoms of Dementia. Here is another fruit which is common throughout India and the world. Banana, *Kela* of the common man has sucrose, fructose, glucose and also fibres. Research has shown that after one and a half hours of eating two bananas, most of the nutrition necessary for the body will be available. This also produces resistance to diseases.

A mixture of banana, honey and milk improves the intelligence of children. As bananas contain potassium, it controls the heartbeats and water content of the body. We have given here only two samples which have been studied in the universities. Many fruits and vegetables and their properties can be easily found in the Indian medical books. The field of research is waiting for you. Topics are available in plenty. What is needed is, will to continue the work till success.

Anil Ahlawat
Editor

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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.

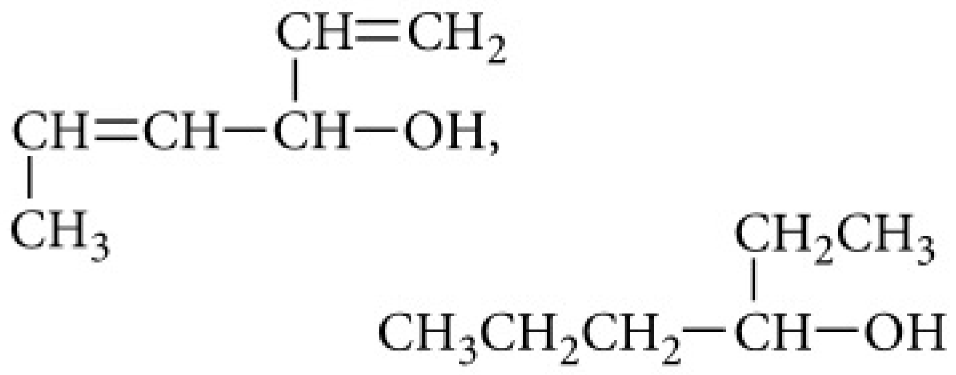
The readers who have solved five or more problems may send their solutions. The names of those who send atleast five correct solutions will be published in the next issue.

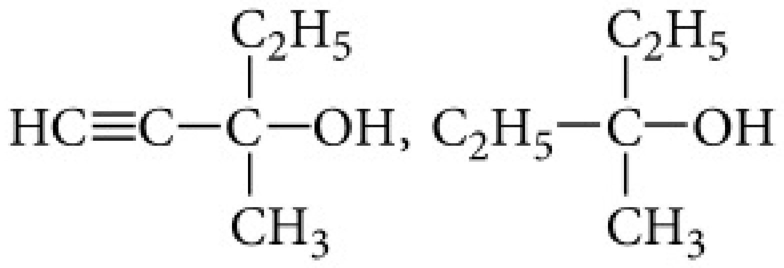
We hope that our readers will enrich their problem solving skills through "Chemistry Musing" and stand in better stead while facing the competitive exams.

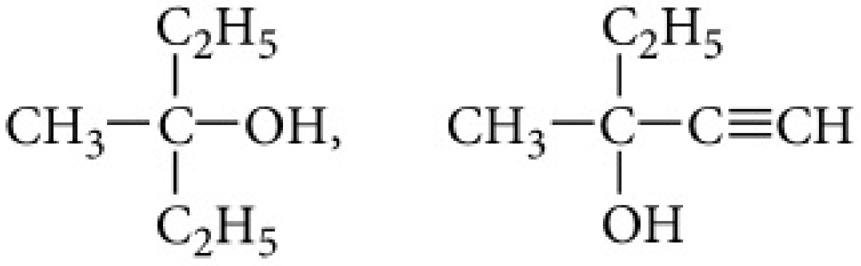
PROBLEM
Set 15

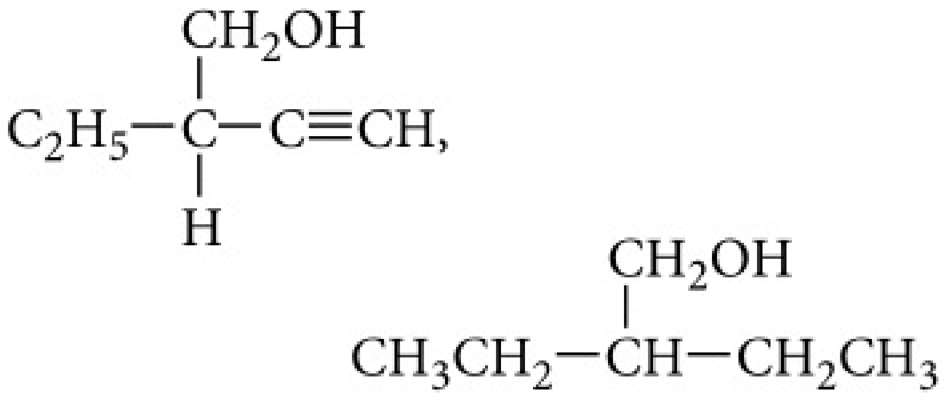
JEE MAIN/PMTs

1. An optically active alcohol (*P*) $C_6H_{10}O$ upon catalytic hydrogenation absorbs two moles of hydrogen per mole of (*P*) and gives a product (*Q*). The compound (*Q*) is optically inactive and resistant to oxidation by CrO_3. Structures of (*P*) and (*Q*) respectively are

(a)

$\underset{\displaystyle CH_3}{\underset{|}{CH}}=CH-\overset{\displaystyle CH=CH_2}{\overset{|}{CH}}-OH$, $CH_3CH_2CH_2-\overset{\displaystyle CH_2CH_3}{\overset{|}{CH}}-OH$

(b)

$HC\equiv C-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle C_2H_5}{\overset{|}{C}}}}-OH$, $C_2H_5-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle C_2H_5}{\overset{|}{C}}}}-OH$

(c)

$CH_3-\underset{\displaystyle C_2H_5}{\underset{|}{\overset{\displaystyle C_2H_5}{\overset{|}{C}}}}-OH$, $CH_3-\underset{\displaystyle OH}{\underset{|}{\overset{\displaystyle C_2H_5}{\overset{|}{C}}}}-C\equiv CH$

(d)

$C_2H_5-\underset{\displaystyle H}{\underset{|}{\overset{\displaystyle CH_2OH}{\overset{|}{C}}}}-C\equiv CH$, $CH_3CH_2-\overset{\displaystyle CH_2OH}{\overset{|}{CH}}-CH_2CH_3$

2. The volume strength of perhydrol is

(a) 20 (b) 30

(c) 99 (d) 10

3. The pH of gastric juice in human stomach is about 2-3 and in the small intestine is about 8. The pK_a of aspirin (acetylsalicylic acid) is 3.5. Aspirin will be

(a) unionised both in small intestine and stomach

(b) completely ionised both in small intestine and stomach

(c) ionised in the stomach and almost unionised in the small intestine

(d) ionised in the small intestine and almost unionised in the stomach.

Solution Senders of Chemistry Musing

SET 13

1. Rushikesh Joshi, Nagpur (Maharashtra)
2. Soumik Chatterjee, Kolkata (West Bengal)
3. Saurabh B. Kasote, Kolhapur (Maharashtra)
4. Namit Bhasin, Ludhiana (Punjab)
5. Khwaja Sami Baig, Azamgarh (Uttar Pradesh)
6. Sakshi Patel, Kota (Rajasthan)

4. On heating a gas, its pressure and volume both become double. By lowering temperature, one fourth of initial number of moles of air are taken in to maintain the double pressure and volume. By what fraction, the temperature must have been raised finally?

(a) $\frac{1}{5}$ times (b) $\frac{4}{5}$ times

(c) $\frac{16}{5}$ times (d) $\frac{8}{5}$ times

5. Which of the following statements is correct?

(a) Pu^{4+} disproportionates to Pu^{3+} and PuO_2^{2+} in strongly acidic medium.

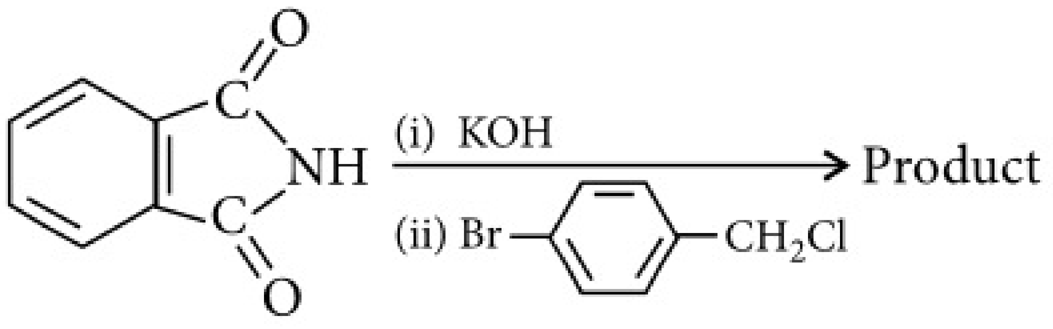
(b) Maximum oxidation state of Np is +7.

(c) UO_2^{2+} is stable.

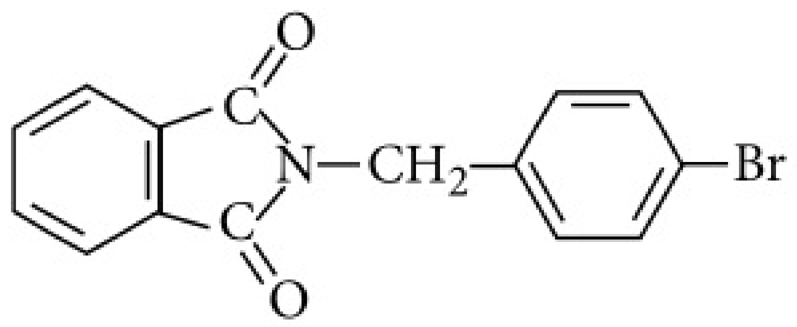
(d) All of the above.

JEE ADVANCED

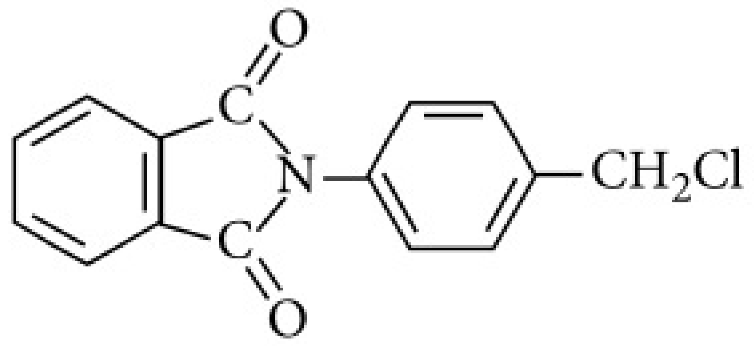
6. The major product of the following reaction is



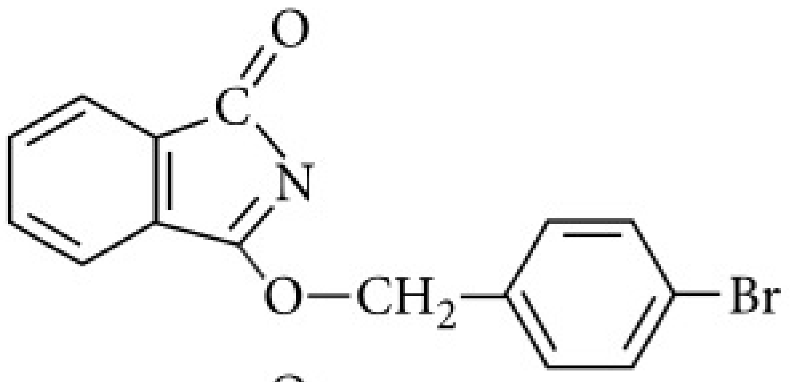
(a)



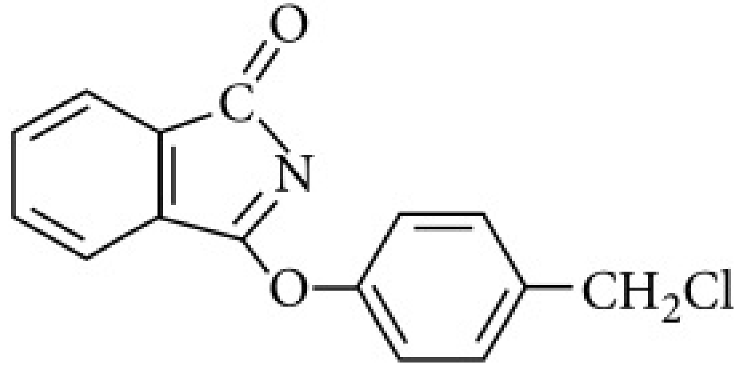
(b)



(c)



(d)



COMPREHENSION

Metallic sulphates can be obtained by reacting the metals (above hydrogen in electrochemical series), or its oxide, hydroxide or carbonate with dil. H_2SO_4. Group IA metals also form hydrogen sulphates which can be isolated in solid. In general, metal sulphates are soluble in water and crystallises with water of crystallization. Sulphates are thermally more stable than nitrates.

7. On treatment with dil. H_2SO_4, which of the following *d*-block elements will not give its sulphate?

(a) Ni (b) Cr

(c) Co (d) Cu

8. Which of the following sulphates is completely soluble in water?

(a) Hg_2SO_4 (b) $SrSO_4$

(c) Ag_2SO_4 (d) Rb_2SO_4

INTEGER VALUE

9. 50 mL of 1 M oxalic acid is shaken with 0.5 g wood charcoal. The final concentration of the solution after adsorption is 0.5 M. The amount of oxalic acid adsorbed per gram of charcoal is

10. Based on VSEPR theory, in BrF_5 the total number of F–Br–F angles equal to 90° is

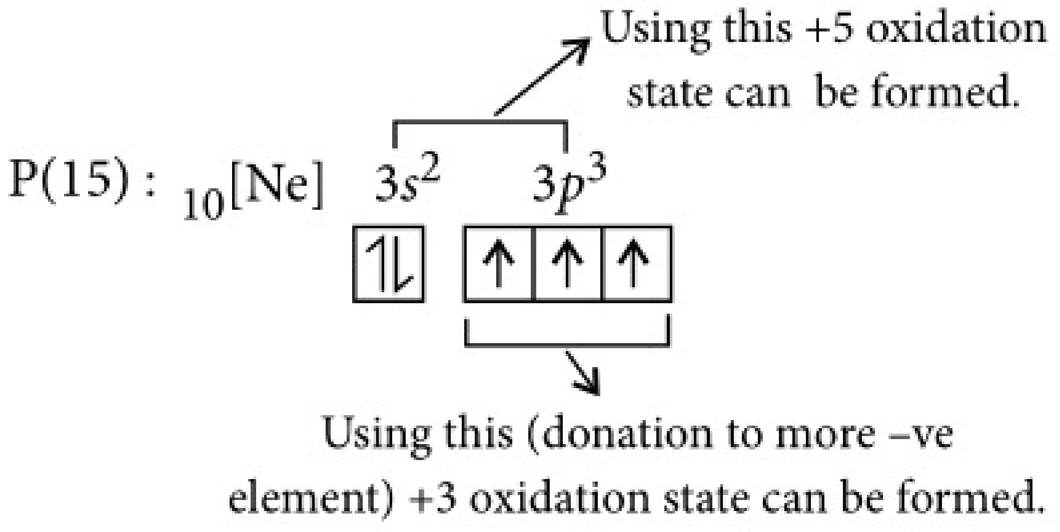
CONCEPT BOOSTER

Dear students!! Here is "The Fun of Inorganic Chemistry" series. Idea behind the topic is to break the saying "Inorganic means nothing but Commit To Memory." Whole topic will be serially presented with the techniques and shortcuts to tackle Inorganic Chemistry. I hope you will like it.

*Arunava Sarkar

GROUP 15 ELEMENTS

- In group 15, main two elements are nitrogen and phosphorus. Nitrogen is very small in size in comparison with the phosphorus and much more electronegative too.
  Electronic configuration of
  $N(7) : 1s^2\, 2s^2\, 2p^3$
  $P(15) : 1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^3$ or $_{10}[Ne]\, 3s^2\, 3p^3$
  To complete the octet, both need three electrons. Nitrogen can afford to take these electrons from metal directly and can form N^{3-} ion whereas phosphorus and other members of group 15 cannot afford this. This is why Ca_3N_2 is fairly ionic while Ca_3P_2 is sufficiently covalent in nature. This can also be seen using Fajan's rule. Covalent character will vary among the group 15 elements as
  $N > P > As > Sb > Bi$
- Members of group 15 can form both +3 and +5 oxidation states.



Using this +5 oxidation state can be formed.

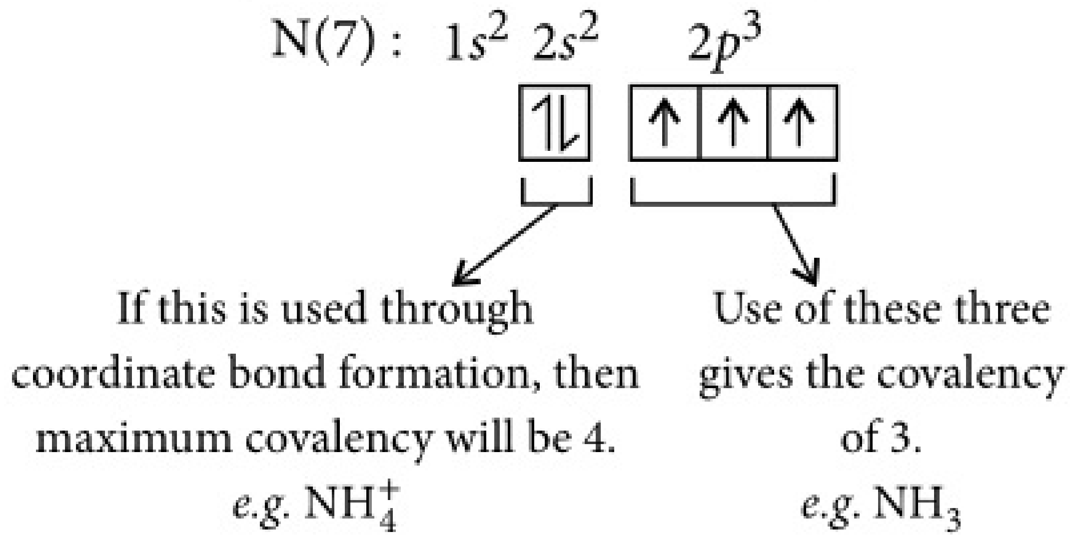
$P(15) :\ _{10}[Ne]\ 3s^2\ 3p^3$

Using this (donation to more –ve element) +3 oxidation state can be formed.

Large amount of energy has to be involved in the formation of E^{5+} (E is group 15 element) and this is why it is not possible to deal with that much high energy and the pentavalent compounds of group 15 are essentially covalent in nature, for example, PCl_5, SbF_5 etc. But, whenever it is the turn of +3 oxidation state, both ionic and covalent compounds are formed. This is because generation of E^{3+} is affordable. Higher two members *i.e.*, Sb and Bi form ionic compounds with fluorine like SbF_3, BiF_3 whereas other members in +3 oxidation state show the dominant nature of covalency in their compounds like NCl_3, PCl_3, $AsCl_3$, $SbCl_3$, NH_3, PH_3, etc.

SbF_3 is ionic but $SbCl_3$ is covalent. Why?
Ans.: Applying Fajan's rule, due to larger size of Cl^- it is more easily polarizable than F^-. More polarization helps to form covalent compounds.

- Nitrogen cannot form NCl_5 whereas phosphorus can easily form PCl_5. This is because nitrogen does not have vacant *d*-orbitals whereas phosphorus and other members have. If an element has vacant *d*-orbitals, it can extend its covalency.



$N(7) :\ 1s^2\ 2s^2\ \ 2p^3$

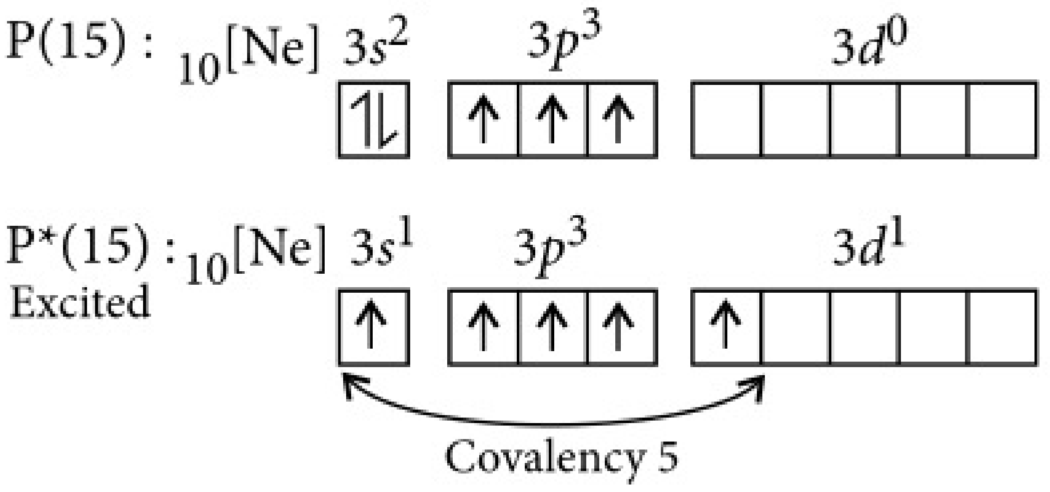
If this is used through coordinate bond formation, then maximum covalency will be 4.
e.g. NH_4^+

Use of these three gives the covalency of 3.
e.g. NH_3

---

* Institute of Chemistry (IOC)- Asansol, Durgapur, Dhanbad, Burdwan, Kolkata, Jamshedpur, Bokaro, Patna 09732313208

On the other hand,



However, phosphorus and other members can show the maximum covalency upto six and this can be done through sp^3d^2 hybridization of P where F^- donates a lone pair to the vacant *d*-orbitals and hence F^- acts as a ligand. So, Nitrogen shows maximum covalency of four. Phosphorus and other members show maximum covalency of six.

- While moving down the group, stability of +3 oxidation state increases. This is expected due to **inert pair effect**.

Nitrogen exhibits all the oxidation states starting from −3 to +5 whereas other members cannot. Why?

Ans.: The reasons are :

1. Small size of nitrogen atom
2. High electronegativity of nitrogen
3. Great tendency of nitrogen to form $p\pi$-$p\pi$ multiple bonds
4. Electron-donating tendency of nitrogen (for example, $\ddot{N}H_3$ is more basic than $\ddot{P}H_3$), and it can better be explained with the help of **Bent's rule**.

Few structures of oxides (with techniques of drawing) and oxyacids of nitrogen are given, which show that how nitrogen is good for the formation of $p\pi$-$p\pi$ multiple bonds.

Oxides of Nitrogen

- **NO :** Lewis dot structure often helps to predict the structure.

In nitrogen, no. of valence electrons = 5

In oxygen, no. of valence electrons = 6

∴ Total no. of valence electrons = 5 + 6 = 11

So, it must be an odd electron molecule.

$$\ddot{N}::\!:\ddot{O}$$

The formal charge on nitrogen is

$$V-L-\frac{1}{2}S=5-2-\frac{1}{2}\times 6=3-3=0$$

The formal charge on oxygen is

$$V-L-\frac{1}{2}S=6-3-\frac{1}{2}\times 6=3-3=0$$

This structure is not the best structure as in this structure, oxygen has surrounded with 9 electrons. So, one bond pair above the nitrogen (lone pair of nitrogen) is added. Hence, the structure becomes

$$\dot{\underset{\cdot\cdot}{N}}::\ddot{O}$$

Here, the formal charge on nitrogen is

$$=5-4-\frac{1}{2}\times 4=1-2=-1$$

The formal charge on oxygen is

$$=6-3-\frac{1}{2}\times 4=3-2=+1$$

The second structure is possibly the best structure. So, the structure of nitric oxide is as shown below :

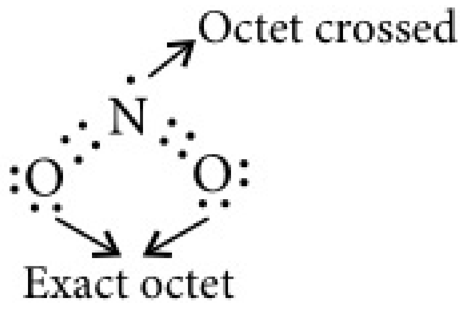
$$\overset{-}{\underset{\cdot\cdot}{\ddot{N}}}=\overset{+}{\ddot{O}}:$$

- **NO_2 :** No. of valence electrons in nitrogen = 5

No. of valence electrons in oxygen = 6

∴ Total no. of valence electrons = 5 + (2 × 6) = 17

So, it must be an odd electron molecule.



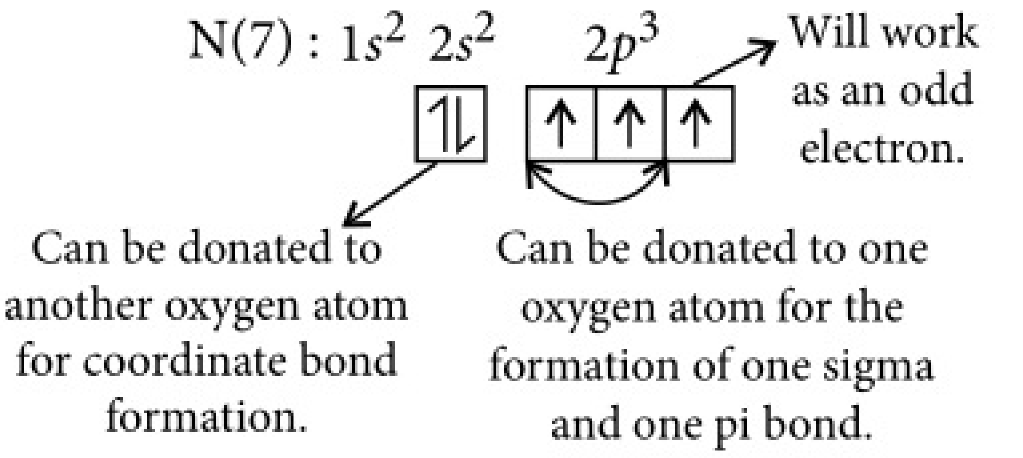
The formal charge on nitrogen is

$$5-1-\frac{1}{2}\times 8=4-4=0$$

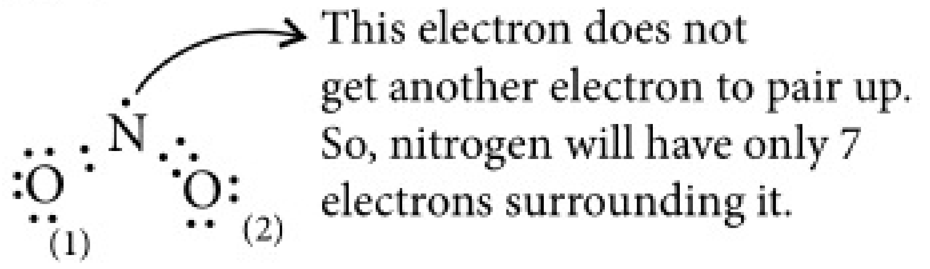
The formal charge on each oxygen atom is

$$6-4-\frac{1}{2}\times 4=2-2=0$$

This may appear to be the best Lewis dot structure as all are having formal charge zero. But this structure is not the best structure as in this structure, nitrogen has 9 electrons surrounding it.



So, the best structure of NO_2 can be as shown below :



The formal charge on N is

$$=5-1-\frac{1}{2}\times 6=4-3=+1$$

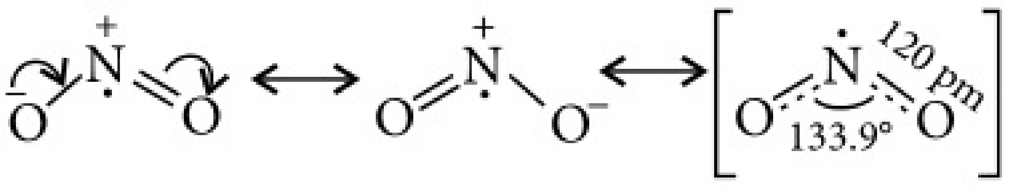
The formal charge on $O_{(1)}$ is

$$=6-6-\frac{1}{2}\times 2=0-1=-1$$

The formal charge on $O_{(2)}$ is

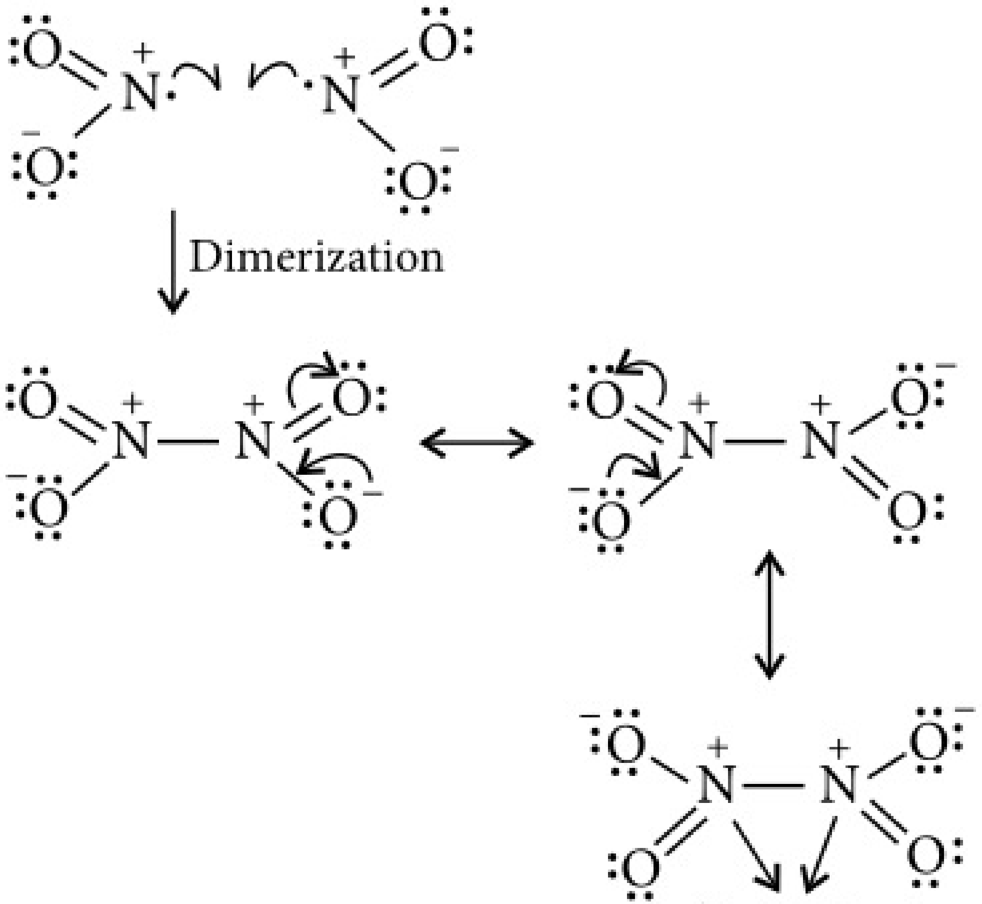
$$=6-4-\frac{1}{2}\times 4=2-2=0$$

So, NO_2 can undergo resonance as shown below :



Angular structure
(Resonance hybrid)

The odd electron over the nitrogen makes it possible for the formation of the dimer of NO_2 *i.e.* N_2O_4 on cooling.



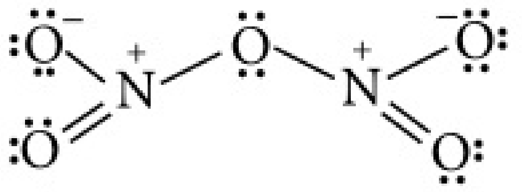
sp^2 hybridized
(Planar structure)

N_2O_4 is resonance stabilized.

So, N_2O_4 is diamagnetic and can give back to NO_2 on heating.

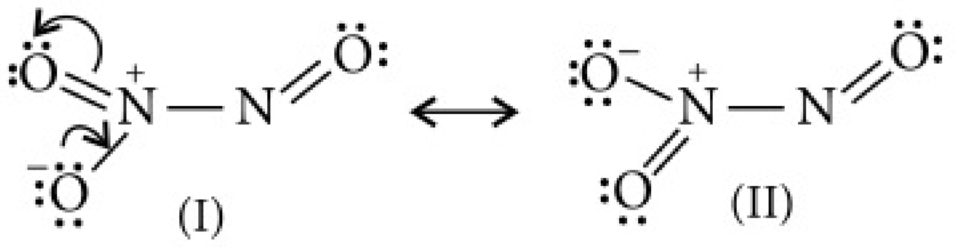
- **N_2O_5 :** In N_2O_4 molecule, putting a complete oxygen atom in between two nitrogen atoms, the structure of N_2O_5 is obtained. It exists as a combination of two ionic parts *i.e.* NO_2^+ and NO_3^- and may be called it as nitronium nitrate $(NO_2^+)\,(NO_3^-)$.

  So, the structure is

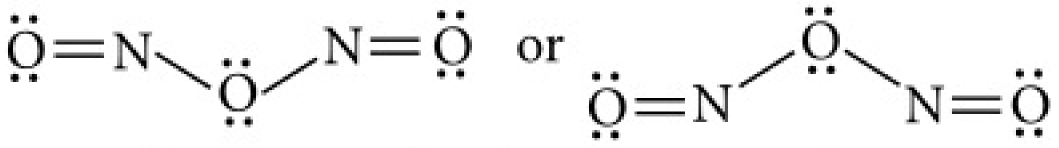


It is also a planar structure.

- **N_2O_3 :** The structure can be given as



Logically (I) and (II) are asymmetric forms. A symmetric form can be as shown below :



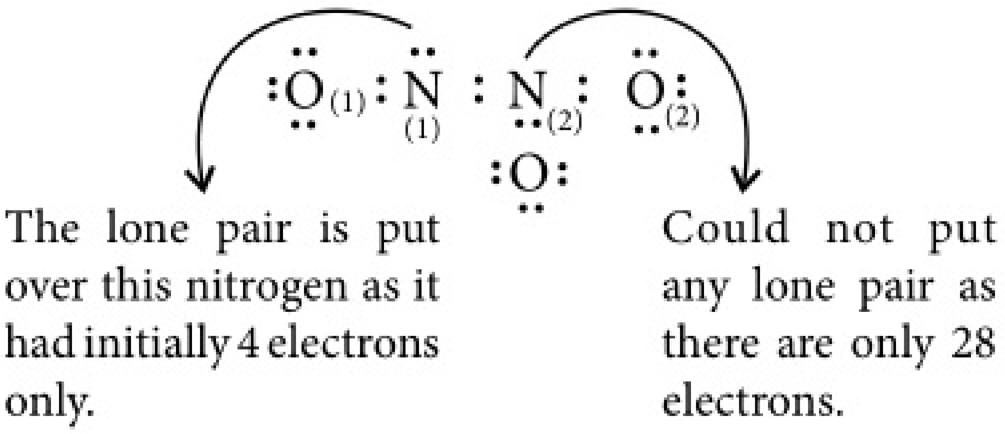
Now, the strategy for the structure of N_2O_3 is

Total no. of valence electrons = 28

Step 1 : First draw the skeleton which is as shown below :

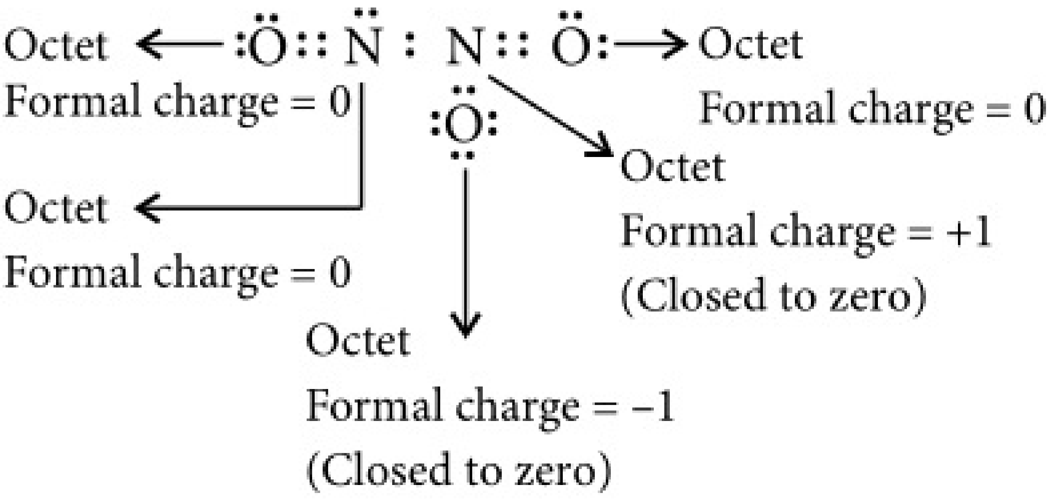
O N N O
O

Step 2 : Now put one shared pair in between two atoms to ascertain minimum one bond in between two atoms. Then fill up the octet for every atom through putting the lone pair(s). So, it looks as shown below :



At the present scenario, all the oxygen atoms have filled their octet but nitrogen atoms have only six electrons surrounding them. So, the double bond exists between nitrogen and oxygen.

Step 3 : From $O_{(2)}$ take one lone pair and put it in between $N_{(2)}$ and $O_{(2)}$. Similarly, take one lone pair from $O_{(1)}$ and put it in between $O_{(1)}$ and $N_{(1)}$. So, the structure looks as shown below :

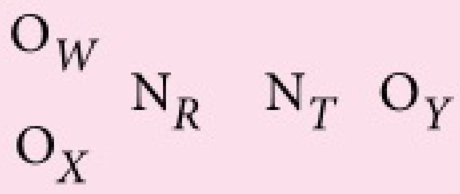


Draw the structure of $N_2O_3^{2-}$.

Ans.: The electron spectroscopy has confirmed its existence. This is known as α-oxyhyponitrite ion.

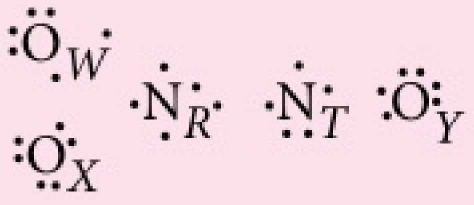
Step 1 : First of all count the number of valence electrons. It must be 28.

Skeleton will be as shown below :

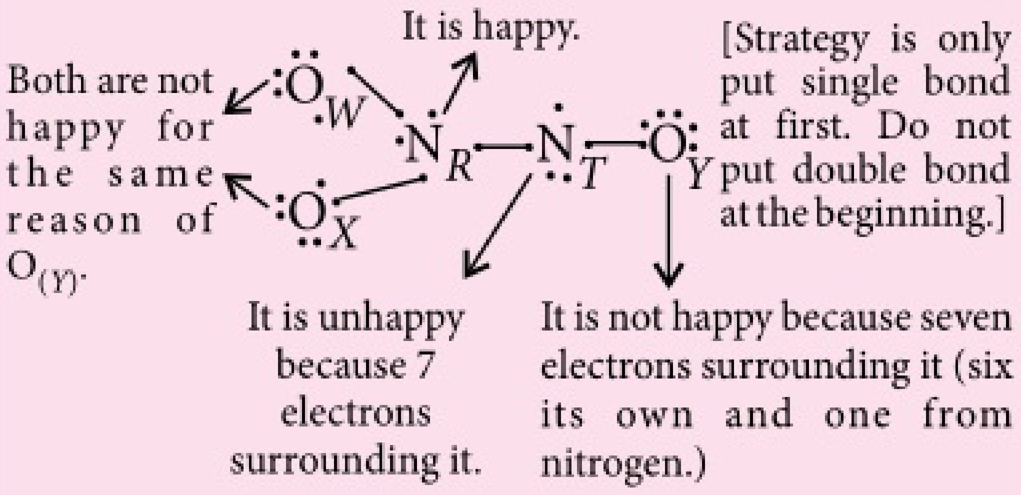


(*W, X, R, T, Y* are the notations at subscript.)

Step 2 : Put the valence electrons accordingly.



Connect the electrons to make bonds.



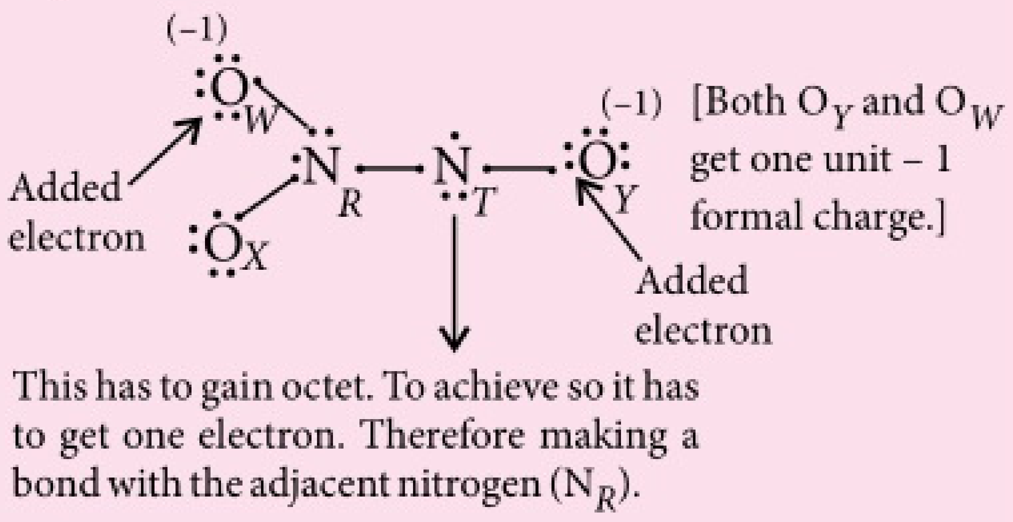
[Strategy is only put single bond at first. Do not put double bond at the beginning.]

It is unhappy because 7 electrons surrounding it.

It is not happy because seven electrons surrounding it (six its own and one from nitrogen.)

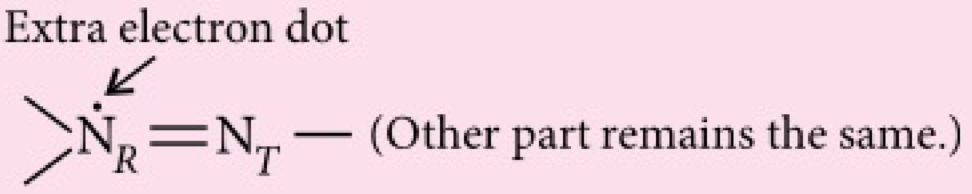
Now, the two extra electrons due to two –ve charges are to be utilized by them. These two electrons are to be donated to the more –ve oxygen atoms. But to which oxygen atoms? One is of course O_Y and another is any one out of the O_W and O_X.

So, it looks as shown below :

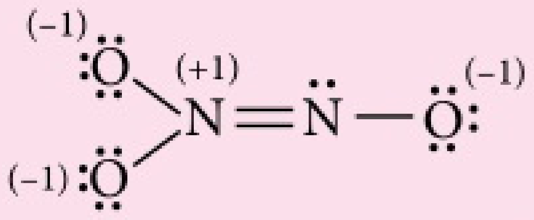


[Both O_Y and O_W get one unit – 1 formal charge.]

This has to gain octet. To achieve so it has to get one electron. Therefore making a bond with the adjacent nitrogen (N_R).

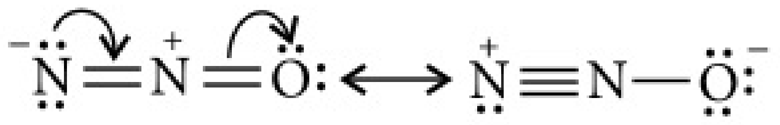


But, there is a problem. N_R gets nine electrons surrounding it. So it has to give up this electron. The O_X has got one electron dot and overall it has got seven electrons surrounding it. Whereas N_R has filled its octet and has one electron dot extra. Take this electron dot from N_R and put on O_X. So, finally the structure will be



α-Oxyhyponitrite ion

- **N_2O :** It has linear structure.



Bond order between N and N is higher than that between N and O.

Preparation of Oxides of Nitrogen

- **NO_2** : It has brown colour and on dissolving in water, it gives HNO_3 so it is acidic in nature. There are two best processes to prepare NO_2 in the laboratory.

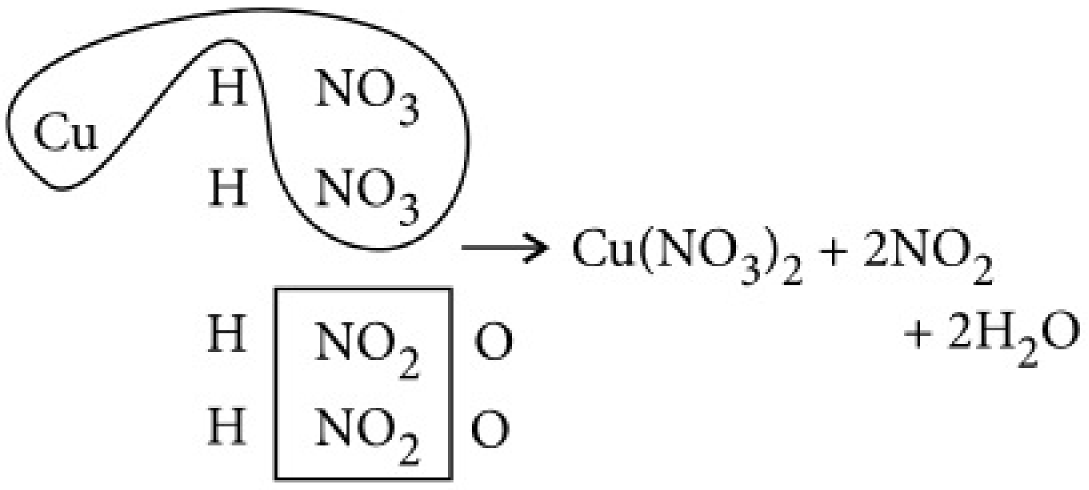
Process 1 : Heating lead nitrate

$$2Pb(NO_3)_2 \rightarrow 2PbO + 4NO_2 + O_2$$

In this type of reaction whenever metal nitrate is heated, metal oxide is an inevitable product, in general.

Process 2 : Reaction between copper chips and conc. HNO_3

$$Cu + \underset{\text{(Conc.)}}{4HNO_3} \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$



- **NO : Process 1 :** Reaction between copper chips and dil. HNO_3

  It is analogous to the previous one.

  $$\underset{\text{(Dilute)}}{3Cu + 8HNO_3} \to 3Cu(NO_3)_2 + 2NO + 4H_2O$$

Question from student's mind

Why is this happening that whenever conc. HNO_3 is used, it is NO_2 which is the product and whenever dil. HNO_3 is used, it is NO as a product?

Ans.: 99% of these inorganic reactions are driven by the concept of (or mechanism of) oxidation-reduction and a few with the electrochemical concepts.

$$3\,NO_{2(g)} + \underset{\substack{\Downarrow \\ \text{Water (Dilution)}}}{H_2O_{(l)}} \to 2HNO_{3(aq)} + NO_{(g)}$$

Whenever copper chips come in contact with HNO_3, NO_2 will be produced. Now, in the diluted solution this NO_2 gives NO as the major outcome. This is only a crude analysis and shortcut methodology to remember the reaction.

Process 2 : NO can also be produced in the following manner :

$$\underbrace{\overset{+3}{2NaNO_2}}_{\text{Nitrite salt}} + \underbrace{\overset{+2}{2FeSO_4}}_{\text{Fe is in +2 state}} + \underbrace{3H_2SO_4}_{\text{Acidic medium}}$$

$$\to \underbrace{\overset{+3}{Fe_2(SO_4)_3}}_{\text{Fe is in +3 state}} + \overset{+2}{2NO} + 2NaHSO_4 + 2H_2O$$

Shortcut Trick : Exchange of oxidation number between N and Fe in the products

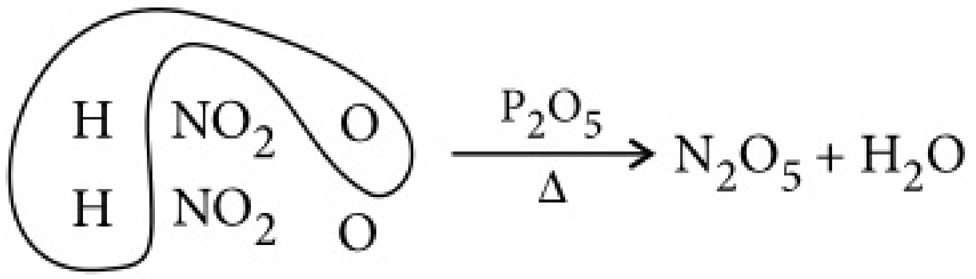
NO is highly reactive due to the odd electron present on oxygen. This is why NO can easily get converted to NO_2.

- **N_2O :** Heating ammonium nitrate

  $$NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$$

  N_2O is a colourless gas.

- **N_2O_5 :** N_2O_5 is the anhydride of HNO_3.



So, as P_2O_5 exists in P_4O_{10} state (dimer), the reaction can be shown as :

$$4HNO_3 + P_4O_{10} \to 4HPO_3 + 2N_2O_5$$

N_2O_5 is a colourless solid.

- **N_2O_3 :** $2NO + \underset{[2NO_2]}{N_2O_4} \xrightarrow{200°C - 230°C} 2N_2O_3$

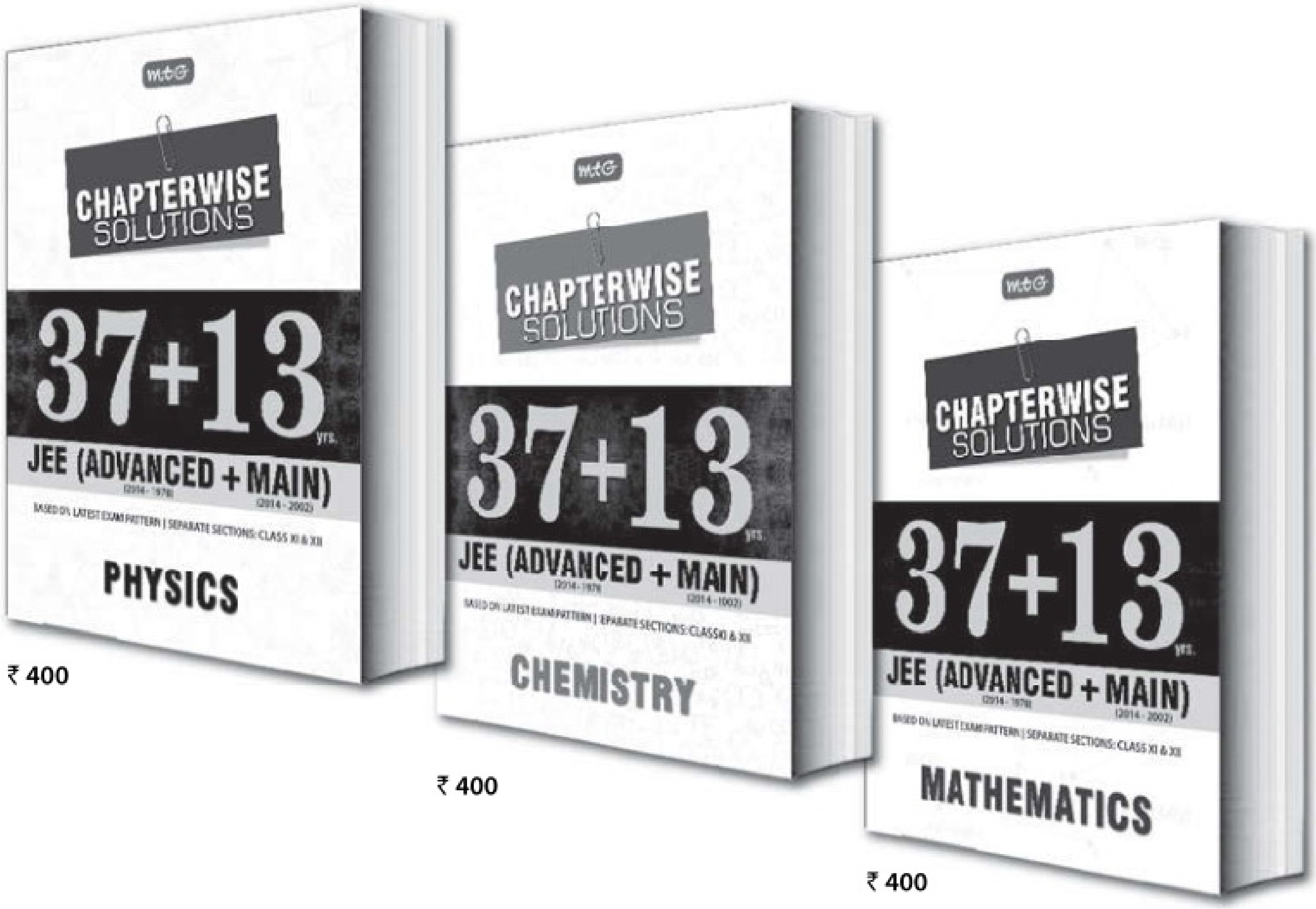
  N_2O_3 is a blue solid.

