NCERT

TEXTBOOK

SOLUTION

Environmental Chemistry

SARASWATI CHEMISTRY

Q-1 Define environmental chemistry.

Sol. Environmental chemistry deals with the chemical phenomenon occurring in our environment, *i.e.*, study of the origin, transport, reactions, effects and fates of chemical species in the environment.

Which gases are responsible for green house effect? List some of them

Sol. Green house gases namely carbon dioxide, methane, nitrous oxide (N_2O), ozone and chlorofluorocarbons (CFC's) are responsible for green house effect, *i.e.*, for maintaining temperature of the earth as these absorb the outgoing radiations from the earth's surface.

Q-2 Carbon monoxide gas is more dangerous than carbon dioxide gas, why?

Sol. Carbon monoxide gas is a poisonous gas. It binds to haemoglobin of the blood to form carboxyhaemoglobin complex which is 300 times more stable than oxyhaemoglobin complex.

When concentration of carboxyhaemoglobin reaches about 3-4%, the oxygen carrying capacity of blood is greatly reduced. This results into headache, nervousness and cardiovascular disorder.

CO_2 gas does not combine with haemoglobin so it is less harmful as a pollutant. Its increased amount in air is mainly responsible for global warming.

Q-3 What would have happened if the green house gases were totally missing in the earth's atmosphere? Discuss.

Sol. Carbon dioxide, methane, water vapours, nitrous oxide, CFCs and ozone are green house gases. These gases trap some of the heat radiated by the earth's object near the earth's surface and keep it warm.

Q-4 Statues and monuments in India are affected by acid rain. How?

Sol. The air around the statues and monuments in India contains fairly high levels of oxides of sulphur and nitrogen. It is mainly due to a large number of industries and power plants around areas. Oxides of nitrogen and sulphur are acidic in nature. SO_2 and NO_2 after oxidation and reaction with water are major contributors to acid rain.

$$2\,SO_2(g) + O_2(g) + 2\,H_2O(l) \longrightarrow 2\,H_2SO_4(aq)$$

$$4\,NO_2\,(g) + O_2(g) + 2\,H_2O(l) \longrightarrow 4\,HNO_3\,(aq)$$

This acid rain reacts with marble of statues and monuments causing damage to these.

$$CaCO_3\,(s) + H_2SO_4(aq) \longrightarrow CaSO_4\,(s) + H_2O(l) + CO_2(g)$$

Q-5 (*i*) What are the reactions involved in removing SO_2 from the atmosphere by passing it through a solution containing citrate ions?.

(*ii*) What is the most important sink of CO pollutant?

(*iii*) How are flue gases from industries freed from oxides of nitrogen and sulphur?

Sol. (*i*) $SO_2(g) + H_2O(l) \rightleftharpoons HSO_3^-(aq) + H^+(aq)$

$$HSO_3^- + H_2Cit^- \longrightarrow \underset{\text{(Complex)}}{(HSO_3 \cdot H_2Cit)^{2-}}$$

(*ii*) Soil microorganisms

(*iii*) By scrubbing them with conc. H_2SO_4 or with alkaline solutions like $Ca(OH)_2$ and $Mg(OH)_2$.

Q-6 What are the harmful effects of photochemical smog and how can they be controlled?

Sol. Photochemical smog consists of O_3, NO, acrolein, formaldehyde and PAN. O_3 and NO irritate the nose and throat and their high concentration causes headache, chest pain, dryness of throat, cough, difficulty in breathing. Aldehydes and PAN cause irritation in eyes. PAN is highly toxic substance to plants and causes bronzing of tender leaves. Ozone also affects the rubber articles and causes cracking and ageing.

Control of photochemical smog If primary precursors of photochemical smog such as hydrocarbons and NO_2 are controlled, the secondary precursors such as O_3 and PAN will automatically be reduced. In automobiles, catalytic converters are used to prevent the release of nitrogen oxide and hydrocarbons to the atmosphere.

Q-7 How can domestic waste be used as manure?

Sol. Domestic wastes are collected in small bins and carried to the disposable site. At the site garbage is sorted out and separated into biodegradable and non-biodegradable wastes. Biodegradable wastes such as vegetable and fruits waste, animal waste, etc., are deposited in land fills and are converted into manure.

Q-8 A large number of fish are suddenly found floating dead on a lake. There is no evidence of toxic dumping but you find an abundance of phytoplankton. Suggest a reason for the fish kill.

Sol. Large quantities of phosphates and nitrates increase the growth of phytoplanktons. These phytoplankton use so much oxygen that it is not sufficiently available for other organisms to use in respiration. Moreover, a large population of bacteria decomposes organic matter such as leaves, grass, etc., in water. During this process, they consume the oxygen dissolved in water. Microorganisms may become so abundant that they form a mat covering on the water surface and preventing sunlight from penetrating the surface and thereby preventing photosynthesis. In all these processes concentration of dissolved oxygen in water decreases. When the concentration of dissolved oxygen of water is below 6 ppm, the growth of fish gets inhibited and they cannot survive.

Q-9 For your agricultural field or garden, you have developed a compost producing pit. Discuss the process in the light of bad odour, flies and recycling of wastes for a good produce.

Sol. The compost producing pit should be set up at a suitable place to protect ourselves from bad odour and flies. Biodegradable domestic wastes *e.g.*, used tea leaves, vegetable and fruits waste are put in the compost pit and it is covered with a little sand. After some time, it is converted into compost by the action of heat and bacteria. Compost pit should be kept covered so that flies cannot make entry into it and the foul odour is minimise. Non-biodegradable domestic waste such as plastic, glass, metal scraps, polythene bags, etc., are sent for recycling. Recycling converts waste into wealth.

Hydrocarbons

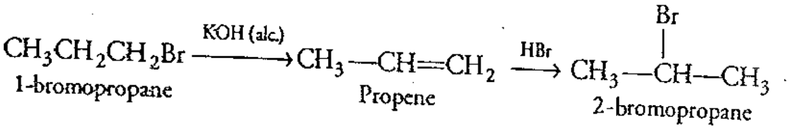
SARASWATI CHEMISTRY

Q-1 Why do the C—C bonds rather than C—H bonds break during cracking of alkanes?

Sol. Since, the bond dissociation energy of C—C bonds (348 kJ mol^{-1}) is lower than bond dissociation energy of C—H bonds (414 kJ mol^{-1}), therefore, during cracking of alkanes, C—C bonds break more easily than C—H bonds.

Q-2 Convert 1-bromopropane to 2-bromopropane.

Sol.

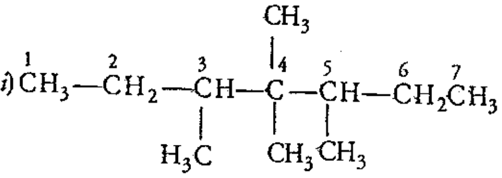


$$\underset{\text{1-bromopropane}}{CH_3CH_2CH_2Br} \xrightarrow{\text{KOH (alc.)}} \underset{\text{Propene}}{CH_3-CH=CH_2} \xrightarrow{HBr} \underset{\text{2-bromopropane}}{CH_3-\overset{\overset{Br}{|}}{C}H-CH_3}$$

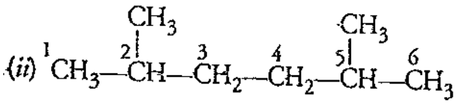
Q-3 Write structural formulae of the following compounds.

(i) 3, 4, 4, 5-tetramethylheptane (ii) 2, 5-dimethylhexane

Sol.



$$(i)\ \overset{1}{C}H_3-\overset{2}{C}H_2-\underset{\underset{H_3C}{|}}{\overset{3}{C}H}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{\overset{4}{C}}}-\underset{\underset{CH_3}{|}}{\overset{5}{C}H}-\overset{6}{C}H_2\overset{7}{C}H_3$$



$$(ii)\ \overset{1}{C}H_3-\overset{\overset{CH_3}{|}}{\overset{2}{C}H}-\overset{3}{C}H_2-\overset{4}{C}H_2-\overset{\overset{CH_3}{|}}{\overset{5}{C}H}-\overset{6}{C}H_3$$

Q-4 Why is Wurtz reaction not preferred for the preparation of alkanes containing odd number of carbon atoms? Illustrate your answer by taking one example.

Sol. For the preparation of alkanes containing odd number of carbon atoms, two different alkyl halides are taken and two different alkyl halides can react in three different ways. Therefore, a mixture of alkanes is produced, *e.g.*,

$$3CH_3I + 6Na + 3C_2H_5I \xrightarrow{\text{Dry ether}} \underset{\text{Ethane}}{CH_3-CH_3} + \underset{\text{Propane}}{CH_3CH_2CH_3} + \underset{\text{Butane}}{CH_3CH_2CH_2CH_3} + 6NaI$$

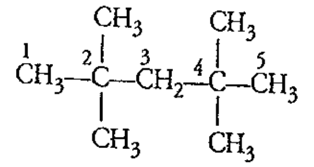
That's why this method (Wurtz reaction) is not suitable for the preparation of odd number alkanes.

Q-5 Write IUPAC names of the following compounds

(i) $(CH_3)_3CCH_2C(CH_3)_3$ (ii) $(CH_3)_2C(C_2H_5)_2$

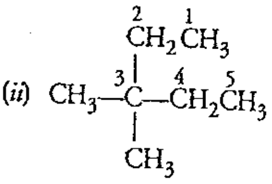
(iii) Tetra-*tert*-butylmethane

Sol. The expanded structures of these alkanes are



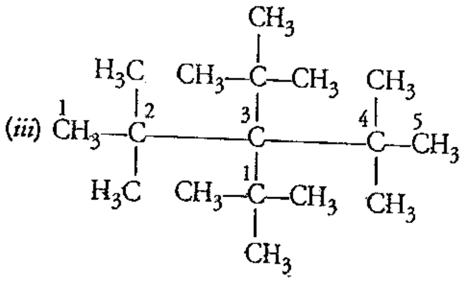
$$(i)\ \overset{1}{C}H_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{\overset{2}{C}}}-\overset{3}{C}H_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{\overset{4}{C}}}-\overset{5}{C}H_3$$

2,2,4, 4-tetramethylpentane



$$(ii)\ CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{\overset{2}{C}H_2\overset{1}{C}H_3}{|}}{\overset{3}{C}}}-\overset{4}{C}H_2\overset{5}{C}H_3$$

3, 3-dimethylpentane



$$(iii)\ \overset{1}{C}H_3-\underset{\underset{H_3C}{|}}{\overset{\overset{H_3C}{|}}{\overset{2}{C}}}-\underset{\underset{CH_3-\underset{\underset{CH_3}{|}}{\overset{1}{C}}-CH_3}{|}}{\overset{\overset{CH_3-\overset{\overset{CH_3}{|}}{C}-CH_3}{|}}{\overset{3}{C}}}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{\overset{4}{C}}}-\overset{5}{C}H_3$$

Q-6 What are pesticides and herbicides? Explain giving examples.

Sol. Pesticides These are the substances that are used to kill or block the reproductive processes of pests. These are basically synthetic toxic chemicals with ecological repercussions. Their accumulation in higher animals (through food chain) causes serious metabolic and physiological disorders. DDT, aldrin, dieldrin, organophosphates and carbamates are some examples of pesticides.

Herbicides These are weed killers, *e.g.*, sodium chlorate ($NaClO_3$) and sodium arsenite (Na_3AsO_3). These are toxic to mammals. Some herbicides cause birth defects. Now a days triazines, better herbicides are used for the corn fields.

Q-7 Have you ever observed any water pollution in your area? What measures would you suggest to control it?

Sol. Yes, polluted water is the water whose quality has been degraded by the addition of substances such as chemical effluents, metal residues, sewage, oil, fertilisers, detergents, etc. *It can be controlled by the following methods*

(*i*) Industrial waste discharge from paper, fertilisers, pesticides, detergents, drugs industries and refineries should not be allowed to get mixed in water bodies such as river, lakes, etc.

(*ii*) Non-biodegradable detergents should be avoided and only biodegradable detergents should be used for cleaning of clothes.

(*iii*) The pH of water should be checked.

(*iv*) Excessive use of fertilisers should be prevented.

(*v*) Oil spills should be avoided as much as possible.

(*vi*) Domestic waste water should be properly discharged and treated.

(*vii*) Avoid the use of DDT, malathion at home.

(*viii*) Waste water should be treated in sewage treatment plant.

Q-8 Do you observe any soil pollution in your neighbourhood? What efforts will you make for controlling the soil pollution?

Sol. *Yes, it can be controlled by the following methods*

(*i*) Insecticides, pesticides which are used for the protection of our crops cause soil pollution. Herbicides (weed killers) also cause soil pollution. Therefore, there is a need for their judicious use.

(*ii*) After the World War-II DDT was put to use in agriculture to control the damages caused by insects, rodents, weeds and various crop diseases. However, due to adverse effects, its use has been banned in India. Pesticides such as aldrin and dieldrin are organic toxins. These are water insoluble and non-biodegradable. These causes serious metabolic and physiological disorders in animals. Now a days organophosphates and carbamates are also used as pesticides. These are more biodegradable but these chemicals are severe nerve toxins and hence, more harmful to humans.

Therefore, chemicals like fertilisers, detergents, pesticides, polymers, should be used only when necessary.

(*iii*) Biodegradable domestic waste should be deposited in land fills.

(*iv*) Non-biodegradable waste should be recycled.

(*v*) Use of polythene should be avoided.

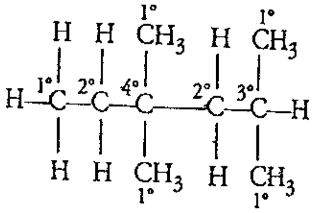
(*vi*) Household waste, biological waste and chemical waste is often incinerated. Incineration greatly reduces the waste volume.

3, 3-di(1, 1-dimethylethyl)-2,2,4,4-tetramethylpentane
or 3,3-bis (1, 1-dimethylethyl)-2,2,4,4-tetramethylpentane

Q-9 In the alkane $H_3CCH_2-C(CH_3)_2-CH_2CH(CH_3)_2$, identify 1°, 2°, 3° carbon atoms and give the number of H-atoms bonded to each one of these.

The carbon which is attached with only 1 or no other carbon atom, is called 1° carbon. Similarly, carbon attached with 2, 3 or 4 other carbon atoms is called 2°, 3°, or 4° carbon atoms respectively. Similarly, hydrogens attached with 1°, 2° or 3° carbon atoms are called 1°, 2° or 3° hydrogens respectively.

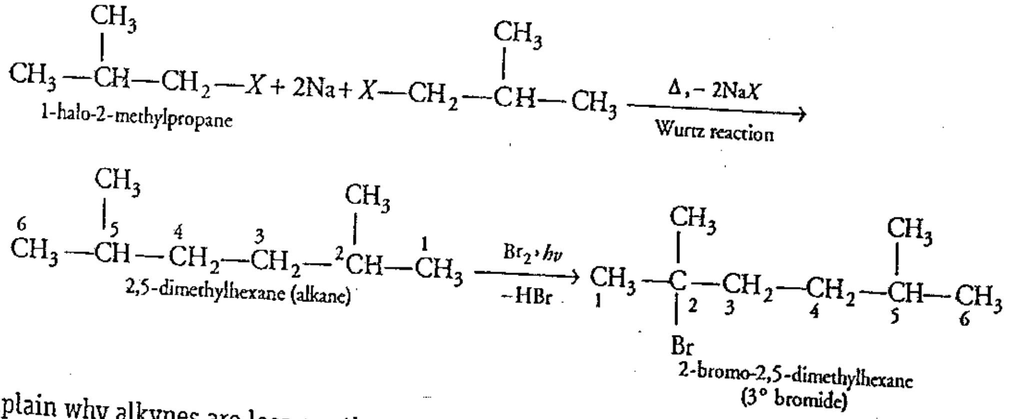
Sol.



15 H-bonded to five 1°C-atoms
4 H-bonded to two 2°C-atoms
1 H-bonded to one 3°C-atom

Q-10 An alkane C_8H_{18} is obtained as the only product on subjecting a primary alkyl halide to Wurtz reaction. On monobromination this alkane yields a single isomer of a tertiary bromide. Write the structure of alkane and the tertiary bromide.

Sol. Since, alkane C_8H_{18} on monobromination yields a single isomer of a tertiary bromide, therefore alkane must contain tertiary hydrogen. This is possible if primary alkyl halide (which undergoes Wurtz reaction) has a tertiary hydrogen.

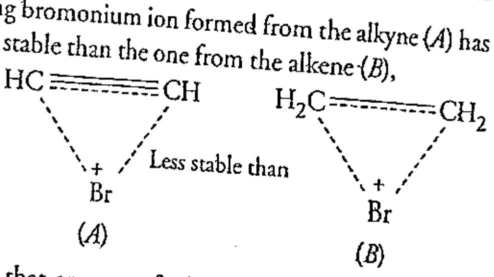


$$\underset{\text{1-halo-2-methylpropane}}{CH_3-\overset{\overset{CH_3}{|}}{C}H-CH_2-X} + 2Na + X-CH_2-\overset{\overset{CH_3}{|}}{C}H-CH_3 \xrightarrow[\text{Wurtz reaction}]{\Delta, -2NaX}$$

$$\underset{\text{2,5-dimethylhexane (alkane)}}{\overset{6}{C}H_3-\overset{\overset{CH_3}{|}}{\underset{5}{C}}H-\overset{4}{C}H_2-\overset{3}{C}H_2-\overset{\overset{CH_3}{|}}{{}^2C}H-\overset{1}{C}H_3} \xrightarrow[-HBr]{Br_2, h\nu} \underset{\substack{\text{2-bromo-2,5-dimethylhexane} \\ \text{(3° bromide)}}}{\underset{1}{C}H_3-\overset{\overset{CH_3}{|}}{\underset{\underset{Br}{|}}{C}}{}_2-\underset{3}{C}H_2-\underset{4}{C}H_2-\overset{\overset{CH_3}{|}}{\underset{5}{C}}H-\underset{6}{C}H_3}$$

Q-11 Explain why alkynes are less reactive than alkenes toward addition of Br_2.