  Note : NO_2 is generally always a product whenever non-metals react with nitric acid. Some very famous reactions are :

  - $C + 4HNO_3 \to H_2CO_3 + H_2O + 4NO_2\uparrow$
  - $S_8 + 48HNO_3 \to 8H_2SO_4 + 48NO_2\uparrow + 16H_2O$
  - $P_4 + 20HNO_3 \to 4H_3PO_4 + 20NO_2\uparrow + 4H_2O$
  - $I_2 + 10HNO_3 \to 2HIO_3 + 10NO_2\uparrow + 4H_2O$
  - $As + 5HNO_3 \to \underset{\text{Arsenic acid}}{H_3AsO_4} + H_2O + 5NO_2\uparrow$
  - $Sb + 5HNO_3 \to \underset{\text{Antimonic acid}}{H_3SbO_4} + H_2O + 5NO_2\uparrow$

  Practice these reactions a number of times.

... To be continued on the next issue.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Thermodynamics

- The study of the flow of heat or any other form of energy into or out of a system as it undergoes a physical or chemical transformation is called **thermodynamics**.
- A **system** may be defined as any specified portion of universe under study which is separated from the rest of the universe with a definite boundary.
- The part of the universe other than the system is known as **surroundings**.
- A system which can exchange neither energy nor matter with its surroundings is called an **isolated system**.
- A system which can exchange energy but not matter with its surroundings is called a **closed system**.
- A system which can exchange matter as well as energy with its surroundings is called an **open system**.
- The properties associated with a macroscopic system (*i.e.* consisting of large number of particles) are called **macroscopic properties**. These properties are pressure, volume, temperature, density, etc.
- A system is said to be **homogeneou**s if it consists of one phase only and **heterogeneous** if it consists of more than one phases.
- A system consisting of two or more immiscible liquids or a solid in contact with a liquid in which it does not dissolve is a **heterogeneous system**.
- A system is said to be in **thermal equilibrium** if there is no flow of heat from one portion of the system to another. This is possible if the temperature remains the same throughout in all parts of the system.
- A system is said to be in **chemical equilibrium** if the composition of the various phases in the system remains same throughout.
- The properties of a system which depend on the quantity of matter contained in it are called **extensive properties** *e.g.*, mass, volume, energy etc.
- The properties of a system which are independent of the quantity of matter present in it are called **intensive properties** *e.g.*, temperature, pressure, viscosity, specific heat etc.
- A physical quantity is said to be a **state function** if its value depends only upon the state of the system and does not depend upon the path by which this state has been attained.
- A **thermodynamic process** is said to occur when the system changes from one state (initial state) to another state (final state).

  The five most common thermodynamic processes are
  - An **isobaric process** occurs at constant pressure.
  - An **isochoric process** occurs at constant volume.
  - An **isothermal process** occurs at constant temperature.
  - An **isoentropic process** occurs at constant entropy.
  - An **adiabatic process** occurs without loss or gain of heat.
- In C.G.S. system, the **unit of energy** is ergs. It is defined as the work done when a resistance of 1 dyne is moved through a distance of 1 centimetre.
- If a system **absorbs heat** q from the surroundings, q is **positive** and if the system **gives out heat** q to the surroundings, q is taken as **negative**.
- **Heat energy** is measured by the product of temperature and the heat capacity of the system.

- The **first law of thermodynamics** states that energy can neither be created nor destroyed although it can be transformed from one form to another. This is also known as **law of conservation of energy**.
- **Internal energy** of a substance or a system is a definite quantity and it is a function only of the state (*i.e.*, chemical nature, composition, temperature, pressure and volume) of the system at the given moment, irrespective of the manner in which that state has been brought about.
- The **change in internal energy** ΔU is given as

  $$\Delta U = U_B - U_A = q - w$$

  where U_A and U_B are the energies of a system in its state A and state B, q is the heat absorbed by the system while undergoing change from state A to state B, and w is the work done by the system. The above equation is the **mathematical statement of the first law of thermodynamics**.
- **Enthalpy** of a system may be defined as the sum of its internal energy and pressure-volume (PV) energy. It is denoted by H. Thus

  $$H = U + PV$$

  where U is the internal energy and P and V are pressure and volume of the system.
- $\boldsymbol{\Delta H = \Delta U + \Delta n_g RT}$

  where ΔH is change in enthalpy, ΔU is change in internal energy, R is a gas constant, T is the temperature on kelvin scale and Δn_g is the change in number of moles of gaseous products and gaseous reactants.
- For a reaction (or a process) taking place at constant temperature and at constant pressure the enthalpy change is equal to the amount of heat evolved or absorbed (q_p) in it.

  $$\Delta H = q_p$$
- The **total amount of work done by the isothermal reversible expansion** of the ideal gas from V_1 to V_2 is

  $$w = -nRT \ln \frac{V_2}{V_1}$$
- **Enthalpy of formation** is defined as the enthalpy change accompanying the formation of one mole of a compound from its constituent elements at a given temperature and pressure. It is denoted by ΔH_f.
- The **standard state** of an element is the pure element in its stable form or more common form under standard conditions of 1 bar and 298 K.
- The standard states of oxygen, carbon, mercury and sulphur are oxygen gas, graphite, liquid mercury and rhombic sulphur at 1 bar pressure and 298 K.
- The enthalpy of formation of any element in the standard state is taken as zero. *i.e.*, $\Delta H_f^\circ = 0$.
- The standard heat of formation of graphite is 0.0 whereas that of diamond is not zero but equal to 1.896 kJ mol^{-1}.
- The **enthalpy of combustion** of a substance is defined as the amount of heat evolved when one mole of the substance is completely burnt or oxidised.
- The change in enthalpy (ΔH) when a liquid changes into vapour state at its boiling point is known as **enthalpy of vaporisation**.
- The integral **enthalpy of solution** is defined as the enthalpy change when one mole of solute is dissolved in a definite quantity say '*n*' moles of solvent to get a solution of specified concentration.
- **Enthalpy of dilution** is defined as the enthalpy change that occurs when a solution containing one mole of a solute is diluted from one concentration to another concentration.
- **Enthalpy of sublimation** is defined as the amount of heat required to change one mole of the solid completely into vapours at a constant temperature.
- **Enthalpy of neutralisation** is defined as the enthalpy change which accompanies the complete neutralisation of one gram equivalent of an acid by a base.
- $\Delta H_{\text{neutralisation}}$ is constant for strong acid and base neutralisation.

  $$\Delta H = -13.7 \text{ kcal/mol} = -57.27 \text{ kJ/mol}$$
- Heat of neutralisation for weak acids (HCN, CH_3COOH, benzoic acid) and weak bases (NH_4OH, amines) is lower than that for strong acids and bases. The reason is that heat is absorbed in complete ionisation of weak acids and bases (unlike in case of strong acids and bases where no heat is required).

- The **standard enthalpy of a reaction** (ΔH°) is the difference of the standard enthalpies of all the products and standard enthalpies of all the reactants.

  $\Delta H^\circ = \Sigma\Delta H^\circ_{f\,\text{(products)}} - \Sigma\Delta H^\circ_{f\,\text{(reactants)}}$
- **Heat capacity** of a system between any two temperatures is defined as the quantity of heat required to raise the temperature of the system through 1°C.

  $$C = \frac{q}{T_2 - T_1} = \frac{q}{\Delta T}$$
- **Heat capacity at constant volume** is defined as the rate of change of internal energy with temperature at constant volume.

  $$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$
- **Heat capacity at constant pressure** is defined as the rate of change of enthalpy with temperature at constant pressure.

  $$C_P = \left(\frac{\partial H}{\partial T}\right)_P$$
- For one mole, the heat capacities at constant volume and at constant pressure are denoted by C_V and C_P respectively. These are termed as **molar heat capacities.** Thus for one mole of the gas

  $$C_V = \left(\frac{\partial U}{\partial T}\right)_V, \quad C_P = \left(\frac{\partial H}{\partial T}\right)_P$$
- The difference between the molar heat capacities of a gas at constant pressure (C_P) and at constant volume (C_V) is equal to the gas constant R *viz.* 1.987 cal or 8.314 J.

  $C_P - C_V = R$
- When a gas is heated at constant volume, no external work is done by the gas. But when a gas is heated at constant pressure, the gas will expand and do some external work. Hence the molar heat capacity of a gas at constant pressure (C_P) must be greater than (C_V) *i.e.*, $C_P > C_V$.
- Ratio of two specific heats, *i.e.* $\dfrac{C_P}{C_V} = \gamma$

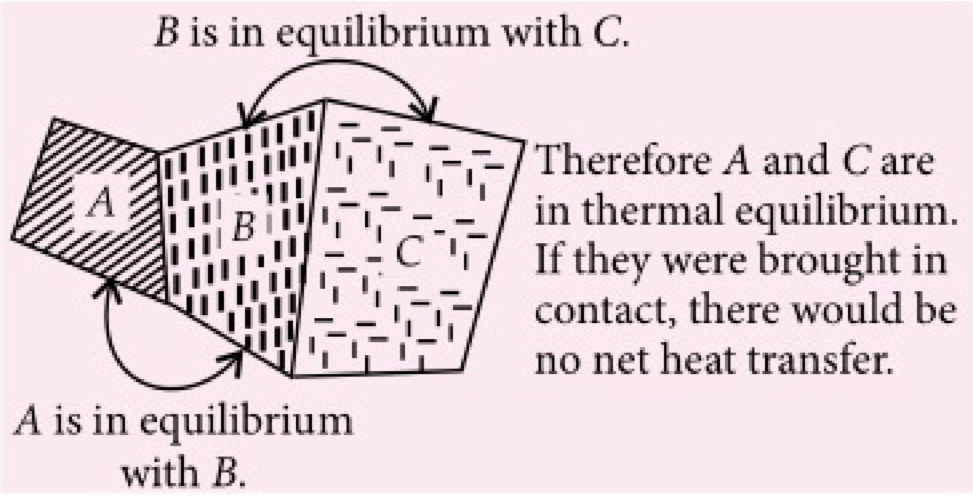
  $\gamma = 1.66$, the gas is monatomic.
    e.g. He, Ne, Ar, Kr, Xe, etc.

  $\gamma = 1.40$, the gas is diatomic.
    e.g. O_2, H_2, Cl_2, N_2, etc.

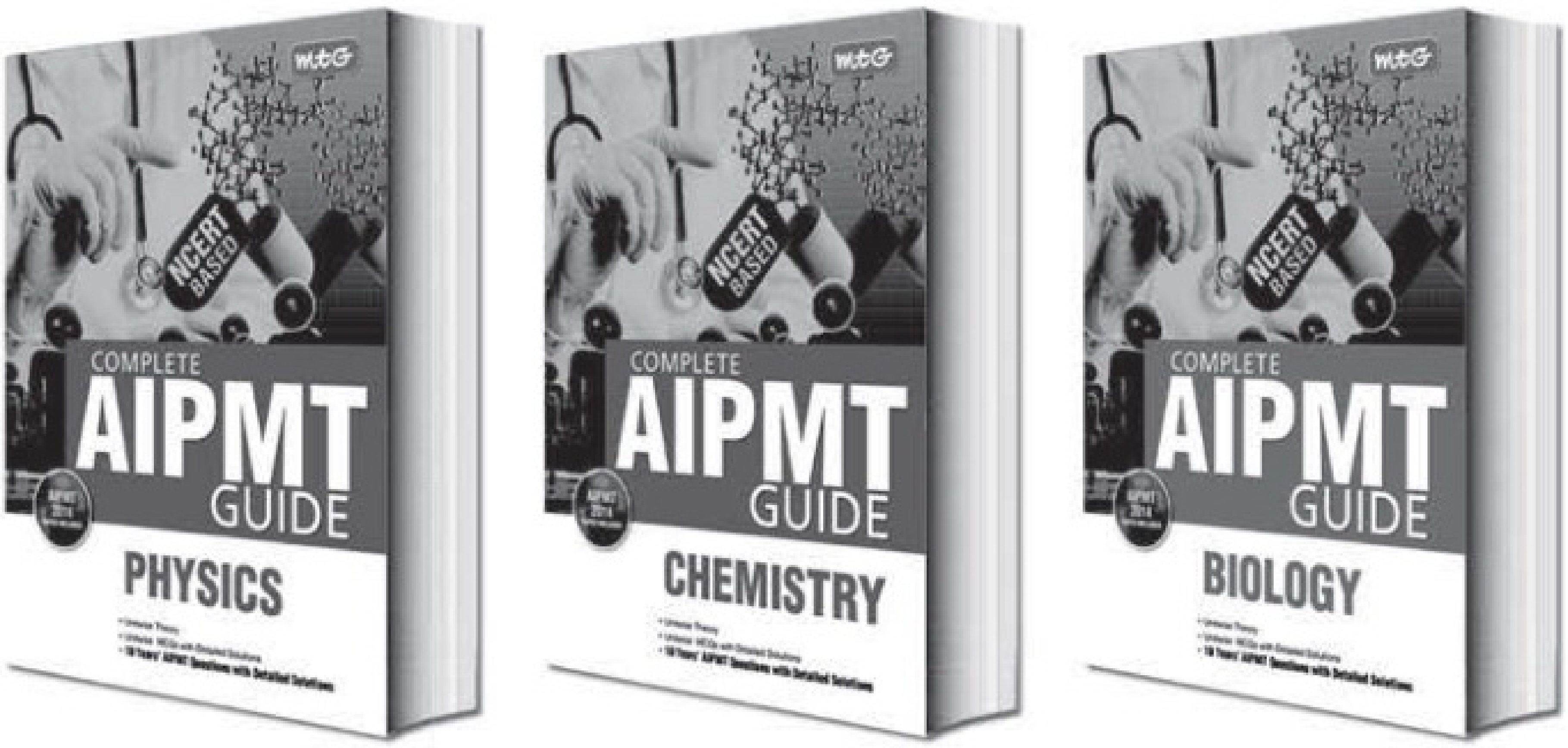
  $\gamma = 1.33$, the gas is polyatomic.
    e.g. SO_3, O_3, CO_2, etc.
- For an isothermal process, ΔT, ΔU and ΔH are zero.
- In an **isothermal expansion**, the work is done at the expense of the heat absorbed.

  $q = w$
- The temperature below which a gas becomes cooler on expansion is known as the **inversion temperature**.
- The phenomenon of change of temperature produced when a gas is made to expand adiabatically from a region of high pressure to a region of extremely low pressure is known as the **Joule-Thomson effect.**
- The number of degrees temperature produced per atmosphere drop in pressure under constant enthalpy conditions on passing a gas through the porous plug is called **Joule-Thomson coefficient**.

  $$\mu = \frac{dT}{dP}$$
- Joule-Thomson effect is zero in an ideal gas in which van der Waals' forces of attraction are negligible and there is no expenditure of energy in overcoming these forces of attraction.
- When an ideal gas undergoes expansion under adiabatic conditions in vacuum, no change takes place in its internal energy. *i.e.* $\left(\frac{\partial E}{\partial V}\right)_T = 0.$
- The quantity $\left(\frac{\partial E}{\partial V}\right)_T$ is called the **internal pressure**. Thus internal pressure of an ideal gas is zero.
- **Zeroth law of thermodynamics** states that if two systems are at the same time in thermal equilibrium with a third system, they are in thermal equilibrium with each other.



If A and C are in thermal equilibrium with B, then A is in thermal equilibrium with B.



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Practically this means that all three are at the same temperature, and it forms the basis for comparison of temperatures. It is so named because it logically precedes the first and second law of thermodynamics.

- Work done in reversible compression of an ideal gas is given by

$$w = nRT\ln\left(\frac{V_1}{V_2}\right) = nRT\ln\left(\frac{P_2}{P_1}\right)$$

- In the case of **expansion of a gas** the work is done by the system on the surroundings and w has a **positive** sign.
- In the case of **compression of a gas**, the work is done by the surroundings on the system and w has a **negative** sign.
- When a gas expands freely, *i.e.*, when it expands against vacuum such as $p_{ext} = 0$, no work is done by the system.

  i.e. work of expansion, $w = -p_{ext}\Delta V$

  $w = 0$.
- For an isochoric process, *i.e.* for which $\Delta V = 0$, change in internal energy, $\Delta U = q_V$.
- For an isobaric process, *i.e.* for which $\Delta P = 0$, change in enthalpy, $\Delta H = q_P$, where q_P is the amount of heat change at constant pressure.
- For an **adiabatic process**, *i.e.* for which $q = 0$, work done, $w = \dfrac{nR(T_2 - T_1)}{\gamma - 1}$

  where R is gas constant (8.314 J K^{-1} mol^{-1}) and $\gamma = C_P/C_V$ (where C_P and C_V are molar heat capacities at constant pressure and constant volume). T_2 and T_1 are final and initial temperatures on kelvin scale.
- **Hess's law** states that the enthalpy change in a chemical or a physical process is same whether the process is carried out in one step or in several steps.

  $\Delta H = \Delta H_1 + \Delta H_2 + \ldots$
- Hess's law is useful in determining the enthalpies of transition of allotropic modifications such as graphite to diamond, rhombic sulphur to monoclinic sulphur, yellow phosphorus to red phosphorus, etc.
- **Bond energy** is the energy released when gaseous atoms form molecules.
- **Bond dissociation energy** can be defined as the energy required to break one mole of a particular type of bonds in gaseous molecules so as to get the separated atoms in gaseous state.
- The branch of chemistry which deals with energy changes in chemical reactions is called **thermochemistry**.
- **Heat of reaction at constant volume** and at a given temperature is given by the difference in the internal energies of the products and that of the reactants, the quantities of the products and the reactants being the same as represented by the chemical equation.

  $q_V = \Delta U = U_P - U_R$
- **Heat of reaction at constant pressure** and at a given temperature is given by the difference in the enthalpies of the products and that of the reactants, the quantities of the products and the reactants being the same as represented by the chemical equation.

  $q_P = \Delta H = H_P - H_R$
- In all **exothermic reactions** taking place at a constant temperature, ΔU has a **negative** sign.
- In all **endothermic reactions** taking place at a constant temperature, ΔU has a **positive** sign.
- In all **exothermic reactions** taking place at a constant temperature, ΔH has a **negative** sign.
- In all **endothermic reactions** taking place at a constant temperature, ΔH has a **positive** sign.
- Variation of heat of reaction with temperature is given by **Kirchhoff's equation**.

$$\left(\frac{\partial(\Delta H)}{\partial T}\right)_P = \Delta C_P \quad \text{or,} \quad \frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta C_P$$

  where $\Delta C_P = \Sigma$ heat capacities of products $- \Sigma$ heat capacities of reactants
- A process which proceeds on its own accord without any outside assistance is termed a **spontaneous** or **natural process**.
- The process which has no natural tendency or an urge to occur is said to be a **non-spontaneous process**.

- The tendency to attain minimum energy *i.e.* a negative value of enthalpy change (ΔH) might be responsible for a process or a reaction to be spontaneous or feasible.
- Dissolution of common salt in water, evaporation of water in an open vessel and flow of water down a hill are spontaneous processes.
- Flow of water up a hill, flow of heat from a cold body to a hot body and dissolution of sand in water are non-spontaneous processes.
- **Entropy** is a measure of randomness or disorder of the system.
- For a given substance, the crystalline solid state has the lowest entropy, the gaseous state has the highest entropy and the liquid state has the entropy between the two.
- The greater the randomness of a system, higher is its entropy.
- At absolute zero, a perfectly crystalline substance has zero entropy.
- **Entropy change** during a process is defined as the amount of heat (q) absorbed isothermally and reversibly (infinitesimally slowly) divided by the absolute temperature (T) at which the heat is absorbed.

$$\Delta S = \frac{q_{\text{rev}}}{T}$$

- The total entropy change (ΔS) of A and B involving transfer of heat from a body B at a higher temperature T_2 to a body A at a lower temperature T_1, is given by

$$\Delta S = \frac{q_{\text{rev}}(T_2 - T_1)}{T_1 T_2}$$

- The entropy change of a chemical reaction is given by the difference between the sum of the entropies of all the products and the sum of entropies of all the reactants.

$$\Delta S = \Sigma S_{(\text{products})} - \Sigma S_{(\text{reactants})}$$

- Entropy of one mole of a substance in pure state at one atmospheric pressure and 25°C is termed as **standard entropy** of that substance and is denoted as $S°$.

$$\Delta S° = \Sigma S°_{(\text{products})} - \Sigma S°_{(\text{reactants})}$$

- **Entropy of fusion** may be defined as the entropy change taking place when one mole of the substance changes from solid state into liquid state at its melting point.
- **Entropy of vaporisation** may be defined as the entropy change taking place when one mole of the substance changes from liquid state into vapours at its boiling point.
- Suppose one mole of a substance melts reversibly at the fusion point T_f, at constant pressure. If ΔH_f be the molar heat of fusion, then the entropy change of the process, ΔS_f will be given by

$$\Delta S_f = \frac{\Delta H_f}{T_f}$$

- Suppose one mole of a substance changes from liquid to vapour state reversibly at its boiling point T_b under a constant pressure. If ΔH_v is the molar heat of vaporisation, then the entropy change accompanying the process will be given by

$$\Delta S_v = \frac{\Delta H_v}{T_b}$$

- If we consider the change of state from vapour to liquid or from liquid to solid, ΔH_v and ΔH_f will be both negative and hence the process of condensation of vapour or freezing of a liquid is accompanied by decrease of entropy.
- The change in entropy when one mole of a solid substance undergoes change of state from one crystalline form (say rhombic form) to another crystalline form (say monoclinic form) at the transition temperature T, is given by

$$\Delta S_T = \frac{\Delta H_t}{T}$$

where ΔH_t is the molar heat of transition of the substance.

- **Molar heat of transition** of the substance ΔH_t is the amount of heat absorbed or evolved by one mole of a substance when it undergoes change of state from one crystalline form to another at transition temperature T.

- According to **second law of thermodynamics,** entropy of the universe is continuously increasing and tends to be maximum.
- **Gibbs free energy** is defined as the amount of energy available from a system that can be put into useful work. Mathematically, free energy G is given by the relation, $G = H - TS$

  where H is enthalpy of the system, S is entropy of the system and T is temperature on kelvin scale.
- **Gibbs—Helmholtz equation** is

  $\Delta G = \Delta H - T\Delta S$

  where $\Delta H = H_2 - H_1$ is the change in enthalpy of the system, $\Delta S = S_2 - S_1$ is the change in entropy of the system, T is absolute temperature and $\Delta G = G_2 - G_1$ is the change in free energy of the system
  - If ΔG is negative, the process will be spontaneous.
  - If ΔG is zero, the process is in equilibrium.
  - If ΔG is positive, the direct process is non-spontaneous; the reverse process may be spontaneous.
- The **standard free energy change** is defined as the free energy change for a process in which reactants in their standard state are converted into the products in their standard state. It is denoted by the symbol $\Delta G°$.
- The **standard free energy of formation** of a compound is defined as the free energy change which takes place when one mole of the compound is formed from its elements taken in their standard states.
- For a reaction in equilibrium, the standard free energy change is related to the equilibrium constant of the reaction according to the relation

  $\Delta G° = -RT \ln K$ or $\Delta G° = -2.303\, RT \log K$

  where R is the gas constant.
- Entropy change of an ideal gas (for 1 mole),

$$\Delta S = C_V \ln\frac{T_2}{T_1} + R\ln\frac{V_2}{V_1} = C_P \ln\frac{T_2}{T_1} + R\ln\frac{P_1}{P_2}$$

At constant temperature (isothermal process),

$$\Delta S_T = R\ln\frac{V_2}{V_1} = R\ln\frac{P_1}{P_2}$$

At constant volume (isochoric process),

$$\Delta S_V = C_V \ln\frac{T_2}{T_1}$$

At constant pressure (isobaric process),

$$\Delta S_P = C_P \ln\frac{T_2}{T_1}$$

- $\Delta G°_{\text{reaction}} = \Sigma\Delta G°_{f\,(\text{products})} - \Sigma\Delta G°_{f\,(\text{reactants})}$
- For elementary substances, $\Delta G°_f = 0$.
- The **entropy of a perfectly crystalline solid** is zero at the absolute zero of temperature.
- Entropy of every substance (element or compound) in the standard state is not equal to zero.
- Nernst in 1906 formulated the **third law of thermodynamics** which states that "at absolute zero the entropy of a perfectly crystalline substance is zero".
- In a perfect crystal, at absolute zero temperature, each atom must be at a crystal lattice point and it must have lowest energy. This means that this particular state is of perfect order, *i.e.*, zero disorder and hence of zero entropy.
- In case of solids,

$$\Delta S = \int_0^T \frac{C_P dT}{T} = C_P \ln T = 2.303 C_P \log T$$

where C_P is the heat capacity of the substance at constant pressure and is supposed to remain constant in the range 0 to T K.

- If a system returns to its original state after undergoing a number of successive changes, it is said to be a cyclic process.
- The fraction of the heat absorbed by a machine that is converted into work is called the **efficiency of the machine**. It is given by

$$\eta = \frac{w}{q_2} = \frac{q_2 - q_1}{q_2} = \frac{T_2 - T_1}{T_2}$$

where q_2 is heat absorbed from the source at temperature T_2, q_1 is heat rejected to the sink at temperature T_1.

EXAMINER'S MIND NCERT 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 | THE *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.

1. Compound that retards the decomposition of H_2O_2 solution is

(a) NH_2CONH_2 (b) $Na_6P_6O_{18}$
(c) $LiAlH_4$ (d) $K_2S_2O_8$

2. The compound *A* on heating gives a colourless gas and a residue that is dissolved in water to obtain *B*. Excess of CO_2 is bubbled through aqueous solution of *B*, *C* is formed which is recovered in the solid form. Solid *C* on gentle heating gives back *A*. The compound is

(a) $CaCO_3$ (b) Na_2CO_3
(c) K_2CO_3 (d) $CaSO_4 \cdot 2H_2O$

3. $$Mg \xrightarrow[\text{Heat}]{\text{Air}} X + Y \xrightarrow{H_2O} \underset{\text{Colourless gas}}{Z}$$

$$Z \xrightarrow{H_2O} \text{Solution} \xrightarrow{CuSO_4} \underset{\text{Blue coloured solution}}{(A)}$$

Substances *X, Y, Z* and *A* are respectively

(a) Mg_3N_2, MgO, NH_3, $CuSO_4 \cdot 5H_2O$
(b) $Mg(NO_3)_2$, MgO, H_2, $CuSO_4 \cdot 5H_2O$
(c) MgO, Mg_3N_2, NH_3, $[Cu(NH_3)_4]SO_4$
(d) $Mg(NO_3)_2$, MgO_2, H_2O_2, $CuSO_4 \cdot 5H_2O$

4. Calculate the amount of $Ca(OH)_2$ required to remove the hardness of water from 60,000 litres containing 16.2 g of $Ca(HCO_3)_2$ per 100 litre.

(a) 1.11 kg (b) 2.22 kg
(c) 3.33 kg (d) 4.44 kg

5. The alkali metal which can emit its outermost electron under the influence of even candle light is

(a) Na (b) Rb
(c) K (d) Cs

6. Which of the following is used in the treatment of manic depression disorders?

(a) Na_2CO_3 (b) Li_2CO_3
(c) K_2CO_3 (d) $MgCO_3$

7. Which one of the following undergoes reduction with hydrogen peroxide in acidic medium?

(a) Mn^{2+} (b) HOCl
(c) PbS (d) Fe^{2+}

8. The formula of microcosmic salt and the product obtained by heating it is

(a) $Na(NH_4)PO_4$; $NaPO_3$
(b) $Na(NH_4)_2HPO_4$; $NaPO_3$
(c) $Na(NH_4)HPO_4$; $NaPO_4$
(d) $Na(NH_4)HPO_4$; $NaPO_3$

9. Which of the following alkaline earth metal sulphates is least soluble in water?

(a) $BaSO_4$ (b) $MgSO_4$
(c) $SrSO_4$ (d) $CaSO_4$

10. Hydrogen can be fused to form helium at

(a) high temperature and high pressure
(b) high temperature and low pressure
(c) low temperature and high pressure
(d) low temperature and low pressure.

11. Consider the following abbrevations for hydrated alkali metal ions :

$X = [Li(H_2O)_n]^+$; $Y = [K(H_2O)_n]^+$; $Z = [Cs(H_2O)_n]^+$

Which is the correct order of size of these hydrated alkali metal ions?

(a) $X > Y > Z$ (b) $Z > Y > X$
(c) $X = Y = Z$ (d) $Z > X > Y$

12. Which is correct order of solubility in water?
(a) $Ba(OH)_2 < Mg(OH)_2$
(b) $BaCO_3 > CaCO_3$
(c) $CaSO_4 < MgSO_4$
(d) $Ca(OH)_2 \simeq Mg(OH)_2$

13. Which of the following is the best scientific method to test presence of water in a liquid?
(a) Use of litmus paper
(b) Taste
(c) Smell
(d) Use of anhydrous copper sulphate

14. Correct order of stability of group IIA metal carbonates is
(a) $MgCO_3 > CaCO_3 > SrCO_3 > BaCO_3$
(b) $BaCO_3 > SrCO_3 > CaCO_3 > MgCO_3$
(c) $SrCO_3 > BaCO_3 > CaCO_3 > MgCO_3$
(d) $CaCO_3 > MgCO_3 > BaCO_3 > SrCO_3$

15. Which of the following has highest hydration energy?
(a) $MgCl_2$ (b) $CaCl_2$
(c) $BaCl_2$ (d) $SrCl_2$

16. Which of the following cannot be used for the preparation of H_2?
(a) $Zn + HCl(dil.) \rightarrow$
(b) $NaH + H_2O \rightarrow$
(c) $Zn + HNO_3(dil.) \rightarrow$
(d) $HCOONa \xrightarrow{\Delta}$

17. $Be + 2NH_3 + 4HF \longrightarrow A \xrightarrow{\Delta} BeF_2 + 2NH_4F$
The compound (A) in the reaction is
(a) NF_3 (b) $NH_3 - BeF_2$
(c) $(NH_4)_2[BeF_4]$ (d) NF_3NH_3

18. Which of the following on thermal decomposition yields a basic as well as an acidic oxide?
(a) $KClO_3$ (b) Na_2CO_3
(c) $NaNO_3$ (d) $CaCO_3$

19. Water softening by Clark's process uses
(a) calcium bicarbonate
(b) sodium bicarbonate
(c) potash alum
(d) calcium hydroxide.

20. If 2 g of aluminium is treated, first with excess of dilute H_2SO_4 and then with excess of NaOH, the ratio of the volumes of hydrogen evolved is
(a) 1 : 1 (b) 1 : 2
(c) 2 : 3 (d) 2 : 1

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. Highly pure dilute solution of sodium in liquid ammonia
(a) shows blue colour
(b) exhibits electrical conductivity
(c) produces sodium amide
(d) produces hydrogen gas.

22. Which of the following pairs of substances on reaction will evolve H_2 gas?
(a) Iron and dilute H_2SO_4
(b) Copper and dilute HCl
(c) Sodium and ethyl alcohol
(d) Iron and steam

23. Which of the following chlorides is (are) soluble in pyridine?
(a) LiCl (b) CsCl
(c) NaCl (d) $BeCl_2$

24. Which of the following statements is (are) correct?
(a) Hydrides of group 13 act as Lewis acids.
(b) Hydrides of group 14 are electron deficient hydrides.
(c) Hydrides of group 14 act as Lewis acids.
(d) Hydrides of group 15 act as Lewis bases.

25. The compounds used in Solvay process is (are)
(a) Na_2SO_4 (b) NaCl
(c) NH_3 (d) $CaCO_3$

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

Presence of calcium and magnesium salts in the form of hydrogencarbonates, chlorides and sulphates in water makes water hard. Hard water does not give lather with soap. Water free from soluble salts of calcium and magnesium is called soft water. It gives lather with soap easily.

The hardness of water is of two types : (i) temporary hardness, and (ii) permanent hardness.

Both temporary and permanent hardness can be removed by different methods.

26. Substances that cause temporary and permanent hardness of water are respectively

(a) $MgCO_3$, $MgSO_4$

(b) $CaSO_4$, $MgCl_2$

(c) $Mg(HCO_3)_2$, $CaCl_2$

(d) $CaCl_2$, $Ca(HCO_3)_2$

27. In a permutit, the calcium and magnesium ions of hard water are exchanged by

(a) CO_3^{2-} and HCO_3^- ions of permutit

(b) Na^+ ions of permutit

(c) Al^{3+} ions of permutit

(d) Si^{4+} ions of permutit.

28. Temporary hardness and permanent hardness can be removed respectively by addition of

(a) CaO, $CaCO_3$ (b) CaO, Na_2CO_3

(c) Na_2CO_3, CaO (d) $NaHCO_3$, $CaCl_2$

Paragraph for Questions 29 to 31

Both alkali and alkaline earth metals and their salts impart characteristic colours to the flame. This is because the heat from the flame excites the outermost orbital electron to a higher energy level. When the excited electron comes back to the ground state, there is emission of radiation in the visible region. Therefore, the flame test is helpful in their detection in qualitative analysis and estimation by flame photometry.

29. Sodium chloride imparts golden yellow colour to the Bunsen flame. This can be interpreted due to

(a) low ionisation potential of sodium

(b) photosensitivity of sodium

(c) sublimation of metallic sodium to give yellow vapours

(d) emission of energy absorbed as a radiation in the ultraviolet region.

30. Which of the following pairs do not impart any colour to the flame?

(a) Ca and Mg (b) Be and Ba

(c) Na and K (d) Be and Mg

31. A substance which gives a brick red flame and breaks down on heating giving oxygen and a brown gas is

(a) calcium carbonate

(b) magnesium carbonate

(c) magnesium nitrate

(d) calcium nitrate.

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

	List I		List II
P.	Quick lime	1.	Setting fractured bones
Q.	Plaster of Paris	2.	A constituent of chewing gum
R.	Slaked lime	3.	Manufacture of bleaching powder
S.	Limestone	4.	Manufacture of dyestuffs

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

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.	Clark's method	1.	$Na_6P_6O_{18}$
Q.	Calgon's method	2.	$NaAlSiO_4$
R.	Ion- exchange method	3.	RSO_3H
S.	Synthetic resins method	4.	$Ca(OH)_2$

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

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

	List I		List II
P.	Strongest reducing agent in aqueous solution	1.	Magnesium
Q.	Does not give flame colouration	2.	Caesium
R.	Forms peroxides on heating with excess oxygen	3.	Lithium
S.	Used in photoelectric cells	4.	Sodium

	P	Q	R	S
(a)	3	1	4	2
(b)	2	1	4	3
(c)	1	2	3	4
(d)	3	4	1	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 :** Hydrides of N, O and F have lower boiling points than the hydrides of their subsequent group members.

Reason : Boiling point depends upon the molecular mass only.

36. **Assertion :** The carbonate of lithium decomposes easily on heating to form lithium oxide and CO_2.

Reason : Lithium being very small in size polarises large carbonate ion leading to the formation of more stable Li_2O and CO_2.

37. **Assertion :** Helium and beryllium have similar outer electronic configuration of type ns^2.

Reason : Both are chemically inert.

38. **Assertion :** The colour of old lead paintings can be restored by washing with a dilute solution of H_2O_2.

Reason : Hydrogen peroxide oxidises black lead sulphide to white lead sulphate.

39. **Assertion :** Lithium resembles magnesium diagonally placed in next group.

Reason : The size of Li^+ and Mg^{2+} are different but their electropositive character is same.

40. **Assertion :** The O—O bond length in H_2O_2 is shorter than that of O_2F_2.

Reason : H_2O_2 is an ionic compound.

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. Commercial 11.2 volume H_2O_2 solution has a molarity of

42. 1 mole mixture of Li_2CO_3 and K_2CO_3 on strongly heating gave 0.25 mol of CO_2. The two compounds are present in the ratio $x : y$ (*i.e.*, $Li_2CO_3 : K_2CO_3$). The value of y is

43. Moles of nitrogen dioxide formed on decomposition of 2 moles of lithium nitrate is

44. Potassium has highest solubility in liquid ammonia at x°C. The value of x is

45. The chloride of an element A gives a neutral solution in water. In periodic table, the element A belongs to group

46. Weight of H_2O_2 in grams required to oxidise 3.5 g H_2S gas is

47. On decomposition of 1 mole of hydrolith by water, *n* number of H_2 molecules are liberated. The value of *n* is

48. The sum of protons, electrons and neutrons in the heaviest isotope of hydrogen is

49. *X* is used for immobilising the affected part of organ where there is a sprain. *X* is obtained on heating gypsum at 393 K. The number of expelled water molecules when *X* is obtained by heating 2 molecules of gypsum is

50. 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

SOLUTIONS

1. **(a) :** Urea (NH_2CONH_2) acts as stabiliser.

2. **(a) :** The reactions can be summarised as follows :

$$A \xrightarrow{\Delta} \text{colourless gas} + \text{residue}$$

$$\text{Residue} + H_2O \longrightarrow B \xrightarrow[\text{excess}]{CO_2} C \xrightarrow{\Delta} A$$

This is possible only when *A* is $CaCO_3$.
The reactions are as follows :

$$\underset{(A)}{CaCO_3} \xrightarrow{\Delta} \underset{\text{(colourless gas)}}{CO_2} + \underset{\text{(residue)}}{CaO}$$

$$CaO + H_2O \longrightarrow \underset{(B)}{Ca(OH)_2} \xrightarrow[\text{(excess)}]{CO_2}$$

$$\underset{(C)}{Ca(HCO_3)_2} \xrightarrow{\Delta} \underset{(A)}{CaCO_3}$$

3. **(c)**

4. **(d) :** Amount of $Ca(HCO_3)_2$ in 60,000 litres of

$$\text{water} = \frac{16.2 \times 60{,}000}{100} = 9720 \text{ g}$$

$$= \frac{9720}{162} = 60 \text{ moles}$$

[$\because$ mol. wt. of $Ca(HCO_3)_2 = 162$]

$$\underset{\text{1 mole}}{Ca(OH)_2} + \underset{\text{1mole}}{Ca(HCO_3)_2} \rightarrow 2CaCO_3\downarrow + 2H_2O$$

Amount of $Ca(OH)_2$ required = 60 moles

$= 60 \times 74 = 4440$ g $= 4.44$ kg

[$\because$ mol. wt. of $Ca(OH)_2 = 74$]

5. **(d) :** Cs because of its low *IE* emits electron under the influence of even candle light.

6. **(b)**

7. **(b) :** $HOCl + H_2O_2 \longrightarrow HCl + H_2O + O_2$

8. **(d) :** Microcosmic salt is $Na(NH_4)HPO_4{\cdot}4H_2O$

$$Na(NH_4)HPO_4{\cdot}4H_2O \xrightarrow{\Delta} NaPO_3 + 5H_2O + NH_3$$

It is prepared by :

$$NH_4Cl + Na_2HPO_4 + 4H_2O \rightarrow Na(NH_4)HPO_4{\cdot}4H_2O + NaCl$$

9. **(a) :** The lattice energies of alkaline earth metal sulphates remain almost constant but their hydration energies decrease down the group. Therefore, $BaSO_4$ is least soluble in water.

10. **(a) :** A fusion reaction is difficult to occur because positively charged nuclei repel each other. At very high temperatures of the order of 10^6 to 10^7 K, the nuclei may have sufficient energy to overcome the repulsive forces and fuse. It is for this reason, fusion reactions are also called thermonuclear reactions. Hence, hydrogen can be fused to form helium at high temperature and high pressure.

11. **(a) :** Smaller the cation, greater is the degree of hydration, hence the degree of hydration decreases from Li^+ to Cs^+.

12. **(c) :** $MgSO_4$ is readily soluble in water. The solubility of the sulphates of alkaline earth metals decreases with increase in size of the central metal ion. The greater hydration enthalpy of Mg^{2+} ion overcomes the lattice enthalpy factor therefore, $MgSO_4$ is more soluble in water.

13. **(d) :** Interaction of water in a liquid with anhydrous copper sulphate ($CuSO_4$, white) will produce blue colour ($CuSO_4{\cdot}5H_2O$) so, the presence of water can be detected.

14. (b) : Mg^{2+} is smallest in size hence show high polarising power. Thus, $MgCO_3$ is most covalent and least stable. Thermal stability increases down the group.

15. (a) : Smaller sized and highly charged metal ions have higher hydration energy.
Therefore, order of hydration energy in this group is $Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$.

16. (c) : $4Zn + 10HNO_3(\text{dil.}) \longrightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O$

17. (c) : $Be + 2NH_3 + 4HF \longrightarrow \underset{(A)}{(NH_4)_2[BeF_4]} \xrightarrow{\Delta} BeF_2 + 2NH_4F$

18. (d) : $CaCO_3 \xrightarrow{\Delta} \underset{\text{(basic)}}{CaO} + \underset{\text{(acidic)}}{CO_2}$

19. (d) : In Clark's process quick lime is added to hard water which produces $Ca(OH)_2$ which further converts bicarbonates into insoluble carbonates.

20. (a) : In first case,
$2Al + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3H_2\uparrow$ ...(i)
and in second case,
$2Al + 2NaOH + 2H_2O \rightarrow 2NaAlO_2 + 3H_2\uparrow$ ...(ii)
Thus, in reactions (i) and (ii) hydrogen (H_2) evolved is 3 and 3 moles respectively. Therefore ratio of the volumes of H_2 evolved is 1 : 1.

21. (a, b) : Dilute solution of sodium in liquid ammonia contains ammoniated cations and ammoniated electrons as shown below and hence, is good conductor of electricity.

$$M + (x + y)NH_3 \longrightarrow M^+(NH_3)_x + e^-(NH_3)_y$$

When ordinary light falls on these ammoniated electrons, they get excited to higher energy levels by absorbing energy corresponding to red region of the visible light. As a result, transmitted light is blue which imparts blue colour to the solution.

22. (a, c, d)

23. (a, d) : Being covalent LiCl and $BeCl_2$ are soluble in pyridine.

24. (a, d) : Hydrides of group 13, *i.e.*, BF_3, $AlCl_3$, etc. act as Lewis acids while those of group 15 such as NH_3 act as Lewis bases.

25. (b, c, d)

26. (c) : Temporary hardness is due to the presence of magnesium and calcium hydrogencarbonates while permanent hardness is due to the presence of soluble salts of magnesium and calcium in the form of chlorides and sulphates in water.

27. (b) : $\underset{\text{Permutit}}{Na_2Al_2Si_2O_8.xH_2O} + Ca^{2+} \text{ (or } Mg^{2+}) \rightarrow CaAl_2Si_2O_8.xH_2O + 2Na^+$
or $MgAl_2Si_2O_8.xH_2O$

28. (b) : Temporary hardness can be removed by addition of CaO.
$CaO + H_2O \longrightarrow Ca(OH)_2$
$\underset{\substack{\text{From hard water} \\ (M = \text{Ca, Mg})}}{M(HCO_3)_2} + Ca(OH)_2 \longrightarrow MCO_3\downarrow + CaCO_3\downarrow + 2H_2O$
Permanent hardness can be removed by addition of Na_2CO_3.
$\underset{\substack{\text{From hard water} \\ (M = \text{Ca, Mg})}}{MSO_4} + Na_2CO_3 \longrightarrow MCO_3\downarrow + Na_2SO_4$

29. (a) : Metals with low ionisation potential impart colour to Bunsen flame.

30. (d) : The electrons in Be and Mg are too strongly held to get excited by flame. Hence, these elements do not impart any colour to the flame.

31. (d) : $\underset{\text{Brick red flame}}{2Ca(NO_3)_2} \xrightarrow{\text{Heat}} 2CaO + \underset{\text{brown gas}}{4NO_2\uparrow} + O_2\uparrow$

32. (b) : Quick lime is used for the manufacture of dyestuffs.
Plaster of Paris is used for setting of fractured bones.
Slaked lime is used for the manufacture of bleaching powder.
Limestone is a constituent of chewing gum.

33. (c) **34. (a)**

35. (d) : Boiling point depends upon intermolecular forces. Due to higher electronegativity of N, O and F, the magnitude of hydrogen bonding in their hydrides will be quite high. Hence their boiling points will be higher than the hydrides of their subsequent group members.

36. (a)

37. (c) : Helium : $Z = 2;\quad 1s^2$

Beryllium : $Z = 4;\ 1s^2, 2s^2$

Helium is an inert gas while beryllium is reactive due to vacant $2p$ orbitals.

38. (a)

39. (c) : The size of Li^+ and Mg^{2+} is nearly the same.

40. (d) : The O—O bond length in H_2O_2 is much longer than that in O_2F_2. This is because the lone pairs of electrons on the O atoms are strongly attracted by the electronegative F atoms. As a result, lone pair-lone pair repulsion of the two oxygen atoms is far less in O_2F_2 than in H_2O_2. As a result, O—O bond length in O_2F_2 (1.22 Å) is much shorter than in H_2O_2 (1.48 Å).

H_2O_2 is a covalent compound.

41. (1) : Volume strength = 11.2 × Molarity

$$\text{Molarity} = \frac{\text{Volume strength}}{11.2} = \frac{11.2}{11.2} = 1$$

42. (3) : $Li_2CO_3 \xrightarrow{\Delta} Li_2O + CO_2\uparrow$

$K_2CO_3 \xrightarrow{\Delta}$ No effect

CO_2 is evolved due to Li_2CO_3 only.

0.25 mol CO_2 = 0.25 mol Li_2CO_3

$\therefore$ mixture contains 0.25 mol Li_2CO_3 and 0.75 mol K_2CO_3

$$\Rightarrow \quad \text{ratio } x : y = \frac{0.25}{0.75} = \frac{1}{3}$$

$\therefore$ Value of $y = 3$

43. (2) : $2LiNO_3 \rightarrow Li_2O + 2NO_2 + \frac{1}{2}O_2$

No. of moles of NO_2 = 2

44. (0) : Potassium has highest solubility in liquid ammonia at 0°C.

45. (1) : The chlorides of 1st group elements (*e.g.*, NaCl) are salts of strong acids (HCl) and strong bases (NaOH). As such, they do not undergo hydrolysis thereby yielding neutral solutions.

46. (7) : H_2O_2 is marked "22.4 volume" which means 1 mL of H_2O_2 at NTP gives 22.4 mL of O_2 at NTP.

$$\underset{(2\times 34 = 68\text{ g})}{2H_2O_2} \longrightarrow 2H_2O + \underset{22400\text{ mL at NTP}}{O_2}$$

22400 mL of O_2 is liberated from 68 g of H_2O_2

$$\underset{34\text{ g}}{H_2S} + \underset{68\text{ g}}{H_2O_2} \longrightarrow 2H_2O + S$$

34 g H_2S is oxidised by = 68 g H_2O_2

$$\therefore \quad 3.5\text{ g } H_2S \text{ is oxidised by} = \frac{68}{34}\times 3.5 = 7\text{ g } H_2O_2$$

47. (2) : $\underset{\text{(Hydrolith)}}{CaH_2} + 2H_2O \rightarrow Ca(OH)_2 + 2H_2$

48. (4) : Heaviest isotope of hydrogen is ${}^3_1H$.

Number of protons = 1

Number of electrons = 1

Number of neutrons = 3 – 1 = 2

Sum = 1 + 1 + 2 = 4

49. (3) : X is plaster of Paris.

$$\underset{\text{Gypsum}}{2(CaSO_4\cdot 2H_2O)} \xrightarrow[393\text{ K}]{\Delta} \underset{\text{Plaster of Paris }(X)}{2(CaSO_4)\cdot H_2O} + 3H_2O$$

$\therefore$ 3 molecules of water are expelled.

50. (4) : $H_2O_2 + 2I^- + 2H^+ \rightarrow 2H_2O + I_2$

$$I_2 + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2I^-$$

$$\underset{(H_2O_2)}{N_1V_1} = \underset{(Na_2S_2O_3)}{N_2V_2}$$

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

Normality of H_2O_2 is related to x volume strength by relation $N_1 = \frac{x}{5.6}$

$\Rightarrow \quad x = N_1 \times 5.6 = 0.7143 \times 5.6 = 4$

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UNIT-4

Classification of Elements and Periodicity in Properties | General Principles and Processes of Isolation of Metals | Hydrogen | *s*-Block Elements | *p*-Block Elements (Group 13 and 14)

CLASSIFICATION OF ELEMENTS AND PERIODICITY IN PROPERTIES

- Modern Periodic Law
- Present Form of the Periodic Table
- *s*, *p*, *d* and *f*-Block Elements
- Periodic Trends

TIPS TO REMEMBER

Modern Periodic Law

- ❑ The physical and chemical properties of the elements are periodic functions of their atomic numbers.
- ❑ **Cause of Periodicity**
  - ❍ The cause of periodicity in properties is the repetition of similar outer electronic configurations after certain regular intervals.

Present Form of the Periodic Table

- ❑ **Groups**
  - ❍ The vertical columns in the modern periodic table are called *groups*.
  - ❍ The *group number* corresponds to the number of electrons in the outermost shell of the element.
- ❑ **Periods**
  - ❍ The horizontal rows in the modern periodic table are called *periods*.
  - ❍ The *period number* corresponds to the highest principal quantum number (n) of the elements in the periodic table.

s, *p*, *d* and *f*-Block Elements

- ❑ ***s*-Block Elements**
  - ❍ Elements in which the last electron enters the *s*-orbital of their respective outermost shells are called *s-block elements*.
  - ❍ General outer shell electronic configuration of *s*-block elements is $ns^{1\text{-}2}$, where $n = 2\text{-}7$.
- ❑ ***p*-Block Elements**
  - ❍ Elements in which the last electron enters any one of the three *p*-orbitals of their respective outermost shells are called *p-block elements*.
  - ❍ General outer shell electronic configuration of *p*-block elements is $ns^2np^{1\text{-}6}$, where $n = 2\text{-}7$.
- ❑ ***d*-Block Elements**
  - ❍ Elements in which the last electron enters any one of the five *d*-orbitals of their respective penultimate shells are called *d-block elements*.
  - ❍ General outer shell electronic configuration of *d*-block elements is $(n-1)d^{1\text{-}10}ns^{0\text{-}2}$, where $n = 4\text{-}7$.

- **f-Block Elements**
  - Elements in which the last electron enters any one of the seven f-orbitals of their respective ante-penultimate shells are called *f-block elements.*
  - General outer shell electronic configuration of f-block elements is $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$, where n = 6-7.

Periodic Trends

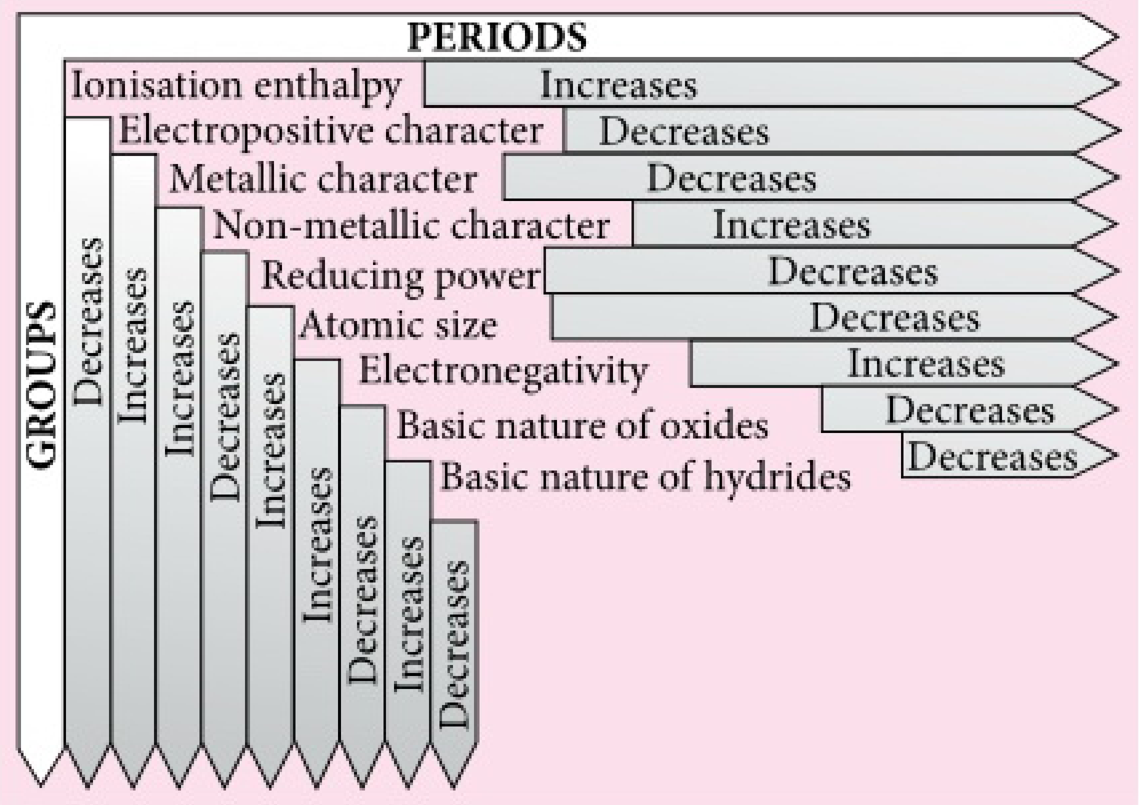
- **Atomic Radius :** It is the distance from the centre of the nucleus to the outermost shell containing electrons.
- **Ionic Radius :** It is the distance between the nucleus and outermost shell of an ion.
  - The ionic radii of cations increase as we move from top to bottom within a group.
  - The ionic radii of isoelectronic ions decrease with the increase in the magnitude of the nuclear charge.
- **Ionisation Enthalpy :** It is defined as the amount of energy required to remove an electron from an isolated gaseous atom of an element resulting in the formation of positive ion.

  $$M_{(g)} + I.E. \longrightarrow M^{+}_{(g)} + e^{-}$$

  - Factors affecting Ionisation Enthalpy
    - *Size of atom :* $I.E. \propto \dfrac{1}{\text{Size of atom}}$
    - *Nuclear charge :* $I.E. \propto$ Nuclear charge
    - *Screening effect :* $I.E. \propto \dfrac{1}{\text{Screening effect}}$
    - *Completely filled or half-filled orbitals :* It is comparatively difficult to remove the electrons from these orbitals (being more stable).
    - *Type of electrons involved :* Ionization energy decreases in the order of $s > p > d > f$-orbitals.
- **Electron Gain Enthalpy :** It is the amount of energy released when an electron is added to an isolated gaseous atom.

  $$M_{(g)} + e^{-} \rightarrow M^{-}_{(g)} + EA$$

  - Factors affecting Electron Gain Enthalpy
    - *Size of the atom :* $EA \propto \dfrac{1}{\text{Size of atom}}$
    - *Nuclear charge :* $EA \propto$ Effective nuclear charge
    - *Screening effect :* $EA \propto \dfrac{1}{\text{Screening effect}}$
  - Electron gain enthalpy becomes less negative as we move down the group.
  - Electron gain enthalpy becomes more and more negative from left to right in a period.
- **Electronegativity :** The relative tendency of an atom to attract the shared electron pair towards itself is called electronegativity.
- **Valency :** The combining capacity of an element is termed as its valency *i.e.*, the number of electrons present in the outermost shell of the atom which are required for bonding.
  - Valency of the elements increases from 1 to 7 from left to right if oxygen is taken as standard (*i.e.*, from Na_2O to Cl_2O_7). The valency of the elements with respect to hydrogen increases from 1 to 4 (*i.e.*, from NaH to SiH_4) and then decreases from 4 to 1 (*i.e.*, from SiH_4 to HCl) in a period.
  - When we move down the group, the number of valence electrons remains the same, therefore, all the elements in a group exhibit the same valency.
- **Chemical Reactivity**
  - *Nature of oxides* : s-Block elements form basic oxides, p-block elements form weakly acidic, acidic or amphoteric oxides.
  - *Nature of oxyacids* : In non-metallic oxy-acids the acidic strength increases with increase in percentage of oxygen.
  - *Metallic nature* : The smaller the ionisation energy of an element, greater will be its tendency to lose electrons and thus, greater will be its metallic character.



Key Points

- Types of atomic radii

  Covalent radius

  – Homonuclear diatomic molecule
  $= 1/2$ [bond length]

  – Heteronuclear diatomic molecule (*having same electronegativities*)
  $d_{A-B} = r_A + r_B$
  (*having different electronegativities*)
  $d_{A-B} = r_A + r_B - 0.09(\chi_A - \chi_B)$

  van der Waals' radius
  $= 1/2$ [distance between nuclei of two non- bonded atoms]

  Metallic radius
  $= 1/2$ [distance between two adjacent metal ions]

  Ionic radius
  = distance between the nucleus and outermost orbit of an ion.

- $r_{\text{van der Waals'}} > r_{\text{metallic}} > r_{\text{covalent}}$
- Scales of electronegativity

  – *Pauling scale* : $\chi_A - \chi_B = 0.1017\sqrt{\Delta}$

  where, $\Delta = E_{A-B} - \frac{1}{2}\sqrt{E_{A-A} + E_{B-B}}$

- Predicting the nature of $A - B$ bond

Percentage ionic character
$= 16(\chi_A - \chi_B) + 3.5(\chi_A - \chi_B)^2$

– If $\chi_A - \chi_B = 1.7$, bond is 50% covalent and 50% ionic.

– If $\chi_A - \chi_B > 1.7$, bond is predominately ionic.

– If $\chi_A \approx \chi_B$, $A — B$ bond is purely covalent.

GENERAL PRINCIPLES AND PROCESSES OF ISOLATION OF METALS

- Modes of Occurrence of Elements
- Steps involved in the Extraction
- Extraction of Al, Fe, Cu and Zn.
- Principles involved in the Extraction

TIPS TO REMEMBER

Modes of Occurrence of Elements

- Depending on chemical reactivity, elements are found in nature either in free (native) state or in combined state.
  - *Minerals* : The naturally occurring chemical substances in form of which the metals occur in the earth along with impurities are called minerals.
  - *Ores* : The mineral from which the metal is conveniently and economically extracted is called an ore. Thus, all ores are minerals but all minerals are not ores.

Metallurgy

The whole process of extracting metals from their ores is called *metallurgy*.

Steps Involved in the Extraction

Metallurgy of a metal involves three main operations :

Step 1 : Concentration or Dressing of the ore

Crushed ore is concentrated by

- **Gravity separation :** This separation is based on the difference in the specific gravities of the gangue particles and the ore particles. The powdered ore is agitated with water. The heavy ore particles settle down while the lighter particles of sand, clay, etc. are washed away.
- **Electromagnetic separation :** This method can be used for separation when either the ores or the impurities are magnetic in nature. The powdered ore is dropped on the belt from one end (non-magnetic) and at the other end (magnetic) the magnetic particles get attracted and fall nearer to the roller while non-magnetic particles fall away from the roller.
- **Froth-floatation process :** It is a physical method of separating minerals from the gangue

that depends on difference in their wettabilities by a liquid solution. This method is used for the concentration of sulphide ores and is based upon the preferential wetting of ore particles by oil and gangue particles by water.

- **Leaching :** It is a chemical separation. It involves the treatment of the ore with a suitable reagent as to make it soluble while impurities remain insoluble and the ore is recovered from the solution by suitable chemical methods.
  - *Baeyer's process* : It is used for extraction of pure alumina from bauxite ore by leaching.

    $$Al_2O_3{\cdot}2H_2O + 2NaOH + H_2O \longrightarrow 2Na[Al(OH)_4]$$

    $$2Na[Al(OH)_4] + 2CO_2 \longrightarrow Al_2O_3{\cdot}xH_2O + 2NaHCO_3$$

    $$Al_2O_3{\cdot}xH_2O \xrightarrow{1200°C} Al_2O_3 + xH_2O$$
  - *Mac Arthur Forest cyanide process* : It is used for extraction of Au or Ag and is based on the principle of leaching. *e.g.*,

    $$4Ag + 8NaCN + 2H_2O + O_2 \longrightarrow 4Na[Ag(CN)_2] + 4NaOH$$

    $$2Na[Ag(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + 2Ag\downarrow$$

Step 2 : Extraction and isolation of metal

The concentrated ore is converted into a form which is suitable for reduction. Since, oxides are easier to reduce, therefore, the extraction of metals involves two processes :

- **Conversion of ore into metallic oxides :** Depending upon the nature of the ores, two methods are used for conversion of oxides :
  - *Calcination* : This method involves heating of the ore below its fusion temperature in the absence of air. During calcination, moisture is driven out, water is removed from hydrated oxides or hydroxides.

    e.g., $Al_2O_3{\cdot}2H_2O \xrightarrow{\Delta} Al_2O_3 + 2H_2O$

    Carbonates lose CO_2 and the ore is converted into its corresponding oxides.

    e.g., $CaCO_3 \xrightarrow{\Delta} CaO + CO_2$

    The material becomes porous which can be easily reduced in the subsequent step.
  - *Roasting* : It is a process in which the ore is heated in the presence of air. As a result of roasting, moisture is driven out, organic matter is burnt and non-metallic impurities such as sulphur, phosphorus, arsenic are converted into respective volatile oxides which get removed.

    e.g., $2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$
- **Reduction of metallic oxide to the free metal :** The crude metal is obtained when roasted or calcined ore is put to reduction by using a suitable reducing agent.
  - *Smelting* : This involves reduction of ore to the molten metal at a high temperature. For the extraction of less electropositive metals such as Pb, Zn, Fe, Sn, etc., powerful reducing agents such as C, H_2, CO, water gas, Na, K, Mg, may be used.

    e.g., $PbO + C \longrightarrow Pb + CO$
    - *Carbon reduction process* : In this process, oxides of less electropositive metals are reduced by strongly heating them with coal or coke.

      e.g., $M_xO_y + yC \longrightarrow xM + yCO$

      i.e., $Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO$
    - *Gold-Schmidt aluminothermic process* : If the temperature needed for carbon to reduce an oxide is too high for economic or practical purpose, the reduction may be affected by another highly electropositive metal such as aluminium, which liberates a large amount of energy on oxidation to Al_2O_3. This is the basis of thermite process.

      $3Mn_3O_4 + 8Al \longrightarrow 9Mn + 4Al_2O_3$
  - *Self-reduction process* : This process is also called *autoreduction process or air reduction process*. The sulphide ores of less electropositive metals like Hg, Pb, Cu, etc., are heated in air as to convert part of the ore into oxide or sulphate which then reacts with the remaining sulphide ore to give the metal and sulphur dioxide. No external reducing agent is used in this process.

    e.g., $2HgS + 3O_2 \longrightarrow 2HgO + 2SO_2$

    $2HgO + HgS \longrightarrow 3Hg + SO_2$

    (Extraction of Hg from cinnabar ore)

- *Electrolytic reduction* : The oxides of the highly electropositive metals like Na, K, Mg, Ca, Al, etc. cannot be reduced easily with carbon at moderate temperatures. For reduction, a very high temperature is required at which the metal may combine with carbon to form a carbide. These metals are thus extracted by the electrolysis of their oxides, hydroxides or chlorides in fused state.

Step 3 : Purification or refining

A metal extracted by any method is usually contaminated with some impurity. For obtaining metals of high purity, several techniques are used depending upon the difference in properties of metal and the impurities.

- **Distillation :** This process is used for those metals which are highly volatile. The impure metal is heated in a retort and its vapours are separately condensed in a receiver. The non-volatile impurities are left behind in the retort. This is used for the purification of Zn, Cd, Hg, etc.
- **Liquation :** This process is based on the difference in fusibility of the metal and impurities. When the impurities are less fusible than the metal itself, this process is employed. This method is used to purify the metals like Bi, Sn, Pb, Hg, etc.
- **Electrolysis :** Many of the metals such as copper, silver, gold, aluminium, lead, etc. are purified by this method. The impure metal is made anode, a thin sheet of pure metal acts as a cathode while electrolytic solution consists of a solution of a suitable salt of the metal.
- **Zone refining :** Elements such as Si, Ge, Ga, etc., which are used as semiconductors are refined by this method. Highly pure metals are obtained. The method is based on the difference in solubility of impurities in molten and solid state of the metal.
- **Vapour phase refining :** In this method, the metal is converted into its volatile compound and collected elsewhere. It is then decomposed to give pure metal. So, the two requirements are

  (i) the metal should form a volatile compound with the available reagent.

  (ii) the volatile compound should be easily decomposable, so that the recovery is easy.

  - *Mond's process for refining nickel* : In this process, nickel is heated in a stream of carbon monoxide forming a volatile complex, nickel tetracarbonyl.

    $$Ni + 4CO \xrightarrow{330\text{-}350\ K} Ni(CO)_4$$

    The carbonyl is subjected to higher temperature so that it is decomposed giving the pure metal.

    $$Ni(CO)_4 \xrightarrow{450\text{-}470\ K} Ni + 4CO$$

  - *van Arkel method for refining Zr and Ti* : This method is very useful for removing all the oxygen and nitrogen present in the form of impurity in certain metals like Zr and Ti. The crude metal is heated in an evacuated vessel with iodine. The metal iodide being more covalent and volatile separates.

    $$Zr + 2I_2 \longrightarrow ZrI_4$$

    The metal iodide is decomposed on a tungsten filament, electrically heated to about 2075 K. The pure metal is thus deposited on the filament.

    $$ZrI_4 \longrightarrow Zr + 2I_2$$

- **Chromatographic methods :** This method is based on the principle that different components of a mixture are differently adsorbed on an adsorbent. The mixture is put in a liquid or gaseous medium which is moved through the adsorbent. Different components are adsorbed at different levels on the column. Later the adsorbed components are removed (eluted) by using suitable solvents (eluant).

Extraction of Fe, Cu, Al and Zn

Metal	Occurrence	Common methods of extraction	Purification/Refining
ALUMINIUM	**(i) Bauxite :** $Al_2O_3\cdot 2H_2O$ **(ii) Cryolite :** Na_3AlF_6	**Concentration :** (Leaching) $Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2 + H_2O$ $NaAlO_2 + 2H_2O \rightarrow NaOH + Al(OH)_3$ $2Al(OH)_3 \xrightarrow{\Delta} \underset{\text{Pure}}{Al_2O_3} + 3H_2O$ **Electrolytic reduction** **(Hall and Heroult process) :** Pure Al_2O_3 + cryolite: $Al_2O_3 \rightarrow 2Al^{3+} + 3O^{2-}$; $Al^{3+} + 3e^- \rightarrow Al$	Hoop's process
ZINC	**(i) Zinc blende :** ZnS **(ii) Calamine :** $ZnCO_3$ **(iii) Zincite :** ZnO	**Concentration :** (Froth floatation method) **Roasting :** $2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$ $ZnS + 2O_2 \rightarrow ZnSO_4$ $2ZnSO_4 \xrightarrow{\Delta} 2ZnO + 2SO_2 + O_2$ **Reduction:** $ZnO + C \rightarrow Zn + CO$	Electrolytic refining, distillation
IRON	**Haematite :** Fe_2O_3	**Concentration :** (Electromagnetic separation) **Calcination and roasting :** (Removal of H_2O, S, C and As) $2Fe_2O_3\cdot 3H_2O \rightarrow 2Fe_2O_3 + 3H_2O$ $FeCO_3 \rightarrow FeO + CO_2$ $S + O_2 \rightarrow SO_2$ $4As + 3O_2 \rightarrow 2As_2O_3$ $2Fe + \frac{3}{2}O_2 \rightarrow Fe_2O_3$ **Smelting :** (Blast furnace) $Fe_2O_3 + 3CO \xrightarrow{400\text{-}700°C} 2Fe + 3CO_2$ $CaCO_3 \xrightarrow{\Delta} CaO + CO_2$ $CaO + SiO_2 \rightarrow CaSiO_3(\text{slag})$ $2CO \xrightarrow{\text{Hot iron}} CO_2 + C$ $SiO_2 + 2C \xrightarrow{1200°C} Si + 2CO$ $MnO_2 + 2C \rightarrow Mn + 2CO$ $P_4O_{10} + 10C \rightarrow 4P + 10CO$ Pig iron so formed is then remelted and cooled to form cast iron.	By oxidising impurities in reverberatory furnace lined with haematite. $Fe_2O_3 + 3C \rightarrow 2Fe + 3CO$

COPPER	**Copper pyrites :** $CuFeS_2$	**Concentration :** (Froth floatation process) **Roasting :** $2CuFeS_2 + O_2 \rightarrow Cu_2S + 2FeS + SO_2\uparrow$ **Smelting :** Sand + coke $2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$ $FeO + SiO_2 \rightarrow FeSiO_{3(Slag)}$ **Bessemerisation:** Sand + hot blast of air $2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$ $2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2$ The copper so obtained upon bessemerisation is called *blister copper*.	Blister copper can be purified by poling or electrolytic refining to get pure copper.

Thermodynamic Principles of Extraction

- For any process, Gibbs free energy change (ΔG) is given by the equation,

  $$\Delta G = \Delta H - T\Delta S$$

- The criterion of feasibility of a reaction at any temperature is that, ΔG of the reaction must be negative.
- A reaction with ΔG positive can still be made to occur by coupling it with another reaction having large negative ΔG so that net ΔG of the two reactions is negative.
- **Ellingham diagram :** It normally consists of plots of $\Delta_f G°$ *vs* T for formation of oxides of elements. These diagrams help us in predicting the feasibility of thermal reduction of an ore.
- **Characteristics of Ellingham Diagram**
  - All metal oxide curves slope upwards.
  - If materials melt/vaporize, the slope changes.
  - When the curve crosses $\Delta G° = 0$, decomposition of oxide begins (Ag, Au, Hg).
  - Electropositive metal curves are at the bottom of the Ellingham diagram.
  - Any metal will reduce the oxide of other metal which is above in Ellingham diagram ($\Delta G°$ will become more negative by an amount equal to the difference between the two graphs at a particular temperature).
    - When $C \rightarrow CO$ line is below $M \rightarrow MO$ line, C reduces the MO and produces CO.
    - When $C \rightarrow CO_2$ line is below $M \rightarrow MO$ line, C reduces the MO and produces CO_2.
    - When $CO \rightarrow CO_2$ line is below $M \rightarrow MO$ line, CO reduces the MO and produces CO_2.
  - The three curves intersect at 710°C.
    - Below 710°C, CO is better reducing agent.
    - Above 710°C, carbon is better reducing agent.

Electrochemical Principles of Extraction

- The reduction of a molten metal salt is done by electrolysis. This method is based on electrochemical principles.
- The Gibbs energy change is related to electrode potential of the redox couple formed in the system as :

  $$\Delta G° = -nFE°$$

- More reactive metals have large negative values of the electrode potential and therefore, their reduction is difficult.
- If the difference of two $E°$ values of a redox system corresponds to a positive $E°$ value and consequently negative $\Delta G°$, then the less reactive metal will come out of the solution and more reactive metal will go into the solution.

Key Points

- Collectors (*e.g.*, pine oils, fatty acids, xanthates, etc.) enhance non-wettability of the mineral particles.
- Froth stabilisers (*e.g.*, cresols, aniline) stabilise the froth.
- Depressants (*e.g.*, NaCN) are added to separate two sulphide ores.
- During smelting, a chemical called *flux* is added to the ore which combines with gangue to form fusible mass called *slag*.
  - For basic gangue, acidic flux (SiO_2, $Na_2B_4O_7$) is added.

$$\underset{\text{Basic gangue}}{CaO} + \underset{\text{Flux}}{SiO_2} \longrightarrow \underset{\text{Slag}}{CaSiO_3}$$

  - For acidic gangue, basic flux ($CaCO_3$, $MgCO_3$, FeO) is added.

$$\underset{\text{Acidic gangue}}{SiO_2} + \underset{\text{Flux}}{MgCO_3} \longrightarrow \underset{\text{Slag}}{MgSiO_3} + \underset{\text{Flue gas}}{CO_2}$$

The waste gases produced during metallurgical process are called flue gases.

  - Neutral flux is added to decrease the m.p. and b.p. and to make the ore conducting in an electrolytic cell. *e.g.* CaF_2, Na_3AlF_6, KF etc.

HYDROGEN

- Position in the Periodic Table
- Isotopes
- Preparation, Properties and Uses
- Compounds of Hydrogen
- Hydrogen as a Fuel

TIPS TO REMEMBER

Hydrogen

Symbol : H, **Atomic no. :** 1

Electronic configuration : $1s^1$

Position in the Periodic Table

- Hydrogen is the first element in the periodic table and its position in the periodic table is anomalous.
- **Resemblance of Hydrogen with**
  - *Alkali Metals :*
    - Electronic configuration : H ($1s^1$), Alkali metals (ns^1)
    - Electropositive character : $H \longrightarrow H^+ + e^-$, $Na \longrightarrow Na^+ + e^-$
    - Oxidation state : H (+1), Alkali metals (+1) *e.g.*, H^+Cl^-, Na^+Cl^-
    - Combination with electronegative elements or non-metals : H (H_2S, H_2O, HCl); Na (Na_2S, Na_2O, NaCl)
    - Liberation at cathode :

At cathode At anode

$$2HCl_{(aq)} \xrightarrow{\text{Electrolysis}} H_{2(g)} + Cl_{2(g)}$$
$$2NaCl_{(l)} \xrightarrow{\text{Electrolysis}} 2Na_{(l)} + Cl_{2(g)}$$

    - Reducing nature : $CuO + H_2 \longrightarrow Cu + H_2O$, $CuO + 2Na \longrightarrow Cu + Na_2O$
  - *Halogens :*
    - Electronic configuration : (one electron less than noble gas configuration) H ($1s^1$), F ($1s^2, 2s^2, 2p^5$)
    - Electronegative character : $H + e^- \longrightarrow H^-$, $F + e^- \longrightarrow F^-$
    - Oxidation state : H (–1), Halogens (–1) *e.g.*, Na^+H^-, Na^+Cl^-
    - Combination with electropositive elements or metals : H (NaH, CaH_2); Cl (NaCl, $CaCl_2$)
    - Liberation at anode :

At anode At cathode

$$2NaH_{(l)} \xrightarrow{\text{Electrolysis}} H_{2(g)} + 2Na_{(l)}$$
$$2NaCl_{(l)} \xrightarrow{\text{Electrolysis}} Cl_{2(g)} + 2Na_{(l)}$$

    - Ionisation enthalpy : H (312 kJ mol^{-1}), Cl (1255 kJ mol^{-1})
    - Atomicity (Diatomic) : *e.g.*, H_2, Cl_2
    - Non-metallic character : H (Non-metals), Halogens (Non-metals)
    - Formation of covalent compounds : H (CH_4, NH_3), Cl (CCl_4, NCl_3)
- **Difference of Hydrogen from**
  - *Alkali Metals :*
    - H is less electropositive than alkali metals.

- Ionisation enthalpy : H (1312 kJ mol^{-1}), Li (520 kJ mol^{-1})
- Metallic/non-metallic character : H (Non-metal), Alkali metals (Metals)
- Atomicity : H [Diatomic (H_2)], Alkali metals [Monatomic (Na)]
- Covalent/ionic compounds : H [Covalent compounds (HCl)], Alkali metals [Ionic compounds (NaCl)]
- Nature of oxides : H [Hydrogen oxide (H_2O)-Neutral], Alkali metals [Oxides (Na_2O)-Basic]

- *Halogens :*
  - H is less electronegative than halogens.
  - Lone pairs of electrons : H (No lone pair, H : H), Halogen (Lone pair, $:\ddot{\underset{..}{Cl}}:\ddot{\underset{..}{Cl}}:$)
  - Nature of Oxides : H [Hydrogen oxide (H_2O) Neutral], Halogens [Halogen oxide (Cl_2O) – Acidic]

Isotopes

Hydrogen (Protium)	Deuterium	Tritium
^1_1H or H ($e = 1, p = 1, n = 0$), Abundance - 99.98% Stable	^2_1H or D ($e = 1, p = 1, n = 1$), 0.016% Stable	^3_1H or T ($e = 1, p = 1, n = 2$), 10^{-15}%, Unstable (Radioactive)

Preparation

From Water

- *By the action of water on metals :*

$$2Na + 2H_2O \longrightarrow 2NaOH + H_2$$

$$3Fe + 4H_2O \xrightarrow[\Delta]{\text{Steam}} Fe_3O_4 + 4H_2$$

(Lane's process)

- *By the action of water on ionic hydrides :*

$$NaH + H_2O \longrightarrow NaOH + H_2$$

$$CaH_2 + 2H_2O \longrightarrow Ca(OH)_2 + 2H_2$$

- *By the electrolysis of water :*

$$2H_2O_{(l)} \xrightarrow[\text{Traces of acid/base}]{\text{Electrolysis}} \underset{\text{At cathode}}{2H_{2(g)}} + \underset{\text{At anode}}{O_{2(g)}}$$

- *Bosch's process :*

$$\underset{\text{(Steam)}}{C + H_2O} \xrightarrow[\text{Ni}]{1000°C} \underbrace{CO + H_2}_{\text{Water gas}}$$

$$\underbrace{H_2 + CO}_{\text{Water gas}} + \underset{\text{(Steam)}}{H_2O} \xrightarrow[500°C]{Fe_2O_3 \cdot Cr_2O_3} CO_2 + 2H_2$$

From acids :

(Active metals which lie above hydrogen in the electrochemical series)

$$Zn + H_2SO_{4(dil.)} \longrightarrow ZnSO_4 + H_2$$

(Laboratory preparation)

From Alkalies

$$2Al + 2NaOH + 2H_2O \xrightarrow{\Delta} 2NaAlO_2 + 3H_2$$

$$Zn + 2NaOH \xrightarrow{\Delta} Na_2ZnO_2 + H_2$$

From Hydrocarbons

$$C_nH_{2n+2} + nH_2O \xrightarrow[\text{Ni}]{1270\text{ K}} nCO + (2n + 1)H_2$$

Pure Hydrogen

$$2Al + 2KOH + 2H_2O \longrightarrow 2KAlO_2 + 3H_2$$

(Uyeno's method)

Properties

Physical Properties

- It is a colourless, tasteless and odourless gas.
- It is slightly soluble in water.
- It is lightest substance known.
- It is highly combustible and burns with pale blue flame.
- It is non-poisonous and lighter than air.

Chemical Properties

- *Reactivity* : Dihydrogen is quite stable and almost inert at room temperature. It dissociates into hydrogen atoms only when heated above 2000 K temperature.

$$H_2 \rightarrow H + H$$

- *Action with metals :*

$$2M + H_2 \xrightarrow{\text{Heat}} 2MH \ (M = \text{Na, K, Ca})$$

- *Reaction with non-metals :*
  - With dioxygen :

$$2H_{2(g)} + O_{2(g)} \xrightarrow{700°C} 2H_2O$$

  - With dinitrogen :

$$N_{2(g)} + 3H_{2(g)} \xrightarrow[475°C,\text{ pressure}]{\text{Fe, Mo}} 2NH_3$$

  - With halogens :

$$H_{2(g)} + Cl_{2(g)} \xrightarrow[400°C,\text{ pressure}]{\text{Diffused sunlight}} 2HCl$$

- *Reducing character* : Hydrogen has great affinity for oxygen and thus act as a strong reducing agent. It reduces oxides of less electropositive metals to corresponding metals.

$$PbO + H_2 \longrightarrow Pb + H_2O$$

$$Fe_3O_4 + 4H_2 \xrightarrow{\text{Heat}} 3Fe + 4H_2O$$

- *Reaction with unsaturated hydrocarbons* : Unsaturated hydrocarbons such as ethylene and acetylene react with dihydrogen to give saturated hydrocarbons.

$$\underset{\text{Ethene}}{H_2C{=}CH_2} + H_2 \xrightarrow[200°C]{\text{Ni or Pt or Pd}} \underset{\text{Ethane}}{H_3C{-}CH_3}$$

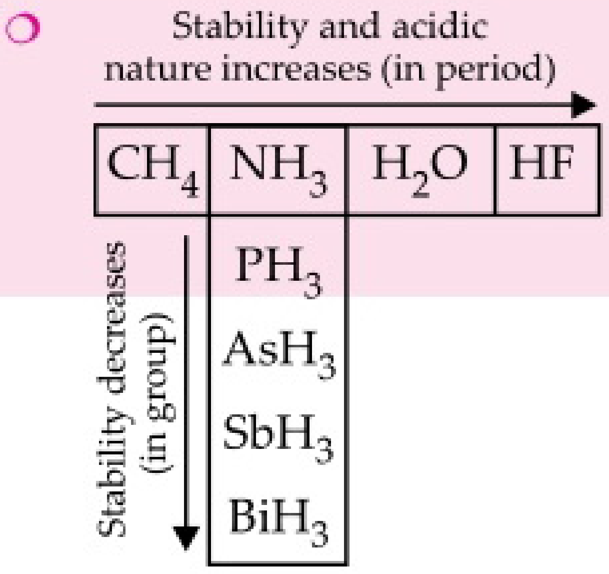
Uses

It is used

- as a reducing agent in industry and laboratories.
- in the preparation of many compounds such as methane, ammonia, water gas, and fertilizers such as urea, ammonium sulphate, etc.

Compounds of Hydrogen

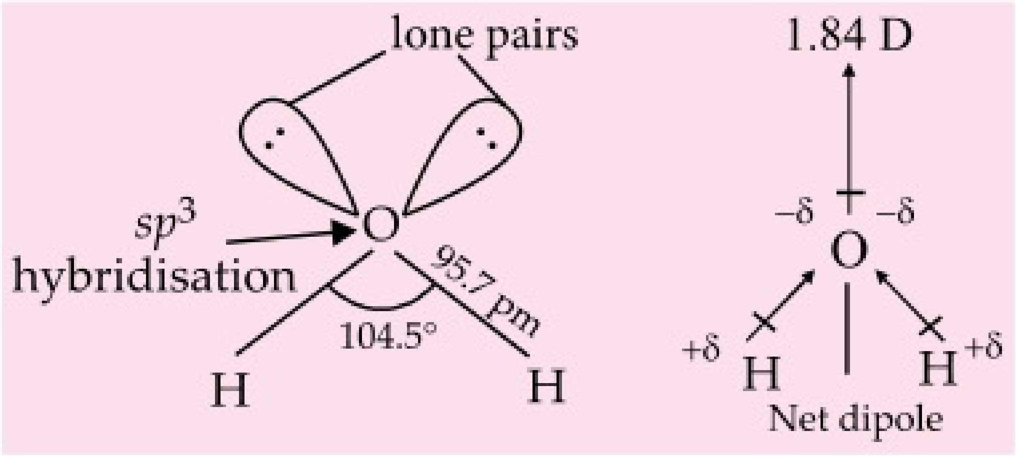
Hydrides

Ionic, saline or salt like hydrides	Molecular or covalent hydrides	Metallic or interstitial hydrides
❍ Formed by *s*-block elements (highly electropositive), except Be and Mg which form polymeric hydrides.	❍ Formed by highly electronegative elements (like non-metals) which share electrons with hydrogen.	❍ Formed by transition and inner-transition elements.
❍ These are solids with ionic lattices and behave like salts.	❍ Molecules are held together by van der Waals' forces.	❍ In them, the hydrogen atoms occupy some of the holes in the metal lattices.
❍ They have, hydrogen as anion. $2Na + H_2 \rightarrow \underset{\text{Sod. hydride}}{2NaH}$	❍ They have low m.pt., b.pt. and electrical conductivity.	❍ These are non-stoichiometric compounds ($TiH_{1.73}$, $PdH_{0.6\text{-}0.8}$, $VH_{0.6}$) and give out hydrogen easily.
❍ They have high m.pt., b.pt. and density.	❍ 	❍ They act as a strong reducing agents and have high conductivity.
❍ The thermal stability decreases with increasing size of cations. LiH > NaH > KH > RbH > CsH $CaH_2 > SrH_2 > BaH_2$		❍ These hydrides are used for the ultrapurification of hydrogen and as hydrogen storage media.

Water

- Water is essential for life. In nature, it exists in three phases - solid, liquid and gas.

Structure



- In gaseous state, water exists as discrete molecules.
- In the liquid state, the water molecules are held together by intermolecular H-bonds. Each water molecule is generally H-bonded to four other water molecules.
- In ice, each molecule of water is surrounded by three water molecules, helping to create an open hexagonal honey-comb lattice.
- The density of ice is less than that of water at the same temperature. Thus, ice floats on water.

Properties

Physical Properties

- Pure water is colourless, tasteless and odourless. It gives bluish tinge in thick layers.
- It freezes at 0°C and boils at 100°C.
- Its maximum density is 1.00 g cm^{-3} at 4°C.
- It has a high dielectric constant. The polar character of water makes it an excellent solvent for polar and ionic substances.
- It is a poor conductor of electricity.

Chemical Properties : Water shows a wide variety of chemical reactions, because it can act as an acid, a base, an oxidizing agent, a reducing agent, and as a ligand to metal ions.

- *Decomposition* :

$$2H_2O_{(g)} \xrightarrow{1200°C} 2H_{2(g)} + O_{2(g)}$$

- *Self-ionization (or Autoprotolysis) of water* :

$$H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$$

$$K_w = [H_3O^+][OH^-]$$

At 298, $K_w = 1.0 \times 10^{-14}\ mol^2\ L^{-2}$

- *Amphoteric character of water* :

$$\underset{\text{Base}}{H_2O_{(l)}} + \underset{\text{Acid}}{HCl_{(aq)}} \rightleftharpoons \underset{\text{Acid}}{H_3O^+_{(aq)}} + \underset{\text{Base}}{Cl^-_{(aq)}}$$

$$\underset{\text{Acid}}{H_2O_{(l)}} + \underset{\text{Base}}{NH_{3(aq)}} \rightleftharpoons \underset{\text{Acid}}{NH^+_{4(aq)}} + \underset{\text{Base}}{OH^-_{(aq)}}$$

- *Oxidizing and reducing nature of water* :

Reduction

$$2Na_{(s)} + 2H_2O_{(l)} \longrightarrow 2Na^+OH^-_{(aq)} + 2H_{2(g)}$$

Oxidation

$$nCO_{2(g)} + nH_2O_{(l)} \xrightarrow[\text{Chlorophyll}]{\text{Sunlight}} \underset{\text{(Carbohydrate)}}{(CH_2O)_n} + nO_{2(g)}$$

- *Hydrolysis reactions* :

$$Na_2CO_{3(s)} + 2H_2O_{(excess)} \longrightarrow 2NaOH_{(aq)} + H_2CO_{3(aq)}$$

$$PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$$

$$SiCl_{4(l)} + 4H_2O_{(l)} \longrightarrow SiO_2.2H_2O_{(s)} + 4HCl_{(aq)}$$

- *Other reactions* :

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

$$Na_2O + H_2O \longrightarrow 2NaOH$$

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

$$P_2O_5 + 3H_2O \longrightarrow 2H_3PO_4$$

$$Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4$$

$$Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3$$

$$Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + \underset{\text{Phosphine}}{2PH_3}$$

- *Formation of hydrates* : Water forms complexes with some metal salts called hydrates which have been grouped in three categories :
  - Water molecules coordinated to the central metal ion, in a complex ion. *e.g.*, $[Cr(H_2O)_6]^{3+}3Cl^-$, $[Ni(H_2O)_6]^{2+}2Cl^-$, $[Fe(H_2O)_6]^{3+}3Cl^-$
  - Water molecules hydrogen bonded to certain oxygen containing anions. *e.g.*, $CuSO_4 \cdot 5H_2O$.
  - Water molecules occupying voids (interstitial sites) in the crystal lattice, *e.g.*, in $BaCl_2.2H_2O$.

Heavy Water

- Deuterium oxide (D_2O) is known as heavy water. It is present in trace amount in ordinary water (1 part in 6000 parts).

Preparation

- It is prepared either by prolonged electrolysis or by fractional distillation of ordinary water.

Properties

Physical Properties

- Heavy water is colourless, tasteless and odourless liquid.
- Its physical constant values are higher than the corresponding values of ordinary water.

Chemical Properties

- Although heavy water is chemically similar to ordinary water, chemical reactions of heavy water are slower than those of ordinary water. This is because of the fact that O—D bond is stronger than O—H bond.
- Heavy water like ordinary water may be associated with salts as water of crystallization, giving deutero hydrates. *e.g.*, $Na_2SO_4 \cdot 10D_2O$, $CuSO_4 \cdot 5D_2O$, $MgSO_4 \cdot 7D_2O$, etc.

$$D_2O \xrightarrow{\text{Electrolysis}} \underset{\text{(at cathode)}}{D_2} + \underset{\text{(at anode)}}{O_2}$$
$$D_2O \xrightarrow{Na} NaOD + D_2$$
$$D_2O \xrightarrow{Ca,\ \Delta} Ca(OD)_2 + D_2$$
$$D_2O \xrightarrow{Fe,\ \Delta} Fe_3O_4 + D_2$$
$$D_2O \xrightarrow{Na_2O} NaOD$$
$$D_2O \xrightarrow{CaO} Ca(OD)_2$$
$$D_2O \xrightarrow{N_2O_5} DNO_3 \text{ (Deuteronitric acid)}$$
$$D_2O \xrightarrow{SO_3} D_2SO_4 \text{ (Deuterosulphuric acid)}$$
$$D_2O \xrightarrow{P_2O_5} D_3PO_4 \text{ (Deuterophosphoric acid)}$$
$$D_2O \xrightarrow{CaC_2} Ca(OD)_2 + \underset{\text{(Deuteroacetylene)}}{DC{\equiv}CD}$$
$$D_2O \xrightarrow{Al_4C_3} Al(OD)_3 + CD_4 \text{ (Deuteromethane)}$$
$$D_2O \xrightarrow{Ca_3P_2} Ca(OD)_2 + PD_3 \text{ (Deuterophosphine)}$$
$$D_2O \xrightarrow{Mg_3N_2} Mg(OD)_2 + ND_3 \text{ (Deuteroammonia)}$$
$$D_2O \xrightarrow{NaOH} NaOD + HDO$$
$$D_2O \xrightarrow{HCl} DCl + HDO$$
$$D_2O \xrightarrow{NH_4Cl} ND_4Cl + HDO$$
$$D_2O \xrightarrow[\text{Deuterolysis}]{AlCl_3} Al(OD)_3 + DCl$$
$$D_2O \xrightarrow[\text{Deuterolysis}]{BaS} Ba(OD)_2 + D_2S$$

Uses

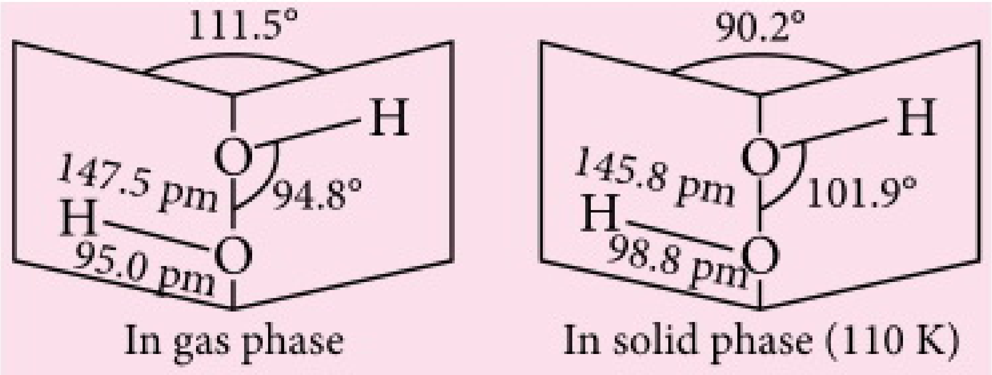
It is used as

- moderator and coolant in nuclear reactor.
- a germicide and bactericide.

Hydrogen Peroxide

- Hydrogen peroxide (H_2O_2) is also known as oxygenated water.

Structure



Preparation

- **From sodium peroxide :**

$$Na_2O_2 + \underset{\text{Ice cold}}{H_2SO_4} \longrightarrow Na_2SO_4 + H_2O_2$$

- **From barium peroxide :**

$$BaO_2{\cdot}8H_2O + \underset{\text{Ice cold}}{H_2SO_4} \rightarrow BaSO_4 + H_2O_2 + 8H_2O$$

- *By the action of CO_2 or carbonic acid (Merck's process)* :

$$BaO_2 + CO_2 + H_2O \rightarrow BaCO_3\downarrow + H_2O_2$$

Manufacture

- **By electrolysis of 50% sulphuric acid :**

$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$

At cathode : $2H^+ + 2e^- \longrightarrow H_2$

At anode : $2HSO_4^- \longrightarrow H_2S_2O_8 + 2e^-$

- **By electrolysis of equimolar mixture of H_2SO_4 and $(NH_4)_2SO_4$:**

$(NH_4)_2SO_4 + H_2SO_4 \longrightarrow 2NH_4HSO_4$

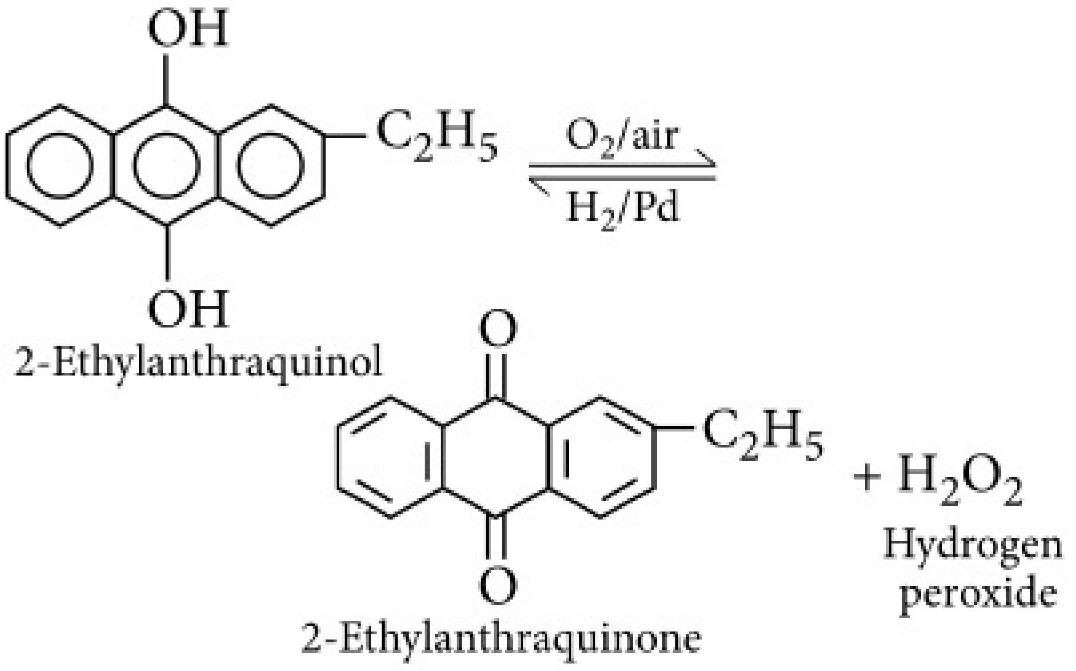
$NH_4HSO_4 \rightleftharpoons H^+ + NH_4SO_4^-$ (dissociation)

At anode: $2NH_4SO_4^- \longrightarrow (NH_4)_2S_2O_8 + 2e^-$

At cathode: $2H^+ + 2e^- \longrightarrow H_2$

$$(NH_4)_2S_2O_8 + 2H_2O \xrightarrow{\text{Hydrolysis}} 2NH_4HSO_4 + H_2O_2$$

- **By autoxidation of 2-ethylanthraquinol :**



Properties

- **Physical Properties**
  - Pure hydrogen peroxide is a pale-blue syrupy liquid with a bitter taste.
  - It is completely soluble in water, alcohol and ether.
  - It is heavier than water (density = 1.469g/mL).
  - It melts at 272.4 K (–0.7°C) and boils under 760 mm of Hg pressure at 423.2 K (150°C) with violent decomposition.
  - It is diamagnetic.
  - It behaves as an excellent solvent for electrolytes, due to its high dielectric constant (93.7 for pure H_2O_2).
  - It is more extensively associated by H-bonding than water.

- **Chemical Properties**
  - *Decomposition* :

    $$2H_2O_{2(l)} \longrightarrow 2H_2O_{(l)} + O_{2(g)}$$
  - *Acidic nature* :

    $$H_2O_2 + NaOH \longrightarrow NaHO_2 + H_2O$$
    $$H_2O_2 + 2NaOH \longrightarrow Na_2O_2 + 2H_2O$$
  - *Oxidising properties* : It acts as a strong oxidising agent in acidic as well as alkaline solution, since it provides nascent oxygen readily.

    $$H_2O_2 \longrightarrow H_2O + [O]$$
    $$4H_2O_2 + PbS \longrightarrow 4H_2O + PbSO_4$$
    $$2FeSO_4 + H_2SO_4 + H_2O_2 \longrightarrow Fe_2(SO_4)_3 + 2H_2O$$
    $$2KI + H_2O_2 + H_2SO_4 \longrightarrow K_2SO_4 + I_2 + 2H_2O$$
    $$HCHO + H_2O_2 \longrightarrow HCOOH + H_2O$$
    $$C_6H_6 + H_2O_2 \longrightarrow C_6H_5OH + H_2O$$
  - *Reducing properties* :

    $$H_2O_2 + [O] \longrightarrow H_2O + O_2$$
    $$Cl_2 + H_2O_2 \longrightarrow 2HCl + O_2$$
    $$O_3 + H_2O_2 \longrightarrow H_2O + 2O_2$$
    $$Ag_2O + H_2O_2 \longrightarrow 2Ag + H_2O + O_2$$
    $$I_2 + H_2O_2 + 2KOH \longrightarrow 2KI + 2H_2O + O_2$$
    $$NaOBr + H_2O_2 \longrightarrow NaBr + H_2O + O_2$$
    $$CaOCl_2 + H_2O_2 \longrightarrow CaCl_2 + H_2O + O_2$$
  - *As a bleaching agent* :

    $$H_2O_2 \longrightarrow H_2O + [O]$$
    $$\text{Colouring matter} + [O] \longrightarrow \text{Colourless}$$

Uses

It is used as

- a mild bleaching agent for bleaching delicate articles such as hair, silk, wool, etc.
- an antiseptic for washing wounds.

Hydrogen as a Fuel

- Hydrogen is considered as one of the alternate sources of energy as it is eco-friendly, producing only water as the by-product and having high heat of combustion.
- Although it is quite useful as a fuel but storage and transportation is one of the major disadvantages.

Key Points

- Ordinary dihydrogen is an equilibrium mixture of *ortho* and *para* hydrogen.
- *Ortho* hydrogen molecules are those in which the spins of both the protons are in the same direction.
- Molecules of hydrogen in which the spins of both the proton are in the opposite direction are called *para* hydrogen.
- Concentration of H_2O_2 is expressed in terms of volume strength.
  - 10 volume of H_2O_2 solution means 1 mL of this solution on decomposition evolves 10 mL of O_2 at NTP.
  - '10 volume' solution of H_2O_2 is 3.035% solution. Strength of '10 volume' H_2O_2 solution is 30.35 g/litre.

    Volume strength = 5.6 × Normality

    Volume strength = 11.2 × Molarity

s-BLOCK ELEMENTS

- General Trends in Physical and Chemical Properties
- Anomalous Properties of the First Element
- Diagonal Relationship
- Preparation, Properties and Uses of Some Important Compounds
- Biological Significance of Na, K, Mg and Ca

TIPS TO REMEMBER

- Elements in which the last electron enters the *s*-orbital are called *s-block elements*. Elements of group 1 or IA (alkali metals) and group 2 or IIA (alkaline earth metals) constitute *s*-block elements.

GROUP-1 ELEMENTS (ALKALI METALS)

- **Electronic Configuration :** [Noble gas] ns^1
- **Elements :** ${}_3Li$, ${}_{11}Na$, ${}_{19}K$, ${}_{37}Rb$, ${}_{55}Cs$, ${}_{87}Fr$

Properties

- **Physical Properties**
  - Alkali metals are silvery white, soft and light metals having low ionization energies.
  - They are largest in their corresponding periods in periodic table.

- Their densities are quite low.
- They are strongly electropositive because of their low ionisation energies thus, have low electronegativity.
- Alkali metals and their salts, when introduced into the flame impart characteristic colour to the flame.
- They show conducting behaviour for heat as well as for electricity due to loosely held valence electrons.
- They show only +1 oxidation state. Therefore, alkali metals are univalent and form ionic compounds.

- **Chemical Properties**
  - *Action of air* : The alkali metals tarnish in air due to the formation of oxides, hydroxides and carbonates at their surface and hence they are stored in kerosene oil or paraffin wax.
  - *Reaction with hydrogen* : $2M + H_2 \rightarrow 2M^+H^-$
  - *Reaction with water* :

    $$2M + 2H_2O \rightarrow 2MOH + H_2$$
  - *Reaction with compounds containing acidic hydrogen* :

    $$2M + \underset{\text{Ethyl alcohol}}{2C_2H_5OH} \longrightarrow \underset{\text{Metal ethoxide}}{2C_2H_5OM} + H_2$$

    $$2M + \underset{\text{Acetylene}}{HC{\equiv}CH} \longrightarrow \underset{\text{Alkali metal acetylide}}{M{-}C{\equiv}C{-}M} + H_2$$
  - *Reaction with halogens* : $2M + X_2 \rightarrow 2M^+X^-$
  - *Solubility in liquid NH_3* :

    $$M + (x+y)NH_3 \longrightarrow \underset{\substack{\text{Ammoniated cation}\\ \text{causes conductivity}}}{[M(NH_3)_x]^+} + \underset{\substack{\text{Ammoniated}\\ \text{electron}\\ \text{responsible for}\\ \text{blue colour and}\\ \text{paramagnetism}}}{[e(NH_3)_y]^-}$$

- **Nature of oxides / hydroxides :** They are basic in nature and their basic character increases gradually on moving down the group.
  - The thermal stability of hydroxides also increases on moving from Li to Cs.
- **Nature of hydrides :** Thermal stability of alkali metal hydrides decreases down the group, hence reactivity of these hydrides increases on moving down the group.
- **Nature of halides :** The solubility of most of the alkali metal halides except those of fluorides decreases on descending the group.
- **Complex formation :** Alkali metals have little tendency to form complexes.
- **Alum formation :** Alums are the double sulphate compounds having formula

  $$M_2^+SO_4 \cdot M_2^{3+}(SO_4)_3 \cdot 24H_2O$$

  or $M^+M^{3+}(SO_4)_2 \cdot 12H_2O$

  where, $M^+ = Na^+, K^+, Rb^+$ and Cs^+ (except Li^+)
- **Alloy formation :** Alkali metals form alloys amongst themselves as well as with other metals. They also form amalgam with mercury.
- **Anomalous Properties of Lithium**

  The anomalous behaviour of lithium is due to extremely small size of lithium atom and its ion. The main points of difference are
  - Li is much harder than the other alkali metals and its melting and boiling points are comparatively high.
  - Li reacts less readily with O_2 forming normal oxide, while the other alkali metals can form peroxides and superoxides.
  - Unlike other alkali metals, Li directly combines with N_2 to form nitride.
  - LiOH is less basic than other alkali metal hydroxides.
  - $LiHCO_3$ is known in solution, but not in solid state, while other alkali metal bicarbonates are known in solid state.
  - Unlike sulphates of other alkali metals, Li_2SO_4 does not form alums.
  - Li reacts with NH_3 to form imide, Li_2NH whereas other alkali metals form amides, MNH_2.
- **Diagonal Relationship**

  Due to the same polarising power, quite comparable electronegativities and nearly same atomic radii and ionic radii, Li resembles Mg through diagonal relationship.
  - Li and Mg both form nitrides.
  - Like $MgCO_3$, Li_2CO_3 is decomposed by heat, both carbonates are insoluble.
  - $LiNO_3$ decomposes to give Li_2O like $Mg(NO_3)_2$.

- Both give their normal oxides, Li_2O, MgO when they burn in oxygen.
- Both Li^+ and Mg^{2+} are heavily hydrated.

Key Points

- K is lighter than Na due to an unusual increase in atomic size of K.
- Li is the strongest reducing agent in solution inspite of its highest ionisation enthalpy in the group.