Sol. The three-membered ring bromonium ion formed from the alkyne (*A*) has a full double bond causing it to be more stained and less stable than the one from the alkene (*B*),



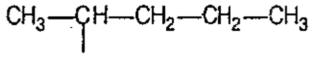
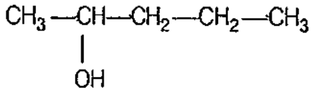
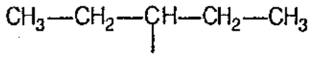
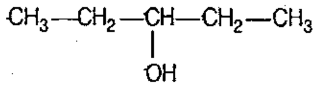
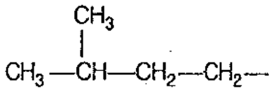
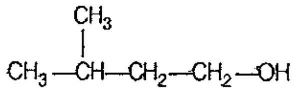
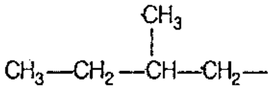
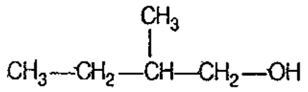
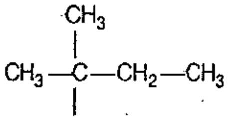
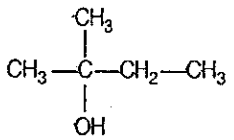
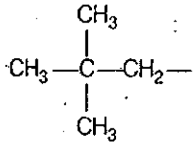
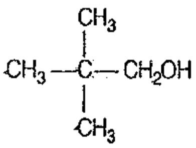
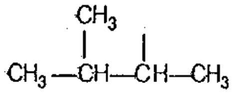
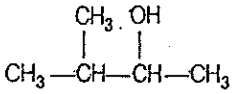
Also, the carbon's of (*A*) that are part of the bromonium ion have more *s*-character than (*B*), further making (*A*) less stable than (*B*).

Q-12 Write chemical equation for the combustion of hexyne.

Sol. $C_6H_{10}(g)+\frac{17}{2}O_2(g) \xrightarrow{\text{Heat}} 6CO_2(g)+5H_2O(g)$

Q-13 Write structures of different isomeric alkyl groups corresponding to the molecular formula C_5H_{11}. Write IUPAC names of alcohols obtained by attachment of —OH groups at different carbons of the chain.

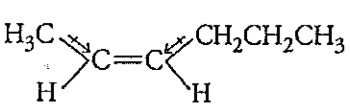
Sol.

	Structures of — C_5H_{11} group	Corresponding alcohols	Name of alcohol
(i)	$CH_3-CH_2-CH_2-CH_2-CH_2-$	$CH_3-CH_2-CH_2-CH_2-CH_2-OH$	Pentan-1-ol
(ii)	 $CH_3-\underset{\vert}{C}H-CH_2-CH_2-CH_3$	 $CH_3-\underset{OH}{\underset{\vert}{C}H}-CH_2-CH_2-CH_3$	Pentan-2-ol
(iii)	 $CH_3-CH_2-\underset{\vert}{C}H-CH_2-CH_3$	 $CH_3-CH_2-\underset{OH}{\underset{\vert}{C}H}-CH_2-CH_3$	Pentan-3-ol
(iv)	 $CH_3-\overset{CH_3}{\overset{\vert}{C}H}-CH_2-CH_2-$	 $CH_3-\overset{CH_3}{\overset{\vert}{C}H}-CH_2-CH_2-OH$	3-methylbutan-1-ol
(v)	 $CH_3-CH_2-\overset{CH_3}{\overset{\vert}{C}H}-CH_2-$	 $CH_3-CH_2-\overset{CH_3}{\overset{\vert}{C}H}-CH_2-OH$	2-methylbutan-1-ol
(vi)	 $CH_3-\overset{CH_3}{\overset{\vert}{\underset{\vert}{C}}}-CH_2-CH_3$	 $CH_3-\overset{CH_3}{\overset{\vert}{\underset{OH}{\underset{\vert}{C}}}}-CH_2-CH_3$	2-methylbutan-2-ol
(vii)	 $CH_3-\overset{CH_3}{\overset{\vert}{\underset{CH_3}{\underset{\vert}{C}}}}-CH_2-$	 $CH_3-\overset{CH_3}{\overset{\vert}{\underset{CH_3}{\underset{\vert}{C}}}}-CH_2OH$	2,2-dimethyl propan-1-ol
(viii)	 $CH_3-\overset{CH_3}{\overset{\vert}{C}H}-\overset{\vert}{C}H-CH_3$	 $CH_3-\overset{CH_3}{\overset{\vert}{C}H}-\overset{OH}{\overset{\vert}{C}H}-CH_3$	3-methylbutan-2-ol

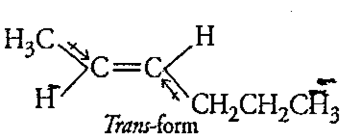
Q-14 Draw the *cis*- and *trans*- structures of hex-2-ene. Which isomer will have higher boiling point and why?

Sol. Hex-2-ene is $CH_3-CH_2-CH_2-CH=CH-CH_3$.

The structures of *cis*- and *trans*- isomers of hex-2-ene are



Cis-form

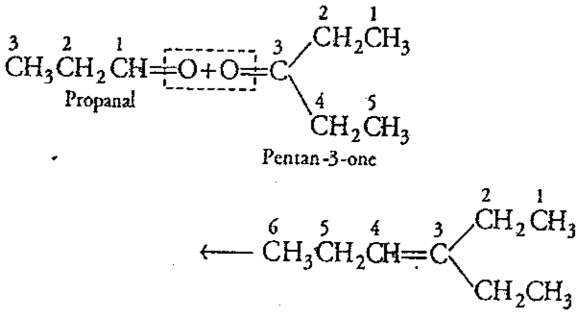


Trans-form

Cis- form is more polar than *trans*-form *i.e.*, *cis*-form has higher dipole moment than *trans*-form. Thus, the boiling point of *cis*-isomer is greater than that of *trans*-isomer because of the greater dipole-dipole interactions between the molecules in it. further more *trans*-isomer of hex-2-ene is almost non-polar.

Q-15 Propanal and pentan-3-one are the ozonolysis products of an alkene. What is the structural formula of the alkene?

Sol.



Propanal

Pentan-3-one

3-ethylhex-3-ene

Q-16 An alkene (molecular weight = 56) on reaction with trioxygen followed by zinc/CH_3COOH gave only ethanal. Identify the structure of the alkene.

Sol. First of all we will derive the molecular formula of alkene, C_nH_{2n}

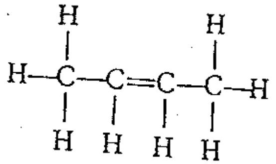
$$12n + 2n = 56$$

or
$$14n = 56$$

$\therefore$
$$n = 4$$

Thus, the molecular formula of alkene is C_4H_8.

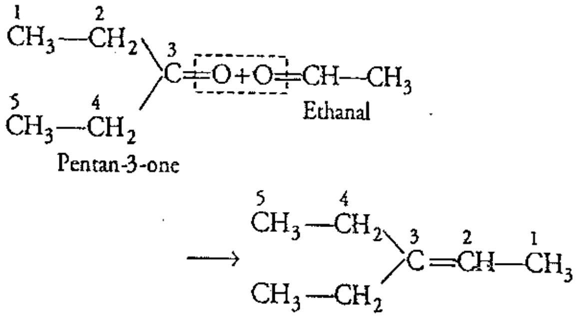
As it is giving only ethanal on reaction with O_3 followed by reduction, the alkene is symmetrical and its structure is



2-butene

Q-17 An alkene *A* on ozonolysis gives a mixture of ethanal and pentan-3-one. Write structure and IUPAC name of *A*.

Sol.



3-ethylpent-2-ene
(*A*)

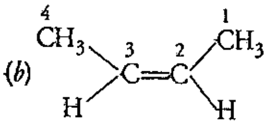
Q-18. For the following compounds, write structural formulae and IUPAC names for all possible isomers having the number of double or triple bond as indicated

(*i*) C_4H_8 (one double bond)
(*ii*) C_5H_8 (one triple bond)

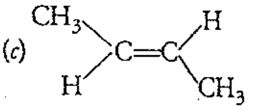
Isomers have the same molecular formula but different structure, so draw all the possible structures for $C_4H_8(C_nH_{2n})$ and C_5H_8 (*i.e.*,C_nH_{2n-2}).

Sol. (*i*) Isomers of C_4H_8 having one double bond are

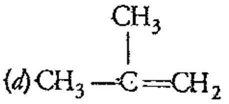
(*a*) $\overset{4}{C}H_3\overset{3}{C}H_2-\overset{2}{C}H=\overset{1}{C}H_2$
But-1-ene

(*b*)


Cis-but-2-ene

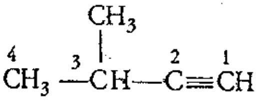
(*c*)


Trans-but-2-ene

(*d*)

$CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2$
2-methylprop-1-ene

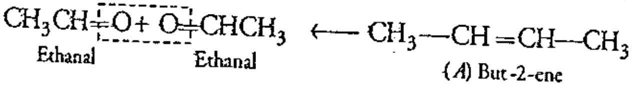
(*ii*) (*a*) $\overset{5}{C}H_3\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{C}\equiv\overset{1}{C}H$
Pent-1-yne

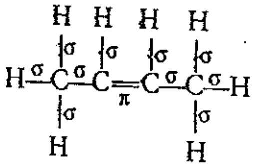
(*b*) $\overset{5}{C}H_3\,\overset{4}{C}H_2-\overset{3}{C}\equiv\overset{2}{C}-\overset{1}{C}H_3$
Pent-2-yne

(*c*)

$\overset{4}{C}H_3-\overset{\overset{CH_3}{|}}{\overset{3}{C}}H-\overset{2}{C}\equiv\overset{1}{C}H$
3-methylbut-1-yne

Q-19, An alkene '*A*' contains three C—C σ-bonds, eight C—H σ-bonds and one C—C π-bond. '*A*' on ozonolysis gives two moles of an aldehyde of molar mass 44 u. Write IUPAC name of '*A*'.

Sol. An aldehyde having molar mass 44 u is ethanal, CH_3CHO. Write the structures of two molecules of ethanal in such a way that their oxygen atoms pointing towards each other. Join the two ends through the double bond with the removal of both of the oxygen atoms to obtain alkene *A*.





Hence, alkene (*A*) is but-2-ene which contains three C—C, eight C—H, σ-bonds and one C—C π-bond (as given in the question).

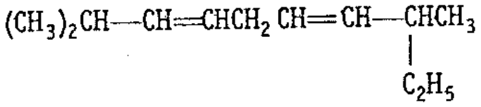
Q-20 Write IUPAC names of the products obtained by the ozonolysis of the following compounds.

(i) Pent-2-ene
(ii) 3,4-dimethylhept-3-ene
(iii) 2-ethylbut-1-ene
(iv) 1-phenylbut-1-ene

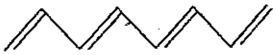
Sol. Solve as before.

(i) propanal + ethanal
(ii) pentan-2-one + butan-2-one
(iii) pentan-2-one + methanal
(iv) propanal + benzaldehyde

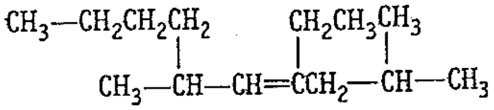
Q-21 Write the IUPAC names of the following compounds.

(i)


$(CH_3)_2CH—CH=CHCH_2\,CH=CH—\underset{\underset{C_2H_5}{|}}{C}HCH_3$

(ii)


(iii) $CH_2=C(CH_2CH_2CH_3)_2$

(iv)


$CH_3—\underset{}{\overset{\overset{CH_3—CH_2CH_2CH_2}{|}}{C}}H—CH=\overset{\overset{CH_2CH_3}{|}}{C}CH_2—\overset{\overset{CH_3}{|}}{C}H—CH_3$

Also calculate the number of σ and π-bonds.

Sol. (i) 2, 8-dimethyldeca-3, 6-diene
σ-bonds = 33, π-bonds = 2

(ii) Octa-1, 3, 5, 7-tetraene
σ-bonds = 17, π-bonds = 4

(iii) 2-propylpent-1-ene
σ-bonds = 23, π-bonds = 1

(iv) 4-ethyl-2, 6-dimethyldec-4-ene
σ-bonds = 41, π-bonds = 1

Q-22 An alkyl halide $C_5H_{11}Br(A)$ reacts with ethanolic KOH to give an alkene '*B*', which reacts with Br_2 to give a compound '*C*', which on dehydrobromination gives an alkyne '*D*'. On treatment with sodium metal in liquid ammonia, one mole of '*D*' gives one mole of the sodium salt of '*D*' and half a mole of hydrogen gas. Complete hydrogenation of '*D*' yields a straight chain alkane. Identify *A*, *B*, *C* and *D*. Give the reactions involved.

Sol. 1 mole of alkyne *D* gives 1 mole of sodium alkynide and $\frac{1}{2}$ mole of H_2. Further more *D* gives straight chain alkane on hydrogenation, and is obtained from five membered compound therefore, *D* must be five membered straight chain terminal alkyne, *i.e.*, 1-pentyne. Since, alkene *B* on reaction with Br_2 forms a compound '*C*' which on dehydrohalogenation, gives 1-pentyne, therefore, '*C*' must be 1,2-dibromopentane and alkene '*B*' must be 1-pentene.

Since, alkene '*B*' is obtained by dehydrohalogenation of alkyl halide, therefore, alkyl halide *A* must be 1-bromopentane. Reactions are as follows

$$\underset{\text{1-bromopentane }(A)}{CH_3CH_2CH_2CH_2CH_2Br} \xrightarrow[-\,HBr]{\text{Alc. KOH},\,\Delta} \underset{\text{1-pentene }(B)}{CH_3CH_2CH_2CH=CH_2} \xrightarrow{Br_2\text{ in }CS_2}$$

$$\underset{\text{1, 2-dibromopentane }(C)}{CH_3CH_2CH_2—\overset{2}{C}HBr—\overset{1}{C}H_2Br} \xrightarrow[-\,2HBr]{\text{Alc. KOH},\,\Delta} \underset{\text{1-pentyne }(D)}{CH_3CH_2CH_2C\equiv CH}$$

$$\xrightarrow{\text{Na in liq. }NH_3} \underset{\text{Sodium 1-pentynide}}{CH_3CH_2CH_2C\equiv C^-Na^+} + \frac{1}{2}H_2$$

Q-23. Suggest the name of a Lewis acid other than anhydrous aluminium chloride which can be used during ethylation of benzene.

Sol. In this reaction, anhydrous $FeCl_3$ or $SnCl_4$ can be used in place of anhydrous $AlCl_3$ as a catalyst.

Q-24 Why does benzene undergo electrophilic substitution reactions easily and nucleophilic substitutions with difficulty?

Sol. Due to the presence of delocalised 6π-electrons, benzene acts as a rich source of electrons. So, it attracts the electrophilic reagent (electron deficient species) towards itself but repels the nucleophilic reagents.

That's why benzene gives electrophilic substitution reactions easily and nucleophilic substitution reaction with difficulty.

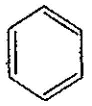
Q-25 Write chemical equation for combustion reaction of toluene.

Sol. $C_7H_8(g) + 9O_2(g) \xrightarrow{\Delta} 7CO_2 + 4H_2O(g)$

Q-26 Arrange benzene, *n*-hexane and ethyne in decreasing order of acidic behaviour. Also give reason for this behaviour.

Higher the s-character, higher is the acidity, so first find hybridisation of all the given compounds and then compare their acidity.

Sol. The hybridisation state of carbon in the given compounds is.


; $CH_3—(CH_2)_4—CH_3$; $H—C \equiv C—H$

Benzene   *n*-hexane   Ethyne

Type of hybridisation	sp^2	sp^3	sp
s-character	33.33%	25%	50%

Acidic character increases with increase in *s*-character of the orbital. Hence, decreasing order of acidic behaviour of ethyne > benzene > hexane

Q-27. Out of benzene, *m*-dinitrobenzene and toluene which will undergo nitration most easily and why?

Nitration is an electrophilic substitution reaction and reactivity of benzene nucleus towards E^+ decreases in the presence of electron withdrawing group while increases in the presence of electron releasing group.

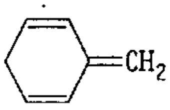
Sol. Nitration of benzene is an electrophilic substitution reaction. Presence of electron releasing group such as $—CH_3$ activates the benzene nucleus towards electrophilic substitution while presence of electron withdrawing group such as $—NO_2$ deactivates the benzene nucleus towards electrophilic substitution. Therefore, the ease of nitration decreases in the order

Toluene > benzene > *m*-dinitrobenzene

Thus, toluene will undergo nitration most easily.

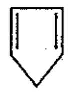
Q-28 Explain why the following systems are not aromatic?

(*i*)



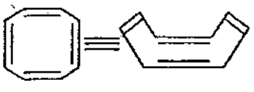
Non-atomatic

(*ii*)



Non-aromatic

(*iii*)



Non-aromatic

For a molecule to be aromatic. It should be planar *i.e.*, all the carbons are sp^2 hybridised. It contains $(4n+2)$ π electron.

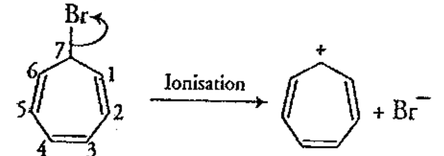
Sol. (*i*) The molecule is non-planar because of the presence of sp^3 hybridised carbon atom. It contains six π-electrons but its π-electron cloud does not surround all the carbon atoms of the ring. Therefore, it is not an aromatic compound.

(*ii*) The molecule is not planar because of the presence of sp^3 hybridised carbon atom Moreover, it contains only 4π-electrons.Thus the molecule is not aromatic as it does not contain planar cyclic electron cloud, having $(4n+2)$ π-electrons.

(*iii*) Cyclo octatetraene is non-planar with 8π-electrons and hence, it is not aromatic.

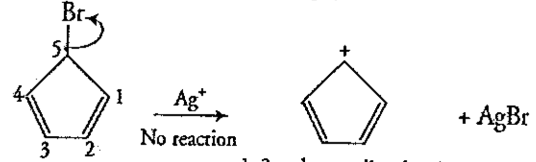
Q-29. 7-bromo-1, 3, 5-cycloheptatriene exists as an ion whereas 5-bromo-1, 3-cyclopentadiene does not form an ion even in presence of Ag^+. Explain.

Sol. 7-bromo-1, 3, 5-cycloheptatriene, on ionisation, gives tropylium ion. Since, tropylium ion contains 6π-electrons which are completely delocalised, therefore, according to Huckel rule, it is aromatic and hence stable. Being highly stable, it is easily formed.