Some Important Compounds

Sodium Hydroxide (NaOH) or Caustic Soda

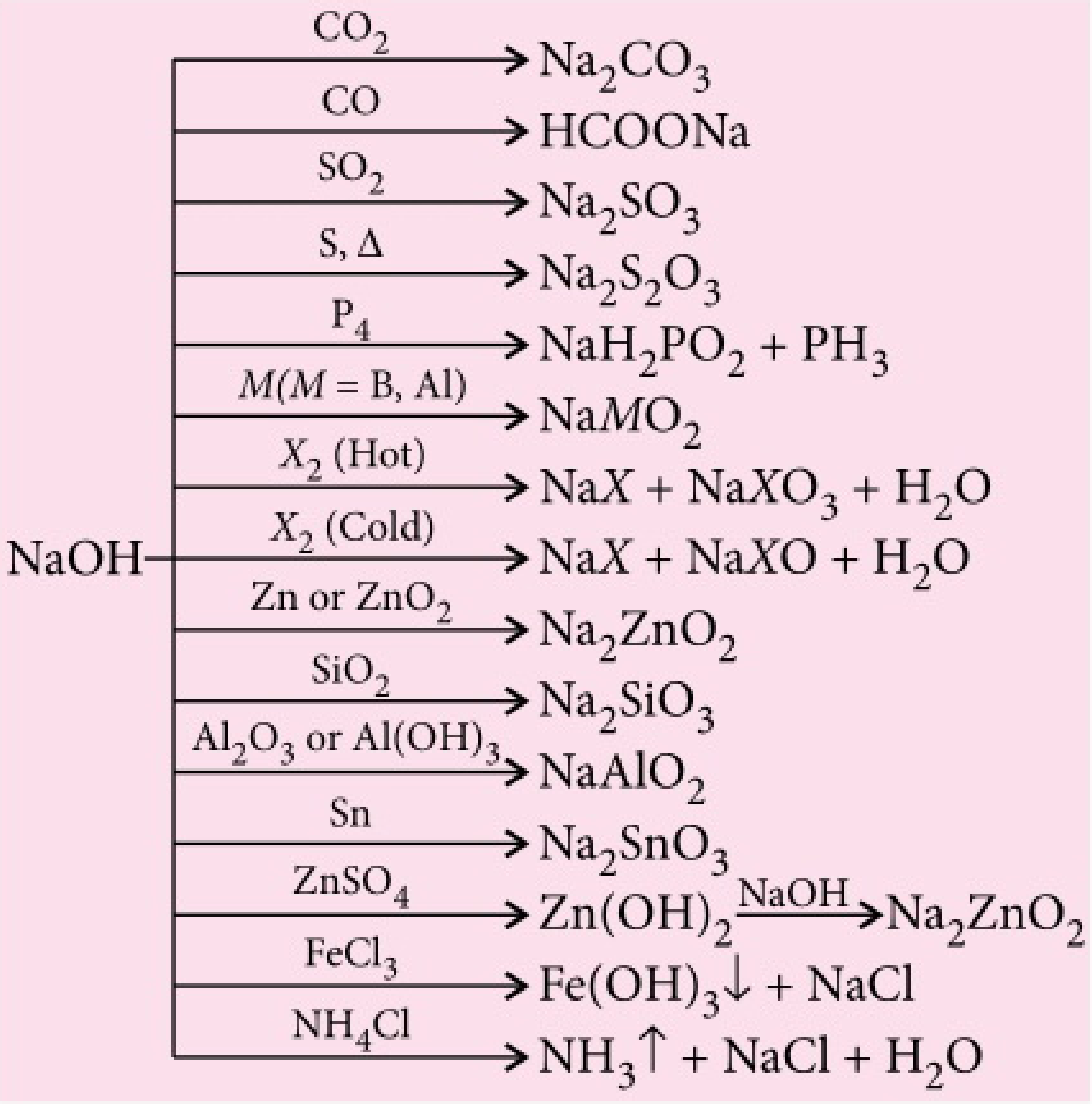
Preparation

- **By electrolysis of NaCl (brine) solution**

$$2NaCl_{(aq)} + 2H_2O_{(l)} \longrightarrow \underbrace{Cl_{2(g)}}_{\text{At anode}} + \underbrace{H_{2(g)} + 2NaOH_{(aq)}}_{\text{At cathode}}$$

Properties

- **Physical Properties**
  - NaOH is deliquescent, white crystalline solid.
  - NaOH dissolves readily in water to yield highly alkaline solution which is corrosive, soapy in touch and bitter in taste.
- **Chemical Properties**



Uses

It is used

- in the manufacture of sodium metal, soap, rayon, paper, dyes, drugs, etc.
- as a laboratory reagent.

Sodium Carbonate ($Na_2CO_3 \cdot 10H_2O$) or Washing Soda

Preparation

- Sodium carbonate is manufactured by *Solvay process.*
- Sodium bicarbonate being sparingly soluble, crystallizes out. This is finally calcined to form sodium carbonate.

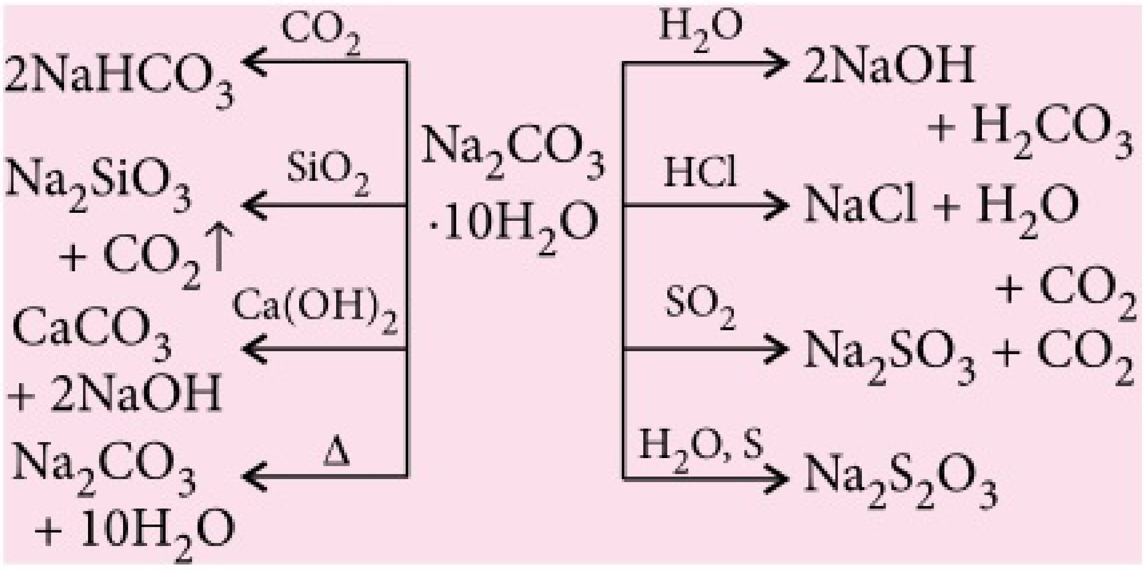
$$Na^+ + Cl^- + NH_4^+ + OH^- + CO_2 \longrightarrow Na^+ + HCO_3^- + NH_4^+ + Cl^-$$

$$Na^+ + HCO_3^- \longrightarrow NaHCO_3 \text{ (as precipitate)}$$

$$2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + CO_2 + H_2O$$

Properties

- **Physical Properties**
  - Sodium carbonate is a white crystalline solid which readily dissolves in water. Its solubility decreases with increase of temperature.
- **Chemical Properties**



Uses

It is used

- in laundries and in softening of water.
- in manufacture of glass, caustic soda, etc.

Key Point

- Potassium carbonate K_2CO_3 cannot be prepared by Solvay ammonia method as $KHCO_3$ being fairly soluble in water will not get precipitated on passing CO_2 through ammoniated KCl solution.

Sodium Hydrogencarbonate ($NaHCO_3$) or Baking Soda

Preparation

- **Obtained as an intermediate product in Solvay process**

  $$NaCl + NH_3 + CO_2 + H_2O \longrightarrow NaHCO_3 + NH_4Cl$$

- It can also be prepared by passing CO_2 through solution of sodium carbonate.

  $$Na_2CO_3 + CO_2 + H_2O \longrightarrow 2NaHCO_3$$

Properties

- $NaHCO_3$ on heating decomposes to produce bubbles of CO_2 which make the cakes and pastries fluffy.

  $$2NaHCO_3 \xrightarrow[100°C]{\Delta} Na_2CO_3 + H_2O + CO_2$$

- It is amphiprotic *i.e.*, it can act as H^+ donor as well as H^+ acceptor.

  $$HCO_3^- + H^+ \rightleftharpoons H_2CO_3; HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$$

Uses

It is used

- in medicines to remove acidity of the stomach.
- in fire extinguishers.

Biological Significance of Na and K

- Na^+ and K^+ are essential for proper functioning of human body.
  - Different ratio of Na^+ to K^+ inside and outside cells produce an electrical potential across the cell membrane which is essential for functioning of nerve and muscle cells.
  - These ions activate many enzymes.
  - These ions primarily help in transmission of nerve signals, in regulating the flow of water across cell membrane, transport of sugars and amino acids into the cells, etc.

GROUP-2 ELEMENTS (ALKALINE EARTH METALS)

- **Electronic Configuration :** [Noble gas] ns^2
- **Elements :** $_4Be$, $_{12}Mg$, $_{20}Ca$, $_{38}Sr$, $_{56}Ba$, $_{88}Ra$

Properties

- **Physical Properties**
  - Alkaline earth metals have a greyish white lustre when freshly cut and are malleable and ductile.
  - They are also light metals but their density is greater than those of the alkali metals.
  - These elements have low melting and boiling points but higher than those of alkali metals.
  - The second ionization energies IE_2 of the elements of group 1 are higher than those of the elements of group 2.
  - They are harder than alkali metals.
  - Due to smaller size of the kernels and greater number of valence electrons, the metallic bonding in alkaline earth metals is stronger as compared to alkali metals.
  - The hydration energies of the group 2 ions (M^{2+}) are four to five times greater than for group 1 ions (M^+) because of their smaller size and increased charge.
  - Because of higher values of hydration energy the crystalline compounds of group 2 are extensively hydrated than the corresponding group 1 compounds.
  - They show dipositive oxidation state in their compounds.
  - They predominantly form ionic compounds which are, however, less ionic than the corresponding alkali metal compounds because of greater ionization energies and high polarising power.
  - Alkaline earth metals and their compounds except Be and Mg impart characteristic colours to the flame.
  - The alkaline earth metals are good conductors of heat and electricity.
  - They are strong reducing agents but weaker than alkali metal.
  - The density firstly decreases slightly from Be to Ca then increases upto radium.
  - The melting and boiling points do not vary regularly due to different crystal structures adopted by metals.
  - $\Delta H_{hydration}$ decreases down the group as the size of the ions increases.
  - The number of molecules of water of crystallization decreases as the ion becomes larger.

- **Chemical Properties**
  - *Action of air* : These metals, except Be, are easily tarnished in air due to the formation of ionic oxides of the type MO (except Ba and Ra, which give peroxides).
  - *Reaction with water* :
    $M + 2H_2O \longrightarrow M(OH)_2 + H_2\uparrow$
    Be reacts with steam, Mg reacts with hot water, Ca, Sr and Ba react rapidly with cold water.
  - *Reaction with hydrogen* : Ionic salts like hydrides are formed at high temperatures by Ca, Sr and Ba.
  - *Reaction with halogens* :
    $M + X_2 \longrightarrow MX_2$
    - Due to the small size and high charge of Be^{2+} ions, BeX_2 are covalent in nature.
    - The halides of other alkaline earth metals are ionic in nature.
  - *Reaction with nitrogen* :
    $3M + N_2 \longrightarrow M_3N_2$
  - *Reaction with carbon* : Except Be, other metals when heated with carbon in an electric furnace form carbides (MC_2).
  - *Solubility in liquid NH_3* :
    $$M + (x + y)NH_3 \longrightarrow [M(NH_3)_x]^{2+} + 2[e(NH_3)_y]^-$$
  - *Action of acids* :
    $M + 2HCl \longrightarrow MCl_2 + H_2\uparrow$
    Be reacts very slowly, Mg reacts very rapidly while Ca, Sr and Ba react explosively.
    With HNO_3, Be becomes passive due to formation of oxide layer.
  - *Formation of amalgams* : Alkaline earth metals combine with mercury to form amalgams.
  - *Formation of nitrates* :
    $MO + 2HNO_3 \longrightarrow M(NO_3)_2 + H_2O$
    $M(OH)_2 + 2HNO_3 \longrightarrow M(NO_3)_2 + 2H_2O$
    $MCO_3 + 2HNO_3 \longrightarrow M(NO_3)_2 + CO_2 + H_2O$
  - *Formation of sulphates* :
    $M + H_2SO_4 \longrightarrow MSO_4 + H_2$
    $MO + H_2SO_4 \longrightarrow MSO_4 + H_2O$
    $M(OH)_2 + H_2SO_4 \longrightarrow MSO_4 + 2H_2O$
    $MCO_3 + H_2SO_4 \longrightarrow MSO_4 + CO_2 + H_2O$
  - *Formation of carbonates* :
    $M(OH)_{2(aq)} + CO_{2(g)} \longrightarrow MCO_{3(s)} + H_2O_{(l)}$
  - Bicarbonates of alkaline earth metals do not exist in solid state. They exist in solutions only.
    $M(HCO_3)_2 \xrightarrow{\Delta} MCO_3 + CO_2 + H_2O$
- **Nature of oxides and peroxides :** Oxides of group 2 elements are basic in nature. Their basic strength increases down the group.
- **Nature of hydroxides :** Solubility of hydroxides increases down the group.
- **Nature of halides :** Due to small size and high charge density, all beryllium halides are essentially covalent and are soluble in organic solvents.
  - The halides of all other alkaline earth metals are ionic. Their ionic character, however, increases as the size of the metal ion increases.
  - The solubility in water decreases from Be to Ba due to the decrease in the hydration energy.
- **Nature of sulphates :** The solubilities of sulphates of alkaline earth metals decrease down the group.
  - Basic nature of metals increases down the group thus thermal stability of sulphates increases on descending the group.
- **Nature of carbonates :** Solubility of carbonates decreases down the group from Be to Ba.
  - Thermal stability of these carbonates, however, increases down the group.
- **Formation of organometallic compounds :** Both Be and Mg form an appreciable number of organometallic compounds.
- **Complex formation :** Be^{2+} being smallest in size shows a great tendency to form complexes such as $[BeF_3]^-$, $[BeF_4]^{2-}$. Tendency of other ions (M^{2+}) to form complexes decreases with the increase of size of M^{2+} ion on descending the group.
- **Anomalous Properties of Beryllium**
  The anomalous behaviour of beryllium is due to its small size and high electronegativity.

The main points of difference are

- Be is harder than other alkaline earth metals.
- Be is less reactive than the other alkaline earth metals.
- Be when treated with concentrated NaOH becomes passive.
- Be reacts with caustic alkalies to form beryllate.
- Among the alkaline earth metal carbides, only beryllium carbide gives methane on hydrolysis.
- $Be(OH)_2$ is amphoteric and covalent.
- Be_3N_2 is covalent.
- Be does not exhibit coordination number more than 4.

- **Diagonal Relationship**

Due to the high polarising power, nearly equal standard oxidation potential values and equal electronegativities, Be resembles Al through diagonal relationship.

- Both metals do not decompose in water even on boiling because of their weak electropositive character.
- Both metals become passive when treated with concentrated HNO_3.
- Both metals react with caustic alkalies to form beryllate and aluminate respectively.
- Both metals react very slowly with dilute mineral acids liberating hydrogen.
- Both metals have a strong tendency to form covalent compounds.
- Both metals form polymeric covalent hydrides.
- Both BeO and Al_2O_3 are hard, high melting solids.

Key Point

- According to Fajan rule polarising power decreases from Be^{2+} to Ba^{2+} because of the increase in ionic radii down the group. Thus Be^{2+} has a tendency to form covalent compounds. Mg also shows some tendency for covalency.

Biological Significance of Mg and Ca

- Mg^{2+} ions form a complex with ATP. They are also essential for the transmission of impulse along nerve fibres.
- Mg^{2+} is an important constituent of chlorophyll, in the green parts of plants.
- Ca^{2+} is present in bones and teeth as apatite $Ca_3(PO_4)_2$, and the enamel on teeth as fluoroapatite $[3(Ca_3(PO_4)_2)\cdot CaF_2]$.
- Ca^{2+} ions are important in blood clotting, and are required to trigger the contraction of muscles and to maintain the regular beating of the heart.

- **Industrial Uses**

Quick lime (CaO)	Limestone ($CaCO_3$)	Plaster of Paris ($CaSO_4\cdot{}^1/_2H_2O$)
○ In steel industry to remove phosphates and silicates as slag. ○ In making cement by mixing it with silica, alumina or clay. ○ In making glass. ○ In lime soda process for the conversion of Na_2CO_3 to NaOH. ○ For softening of water, for making slaked lime, $[Ca(OH)_2]$ and calcium carbide (CaC_2).	○ As building material in the form of marble. ○ In manufacture of quick lime (CaO). ○ As a raw material for the manufacture of Na_2CO_3 in solvay ammonia process. ○ As a fertilizer.	○ For producing moulds for pottery and ceramics and casts of statues and busts. ○ In surgical bandages used for plastering broken or fractured bones. ○ In dentistry.

- **Cement :** Cement is greyish, finely powdered mixture of calcium silicates and aluminates along with small quantities of gypsum which sets into hard mass when mixed with water.

p-BLOCK ELEMENTS (GROUP 13 AND 14)

- General Trends in Physical and Chemical Properties
- Anomalous Properties of the First Element
- 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 shells are called *p-block elements.*

GROUP-13 ELEMENTS (BORON FAMILY)

❑ **Electronic Configuration :** [Noble gas] $ns^2\ np^1$

❑ **Elements :** ${}_5B$, ${}_{13}Al$, ${}_{31}Ga$, ${}_{49}In$, ${}_{81}Tl$

Properties

❑ **Physical Properties**

- Group 13 elements and their ions have smaller size than the corresponding group 2 elements because of the increase in nuclear charge.
- They have higher density as compared to elements of group 2 due to smaller atomic and ionic radii.
- The first ionization energies of these element are less than the corresponding values of *s*-block elements because of less penetrating effect of *p*-electrons than *s*-electrons.
- They show +1 and +3 oxidation states. Boron shows only +3 oxidation state while others show +1 as well as +3 oxidation states.
- They are less electropositive and more electronegative than group 1 and group 2 elements.
- Density increases from B to Tl.
- The melting point decreases from B to Ga and then increases.
- As we move down the group, the stability for the +3 oxidation state decreases while that of +1 oxidation state increases (due to inert pair effect).
- Electronegativity first decreases from B to Al and then increases due to poor shielding by inner *d*- and *f*-electrons.
- The tendency of formation of ionic compounds increases from B to Tl, since ionization energy decreases and ionic size increases from B to Tl.
- The reducing power of the elements of group 13 decreases down the group.

❑ **Chemical Properties**

- *Action of air* : $4M + 3O_2 \longrightarrow 2M_2O_3$
  Reaction occurs at high temperature. With Al, a protective oxide layer is formed which makes it passive. Tl also forms Tl_2O. Ga and In are not affected by air.
- *Reaction with water* :
  $2M + 3H_2O \longrightarrow M_2O_3 + 3H_2$
  Boron is not affected by water. It reacts with steam when red hot. Al decomposes cold water if it is not passive by oxide layer formation. Ga and In are not attacked by cold or hot water unless oxygen is present. Tl reacts with moist air to form TlOH.
- *Reaction with nitrogen* : $2M + N_2 \longrightarrow 2MN$
  Only B and Al form nitrides. BN is a slippery white solid with layer structure similar to graphite.
- *Reaction with halogen* : $2M + 3X_2 \longrightarrow 2MX_3$
  All the group 13 elements form trihalides except TlI_3 which is unknown.
- *Reaction with carbon* : Only B and Al form carbides.
  $4B + C \longrightarrow B_4C$; $4Al + 3C \longrightarrow Al_4C_3$
- *Reaction with acids* :
  $2M + 6H^+ \longrightarrow 2M^{3+} + 3H_2$
  Boron is not affected by non-oxidising acids like HCl and dilute H_2SO_4 while other elements dissolve to form trivalent salts.
  Conc. HNO_3 and conc. H_2SO_4 react with all the group 13 elements, but HNO_3 makes Al passive.
  $2B + 3H_2SO_4 \longrightarrow 2H_3BO_3 + 3SO_2$
  $B + 3HNO_3 \longrightarrow H_3BO_3 + 3NO_2$
  $2Al + 6H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 3SO_2 + 6H_2O$
- *Reaction with alkalies* :
  $2M + 2NaOH + 2H_2O \longrightarrow 2NaMO_2 + 3H_2$
  Only B, Al and Ga react with alkalies.

CONCEPT MAP

GENERAL ORGANIC CHEMISTRY (Part-2)

Organic Compounds

I : Nature of Attacking Reagents

Types

Nucleophiles (nucleus loving)	Electrophiles (electron loving)
Expressed by a symbol : Nu^-	Expressed by a symbol E^+
Electron rich	Electron deficient
Donate an electron pair	Accept an electron pair
Attack on electron deficient atoms (*i.e.*, low e^- density)	Attack on electron rich atoms (*i.e.*, high e^- density)
Lewis bases (e^- pair donor)	Lewis acids (e^- pair acceptors)
Carry neutral or –ve charge	Carry neutral or +ve charge
Possess an unshared pair of electrons which are not too strongly held to the atomic nucleus.	Possess an empty orbital to receive the electron pair from the nucleophile.
Able to increase their covalency by one unit.	Able to form an extra or alternative bond with the nucleophile.
e.g., $\ddot{N}H_3$, $R-\ddot{N}H_2$, CN^-, OH^-	*e.g.*, BF_3, $AlCl_3$, Cl^+, NO^+

II : Electronic Displacements in Organic Molecules

Organic compounds undergo electronic displacements on their own or under the influence of an attacking agent.

Inductive effect :

- Permanent effect
- Observed in saturated compounds
- Operate through σ-bonds
- Represented by ≻ arrow
- **+*I* effect :** $\overset{\delta\delta\delta^-}{C} \leftarrow \overset{\delta\delta^-}{C} \leftarrow \overset{\delta^-}{C} \leftarrow \overset{\delta^+}{CH_3}$

  [Substituent attached to the end of the carbon chain is electron-donating.]
- **–*I* effect :** $\overset{\delta\delta\delta^+}{C} \rightarrow \overset{\delta\delta^+}{C} \rightarrow \overset{\delta^+}{C} \rightarrow \overset{\delta^-}{X}$

  [Substituent attached to the end of the carbon chain is electron-withdrawing, (X = F, Cl, CN etc.)]

◆ Stability of carbocation/free radical

$\propto +I \propto \frac{1}{-I} \propto$ Strength of base cation (conjugate acid)

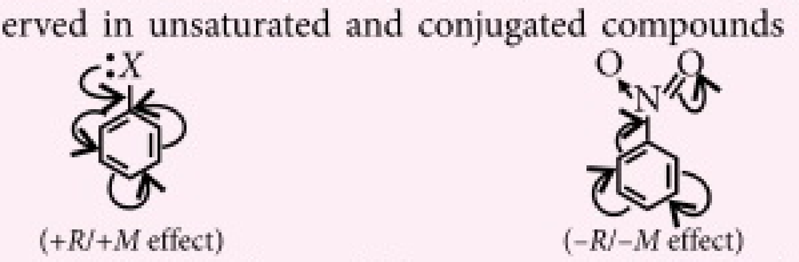
Thus, order is 1° < 2° < 3°.

◆ Stability of carbanion $\propto -I \propto \frac{1}{+I} \propto$ Strength of acid anion (conjugate base)

Thus, order is 1° > 2° > 3°.

Mesomeric/Resonance effect :

- Permanent effect
- Represented by a curved (↷) arrow
- Operate through two π-bonds or a π-bond with the lone pair
- Observed in unsaturated and conjugated compounds

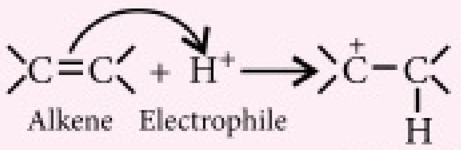


(+*R*/+*M* effect) [Electrons move away from the atom.]

(–*R*/–*M* effect) [Electrons are transferred towards the atom.]

Electromeric effect :

- Temporary effect
- Represented by a curved (↷) arrow
- Operates in multiple covalent bonds or an atom with a lone pair of electrons
- **+*E* effect :**

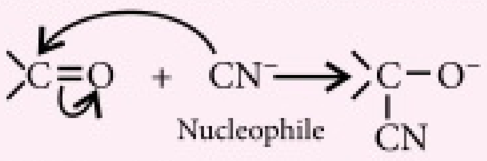


$>C=C< + H^+ \rightarrow >\overset{+}{C}-\underset{H}{C}<$

Alkene Electrophile Carbocation

(Transfer of electrons of the π-bond towards the attacking reagent.)

- **–*E* effect :**



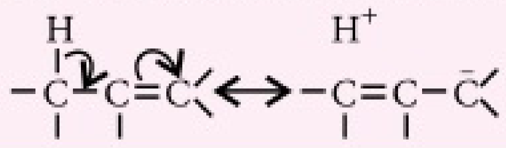
$>C=O + CN^- \rightarrow >\underset{CN}{C}-O^-$

Nucleophile

(Transfer of π-electrons takes place to more electronegative atom (*i.e.*, O, N, S) joined by multiple bonds.)

Hyperconjugation/No bond resonance/σ-π conjugation :

- Permanent effect
- Delocalization of σ and π-bond orbitals



$-\overset{H}{C}-C=C< \longleftrightarrow -C=C-C<$ H^+

III : Types of Organic Reactions

Substitution Reactions

(*Replacement of an atom by a different atom.*)

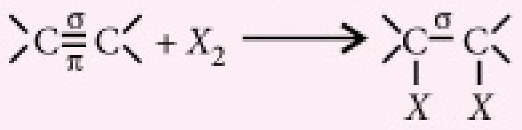
Reaction is done by –

- **Free radical:** (*e.g.*, Wurtz reaction)
- **Ionic**
  - Electrophilic (by electrophiles), S_E
  - Nucleophilic (by nucleophiles), S_N

S_N1	S_N2
Unimolecular	Bimolecular
First order	Second order
Two steps reaction (i) $R:X \xrightleftharpoons[\text{Carbocation}]{\text{Slow}} R^+ + X^-$ (ii) $R^+ + :Nu^- \xrightarrow{\text{Fast}} R:Nu$	One step reaction $R:X + :Nu^- \longrightarrow R:Nu + :X^-$ (through transition state)
Low and mild concentration of nucleophile.	High and strong concentration of nucleophile.
Solvents of high polarity.	Solvents of low polarity.
Catalysed by Lewis and Brönsted acids.	Catalyst not involved.
e.g., Hydrolysis of *tert*.butyl halide.	*e.g.*, Hydrolysis of methyl halide.

Addition Reactions

(*Compounds containing = or ≡ bonds.*)



$>C\overset{\sigma}{\underset{\pi}{=}}C< + X_2 \longrightarrow >\underset{X}{C}\overset{\sigma}{-}\underset{X}{C}<$

Reaction is done by –

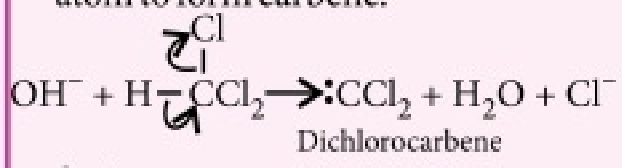
- **Free radical** -(*e.g.*, Peroxide effect)
- **Ionic**
  - Nucleophilic, A_N
  - Electrophilic, A_E

(*e.g.*, Markownikoff's rule)

Elimination Reactions

(*Reverse of addition reaction.*)

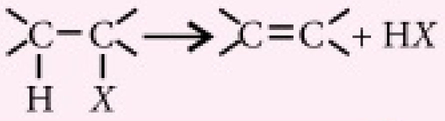
- **α-elimination :** Two atoms or groups are lost from the same carbon atom to form carbene.



$OH^- + H-CCl_2Cl \longrightarrow :CCl_2 + H_2O + Cl^-$

Dichlorocarbene

- **β-elimination :** Two atoms or groups are lost from adjacent carbon atoms to form an unsaturated compound.



$>\underset{H}{C}-\underset{X}{C}< \longrightarrow >C=C< + HX$

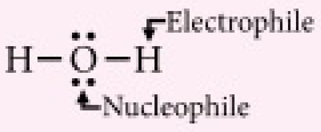
Rearrangement Reactions

(*Migration of an atom/group within the molecule.*)

$NH_4CNO \xrightarrow{\Delta} NH_2CONH_2$

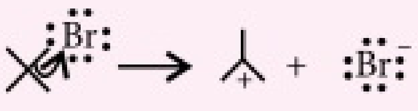
Have A Look!

- Lewis acid and base are terms that are used generally, but when one or the other reacts to form a bond to a carbon atom, we usually call it an *electrophile* or a *nucleophile*.
- Ambiphile (ambident) reagents, behave both like electrophiles and nucleophiles.



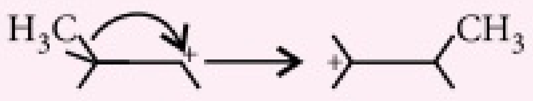
- 4-Characteristic patterns of electron flow are
  - Nucleophilic attack ➡

  - Loss of leaving group ➡

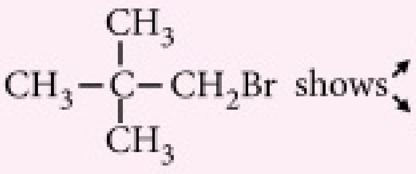


  - Proton transfer ➡

  - Rearrangement ➡



- When inductive and electromeric effects both are operative in the same molecule but in the opposite directions, the *electromeric effect* predominates.
-



$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2Br$ shows

  - S_N1 reaction with C_2H_5OH
  - S_N2 reaction with $C_2H_5O^-$
- If the reactant is a 1° alkyl halide → Undergoes only $S_N2/E2$ reactions.
- If the reactant is a 2°/3° alkyl halide,
  - Undergoes $S_N2/E2$ reactions favoured by a high concentration of a good nucleophile/strong base.
  - Undergoes $S_N1/E1$ reactions favoured by a poor nucleophile/weak base.

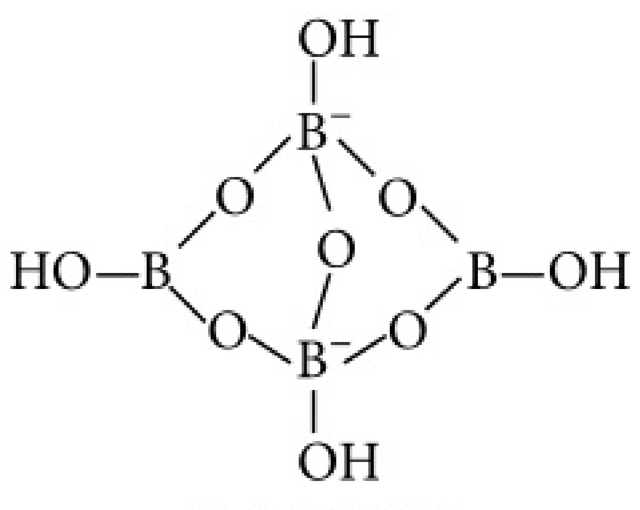
- *Reaction with ammonia* :
  $2M + 6NH_3 \longrightarrow 2M(NH_2)_3 + 3H_2$
  All the elements form amides except B which forms nitrides.
  $2B + 2NH_3 \longrightarrow 2BN + 3H_2$

- **Nature of oxides and hydroxides :** On moving down the group their basic character increases or conversely acidic character decreases.
- **Nature of hydrides :** Stability decreases as we move down the group due to corresponding decrease in the strength of M—H bond as the size of atom increases.
- **Nature of halides :** Lewis acid character of halides of group 13 elements decreases in the order : $BX_3 > AlX_3 > GaX_3 > InX_3$
  - All boron halides are covalent and covalent character decreases down the group.
  - The Lewis acid strength of boron halides follows the order : $BF_3 < BCl_3 < BBr_3 < BI_3$
- **Anomalous Properties of Boron**
  Boron shows anomalous behaviour due to its small size, high nuclear charge, high electronegativity and non-availability of *d*-electrons.
  The main points of difference are
  - Boron is a typical non-metal whereas other members are metals.
  - It alone exhibits allotropy.
  - It is a bad conductor of electricity whereas others are good conductors.
  - It forms only covalent compounds whereas other elements also form some ionic compounds.
  - Hydroxides and oxides of boron are acidic in nature whereas those of others are amphoteric and basic.
  - The trihalides of boron (BX_3) exist as monomer whereas others exist as dimers.
  - Borates are more stable than aluminates.
  - It exhibits maximum covalency of 4 while others exhibit a maximum covalency of 6.
  - It does not decompose steam while other members do so.
  - Concentrated nitric acid oxidises boron to boric acid while other elements become passive specially Al and Ga.
    $B + 3HNO_3 \longrightarrow H_3BO_3 + 3NO_2$

Preparation, Properties and Uses of Some Important Compounds

Borax ($Na_2B_4O_7 \cdot 10H_2O$) or $Na_2[B_4O_5(OH)_4] \cdot 8H_2O$

Structure



$[B_4O_5(OH)_4]^{2-}$

Preparation

- **From colemanite :**
  $$Ca_2B_6O_{11} + 2Na_2CO_3 \xrightarrow{\Delta} 2CaCO_3\downarrow + Na_2B_4O_7 + 2NaBO_2$$
  $$4NaBO_2 + CO_2 \longrightarrow Na_2CO_3 + Na_2B_4O_7$$

Properties

- Its solution is basic in nature due to hydrolysis.
  $$Na_2B_4O_7 + 7H_2O \rightleftharpoons \underset{\text{Strong base}}{2NaOH} + \underset{\text{Weak acid}}{4H_3BO_3}$$
- **Action of heat :**
  $$Na_2B_4O_7.10H_2O \xrightarrow[-10H_2O]{\Delta} \underset{\text{Anhydrous}}{Na_2B_4O_7} \xrightarrow{740°C} \underbrace{2NaBO_2 + B_2O_3}_{\text{Transparent bead}}$$

Uses

It is used

- as water softener and cleansing agent.
- in the laboratory for borax bead test.

Boric acid or Orthoboric acid (H_3BO_3) or $B(OH)_3$

Preparation

- **From borax :**
  $$Na_2B_4O_7 + 2HCl + 5H_2O \longrightarrow 4H_3BO_3 + 2NaCl$$
  $$Na_2B_4O_7 + H_2SO_4 + 5H_2O \longrightarrow 4H_3BO_3 + Na_2SO_4$$
- **By hydrolysis of boron compounds :**
  $$BCl_3 + 3H_2O \longrightarrow H_3BO_3 + 3HCl$$
  $$B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3 + 6H_2$$
  $$BN + 3H_2O \longrightarrow H_3BO_3 + NH_3$$

Properties

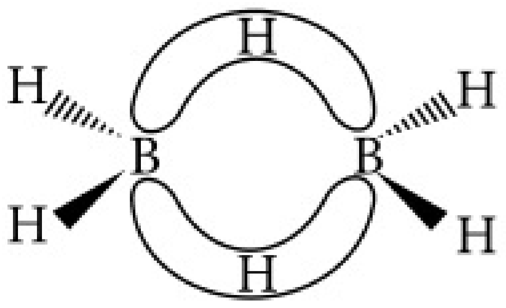
- It is a weak monobasic acid. It is not a protonic acid but acts as Lewis acid.
  $B(OH)_3 + 2HOH \longrightarrow [B(OH)_4]^- + H_3O^+$
- **Action of heat :**
  $H_3BO_3 \xrightarrow{370\ K} HBO_2 + H_2O$
  Boric acid Metaboric acid
  $4HBO_2 \xrightarrow[-H_2O]{410\ K} H_2B_4O_7 \xrightarrow[heat]{Red} 2B_2O_3 + H_2O$
  Metaboric acid Tetraboric acid Boron trioxide

Uses

- It is used in the manufacture of heat resistant borosilicate glass.
- The aqueous solution of boric acid is used as a mild antiseptic especially as eye wash under the name *boric lotion*.

Diborane (B_2H_6)

Structure



Four 2*c*-2*e* B-H terminal bonds
Two 3*c*-2*e* B-H bridging bonds

Preparation

- $4BF_3 + 3LiAlH_4 \xrightarrow[ether]{Diethyl} 2B_2H_6 + 3LiF + 3AlF_3$
- **Laboratory Method**
  $2NaBH_4 + I_2 \longrightarrow B_2H_6 + 2NaI + H_2$
- $2BF_3 + 6NaH \xrightarrow{450\ K} B_2H_6 + 6NaF$

Properties

- It catches fire spontaneously upon exposure to air.
  $B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O$
- Boranes are readily hydrolysed by water to form boric acid.
  $B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3 + 6H_2$
- With methanol, trimethylborate is formed.
  $B_2H_6 + 6CH_3OH \longrightarrow 2B(OCH_3)_3 + 6H_2$
- Diborane undergoes cleavage reactions with Lewis bases to give borane adducts.
  $B_2H_6 + 2NMe_3 \longrightarrow 2BH_3.NMe_3$
  $B_2H_6 + 2CO \longrightarrow 2BH_3.CO$
- **Reaction with metal hydrides :**
  $2NaH + B_2H_6 \xrightarrow[ether]{Diethyl} 2Na^+[BH_4]^-$
  Sod. hydride Sod. borohydride
  $2LiH + B_2H_6 \xrightarrow[ether]{Diethyl} 2Li^+[BH_4]^-$
  Lithium hydride Lithium borohydride
- **Reaction with ammonia :**
  $3B_2H_6 + 6NH_3 \longrightarrow 3[BH_2(NH_3)_2]^+[BH_4]^- \xrightarrow{\Delta} 2B_3N_3H_6 + 12H_2$
  Inorganic benzene

Uses

It is used

- for preparing a number of borohydrides such as $LiBH_4$, $NaBH_4$, etc.
- as a reducing agent in organic reactions.

Boron Trifluoride (BF_3)

Preparation

- $B_2O_3 + 6HF \longrightarrow 2BF_3 + 3H_2O$

Properties

- It undergoes rapid halide exchange reactions.
  $BF_3 + BCl_3 \longrightarrow BF_2Cl + BCl_2F$
- It is electron deficient hence acts as Lewis acid that forms adducts with Lewis bases.
  $BF_3 + (C_2H_5)_2O \longrightarrow BF_3.O(C_2H_5)_2$
- It reacts with water to give boric acid and fluoroboric acid.
  $4BF_3 + 3H_2O \longrightarrow 3HBF_4 + B(OH)_3$

Uses

- It acts as a catalyst in organic reactions.
- It is used as an important reagent in organic chemistry as a Lewis acid.

Aluminium Chloride (Al_2Cl_6)

- It exists both as an anhydrous and hexahydrate compounds.
- Anhydrous $AlCl_3$ is covalent in nature while hydrated or aqueous $AlCl_3$ is ionic. Hydrated $AlCl_3$ exists as follows in aqueous solution.
  $2AlCl_3 + 6H_2O \rightleftharpoons [AlCl_2(H_2O)_4]^+_{(aq)} + [AlCl_4(H_2O)_2]^-_{(aq)}$

Preparation

- $2Al + 3Cl_2 \longrightarrow 2AlCl_3$
  $2Al + 6HCl \longrightarrow 2AlCl_3 + 3H_2$
- $Al_2O_3 + 3C + 3Cl_2 \xrightarrow{100°C} 2AlCl_3 + 3CO$

Properties

- Anhydrous $AlCl_3$ fumes in moist air due to hydrolysis and the resulting solution is acidic.
  $AlCl_3 + 3H_2O \longrightarrow Al(OH)_3 + 3HCl$
- $$AlCl_3 + 3NH_4OH \longrightarrow \underset{\substack{\text{Gelatinous ppt.}\\ \text{(Insoluble in } NH_4OH)}}{Al(OH)_3\downarrow} + 3NH_4Cl$$
  $$AlCl_3 + 3NaOH \longrightarrow \underset{\substack{\text{(Soluble in}\\ \text{excess NaOH)}}}{Al(OH)_3\downarrow} + 3NaCl$$
  $$Al(OH)_3 + NaOH \longrightarrow \underset{\text{(Soluble metaaluminate)}}{NaAlO_2 \quad + \quad 2H_2O}$$
- **Alums :** Alums are double sulphates of the type $M_2SO_4 \cdot M_2'(SO_4)_3{\cdot}24H_2O$ where M is a univalent cation like Na^+, K^+ and NH_4^+ and M' is a trivalent cation like Al^{3+}, Fe^{3+} and Cr^{3+}.

Potash alum	$K_2SO_4{\cdot}Al_2(SO_4)_3{\cdot}24H_2O$
Sodium alum	$Na_2SO_4{\cdot}Al_2(SO_4)_3{\cdot}24H_2O$

GROUP-14 ELEMENTS (CARBON FAMILY)

- **Electronic Configuration :** [Noble gas] $ns^2\, np^2$
- **Elements :** ${}_6C$, ${}_{14}Si$, ${}_{32}Ge$, ${}_{50}Sn$, ${}_{82}Pb$

Properties

- **Physical Properties**
  - The melting and boiling points of group 14 elements are much higher than those of the elements of group 13.
  - Elements of group 14 exist in both +4 and +2 oxidation states.
  - The melting and boiling points decrease on descending the group form carbon to lead.
  - The density of group 14 elements increases regularly on moving down the group, from C to Pb.
  - The stability for +2 oxidation state increases and stability of +4 oxidation state decreases down the group due to inert pair effect.
  - **Multiple Bonding :** C has strong tendency to show $p\pi$-$p\pi$ multiple bond either with itself ($C = C$, $C \equiv C$) or with atoms like N, O ($C \equiv N$, $C = O$ etc.). Carbon does not have d-orbitals and never forms $d\pi$-$p\pi$ or $d\pi$-$d\pi$ bonds. Silicon on the other hand forms $d\pi$-$d\pi$ bonds.
- **Chemical properties**
  - *Action of air :*
    - *Monoxides* : $2M + O_2 \longrightarrow 2MO$
    - *Dioxides* : $M + O_2 \longrightarrow MO_2$
  - *Reaction with water* : C, Si, Ge and Pb are unaffected by H_2O.
    $$Sn + \underset{\text{Steam}}{2H_2O} \longrightarrow SnO_2 + 2H_2\uparrow$$
  - *Reaction with acids* : Non-oxidising acids do not attack C and Si. Ge is not attacked by dilute HCl.
    $Ge + 3HCl \longrightarrow GeHCl_3 + H_2$
    Sn dissolves slowly in dilute HCl but readily in concentrated HCl.
    $Sn + 2HCl \longrightarrow SnCl_2 + H_2$
    Pb dissolves in conc. HCl forming chloroplumbous acid, but the reaction stops after sometime due to deposition of $PbCl_2$.
  - *Reaction with alkali* : C is unaffected by cold alkali. Si reacts slowly with cold aqueous NaOH and readily with hot NaOH forming silicate.
    $Si + 2NaOH + H_2O \longrightarrow Na_2SiO_3 + 2H_2\uparrow$
    Sn and Pb form stannate and plumbate respectively on reaction with hot alkali.
- **Nature of oxides :** The acidic nature decreases with increase of atomic number. CO_2 and SiO_2 are acidic while GeO_2, SnO_2 and PbO_2 are amphoteric. All these dissolve in alkalies giving carbonates, silicates, germanates, stannates and plumbates, respectively.
  $$MO_2 + 2NaOH \longrightarrow Na_2MO_3 + H_2O$$
  The dioxides of Ge, Sn and Pb also dissolve in acids.
- **Nature of hydrides :** All the members of this group form covalent hydrides of the type MH_4.
  - The stability of hydrides decreases, consequently reducing nature increases as we move down from carbon to lead.
- **Nature of halides :** The members of this group form tetrahalides of the type MX_4 except $PbBr_4$ and PbI_4. The halides are covalent.
  - The order of thermal stability of halides :
    $CX_4 > SiX_4 > GeX_4 > SnX_4 > PbX_4$
    $CF_4 > CCl_4 > CBr_4 > CI_4$

  - Carbon does not form dihalides. All the other elements do form dihalides. There is a steady increase in the stability of dihaldies down the group. $SiX_2 < GeX_2 < SnX_2 < PbX_2$

- **Allotropy :** Except lead, all other elements of group 14 show allotropy.
- **Anomalous Properties of Carbon**
  Carbon differs from the rest of the members of group 14 because of its small size, high electronegativity, property of catenation and absence of *d*-orbitals.
  The main points of difference are
  - The melting and boiling points, ionisation energy and electronegativity of carbon are very high as compared to the rest of the members of the family.
  - It has maximum tendency to show catenation as compared to other members of the family.
  - It has high tendency to form $p\pi$-$p\pi$ multiple bonds while others form $p\pi$-$d\pi$ bonds and that also to a lesser extent.
  - CO_2 is a gas while the dioxides of all other members are solids.

Some Important Compounds

- **Allotropes of carbon :** Diamond and graphite are two allotropes of carbon.
  - Diamond is hard and non-conducting while graphite is soft and a good conductor of electricity.
  - Another allotrope of carbon is buckminsterfullerene, C_{60} which looks like a soccer ball and is sometimes called a *bucky ball.*

Silicon Tetrachloride

Preparation

- $Si_{(s)} + 2Cl_{2(g)} \xrightarrow{\Delta} SiCl_{4(l)}$
- $SiC_{(s)} + 4Cl_{2(g)} \xrightarrow{\Delta} SiCl_{4(l)} + CCl_{4(l)}$

Properties

- $SiCl_{4(l)} + 2H_2O_{(l)} \xrightarrow{\Delta} \underset{\text{Silicic acid}}{Si(OH)_{4(aq)}} \xrightarrow{\Delta} \underset{\text{Silica gel}}{SiO_2.xH_2O_{(s)}}$
- $SiCl_{4(g)} + 4H_2O_{(l)} \xrightarrow[O_2-H_2\text{ flame}]{\text{High temp.}} SiO_{2(s)} + 4HCl_{(g)}$
- $SiCl_{4(g)} + 2H_{2(g)} \xrightarrow{\Delta} Si_{(s)} + 4HCl_{(g)}$

Silicates

- Silicates are metal derivatives of silicic acid, H_4SiO_4 or $Si(OH)_4$.
- The basic structural unit of silicates is SiO_4^{4-} in which silicon atom is bonded to four oxygen atoms in tetrahedron fashion.
  e.g. zeolites, feldspar, mica, asbestos.
- In silicates either the discrete unit is present or a number of such units are joined together *via* corners by sharing 1, 2, 3 or 4 oxygen atoms per silicate units.
- When silicate units are linked together, they form chain, ring, sheet or three-dimensional structures.
  Orthosilicates (SiO_4^{4-}), Pyrosilicates ($Si_2O_7^{6-}$),
  Cyclic silicates ($Si_3O_9^{6-}$, $Si_6O_{18}^{12-}$),
  Chain silicates $(SiO_3)_n^{2n-}$, $(Si_4O_{11})_n^{6n-}$

Zeolites

- These are a class of three dimensional aluminosilicates. Their general formula is $M_{x/n}[AlO_2]_x[SiO_2]_y{\cdot}mH_2O$.
  where, M = Na^+, K^+ or Ca^{2+}, n = charge on the simple cation, m = no. of molecules of water of hydration.

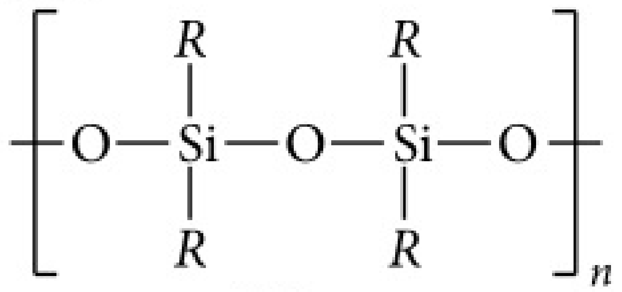
Silicones

- Silicones are polymeric organo-silicon compounds containing Si – O – Si linkages.

Preparation

- $2RCl + Si \xrightarrow[570\text{ K}]{\text{Cu powder}} \underset{\text{Dialkyldichloro silane}}{R_2SiCl_2}$

$$R_2SiCl_2 \xrightarrow[-HCl]{+H_2O} \underset{\text{Dialkyldihydro silane}}{R_2Si(OH)_2} \xrightarrow{H_2O}$$



Silicone

Uses

- They have good thermal oxidative stability. These are excellent water repellants and chemically inert substances. Liquid silicones are used as excellent lubricants.

Questions for Practice

1. In the periodic table, with the increase in the atomic number, the metallic character of the elements
(a) decreases in a period and increases in a group
(b) increases in a period and decreases in a group
(c) increases both in a period and a group
(d) decreases both in a period and a group.

2. Cyanide process is used for the extraction of
(a) barium (b) aluminium
(c) boron (d) silver.

3. H_2O_2 cannot oxidise
(a) PbS (b) O_3
(c) Na_2SO_3 (d) KI

4. During electrolysis of sodium chloride in Castner-Kellner cell, the products obtained at the cathode and anode are respectively
(a) Na, O_2 (b) H_2, O_2
(c) Na-Hg, Cl_2 (d) Cl_2, Na-Hg

5. In the given reactions,

$$Na_2B_4O_7\cdot 10H_2O \xrightarrow{\Delta} NaBO_2 + (P) + H_2O$$

$$(P) + MnO \xrightarrow{\Delta} (Q)$$

(*P*) and (*Q*) are respectively
(a) Na_3BO_3, $Mn_3(BO_3)_2$
(b) $Na_2(BO_2)_2$, $Mn(BO_2)_2$
(c) B_2O_3, $Mn(BO_2)_2$
(d) None of the above.

6. Which silicates is formed from SiO_4^{4-} tetrahedral units by sharing three oxygen atoms?
(a) Sheet silicates
(b) Pyrosilicates
(c) Linear chain silicates
(d) Three dimensional silicates

7. Phosphine, acetylene and ammonia can be formed by treating water with
(a) Mg_3P_2, Al_4C_3, Li_3N
(b) Ca_3P_2, CaC_2, $Mg(NO_3)_2$
(c) Ca_3P_2, CaC_2, CaNCN
(d) Ca_3P_2, MgC_2, NH_4NO_3

8. For the process :

$$X_{(g)} + e^- \longrightarrow X^-_{(g)}, \quad \Delta H = x$$

and $$X^-_{(g)} \longrightarrow X_{(g)} + e^-, \quad \Delta H = y$$

Select the correct alternate.
(a) Ionisation energy of $X^-_{(g)}$ is y.
(b) Electron affinity of $X_{(g)}$ is x.
(c) Electron affinity of $X_{(g)}$ is $-y$.
(d) All the above.

9. Which of the following statements is correct regarding the slag obtained during the extraction of a metal like copper or iron?
(a) The slag is lighter and has lower melting point than metal.
(b) The slag is heavier and has lower melting point than metal.
(c) The slag is lighter and has higher melting point than metal.
(d) The slag is heavier and has higher melting point than metal.

10. The oxide that gives hydrogen peroxide on treatment with a dilute acid is
(a) PbO_2 (b) Na_2O_2 (c) MnO_2 (d) TiO_2

11. $AlCl_3$ is
(a) covalent and basic
(b) anhydrous and ionic
(c) anhydrous and covalent
(d) co-ordinate and acidic.

12. A metal *M* readily forms water soluble sulphate MSO_4, water insoluble hydroxide $M(OH)_2$ and oxide *MO* which becomes inert on heating. The hydroxide is soluble in NaOH. The metal *M* is
(a) Be (b) Mg (c) Ca (d) Sr

13. Hydride of boron occurs as B_2H_6 but B_2Cl_6 does not exist. This is because
(a) $p\pi$–$d\pi$ back bonding is possible in B_2H_6 but not in B_2Cl_6
(b) boron and hydrogen have almost equal values of electronegativity
(c) boron and chlorine have almost equal atomic sizes
(d) small hydrogen atoms can easily fit in between boron atoms but large chlorine atoms do not.

14. In which of the following, the hydration energy is higher than the lattice energy?
(a) $SrSO_4$ (b) $BaSO_4$
(c) $MgSO_4$ (d) $RaSO_4$

15. For one of the element various successive ionisation energies (in kJ mol^{-1}) are given below:

Ionisation energy	1st	2nd	3rd	4th	5th
	577.5	1810	2750	11580	14820

The element is
(a) magnesium (b) aluminium
(c) silicon (d) phosphorus.

16. Copper is extracted from copper pyrites ore by heating in a bessemer converter. The method is based on the principle that
(a) copper has more affinity for oxygen than sulphur at high temperature
(b) iron has less affinity for oxygen than sulphur at high temperature
(c) sulphur has less affinity for oxygen at high temperature
(d) copper has less affinity for oxygen than sulphur at high temperature.

17. Which of the following explanation justifies for not placing hydrogen in either the group of alkali metals or halogens?
(a) Hydrogen is much lighter than alkali metals or halogens.
(b) Hydrogen exhibits same valency as that of alkali metals and halogens.
(c) Hydrogen is comparatively less electropositive than alkali metals and less electronegative than halogens.
(d) Hydrogen can form compounds with almost all other elements.

18. An alkali metal hydride (NaH) reacts with diborane in *Y* to give a tetrahedral compound *Z* which is extensively used as reducing agent in organic synthesis. The *Y* and *Z* respectively are
(a) C_2H_6, C_2H_5Na (b) $(C_2H_5)_2O$, $NaBH_4$
(c) NH_3, $B_3N_3H_6$ (d) C_3H_8, C_3H_7Na

19. Photoelectric effect is maximum in
(a) Cs (b) Na (c) K (d) Li

20. Which one of the following statements about the zeolites is false?
(a) They are used as cation exchangers.
(b) They have open structure which enables them to take up small molecules.
(c) Zeolites are aluminosilicates having three dimensional network.
(d) Some of the SiO_4^{4-} units are replaced by AlO_4^{5-} and AlO_6^{9-} ions in zeolites.