7-bromo-1, 3, 5-cycloheptatriene

Tropylium ion (6π-electrons, aromatic, highly stable)



5-bromo-1, 3-cyclopentadiene

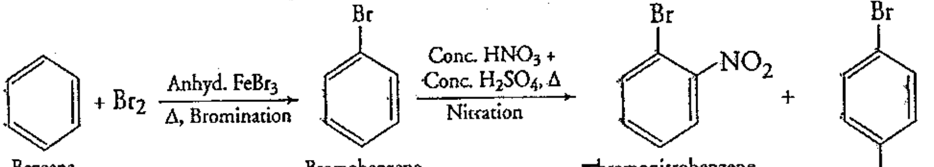
1, 3-cyclopentadienyl cation (4π-electrons, aromatic, highly stable)

In contrast, 5-bromo-1,3-cyclopentadiene, on ionisation, will give 1, 3-cyclopentadienyl cation which contains 4π-electrons and hence, is anti-aromatic. Being anti-aromatic, it is highly unstable and hence is not formed even in the presence of Ag^+ ion which otherwise facilitates ionisation.

Q-30. How will you convert benzene into

(*i*) *p*-nitrobromobenzene (*ii*) *m*-nitrochlorobenzene
(*iii*) *p*-nitrotoluene (*iv*) acetophenone?

Sol. (*i*) Since, the two substituents in the benzene ring are present at *p*-position, therefore, the first substituent in the benzene ring should be an *o*, *p*-directing group



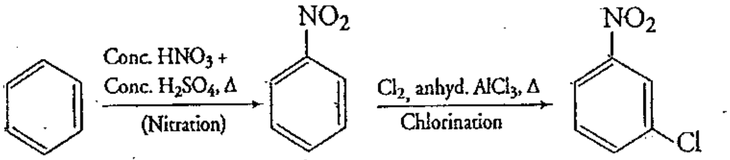
Benzene

Bromobenzene

[illegible]-bromonitrobenzene (minor)

p-bromonitrobenzene (major)

(*ii*) Since, the two substituents in the benzene ring are present at *m*-positions, therefore, the first substituent in the benzene ring should be *m*-directing.

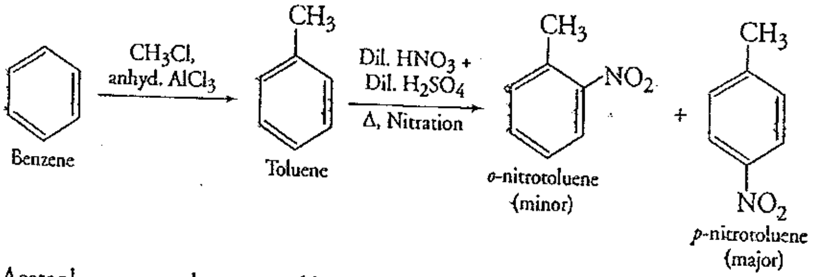


Benzene

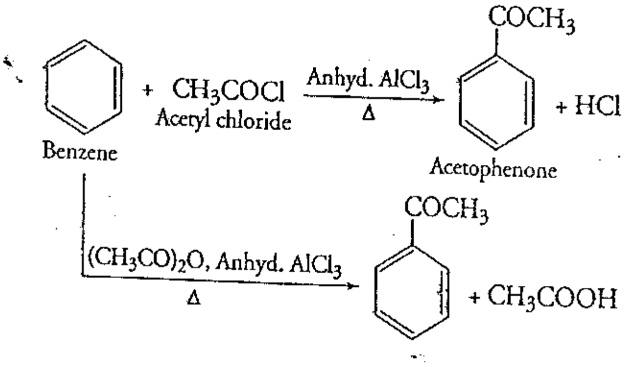
Nitrobenzene

m-chloronitrobenzene

(iii)



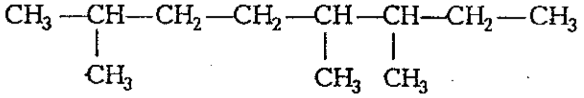
(iv) Acetophenone can be prepared by Friedel Crafts acylation.



SARASWATI CHEMISTRY

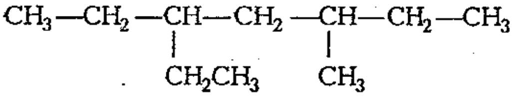
Organic Chemistry Some Basic Principles and Techniques

Q-1 Structures and IUPAC names of some hydrocarbons are given below. Explain why the names given in the parentheses are incorrect.

(*i*)


$CH_3-CH(CH_3)-CH_2-CH_2-CH(CH_3)-CH(CH_3)-CH_2-CH_3$

2,5,6-trimethylocatane
[and not 3,4,7-trimethyloctane]

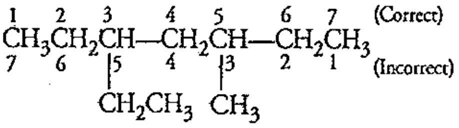
(*ii*)


$CH_3-CH_2-CH(CH_2CH_3)-CH_2-CH(CH_3)-CH_2-CH_3$

3-ethyl-5-methylheptane
[and not 5-ethyl-3-methylheptane]

Solution

(*i*) Because locant number, 2, 5, 6 is lower than 3, 4, 7,

(*ii*)


$\overset{1}{C}H_3\overset{2}{C}H_2\overset{3}{C}H(CH_2CH_3)-\overset{4}{C}H_2\overset{5}{C}H(CH_3)-\overset{6}{C}H_2\overset{7}{C}H_3$ (Correct)

7 6 5 4 3 2 1 (Incorrect)

Since, substituents are in equivalent position so lower number is given to ethyl which comes first in the name according to alphabetical order.

Q-2 What is the shape of the following compounds?

(*i*) $H_2C{=}O$ (*ii*) CH_3F (*iii*) $HC{\equiv}N$

Sol. (*i*) sp^2 hybridised carbon ⟶ trigonal planar

(*ii*) sp^3 hybridised carbon ⟶ tetrahedral

(*iii*) *sp* hybridised carbon ⟶ linear

Q-3 What are primary and secondary suffixes as applied to IUPAC nomenclature?

Sol. The primary suffix indicates whether the carbon chain is saturated or unsaturated while the secondary suffix indicates the functional group present in the molecule.

Q-4 Which of the following represents the correct IUPAC name for the compounds concerned?

(*i*) 2,2-dimethylpentane or 2-dimethylpentane

(*ii*) 2,4,7-trimethyloctane or 2,5,7-trimethyloctane

(*iii*) 2-choloro-4-methylpentane or 4-chloro-2-methylpentane

(*iv*) But -3-yn-1-ol or But-4-ol-1-yne

Sol. (*i*) 2,2-dimethylpentane (because for the two alkyl groups o the same carbon, its locant is repeated twice)

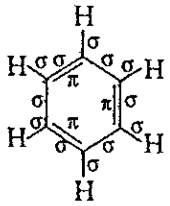
(*ii*) 2, 4, 7-trimethyloctane (because 2, 4, 7-locant set is lowe than 2, 5, 7).

(*iii*) 2-chloro-4-methylpentane. (Alphabetical order substituents) (iv) But-3-yn-1-ol (because lower locant fc the principal functional group, *i.e.*, alcohol).

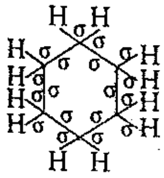
Q-5 Indicate the σ- and π-bonds in the following molecules. C_6H_6, C_6H_{12}, CH_2Cl_2, $CH_2{=}C{=}CH_2$, CH_3NO_2, $HCONHCH_3$

Single bonds are only σ bonds, double bond contains one σ and one π bond and triple bond contains one σ and two π bonds. Mark σ and π bonds on this basis.

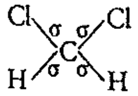
Sol.



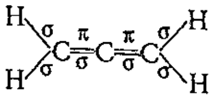
(12σ, 3π)



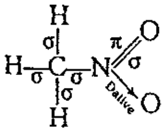
(18σ)



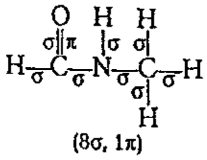
(4σ)



(6σ, 2π)



(6σ, 1π)

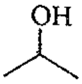


(8σ, 1π)

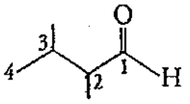
Q-6 Write bond-line formulas for : *Iso*-propyl alcohol, 2,3-dimethylbutanal, heptan-4-one.

To draw the bond line formulae of the given compounds, first draw the complete structure of each compound and then convert it into bond line formula in which joint represent the carbon atoms. In such a structure, H-atoms remain hidden.

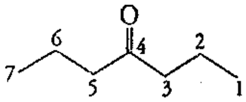
Sol.



Iso-propyl alcohol ,



2,3-dimethylbutanal ,



Heptan-4-one

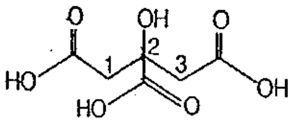
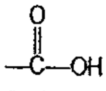
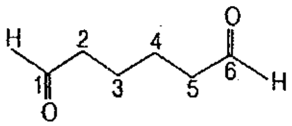
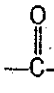
Q-7 Give condensed and bond line structural formulae and identify the functional group(s) present, if any, for

(*i*) 2,2,4-trimethylpentane

(*ii*) 2-hydroxy-1,2,3-propanetricarboxylic acid

(*iii*) Hexanedial.

Sol.

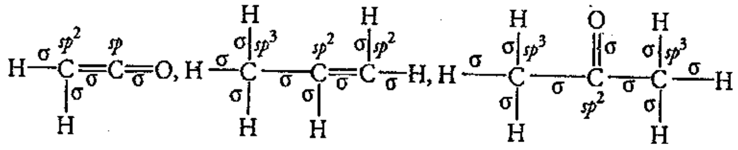
S. No.	Condensed formula	Bond line formula	Functional groups
(i)	$(CH_3)_3CCH_2CH(CH_3)_2$		—
(ii)	$HOOCCH_2C(OH)(COOH)CH_2COOH$		 $-\overset{\overset{O}{\parallel}}{C}-OH$ (carboxyl) and —OH (hydroxyl)
(iii)	$OHC(CH_2)_4CHO$		 $-\overset{\overset{O}{\parallel}}{C}-H$ (aldehyde)

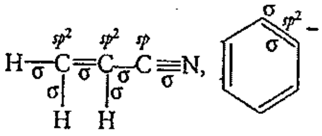
Q-8 What are hybridisation states of each carbon atom in the following compounds?

$CH_2{=}C{=}O, CH_3CH{=}CH_2, (CH_3)_2CO, CH_2{=}CHCN, C_6H_6$

- Hybridisation depends upon the number of σ bond formed by an atom. If number of σ bonds is 2, hybridisation is sp, if 3, sp^2, if 4, sp^3 and so on. So count the number of σ bonds and find the hybridisation.

Sol.

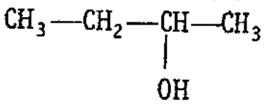


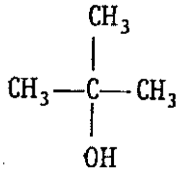


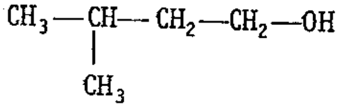
In benzene, each C is sp^2-hybridised

Q-9 Consider structures I to VII and answer following the questions (I) to (II).

I. $CH_3{-}CH_2{-}CH_2{-}CH_2{-}OH$

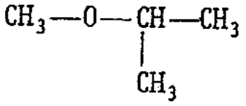
II. 
$CH_3{-}CH_2{-}\underset{\underset{\displaystyle OH}{|}}{CH}{-}CH_3$

III. 
$CH_3{-}\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}{-}CH_3$

IV. 
$CH_3{-}\underset{\underset{\displaystyle CH_3}{|}}{CH}{-}CH_2{-}CH_2{-}OH$

V. $CH_2{-}CH_2{-}O{-}CH_2{-}CH_3$

VI. $CH_2{-}O{-}CH_2{-}CH_2{-}CH_3$

VII. 
$CH_3{-}O{-}\underset{\underset{\displaystyle CH_3}{|}}{CH}{-}CH_3$

(*i*) Which of the above compounds form metamer's pairs?

(*ii*) Identify the pairs of compounds which are functional group isomers.

(*iii*) Identify the pairs of compounds that represent position isomerism.

(*iv*) Identify the pairs of compounds that represent chain isomerism.

Sol. (*i*) V and VI or V and VII form a pair of metamers since they differ in the number of carbon atoms on the either side fo the functional group, *i.e.*, O-atom.

(*ii*) I and V, I and VI, I and VII; II and V, II and VI, II and VII; III and VII; III and V, II and VI; III and VII; IV and V; IV and VI and IV and VII are all functional group isomers.

(*iii*) I and II, III and IV and, VI and VII represent position isomerism.

(*iv*) I and III, I and IV, II and III and II and IV represent chain isomerism.

Q-10 Classify the following reactions in one of the reaction type studied in this unit.

(*i*) $CH_3CH_2Br + HS^- \longrightarrow CH_3CH_2SH + Br^-$

(*ii*) $(CH_3)_2C{=}CH_2 + HCl \longrightarrow (CH_3)_2CCl{-}CH_3$

(*iii*) $CH_3CH_2Br + HO^- \longrightarrow CH_2{=}CH_2 + H_2O + Br^-$

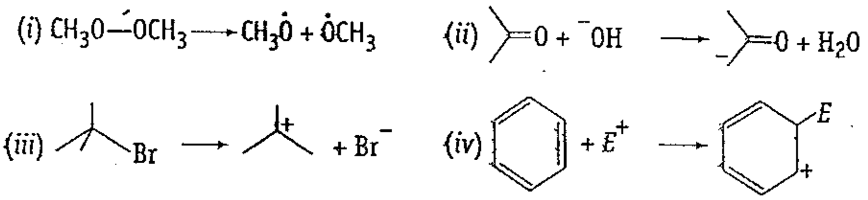
(*iv*) $(CH_3)_3C{-}CH_2OH + HBr \longrightarrow (CH_3)_2CBrCH_2CH_3 + H_2O$

- A nucleophile (Br^-) is substituted by other nucleophile (HS^-).
- HCl is added to the double bond (C=C).
- H and Br are eliminated from successive carbon atoms.
- Nucleophile (OH^-) is substituted by Br^-.

Sol. (*i*) Nucleophilic substitution reaction (*ii*) Electrophilic addition reaction

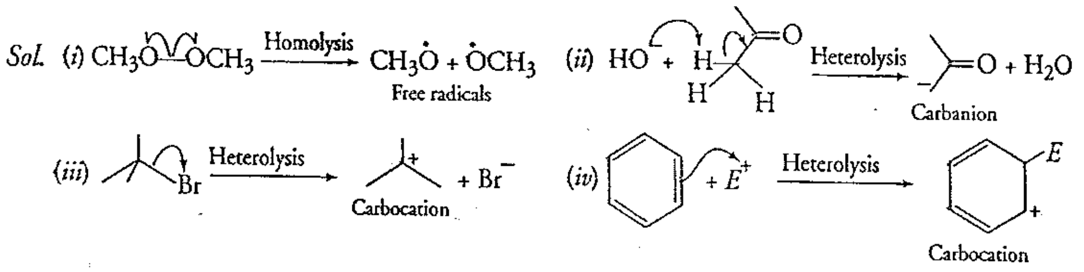
(*iii*) β-elimination reaction (*iv*) Nucleophilic substitution reaction with rearrangement.

Q-11 For the following bond cleavages, use curved-arrows to show the electron flow and classify each as homolysis or heterolysis. Identify reactive intermediate produced as free radical, carbocation and carbanion.



Free radicals are the result of homolysis while ions (carbanion or carbocation) are formed when reactant undergoes heterolysis.

Sol.



Q-12 On complete combustion, 0.246 g of an organic compound gave 0.198 g of carbon dioxide and 0.1014 g of water. Determine the percentage composition of carbon and hydrogen in the compound.

Solution Percentage of carbon $= \dfrac{12 \times 0.198 \times 100}{44 \times 0.246} = 21.95\%$

Percentage of hydrogen $= \dfrac{2 \times 0.1014 \times 100}{18 \times 0.246} = 4.58\%$

Q-13 In Dumas method for estimation of nitrogen, 0.3 g of an organic compound gave 50 mL of nitrogen collected at 300 K temperature and 715 mm pressure. Calculate the percentage composition of nitrogen in the compound. (Aqueous tension at 300 K = 15 mm).

Solution Volume of nitrogen collected at 300 K and 715 mm pressure = 50 mL

Actual pressure = 715 − 15 = 700 mm

Volume of nitrogen at STP $= \dfrac{273 \times 700 \times 50}{300 \times 760} = 41.9$ mL

22,400 mL of N_2 at STP weighs = 28 g

∴ 41.9 mL of nitrogen weighs $= \dfrac{28 \times 41.9}{22400}$ g

∴ Percentage of nitrogen $= \dfrac{28 \times 41.9 \times 100}{22400 \times 0.3} = 17.46\%$

Q-14 During estimation of nitrogen present in an organic compound by Kjeldahl's method, the ammonia evolved from 0.5 g of the compound in Kjeldahl's estimation of nitrogen, neutralized 10 mL of 1 M H_2SO_4. Find out the percentage of nitrogen in the compound.

Solution 1 M of 10 mL H_2SO_4 = 1 M of 20 mL NH_3

1000 mL of 1 M ammonia contains nitrogen = 14 g

$\therefore$ 20 mL of 1 M ammonia will contain nitrogen $= \dfrac{14 \times 20}{1000}$ g

$\therefore$ Percentage of nitrogen $= \dfrac{14 \times 20 \times 100}{1000 \times 0.5} = 56.0\%$

Kjeldahl's method is not applicable to compounds containing nitrogen in nitro and azo groups and nitrogen present in the ring, as nitrogen of these compounds is not quantitatively converted into ammonium sulphate.

Q-15 In carius method of estimation of halogen, 0.15 g of an organic compound gave 0.12 of AgBr. Find out the percentage of bromine in the compound.

Solution $\dfrac{80}{188} \times \dfrac{\text{wt. of AgBr} \times 100}{\text{wt. of compound}}$

Percentage of bromine $= \dfrac{80 \times 0.12 \times 100}{188 \times 0.15} = 34.04\%$

Q-16 In sulphur estimation, 0.157 g of an organic compound gave 0.4813 g of barium sulphate. What is the percentage of sulphur in the compound ?