21. Lattice energies of BeF_2, MgF_2, CaF_2 and BaF_2 are –2906, – 2610, – 2459 and –2367 kJ mol^{-1} respectively. Hydration energies of Be^{2+}, Mg^{2+}, Ca^{2+}, Ba^{2+} and F^- are –2494, –1921, –1577, –1305 and –457 kJ mol^{-1} respectively. Which of the fluorides is soluble in water?
(a) BeF_2 (b) MgF_2 (c) CaF_2 (d) BaF_2

22. The correct order of radii is
(a) $N < Be < B$ (b) $F^- < O^{2-} < N^{3-}$
(c) $Na < Li < K$ (d) $Fe^{3+} < Fe^{2+} < Fe^{4+}$

23. Match the following :

	Column I		**Column II**
(i)	Smelting	**p.**	Copper glance
(ii)	Self reduction	**q.**	Malachite
(iii)	Electrolytic reduction	**r.**	Haematite
(iv)	Hydrometallurgy	**s.**	Bauxite

(a) (i) – (r), (ii) – (p), (iii) – (s), (iv) – (q)
(b) (i) – (q), (ii) – (p), (iii) – (r), (iv) – (s)
(c) (i) – (r), (ii) – (s), (iii) – (q), (iv) – (p)
(d) (i) – (r), (ii) – (s), (iii) – (p), (iv) – (q)

24. The amount of H_2O_2 present in 1L of 1.5 N H_2O_2 solution is
(a) 2.5 g (b) 25.5 g (c) 3.0 g (d) 8.0 g

25. Consider the following boron halides
1. BF_3 2. BCl_3 3. BBr_3 4. BI_3
The Lewis acid character of these halides is in the order
(a) $1 > 2 > 3 > 4$ (b) $1 > 3 > 2 > 4$
(c) $4 > 3 > 2 > 1$ (d) $4 > 2 > 3 > 1$

26. A metal *M* forms chlorides in +2 and +4 oxidation states. Which of the following statements about these chlorides is correct?
(a) MCl_2 is more volatile than MCl_4.
(b) MCl_2 is more soluble in anhydrous ethanol than MCl_4.
(c) MCl_2 is more ionic than MCl_4.
(d) MCl_2 is more easily hydrolysed than MCl_4.

27. RbO_2 is
(a) peroxide and paramagnetic
(b) peroxide and diamagnetic
(c) superoxide and paramagnetic
(d) superoxide and diamagnetic.

28. Which of the following is the strongest base?
(a) $Ca(OH)_2$ (b) $Sr(OH)_2$
(c) $Ba(OH)_2$ (d) $Mg(OH)_2$

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

List I	**List II**
1. Heavy water	(a) Bicarbonates of Mg and Ca in water
2. Temporary hard water	(b) No foreign ions in water
3. Soft water	(c) D_2O
4. Permanent hard water	(d) Sulphates and chlorides of Mg and Ca in water

Code :
(a) 1-c, 2-d, 3-b, 4-a (b) 1-b, 2-a, 3-c, 4-d
(c) 1-b, 2-d, 3-c, 4-a (d) 1-c, 2-a, 3-b, 4-d

30. In which of the following arrangements the order is not according to the property indicated against it?
(a) $Al^{3+} < Mg^{2+} < Na^+ < F^-$ - increasing ionic size
(b) $B < C < N < O$ - increasing first ionisation enthalpy
(c) $I < Br < F < Cl$ - increasing electron gain enthalpy (with negative sign)
(d) $Li < Na < K < Rb$ - increasing metallic radius

SOLUTIONS

1. (a) : In the periodic table, with the increase in atomic number, the metallic character of the elements decreases in a period and increases in a group.

2. (d) : Gold and silver are extracted from their native ores by Mac-Arthur forest cyanide process.

3. (b) : O_3 is a stronger oxidising agent than H_2O_2 and thus is not oxidised by H_2O_2, rather it is reduced in the reaction :

$$O_3 + H_2O_2 \longrightarrow 2O_2 + H_2O$$

4. (c) : A brine solution is electrolysed using a mercury cathode and a carbon anode.

At cathode : $Na^+ + e^- \xrightarrow{Hg} \text{Na-amalgam}$

At anode : $Cl^- \longrightarrow \frac{1}{2}Cl_2 + e^-$

5. (c) : $Na_2B_4O_7.10H_2O \xrightarrow{\Delta} 2NaBO_2 + \underset{(P)}{B_2O_3} + 10H_2O$

$$\underset{(P)}{B_2O_3} + MnO \xrightarrow{\Delta} \underset{(Q)}{Mn(BO_2)_2}$$

6. (a) : The sharing of three corners *i.e* three oxygen of each tetrahedron (SiO_4^{4-}) results in an infinite two dimensional sheet structure of the formula $(Si_2O_5)_n^{2n-}$.

7. (c) : $Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$
$CaNCN + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$
$CaNCN + 3H_2O \longrightarrow CaCO_3 + 2NH_3$

8. (d) : $X_{(g)} + e^- \longrightarrow X^-_{(g)}$, $\Delta H = x$ (EA of $X_{(g)}$)
$X^-_{(g)} \longrightarrow X_{(g)} + e^-$, $\Delta H = y$ (IE of $X^-_{(g)}$ or $-EA$ of $X_{(g)}$)
Thus, (a), (b) and (c) all are correct alternates.

9. (a) : The slag is lighter and has lower melting alternate point than metal.

10. (b) : $Na_2O_2 + \underset{\text{(20\% ice cold)}}{H_2SO_4} \longrightarrow Na_2SO_4 + H_2O_2$

11. (c) : $AlCl_3$ is anhydrous and covalent.

12. (a) : The metal M is Be. Its oxide BeO has high melting point. Its hydroxide dissolves in NaOH to form sodium beryllate.

$$Be(OH)_2 + 2NaOH \longrightarrow \underset{\text{Sodium beryllate}}{Na_2[Be(OH)_4]}$$

$BeSO_4$ is highly soluble in water. $Be(OH)_2$ is insoluble in water.

13. (d) : Trihalides of B are electron deficient compounds and do not exist as dimers. B_2H_6 has different types of bonding in which two H atoms act as bridged atoms.

14. (c) : $MgSO_4$ is water soluble due to its high hydration enthalpy because of smaller size of Mg^{2+} ions.

15. (b) : 3rd ionisation energy = 2750 kJ/mol
4th ionisation energy = 11580 kJ/mol
4th ionisation energy is much higher than 3rd ionisation energy, it means removal of

4th electron is from the stable configuration $Al^{3+}(2s^2, 2p^6)$, hence aluminium is the element.

16. **(a) :** Extraction of copper from copper pyrites ore by heating it in a bessemer converter is based on the fact that copper has more affinity for oxygen than sulphur at high temperature.

17. **(c) :** Hydrogen is comparatively less electropositive than alkali metals and less electronegative than halogens. For example, hydrogen has less tendency to form H^+ ions as compared to alkali metals which readily form monovalent cations. Similarly, hydrogen has less tendency to form H^- ions as compared to halogens which readily form halide (X^-) ions.

18. **(b) :** $2NaH + B_2H_6 \xrightarrow[Y]{(C_2H_5)_2O} \underset{Z}{2NaBH_4}$

19. **(a)** 20. **(d)**

21. **(d) : BeF_2 :**

$$\text{Hydration energy} = -2494 + 2 \times (-457) = -3408 \text{ kJ mol}^{-1}$$
$$\text{Lattice energy} = -2906 \text{ kJ mol}^{-1}$$
$$\Delta H_{\text{solution}} = -3408 - (-2906) = -502 \text{ kJ mol}^{-1}$$

MgF_2 :

$$\text{Hydration energy} = -1921 + 2 \times (-457) = -2835 \text{ kJ mol}^{-1}$$
$$\text{Lattice energy} = -2610 \text{ kJ mol}^{-1}$$
$$\Delta H_{\text{solution}} = -2835 - (-2610) = -225 \text{ kJ mol}^{-1}$$

CaF_2 :

$$\text{Hydration energy} = -1577 + 2 \times (-457) = -2491 \text{ kJ mol}^{-1}$$
$$\text{Lattice energy} = -2459 \text{ kJ mol}^{-1}$$
$$\Delta H_{\text{solution}} = -2491 - (-2459) = -32 \text{ kJ mol}^{-1}$$

BaF_2 :

$$\text{Hydration energy} = -1305 + 2 \times (-457) = -2219 \text{ kJ mol}^{-1}$$
$$\text{Lattice energy} = -2367 \text{ kJ mol}^{-1}$$
$$\Delta H_{\text{solution}} = -2219 - (-2367) = +148 \text{ kJ mol}^{-1}$$

$\Delta H_{\text{solution}}$ is +ve in BaF_2, hence BaF_2 is easily soluble in water.

22. **(b) :** There is a decrease in effective nuclear charge (*i.e.* Z/e ratio) from F^- to N^{3-}. The size decreases with increase in effective nuclear charge. Hence, the correct order of radii is $F^- < O^{2-} < N^{3-}$.

$$\left[\because \; Z/e \text{ for } F^- = 9/10 \text{ or } 0.9; \; O^{2-} = 8/10 \text{ or } 0.8, N^{3-} = 7/10 \text{ or } 0.7\right]$$

23. **(a) : Smelting** : $Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO$

Self-reduction :

$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$$
$$Cu_2S + 2Cu_2O \longrightarrow 6Cu + SO_2$$

Electrolytic reduction :

$$\text{Cathode} : Al^{3+} + 3e^- \longrightarrow Al$$
$$\text{Anode} : C + 2O^{2-} \longrightarrow CO_2 + 4e^-$$
$$C + O^{2-} \longrightarrow CO + 2e^-$$

Hydrometallurgy :

Hydrometallurgical processes are used to treat oxide ores dominated by $CuCO_3$ minerals like malachite and azurite.

24. **(b) :** Strength = Normality × equivalent weight
$= 1.5 \times 17$ ($\because$ eq. wt. of $H_2O_2 = 34/2 = 17$)
$= 25.5 \text{ g L}^{-1}$

25. **(c) :** The Lewis acid strength decreases in the order : $BI_3 > BBr_3 > BCl_3 > BF_3$
This can be explained on the basis of the tendency of the halogen atom to back donate its lone pair of electrons to the boron atom through $p\pi - p\pi$ bonding, which is maximum in BF_3.

26. **(c)** 27. **(c)**

28. **(c) :** Basic strength increases down the group
$Mg(OH)_2 < Ca(OH)_2 < Sr(OH)_2 < Ba(OH)_2$

29. **(d) :** Heavy water – D_2O
Temporary hard water – Bicarbonates of Mg/Ca in water.
Soft water – No foreign ions in water
Permanent hard water – Sulphates and chlorides of Mg/Ca in water.

30. **(b) :** As we move from left to right across a period, ionisation enthalpy increases with increasing atomic number. So the order of increasing ionisation enthalpy should be $B < C < N < O$.
But $N(1s^2 2s^2 2p^3)$ has a stable half filled electronic configuration. So, ionisation enthalpy of nitrogen is greater than oxygen.
So, the correct order of increasing first ionisation enthalpy is $B < C < O < N$.

2015
CBSE-BOARD
CHAPTERWISE PRACTICE PAPER

Series- 5 The *d- and f-* Block Elements / Coordination Compounds

Time : 3 hrs. Marks : 70

GENERAL INSTRUCTIONS

(i) All questions are compulsory.
(ii) Question numbers 1 to 8 are very short-answer questions and carry 1 mark each.
(iii) Question numbers 9 to 18 are short-answer questions and carry 2 marks each.
(iv) Question numbers 19 to 27 are also short-answer questions and carry 3 marks each.
(v) Question numbers 28 to 30 are long-answer questions and carry 5 marks each.
(vi) Use Log Tables, if necessary. Use of calculator is not allowed.

1. Write the formula of a compound where the transition metal is in + 7 oxidation state.

2. Vitamin B_{12} is a coordination compound of which metal?

3. Why does surface of polished zinc gradually become dull in moist air?

4. Indicate the steps in the preparation of $KMnO_4$ from pyrolusite ore.

5. Write IUPAC name of any of the isomers with molecular formula :

(i) $[Pt(NH_3)_2Cl_2]Cl_2$
(ii) $[Cr(NH_3)_4Cl_2]^+$

6. Why do Zr and Hf exhibit similar properties?

7. Give an example of linkage isomerism.

8. Calculate the 'spin only' magnetic moment of $M^{2+}_{(aq)}$ ion ($Z = 27$).

9. What are the different oxidation states exhibited by the lanthanoids?

10. (i) What is a ligand? Give an example of bidentate ligand.

(ii) Explain as to how the two complexes of nickel $[Ni(CN)_4]^{2-}$ and $[Ni(CO)_4]$ have different structures but do not differ in their magnetic behaviour (Ni = 28).

OR

(i) What is the basis of formation of the spectrochemical series?

(ii) Draw the structures of geometrical isomers of the following coordination complexes : $[Co(NH_3)_3Cl_3]$ and $[CoCl_2(en)_2]^+$ (*en* = ethylenediamine and atomic number of Co is 27)

11. Which metal in the first series of transition metals exhibits +1 oxidation state most frequently and why?

12. What are alloys? Write the percentage (%) composition of alnico.

13. How do you account for the following :

(i) All scandium salts are white.

[At. no. of Sc = 21]

(ii) The first ionisation energies of the 5*d* transition elements are higher than those of the 3*d* and 4*d* transition elements in respective groups.

14 . What do you mean by denticity and chelation?

15. **(i)** Of the ions Ag^+, Co^{2+} and Ti^{4+}, which one will be coloured in aqueous solution? (Atomic nos : Ag = 47, Co = 27, Ti = 22).

(ii) If each one of the above ionic species is in turn placed in a magnetic field how will it respond and why?

16. In the transition series, with an increase in atomic number the atomic radius does not change very much. Why is it so?

17. How many stereoisomers are possible in the following coordination entities?

(i) $[Cr(ox)_3]^{3-}$

(ii) $[CoCl_3(NH_3)_3]$

18. Draw the structures of

(i) *cis*-dichloridotetracyanochromate(III)

(ii) *mer*-triamminetrichloridocobalt(III)

19. **(i)** Give reasons for each of the following :

(a) Size of trivalent lanthanoid cations decreases with increase in the atomic number.

(b) Transition metal fluorides are ionic in nature whereas bromides and chlorides are usually covalent in nature.

(ii) What happens when aqueous ammonia reacts with

(a) Mercury(I) chloride

(b) Silver chloride?

Write balanced chemical equations.

20. How does the acidified $KMnO_4$ reacts with the following :

(i) Iodide (I^-) ion

(ii) Oxalate ion ($C_2O_4^{2-}$)

(iii) Sulphide ion (S^{2-})

21. How would you account for the following :

(i) Of the d^4 species Cr^{2+} is strongly reducing while Mn^{3+} is strongly oxidising.

(ii) Cobalt (II) is stable in aqueous solution but in the presence of complexing reagents it is easily oxidised.

(iii) The d^1 configuration is very unstable in ions.

OR

For M^{2+}/M and M^{3+}/M^{2+} systems the $E°$ values for some metals are as follows :

Cr^{2+}/Cr	−0.9 V	Cr^{3+}/Cr^{2+}	−0.4 V
Mn^{2+}/Mn	−1.2 V	Mn^{3+}/Mn^{2+}	+1.5 V
Fe^{2+}/Fe	−0.4 V	Fe^{3+}/Fe^{2+}	+0.8 V

Use this data to comment upon :

(i) the stability of Fe^{3+} in acid solution as compared to that of Cr^{3+} or Mn^{3+} and

(ii) the ease with which iron can be oxidised as compared to a similar process for either chromium or manganese metal.

22. Assign reasons for the following observations :

(i) Mn^{2+} compounds are more stable than Fe^{2+} compounds towards oxidation to their +3 oxidation state.

(ii) Interstitial compounds are well known for transition elements.

(iii) An aqueous solution of potassium chromate is yellow but changes its colour on decreasing the pH of the solution.

23. Describe for any two of the following complex ions, the type of hybridization, shape and magnetic property :

(i) $[Fe(H_2O)_6]^{2+}$

(ii) $[Co(NH_3)_6]^{3+}$

(iii) $[NiCl_4]^{2-}$

[At. Nos. Fe = 26, Co = 27, Ni = 28]

24. Ravi and Sohan were given same project of synthesis of complex compound in the school. Ravi prepared a complex compound of cobalt with NH_3 and NO_2 as donor ligands. He got a red precipitate. Sohan also prepared the same complex using same metal salt solution and same ligands. He obtained yellow crystals. Sohan complained his teacher that his chemicals were different so he got different product. But their teacher is satisfied with both the results.

Now answer the following questions :

(i) What is the reason for different colours?

(ii) Write IUPAC name of both the compounds.

(iii) What value is associated with this observation?

25. Give examples and suggest reasons for the following features of the transition metal chemistry :

(i) The lowest oxide of transition metal is basic, the highest is amphoteric/acidic.

(ii) A transition metal exhibits highest oxidation state in oxides and fluorides.

(iii) The highest oxidation state is exhibited in oxoanions of a metal.

26. Compare the chemistry of actinoids with that of the lanthanoids with special reference to :

(i) atomic and ionic sizes

(ii) oxidation state and

(iii) chemical reactivity.

27. Draw a sketch to show the splitting of *d*-orbitals in an octahedral crystal field. For a d^6 ion the actual configuration in split *d*-orbitals in an octahedral crystal field is decided by the magnitude of Δ_o and *P*. Explain.

28. (i) Given below are the electrode potential values, *E*° for some of the first row transition elements :

Element	$E^\circ_{M^{2+}/M}$ (V)
V(23)	–1.18
Cr(24)	–0.91
Mn(25)	–1.18
Fe(26)	–0.44
Co(27)	–0.28
Ni(28)	–0.25
Cu(29)	+0.34

Explain the irregularities in these values on the basis of electronic structures of atoms.

(ii) Complete the following chemical equations:

(a) $Cr_2O_7^{2-} + Sn^{2+} + H^+ \longrightarrow$

(b) $MnO_4^- + Fe^{2+} + H^+ \longrightarrow$

OR

(i) Explain the following :

(a) Transition elements tend to be unreactive with increasing atomic number in the series.

(b) *d*-Block elements exhibit more oxidation states than *f*-block elements.

(ii) A green chromium compound (*A*) on fusion with alkali gives a yellow compound (*B*) which on acidification gives an orange coloured compound (*C*). (*C*) on treatment with NH_4Cl gives an orange coloured product (*D*), which on heating decomposes to give back (*A*). Identify *A*, *B*, *C* and *D*. Write balanced equations for reactions.

29. (a) For the complex $[Fe(en)_2Cl_2]Cl$, (*en* = ethylenediamine), identify :

(i) the oxidation number of iron

(ii) the hybrid orbitals and the shape of the complex

(iii) the magnetic behaviour of the complex

(iv) the number of geometrical isomers

(v) whether there is an optical isomer also, and

(vi) Name of the complex

(Atomic number of Fe = 26).

(b) (i) Draw the structure of ferrocene.

(ii) Using valence bond theory explain the geometry and magnetic behaviour of pentacarbonyliron (0).

OR

(a) (i) Give the IUPAC name of $[PtCl(NH_2CH_3)(NH_3)_2]Cl$.

(ii) Compare the magnetic behaviour of the complex entities $[Fe(CN)_6]^{4-}$ and $[FeF_6]^{3-}$(Fe = 26).

(b) Explain the following cases giving appropriate reasons :

(i) Nickel does not form low spin octahedral complexes.

(ii) The π-complexes are known for the transition metals only.

(iii) Co^{2+} is easily oxidised to Co^{3+} in the presence of a strong field ligand.

30. (i) Complete the following chemical equations :

(a) $MnO^-_{4(aq)} + S_2O^{2-}_{3\,(aq)} + H_2O_{(l)} \longrightarrow$

(b) $Cr_2O^{2-}_{7\,(aq)} + H_2S_{(g)} + H^+_{(aq)} \longrightarrow$

(ii) Give an explanation for each of the following observations.

(a) The gradual decrease in size (actinoid contraction) from element to element is greater among the actinoids than among the lanthanoids (lanthanoid contraction).

(b) The greater number of oxidation states are exhibited by the members in the middle of a transition series.

(c) Chromium is a typically hard metal while mercury is a liquid.

OR

(a) Complete the following chemical equations :

(i) $MnO^-_{4\,(aq)} + C_2O^{2-}_{4\,(aq)} + H^+_{(aq)} \longrightarrow$

(ii) $Cr_2O^{2-}_{7\,(aq)} + Fe^{2+}_{(aq)} + H^+_{(aq)} \longrightarrow$

(b) Explain the following observations about the transition/inner transition element :

(i) There is in general an increase in density of element from titanium ($Z = 22$) to copper ($Z = 29$).

(ii) There occurs much more frequent metal-metal bonding in compounds of heavy transition elements (3rd series).

(iii) The members in the actinoid series exhibit a larger number of oxidation states than the corresponding members in the lanthanoid series.

SOLUTIONS

1. In $KMnO_4$, the transition metal, Mn has +7 oxidation state.

2. Cobalt is present in vitamin B_{12}.

3. This is because of formation of a thin film of basic carbonate.

$$4Zn + 3H_2O + 2O_2 + CO_2 \longrightarrow ZnCO_3.3Zn(OH)_2$$

4. $$2MnO_2 + 4KOH + O_2 \xrightarrow{\Delta} 2K_2MnO_4 + 2H_2O$$

$$3MnO_4^{2-} + 4H^+ \longrightarrow 2MnO_4^- + MnO_2 + 2H_2O$$

5. **(i)** *cis*-Diamminedichloridoplatinum(IV) chloride.

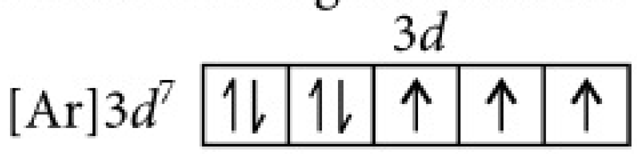
(ii) *cis*-Tetraamminedichloridochromium(III) ion

6. Due to lanthanoid contraction Zr and Hf have nearly equal atomic and ionic radii, hence show similar properties.

7. $[Co(NH_3)_5(NO_2)]Cl_2$ and $[Co(NH_3)_5(ONO)]Cl_2$

8. Electronic configuration of M atom with $Z = 27$ is $[Ar]\ 3d^7 4s^2$.

∴ Electronic configuration of M^{2+} ion :



Thus, it has three unpaired electrons.

∴ Spin only magnetic moment

$$(\mu) = \sqrt{n(n+2)}\ \text{BM}$$

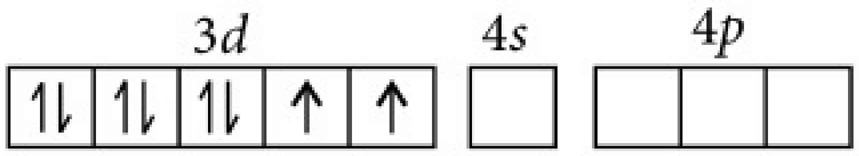
$$= \sqrt{3(3+2)} = \sqrt{15}\ \text{BM} = 3.87\ \text{BM}$$

9. The most common oxidation state exhibited by lanthanoids is +3. However, some of the lanthanoids also show +2 and +4 oxidation states in solution or in solid compounds.

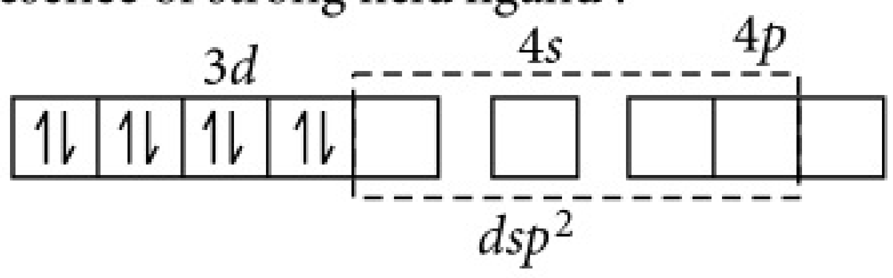
10. **(i)** The ions or molecules bound to the central atom or ion in the coordination entity are called ligands. Example of a bidentate ligand is $H_2N—CH_2—CH_2—NH_2$.
(Ethylenediamine)

(ii) $[Ni(CN)_4]^{2-}$ contains Ni^{2+} ion which is $3d^8$ system having dsp^2 hybridisation and square planar geometry.

$Ni^{2+} : [Ar]\ 3d^8\ 4s^0\ 4p^0$

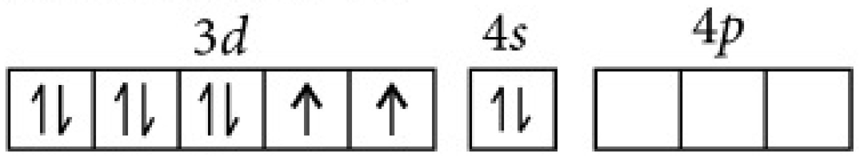


Pairing of electrons takes place in the presence of strong field ligand :

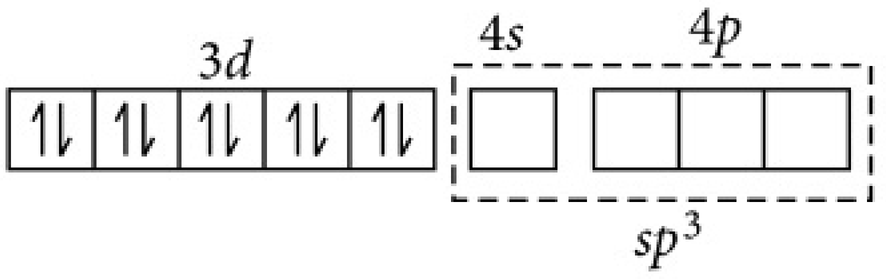


$[Ni(CO)_4]$ contains Ni^0 which is $3d^8 4s^2$ system having sp^3 hybridisation and tetrahedral geometry.

$Ni(0) : [Ar]\ 3d^8\ 4s^2$



In the presence of strong field ligand CO two electrons of 4s orbital shift to 3d orbitals.

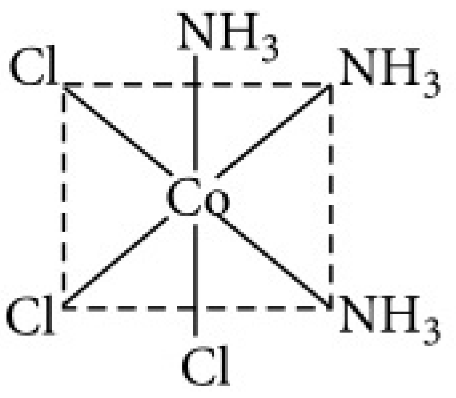


It has no unpaired electrons, hence it is diamagnetic.
Thus, $[Ni(CN)_4]^{2-}$ and $[Ni(CO)_4]$ have different structures but same magnetic behaviour.

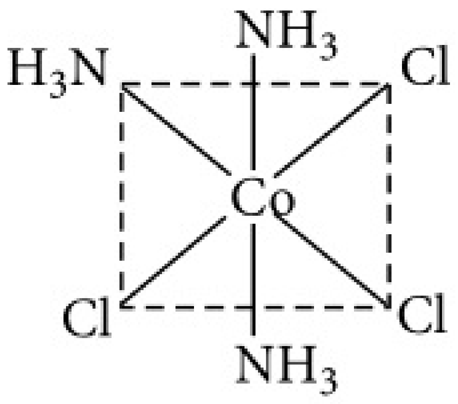
OR

(i) Spectrochemical series is the arrangement of ligands in order of their increasing field strength and is based upon crystal field splitting energy (CFSE). The ligands with small value of CFSE are called weak field ligands whereas those with large value of CFSE are called strong field ligands.

(ii) **(a)** The facial and meridional isomers of $[Co(NH_3)_3Cl_3]$ may be represented as :

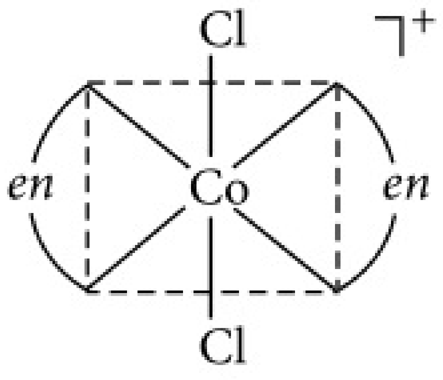


Facial-isomer

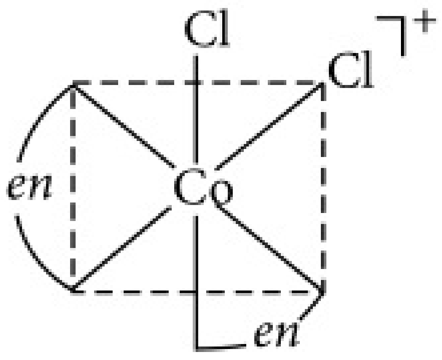


Meridional-isomer

(b) $[CoCl_2(en)_2]^+$ ion exists in two geometrical isomers as shown below :



trans-form



cis-form

11. Copper exhibits +1 oxidation state in its compounds. Electronic configuration of Cu in the ground state is $3d^{10}4s^1$. So, Cu can easily lose $4s^1$ electron to give a stable $3d^{10}$ configuration.

12. Alloys are homogeneous mixture of two or more elements in which atleast one of the element is a metal. Since *d*-block elements have nearly same atomic sizes, they can easily take up position of one another in crystal lattices and form alloys. In alnico, Al = 12%, Ni = 20%, Co = 8% and Fe = 60%.

13. **(i)** Sc^{3+} has $3d^0$ configuration. So no *d-d* transitions are possible and hence, all scandium salts are white.

(ii) The first ionisation energies of 5*d* transition elements are higher due to their higher effective nuclear charge which is caused by the poor shielding effect of 4*f*-electrons (lanthanoid contraction).

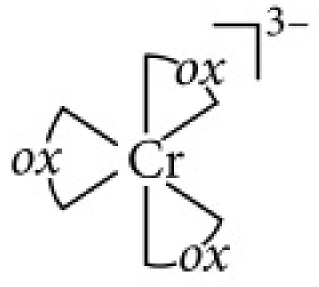
14. The number of atoms through which the ligand can donate a pair of electrons is called denticity of a ligand. Ligands on this basis can be unidentate, tridentate or polydentate.
When coordination of central metal atom or ion with ligand takes place from two or more groups of the same ligand in such a way that a five or six membered ring is formed with metal atom or ion, then it is called chelation and such ligands are called chelating ligands.

15. **(i)** Ag^+ $(4d^{10}5s^0)$ and Ti^{4+} $(3d^04s^0)$ have no incompletely filled *d*-orbital while Co^{2+} $(3d^74s^0)$ has so. Thus, Ag^+ and Ti^{4+} ions are colourless and Co^{2+} ions are coloured in aqueous solutions.

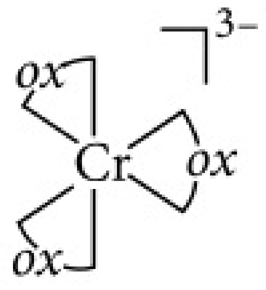
(ii) Co^{2+} ions will get attracted in a magnetic field while Ag^+ and Ti^{4+} ions will get repelled in the magnetic field *i.e.* Co^{2+} ions are paramagnetic while Ag^+ and Ti^{4+} ions are diamagnetic in nature.

16. As one proceeds along a transition series, the nuclear charge increases which tends to decrease the size but the addition of electrons in the *d*-subshell increases the screening effect which counterbalances the effect of increased nuclear charge.

17. **(i)** $[Cr(ox)_3]^{3-}$ shows two optical isomers :

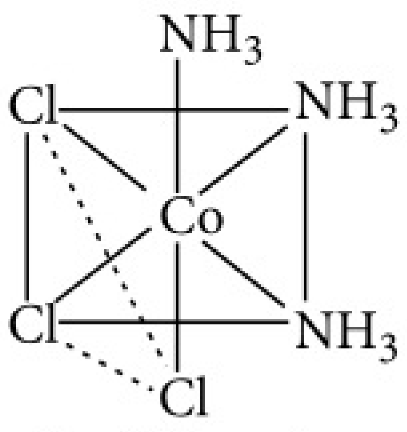


dextro

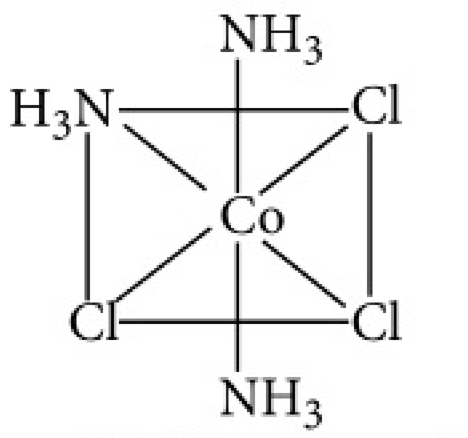


laevo

(ii) $[CoCl_3(NH_3)_3]$ shows two geometrical isomers :

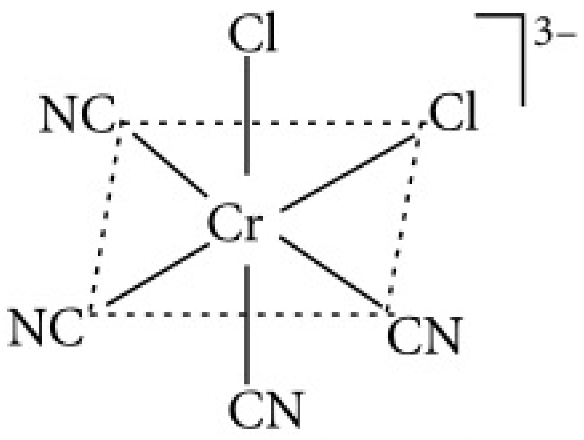


(Facial-isomer)

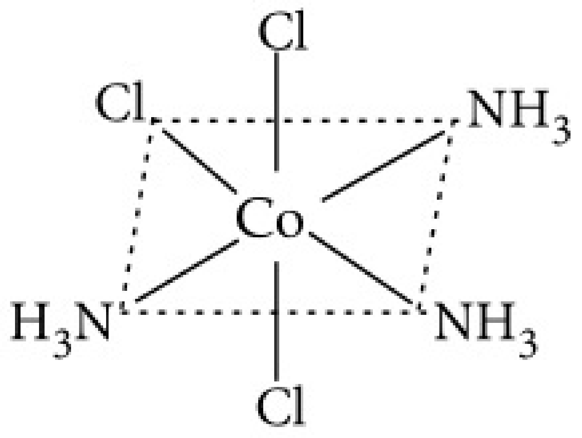


(Meridional-isomer)

18. (i) *cis*-Dichloridotetracyanochromate(III)



(ii) *mer*-Triamminetrichloridocobalt(III)



19. (i) **(a)** As we move through the lanthanoid series, 4*f*-electrons are being added one at each step. The mutual shielding of 4*f*-electrons is very little due to the shape of 4*f*-orbitals. The nuclear charge increases by one at each step and the inward pull experienced by 4*f*-electrons increases. Hence the size of the trivalent lanthanoid cations decreases with the increase in atomic number.

(b) As the electronegativity of halogens decreases down the group, the ionic character also decreases in the order :

$M\text{-F} > M\text{-Cl} > M\text{-Br}$

So transition metal fluorides are ionic in nature whereas bromides and chlorides are covalent in nature.

(ii) **(a)** When mercury (I) chloride reacts with aqueous ammonia, Hg_2Cl_2 disproportionates into Hg and mercury aminochloride.

$$Hg_2Cl_2 + 2NH_{3(aq)} \longrightarrow Hg + Hg(NH_2)Cl + NH_4Cl$$

(b) A soluble linear complex $[Ag(NH_3)_2]Cl$ is formed.

$$AgCl_{(s)} + 2NH_{3(aq)} \longrightarrow \underset{\text{Diamminesilver (I) chloride}}{[Ag(NH_3)_2]Cl_{(aq)}}$$

20. In acidic medium :

(i) Iodine is liberated from potassium iodide :

$$10I^- + 2MnO_4^- + 16H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 5I_2$$

(ii) Oxalate ion or oxalic acid is oxidised at 333 K :

$$5C_2O_4^{2-} + 2MnO_4^- + 16H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 10CO_2$$

(iii) Hydrogen sulphide is oxidised, sulphur being precipitated :

$$5S^{2-} + 2MnO_4^- + 16H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 5S$$

21. (i) Cr^{2+} is reducing as its configuration changes from d^4 to d^3, the latter having a half filled t_{2g} level. On the other hand, the change from Mn^{3+} to Mn^{2+} results in the half filled d^5 configuration which has extra stability.

(ii) The tendency to form complexes is high for Co(III) as compared to Co(II). Co^{2+} ions are very stable and are difficult to oxidise. Co^{3+} ions are less stable and are reduced by water. In contrast many Co(II) complexes are readily oxidised to Co(III) complexes and Co(III) complexes are very stable, *e.g.*,

$$[Co(NH_3)_6]^{2+} \xrightarrow{\text{Air}} [Co(NH_3)_6]^{3+}$$

This happens because the crystal field stabilisation energy of Co(III) with a $d^6(t_{2g}^6)$ configuration is higher than for Co(II) with a $d^7(t_{2g}^6 e_g^1)$arrangement.

(iii) Transition metal ions with d^1 configuration have a tendency to lose this single electron and give ion with a noble gas configuration.

OR

(i) Consider the half-reaction,

$M^{n+}_{(aq)} + ne^- \longrightarrow M_{(s)};\ E° = x\text{ V}$

If $E°$ value is negative then the metal M has the tendency to go into solution and form M^{n+} ions. This tendency is reversed for positive $E°$ values.

Now, for

$Fe^{3+}_{(aq)} + e^{-} \longrightarrow Fe^{2+}_{(aq)}$; $E° = +0.8$ V

$Cr^{3+}_{(aq)} + e^{-} \longrightarrow Cr^{2+}_{(aq)}$; $E° = -0.4$ V

and $Mn^{3+}_{(aq)} + e^{-} \longrightarrow Mn^{2+}_{(aq)}$; $E° = +1.5$ V

These values suggest that relative stabilities of the ions would be in the order $Cr^{3+} > Fe^{3+} > Mn^{3+}$.

(ii) Higher the value of $E°_{M^{2+}/M}$, lesser will be the ease to get oxidised. Hence, on the basis of $E°_{M^{2+}/M}$ values, the ease of oxidation of metals is in the order : Mn > Cr > Fe.

22. **(i)** Electronic configuration of $_{25}Mn^{2+}$ is [Ar] $3d^5 4s^0$ whereas that of $_{25}Mn^{3+}$ is [Ar] $3d^4 4s^0$. As half filled orbitals are more stable, Mn^{2+} compounds are more stable than Mn^{3+} compounds.

The electronic configuration of $_{26}Fe^{2+}$ is [Ar] $3d^6 4s^0$ and that of $_{26}Fe^{3+}$ is [Ar] $3d^5 4s^0$. So, Fe^{3+} compounds are more stable than Fe^{2+} compounds due to stable configuration.

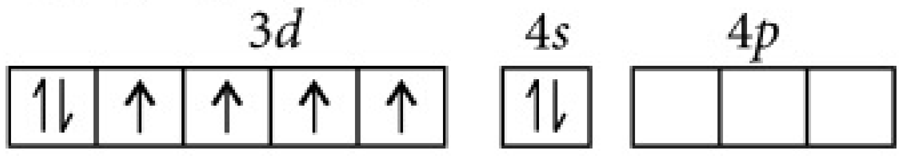
(ii) In a crystal lattice, transition elements have interstitial vacant spaces into which small sized non-metal atoms (H, C, N, B) can fit resulting in the formation of interstitial compounds.

(iii) When the pH of the solution of potassium chromate is decreased, the colour of the solution changes from yellow to orange due to the conversion of CrO_4^{2-} ions into $Cr_2O_7^{2-}$ ions.

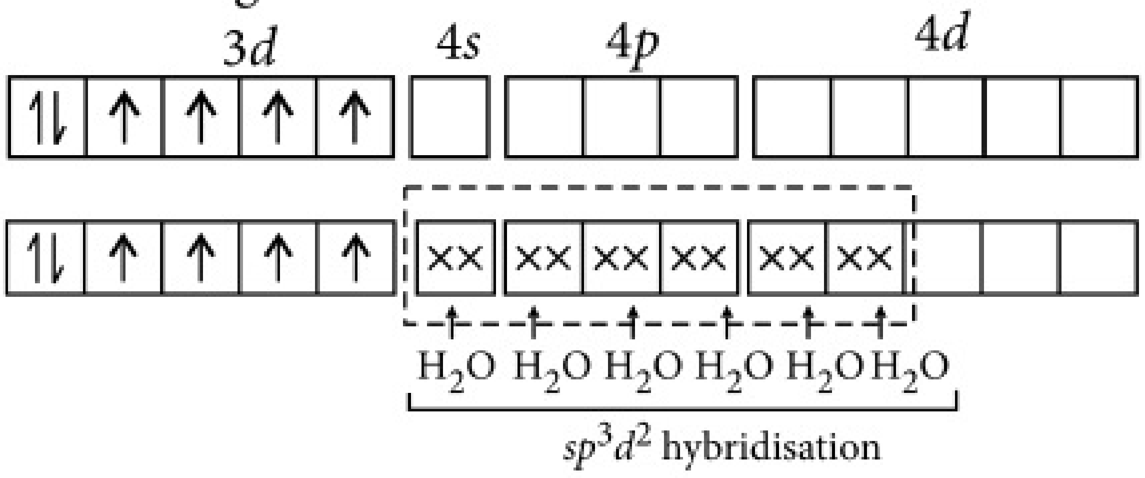
$$\underset{\text{Yellow}}{2CrO_4^{2-}} + 2H^+ \longrightarrow \underset{\text{Orange}}{Cr_2O_7^{2-}} + H_2O$$

23. **(i)** $[Fe(H_2O)_6]^{2+}$

Fe(26) = [Ar] $3d^6 4s^2$



Configuration of Fe^{2+} in the presence of weak field ligand :



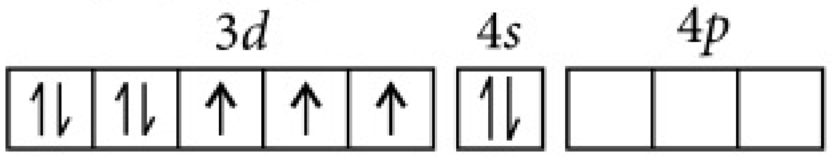
Hybridisation - sp^3d^2

Shape - octahedral

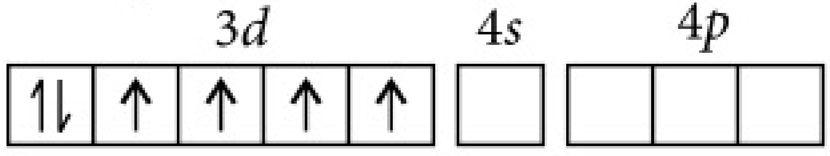
Magnetic property - paramagnetic

(ii) $[Co(NH_3)_6]^{3+}$

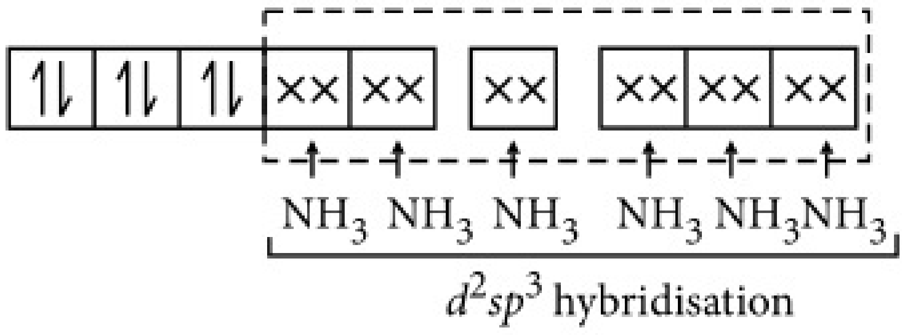
Co (27) : [Ar]$3d^7 4s^2$



Configuration of Co^{3+} :



In the presence of strong field ligand NH_3, pairing of electrons takes place.



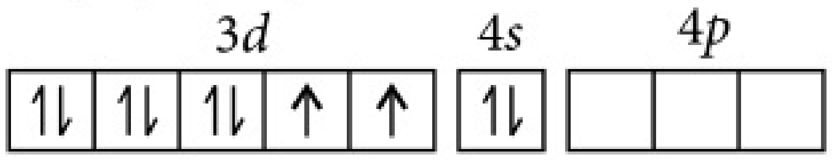
Hybridisation - d^2sp^3

Shape - octahedral

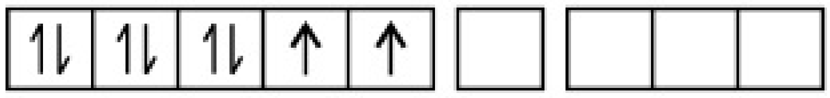
Magnetic property - diamagnetic

(iii) $[NiCl_4]^{2-}$

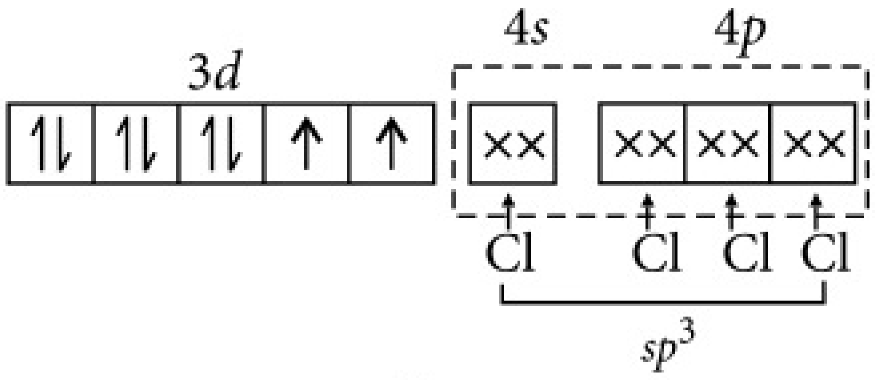
Ni (28) : [Ar]$3d^8 4s^2$



Configuration of Ni^{2+} :



In presence of weak field ligand :



Hybridisation - sp^3

Shape - tetrahedral

Magnetic property - paramagnetic

24. **(i)** Reason for different colours is different linkage of ligands with the metal *i.e.* formation of linkage isomers.

(ii) $[Co(NH_3)_5(NO_2)]Cl_2$-Yellow

Pentaamminenitrito-N-cobalt(III)chloride

$[Co(NH_3)_5(ONO)]Cl_2$-Red

Pentaamminenitrito-O-cobalt(III) chloride

(iii) Same thing can show different properties in different conditions of synthesis. Similarly, people respond differently in same situation.

25. (i) Lowest oxides of transition metals are basic due to their ability to get oxidised to higher oxidation states by donating electrons.

(ii) Being small in size and high in electronegativity fluorine and oxygen can bring about higher oxidation states in the compounds of transition elements. Examples are Mn_2O_7, CrO_3, OsF_6.

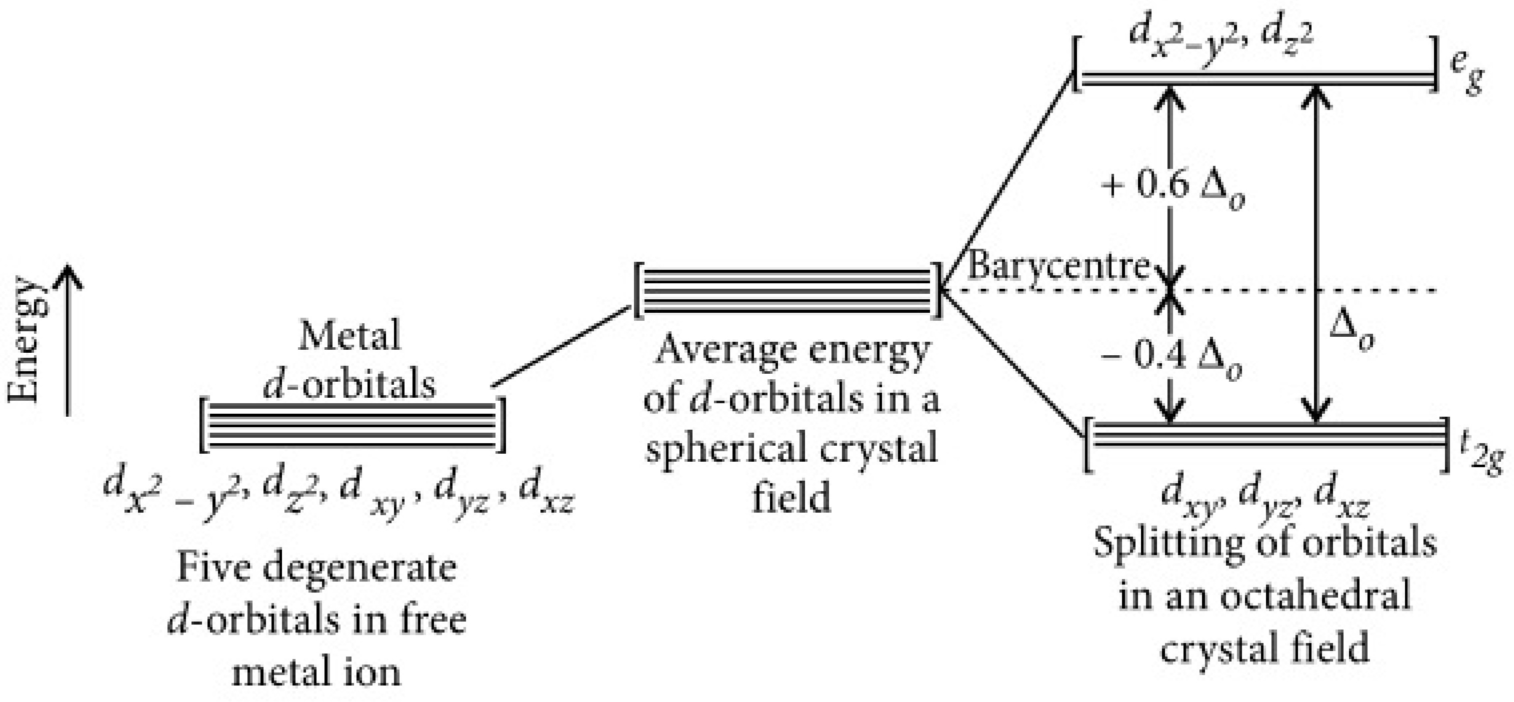
(iii) Transition metals showing higher oxidation states in the oxoanions are Cr and Mn, *e.g.*, CrO_4^{2-}, $Cr_2O_7^{2-}$, MnO_4^{2-}, MnO_4^-. This is due to the small size and high electronegativity of oxygen and its ability to form multiple π-bonds with the metal.

26. (i) **Atomic and ionic sizes :** The decrease in atomic and ionic radii from element to element is greater in actinoids than the lanthanoids due to poorer shielding by $5f$ electrons.

(ii) **Oxidation state :** Lanthanoids show oxidation states +2 , +3 and +4 (+3 oxidation state is the most stable). Actinoids exhibit large number of oxidation states (+3, +4, +5, +6, +7) because of the small energy gap between $5f$, $6d$ and $7s$ orbitals.

(iii) **Chemical reactivity :** Actinoids are more reactive than lanthanoids. This is due the reason that $5f$ electrons penetrate less into the inner core of electrons and hence are more effectively shielded from the nuclear charge than the $4f$ electrons of the corresponding lanthanoids. Because the outer electrons are less firmly held, they are available for bonding in the actinoids.

27.



Obeying the Hund's rule of maximum multiplicity, one (d^1), two (d^2) and three (d^3) electrons are placed in the more stable t_{2g} orbitals with their parallel spins. Similarly, eight (d^8), nine (d^9) and ten (d^{10}) electrons occupy the e_g orbitals.

For four (d^4), five (d^5), six (d^6) and seven (d^7) electrons in the d-orbitals, there are two ways of placing them which is determined by the magnitude of Δ_o and the average pairing energy P.

(i) When $\Delta_o > P$, pairing of electrons will take place and the electrons will occupy the more stable t_{2g} orbitals (strong field case) *i.e.*, $d^6(t_{2g}^{\ 6}e_g^{\ 0})$.

(ii) When $\Delta_o < P$, pairing of electrons will take place only after all the d-orbitals (t_{2g} and e_g) are singly filled as in the free metal ion (weak field case) *i.e.*; $d^6(t_{2g}^{\ 4}e_g^{\ 2})$.