Solution Percentage of sulphur

$$= \frac{32 \times \text{mass of } BaSO_4 \times 100}{233 \times \text{mass of compound}} = \frac{32 \times 0.4813 \times 100}{233 \times 0.157}$$

= 42.10%

Q-17 Name a suitable technique of separation of the components from a mixture of calcium sulphate and camphor.

Camphor is a suplimate while $CaSO_4$ is not. A sublimate from a non-sublimate is separated by sublimation.

Sol. A mixture of $CaSO_4$ and camphor can be separated by sublimation. Because camphor is sublimable but $CaSO_4$ is not therefore, sublimation of the mixture gives camphor on the sides of funnel while $CaSO_4$ is left in the China dish.

Q-18 Explain the reason for the fusion of an organic compound with metallic sodium for testing nitrogen, sulphur and halogens.

Sol. Nitrogen, sulphur and halogens are present in an organic compound in covalent form so their detection is not easy.

Q-19. Lassaigne's test is not shown by diazonium salts, though they contain nitrogen. Why?

Sol. Diazonium salts ($C_6H_5N_2^+X^-$) readily lose N_2 on heating before reacting with fused sodium metal. Therefore, these do not give positive Lassaigne's test for nitrogen.

Q-20 Will CCl_4 give white precipitate of AgCl on heating it with silver nitrate? Give reason for your answer.

CCl_4 is a covalent compound and does not give Cl^- ions.

Sol. CCl_4 will not give a white ppt of AgCl with $AgNO_3$ solution because CCl_4 is a covalent compound. It does not ionise to give Cl^- ions required for the formation of AgCl precipitate.

Q-21. Suggest methods for the separation of the following mixtures

(*i*) a mixture of liquid *A* (bp 365K) and liquid *B* (bp 355 K)

(*ii*) a mixture of liquid *C* (bp 348 K) and liquid *D* (bp 478 K).

Sol. (*i*) Fractional distillation because the boiling points of the two liquids differ by only 10°.

(*ii*) Simple distillation because the boiling points of the two liquids differ much.

Q-22 Why is it necessary to use acetic acid and not sulphuric acid for acidification of sodium extract for testing sulphur by lead acetate test?

Sol. If H_2SO_4 is used, lead acetate itself will react with H_2SO_4 to form white ppt. of lead sulphate.

$$\underset{\text{Lead acetate}}{Pb(OCOCH_3)_2} + H_2SO_4 \longrightarrow \underset{\text{White ppt}}{PbSO_4\downarrow} + 2CH_3COOH$$

Hence, white precipitate of $PbSO_4$ will interfere with the following test of sulphur.

$$Pb(CH_3COO)_2 + Na_2S \longrightarrow \underset{\text{Black ppt}}{PbS\downarrow} + 2CH_3COONa$$

However, if acetic acid is used, it does not react with lead acetate, so does not interfere in the test.

Q-23 Why is a solution of potassium hydroxide used to absorb carbon dioxide evolved during the estimation of carbon present in an organic compound?

Sol. CO_2 is slightly acidic in nature, therefore, it reacts with the strong base KOH to form K_2CO_3 and from the weight of the CO_2 obtained, percentage of carbon in the organic compound is calculated.

$$2\,KOH + CO_2 \longrightarrow K_2CO_3 + H_2O$$

The increase in the weight of U-tube containing KOH gives the weight of CO_2 produced and from the weight of the CO_2 obtained, percentange of carbon in the organic compound is calculated as,

$$\text{\% of carbon} = \frac{12}{44} \times \frac{\text{weight of } CO_2 \text{ formed}}{\text{weight of substance taken}} \times 100$$

Q-24 In the estimation of sulphur by Carius method, 0.468 g of an organic sulphur compound afforded 0.668 g of barium sulphate. Find the percentage of sulphur in the given compound.

Sol.

$$\text{\% of sulphur} = \frac{32}{233} \times \frac{\text{mass of } BaSO_4 \text{ formed}}{\text{mass of substance taken}} \times 100$$

$$= \frac{32}{233} \times \frac{0.668}{0.468} \times 100 = 19.60\%$$

Q-25 • 0.3780 g of an organic chloro compound gave 0.5740 g of silver chloride in Carius estimation. Calculate the percentage of chlorine present in the compound.

Sol. $\text{\% of chlorine} = \frac{35.5}{143.5} \times \frac{\text{mass of AgCl formed}}{\text{mass of substance taken}} \times 100 = \frac{35.5}{143.5} \times \frac{0.5740}{0.3780} \times 100 = 37.566\%$

Q-26 A sample of 0.50 g of an organic compound was treated according to Kjeldahl's method. The ammonia evolved was absorbed in 50 mL of 0.5 M H_2SO_4. The residual acid required 60 mL of 0.5 M solution of NaOH for neutralisation. Find the percentage composition of nitrogen in the compound.

- Calculate the volume of the H_2SO_4 used to neutralise NaOH.
- Calculate percentage of nitrogen by using the formula $N\% = \frac{1.4 \times NV}{w}$

Sol. Volume of the acid taken = 50 mL of 0.5 M H_2SO_4

= 25 mL of 1.0 M H_2SO_4

Volume of alkali used for neutralisation of excess acid

= 60 mL of 0.5 M NaOH

= 30 mL of 1.0 M NaOH

$$H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2H_2O$$

1 mole of H_2SO_4 = 2 moles of NaOH

Hence, 30 mL of 1.0 M NaOH = 15 mL of 1.0 M H_2SO_4

∴ Volume of acid used by ammonia = 25 − 15 = 10 mL

$$\text{\% of nitrogen} = \frac{1.4 \times N_1 \times \text{vol. of acid used}}{w}$$

(where, N_1 = normality of acid and w = mass of the organic compound taken)

$$\text{\% of nitrogen} = \frac{1.4 \times 2 \times 10}{0.5} = 56.0$$

Q-27 An organic compound contains 69% carbon and 4.8% hydrogen, the remainder being oxygen. Calculate the masses of carbon dioxide and water produced when 0.20 g of this substance is subjected to complete combustion.

Sol.

$$\%C = \frac{12}{44} \times \frac{\text{Mass of } CO_2 \text{ formed}}{\text{Mass of substance taken}} \times 100$$

$$69 = \frac{12}{44} \times \frac{\text{Mass of } CO_2 \text{ formed}}{0.2} \times 100$$

$$\therefore \text{ Mass of } CO_2 \text{ formed} = \frac{69 \times 44 \times 0.2}{12 \times 100} = 0.506 \text{ g}$$

$$\%H = \frac{2}{18} \times \frac{\text{Mass of } H_2O \text{ formed}}{\text{Mass of substance taken}} \times 100$$

$$4.8 = \frac{2}{18} \times \frac{\text{Mass of } H_2O \text{ formed}}{0.2} \times 100$$

$$\therefore \text{ Mass of } H_2O \text{ formed} = \frac{4.8 \times 18 \times 0.2}{2 \times 100} = 0.0864 \text{ g}$$

The *p*-Block Elements

SARASWATI CHEMISTRY

Q-1 Standard electrode potential values, $E^\ominus$ for Al^{3+}/Al is -1.66 V and that of Tl^{3+}/Tl is $+1.26$ V. Predict about the formation of M^{3+} ion in solution and compare the electropositive character of the two metals.

Solution Since, E° values are more negative in case of Al, so it has higher tendency to form $Al^{3+}(aq)$ ions, whereas Tl^{3+} is highly unstable in aqueous solution and acts as a good oxidising agent. It readily reduces to more stable Tl^+ ion. Al^{3+} being stable, exists in this form and hence, Al is more electropositive as compared to Tl.

Q-2 Why is boric acid considered as a weak acid?

Solution Boric acid is incapable to release H^+ ions by its own. It only receives OH^- ions from water molecule to complete its octet and in turn releases H^+ ions. That's why it is considered as a weak acid.

Q-6 Why does boron trifluoride behave as a Lewis acid?

Lewis acids have a tendency to accept electrons, *i.e.*, they are electron deficient.

Sol. BF_3 being electron deficient, is a strong Lewis acid. It reacts with Lewis bases easily to complete the octet around boron.

$$\underset{\text{Lewis acid}}{F_3B} + \underset{\text{Lewis base}}{:NH_3} \longrightarrow F_3B \leftarrow NH_3$$

Q-7 Atomic radius of gallium (135 pm) is less than that of aluminium (143 pm).

Sol. It is due to poor shielding effect of 3*d*-electrons due to which effective nuclear charge increases in Ga, therefore, it is smaller than Al.

Q-3 Is boric acid a protic acid? Explain.

Sol. It is not a protic acid because it does not ionise in H_2O to give a proton. It acts as a Lewis acid by accepting electrons from a hydroxyl ion of water and in turn releases H^+ ions.

$$B(OH)_3 + HOH \longrightarrow [B(OH)_4]^- + H^+$$

Q-4. How can you explain higher stability of BCl_3 as compared to $TlCl_3$?

Sol. Boron exhibits only +3 oxidation state. So, it forms BCl_3, a stable compound. On moving down the group, the inert pair effect becomes more and more pronounced therefore, in thallium +1 oxidation state is more stable than +3 oxidation state. That's why BCl_3 is more stable than $TlCl_3$.

Q-5 Discuss the pattern of variation in the oxidation states of B to Tl.

Sol.

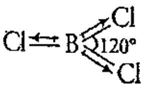
Element	B	Al	Ga	In	Tl
Oxidation state	+3	+3	+3, +1	+3, +1	+1

Boron and aluminium show an oxidation state of +3 only because they do not exhibit inert pair effect due to the absence of *d* or *f*-electrons. Elements from Ga to Tl show two oxidation states, *i.e.*, +1 and +3. The tendency to show +1 oxidation state increases down the group due to the inability of ns^2 electrons of valence shell to participate in bonding which is called inert pair effect.

Therefore, Tl^+ is more stable than Tl^{3+}.

Q-8 If B—Cl bond has a dipole moment, explain why BCl_3 molecule has zero dipole moment?

Sol. Boron in BCl_3 is sp^2 hybridised, due to this the shape of BCl_3 molecule is trigonal planar. It is symmetrical in shape. The net dipole moment for symmetrical molecule is zero (because individual dipole moments cancel out due to the symmetry of the molecule).

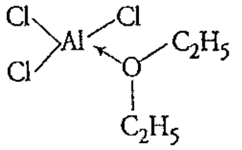


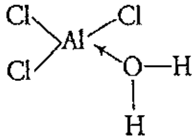
$$\mu = 0$$

Thus, dipole moment of BCl_3 is zero.

Q-9 Which one is more soluble in diethyl ether, anhydrous $AlCl_3$ or hydrated $AlCl_3$? Explain in terms of bonding.

Sol. Anhydrous $AlCl_3$ is an electron-deficient compound while hydrated $AlCl_3$ is not. Therefore, anhydrous $AlCl_3$ is more soluble in diethyl ether because the oxygen atom of ether donates a pair of electrons to the vacant *p*-orbital on the Al atom in $AlCl_3$ forming a coordinate bond.





In case of hydrated $AlCl_3$, Al is not electron deficient since H_2O has already donated a pair of electrons to it.

Q-10 Give reasons

(*i*) Conc. HNO_3 can be transported in aluminium container.

(*ii*) A mixture of dilute NaOH and aluminium pieces is used to open drain.

Sol. (*i*) Al reacts with conc. HNO_3 to form a protective layer of aluminium oxide on its surface which prevents it from further reaction.

$$2Al(s) + 6HNO_3(\text{conc.}) \longrightarrow \underset{\substack{\text{Alumina} \\ \text{(a passive protective layer)}}}{Al_2O_3(s)} + 6NO_2(g) + 3H_2O(l)$$

Therefore, Al becomes passive that's why aluminium containers can be used to transport conc. HNO_3.

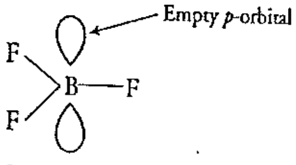
(*ii*) NaOH reacts with Al to evolve dihydrogen gas. The pressure of the hydrogen gas can be used to open drains.

$$2Al(s) + 2NaOH(aq) + 2H_2O(l) \longrightarrow 2NaAlO_2(aq) + 2H_2(g)$$

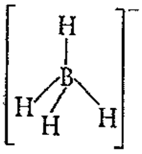
Q-11 Describe the shapes of BF_3 and $[BH_4]^-$. Assign the hybridisation of boron in these species.

Sol. In BF_3, boron is sp^2-hybridised as it contains three bond pairs and, therefore, BF_3 molecule is trigonal planar in shape.

On the other hand, in $[BF_4]^-$ boron is sp^3-hybridised because of the presence of four bond pairs and hence $[BF_4]^-$ species is tetrahedral in shape.



BF_3 sp^2-hybridised
Trigonal planar shape



$[BH_4]^-$, sp^2-hybridised
Tetrahedral shape

Q-12 In some of the reactions, thallium resembles aluminium, whereas in others it resembles with group I metals. Support this statement by giving some evidences.

Sol. Thallium and aluminium both the elements belong to group 13. Their general electronic configuration for the valence shell is ns^2np^1. Aluminium shows only +3 oxidation state.

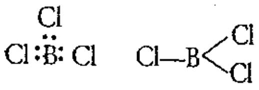
Like Al, thallium also shows +3 oxidation state in some compounds like Tl_2O_3, $TlCl_3$, etc. Like aluminium, thallium also forms octahedral ions like $[AlF_6]^{3-}$ and $[TlF_6]^{3-}$.

Like group-I alkali metals, thallium shows +1 oxidation state due to inert pair effect in some compounds like TlCl, Tl_2O, etc., Like alkali metal hydroxides, TiOH is water soluble and its aqueous solution is strongly alkaline. Tl_2SO_4 also forms alums like alkali metal sulphates. Tl_2CO_3 is soluble in water like alkali metal carbonates.

Q-13 What are electron deficient compounds? Are BCl_3 and $SiCl_4$ electron deficient species? Explain.

Sol. Electron deficient compounds are those in which the octet of all the atoms is not complete *i.e.*, all the elements present in the compound do not have $8\,e^-$ in their outer shell.

In trivalent state, the number of electrons around the central atom B in BCl_3 is six.



Such (electron deficient) molecules have a tendency to accept a pair of electrons to achieve stability and hence, behave as Lewis acids.

Q-14 Aluminium trifluoride is insoluble in anhydrous HF but dissolves on addition of NaF. Aluminium trifluoride precipitates out of the resulting solution when gaseous BF_3 is bubbled through. Give reasons.

Sol. (*i*) Anhydrous HF is a covalent compound and is strongly H-bonded. Therefore, it does not give F^- ions and hence AlF_3 does not dissolve in HF. NaF is an ionic compound. It contains F^- ions which combine with electron deficient AlF_3 to form the soluble complex.

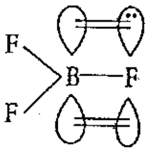
$$3NaF + AlF_3 \longrightarrow \underset{\substack{\text{Sodium hexafluoroaluminate (III)} \\ \text{(soluble complex)}}}{Na_3[AlF_6]}$$

(*ii*) Boron due to its small size and higher electronegativity has greater tendency to form complexes than aluminium. Hence, precipitation of AlF_3 takes place when BF_3 is passed through $Na_3[AlF_6]$ solution.

$$Na_3[AlF_6] + 3BF_3 \longrightarrow \underset{\substack{\text{Sodium tetrafluoroborate (III)} \\ \text{(soluble complex)}}}{3Na^+[BF_4]^-} + AlF_3(g)$$

Q-15 Suggest reason why the B—F bond lengths in BF_3 (130 pm) and BF_4^- (143 pm) differ?

Sol. In BF_3, boron is sp^2 hybridised. It has as vacant 2*p*-orbital. Each fluorine in BF_3 has completely filled unutilised 2*p*-orbitals. Since, both of these orbitals belong to same energy level so $p\pi$-$p\pi$ back bonding occurs in which a lone pair of electrons is transferred from unutilised completely filled 2*p*-orbital of F to vacant 2*p*-orbital of B. This type of bond formation is known as back bonding. Therefore, B—F bond has some double bond character. That's why all the three boron-fluorine bonds are shorter than the usual single boron-fluorine bond. In $[BF_4]^-$ ion, boron is sp^3-hybridised. It does not have empty 2*p*-orbital so there is no back bonding. In $[BF_4]^-$ ion, all the four B—F bonds are purely single bonds and double bonds are shorter than single bonds. Therefore, B—F bond length in BF_3 is shorter (130 pm) than B—F bond length (143 pm) in $[BF_4]^-$.



Back bonding in BF_3 molecule

Q-16 Explain the following.

(*i*) Aluminium alloys are used to make aircraft body.

(*ii*) Aluminium utensils should not be kept in water overnight.

(*iii*) Aluminium wire is used to make transmission cables.

Sol. (*i*) Aluminium alloys such as duralumin is light, tough and resistant to corrosion and hence, it is used in making aircraft body.

(*ii*) Because aluminium reacts with water and oxygen (dissolved in) to form a thin layer of toxic aluminium oxide on the surface of utensils.

$$2Al(s) + O_2(g) + H_2O(l) \longrightarrow Al_2O_3(s) + H_2(g)$$

(*iii*) Aluminium possesses high electrical conductivity. Therefore, it is used in making transmission cables. Further on weight to weight basis conductivity of aluminium is twice as Cu.

Q-17 A non-metallic element of group 13, used in making bulletproof vests is extremely hard solid of black colour. It can exist in many allotropic forms and has unusually high melting point. Its trifluoride acts as Lewis acid towards ammonia. The element exhibits maximum covalency of four. Identify the element and write the reaction of its trifluoride with ammonia. Explain why does the trifluoride act as a Lewis acid?

Sol. The only non-metallic element of group 13 is boron. It is an extremely hard black substance and is used in making bulletproof vests. It exists in many allotropic forms and has usually high melting point. Since, B has only *s* and *p*-orbitals but no *d*-orbitals, therefore, at the maximum it can exhibit a covalency of four.

$$H_3\ddot{N} + BF_3 \longrightarrow H_3N \rightarrow BF_3$$

Since, B in BF_3 has only six electrons in its valence shell, therefore, it needs two more electrons to complete its octet. Thus, BF_3 acts as a Lewis acid.