28. (i) This irregular trend in $E°$ values is because of irregular trends in variation of ionization energy *i.e.*, $(IE_1 + IE_2)$ and also the sublimation energies which are relatively much lower for Mn (240 kJ/mol) and V (470 kJ/mol).

(ii) **(a)** $Cr_2O_7^{2-} + 3Sn^{2+} + 14H^+ \longrightarrow 2Cr^{3+} + 3Sn^{4+} + 7H_2O$

(b) $MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$

OR

(i) **(a)** Reactivity of transition elements decreases with increase in atomic number. This is due to increased nuclear charge which reduces the size of the atom, making the removal of outer electrons difficult.

(b) In *d*-block elements, electrons of *s*-orbitals and *d*-orbitals both take part in bond formation. In *f*-block elements due to poor shielding effect of *f*-electrons effective nuclear charge increases, therefore, lesser number of oxidation states are shown.

(ii) $\underset{(A)\text{(Green)}}{2Cr_2O_3} + 8NaOH + 3O_2 \longrightarrow \underset{(B)\text{(Yellow)}}{4Na_2CrO_4} + 4H_2O$

$\underset{(B)}{2Na_2CrO_4} + H_2SO_4 \longrightarrow \underset{\text{(Orange)}\ (C)}{Na_2Cr_2O_7} + Na_2SO_4 + H_2O$

$2NH_4Cl + \underset{(C)}{Na_2Cr_2O_7} \longrightarrow \underset{\text{(Orange)}\ (D)}{(NH_4)_2Cr_2O_7} + 2NaCl$

$\underset{\text{Ammonium dichromate}}{(NH_4)_2Cr_2O_7} \xrightarrow{\text{heat}} \underset{\text{(Green)}(A)}{Cr_2O_3} + N_2 + 4H_2O$

29. (a) **(i)** Oxidation number : + 3

(ii) d^2sp^3 (octahedral)

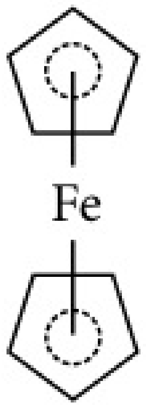
(iii) Paramagnetic

(iv) Two/cis and trans isomers

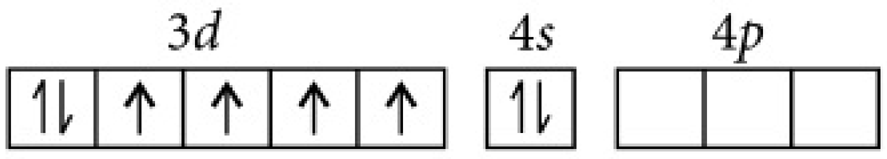
(v) Yes/*cis*(*d*-and *l*-form)

(vi) Dichloridobis(ethane-1,2 -diamine) iron(III) chloride.

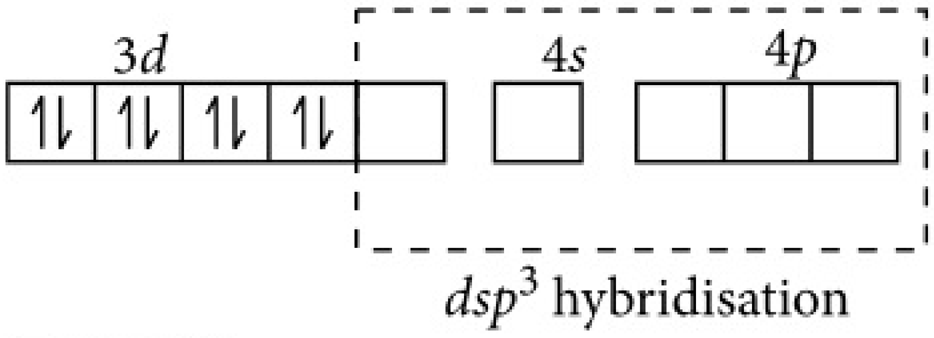
(b) **(i)** Structure of ferrocene



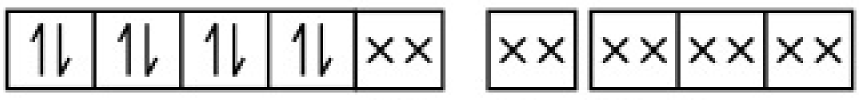
(ii) Fe (Z = 26) ground state :



In presence of strong field ligand, pairing of electrons in 3*d*-orbitals takes place.



[Fe(CO)$_5$]



Five pairs of electrons from five CO molecules

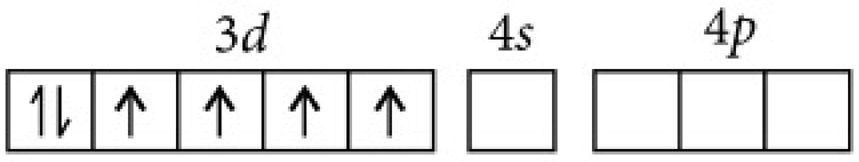
Fe atom is dsp^3 hybridised. Five pairs of electrons from five CO molecules occupy five hybrid orbitals. $Fe(CO)_5$ has trigonal bipyramidal shape. As it has no unpaired electron, so it is diamagnetic .

OR

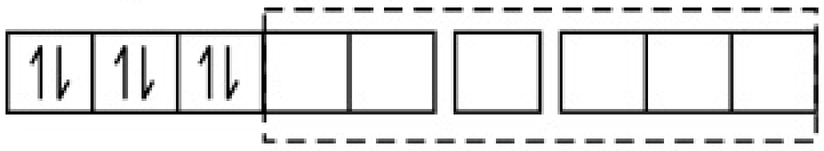
(a) **(i)** Diamminechlorido(methylamine) platinum(II) chloride.

(ii) $[Fe(CN)_6]^{4-}$ ion :

Fe^{2+} ion : $3d^64s^0$

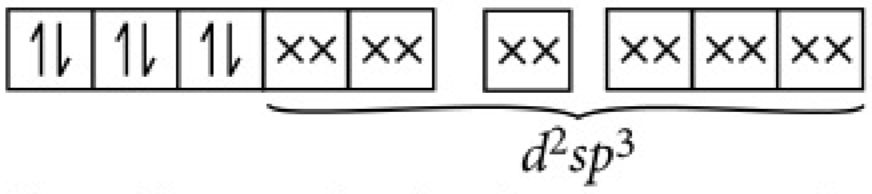


Fe^{2+} ion hybridised (under the influence of strong field ligand).



Six empty d^2sp^3 hybrid orbitals

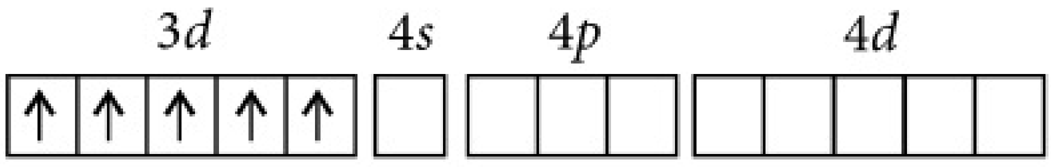
$[Fe(CN)_6]^{4-}$ ion formation :



Since the complex ion does not contain any unpaired electron, so it is diamagnetic.

(ii) $[FeF_6]^{3-}$ ion :

Fe^{3+}ion : $3d^54s^0$



Fe^{3+} ion hybridised (under the influence of weak field ligand).

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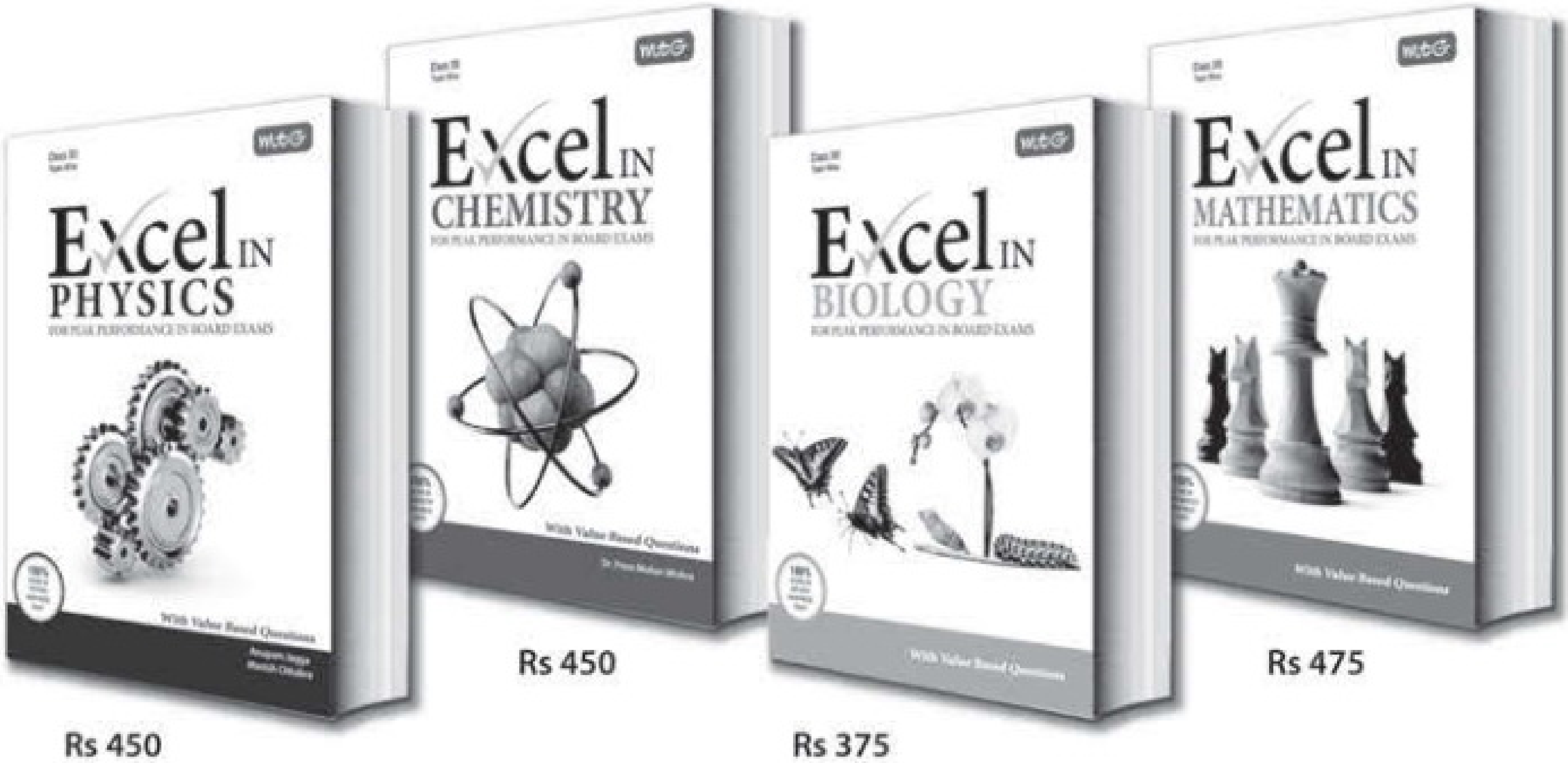

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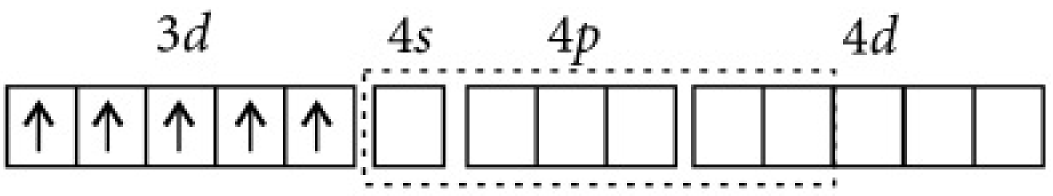
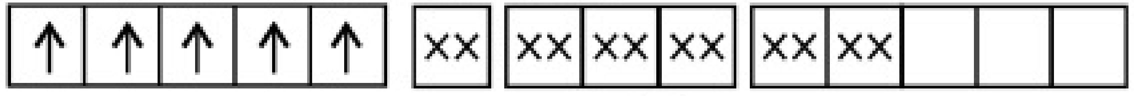


Six empty sp^3d^2 hybrid orbitals

$[FeF_6]^{3-}$ ion formation :

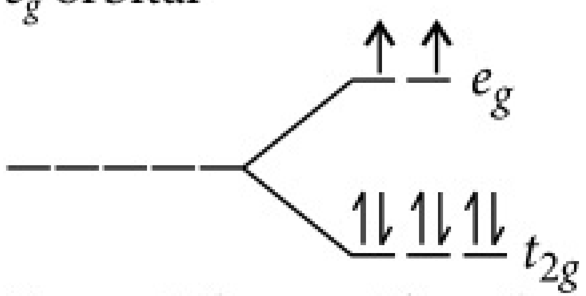


Six pairs of electrons
from six F^- ions

As the complex ion contains five unpaired electrons, it is highly paramagnetic in nature.

$$\mu_s = \sqrt{5(5+2)} = \sqrt{35} = 5.9 \text{ BM}$$

(b) **(i)** Nickel forms octahedral complexes mainly in +2 oxidation state which has d^8 configuration. In presence of strong field ligand also it has two unpaired electrons in e_g orbital

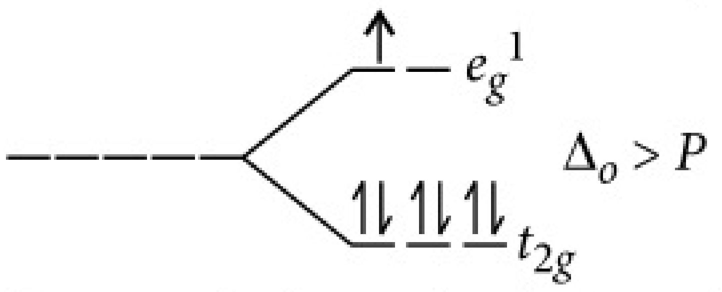


Hence it does not form low spin octahedral complexes.

(ii) The transition metals/ions have empty d-orbitals into which the electron pairs can be donated by ligands containing π electrons.

For example : $CH_2 = CH_2$, C_6H_6, and $C_5H_5^-$.

(iii) In presence of strong field ligand Co(II) has electronic configuration, $t_{2g}^6 e_g^1$.



It can easily lose only electron of e_g orbital to give stable t_{2g}^6 configuration. This is why Co^{2+} is easily oxidised to Co^{3+} in the presence of strong field ligand.

30. **(i)** **(a)** $8MnO^-_{4\,(aq)} + 3S_2O^{2-}_{3(aq)} + H_2O_{(l)} \longrightarrow 8MnO_{2(s)} + 6SO^{2-}_{4(aq)} + 2OH^-_{(aq)}$

(b) $Cr_2O^{2-}_{7\,(aq)} + 3H_2S_{(g)} + 8H^+_{(aq)} \longrightarrow 2Cr^{3+}_{(aq)} + 7H_2O_{(l)} + 3S_{(s)}$

(ii) **(a)** The actinoid contraction is similar to lanthanoid contraction. Actinoid contraction is greater than lanthanoid contraction due to more poor shielding by 5f-electrons in the actinoids than that by 4f-electrons in the lanthanoids. Shielding power of 5f-orbitals is less than that of 4f-orbitals. Hence, effective nuclear charge of actinoids is greater than that of lanthanoids.

(b) The highest number of oxidation states in the middle of the transition series is due to the presence of more number of unpaired electrons in the middle of series.

(c) Chromium has five unpaired electrons in the d-subshell. Hence, metallic bonds are very strong. In mecury, all the d-orbitals are fully filled, hence the metallic bonding is very weak.

OR

(a) **(i)** $5C_2O^{2-}_{4\,(aq)} + 2MnO^-_{4\,(aq)} + 16H^+_{(aq)} \longrightarrow 2Mn^{2+}_{(aq)} + 8H_2O_{(l)} + 10CO_{2(g)}$

(ii) $Cr_2O^{2-}_{7\,(aq)} + 6Fe^{2+}_{(aq)} + 14H^+_{(aq)} \longrightarrow 2Cr^{3+}_{(aq)} + 6Fe^{3+}_{(aq)} + 7H_2O_{(l)}$

(b) **(i)** As we move along transition metal series from left to right (*i.e.* Ti to Cu), the atomic radii decrease due to increase in nuclear charge. Hence the atomic volume decreases. At the same time, atomic mass increases. Hence the density from titanium (Ti) to copper (Cu) increases.

(ii) The metals of 4d and 5d-series have more frequent metal bonding in their compounds than the 3d-metals because 4d and 5d-orbitals are more exposed in space than the 3d orbitals. So, the valence electrons are less tightly held and form metal–metal bonding more frequently.

(iii) Actinoids show a large number of oxidation states because of small energy gap between 5f, 6d and 7s subshells.

■■

PRACTICE PROBLEMS 2015

Chemistry Olympiad

1. For a process to occur spontaneously
(a) only the entropy of the system must increase
(b) only the entropy of the surroundings must increase
(c) either the entropy of the system or that of the surroundings must increase
(d) the total entropy of the system and the surroundings must increase.

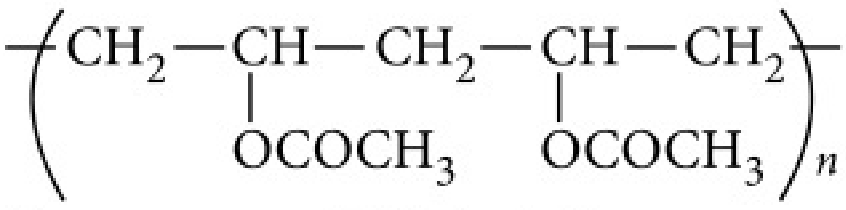
2. Among NH_3, BCl_3, Cl_2 and N_2, the compound that does not satisfy the octet rule is
(a) NH_3 (b) BCl_3
(c) Cl_2 (d) N_2

3. What amount of O_2 (in moles) contains 1.8×10^{22} molecules?
(a) 0.0030 (b) 0.030
(c) 0.30 (d) 3.0

4. In how many elements does the last electron have the quantum numbers $n = 4$ and $l = 1$?
(a) 4 (b) 6
(c) 8 (d) 10

5. For $Fe(OH)_3$, the solubility product K_{sp} is
(a) $27\ S^4$ (b) S^2
(c) $4\ S^3$ (d) $8\ S^4$

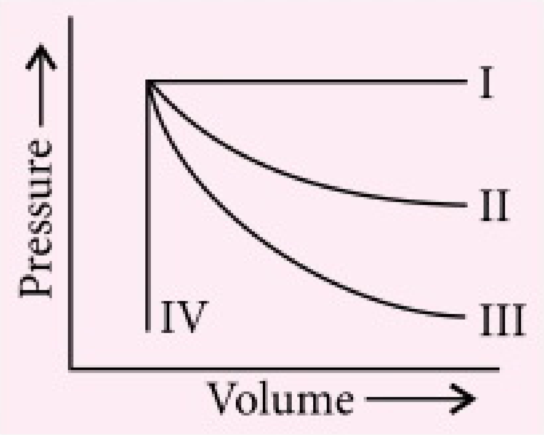
6. The following polymer is used for athletic shoe innersoles because of its resilience and durability:



$$\left(CH_2-\underset{OCOCH_3}{\underset{|}{CH}}-CH_2-\underset{OCOCH_3}{\underset{|}{CH}}-CH_2\right)_n$$

The monomer is likely to be
(a) ethylene + methyl acrylate
(b) allyl acetate
(c) vinyl acetate
(d) vinyl acrylate.

7. Look at the following plots and match entries of column I with appropriate entries of column II and choose the correct answer using the codes given below.



Column I		Column II	
(A)	Plot I	(p)	Isothermal process
(B)	Plot II	(q)	Adiabatic process
(C)	Plot III	(r)	Isochoric process
(D)	Plot IV	(s)	Isobaric process

(a) A-p, B-q, C-r, D-s (b) A-r, B-p, C-q, D-s
(c) A-s, B-p, C-q, D-r (d) A-s, B-q, C-p, D-r

8. The number of sigma(σ) and pi(π) bonds present in 1,3,5,7-octatetraene respectively are
(a) 14 and 3 (b) 17 and 4
(c) 16 and 5 (d) 15 and 4

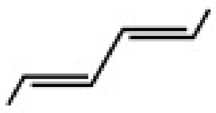
9. Iodoform can be prepared from all except
(a) isopropyl alcohol
(b) 3-methyl-2-butanone
(c) isobutyl alcohol
(d) ethyl methyl ketone.

10. A colourless crystalline solid '*B*' dissolved easily in water. On addition of dilute HCl to the aqueous solution of '*B*', no change was observed. When NaOH was added to the aqueous solution of '*B*', a white ppt. was obtained that dissolved in excess, giving a colourless solution. '*B*' is

(a) $MgSO_4$ (b) $Pb(NO_3)_2$
(c) $AgNO_3$ (d) $ZnSO_4$

11. The hybridization, oxidation number of central metal ion and shape of Wilkinson's catalyst are

(a) dsp^2, +1, square planar
(b) sp^3, +1, tetrahedral
(c) sp^3d, +2, trigonal bipyramidal
(d) d^2sp^3, +6, octahedral.

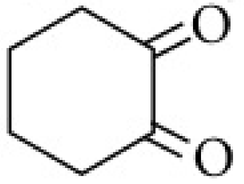
12. The name of the compound  is

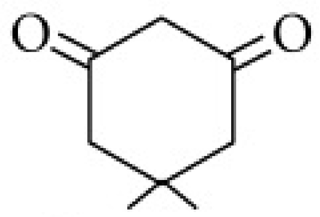
(a) (2*Z*, 4*Z*)-2,4-hexadiene
(b) (2*Z*, 4*E*)-2,4-hexadiene
(c) (2*E*, 4*Z*)-2,4-hexadiene
(d) (2*E*, 4*E*)-2,4-hexadiene.

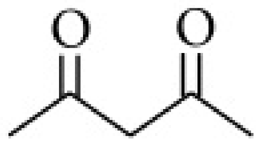
13. A solid has a *bcc* structure. If the distance of closest approach between the two atoms is 1.73 Å the edge length of the cell is

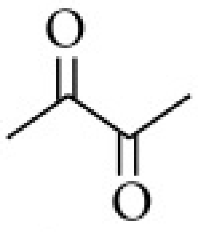
(a) 199 pm (b) $\sqrt{3/2}$ pm
(c) 142.2 pm (d) $\sqrt{2}$ pm

14. Which of the following compounds will have least percentage of enol content?

(a) 

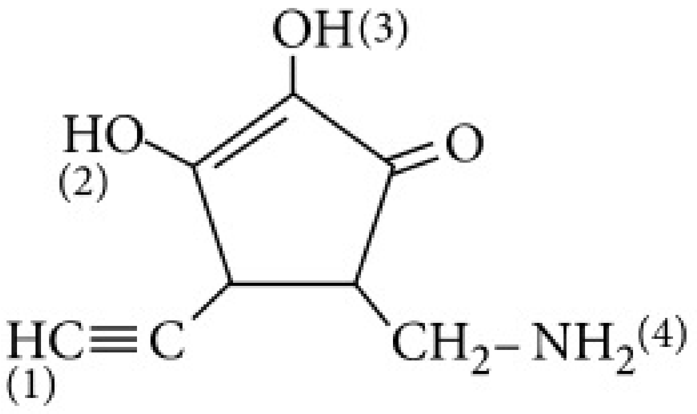
(b) 

(c) 

(d) 

15. The IUPAC name of  is

(a) 4-hydroxy-2-pentanone
(b) 2-hydroxy-4-pentanone
(c) 2-oxo-4-pentanol
(d) 4-keto-2-pentanol.

16. 

Arrange the hydrogens in the decreasing order of acidity.

(a) 1 > 2 > 3 > 4 (b) 4 > 3 > 2 > 1
(c) 2 > 3 > 1 > 4 (d) 2 > 3 > 4 > 1

17. The acid produced (*A*) in the sequence given below is

$$C_2H_5I \xrightarrow[\text{KOH}]{\text{alc.}} X \xrightarrow[CCl_4]{Br_2} Y \xrightarrow{\text{KCN}} Z \xrightarrow{H_3O^+} A$$

(a) succinic acid (b) malonic acid
(c) oxalic acid (d) maleic acid.

18. A positive carbylamine test is given by

1. *N*, *N*-dimethylaniline
2. 2,4-dimethylaniline
3. *N*-methyl-*o*-methylaniline
4. *p*-methylbenzylamine

(a) 2, 4 (b) 2, 3
(c) 1, 2, 4 (d) 2, 3, 4

19. Which of the following compounds is isomeric with 2,2,4,4-tetramethylhexane?

(a) 3-Ethyl-2,2-dimethylpentane
(b) 4-Isopropylheptane
(c) 4-Ethyl-3-methyl-4-(*n*-propyloctane)
(d) 4,4-Diethyl-3-methylheptane

20. Initial rate data at 25°C are listed in the table for the reaction :

$$NH_4^+ + NO_2^- \longrightarrow N_2 + 2H_2O$$

Exp. no.	Initial $[NH_4^+]$	Initial $[NO_2^-]$	Initial rate of consumption
1	0.24	0.10	7.2×10^{-6}
2	0.12	0.10	3.6×10^{-6}
3	0.12	0.15	5.4×10^{-6}

The rate law for the reaction will be

(a) $k[NH_4^+]$ (b) $k[NH_4^+][NO_2^-]$
(c) $k[NH_4^+]^2$ (d) $k[NH_4^+][NO_2^-]^{-1}$

21. Which of the following hormones contains iodine?

(a) Testosterone (b) Adrenaline
(c) Thyroxine (d) Insulin

22. For the reaction,

$$2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$$

the degree of dissociation (α) of $HI_{(g)}$ is related to equilibrium constant K_p by the expression

(a) $\dfrac{1+2\sqrt{K_p}}{2}$ (b) $\sqrt{\dfrac{1+2K_p}{2}}$

(c) $\sqrt{\dfrac{2K_p}{2+2K_p}}$ (d) $\dfrac{2\sqrt{K_p}}{1+2\sqrt{K_p}}$

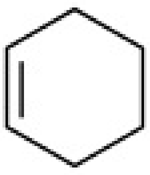
23. Lowering of vapour pressure, Δp; elevation in boiling point, ΔT_b; and depression in freezing point, ΔT_f of a solvent for the same molar concentration of each of the three solutes: (A) sugar, (B) NaCl, and (C) $BaCl_2$ follow the sequence

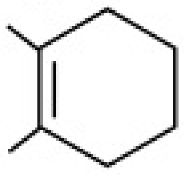
(a) $\Delta p : A < B < C$
(b) $\Delta T_b : C > B > A$
(c) $\Delta T_f : A < B < C$
(d) All of these.

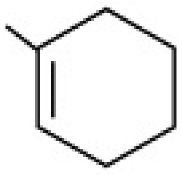
24. The rate of a gaseous reaction, $A + B \rightarrow C + D$ is equal to $k[A][B]$. The volume of the reaction vessel containing these gases is suddenly reduced to one-fourth of the initial volume. The rate of the reaction would be

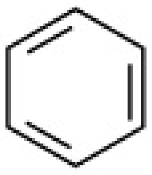
(a) 1/16
(b) 16
(c) 1/8
(d) 8

25. Decreasing order of C$=$C bond length amongst the following is


(1)


(2)


(3)

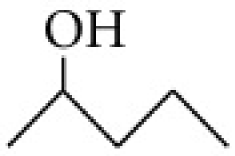

(4)

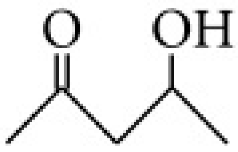
(a) $4 > 3 > 1 > 2$
(b) $2 > 3 > 1 > 4$
(c) $2 > 3 > 4 > 1$
(d) $4 > 2 > 3 > 1$

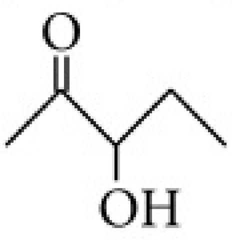
26. Which one of the following is the correct statement?

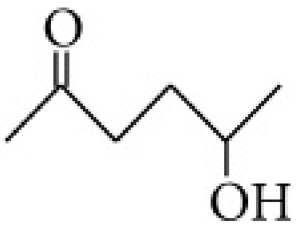
(a) HCO_3^- is the conjugate base of CO_3^{2-}.
(b) NH_2^- is the conjugate acid of NH_3.
(c) H_2SO_4 is the conjugate acid of HSO_4^-.
(d) NH_3 is the conjugate base of NH_2^-.

27. Which one of the following will most readily be dehydrated in acidic solutions?

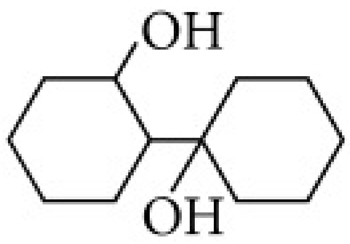
(a)


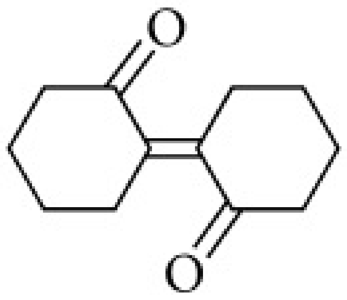
(b)


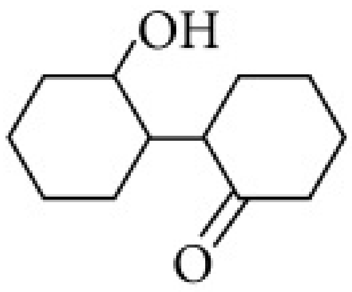
(c)


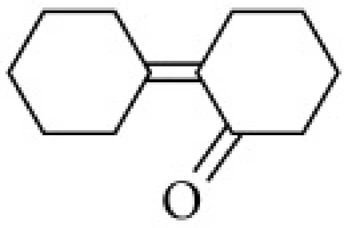
(d)


28. Cyclohexanone on heating with conc. NaOH gives

(a)


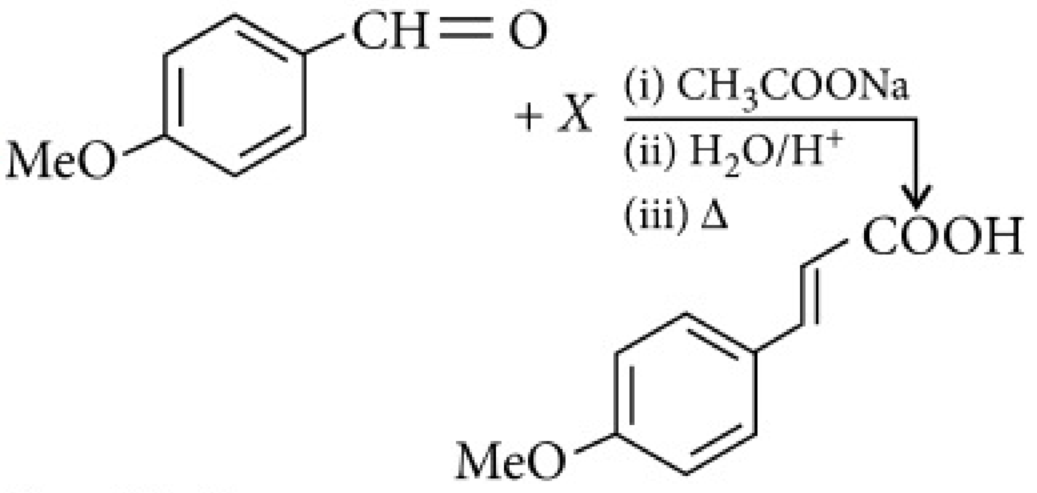
(b)


(c)


(d)


29. A 3 L solution contains 0.06 moles each of $[Co(H_2O)_5SO_4]Br$ and $[Co(H_2O)_5Br]SO_4$. Excess of $AgNO_3$ was added to 1 L of the above solution. 1 L of the remaining solution was reacted with $BaCl_2$ solution. The ratio of the number of moles of the precipitate was

(a) 1 : 1
(b) 1 : 2
(c) 2 : 1
(d) 1 : 3

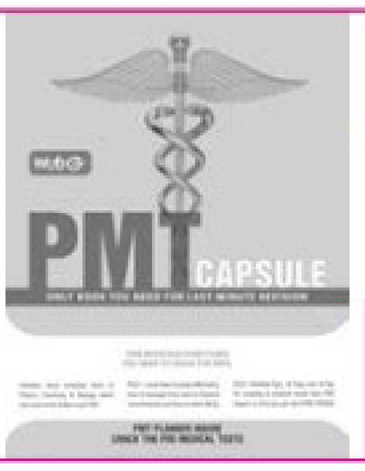
30.


Identify X.

(a) CH_3COOH
(b) $BrCH_2COOH$
(c) $OHC - COOH$
(d) $(CH_3CO)_2O$

ANSWER KEY

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



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Use the vast expertise of our mtg team to get to the bottom of the question. From the serious to the silly, the controversial to the trivial, the team will tackle the questions, easy and tough.

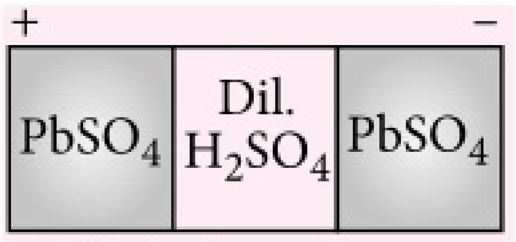
The best questions and their solutions will be printed in this column each month.

Q1. Why do we add water to lead storage battery when the water released during discharging is used up in charging?

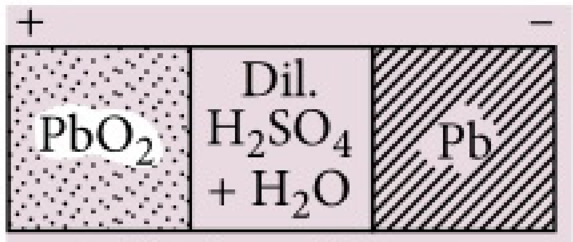
– Navdeep Kumar, Amritsar, Punjab

Ans. The main active materials in lead acid storage battery are :

1. Lead peroxide, $PbO_2 \Rightarrow$ +ve plate, dark brown, hard and brittle substance.
2. Sponge lead, $Pb \Rightarrow$ –ve plate.
3. Dil. $H_2SO_4 \Rightarrow$ Ratio of water : acid = 3 : 1



Fully discharged battery



Fully charged battery

During the discharge operation, acid is consumed and water is produced while during the charge operation, water is consumed and acid is produced. Thus, the reaction occuring in lead storage battery is

$$Pb_{(s)} + PbO_{2(s)} + 2H_2SO_{4(aq)} \underset{\text{Charging}}{\overset{\text{Discharging}}{\rightleftharpoons}} 2PbSO_{4(s)} + 2H_2O_{(l)}$$

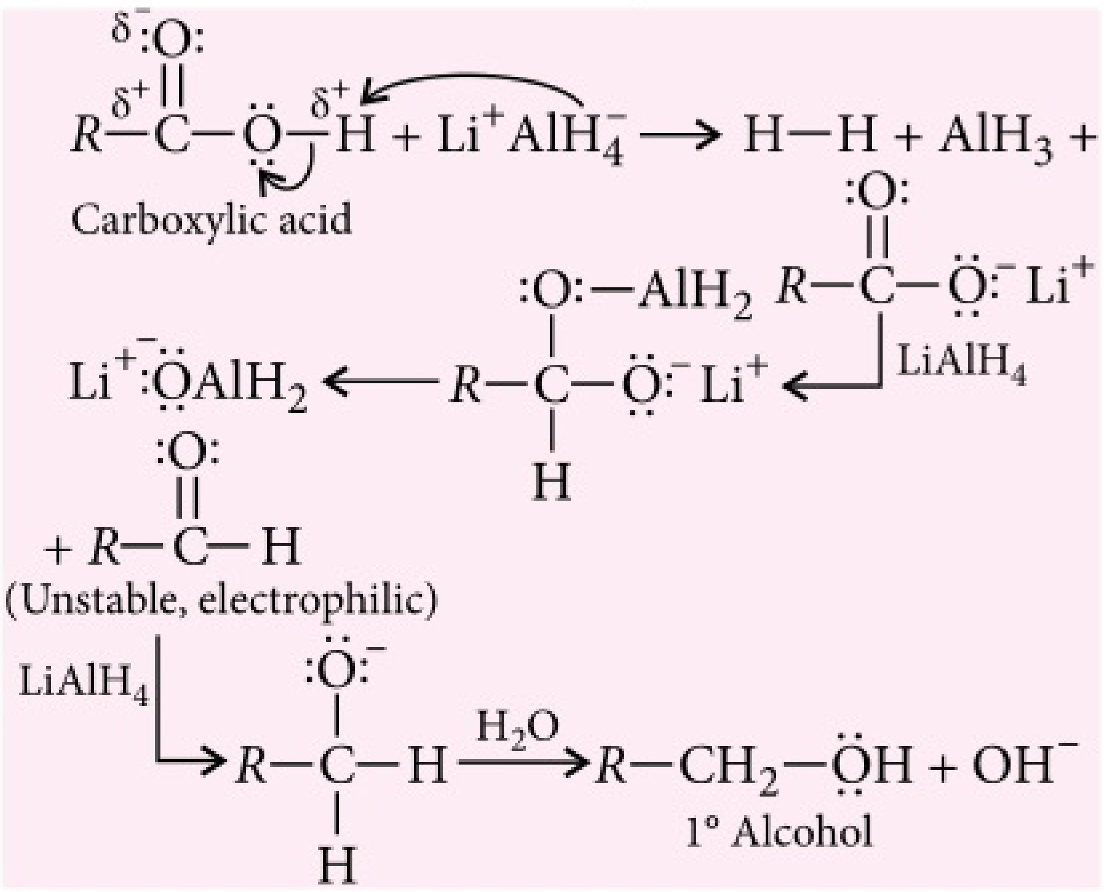
The sulphuric acid, which acts as an electrolyte in the battery is a heavy, oily liquid that does not evaporate. It is only the water in the electrolyte which evaporates. Therefore, when the level of the electrolyte falls, only water should be added to bring the electrolyte to the correct height.

- If there is too much acid in the electrolyte (*i.e.*, under-watering), the plates may be over-discharged, which produces over sulphation.
- If there is too much water in the electrolyte (*i.e.*, over-watering), it results in additional dilution of the electrolyte, resulting in reduced battery performance. Add water to the battery after it has been fully charged, never when the battery is partially discharged.

Q2. Why $NaBH_4$ does not reduce carboxylic acid while $LiAlH_4$ does?

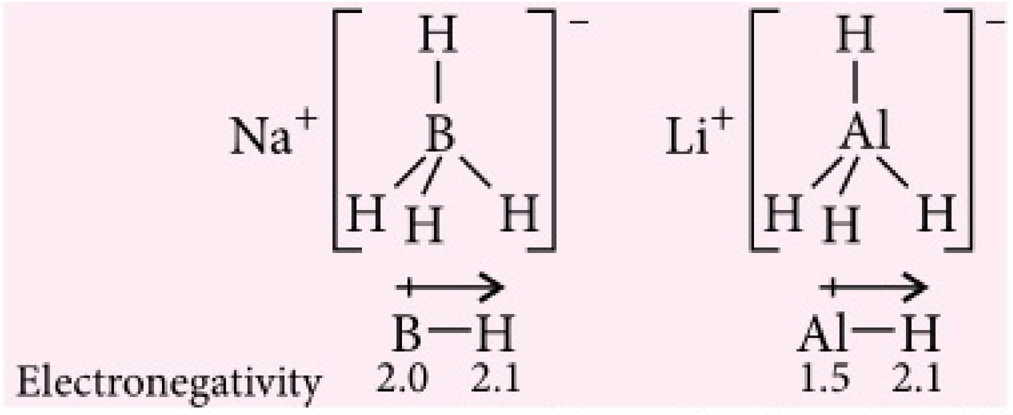
– Shruti Jha

Ans. Reduction with $LiAlH_4$



The two main factors, which affect the reactivity are:

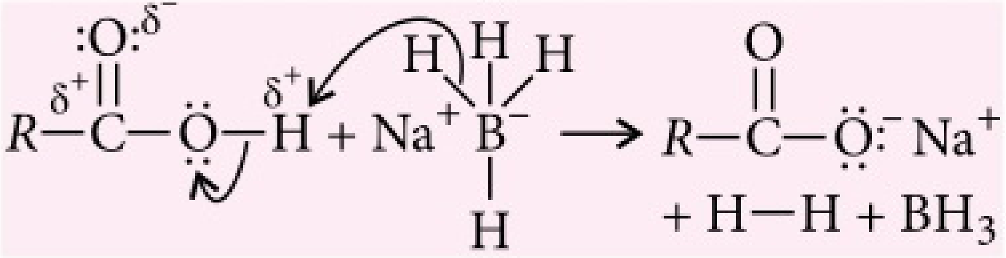
1. Electronegativity : Structures of metal hydride reagents (equivalent to hydride ion, H:⁻) are:



B is more electronegative than Al, thus it will be less likely to share or give up electrons to H to form $H:^-$ ion. So if the hydride is bound to boron, it is less likely to be released for organic transformation when compared to Al.

2. The cation : The lithium is better able to act as a Lewis acid (e^- pair acceptor) than the sodium, the Lewis acid bonds to the carboxyl oxgen. This in turn increases the +ve charge density on the carbonyl carbon thus, favours the reduction more with $LiAlH_4$ than $NaBH_4$.

Reaction with $NaBH_4$



The carbonyl carbon of a carboxylic acid is even more electrophilic than carbonyl carbon of an aldehyde or ketone. However, there is also an acid proton from the carboxylic acid that can react with hydride reagent. For this reason, sodium borohydride does not reduce a carboxylic acid.

ADVANCED CHEMISTRY BLOC

(ELECTROCHEMISTRY)

Mukul C. Ray, Odisha

Cell Potential and EMF of a Cell

The galvanic cell consists of two half-cells. The electrode at higher reduction potential has higher tendency to gain electrons and *vice-versa*. As a result of this potential difference, the electrons flow from the electrode of lower reduction potential (anode) to the electrode of higher reduction potential (cathode).

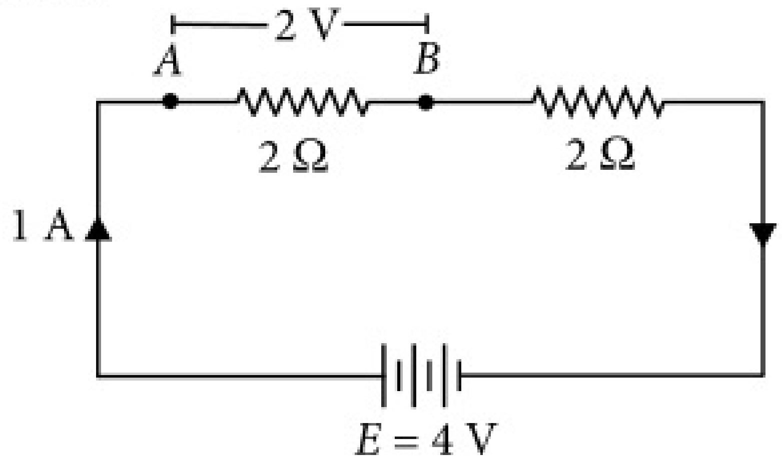
Differences between emf and cell potential or potential difference

EMF	Cell Potential
It is the potential difference between the two electrodes when no current is drawn from the cell.	It is the difference of the electrode potentials of the two electrodes when the cell is sending current through the circuit.
It is the maximum voltage obtainable from the cell.	It is less than the emf of the cell.
The work obtained from the emf is maximum.	The work calculated from the potential difference is less than the maximum work obtainable from the cell.

Potential Difference and EMF

There is a distinction between emf and potential difference. The emf of a device, say, a battery, is a measure of the energy the battery gives to each coulomb of charge. Thus if a battery supplies 4 joules of energy per coulomb of charge then it has an emf of 4 volts. The energy given to each coulomb of charge in a battery is due to chemical reaction.

The potential difference between the two points, say *A* and *B* in the given diagram is a measure of the energy used by one coulomb of charge in moving from *A* to *B*.



Here the battery has an emf of 4 volts, it means battery supplies 4 joules of energy to each coulomb of charge continuously. As each coulomb of charge moves through the circuit starting from positive terminal, it gives off most of its energy to the resistance and rest to the wire. When it returns to the negative terminal it has lost all its energy originally supplied by the battery. Now the battery supplies 4 joules of energy to each coulomb to start a fresh journey. The potential difference between two points *A* and *B* is 2 V which means each coulomb of charge will give up energy of 2 joules while moving from *A* to *B*. This energy will be released as heat.

Overvoltage and Discharge Potential

There is difference between the electrolytic cell and electrochemical or galvanic cell. During electrolysis, it is expected that the decomposition potential of any solution is approximately equal to the reversible emf of the galvanic cell consisting of the products liberated at the electrodes in contact with the same solution. For example, if an attempt is made to electrolyse water, the products expected are hydrogen and oxygen. Construct a galvanic cell consisting of hydrogen and oxygen as electrode components and then calculate the theoretical cell potential. The theoretical decomposition voltage for the electrolysis of water is 1.23 V as shown by the calculation for the cell represented as

$Pt_{(s)}|H_{2(g)}|H_2O_{(l)}|O_{2(g)}|Pt_{(s)}$

Reaction at Left Hand Electrode:

$$H_2 \rightarrow 2H^+ + 2e^-$$

$$E_{\text{LHS}} = E^\circ_{\text{LHS}} - \frac{0.059}{2}\log[H^+]^2$$

Reaction at Right Hand Electrode:

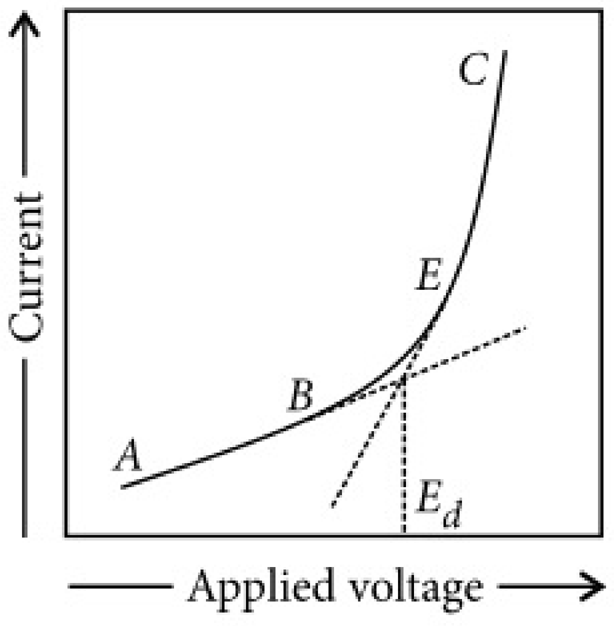
$$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-$$

$$E_{\text{RHS}} = E^\circ_{\text{RHS}} - \frac{0.059}{2}\log[OH^-]^2$$

E°_{RHS} and E°_{LHS} are respectively 0.00 V and 0.401 V. Knowing the ionic product of water as 1×10^{-14}, we can derive E_{cell} as follows:

$$E_{\text{cell}} = E_{\text{RHS}} + E_{\text{LHS}} = 0.401 - 0.059\log 10^{-14}$$
$$= 1.227 \text{ V at } 25°\text{C}$$

However, continuous electrolysis of water acidified with sulphuric acid using smooth platinum electrodes takes place only when the applied emf exceeds 1.7 V, not at 1.227 V as calculated from theory. The difference between the applied potential for continuous electrolysis and the theoretical decomposition potential is called **overvoltage**.



From the graph it can be seen between points *B* and *C* continuous electrolysis has started. This is called as **discharge potential**.

Discharge or decomposition potential at any electrode is the potential at which continuous decomposition or discharge of ions commences at the electrodes. For most of the metals the discharge potential values are almost equal to their reversible electrode potentials but in case of gases like hydrogen and oxygen discharge potentials are appreciably higher than their reversible electrode potentials. The excess voltage is believed to be the overvoltage of the gas. For example, overvoltage of smooth oxygen release over platinum surface is 1.7 – 1.227 = 0.473 V.

Reason for Overvoltage

Of the many steps involved in gas evolution atleast one is rather a slow process and requires extra energy. This extra energy is to be supplied by the applied voltage and is linked to overvoltage.

Another alternative explanation is when electrolysis is carried out the products of electrolysis accumulate at the electrodes and convert even inert electrodes into active electrodes, which can exercise a back emf. For example, in the electrolysis of water using platinum electrodes oxygen and hydrogen are released at the electrodes. The electrolytic cell now consists of one hydrogen electrode and one oxygen electrode, which can be written as

$$Pt|H_{2(g)}|H_2O_{(l)}|O_{2(g)}|Pt$$

This electrochemical cell developed inside the electrolytic cell produces an emf called **back emf** that opposes the applied emf. The cell is said to be polarized and the applied emf must exceed the back emf for continuous electrolysis to take place.

It can be concluded that the decomposition of the electrolyte begins when the applied voltage reaches the reversible emf of the cell but the continuous electrolysis occurs only when the applied emf exceeds the back emf or overvoltage is applied.

The following factors influence the overvoltage:

- Electrode surface
- Nature of the electrolyte
- Nature of the substance to be discharged
- Current density
- Temperature

Illustration of Overvoltage

The electrode potential of Zn^{2+}/Zn is – 0.76 V and that of H^+/H_2 is 0.00 V. This means zinc cannot be electrodeposited from aqueous solution of $ZnSO_4$. Contrary to the expectation, zinc is electrodeposited from acidic solution. Consider 1 M solution of zinc sulphate at pH = 4. Under this condition the reversible reduction potential of hydrogen is – 0.23 V (as the pH has changed it is no more 0.00V). Then comes the overvoltage; for zinc overvoltage is almost nil. So its reversible potential – 0.76 V becomes the discharge potential. For hydrogen on the surface of zinc the overvoltage is 0.7 V and the discharge potential of hydrogen becomes $-0.23 - 0.70 = -0.93$ V. Since this value is more negative than that of zinc, it is zinc that is deposited first.

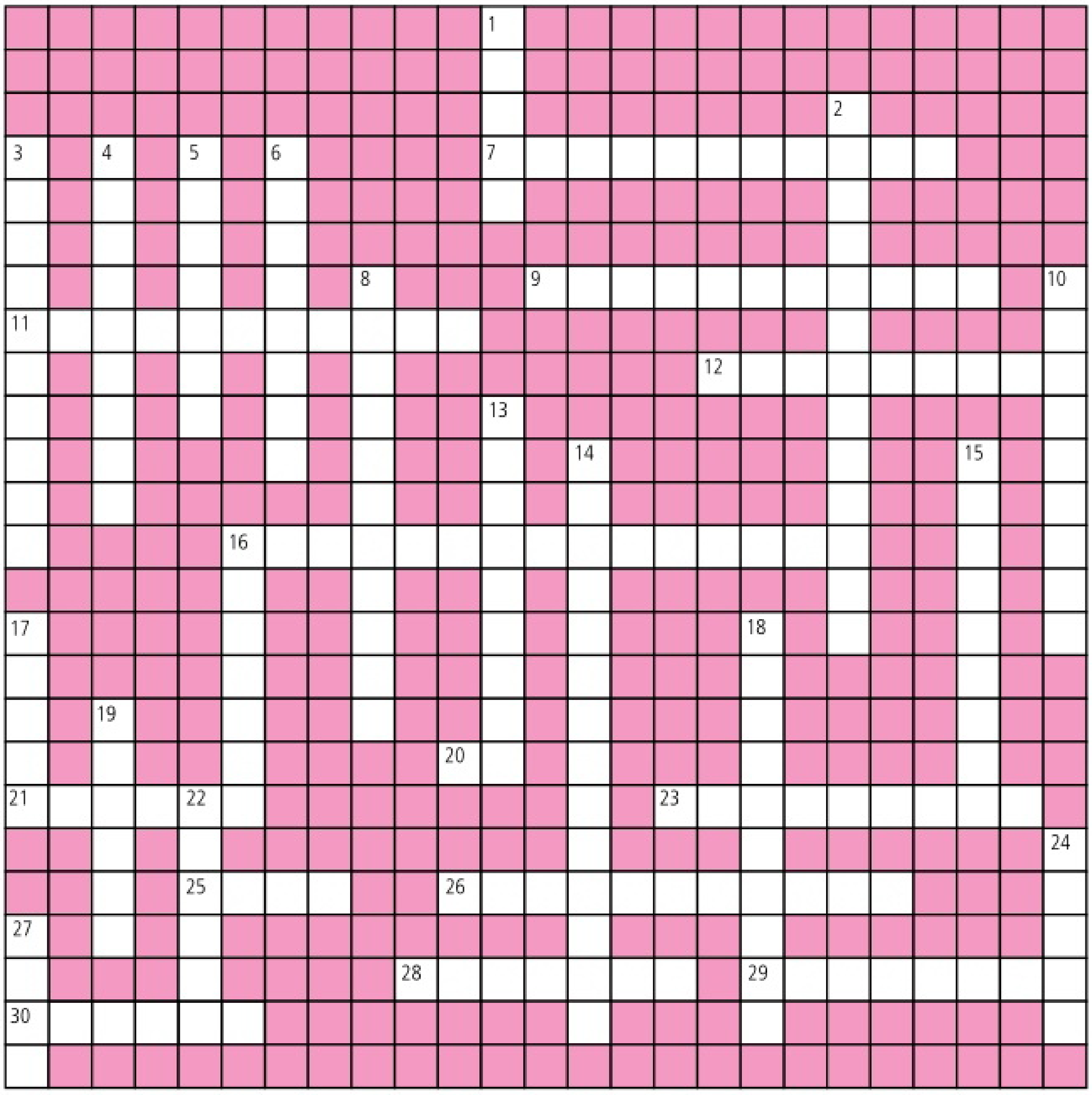
Batteries

The Nickel-Cadmium (NiCd) batteries have an interesting "**memory effect**". Frequent partial battery discharge followed by a full recharge causes this problem. The "NiCd" over such cycles 'learns' that only portion of its capacity is used. This renders the battery unable to deliver a full discharge time when needed. The cause of this effect is unknown. This is a temporary effect that can usually be cleared by forcing the battery to full charge/discharge cycles. Lithium ion batteries are the most popular ones in mobile, laptops. One advantage of lithium ion battery is their low self-discharge rate of only 5 per cent as compared to 20 per cent per month for NiCd. The low self-discharge rate however, does not make Li ion batteries more durable because they lose their charge retention capacity over time. These lithium ion batteries irreversibly lose 20 per cent of their capacity per year from the time when they are manufactured even when unused. This means Li ion batteries degrade over time whether it is left alone in the shelf or recharged 1000 times. For obvious reason, this drawback is never publicized.