Q-18 Write balanced equations for

(*i*) $BF_3 + LiH \longrightarrow$ (*ii*) $B_2H_6 + H_2O \longrightarrow$

(*iii*) $NaH + B_2H_6 \longrightarrow$ (*iv*) $H_3BO_3 \xrightarrow{\Delta}$

(*v*) $Al + NaOH \longrightarrow$ (*vi*) $B_2H_6 + NH_3 \longrightarrow$

Sol. (*i*) $2BF_3 + 6LiH \longrightarrow \underset{\text{Diborane}}{B_2H_6} + 6LiF$

(*ii*) $B_2H_6 + 6H_2O \longrightarrow \underset{\text{Orthoboric acid}}{2H_3BO_3} + 6H_2$

(*iii*) $2NaH + B_2H_6 \longrightarrow \underset{\text{Sodium borohydride}}{2Na^+[BH_4]^-}$

(*iv*) $\underset{\text{Orthoboric acid}}{H_3BO_3} \xrightarrow[370\text{ K}]{\Delta} \underset{\text{Metaboric acid}}{HBO_2} + H_2O$

$$\underset{\text{Metaboric acid}}{4HBO_2} \xrightarrow[-H_2O]{\Delta} \underset{\text{Tetraboric acid}}{H_2B_4O_7} \xrightarrow{\Delta} \underset{\text{Boron trioxide}}{2B_2O_3} + H_2O$$

(*v*) $2Al + 2NaOH + 6H_2O \longrightarrow \underset{\text{Sodium tetrahy-droxoaluminate (III)}}{2Na^+[Al(OH)_4]^-} + 3H_2$

(*vi*) (*a*) $B_2H_6 + 2NH_3 \longrightarrow \underset{\text{Borane-ammonia complex (Adduct)}}{2BH_3 \cdot NH_3}$

or $[BH_2(NH_3)_2]^+ [BH_4]^-$

(*b*) $3B_2H_6 + 6NH_3 \longrightarrow$

$$3[BH_2(NH_3)_2]^+[BH_4]^- \xrightarrow{\Delta} \underset{\text{Borazine (Inorganic benzene)}}{2B_3N_3H_6} + 12H_2$$

Q-19 A certain salt *X*, gives the following results.

(*i*) Its aqueous solution is alkaline to litmus.

(*ii*) It swells up to a glassy material *Y* on strong heating.

(*iii*) When conc. H_2SO_4 is added to a hot solution of *X*, white crystals of an acid *Z* separate out. Write equations for all the above reactions and identify *X*, *Y* and *Z*.

Borax swells up to a glassy mass on strong heating.

Sol. (*i*) Aqueous solution of salt *X* is alkaline. It indicates that '*X*' is the salt of a strong base and a weak acid.

(*ii*) On strong heating, the salt '*X*' swells up to a glassy material *Y*. It indicates that the salt '*X*' is borax.

(*iii*) Hot aqueous solution of borax on reaction with conc. H_2SO_4 gives crystals of orthoboric acid.

The equations for the reactions involved in the question are as follows

(*a*) $Na_2B_4O_7 + 7H_2O \longrightarrow \underset{\text{Strong base}}{2NaOH} + \underset{\text{Weak acid}}{4H_3BO_3}$

(b) $\underset{(X)}{Na_2B_4O_7 \cdot 10H_2O} \xrightarrow{\Delta} \underset{\text{Anhydrous (swollen white mass)}}{Na_2B_4O_7} + 10H_2O$

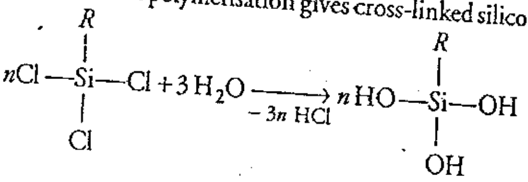
$$Na_2B_4O_7 \xrightarrow{\Delta} \underset{\text{Glassy bead, } Y}{2NaBO_2 + B_2O_3}$$

Glassy material '*Y*' consists of sodium metaborate and boric anhydride.

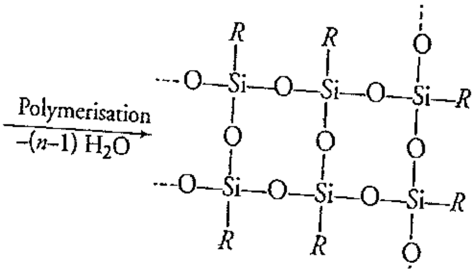
(*iii*) $\underset{(X)}{Na_2B_4O_7 \cdot 10H_2O} + H_2SO_4 \longrightarrow \underset{\substack{\text{Orthoboric acid}\\(Z)}}{4H_3BO_3} + Na_2SO_4 + 5H_2O$

Q-20 If the starting material for the manufacture of silicones is $RSiCl_3$, write the structure of the product formed.

Sol. Hydrolysis of alkyltrichlorosilanes followed by condensation polymerisation gives cross-linked silicones.



$$n\,Cl-\overset{R}{\underset{Cl}{Si}}-Cl + 3H_2O \xrightarrow[-3n\text{ HCl}]{} n\,HO-\overset{R}{\underset{OH}{Si}}-OH$$



Cross-linked silicone

Q-21 Suggest a reason as to why CO is poisonous?

Sol. Carbon monoxide reacts with haemoglobin and form a stable compound carboxyheamoglobin. Carboxyheamoglobin is 300 times more stable than oxyhaemoglobin. Formation of carboxyhaemoglobin reduces the oxygen carrying capacity of the blood, as a result of this suffocation takes place. Low level poisoning results in headache and drowsiness, high level poisoning may cause death.

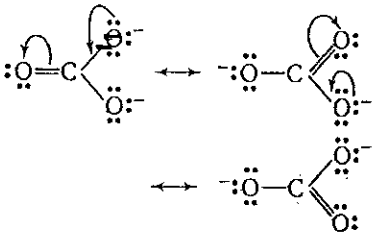
Q-22 Explain why is there a phenomenal decrease in ionisation enthalpy from carbon to silicon?

Sol. As we move from carbon to silicon atomic size increases, *i.e.,* the distance between the outermost electron and nucleus increases. Thus, this electron experience very small attraction from the nucleus and hence, easy to remove. Since, the size of Si atom is larger, the outer electron experience lesser attraction and hence, its ionisation enthalpy (energy required to remove an electron) is smaller.

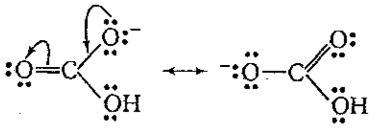
Q-23 Write the resonance structures of CO_3^{2-} and HCO_3^-.

Draw all the possible structures which differ only in the arrangement of electrons.

Sol. Resonance structures of CO_3^{2-} ion



Resonance structures of HCO_3^- ion



Q-24 Consider the compounds, BCl_3 and CCl_4. How will they behave with water? Justify.

Sol. BCl_3 is an electron deficient molecule. It easily accepts a pair of electrons from water and hence, BCl_3 undergoes hydrolysis to form boric acid (H_3BO_3) and HCl.

$$BCl_3 + 3H_2O \longrightarrow H_3BO_3 + 3HCl$$

CCl_4 is an electron precise molecule having absence of *d*-orbitals in C atom and hence, it neither accepts nor donates a pair of electrons. Thus, CCl_4 does not undergo hydrolysis in water.

Q-25 Carbon monoxide is readily absorbed by ammoniacal cuprous chloride solution but carbon dioxide is not. Explain.

Sol. Due to the presence of a lone pair of electrons on carbon in CO, it acts as a Lewis base (or ligand) and thus forms a soluble complex with ammoniacal cuprous chloride solution.

$$\mathrm{CuCl} + \mathrm{NH_3} + :\mathrm{CO} \longrightarrow \underset{\text{Soluble complex}}{[\mathrm{Cu(CO)NH_3}]^+\mathrm{Cl}^-}$$

On the other hand, CO_2 does not act as a Lewis base since it does not have a lone pair of electrons on the carbon atom and hence, does not dissolve in ammoniacal cuprous chloride solution.

Q-26 How is excessive content of CO_2 responsible for global warming?

Sol. CO_2 is a greenhouse gas. About 75% of the solar energy reaching the earth is absorbed by the earth's surface. The rest of the heat radiates back to the atmosphere. But the heat radiated by the heated surface cannot pass freely into the space because excessive CO_2 in the atmosphere absorb more heat. This results in increase in the average temperature of the atmosphere. This is known as global warming.

Q-27 Explain the difference in properties of diamond and graphite on the basis of their structures.

Sol.

S. No.	Diamond	Graphite
1.	C is sp^3 hybridised.	C is sp^2 hybridised.
2.	Three dimensional, tetrahedral structure.	Two dimensional, sheet like (layer like structure).
3.	Crystalline, transparent with extra brilliance (due to high refractive index).	Crystalline, opaque and shiny substance.
4.	Hardest substance with high density and high melting point.	Soft having soapy touch with low density and high melting point.
5.	Bad conductor of heat and electricity (no free electron).	Good conductor of heat and electricity (fourth electron is free).
6.	It is used in glass cutting and jewellery and as abrasive.	It is used as a lubricating agent, in making electrodes, in pencils, crucibles (due to high melting point).

Q-28 (*i*) Classify the following oxides as neutral, acidic, basic or amphoteric $CO, B_2O_3, SiO_2, CO_2, Al_2O_3, PbO_2, Tl_2O_3$.

(*ii*) Write suitable chemical equations to show their nature.

Sol. (*i*) Neutral oxides : CO; Acidic oxides : B_2O_3, SiO_2 and CO_2

Basic oxide : Tl_2O_3;

Amphoteric oxides : Al_2O_3 and PbO_2

(*ii*) (*a*) Being acidic B_2O_3, SiO_2 and CO_2 react with alkalis to form salts.

$$\underset{\text{Boric anhydride}}{B_2O_3} + 2NaOH \longrightarrow \underset{\text{Sodium metaborate}}{2NaBO_2} + H_2O$$

$$\underset{\text{Silica}}{SiO_2} + 2NaOH \xrightarrow{\Delta} \underset{\text{Sodium silicate}}{Na_2SiO_3} + H_2O$$

$$\underset{\text{Carbon dioxide}}{CO_2} + 2NaOH \longrightarrow \underset{\text{Sodium carbonate}}{Na_2CO_3} + H_2O$$

(*b*) Being amphoteric, Al_2O_3 and PbO_2 react with both acids and bases.

$$Al_2O_3 + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 3H_2O$$

$$\underset{\text{Alumina}}{Al_2O_3} + 2NaOH \xrightarrow{\text{Fuse}} \underset{\text{Sodium metaaluminate}}{2NaAlO_2} + H_2O$$

Q-29 Rationalise the given statements and give chemical reactions.

(*i*) Lead (II) chloride reacts with Cl_2 to give $PbCl_4$.

(*ii*) Lead (IV) chloride is highly unstable towards heat.

(*iii*) Lead is known not to form an iodide, PbI_4.

Pb^{2+} is more stable than Pb^{4+} due to inert pair effect.

Sol. (*i*) Due to inert pair effect, Pb is more stable in + 2 state than in + 4 oxidation state. Therefore, lead (II) chloride does not react with Cl_2 to give lead (IV) chloride.

(*ii*) Lead (IV) chloride on heating decomposes to give lead (II) chloride and Cl_2 because lead in + 2 oxidation state is more stable than in + 4 oxidation state.

$$PbCl_4(l) \longrightarrow PbCl_2(s) + Cl_2(g)$$

(*iii*) Due to strong oxidising power of Pb^{4+} ion and reducing power of I^- ion, PbI_4 does not exist.

Q-30 Account for the following.

(*i*) CO is used in the extraction of metals.

(*ii*) CO is poisonous.

(*iii*) CO_2 is used in referigeration.

Sol. (*i*) CO being a good reducing agent, reduces several metal oxides (except alkali and alkaline earth metal oxides) into crude metal. That's why it is used in the extraction of metals.

(*ii*) CO forms carboxy-haemoglobin complex with haemoglobin (the red pigment which carries oxygen) of blood which is about 300 times more stable than oxygen-haemoglobin complex and thus, it stops the supply of oxygen and hence, leads to death of the person.

(*iii*) Solid CO_2, produce cooling and sublimes directly into vapour state. That's why it is used for refrigeration.

Q-31 Explain the following reactions.

(*i*) Silicon is heated with methyl chloride at high temperature in the presence of copper.

(*ii*) Silicon dioxide is treated with hydrogen fluoride.

(*iii*) CO is heated with ZnO.

Sol. (*i*) When Si is heated with CH_3Cl at high temperature in the presence of Cu as a catalyst, a mixture of mono-, di- and trimethylchlorosilanes along with a small amount of tetramethylsilane is formed.

$$\underset{\text{Methyl chloride}}{CH_3Cl} + Si \xrightarrow[\text{570 K}]{\text{Cu powder}} CH_3SiCl_3$$

$$+ (CH_3)_2SiCl_2 + (CH_3)_3SiCl + (CH_3)_4Si$$

(*ii*) When SiO_2 reacts with HF, silicon tetrafluoride is formed which dissolves in HF to from hydrofluorosilicic acid.

$$SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$$

$$SiF_4 + 2HF \longrightarrow H_2SiF_6$$

(*iii*) CO is a strong reducing agent but it cannot reduce ZnO as for $CO \rightarrow CO_2$ $\Delta_r G^\circ$ is always higher than that of ZnO. Thus, no reaction takes place.

Q-32 PbO_2 is a stronger oxidising agent than SnO_2.

Sol. Pb^{4+} is less stable than Pb^{2+}, due to inert pair effect therefore, Pb^{4+} salts act as strong oxidising agent. Sn^{2+} is also less stable, than Sn^{4+}, thus Sn^{4+} can also act as an oxidising agent. But Pb^{4+} is a stronger oxidising agent than Sn^{4+} because inert pair effect increases down the group.

Q-33 When metal *X* is treated with sodium hydroxide, a white precipitate (*A*) is obtained, which is soluble in excess of NaOH to give soluble complex (*B*). Compound (*A*) is soluble in dilute HCl to form compound (*C*). The compound (*A*) when heated strongly gives (*D*), which is used to extract metal. Identify (*X*), (*A*), (*B*), (*C*) and (*D*). Write suitable equations to support their identities.

Sol. Since, metal *X* on treatment with sodium hydroxide gives white precipitate which dissolves in excess of NaOH to give soluble complex (*B*), therefore, the metal *X* is Al.

$$\underset{(X)}{\mathrm{Al}} + 3\mathrm{NaOH} \longrightarrow \underset{\substack{\text{White ppt.}\\(A)}}{\mathrm{Al(OH)_3}\downarrow} + 3\mathrm{Na^+}$$

$$\underset{(A)}{\mathrm{Al(OH)_3}} + \underset{\text{(Excess)}}{\mathrm{NaOH}} \longrightarrow \underset{\substack{\text{Sodium tetrahydroxoaluminate (III)}\\(B)}}{2\mathrm{Na^+[Al(OH)_4]^-}}$$

$$\underset{(A)}{\mathrm{Al(OH)_3}} + 3\mathrm{HCl}(aq) \longrightarrow \underset{(C)}{\mathrm{AlCl_3}} + 3\mathrm{H_2O}$$

$$\underset{(A)}{2\mathrm{Al(OH)_3}} \xrightarrow{\Delta} \underset{(D)}{\mathrm{Al_2O_3}} + 3\mathrm{H_2O}$$

Q-34 (*i*) What happens when

(*a*) borax is heated strongly?

(*b*) boric acid is added to water?

(*c*) aluminium is treated with dilute NaOH?

(*d*) BF_3 is reacted with ammonia?

(*ii*) How does $NaBH_4$ react with iodine?

Sol. (*i*) (*a*) When borax is heated strongly, a transparent glassy bead which consists of sodium metaborate and boric anhydride is formed:

$$\underset{\text{Borax}}{\mathrm{Na_2B_4O_7\cdot 10H_2O}} \xrightarrow{\text{Heat}} \underset{\substack{\text{Anhydrous swollen}\\\text{white mass}}}{\mathrm{Na_2B_4O_7}} + 10\mathrm{H_2O}$$

$$\mathrm{Na_2B_4O_7} \xrightarrow{\text{Heat}} \underbrace{\underset{\text{Sodium metaborate}}{2\mathrm{NaBO_2}} + \underset{\text{Boric anhydride}}{\mathrm{B_2O_3}}}_{\text{Transparent glassy bead}}$$

(*b*) Boric acid is sparingly soluble in cold water, but fairly soluble in hot water. It acts as a weak monobasic acid. It is not a protonic acid but it acts as a Lewis acid by accepting a hydroxide ion of water and releasing a proton into the solution.

$$\mathrm{H{-}OH} + \mathrm{B(OH)_3} \longrightarrow \{\mathrm{B(OH)_4}]^- + \mathrm{H^+}$$

(*c*) When aluminium is treated with dilute NaOH, dihydrogen is evolved.

$$2\mathrm{Al}(s) + 2\mathrm{NaOH}(aq) + 6\mathrm{H_2O}(l) \longrightarrow 2\mathrm{Na^+[Al(OH)_4]^-}(aq) + 3\mathrm{H_2}(g)$$

(*d*) BF_3 being a Lewis acid accepts a pair of electrons from NH_3 to form the corresponding complex.

$$\underset{\text{Lewis acid}}{\mathrm{F_3B}} + \underset{\text{Lewis base}}{:\mathrm{NH_3}} \longrightarrow \underset{\text{Complex}}{\mathrm{F_3B \leftarrow NH_3}}$$

(*ii*) In this reaction, diborane is obtained.

$$2\mathrm{NaBH_4} + \mathrm{I_2} \longrightarrow \underset{\text{Diborane}}{\mathrm{B_2H_6}} + 2\mathrm{NaI} + \mathrm{H_2}$$

SARASWATI CHEMISTRY

The s-Block Elements

1. Why are alkali metals not found in nature?

Alkali metals are highly reactive because of their very low ionisation energy.

Sol. Due to high chemical reactivity alkali metals do not occur free in nature. They are found in the earth's crust in the form of halide, sulphate, carbonate, silicate, borate, oxide ores, etc..

2. Explain why is sodium less reactive than potassium?

Reactivity depends upon the ionization enthalpy and electrode potential ($E°$). As the size increases, ionization enthalpy decreases.

Sol. The ionization enthalpy ($\Delta_i H_1$) of potassium (419 kJ mol^{-1}) is less than that of sodium (496 kJ mol^{-1}) and the standard electrode potential ($E°$) of potassium (– 2.925 V) is more negative than that of sodium (– 2.714 V) that's why potassium is more reactive than sodium.

3. Sodium fire in the laboratory should not be extinguished by pouring water. Why?

Sol. This is because sodium produce hydrogen gas with water which catches fire because of the exothermic nature of the reaction.

NOTE To extinguish sodium fire (or such fires) pyrene, CCl_4 or sand is used.

4. Why are potassium and caesium, rather than lithium used in photoelectric cells?

Metals having very high tendency to lose electrons are used in photoelectric cells. Lower the ionization energy, higher is the tendency to lose electrons.

Sol. Potassium and caesium have much lower ionization enthalpy than that of lithium. Therefore, these metals on exposure to light emit electrons easily but lithium does not. That's why K and Cs rather than Li are used in photoelectric cells.

6. Find out the oxidation state of sodium in Na_2O_2.

Sol. Let x be the oxidation state of Na in Na_2O_2.

Na_2O_2 contains a peroxide linkage in which O has an oxidation state of – 1.

$\overset{x}{Na_2}\overset{-1}{O_2}$ or $2x + 2(-1) = 0$ or $x = +1$.

Thus, the oxidation state of sodium in Na_2O_2 is + 1.

7. How would you explain LiI is more soluble than KI in ethanol?

Sol. LiI is more covalent because Li^+ is smallest and polarised anion (I^-) to maximum extent, so it is more soluble than KI in ethanol.

8. Why is LiF almost insoluble in water whereas LiCl is soluble not only in water but also in acetone?

Sol. LiF is almost insoluble in water due to its high lattice energy. But LiCl is soluble in water due to high hydration energy of Li^+ ion. LiCl is also soluble in acetone due to its predominantly covalent nature. (Because covalent character increases with increase in the size of anion.

$$LiF < LiCl < LiBr < LiI)$$

9. Why is Li_2CO_3 decomposed at a lower temperature whereas Na_2CO_3 at higher temperature?

Sol. Lithium being very small in size polarises a large CO_3^{2-} ion leading to the formation of more stable Li_2O and CO_2. All the carbonates of alkali metals (except lithium carbonate) are thermally quite stable. That's why Li_2CO_3 is decomposed at a lower temperature whereas Na_2CO_3 at higher temperature.

10. State as to why a solution of Na_2CO_3 is alkaline?

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

$$Na_2CO_3(s) + H_2O(l) \rightarrow \underset{\text{Strong base}}{2NaOH(aq)} + \underset{\text{Weak acid}}{H_2CO_3(aq)}$$

11. What is light soda ash? Why is it called so?

Sol. Light soda ash is anhydrous Na_2CO_3. It is called so because it is fluffy solid with a low packing density of about $0.5\,g\,cm^{-3}$.

Q-12 Comment on each of the following observations

(*i*) The mobilities of the alkali metal ions in aqueous solution are
$Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$.

(*ii*) Lithium is the only alkali metal which forms nitride directly.

Sol. (*i*) Smaller the size of the ion, more highly it is hydrated and greater the hydration of the ion, lower is its ionic mobility. Since, the extent of hydration decreases in the order

$$Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$$

Therefore, ionic mobility increases in the reverse order

$$Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$$

Q-13 (*i*) State as to why

(*a*) alkali metals are prepared by electrolysis of their fused chlorides?

(*b*) sodium is found to be more useful than potassium?

(*ii*) Explain what happens when fused sodium metal reacts with ammonia?

- $E°$ of hydrogen is lesser than of Na, so H_2 will liberate, instead of Na if aqueous sodium chloride is used.
- Sodium is a highly reactive metal but less reactive than potassium.

Sol. (*i*) (a) I. Alkali metals are strong reducing agents, hence cannot be extracted by reduction of their oxides and other compounds.

II. Being highly positive in nature it is not possible to displace them from their salt solutions by any other element.

III. Alkali metals cannot be obtained by the electrolysis of the aqueous solution of their salts because H_2 is liberated at cathode instead of alkali metal. That's why alkali metals are prepared by electrolysis of their fused chloride,

$$NaCl \xrightarrow{\text{Fusion}} Na^+ + Cl^-$$

During electrolysis

At anode $\quad 2\,Cl^- \longrightarrow Cl_2 + 2e^-$

At cathode $\quad 2\,Na^+ + 2e^- \longrightarrow 2\,Na$

(*b*) Sodium is found to be more useful than potassium as it is highly reactive but not as reactive as potassium. Sodium is used

I. as a coolant in nuclear reactor.

II. in the manufacture of tetraethyl lead an anti-knock additive for petrol.

$$4C_2H_5Cl + 4Na-Pb \longrightarrow (C_2H_5)_4Pb + 3\,Pb + 4NaCl$$

III. In sodium vapour discharge lamps.

IV. As a laboratory reagent for organic analysis.

(*ii*) $Na + NH_3 \longrightarrow NaNH_2 + H_2$

Q-14 Ions of an element of group 1 participate in the transmission of nerve signals and transport of sugars and amino acids into cells. This element imparts yellow colour to the flame in flame test and forms an oxide and a peroxide with oxygen. Identify the element and write chemical reaction to show the formation of its peroxide. Why does the element impart colour to the flame?

Sol. Yellow colour flame in flame test indicates that the alkali metal must be sodium. It reacts with O_2 to form a mixture of sodium peroxide, Na_2O_2 and sodium oxide, Na_2O.

$$4Na + O_2 \xrightarrow{\Delta} \underset{\text{(Minor)}}{2Na_2O}$$

$$2Na_2O + O_2 \xrightarrow{\Delta} \underset{\text{(Major)}}{2Na_2O_2}$$

$$2Na + O_2 \xrightarrow{\Delta} Na_2O_2$$

Ionisation enthalpy of sodium is low. When sodium metal or its salt is heated in Bunsen flame, the flame energy causes an excitation of the outermost electron which on reverting back to its initial position gives out the absorbed energy as visible light. That's why sodium imparts yellow-colour to the flame.

Q-15 (*i*) Which colour is imparted to flame by sodium?

(*ii*) Why are lithium salts commonly hydrated and those of the other alkali metal ions usually anhydrous?

(*iii*) Out of KOH and NaOH, which is a stronger base and why?

Smaller the size, higher is the hydration enthalpy and size of alkali metal ions increases on moving down the group.

Sol. (*i*) Sodium imparts a golden yellow colour to the flame.

(*ii*) Because of its smallest size among alkali metals. Li^+ has the maximum degree of hydration. That's why lithium salts are commonly hydrated and those of other alkali metal ions usually anhydrous.

$$\xrightarrow[\Delta H_{\text{hydration}}\text{ in decreasing order}]{Li^+ > Na^+ > K^+ > Rb^+ > Cs^+}$$

(*iii*) KOH is a stronger base than NaOH. Due to large size of K, K—O bond is weaker than Na—O bond. KOH has more concentration of OH than NaOH, hence, is a stronger base than NaOH.

Q-16. What happens when

(*i*) sodium metal is dropped in water? (*ii*) sodium metal is heated in free supply of air?
(*iii*) sodium peroxide dissolves in water?

Sol. (*i*) H_2 gas is evolved which catches fire due to the liberation of extreme heat in the reaction.

$$2\,Na(s) + 2\,H_2O(l) \longrightarrow 2NaOH(aq) + H_2(g)$$

(*ii*) Na_2O_2 along with a small amount of Na_2O is formed.

$$4\,Na(s) + O_2(g) \longrightarrow \underset{\text{(Minor)}}{2\,Na_2O(s)}$$

$$Na_2O(s) + \frac{1}{2}O_2(s) \longrightarrow \underset{\text{(Major)}}{Na_2O_2\,(s)}$$

(*iii*) H_2O_2 is formed when sodium peroxide is dissolved in water.

$$Na_2O_2\,(s) + 2\,H_2O(l) \longrightarrow 2\,NaOH(aq) + H_2O_2(l)$$

Q-17 Write the balanced equations for the reactions between

(*i*) Na_2O_2 and water (*ii*) KO_2 and water (*iii*) Na_2O and CO_2.

Sol. (*i*) $Na_2O_2(s) + 2\,H_2O(l) \longrightarrow 2NaOH(aq) + H_2O_2(aq)$

(*ii*) $2\,KO_2(s) + 2H_2O(l) \longrightarrow 2\,KOH(aq) + H_2O_2(aq) + O_2(g)$

or $4KO_2(s) + 2H_2O(l) \longrightarrow 4KOH(aq) + 3O_2(g)$

(*iii*) $Na_2O + CO_2 \longrightarrow Na_2CO_3$

Q-18 (*i*) Name the groups which constitute *s*-block elements.

(*ii*) Why cannot sodium and potassium be prepared by the electrolysis of their aqueous solutions?

(*iii*) Why is the density of potassium less than sodium?

(*iv*) Why are alkali metals soft and have low melting points?

(*v*) What happens when K burns in air? Give chemical equation.

Sol. (*i*) *s*-block contains only two groups; group 1 (alkali metals) and group 2 (alkaline earth metals).

(*ii*) The electrode potential, *i.e.*, reduction potential of Na (– 2.71 V) or K (– 2.92) is much lower than that of H_2O(– 0.83V), therefore, upon electrolysis, water gets reduced in preference to Na^+ or K^+ ions.

In other words, sodium and potassium cannot be obtained by electrolytic reduction of Na^+ and K^+ ions in aqueous solution.

(*iii*) This is due to abnormal increase in the atomic size of potassium.

(*iv*) Alkali metals have only one valence electron per metal atom. As a result, the binding energy of alkali metal ions in the close-packed metal lattices are weak. Therefore these are soft and have low melting points.

(*v*) $K + O_2 \rightarrow KO_2$, potassium superoxide will be formed.

Q-19 Explain why can alkali and alkaline earth metals not be obtained by chemical reduction methods?

Sol. (*i*) Alkali and alkaline earth metals are themselves strong reducing agents. Therefore, these metals cannot be obtained by chemical reduction of their oxides and other compounds.

(*ii*) These metals are highly electropositive in nature. So, these cannot be displaced from the aqueous solutions of their salts by other metals.

Q-20 What happens when (*i*) magnesium is burnt in air (*ii*) quick lime is heated with silica?

Sol. (*i*) $2\,Mg(s) + O_2(g) \longrightarrow 2\,MgO(s)$

(*ii*) $\underset{\text{Quick lime}}{CaO(s)} + \underset{\text{Silica}}{SiO_2(s)} \xrightarrow{\Delta} \underset{\text{Calcium silicate}}{CaSiO_3(s)}$

Q-21 How would you explain

(*i*) BeO is insoluble but $BeSO_4$ is soluble in water?

(*ii*) $Be(OH)_2$ dissolves in NaOH but $Mg(OH)_2$ does not?

Sol. (*i*) Lattice energy of BeO is greater than its hydration energy so, it is insoluble in water while in case of $BeSO_4$, hydration energy is greater than lattice energy, so it is readily soluble in water.

(*ii*) $Be(OH)_2$ is amphoteric and therefore, it dissolves in NaOH forming sodium beryllate

$$Be(OH)_2 + 2\,NaOH \longrightarrow Na_2BeO_2 + 2\,H_2O$$

On the otherhand, $Mg(OH)_2$ is basic and does not dissolve in NaOH.

Q-22 The hydroxides and carbonates of sodium and potassium are easily soluble in water while the corresponding salts of magnesium and calcium are sparingly soluble in water. Explain.

High hydration energy and low lattice energy are the favourable conditions for a salt to be soluble in water.

Sol. The solubility of a salt in water depends upon the lattice energy and hydration energy.

$$\Delta H_{\text{solution}} = \Delta H_{\text{lattice energy}} + \Delta H_{\text{hydration energy}}$$

More negative is $\Delta H_{\text{solution}}$, more is the solubility of compounds.

For sodium and potassium hydroxides and carbonates, hydration energy is more than that of their lattice energy. Therefore, they are soluble in water. For magnesium and calcium hydroxides and carbonates, lattice energy is greater than that of their hydration energy. Therefore, these are sparingly soluble in water.

Q-23. Compare the alkali metals and alkaline earth metals with respect to

(*i*) ionization enthalpy

(*ii*) basicity of oxides

(*iii*) solubility of hydroxides.

Sol. (*i*) Ionization enthalpies The first ionization enthalpies of the alkaline earth metals are higher than those of the corresponding alkali metals. This is due to their small size as compared to the corresponding alkali metals.

But second ionization enthalpies of the alkaline earth metals are smaller than those of the corresponding alkali metals.

(*ii*) Basicity of oxides The oxides of the alkali and alkaline earth metals dissolves in water to form basic hydroxides. The alkaline earth metal hydroxides are however less basic and less stable than alkali metal hydroxides.

(*iii*) Solubility of hydroxides The solubility of hydroxides of alkaline earth metals is relatively less than their corresponding alkali metal hydroxides.

Q-24 Compare the solubility and thermal stability of the following compounds of the alkali metals with those of alkaline earth metals.

(*i*) Nitrates (*ii*) Carbonates (*iii*) Sulphates

Sol. (*i*) Nitrates of alkali metals and alkaline earth metals

(*a*) Alkali metal and alkaline earth metal nitrates are highly soluble in water.

(*b*) Alkali metal nitrates on strong heating decompose to nitrites (except $LiNO_3$).

On heating further at higher temperature, the products are oxides.

$$2NaNO_3 \overset{500°C}{\rightleftharpoons} 2NaNO_2 + O_2$$

$$4\,NaNO_3 \overset{800°C}{\rightleftharpoons} 2Na_2O + 5\,O_2 + 2N_2$$

$$2LiNO_3 \xrightarrow{\Delta} Li_2O + 2NO_2 + \frac{1}{2}O_2$$

Alkaline earth metal nitrates on heating decompose into their corresponding oxide with the evolution of mixture of NO_2 and O_2 (except $Be(NO_3)_2$).

$$2Mg(NO_3)_2 \xrightarrow{\Delta} 2MgO + 4NO_2 + O_2$$

(*ii*) Carbonates of alkali metals and alkaline earth metals

(*a*) Alkali metal carbonates are thermally quite stable upto 1273 K; above which they melt and then converted into oxides.

$$Na_2CO_3 \xrightarrow{\Delta,\,>1273\text{ K}} Na_2O + CO_2$$

Li_2CO_3 is considerably less stable and decompose readily.

$$Li_2CO_3 \xrightarrow{\Delta} Li_2O + CO_2$$

All alkaline earth metal carbonates decomposes on heating to give CO_2 and metal oxide.

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$

Thermal stability of alkaline earth metal carbonates increases down the group. $BeCO_3$ is least stable.

(*b*) All the alkali metal carbonates are generally soluble in water and their solubility increases down the group because their lattice energy decreases more readily than the hydration energy.

Alkaline earth metal carbonates are sparingly soluble in water and their solubility decreases down the group. However, these are more soluble in the presence of CO_2.

(*iii*) Sulphates of alkali and alkaline earth metals

(*a*) Sulphates of alkali metals are thermally quite stable except Li_2SO_4 while sulphates of alkaline earth metals are decomposed on heating. Their thermal stability increases down the group.

$$Li_2SO_4 \longrightarrow Li_2O + SO_2 + \frac{1}{2}O_2$$

$$2MgSO_4 \xrightarrow{\Delta} 2MgO + 2SO_2 + O_2$$

(*b*) The alkali metal sulphates are soluble in water (except Li_2SO_4). The solubility of alkaline earth metal sulphates in water decreases down the group. $BeSO_4$ and $MgSO_4$ are fairly soluble while $BaSO_4$ is completely insoluble.

Q-25 What happens when

(*i*) magnesium is burnt in air

(*ii*) quicklime is heated with silica

(*iii*) chlorine reacts with slaked lime

(*iv*) calcium nitrate is heated

(*v*) lime is heated with coke?

Sol. (*i*) $2Mg(s) + O_2(g) \xrightarrow{\Delta} 2MgO(s)$

and $3Mg(s) + N_2(g) \xrightarrow{\Delta} Mg_3N_2(s)$

(*ii*) $\underset{\text{Quicklime}}{CaO(s)} + \underset{\text{Silica}}{SiO_2(s)} \xrightarrow{\Delta} \underset{\text{Calcium silicate}}{CaSiO_3(s)}$

(*iii*) It reacts with Cl_2 to form calcium hypochlorite, $Ca(OCl)_2$

$$\underset{\text{Slaked lime}}{2Ca(OH)_2} + 2Cl_2 \rightarrow CaCl_2 + \underset{\text{Bleaching powder}}{Ca(OCl)_2} + 2H_2O$$

(*iv*) $2Ca(NO_3)_2(s) \xrightarrow{\Delta} 2CaO(s) + 4NO_2(g) + O_2(g)$

(*v*) Lime is reduced to calcium carbide.

$$CaO + 3C \longrightarrow \underset{\text{Calcium carbide}}{CaC_2} + CO$$

SARASWATI CHEMISTRY

Hydrogen

Q-1 • Describe the bulk preparation of hydrogen by electrolytic method. What is the role of an electrolyte in this process?

Sol. Electrolysis of acidified water using platinum electrodes gives hydrogen.

$$2H_2O(l) \xrightarrow[\text{Traces of acid / base}]{\text{Electrolysis}} 2H_2(g) + O_2(g)$$

Here, the role of an electrolyte is to make water conducting.

Q-2 • Why does hydrogen occur in a diatomic form rather than in a monoatomic form under normal conditions?

Sol. Hydrogen atom has only one electron in its 1*s*-orbital. So, to achieve stable inert gas configuration of helium, it exists as diatomic molecule and is called dihydrogen.

Q-3 • Why does hydrogen react mostly at higher temperatures?

Or

Discuss the consequences of high enthalpy of H—H bond in terms of chemical reactivity of dihydrogen.

Sol. Due to high bond dissociation enthalpy of H—H bond, hydrogen is relatively unreactive at room temperature.

However, at high temperatures or in the presence of catalysts, it combines with many metals and non-metals to form hydrides.

Q-4 • Why is dihydrogen not preferred in balloons these days?

Sol. Dihydrogen is highly combustible and hence, is likely to catch fire in the presence of excess of air. That's why it is not preferred in balloons now a days.

Q-5 • Write the names of isotopes of hydrogen. What is the mass ratio of these isotopes?

Sol. Protium ${}^1_1H$, deuterium ${}^2_1H$ or D, tritium ${}^3_1H$ or T. The mass ratio protium: deuterium : tritium = 1 : 2 : 3.

Q-6 (*i*) Complete the following reactions,

(*a*) $H_2(g) + M_mO_o(s) \xrightarrow{\Delta}$

(*b*) $CO(g) + H_2(g) \xrightarrow[\text{Catalyst}]{\Delta}$

(*c*) $C_3H_8(g) + 3H_2O(g) \xrightarrow[\text{Catalyst}]{\Delta}$

(*d*) $Zn(s) + NaOH(aq) \xrightarrow{\text{Heat}}$

(*ii*) What do you understand by the term 'syn gas'?