■■

CROSSWORD

Readers can send their answer to win exciting prizes. Winners' name with their valuable feedback will be published in next issue.



ACROSS

7. Law proposed by Guldberg and Waage is applied to a reversible reaction in (11)

9. Change from a solid to a gas. (11)

11. Ion containing atoms of hydrogen, carbon and oxygen. (11)

12. Not crystalline. (9)

16. Meadowsweet. (15)

20. Chloride of this element forms dimer [symbol]. (2)

21. Its atomic number is 47. (6)

23. Holme's signals. (9)

25. Water, unsuitable for washing. (4)

26. Elements 58 to 71. (11)

28. Change in the no. of neutrons does not change the element. (7)

29. The effect of raising temperature on reaction rate. (8)

30. Gas required for combustion. (6)

DOWN

1. A volumetric glassware. (5)

2. Not mirror images of each other. (13)

3. Toluene was first obtained by dry distillation of (10)

4. Process when copper sulphide is converted to copper metal. (9)

5. Equivalent to 4.18 J. (7)

6. Acid in soft drinks. (8)

8. Electrochemical method for the protection of corrosion. (11)

10. Arrow (↔) represents (9)

13. Nobel's oil / powder (9)

14. Transformation of ethene to polythene. (14)

15. Reaction intermediate formed in Aldol condensation. (9)

16. Element present in garlic and hair. (7)

17. Alloy of copper and zinc. (5)

18. Linkage between C-1 of galactose and C-4 of glucose. (10)

19. Great in balloons! (6)

22. Hydrocarbon used in gas stoves. (6)

24. No. of hydrogen bonds between guanine and cytosine. (5)

27. A black material formed in a smoky yellow flame. (4)

■■

EXAMINER'S MIND NCERT 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.

ALCOHOLS, PHENOLS AND ETHERS | ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

SECTION - I

Only One Option Correct Type

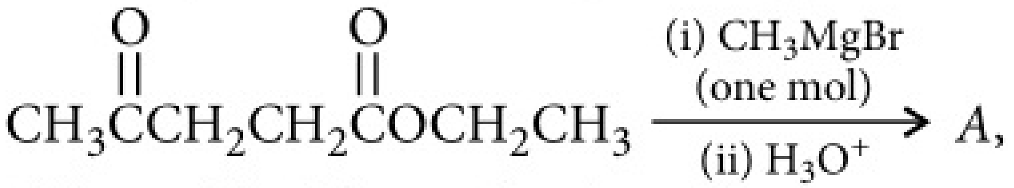
This section contains 20 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

1. In the reaction, $R\text{—}OH + HX \rightarrow RX + H_2O$ the reactivity of alcohols is in the order
(a) tertiary > secondary > primary
(b) tertiary < secondary < primary
(c) tertiary > primary > secondary
(d) secondary > primary > tertiary.

2. The main product formed when benzaldehyde is treated with one mole of acetone in the presence of aqueous alkali is
(a) $C_6H_5CH{=}CHCHO$
(b) $(CH_3)_2C{=}CHCOCH_3$
(c) $C_6H_5CH{=}CHCOCH_3$
(d) $C_6H_5CH(OH)CH_2CHO$

3. $CH_3OC_2H_5$ and $(CH_3)_3C\text{—}OCH_3$ are treated with hydroiodic acid separately. The fragments after reactions obtained are respectively
(a) $CH_3I + C_2H_5OH; (CH_3)_3CI + CH_3OH$
(b) $CH_3OH + C_2H_5I; (CH_3)_3CI + CH_3OH$
(c) $CH_3OH + C_2H_5I; (CH_3)_3COH + CH_3I$
(d) $CH_3I + C_2H_5OH; CH_3I + (CH_3)_3COH$

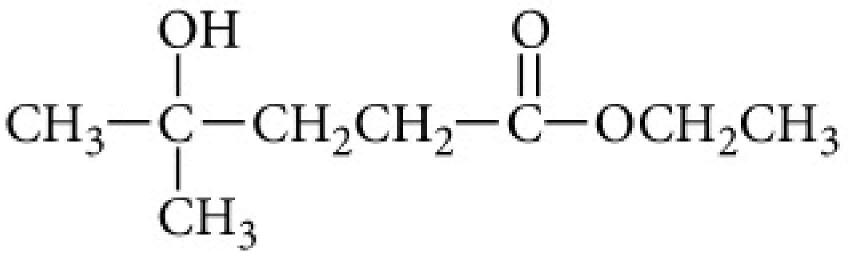
4.



$$CH_3\overset{O}{\overset{\|}{C}}CH_2CH_2\overset{O}{\overset{\|}{C}}OCH_2CH_3 \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } CH_3MgBr \text{ (one mol)}} A,$$

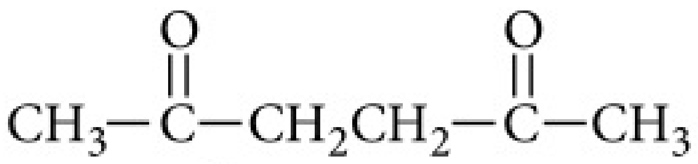
A formed in this reaction is

(a)



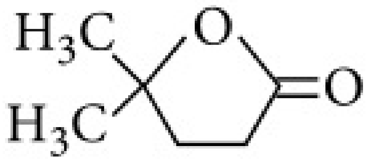
$$CH_3-\underset{CH_3}{\overset{OH}{\overset{|}{C}}}-CH_2CH_2-\overset{O}{\overset{\|}{C}}-OCH_2CH_3$$

(b)

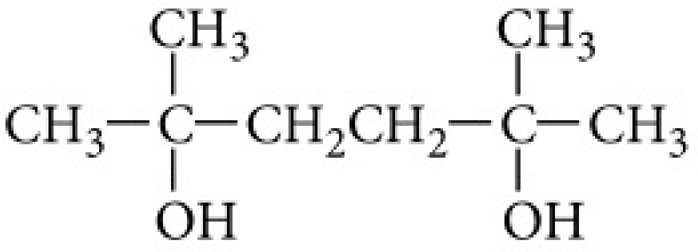


$$CH_3-\overset{O}{\overset{\|}{C}}-CH_2CH_2-\overset{O}{\overset{\|}{C}}-CH_3$$

(c)



(d)



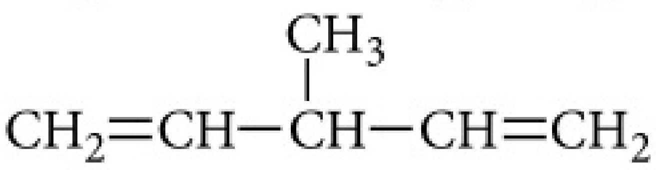
$$CH_3-\underset{OH}{\overset{CH_3}{C}}-CH_2CH_2-\underset{OH}{\overset{CH_3}{C}}-CH_3$$

5. Consider the acidity of the carboxylic acids :
(i) PhCOOH
(ii) $o\text{-}NO_2C_6H_4COOH$
(iii) $p\text{-}NO_2C_6H_4COOH$
(iv) $m\text{-}NO_2C_6H_4COOH$
Which of the following order is correct?
(a) i > ii > iii > iv
(b) ii > iv > iii > i
(c) ii > iv > i > iii
(d) ii > iii > iv > i

6. In the reaction :
Phenol $\xrightarrow[CHCl_3]{NaOH} A \xrightarrow{H^+} B$
B is identified as
(a) benzaldehyde
(b) benzene
(c) benzoic acid
(d) salicylaldehyde.

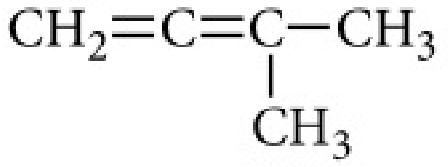
7. An alkene gives two moles of HCHO, one mole of CO_2 and one mole of CH_3COCHO on ozonolysis. What is its structure?
(a) $CH_2{=}C{=}CH{-}CH_2{-}CH_3$

(b)



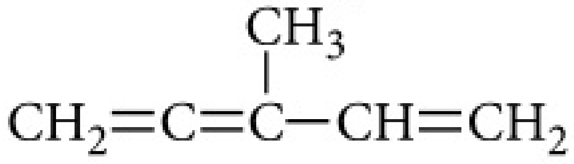
$$CH_2{=}CH{-}\overset{CH_3}{\overset{|}{C}H}{-}CH{=}CH_2$$

(c)



$$CH_2{=}C{=}\underset{CH_3}{\underset{|}{C}}{-}CH_3$$

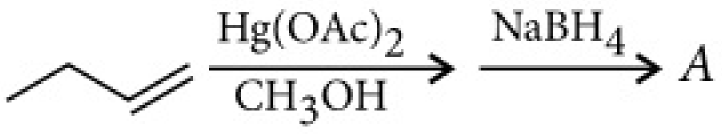
(d)



$$CH_2{=}C{=}\overset{CH_3}{\overset{|}{C}}{-}CH{=}CH_2$$

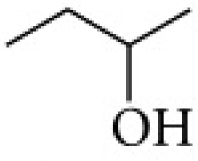
8. The correct order of increasing acidic strength is
(a) phenol < ethanol < chloroacetic acid < acetic acid
(b) ethanol < phenol < chloroacetic acid < acetic acid
(c) ethanol < phenol < acetic acid < chloroacetic acid
(d) chloroacetic acid < acetic acid < phenol < ethanol.

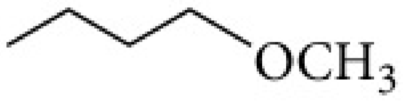
9. In the following reaction sequence,

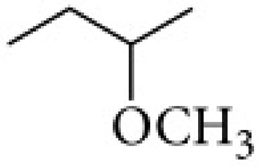


A is

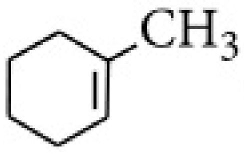
(a) 

(b) 

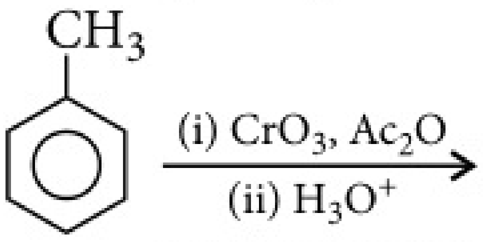
(c) 

(d) 

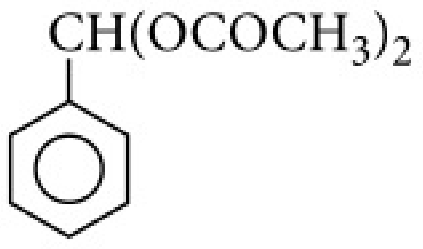
10. To prepare *tert*-butyl ethyl ether by Williamson's synthesis, the reactants needed are
(a) sodium ethoxide and sodium *tert*-butoxide
(b) sodium ethoxide and *tert*-butyl bromide
(c) sodium *tert*-butoxide and ethyl bromide
(d) ethyl alcohol and *tert*-butyl alcohol.

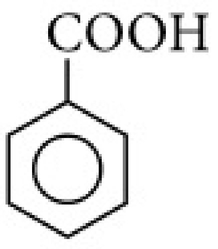
11. 

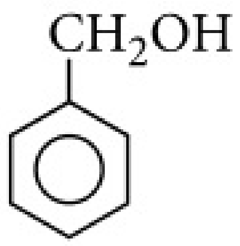
on reductive ozonolysis yields
(a) 6-oxoheptanal (b) 6-oxoheptanoic acid
(c) 6-hydroxyheptanal
(d) 3-hydroxypentanal.

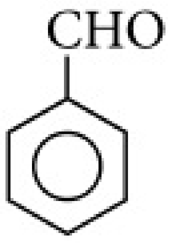
12. 

P; Product *P* is

(a) 

(b) 

(c) 

(d) 

13. Decreasing order of reactivity in Williamson's synthesis of the following :
I. Me_3CCH_2Br II. $CH_3CH_2CH_2Br$
III. $CH_2{=}CHCH_2Cl$ IV. $CH_3CH_2CH_2Cl$
(a) III > II > IV > I (b) I > II > IV > III
(c) II > III > IV > I (d) I > III > II > IV

14. The ozonolysis of C_7H_{14} gave 2-methyl-3-pentanone. The alkene is
(a) 2-ethyl-3-methylbut-1-ene
(b) 3-ethyl-2-methylbut-3-ene
(c) 2, 5-dimethyl-3, 4-dimethylhex-3-ene
(d) 3-ethyl-2-methylbut-1-ene.

15. The compound which does not react with Lucas reagent is
(a) *n*-butyl alcohol (b) *sec*-butyl alcohol
(c) *tert*-butyl alcohol (d) both (a) and (b).

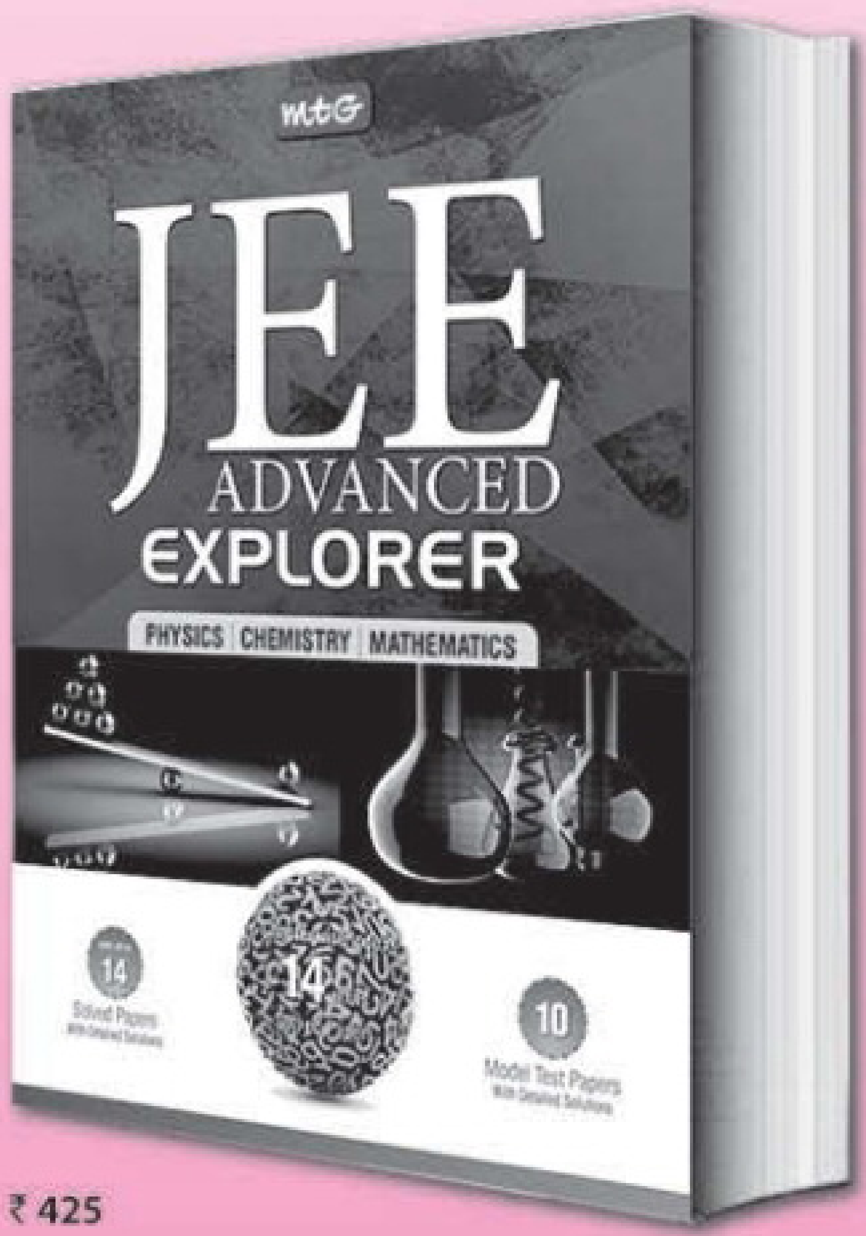
16. Benzoic acid gives benzene on being heated with *X* and phenol gives benzene on being heated with *Y*. *X* and *Y* are respectively
(a) soda-lime and copper
(b) Zn dust and NaOH
(c) Zn dust and soda lime
(d) soda lime and zinc dust.

17. Arrange the following compounds in increasing order of boiling point :
Propan-1-ol, butan-1-ol, butan-2-ol, pentan-1-ol
(a) Propan-1-ol, butan-2-ol, butan-1-ol, pentan-1-ol
(b) Propan-1-ol, butan-1-ol, butan-2-ol, pentan-1-ol
(c) Pentan-1-ol, butan-2-ol, butan-1-ol, propan-1-ol
(d) Pentan-1-ol, butan-1-ol, butan-2-ol, propan-1-ol.

18. The strongest acid amongst the following is
(a) CH_3COOH (b) F_3CCOOH
(c) Cl_3CCOOH (d) Br_3CCOOH

19. The reagent which can be used to distinguish acetophenone from benzophenone is
(a) 2,4-dinitrophenylhydrazine
(b) aqueous solution of $NaHSO_3$
(c) benedict's reagent
(d) I_2 and Na_2CO_3.

20. 1-Propanol and 2-propanol can be distinguished by
(a) oxidation with alkaline $KMnO_4$ followed by reaction with Fehling's solution
(b) oxidation with acidic dichromate followed by reaction with Fehling's solution
(c) oxidation by heating with copper followed by reaction with Fehling's solution
(d) oxidation with concentrated H_2SO_4 followed by reaction with Fehling's solution.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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. Formic acid and acetic acid can be distinguished by the action of

(a) conc. H_2SO_4

(b) Tollens' reagent

(c) Fehling's solution

(d) sodium salt on heating.

22. Ethyl bromide can be converted into diethyl ether by

(a) reacting with sodium ethoxide

(b) heating with moist silver oxide

(c) heating with dry silver oxide

(d) treating with ethyl magnesium bromide.

23. Under Wolff-Kishner reduction conditions, the conversion(s) which may be brought about is (are)

(a) benzophenone into diphenylmethane

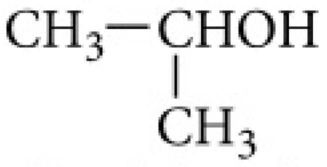
(b) benzaldehyde into benzyl alcohol

(c) cyclohexanone into cyclohexane

(d) cyclohexanone into cyclohexanol.

24. Following compounds are given :

(i) CH_3CH_2OH (ii) CH_3COCH_3

(iii) 
$CH_3-\underset{\substack{|\\CH_3}}{CHOH}$ (iv) CH_3OH

Which of the above compound(s), on being warmed with iodine solution and NaOH, will give iodoform?

(a) (i), (iii) and (iv)

(b) Only (ii)

(c) (i), (ii) and (iii)

(d) (i) and (ii)

25. Which of the following compound(s) will give a yellow precipitate with iodine and alkali?

(a) 2-hydroxypropane

(b) 2-iodobutane

(c) 1-phenylethanol

(d) 1-phenylbromoethane

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

Williamson's synthesis is an important laboratory method for the preparation of symmetrical and unsymmetrical ethers. In this method, an alkyl halide is allowed to react with sodium alkoxide.

$$R-X + R'-\underset{\cdot\cdot}{\dot{\dot{O}}}Na \longrightarrow R-\underset{\cdot\cdot}{\dot{\dot{O}}}-R' + NaX$$

Ethers containing substituted alkyl groups (secondary or tertiary) may also be prepared by this method. The reaction involves S_N2 attack of an alkoxide ion on primary alkyl halide.

Better results are obtained if the alkyl halide is primary. In case of secondary and tertiary alkyl halides, elimination competes over substitution. If a tertiary alkyl halide is used, an alkene is the only reaction product and no ether is formed.

It is because alkoxides are not only nucleophiles but strong bases as well. They react with alkyl halides leading to elimination reactions.

26. Which of the following leads to the formation of methyl *t*-butyl ether?

(a) $(C_2H_5)_3CONa + CH_3Cl$

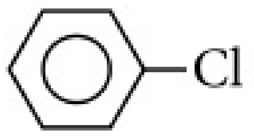
(b) $CH_3ONa + (CH_3)_3CCl$

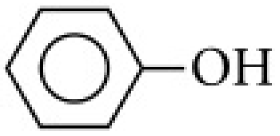
(c) $(CH_3)_3CONa + C_2H_5Cl$

(d) $(CH_3)_3CONa + CH_3Cl$

27. Which of the following reagents are not used in the preparation of anisole via Williamson's synthesis?

(a) Na (b) CH_3-Cl

(c) 

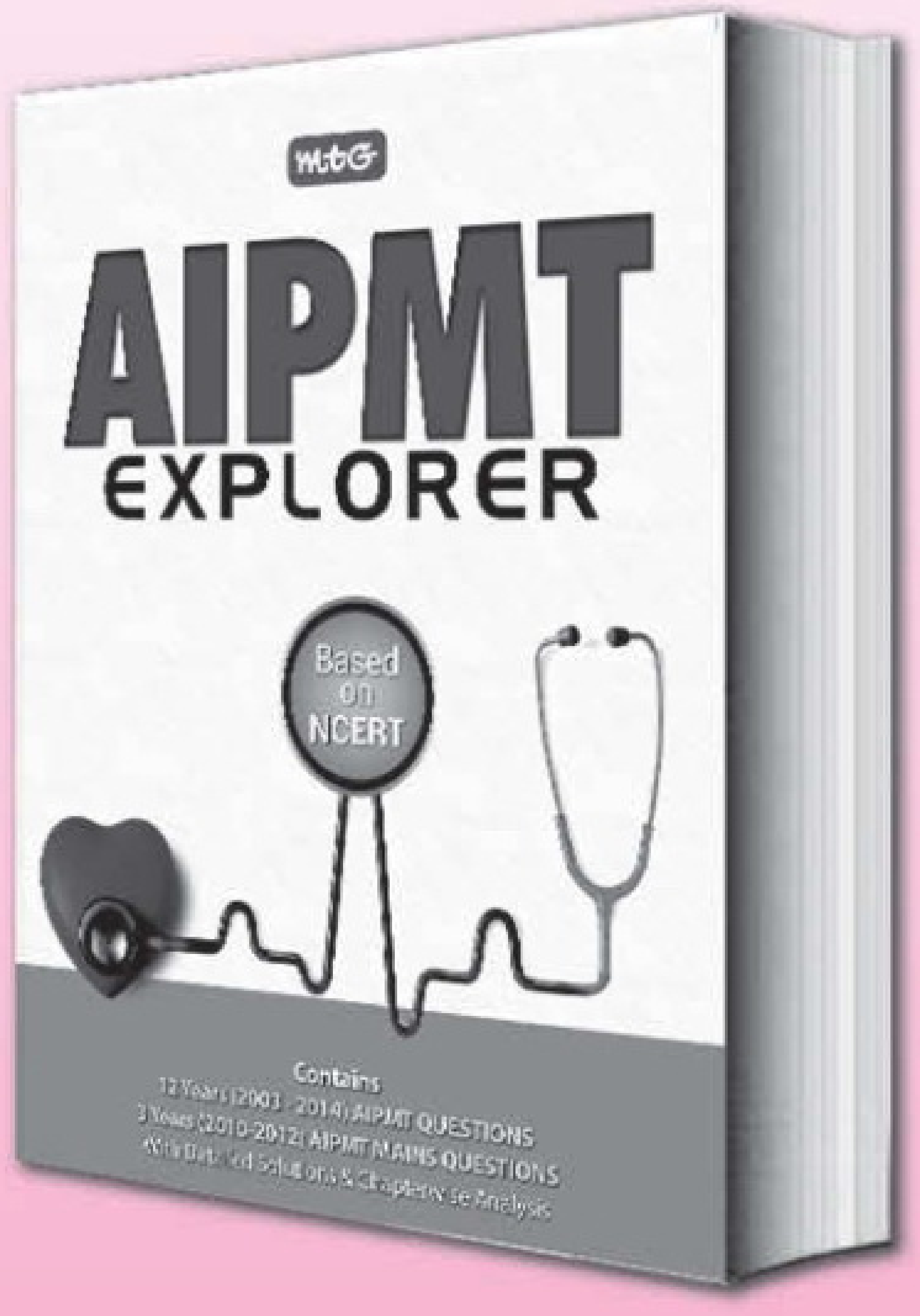
(d) 

28. Consider the following reactions :

(i) $(CH_3)_2CHCH_2Br \xrightarrow{C_2H_5OH} (CH_3)_2CHCH_2OC_2H_5 + HBr$

(ii) $(CH_3)_2CHCH_2Br \xrightarrow{C_2H_5O^-} (CH_3)_2CHCH_2OC_2H_5 + Br^-$

The mechanisms of reactions (i) and (ii) are respectively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(a) S_N1 and S_N2 (b) S_N1 and S_N1
(c) S_N2 and S_N2 (d) S_N2 and S_N1.

Paragraph for Questions 29 to 31

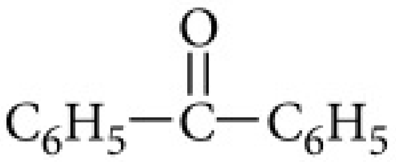
The aldehydes and ketones undergo a number of reactions due to the acidic nature of α-hydrogen. The acidity of α-hydrogen atoms of carbonyl compounds is due to the strong electron withdrawing effect of the carbonyl group and resonance stabilisation of the conjugate base.

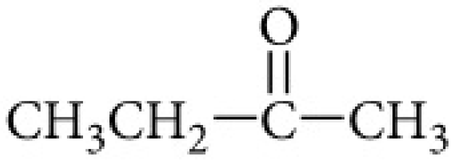
(i) **Aldol condensation:** Aldehydes and ketones having at least one α-hydrogen undergo a reaction in the presence of dilute alkali as catalyst to form β-hydroxyaldehydes (aldol) or β-hydroxyketones (ketol), respectively. This is known as Aldol condensation.

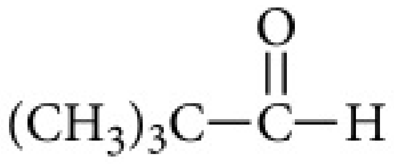
(ii) **Cross aldol condensation:** When aldol condensation is carried out between two different aldehydes and / or ketones, it is called cross aldol condensation. If both of them contain α-hydrogen atoms, it gives a mixture of four products.

29. Which of the following gives aldol condensation reaction?

(a) C_6H_5OH

(b) 
$C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-C_6H_5$

(c) 
$CH_3CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$

(d) 
$(CH_3)_3C-\overset{\overset{\displaystyle O}{\|}}{C}-H$

30. A compound possessing α-hydrogen atom, in the presence of dilute alkali forms β-hydroxy aldehyde. This product on heating with dilute acid forms an unsaturated crotonaldehyde. The compound is

(a) CH_3CHO
(b) CH_3CH_2CHO
(c) $CH_2{=}CH-CHO$
(d) $HC{\equiv}C-CHO$

31. Aldol condensation will not occur in

(a) HCHO (b) CH_3CH_2CHO
(c) CH_3CHO (d) CH_3COCH_3

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 common names given in List I with the IUPAC names in List II and select the correct answer using the code given below the lists :

	List I		List II
P.	Cinnamaldehyde	1.	Pentanal
Q.	Acetophenone	2.	Prop-2-enal
R.	Valeraldehyde	3.	3-Phenylprop-2-enal
S.	Acrolein	4.	1-Phenylethanone

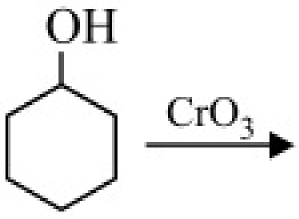
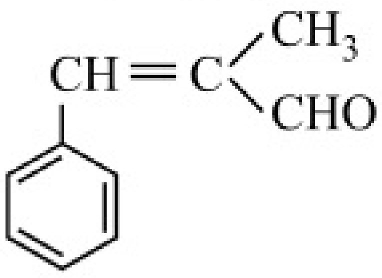
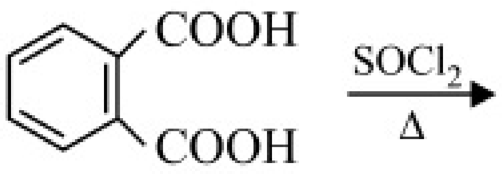
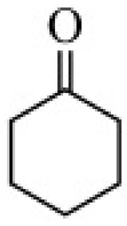
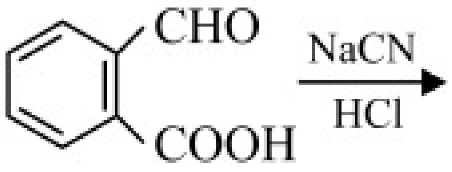
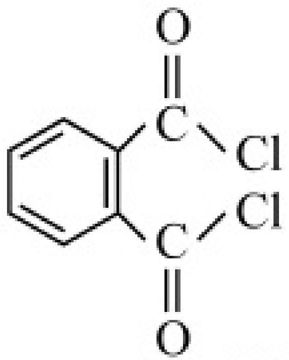
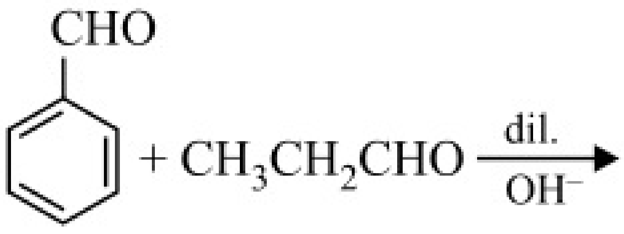
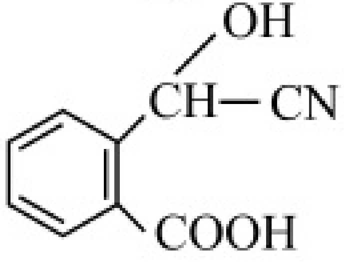
	P	Q	R	S
(a)	3	1	2	4
(b)	2	4	3	1
(c)	1	3	2	4
(d)	3	4	1	2

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.	Solvent used in perfumes	1.	Glycerol
Q.	Starting material for picric acid	2.	Methanol
R.	Wood spirit	3.	Phenol
S.	By product of soap industry used in cosmetics	4.	Ethanol

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

34. 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.	
Q.		2.	
R.		3.	
S.		4.	

	P	Q	R	S
(a)	1	3	4	2
(b)	2	4	1	3
(c)	3	2	4	1
(d)	2	3	4	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 : Benzoic acid and phenol can be distinguished by $NaHCO_3$.
Reason : Benzoic acid is stronger acid than phenol.

36. Assertion : Aromatic aldehydes and formaldehyde undergo Cannizzaro reaction.
Reason : Aromatic aldehydes are almost as reactive as formaldehyde.

37. Assertion : In the presence of alkaline $KMnO_4$ 4-methylacetophenone is oxidised to benzoic acid.
Reason : Only keto group is oxidised to —COOH group.

38. Assertion : Anisole undergoes electrophilic substitution at *o*- and *p*-positions.
Reason : Anisole is less reactive than phenol towards electrophilic substitution reactions.

39. Assertion : β-hydrogen atom of carbonyl compounds is acidic in nature.
Reason : β-hydrogen is directly attached to carbon next to carbonyl carbon.

40. Assertion : CH_3OCH_3 and C_2H_5OH have comparable molecular weight but boiling point of ethanol is more than dimethyl ether.
Reason : C_2H_5OH forms intermolecular H-bonding while CH_3OCH_3 forms intramolecular H-bonding.

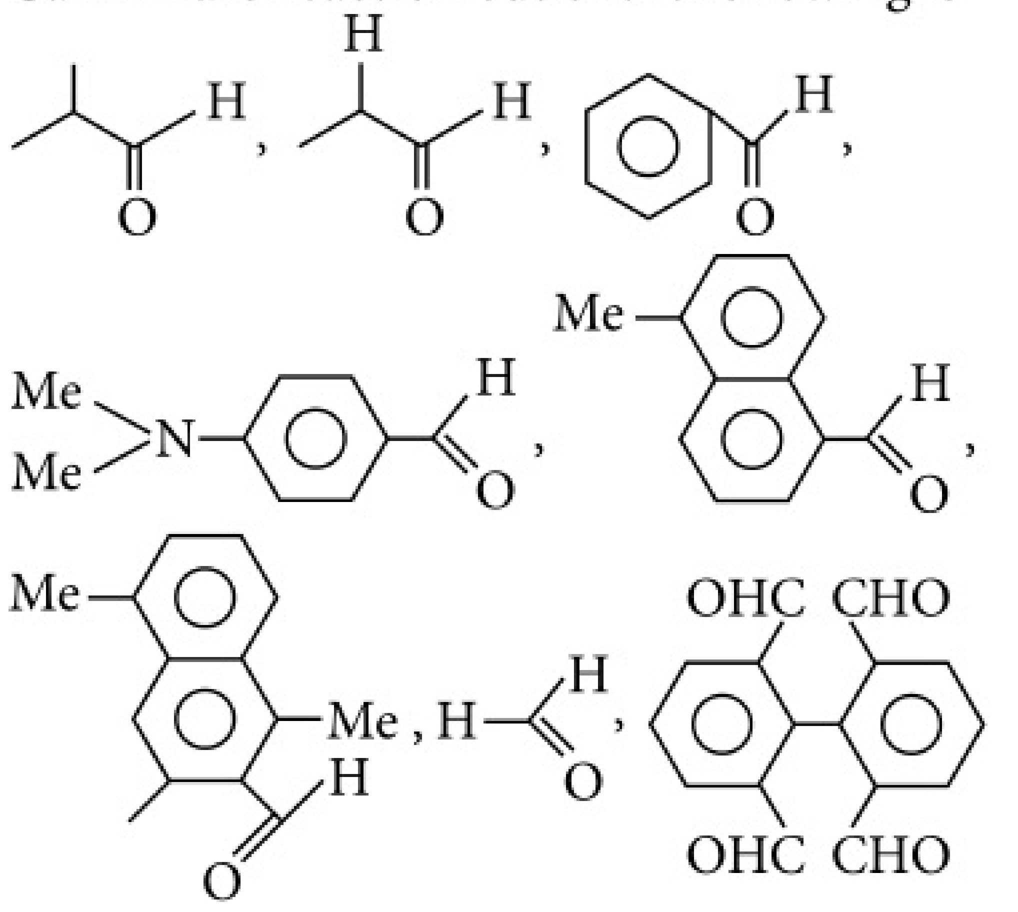
SECTION - VI

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*) $C_6H_{14}O$ (alcohol) gives iodoform test when CHI_3 and (*B*), a salt of monobasic acid is formed. Salt (*B*) on acidification gives 2,2-dimethylpropanoic acid. The nature of alcoholic group in (*A*) is $x°$. x is

42. Number of compounds which can undergo Cannizzaro reaction out of the following is

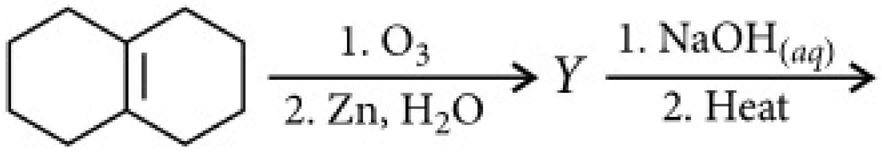


43. The total number of carboxylic acids which are obtained when all the isomeric arenes having the molecular formula C_8H_{10} are oxidised with alk. $KMnO_4$ followed by acidification is

44. Adipic acid on heating at 300°C is converted to a compound having x number of C atoms. The value of x is

45. An organic compound of formula $C_3H_8O_3$ yields on acetylation with acetic anhydride a derivative of the formula $C_9H_{14}O_6$. The number of hydroxyl groups present in the compound is

46. In the scheme given below, the total number of intramolecular aldol condensation products formed from 'Y' is



47. The number of stuctural formulae for all possible ethers having molecular formula $C_4H_{10}O$ are

48. Total number of functional isomers possible for $C_3H_6O_2$ is

49. A compound $A(C_5H_8O_2)$ is reduced to pentane with Zn-Hg/HCl. It forms a dioxime with NH_2OH and also gives positive iodoform and Tollens' tests. The number of ketonic groups present in A is

50. The total number of the structurally isomeric pentyl alcohols that will produce immediate turbidity in Lucas test is

SOLUTIONS

1. **(a) :** Reactions of alcohols involving cleavage of C—OH bond follow the reactivity order : tertiary > secondary > primary, according to the stability of carbocation intermediate.

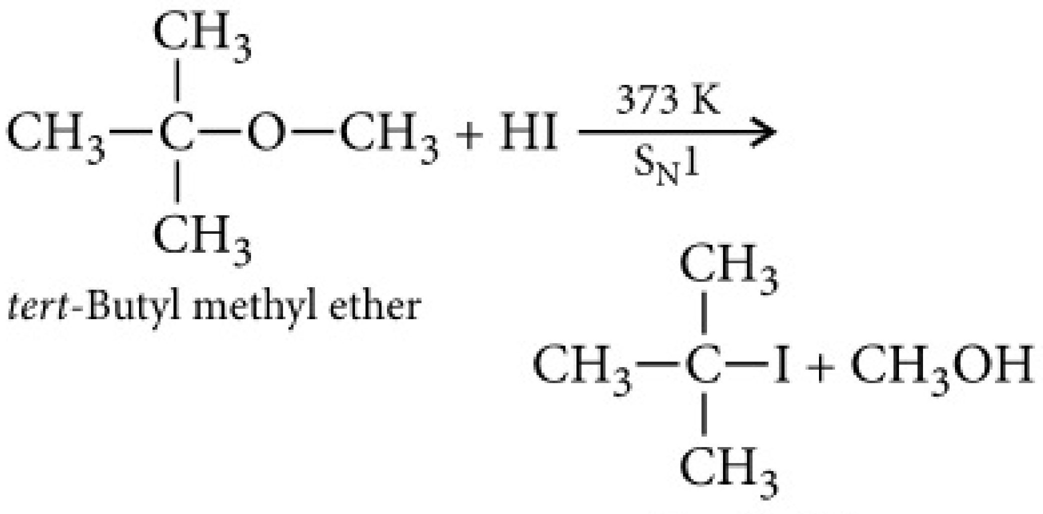
2. **(c) :** $C_6H_5CH\boxed{O + H_2}CHCOCH_3 \xrightarrow{\text{Aq. NaOH}} C_6H_5CH{=}CHCOCH_3 + H_2O$

3. **(a) :** When mixed ethers are used, the alkyl iodide produced depends on the nature of alkyl groups. If one group is Me and the other a primary or secondary alkyl group, then methyl iodide is produced. Here reaction occurs via S_N2 mechanism and because of the steric effect of the larger group, I^- attacks the smaller (Me) group.

$$CH_3OC_2H_5 + HI \rightarrow CH_3I + C_2H_5OH$$

When the substrate is a methyl t-alkyl ether, the products are t-RI and MeOH. Here reaction occurs by S_N1 mechanism and formation of products is controlled by the stability of carbocation. Since carbocation stability order is $3° > 2° > 1° > \overset{+}{C}H_3$.

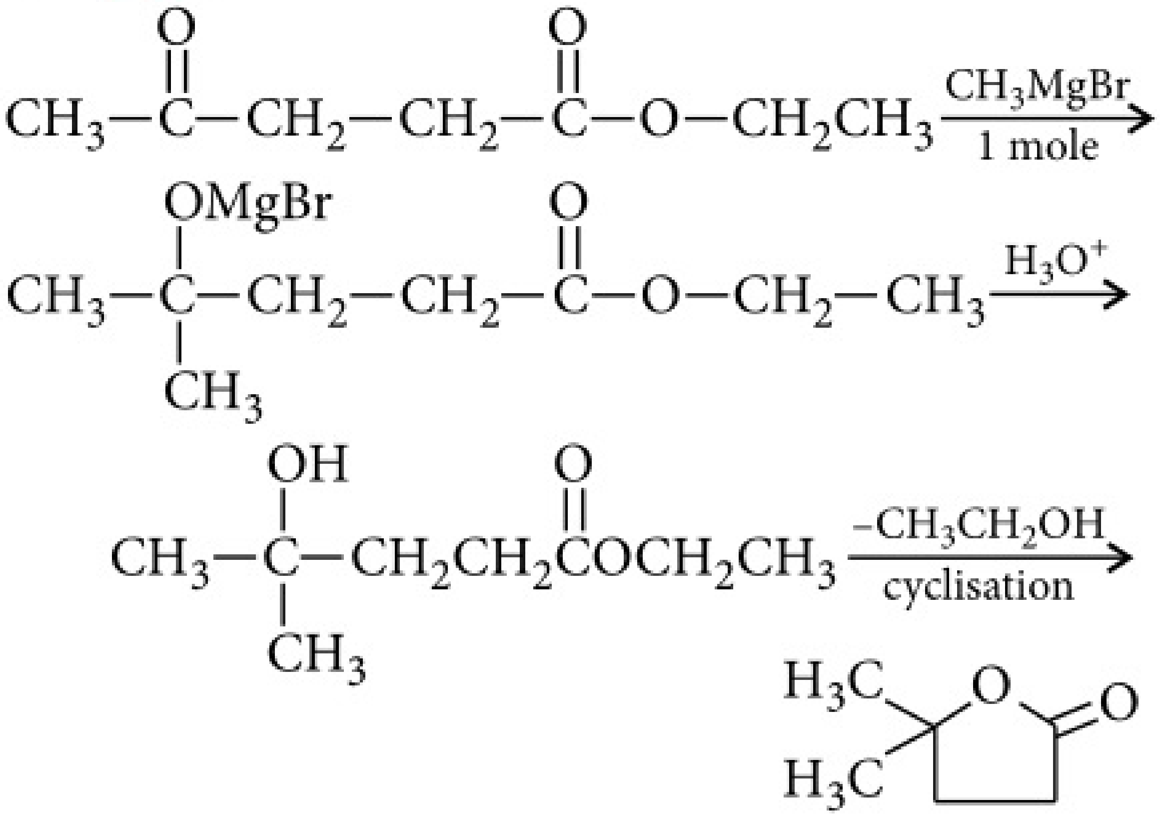
$\therefore$ Alkyl halide is always derived from *tert*-alkyl group.



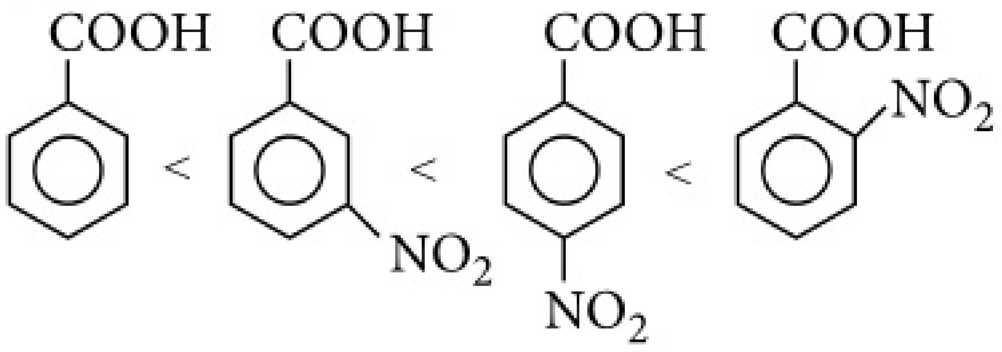
tert-Butyl methyl ether

tert-Butyl iodide

4. **(c) :**

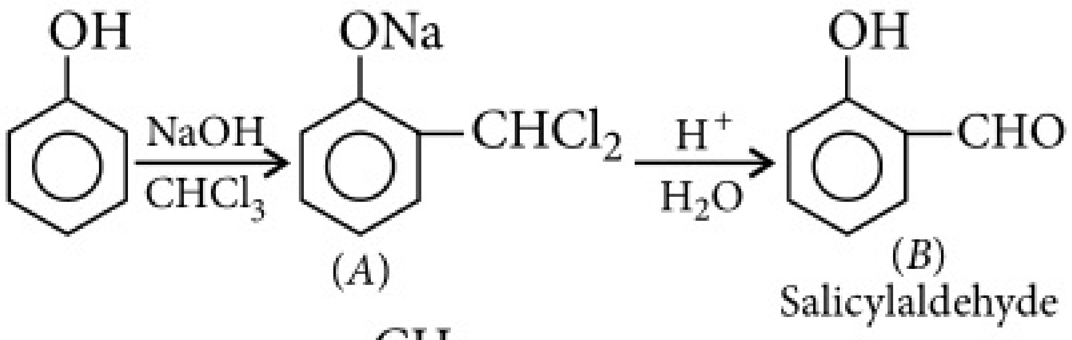


5. **(d) :** Order of acidity is :

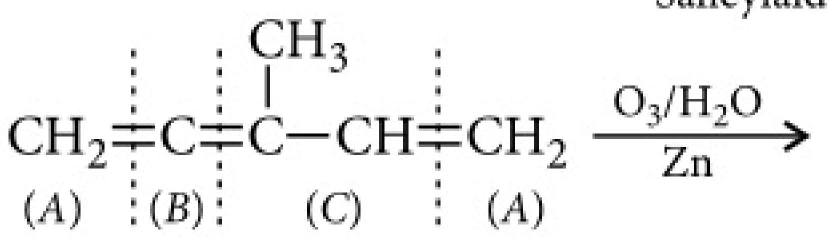


E.W.G. increases the acidity of benzoic acid, o-isomer will have higher acidity than corresponding m- and p-isomers due to *ortho*-effect. In p-nitrobenzoic acid, both $-R$ effect and $-I$ effect of the nitro group increase the acidity while in m-nitrobenzoic acid, only the weaker $-I$ effect increases the acidity. Therefore the correct order of acidity is ii > iii > iv > i.

6. **(d) :** The given reaction is Reimer-Tiemann reaction.



7. **(d) :**

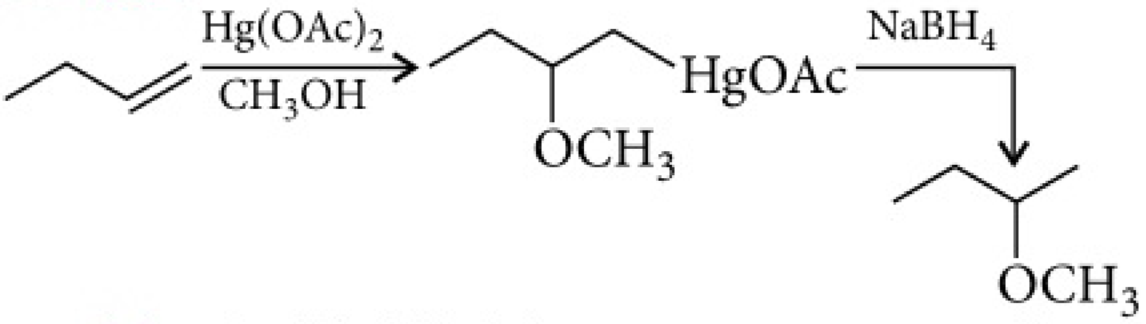


$$\underset{(A)}{CH_2}=\underset{(B)}{C}=\underset{(C)}{\overset{CH_3}{\overset{|}{C}}}-CH=\underset{(A)}{CH_2}\xrightarrow[Zn]{O_3/H_2O}$$

$$\underset{(A)}{2HCHO}+\underset{(B)}{CO_2}+\underset{(C)}{CH_3COCHO}$$

8. **(c) :** Due to $-I$ effect of Cl, chloroacetic acid is a stronger acid than acetic acid. Due to stabilization of phenoxide ion by resonance, phenol is a stronger acid than ethanol.

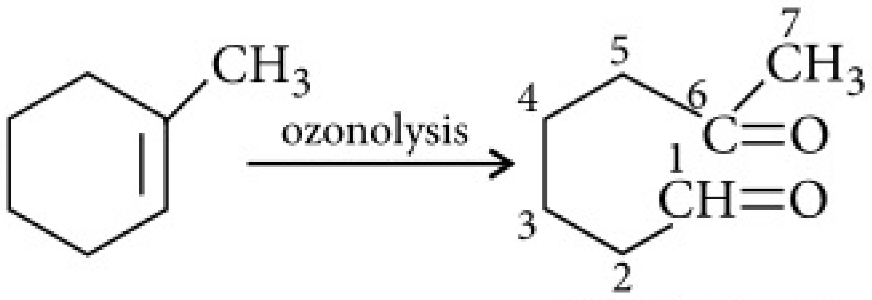
9. **(d) :**



10. **(c) :** 1° Alkyl halides on treatment with an alkoxide ion tend to undergo substitution to form ethers. Thus, sodium *tert*-butoxide and ethyl bromide is the right choice of reagents, *i.e.*,

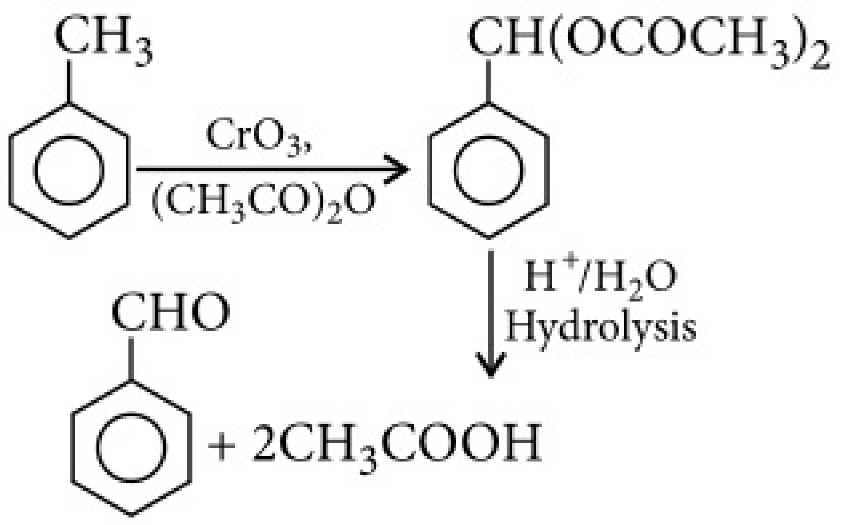
$$(CH_3)_3CO^-Na^+ + CH_3CH_2Br \longrightarrow (CH_3)_3C-O-CH_2CH_3 + NaBr$$

11. **(a) :**



6-Oxoheptanal

12. **(d) :**



(P)

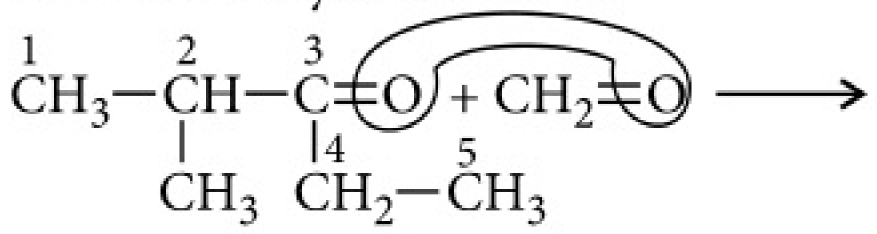
13. **(c) :** C—Br bond is weaker than C—Cl bond, therefore, alkyl bromide (II) reacts faster than alkyl chloride (III) and (IV). Since $CH_2{=}CH-$ is electron withdrawing therefore, CH_2 has more +ve charge on III than on IV.

$$\underset{III}{CH_2=CH\leftarrow\overset{\delta\delta+}{C}H_2-Cl}$$

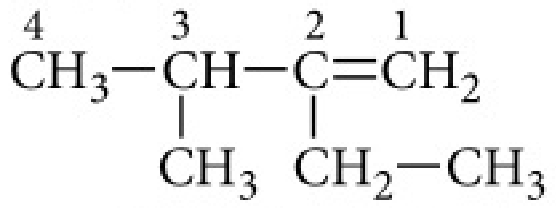
$$\underset{IV}{CH_3-CH_2\rightarrow\overset{\delta+}{C}H_2-Cl}$$

In other words, nucleophilic attack occurs faster on III than on IV. Further, since Williamson's synthesis occurs by S_N2 mechanism, therefore, due to steric hindrance alkyl bromide (I) is the least reactive. Thus, the decreasing order of reactivity is II > III > IV > I.