Sol. (*i*) (*a*) $H_2(g) + M_mO_o(s) \xrightarrow{\Delta} mM(s) + oH_2O(l)$

(*b*) $CO(g) + H_2(g) \xrightarrow[\text{Catalyst}]{\Delta} CH_3OH(l)$

(*c*) $C_3H_8(g) + 3H_2O(g) \xrightarrow{\text{Ni, 1270 K}} 3CO(g) + 7H_2(g)$

(*d*) $Zn(s) + NaOH(aq) \xrightarrow{\text{Heat}} \underset{\text{Sodium zincate}}{Na_2ZnO_2(aq)} + H_2(g)$

(*ii*) Syn gas Mixture of CO and H_2 is known as synthesis gas or syn gas. Reaction of steam on hydrocarbons or coke at high temperatures in the presence of catalyst yields syn gas, *e.g.*,

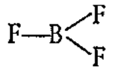
$$CH_4(g) + H_2O(g) \xrightarrow[\text{Ni}]{\text{1270 K}} CO(g) + 3H_2(g)$$

Now a days syn gas is produced from sewage, saw-dust, scrapwood, news papers, etc. The process of production of syn gas from coal is called coal gasification.

$$C(s) + H_2O(g) \xrightarrow[\text{Ni}]{\text{1270 K}} CO(g) + H_2(g)$$

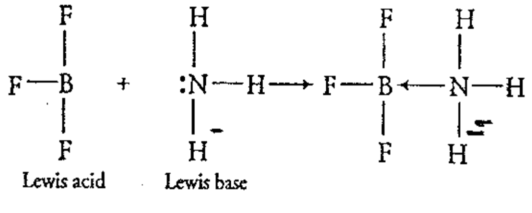
Q-7 What characteristics do you expect from an electron-deficient hydride with respect to its structure and chemical reactions?

Sol. These hydrides do not have sufficient number of electrons to form normal covalent bonds, *e.g.*, B in BF_3 has 6 electrons in its valence shell. These hydrides are trigonal planar in shape.



Trigonal planar
(BF_3)

These hydrides act as Lewis acids, *i.e.*, electron pair acceptor *e.g.*,



To make up the deficiency of electrons, these hydrides exist in polymeric forms, *e.g.*, B_2H_6, B_4H_{10}, etc. Electron deficient hydrides are very reactive. These react with metals and non-metals and their compounds readily, *e.g.*,

$$B_2H_6(g) + 3O_2(g) \longrightarrow B_2O_3(g) + 3H_2O(g)$$

Q-8 • Do you expect the carbon hydrides of the type (C_nH_{2n+2}) to act as Lewis acid or base? Justify your answer.

Sol. Carbon hydrides of the type (C_nH_{2n+2}) are electron-precise hydrides. They have exact number of electrons required to form covalent bonds. Therefore, they neither act as Lewis acids nor Lewis bases.

Q-9 **Among NH_3, H_2O and HF, which would you expect of have highest magnitude of hydrogen bonding and why?**

Sol. Since, electronegativity of F is the highest, therefore, magnitude of the positive charge on hydrogen and negative charge on F is the highest in HF and hence, electrostatic attraction of the H-bonding is the strongest in H—F.

Q-10 **How do you expect the metallic hydrides to be useful for hydrogen storage? Explain**

Sol. In metallic hydrides, hydrogen is adsorbed as H-atoms. This property of adsorption of hydrogen on transition metals is widely used as its storage media. Some of the metals such as Pd, Pt can accommodate a very large volume of hydrogen. This property has high potential for hydrogen storage and as a source of energy. Metallic hydrides on heating decompose to form hydrogen and very finely divided metal.

Q-11. **What is meant by 'demineralised water' and how can it be obtained?**

Sol. Water which is free from all soluble minerals salts is called demineralised water. Demineralised water is obtained by passing water successively through a cation exchange and an anion exchange resins. In cation exchanger, Ca^{2+}, Mg^{2+}, Na^+ and other cations present in water are removed by exchanging them with H^+ ions while in anion exchanger, Cl^-, HCO_3^-, SO_4^{2-}, etc., present in water are removed by exchanging them with OH^- ions.

$$\underset{\substack{\text{(Released in}\\\text{cation}\\\text{exchanger)}}}{H^+} + \underset{\substack{\text{(Released in}\\\text{anion}\\\text{exchanger)}}}{OH^-} \longrightarrow H_2O$$

Q-12 **What is the difference between the terms 'hydrolysis' and 'hydration'?**

Sol. Interaction of H^+ and OH^- ions of H_2O with the anion and the cation of a salt respectively to yield the original acid and the original base is called hydrolysis.

e.g., $$\underset{\text{Salt}}{Na_2CO_3} + 2H_2O \longrightarrow \underset{\text{Base}}{2\,NaOH} + \underset{\text{Acid}}{H_2CO_3}$$

Hydration, on the other hand, means addition of H_2O to ions or molecules to form hydrated ions or hydrated salts. *e.g.,*

$$\underset{\text{Salt}}{KCl(s)} + H_2O(l) \longrightarrow K^+(aq) + Cl^-(aq)$$

$$\underset{\text{(Colourless)}}{CuSO_4(s)} + 5H_2O(l) \longrightarrow \underset{\text{(Blue)}}{CuSO_4 \cdot 5H_2O(s)}$$

Q-13 **Do you except different products in solution when aluminium (III) chloride and potassium chloride are treated separately with (*i*) normal water (*ii*) acidified water, and (*iii*) alkaline water? Write equations wherever necessary.**

Sol. $AlCl_3$ is a salt of weak base, $Al(OH)_3$ and a strong acid, HCl. Therefore, in normal water, it undergoes hydrolysis.

$$AlCl_3(s) + 3H_2O(l) \longrightarrow Al(OH)_3(s) + 3H^+(aq) + 3Cl^-(aq)$$

Its aqueous solution is acidic in nature.

In acidified water, H^+ ions react with $Al(OH)_3$ to produce $Al^{3+}(aq)$ ions and H_2O. Therefore, in acidified water $AlCl_3$ exists as $Al^{3+}(aq)$ and $Cl^-(aq)$ ions.

In alkaline water $AlCl_3$ yields following products

$$AlCl_3(s) \xrightarrow{\text{Alk. water}} Al(OH)_4^-(aq) + 3Cl^-(aq)$$

$$Al[OH]_4^- \longrightarrow AlO_2^-(aq) + 2H_2O(l)$$

KCl is the salt of a strong acid and a strong base. It does not undergo hydrolysis in normal water. It only dissociates in wate [illegible] ve $K^+(sq)$ and $Cl^-(aq)$ ion.

$$KCl(s) \xrightarrow{\text{Water}} K^+(aq) + Cl^-(aq)$$

Aqueous solution of KCl is neutral. Hence, in acidified water or in alkaline water, the ions do not react further.

Q-14 **When the first element of the periodic table is treated with dioxygen, it gives a compound whose solid state floats on its liquid state. This compound has an ability to act as an acid as well as a base. What products will be formed when this compound undergoes auto-ionisation?**

Sol. The first element of the periodic table is H and its molecular form is dihydrogen (H_2). When dihydrogen reacts with dioxygen, water is formed.

Water is a liquid at room temperature. When liquid water freezes, it expands to form ice. In other words, density of ice is lower than that of liquid water and hence, ice floats over water. Water is amphoteric in nature, *i.e.*, it acts as an acid in presence of strong bases and as a base in the presence of strong acids.

$$\underset{\text{Acid}_1}{H_2O(l)} + \underset{\text{Base}_2}{NH_3(aq)} \longrightarrow \underset{\text{Acid}_2}{NH_4^+(aq)} + \underset{\text{Base}_1}{OH^-(aq)}$$

$$\underset{\text{Base}_1}{H_2O(l)} + \underset{\text{Acid}_2}{H_2S(aq)} \longrightarrow \underset{\text{Acid}_1}{H_3O^+(aq)} + \underset{\text{Base}_2}{HS^-(aq)}$$

Due to amphoteric character, water undergoes self ionisation as shown below

$$\underset{\text{Acid}_1}{H_2O(l)} + \underset{\text{Base}_2}{H_2O\text{ (base)}} \rightleftharpoons \underset{\substack{\text{Acid}_2\\\text{(Conjugate acid)}}}{H_3O^+(aq)} + \underset{\substack{\text{Base}_2\\\text{(Conjugate base)}}}{OH^-(aq)}$$

The self ionisation of water is called auto-protolysis.

Q-15. Consider the reaction of water with F_2 and suggest, in terms of oxidation and reduction, which species are oxidised/reduced?

Fluorine being more electronegative removes oxygen from water and itself gets reduced to fluoride ion.

Sol.

$$\underset{\text{Oxidant}}{2F_2(g)} + \underset{\text{Reductant}}{2H_2O(l)} \longrightarrow O_2(g) + 4H^+(aq) + 4F^-(aq)$$

$$\underset{\text{Oxidant}}{3F_2(g)} + \underset{\text{Reductant}}{3H_2O(l)} \longrightarrow O_3(g) + 6H^+(aq) + 6F^-(aq)$$

In these reactions, water acts as reducing agent and hence, itself gets oxidised to either oxygen or ozone. Fluorine acts as an oxidising agent and hence, itself reduced to F^- ion.

Q-16. An ionic hydride of an alkali metal has significant covalent character and is almost unreactive towards oxygen and chlorine. This is used in the synthesis of other useful hydrides. Write the formula of this hydride. Write its reaction with Al_2Cl_6.

Sol. It is LiH because it has significant covalent character due to the smallest alkali metal Li. LiH is very stable. It is almost unreactive towards oxygen and chlorine.

It reacts with Al_2Cl_6 to form lithium aluminium hydride.

$$8LiH + Al_2Cl_6 \longrightarrow 2LiAlH_4 + 6LiCl$$

Q-17 What properties of water make it useful as a solvent? What type of compounds can it

(*i*) dissolve

(*ii*) hydrolyse?

Sol. High dipole moment and high dielectric constant, these are the two properties of water which make it useful as a solvent.

(*i*) It can dissolve both ionic compounds as well as those covalent compounds which can form hydrogen bonds with water such as ethyl alcohol, sugar, glucose, etc.

(*ii*) Water can hydrolyse many metallic and non-metallic oxides, hydrides, phosphides and other salts, *e.g.*,

$$P_4O_{10}(s) + 6H_2O(l) \longrightarrow 4H_3PO_4(aq)$$

Q-18 Describe the industrial applications of hydrogen dependent on

(*i*) the heat liberated when its atoms are made to combine on the surface of a metal.

(*ii*) its effect on the unsaturated organic systems in the presence of a catalyst.

(*iii*) its ability to combine with nitrogen under specific conditions.

Sol. (*i*) Due to this property hydrogen is used in atomic hydrogen welding/cutting torch.

(*ii*) Due to this property hydrogen is used for the manufacture of vanaspati ghee from edible oils such as cotton-seed oil, soyabean oil, corn oil etc.

$$\text{Unsaturated oil} + H_2(g) \xrightarrow{\text{Ni catalyst}} \text{Vanaspati ghee}$$

(*iii*) Due to this property dihydrogen is used for the manufacture of ammonia.

$$N_2(g) + 3H_2(g) \xrightleftharpoons[\text{Fe, Mo}]{\text{673K, 200 atm}} 2NH_3(g)$$

(Haber's process)

Q-19 Describe the usefullness of water in biosphere and biological systems.

Sol. A major part of all living organisms is made up of water. Human body has about 65% water and some plants have as much as 95% water. It is an essential compound for the survival of all life forms. In comparison to other liquids, water has a high specific heat, thermal conductivity, surface tension, dipole moment, dielectric constant, etc.

Q-20 (*i*) What is hydrolith? How is it prepared?

(*ii*) Knowing the properties of H_2O and D_2O, do you think that D_2O can be used for drinking purposes?

(*iii*) Explain why HCl is a gas and HF a liquid?

Sol. (*i*) Calcium hydride is also known as hydrolith. It is obtained by treating calcium with hydrogen;

$$Ca + H_2 \xrightarrow{\Delta} CaH_2 \text{ (hydrolith)}$$

(*ii*) No, because heavy water is injurious to human beings as rate of biochemical reactions decreases in heavy water.

(*iii*) F is smaller and more electronegative than Cl, so it forms stronger H-bonds as compared to Cl. That's why HF is liquid and HCl is a gas.

Q-21 Statues coated with white lead on long exposure to atmosphere turn black and the original colour can be restored on treatment with H_2O_2. Why?

Sol. On long exposure to atmosphere, white lead is converted into black PbS due to the action of H_2S present in the atmosphere. As a result, statues turn black.

$$PbO_2 + 2H_2S \longrightarrow PbS + 2H_2O$$

On treatment of these blackened statues with H_2O_2, the black PbS gets oxidised to white $PbSO_4$ and the colour is restored.

$$PbS + 4H_2O_2 \longrightarrow PbSO_4 + 4H_2O$$

Q-22 Write chemical reactions to justify that hydrogen peroxide can function as an oxidising as well as reducing agent.

Sol. H_2O_2 can act as an oxidising as well as a reducing agent both in acidic and basic media, *e.g.*,

(*i*) Oxidising agent in acidic medium

$$2\,Fe^{2+}(aq) + 2H^+(aq) + H_2O_2(aq) \longrightarrow 2\,Fe^{3+}(aq) + 2\,H_2O\,(l)$$

(*ii*) Oxidising agent in basic medium

$$Mn^{2+}(aq) + H_2O_2(aq) \longrightarrow Mn^{4+}(aq) + 2OH^-(aq)$$

Q-23 (*i*) Why is hydrated barium peroxide used in the preparation of hydrogen peroxide instead of anhydrous barium peroxide?

(*ii*) Phosphoric acid is preferred over sulphuric acid in preparing hydrogen peroxide from peroxides. Why?

(*iii*) Hydrogen peroxide acts both as an oxidising agent as well as a reducing agent in alkaline solution towards certain first row transition metal ions. Illustrate both these properties of H_2O_2 using chemical equations.

Sol. (*i*) Anhydrous BaO_2 is not used because the $BaSO_4$ formed during the reaction forms a protective layer around unreacted BaO_2 and the reaction stops after sometime.

(*ii*) H_2SO_4 acts as a catalyst for decomposition of H_2O_2. Therefore, some weaker acids such as H_3PO_4, H_2CO_3 are preferred over H_2SO_4 for preparing H_2O_2 from peroxides.

$$3BaO_2 + 2H_3PO_4 \longrightarrow \underset{\text{(Insoluble)}}{Ba_3(PO_4)_2} + 3H_2O_2$$

(*iii*) Oxidising agent

$$2Cr(OH)_3 + 4NaOH + 3H_2O_2 \longrightarrow 2Na_2CrO_4 + 8H_2O$$

Here, Cr^{3+} gets oxidised to Cr^{6+}

Reducing agent

$$2K_3[Fe(CN)_6] + 2KOH + H_2O_2 \longrightarrow 2K_4[Fe(CN)_6] + 2H_2O + O_2$$

Here, Fe^{3+} gets reduced to Fe^{2+}.

Q-24 (*i*) Arrange the following.

(*a*) CaH_2, BeH_2 and TiH_2 in the order of increasing electrical conductance.

(*b*) LiH, NaH and CsH in the order of increasing ionic character.

(*c*) H—H, D—D and F—F in the order of increasing bond dissociation enthalpy.

(*d*) NaH, MgH_2 and H_2O in order of increasing reducing property.

Sol. (*i*) (*a*) Element with $Z = 15$, belongs to *p*-block. It forms covalent hydride, PH_3.

(*b*) Element with $Z = 19$ belongs to *s*-block. It forms ionic or saline hydride, KH.

(*c*) Element with $Z = 23$ belongs to *d*-block and Vth group elements. It forms interstitial hydride, $VH_{1.6}$. It is non-stoichiometric hydride.

(*d*) Element with $Z = 44$ belongs to *d*-block and 8th group elements. It is ruthinium. It does not form any hydride because metals of group 7, 8 and 9 do not form hydride (hydride gap). Only ionic hydride, KH reacts violently with water producing dihydrogen gas.

$$KH\,(s) + H_2O\,(aq) \longrightarrow KOH(aq) + H_2(g)$$

SARASWATI CHEMISTRY

Redox Reactions

Q-1 The compound AgF_2 is a unstable compound. However, if formed, the compound acts as a very strong oxidising agent. Why?

- Due to the presence of completely filled configuration Ag^+ is more stable than Ag^{2+}.
- An oxidising agent has a great tendency of accepting electron.

Sol. In AgF_2, Ag is in + 2 oxidation state. It is highly unstable so it readily accepts an electron to attain + 1 oxidation state which is more stable.

$$Ag^{2+} + e^- \longrightarrow Ag^+$$

That's why AgF_2 acts as a strong oxidising agent.

Q-2 Assign oxidation number to the underlined elements in each of the following species.

(i) $NaH_2\underline{P}O_4$ (ii) $NaH\underline{S}O_4$ (iii) $H_4\underline{P}_2O_7$

(iv) $K_2\underline{Mn}O_4$ (v) $Ca\underline{O}_2$ (vi) $Na\underline{B}H_4$

(vii) $H_2\underline{S}_2O_7$ (viii) $KAl(\underline{S}O_4)_2 \cdot 12H_2O$

(carry one mark each)

Sol. (i) $NaH_2\underline{P}O_4$

Let the oxidation number of P be x. Writing the oxidation number of each atom above its symbol, we get $\overset{+1}{Na}\overset{+1}{H_2}\overset{x}{P}\overset{-2}{O_4}$.

Q-3 The compound $YBa_2Cu_3O_7$, which shows superconductivity, has copper in x oxidation state. Assume that the rare earth element yttrium is in its usual +3 oxidation state. Predict the value of x.

Sol. $1 \times (+3) + 2 \times (+2) + 3x + 7 \times (-2) = 0$

or $3 + 4 + 3x - 14 = 0$

or $3x = 7$

$$x = \frac{7}{3}$$

Q-4 Why does fluorine not show disproportionation reaction?