14. **(a) :** Since C_7H_{14} on ozonolysis gives 2-methyl-3-pentanone which contains six carbon atoms hence other product is formaldehyde. Thus, structure of hydrocarbon is



2-Methyl-3-pentanone



2-Ethyl-3-methylbut-1-ene
(C_7H_{14})

15. **(a) :** Primary alcohols such as *n*-butyl alcohol do not react with Lucas reagent.

16. **(d) :** $C_6H_5COOH \xrightarrow[(X)]{\text{Soda lime}} C_6H_6 + Na_2CO_3$

$C_6H_5OH \xrightarrow[(Y)]{\text{Zn dust}} C_6H_6 + ZnO$

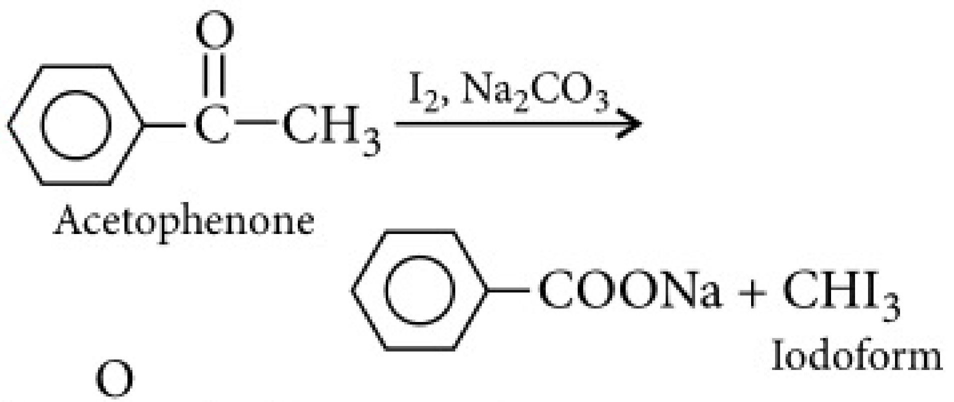
X = soda lime and Y = Zn dust

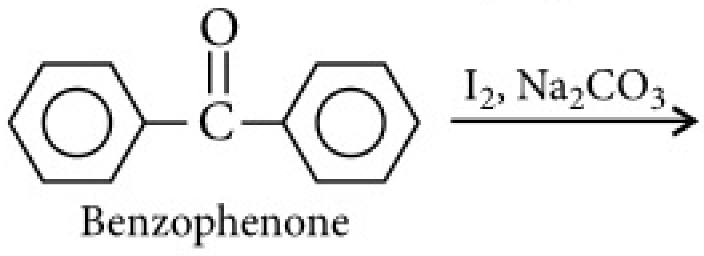
17. **(a) :** Boiling point increases with increase in molecular mass and decreases with increase in branching.

18. **(b) :** Acidity decreases as the $-I$ effect of the halogen group decreases.

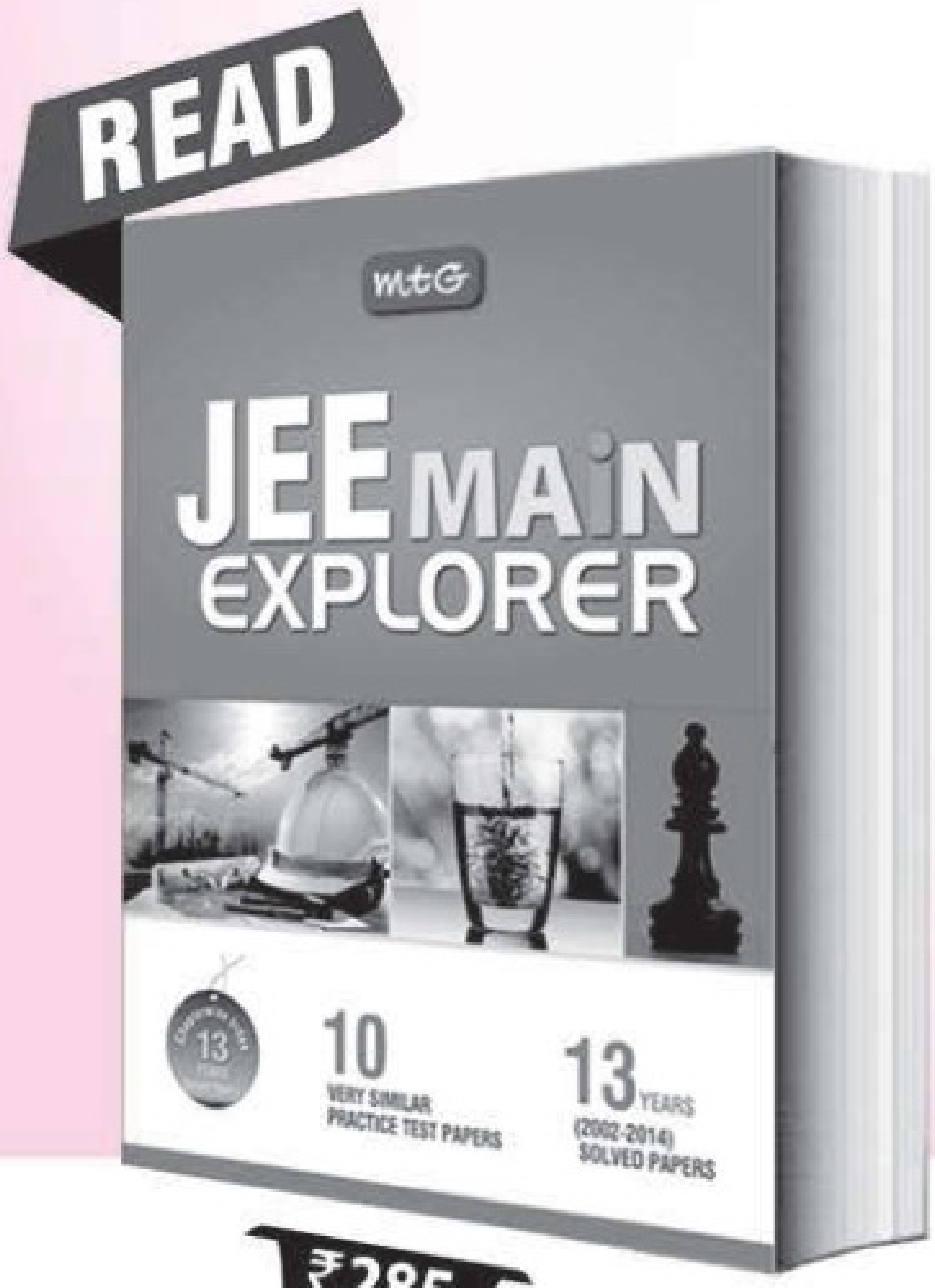
$F_3CCOOH > Cl_3CCOOH > Br_3CCOOH > CH_3COOH$

19. **(d) :**





No iodoform formation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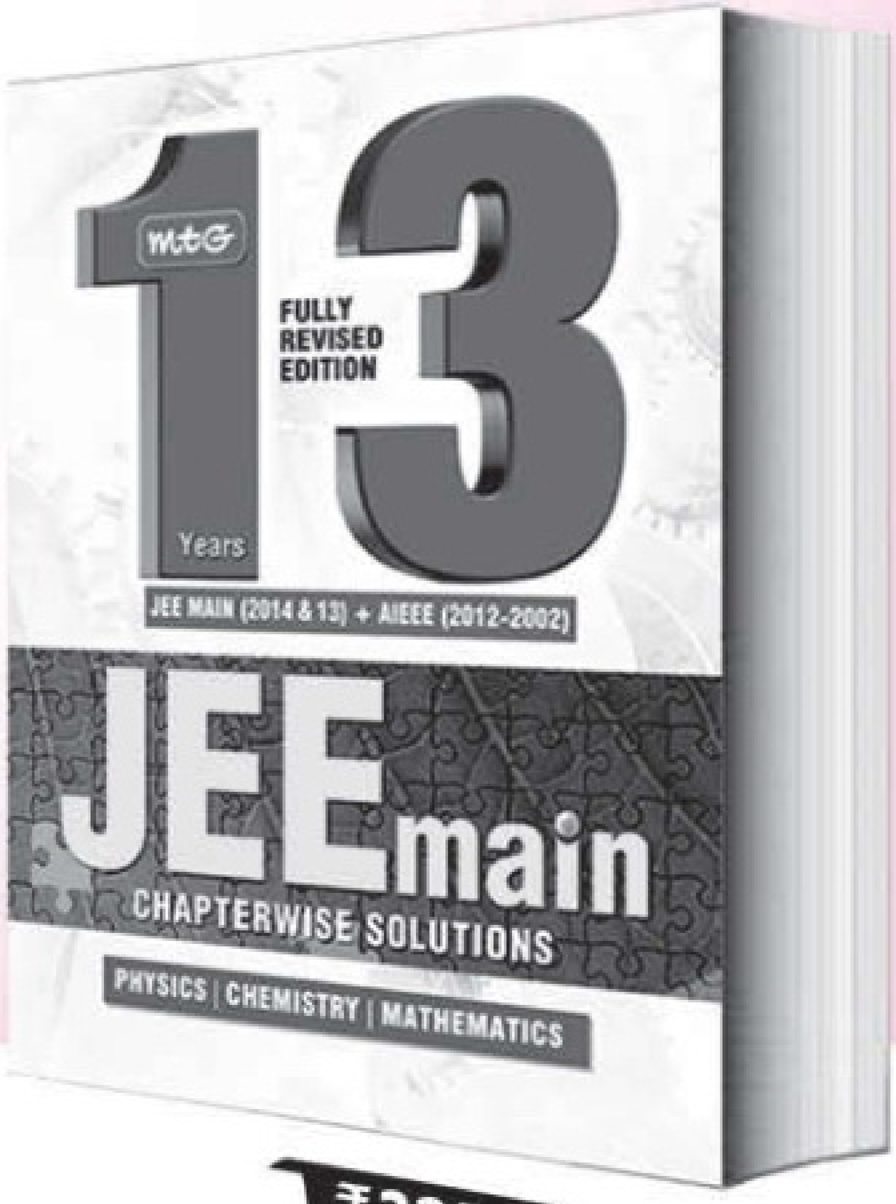
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20. (c) : 1-Propanol and 2-propanol in presence of Cu/Δ undergo dehydrogenation to give acetaldehyde and acetone respectively which can be distinguished by Fehling's solution since acetaldehyde reduces while acetone does not reduce Fehling's solution.

In contrast with alkaline $KMnO_4$ or acidic $K_2Cr_2O_7$, 1-propanol will first give propionaldehyde which will be readily oxidised to propionic acid while 2-propanol will first give acetone and then on further oxidation will give acetic acid. Both these acids cannot be distinguished by Fehling's solution. Option (d) is incorrect since conc. H_2SO_4 does not bring about oxidation of alcohols.

21. (a, b, c, d) :

	Formic acid	**Acetic acid**
Conc. H_2SO_4	$HCOOH \xrightarrow[H_2SO_4]{conc.} CO + H_2O$	No effect
Tollens' Reagent	$HCOOH + Ag_2O \longrightarrow \underset{\text{Black ppt.}}{2Ag} + CO_2 + H_2O$	No effect
Fehling's solution	$HCOOH + 2CuO \longrightarrow \underset{\text{Red ppt.}}{Cu_2O} + CO_2 + H_2O$	No effect
Sodium Salt	$2HCOONa \xrightarrow{\Delta} \begin{matrix} COONa \\ \vert \\ COONa \end{matrix} + H_2$	No effect

22. (a, c) : $\underset{\text{Ethyl bromide}}{C_2H_5Br} + \underset{\text{Sodium ethoxide}}{\overset{+}{Na}\overset{-}{O}CH_2CH_3} \xrightarrow{\Delta} \underset{\text{Diethyl ether}}{CH_3CH_2OCH_2CH_3}$

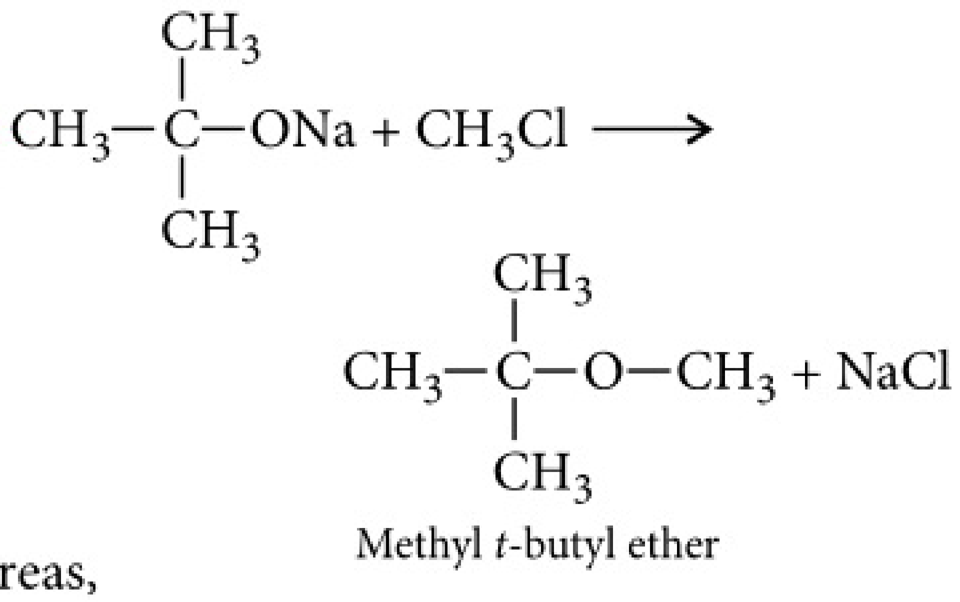
$$\underset{\text{(Dry)}}{2C_2H_5Br + Ag_2O} \xrightarrow{Heat} C_2H_5-O-C_2H_5 + 2AgBr$$

23. (a, c)

24. (c) : Compounds containing CH_3CO— or any group such as $CH_3CH(OH)$— which can be easily oxidised to CH_3CO— group on warming with I_2 and NaOH form iodoform. Hence, compounds (i), (ii) and (iii) will give iodoform while compound (iv), *i.e.*, CH_3OH will not.

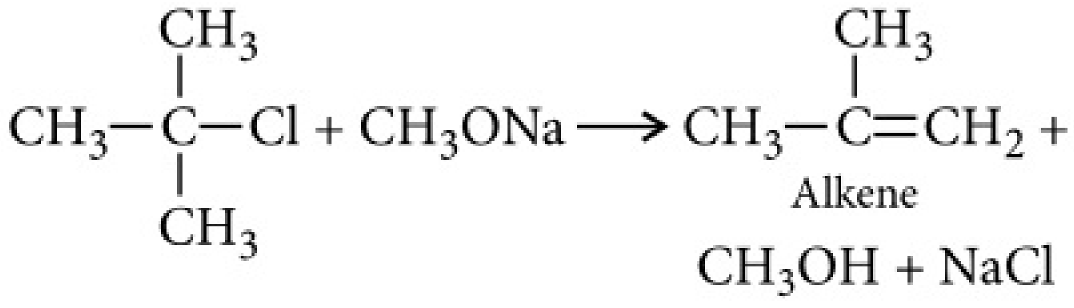
25. (a, b, c, d) : 2-Iodobutane on hydrolysis gives 2-butanol and 1-Phenylbromoethane gives 1-phenylethanol both of which give iodoform test. 1-Phenylethanol ($C_6H_5CHOHCH_3$) and 2-hydroxypropane ($CH_3CHOHCH_3$), of course, contain the grouping CH_3CHOH— and hence give iodoform test. Thus, all options are correct.

26. (d) :



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-ONa + CH_3Cl \longrightarrow \underset{\text{Methyl } t\text{-butyl ether}}{CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O-CH_3} + NaCl$$

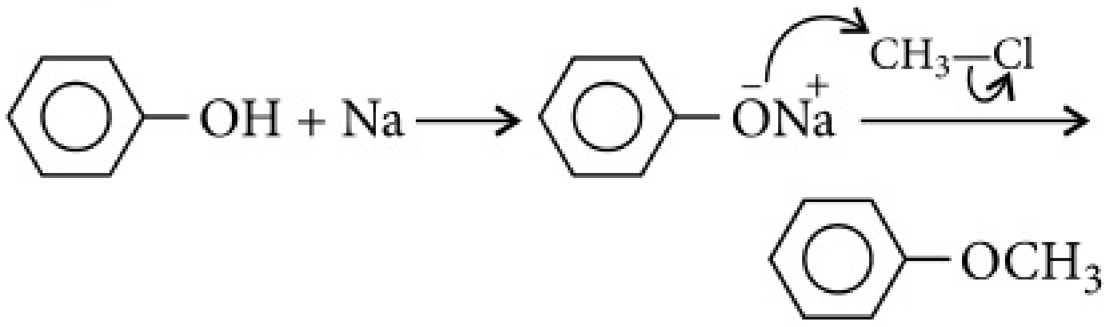
whereas,



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Cl + CH_3ONa \longrightarrow \underset{\text{Alkene}}{CH_3-\overset{CH_3}{C}=CH_2} + CH_3OH + NaCl$$

Secondary and tertiary alkyl halides readily undergo elimination reaction rather than ether formation in the presence of alkoxide.

27. (c) : Williamson's synthesis of anisole

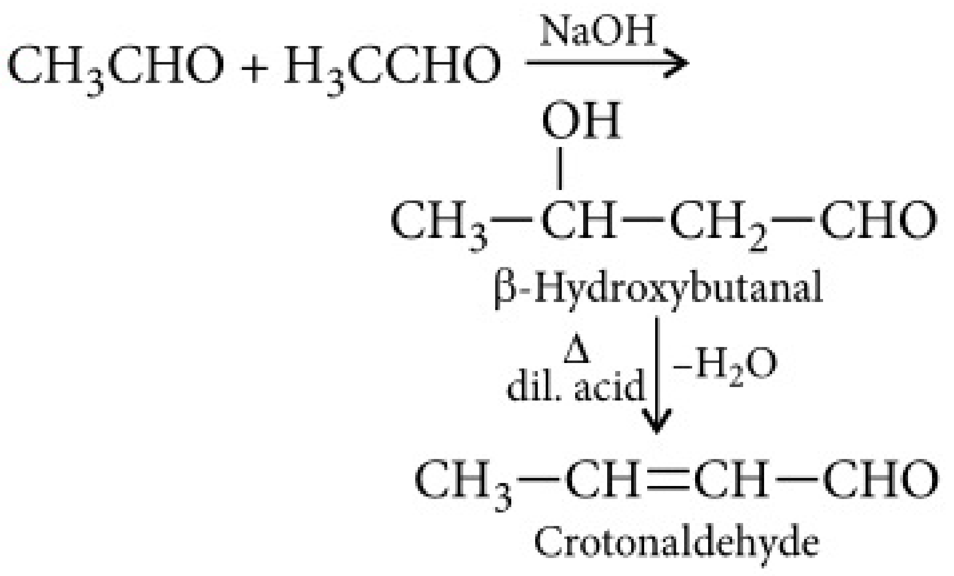


(Anisole)

28. (c) : Since rearrangements do not occur in the given nucleophilic substitution reactions, therefore, carbocations are not the intermediates in these reactions. Thus, both the reactions occur by S_N2 mechanism.

29. (c) : Carbonyl compounds containing α-hydrogen atom give aldol condensation.

30. (a) :



$$CH_3CHO + H_3CCHO \xrightarrow{NaOH} \underset{\beta\text{-Hydroxybutanal}}{CH_3-\overset{OH}{CH}-CH_2-CHO} \xrightarrow[\text{dil. acid}]{\Delta,\ -H_2O} \underset{\text{Crotonaldehyde}}{CH_3-CH=CH-CHO}$$

31. (a) : Aldol condensation is given by compounds containing α-hydrogen.

32. (d) **33. (c)** **34. (d)**

35. (b) : Reaction of carboxylic acids with sodium bicarbonate leads to evolution of CO_2 producing brisk effervescence. However most phenols do not produce effervescence with $NaHCO_3$. Therefore, this reaction is used to distinguish between carboxylic acids and phenols.

36. (c) : Formaldehyde and aromatic aldehydes do not contain α-hydrogen.

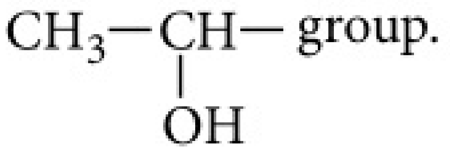
37. (d) : Alkaline $KMnO_4$ will oxidise both, $-CH_3$ and $-COCH_3$ groups to $-COOH$ group. Hence benzene-1,4-dicarboxylic acid (terephthalic acid) will be formed.

38. (b) : $-OCH_3$ group is *o*, *p*-directing.

39. (d) : α-hydrogen is attached to carbon next to carbonyl carbon and it is acidic in nature.

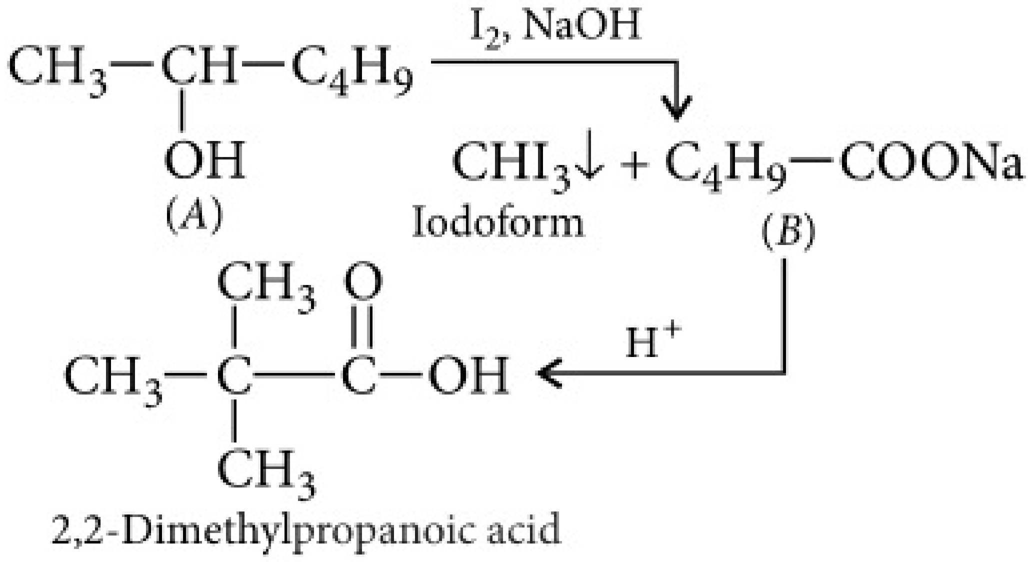
40. (c) : Due to the presence of hydroxyl group (—OH), there is extensive hydrogen bonding between the ethanol molecules (C_2H_5OH) but there is no such hydrogen bonding in dimethyl ether (due to absence of —OH group). So, boiling point of dimethyl ether is much lower than ethanol.

41. (2) : Since alcohol (*A*), ($C_6H_{14}O$) gives iodoform test positively, so, (*A*) should have



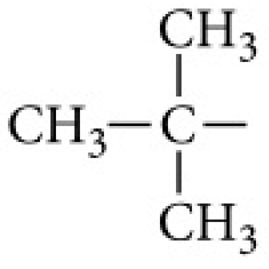
$CH_3-\underset{OH}{\underset{|}{CH}}-$ group.

So, (*A*) is

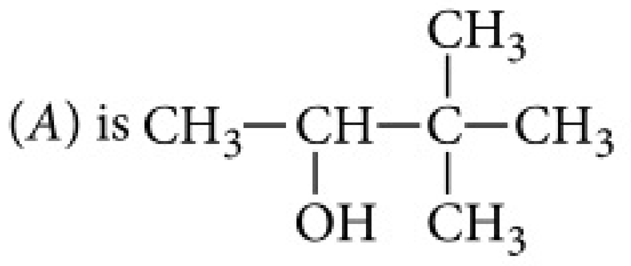


$CH_3-\underset{OH}{\underset{|}{CH}}-C_4H_9 \xrightarrow{I_2,\ NaOH} CHI_3\downarrow + C_4H_9-COONa \xrightarrow{H^+} CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-\overset{O}{\overset{||}{C}}-OH$

Hence, C_4H_9 is

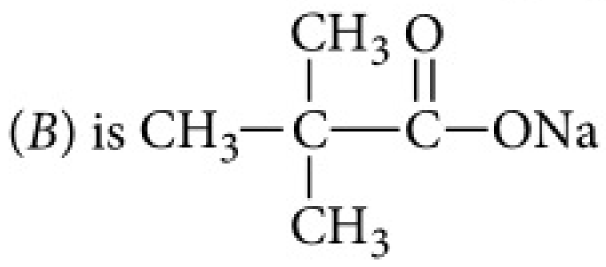


$CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-$ and hence,



(*A*) is $CH_3-\underset{OH}{\underset{|}{CH}}-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_3$ and

(secondary alcoholic group)

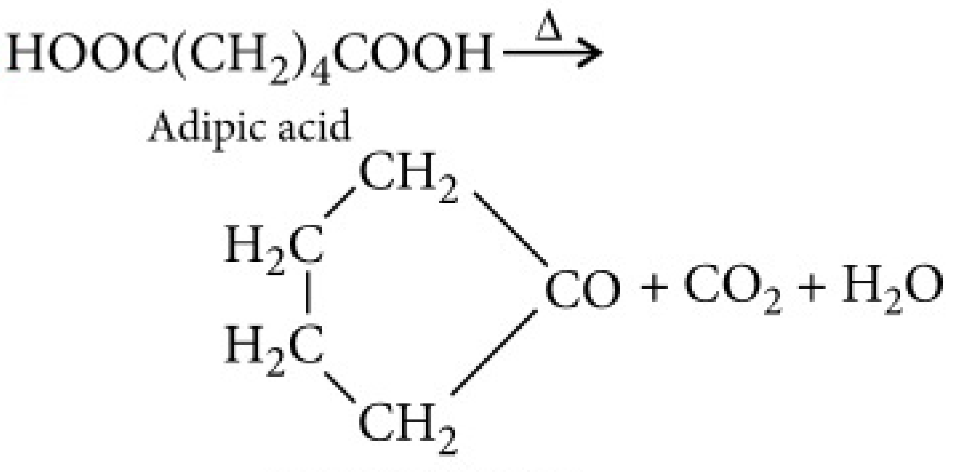


(*B*) is $CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-\overset{O}{\overset{||}{C}}-ONa$

42. (3) : The aldehydes undergo disproportionation reaction in basic medium which is called Cannizzaro reaction. The aldehydes which do not contain α-hydrogen undergo Cannizzaro reaction. If activating groups are present at *ortho* and *para* positions w.r.t. aldehyde group, these type of benzene derivatives do not undergo Cannizzaro reaction.

43. (4) : Isomeric carboxylic acids are formed from four different arenes : ethylbenzene → benzoic acid, *o*-xylene → phthalic acid, *m*-xylene → isophthalic acid and *p*-xylene → terephthalic acid.

44. (5) :



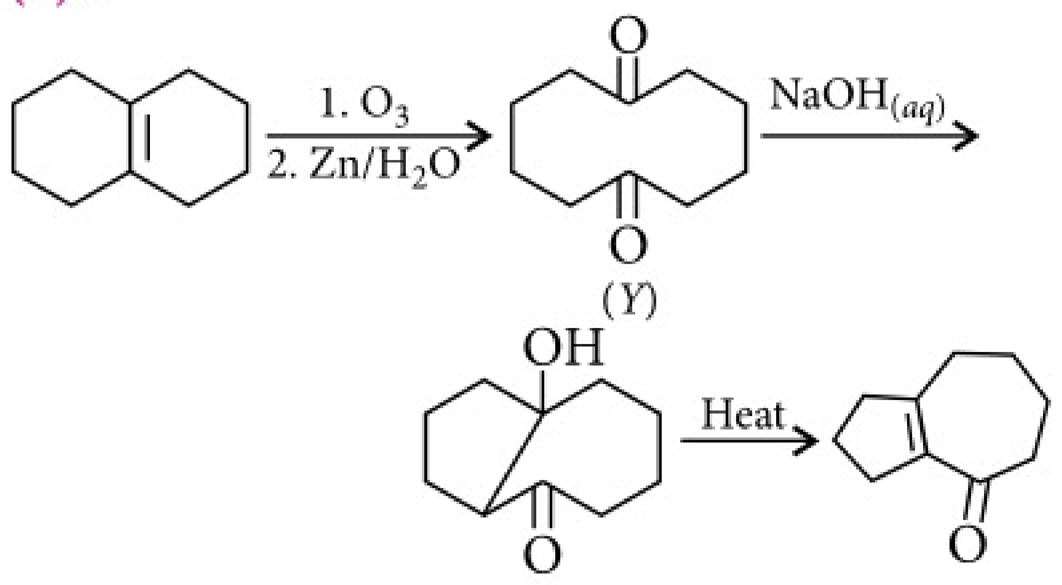
45. (3) : $R-OH \xrightarrow{(CH_3CO)_2O} ROCOCH_3$

In this reaction for every —OH group, C_2H_2O is increased on acetylation.

Total increase = $C_9H_{14}O_6 - C_3H_8O_3 = C_6H_6O_3$

Thus, the increase is equivalent to the presence of 3 – OH groups in the alcohol.

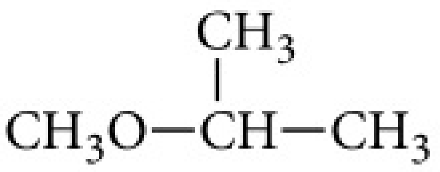
46. (1) :



47. (3) : There are three isomeric ethers of molecular formula $C_4H_{10}O$.

$CH_3CH_2OCH_2CH_3$, Diethyl ether (Ethoxyethane)

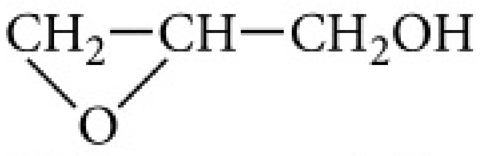
$CH_3OCH_2CH_2CH_3$ Methyl propyl ether (1-Methoxypropane)



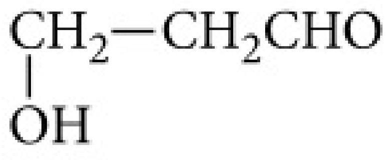
$$CH_3O-\overset{CH_3}{\overset{|}{C}H}-CH_3$$

Methyl isopropyl ether (2-Methoxypropane)

48. (6) : CH_3CH_2COOH , Propionic acid

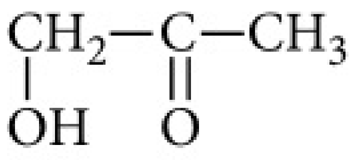


2,3-Epoxypropan-1-ol



$$\underset{OH}{\underset{|}{C}H_2}-CH_2CHO$$

3-Hydroxypropanal ,



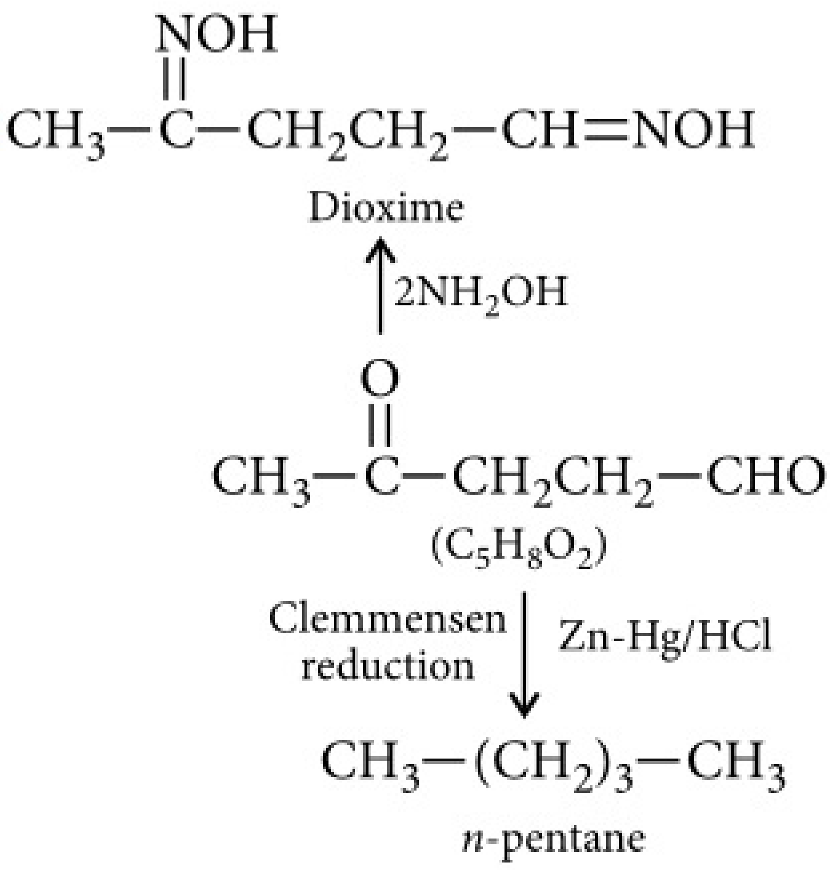
$$\underset{OH}{\underset{|}{C}H_2}-\underset{O}{\underset{||}{C}}-CH_3$$

1-Hydroxypropan-2-one

$HCOOC_2H_5$, Ethyl formate

CH_3COOCH_3 Methyl acetate

49. (1) :



$$CH_3-\overset{NOH}{\overset{||}{C}}-CH_2CH_2-CH{=}NOH$$

Dioxime

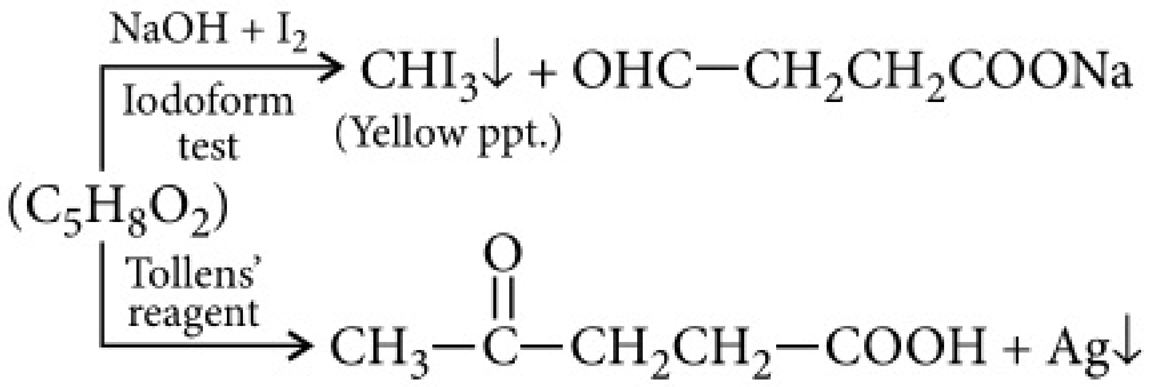
$$\uparrow 2NH_2OH$$

$$CH_3-\overset{O}{\overset{||}{C}}-CH_2CH_2-CHO \quad (C_5H_8O_2)$$

$$\downarrow \text{Clemmensen reduction, Zn-Hg/HCl}$$

$$CH_3-(CH_2)_3-CH_3$$

n-pentane

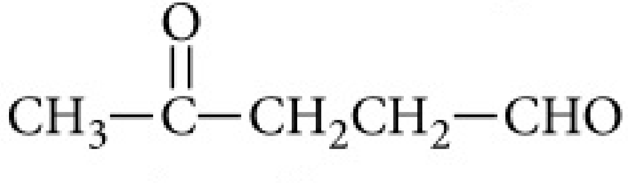


$$(C_5H_8O_2)\xrightarrow[\text{Iodoform test}]{NaOH + I_2} CHI_3\downarrow + OHC-CH_2CH_2COONa$$

(Yellow ppt.)

$$(C_5H_8O_2)\xrightarrow{\text{Tollens' reagent}} CH_3-\overset{O}{\overset{||}{C}}-CH_2CH_2-COOH + Ag\downarrow$$

Hence, the structure of the given compound is



$$CH_3-\overset{O}{\overset{||}{C}}-CH_2CH_2-CHO$$

∴ The number of ketone groups is 1.

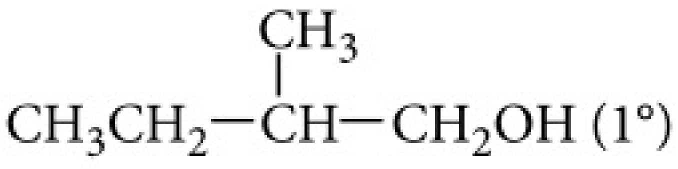
50. (1) : Only 3° alcohols immediately give turbidity in the Lucas Test.

(i) $CH_3CH_2CH_2CH_2CH_2OH$ (1°);

(ii) $CH_3CH_2CH_2-CHOH-CH_3$ (2°);

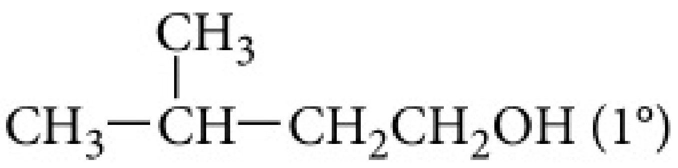
(iii) $CH_3CH_2-CHOH-CH_2CH_3$ (2°);

(iv)



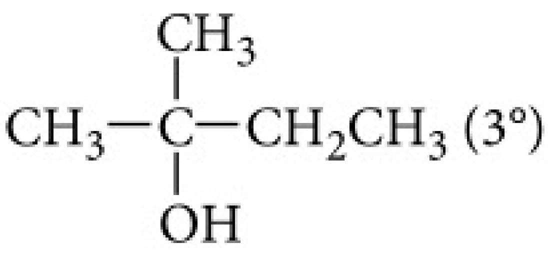
$$CH_3CH_2-\overset{CH_3}{\overset{|}{C}H}-CH_2OH\ (1°)$$

(v)



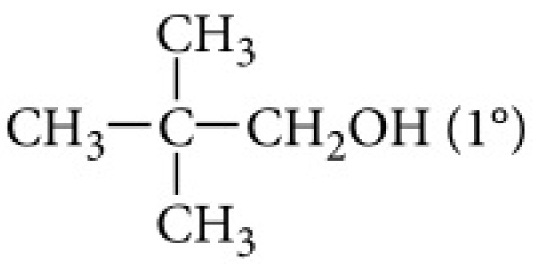
$$CH_3-\overset{CH_3}{\overset{|}{C}H}-CH_2CH_2OH\ (1°)$$

(vi)



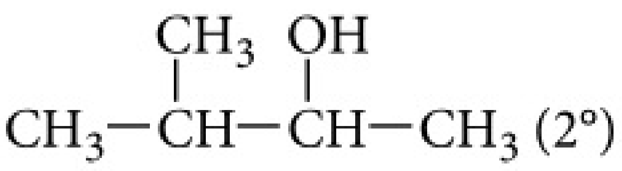
$$CH_3-\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_2CH_3\ (3°)$$

(vii)



$$CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_2OH\ (1°)$$

(viii)



$$CH_3-\overset{CH_3}{\overset{|}{C}H}-\overset{OH}{\overset{|}{C}H}-CH_3\ (2°)$$

SOLUTIONS TO SEPTEMBER 2014 CROSSWORD

1 N	I	C	K	E	L	2 F	L	U	O	R	I	N	E
I						3 O	R	B	4 I	T	5 A	L	
T		6 P	7 A	8 P	E	9 R	E	D	O	X	M	10 G	
R	11 A		C	E		M		12 L	N	13 K	I	L	14 N
15 I	N	T	E	R	H	A	16 L	O	G	E	N	A	E
L	T		T	M		17 L	O	N	E		E	U	U
E	A		O	U		I	W	D			18 S	B	T
	C		N	T		N		19 O	C	T	A	E	R
20 S	I	X	E	I				21 N	E	O	N	R	A
	D	22 C	A	T	A	L	Y	S	T		D	23 W	L
		H	24 P	R	O	T	O	N	25 A	T	I	O	N
		A		26 E	B	O	N	I	T	E		O	
	27 R	I	C	K	E	T	S		O			D	
	28 E	N	T	R	O	P	Y		29 M	E	T	A	L

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Tushar Chatterjee (West Bengal): MTG moulds minds in millions. Crossword is surely an amazing concept, no words to explain. It catalyses my thinking ability.

Dhanraj Hirpara, Jaykishan Pipaliya (Gujarat): The crossword in Chemistry Today was awesome.

M. Krishna, Mangalore (Karnataka)

Aditi Kolhe, Nagpur (Maharashtra)

CHEMISTRY MUSING

SOLUTION SET 14

1. (a) : $\frac{r_A}{r_B} = \sqrt{\frac{M_B}{M_A}}$

(i) $= \sqrt{\frac{44}{44}} = 1$ (ii) $= \sqrt{\frac{28}{28}} = 1$

(iii) $= \sqrt{\frac{48}{32}} = 1.225$ (iv) $= \sqrt{\frac{20}{18}} = 1.054$

(v) $= \sqrt{\frac{352}{349}} = 1.004$

$\therefore$ (i) = (ii) < (v) < (iv) < (iii)

2. (d) : All the alkali metals are highly reactive elements, since they have a strong tendency to lose the single valence *s*-electron to form unipositive ions having inert gas configuration. As we move down the group, the ionization enthalpy of the elements decreases hence, reactivity increases.

However, the reactivity of halogens decreases with increase in atomic number due to following reasons :

1. As the size increases, the attraction for an additional electron by the nucleus becomes less.
2. Due to decrease in electronegativity from F to I, the bond between halogen and other elements becomes weaker and weaker.

3. (d) : Pure $H_2O_2 = \frac{x}{100} g = \frac{x}{1700}$ equivalent

$KMnO_4 = \frac{x\,N}{1000}$ equivalent

$\therefore \frac{Nx}{1000} = \frac{x}{1700}$

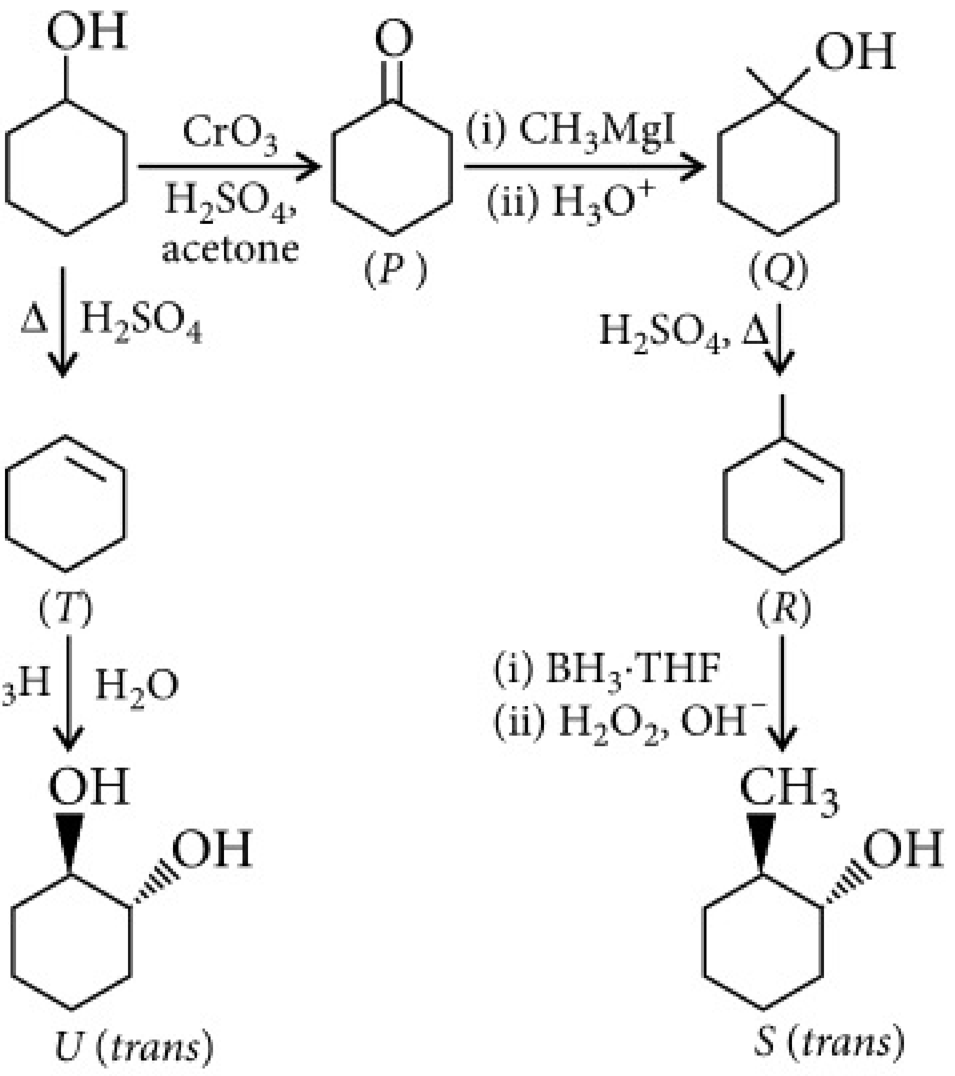
$N = \frac{10}{17} = 0.59$ N

4. (d) : Benzyl chloride on hydrolysis gives benzyl alcohol.

$$\underset{\text{Benzyl chloride}}{C_6H_5CH_2Cl} \xrightarrow[\text{boil, hydrolysis}]{\text{aq. NaOH}} \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} + NaCl$$

5. (c) : (a), (b) and (d) are functional isomers while (c) is a tautomer.

6. (b) :



7. (d) : $E^\circ_{cell} = E^\circ_{oxi} + E^\circ_{red} = E^\circ_{X/X^{2+}} + E^\circ_{Y^{3+}/Y}$
$= E^\circ_{X/X^{2+}} - E^\circ_{Y/Y^{3+}} = 0.20 - 0.40 = -0.20$ V

8. (c) : $K = \frac{[X^{2+}]^3}{[Y^{3+}]^2} = \frac{(0.1)^3}{(0.1)^2} = \frac{1}{10}$

$\therefore \quad E_{cell} = E^\circ_{cell} - \frac{0.0591}{6}\log\frac{1}{10}$

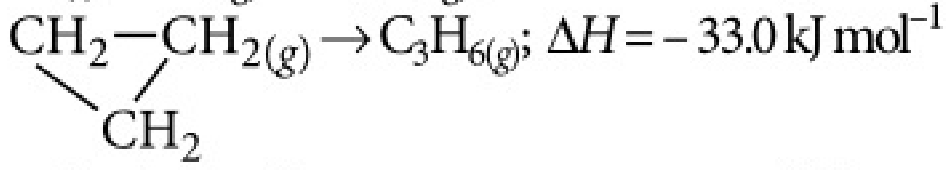
$= \left(-0.20 + \frac{0.0591}{6}\right)$ V

9. (2) : Following equations can be obtained from the available data

(i) $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}; \Delta H = -393.5$ kJ mol^{-1}

(ii) $H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)}; \Delta H = -285.8$ kJ mol^{-1}

(iii) $3C_{(s)} + 3H_{2(g)} \rightarrow C_3H_{6(g)}; \Delta H = +20.42$ kJ mol^{-1}

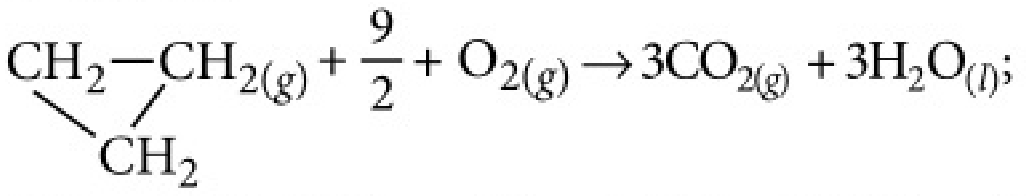
(iv) 

$\underset{\diagdown\ CH_2\ \diagup}{CH_2{-}CH_{2(g)}} \rightarrow C_3H_{6(g)}; \Delta H = -33.0$ kJ mol^{-1}

To get the desired equation compute as follows

[3 × (i) + 3 × (ii)] + [(iv) – (iii)]

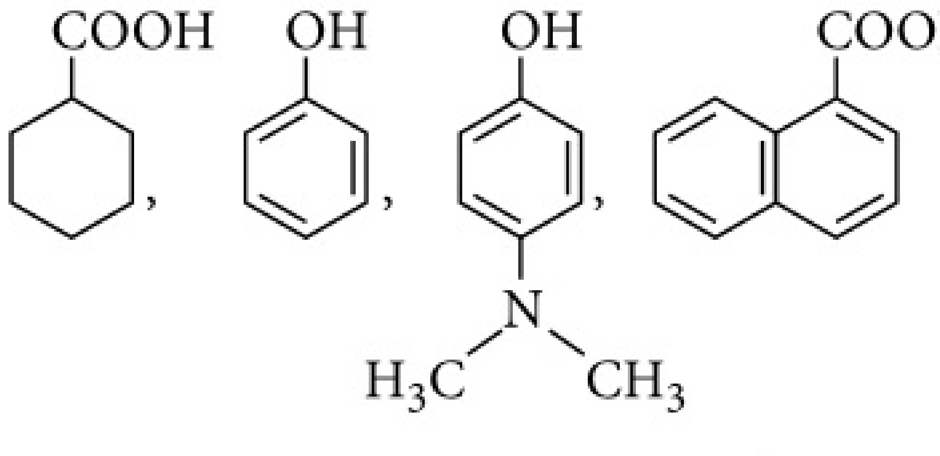
or we have



$\underset{\diagdown\ CH_2\ \diagup}{CH_2{-}CH_{2(g)}} + \frac{9}{2} + O_{2(g)} \rightarrow 3CO_{2(g)} + 3H_2O_{(l)};$

$\Delta H = -2091.32$ kJ mol$^{-1} \approx -2.091 \times 10^3$ kJ mol^{-1}

10. (4) : Out of the given compounds, those soluble in aq.NaOH are :



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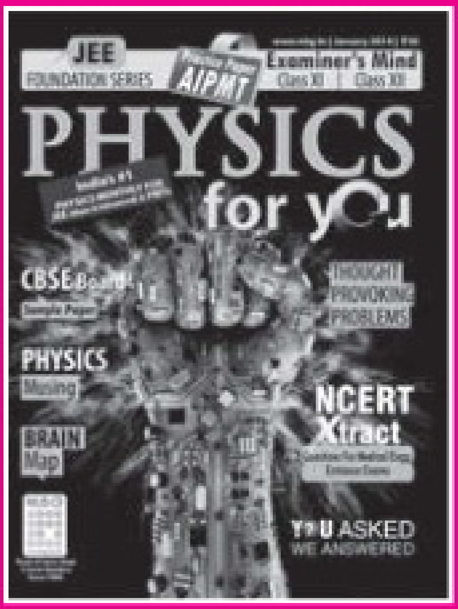

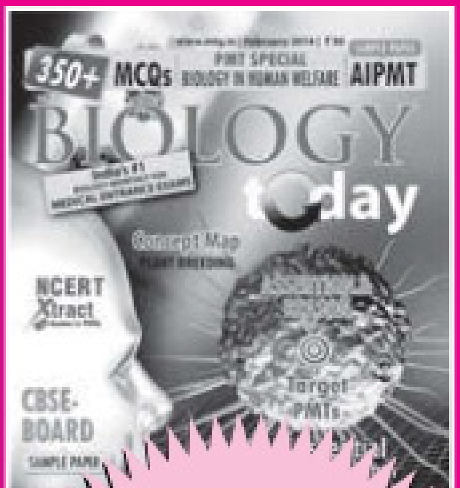

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