Sol. In a disproportionation reaction, the same species is simultaneously oxidised as well as reduced. Therefore, for such a redox reaction to occur, the reacting species must contain an element which has atleast three oxidation states. The element, in reacting species, is present in an intermediate state while lower and higher oxidation states are available for reduction and oxidation to occur (respectively). Fluorine is the strongest oxidising agent. It does not show positive oxidation state. That's why fluorine does not show disproportionation reaction.

Q-5 Fluorine reacts with ice and results in the change

$$H_2O\,(s) + F_2(g) \longrightarrow HF(g) + HOF\,(g)$$

Justify that this reaction is a redox reaction.

Redox reactions involve oxidation and reduction as its two half reactions. So, find the oxidation state of each element given in the equation to find which substance is oxidising and which is reducing, then tell, is the given reaction redox reaction?

Sol. $$\overset{+1}{H_2}\overset{-2}{O}(s) + \overset{0}{F_2}(g) \longrightarrow \overset{+1}{H}\overset{-1}{F}(g) + \overset{+1}{H}\overset{-2}{O}\overset{+1}{F}\,(g)$$

$$\longrightarrow \overset{+1}{H}\overset{-1}{F} + \overset{+1}{H_2}\overset{-2}{O} + \overset{+2}{O}\overset{+1}{F_2}$$

Oxidation number of F decreases from zero (in F_2) to -1 (in HF) and of O increases from -2 to $+2$ (in OF_2). This shows that F_2 is reduced. It is not a disproportionation reaction, but only a redox reaction. In a disproportionation reaction, an element in one oxidation state is simultaneously reduced and oxidised.

Q-6 Consider the reactions,

$$2S_2O_3^{2-}(aq) + I_2\,(s) \longrightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$$

$$S_2O_3^{2-}(aq) + 2Br_2(l) + 5H_2O\,(l) \longrightarrow 2SO_4^{2-}(aq) + 4Br^-(aq) + 10H^+(aq)$$

Why does the same reductant, thiosulphate react differently with iodine and bromine?

Bromine is a stronger oxidising agent than iodine.

Sol. $$2\,\overset{+2}{S_2}\overset{-2}{O_3^{2-}}(aq) + \overset{0}{I_2}(s) \longrightarrow \overset{2.5}{S_4}\overset{-2}{O_6^{2-}}(aq) + 2I^-(aq)$$

$$\overset{+2}{S_2}\overset{-2}{O_3^{2-}}(aq) + 2\overset{0}{Br_2}\,(l) + 5\,H_2O\,(l) \longrightarrow 2\,\overset{+6}{S}\overset{-2}{O_4^{2-}}(aq) + 4\,Br^-(aq) + 10H^+(aq)$$

Bromine is a stronger oxidising agent in comparison to I_2. It oxidises S of $S_2O_3^{2-}$ to a higher oxidation state $+6$ in SO_4^{2-}.

While I_2 oxidises S of $S_2O_3^{2-}$ to a lower oxidation state 2.5 in $S_4O_6^{2-}$. That's why same reductant, thiosulphate react differently with bromine and iodine.

Q-7 . Why does the following reaction occur?

$$XeO_6^{4-}(aq)+2F^-(aq)+6H^+(aq)\longrightarrow XeO_3(g)+F_2(g)+3H_2O(l)$$

What conclusion about the compound Na_4XeO_6 (of which XeO_6^{4-} is a part) can be drawn from the reaction?

Sol. $$\overset{+8}{Xe}O_6^{4-}(aq)+2\overset{-1}{F}{}^-(aq)+6H^+(aq)\longrightarrow \overset{+6}{Xe}O_3(g)+\overset{0}{F_2}+3H_2O(l)$$

In the above reaction, oxidation number of Xe in XeO_6^{4-} decreases from +8 to +6 in XeO_3 and oxidation number of F increases from −1 (in F^-) to zero (in F_2).

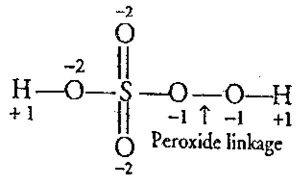
Q-8 Calculate the oxidation number of sulphur, chromium and nitrogen in H_2SO_5, $Cr_2O_7^{2-}$ and NO_3^-. Suggest the structure of these compounds. Count for the fallacy.

Sol. (*i*) Oxidation number of S in H_2SO_5 is

$$2(+1)+x+5(-2)=0 \quad\text{or}\quad x=+8$$

But oxidation number of S cannot be more than 6 because S has only 6 valence electrons. This fallacy is removed by calculating oxidation number of S by chemical bonding method.

Let us consider the structure of H_2SO_5,



In H_2SO_5, two oxygen atoms are in −1 oxidation state.

Let the oxidation number of S be *x*.

$$\underbrace{2(+1)}_{\text{(for H)}}+\underbrace{3(-2)}_{\text{(for three O)}}+x-\underbrace{2(-1)}_{\text{(for O—O)}}=0$$

$$2\times(-6)+x+(-2)=0$$

$$x=+6$$

Therefore, the oxidation number of S in H_2SO_5 is +6.

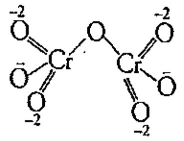
(*ii*) Oxidation number of Cr in $Cr_2O_7^{2-}$ is

$$2x+(-2)7=-2$$

$$2x=+12,$$

$$x=+6$$

Let us consider the structure of $Cr_2O_7^{2-}$ ion



Let the oxidation number of each Cr atom be *x*.

$$4(-2)+(-2)+1(-2)+2x=0$$

$$-8-2-2+2x=0$$

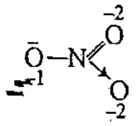
$$2x=+12,\ x=+6$$

Oxidation number of Cr in $Cr_2O_7^{2-}$ is same *i.e.*, +6 whether it is calculated by conventional method or by chemical bonding method. Hence, there is no fallacy.

(*iii*) Oxidation number of N in NO_3^- is

$$+5\ [x+3(-2)=-1 \quad\text{or}\quad x=+5]$$

Let us consider the structure of NO_3^- ion



Let the oxidation number of N be *x*.

$$\underbrace{1(-1)}_{(\text{for }\bar{O})}+x+\underbrace{1(-2)}_{(\text{for}=O)}+\underbrace{1(-2)}_{(\text{for}\rightarrow O)}=0$$

$$x=+5$$

Oxidation number of N in NO_2^- ion is same, *i.e.*, +5 whether it is calculated by conventional method or by chemical bonding method. Hence, there is no fallacy.

Q-9 How does Cu_2O act as both oxidant and reductant? Explain with proper reactions showing the change of oxidation numbers in each example.

Sol. Cu^+ undergoes disproportionation to form Cu^{2+} and Cu.

$$2Cu^+(aq)\longrightarrow Cu^{2+}(aq)+Cu(S)$$

Thus, Cu^+ or Cu_2O acts both as an oxidant as well as reductant.

(*i*) When heated in air, Cu_2O is oxidised to CuO.

$$\overset{+1}{Cu_2}\overset{-2}{O}+\frac{1}{2}\overset{0}{O_2}\longrightarrow 2\overset{+2}{Cu}\overset{-2}{O}$$

i.e., Cu_2O acts as a reductant and reduces O_2 to O^{2-}.

(*ii*) When heated with Cu_2S, it oxidises S^{2-} to SO_2 and hence, Cu_2O acts as an oxidant.

$$2\overset{+1}{Cu_2}\overset{-2}{O}+\overset{+1}{Cu_2}\overset{-2}{S}\longrightarrow 6\overset{0}{Cu}+\overset{+4}{S}O_2$$

Q-10 Why do the following reactions proceed differently?

$Pb_3O_4 + 8HCl \longrightarrow 3PbCl_2 + Cl_2 + 4H_2O$ and

$Pb_3O_4 + 4HNO_3 \longrightarrow 2Pb(NO_3)_2 + PbO_2 + 2H_2O$

Sol. Pb_3O_4 is actually a stoichiometric mixture of 2 moles of PbO and 1 mole of PbO_2. In PbO_2, lead is present in + 4 oxidation state, whereas the stable oxidation state of lead in PbO is + 2. PbO_2 thus can act as an oxidant (oxidising agent) and therefore, can oxidise Cl^- ion of HCl into chlorine. We may also keep in mind that PbO is a basic oxide. Therefore, the reaction

$$Pb_3O_4 + 8HCl \longrightarrow 3PbCl_2 + Cl_2 + 4H_2O$$

can be splitted into two reactions namely;

$$2\,PbO + 4\,HCl \longrightarrow 2\,PbCl_2 + 2H_2O$$

(acid-base reaction)

$$\overset{+4}{Pb}O_2 + 4H\overset{-1}{Cl} \longrightarrow \overset{+2}{Pb}Cl_2 + \overset{0}{Cl_2} + 2H_2O$$

(redox reaction)

Since HNO_3 itself is an oxidising agent, therefore it is unlikely that the reaction may occur between PbO_2 and HNO_3. However, the acid-base reaction occurs between PbO and HNO_3 as

$$2\,PbO + 4\,HNO_3 \longrightarrow 2Pb(NO_3)_2 + 2H_2O$$

It is the passive nature of PbO_2 against HNO_3 that makes the reaction different from the one that follows with HCl.

Q-11 Whenever a reaction between an oxidising agent and a reducing agent is carried out, a compound of lower oxidation state is formed if the reducing agent is in excess and a compound of higher oxidation state is formed if the oxidising agent is in excess. Justify this statement giving three illustrations.

Sol. (*i*) P_4 is a reducing agent and Cl_2 is an oxidising agent.

(*a*) $\underset{\text{Excess}}{\overset{0}{P_4}}\,(s) + 6\,Cl_2(g) \longrightarrow \underset{\text{Lower oxidation state of P}}{4\,\overset{+3}{P}Cl_3}$

(*b*) $\overset{0}{P_4}(2) + \underset{\text{Excess}}{10\,Cl_2} \longrightarrow \underset{\text{Higher oxidation state of P}}{4\,\overset{+5}{P}Cl_5}$

Therefore, when P_4 (reducing agent) is in excess, PCl_3 is formed in which oxidation state of P is + 3 and if Cl_2 (oxidising agent) is in excess, PCl_5 is formed in which oxidation state of P is + 5. Other two examples are

(*ii*) C is a reducing agent while O_2 is an oxidising agent.

(*a*) $\underset{\text{Excess}}{2\overset{0}{C}(s)} + O_2(g) \longrightarrow 2\overset{+2}{C}O\,(g)$

(*b*) $\overset{0}{C}(s) + \underset{\text{Excess}}{O_2} \longrightarrow \overset{+4}{C}O_2(g)$

Q-12 . Consider the elements : Cs, Ne, I and F

(*i*) Identify the element that exhibits only negative oxidation state.

(*ii*) Identify the element that exhibits only positive oxidation state.

(*iii*) Identify the element that exhibits both positive and negative oxidation states.

(*iv*) Identify the element which exhibits neither the negative nor does the positive oxidation state.

Sol. (*i*) F exhibits only negative oxidation state because it is the most electronegative element.

(*ii*) Cs exhibits only positive oxidation state because it is the most electropositive element.

(*iii*) I exhibits both positive and negative oxidation states. Iodine exhibits $-1, 0, +1, 3, +5$ and $+7$ oxidation states ($+3$, $+5$ and $+7$ oxidation states are exhibited by I due to the presence of vacant *d*-orbitals).

(*iv*) Ne is an inert gas, so it neither exhibits negative nor positive oxidation states.

Q-13 Write formulae for the following compounds.

(*i*) Mercury (II) chloride (*ii*) Nickel (II) sulphate

(*iii*) Tin (IV) oxide (*iv*) Thallium (I) sulphate

(*v*) Iron (III) sulphate

(*vi*) Chromium (III) oxide

- While writing the formula of a compound, oxidation state (or valency) of cation is written as the subscript of anion and valency of anion is written as the subscript of cation.
- Valency of chloride (Cl^-), sulphate (SO_4^{2-}) and oxide (O^{2-}) are $-1, -2$ and -2 respectively. Valencies of metals are given in brackets.

Sol. (*i*) Hg (II) Cl_2 (*ii*) Ni (II) SO_4

(*iii*) Sn (IV) O_2 (*iv*) Th_2(I) SO_4

(*v*) Fe_2 (III) $(SO_4)_3$ (*vi*) Cr_2 (III) O_3

Q-14 . While sulphur dioxide and hydrogen peroxide can act as oxidising as well as reducing agents in their reactions, ozone and nitric acid act only as oxidants. Why?

Sol. (*i*) In SO_2, S is in $+4$ oxidation state. It can have minimum oxidation number -2 and maximum oxidation number $+6$. Therefore, S in SO_2 can either decrease or increase its oxidation number. So, SO_2 can act both as oxidising as well as reducing agent.

(*ii*) In H_2O_2, O is in -1 oxidation state. It can have minimum oxidation number -2 and maximum oxidation number zero ($+1$ and $+2$ also possible in O_2F_2 and OF_2 respectively). Therefore, O in H_2O_2 can either decrease or increase its oxidation number. So, H_2O_2 can act both as oxidising as well as reducing agent.

(*iii*) In O_3, O is in zero oxidation state. It cannot increase its oxidation number, it can only decrease its oxidation number from zero to -1 or -2. So, ozone can act only as an oxidising agent.

(*iv*) In HNO_3, the oxidation number of N is $+5$. It is maximum. So, N in HNO_3 can only decrease its oxidation number. So, it can act as an oxidising agent only.

Q-15 One mole of N_2H_4 loses 10 moles electrons to form a new compound Y. Assuming that all the nitrogen appears in the new compound, what is the oxidation number of N in Y? There is no change in oxidation state of H.

Sol. Suppose the oxidation number of N in Y is x

$$(N^{2-})_2 \longrightarrow (2\,N)^x + 10e^-$$

$$(\text{as } N_2H_4 \longrightarrow Y + 10e^-)$$

Therefore, $2x - 10 = -4$, which gives $x = +3$. Hence oxidation number of N in $Y = 3$.

16 Permanganate ion reacts with bromide ion in basic medium to give manganese dioxide and bromate ion. Write the balanced ionic equation for the reaction.

Sol. *Step* 1 The skeletal ionic equation is

$$MnO_4^-(aq) + Br^-(aq) \longrightarrow MnO_2(s) + BrO_3^-(aq)$$

Step 2 Assign oxidation numbers for Mn and Br

$$\overset{+7}{Mn}O_4^-(aq) + \overset{-1}{Br^-}(aq) \longrightarrow \overset{+4}{Mn}O_2(s) + \overset{+5}{Br}O_3^-(aq)$$

this indicates that permanganate ion is the oxidant and bromide ion is the reductant.

Step 3 Calculate the increase and decrease of oxidation number, and make the increase equal to the decrease.

$$2\overset{+7}{Mn}O_4^-(aq) + \overset{-1}{Br^-}(aq) \longrightarrow 2\overset{+4}{Mn}O_2(s) + \overset{+5}{Br}O_3^-(aq)$$

Step 4 As the reaction occurs in the basic medium and the ionic charges are not equal on both sides, add $2\,OH^-$ ions on the right to make ionic charges equal.

$$2MnO_4^-(aq) + Br^-(aq) \longrightarrow 2MnO_2(s) + BrO_3^-(aq) + 2OH^-(aq)$$

Step 5 Finally, count the hydrogen atoms and add appropriate number of water molecules (*i.e.*, one H_2O molecule) on the left side to achieve balanced redox change).

$$2MnO_4^-(aq) + Br^-(aq) + H_2O(l) \longrightarrow 2MnO_2(s) + BrO_3^-(aq) + 2OH^-(aq)$$

Q-17 The Mn^{3+} ion is unstable in solution and undergoes disproportionation to give Mn^{2+}, MnO_2 and H^+ ions. Write a balanced ionic equation for the reaction.

Sol. The skeletal equation is,

$$Mn^{3+}(aq) \longrightarrow Mn^{2+}(aq) + MnO_2(s) + H^+(aq)$$

On solving similar to Q. No. 3.

$$2Mn^{3+}(aq) + 2H_2O(l) \longrightarrow Mn^{2+} + MnO_2(s) + 4H^+(aq)$$

Q-18 Balance the following equations in basic medium by ion electron and oxidation number methods and identify the oxidising agent and the reducing agent.

(*i*) $P_4(s) + OH^-(aq) \longrightarrow PH_3(g) + H_2PO_2^-(aq)$

(*ii*) $N_2H_4(l) + ClO_3^-(aq) \longrightarrow NO(g) + Cl^-(g)$

(*iii*) $Cl_2O_7(g) + H_2O_2(aq) \longrightarrow ClO_2^-(aq) + O_2(g)$

(Each carries 2 Marks)

Sol. (*i*) On solving as in Q. No. 3 and 4, we get following balanced equations

$$P_4(s) + 3OH^-(aq) + 3H_2O \longrightarrow 4PH_3(g) + 3H_2PO_2^-(aq)$$

(*ii*) $3N_2H_4(l) + 4ClO_3^-(aq) \longrightarrow 6NO(g) + 4Cl^-(aq) + 6H_2O(l)$

(*iii*) $Cl_2O_7(g) + 4H_2O_2(aq) + 2OH^-(aq) \longrightarrow 2ClO_2^-(aq) + 5H_2O(l) + 4O_2(g)$

Q-19 What short of informations can you draw from the following reaction?

$$(CN)_2(g) + 2OH^-(aq) \longrightarrow CN^-(aq) + CNO^-(aq) + H_2O(l)$$

Sol. $(CN)_2(g) + 2OH^-(aq) \longrightarrow CN^-(aq) + CNO^-(aq) + H_2O(l)$

(*i*) Let the oxidation number of C in $(CN)_2$ be x.

$$2x + 2(-3) = 0 \quad \text{or} \quad x = +3$$

(*ii*) Let the oxidation number of C in CN^- be x.

$$x + (-3) = -1 \quad \text{or} \quad x = +2$$

(*iii*) Let the oxidation number of C in CNO^- be x.

$$x + (-3) + (-2) = -1 \quad \text{or} \quad x = +4$$

$$\overset{+3}{(CN)_2}(g) + 2OH^-(aq) \longrightarrow \overset{+2}{CN^-}(aq) + \overset{+4}{CNO^-}(aq) + H_2O(l)$$

ON decreases

ON increases

The following information we can drawn from the above reaction.

(*i*) Decomposition of cyanogen in the cyanide ion (CN^-) and cyanate ion (CNO^-) occurs in basic medium.

(*ii*) Cyanogen $(CN)_2$ acts as both reducing agent as well as oxidising agent.

(*iii*) The reaction, is an example of disproportionation reaction (a special type of redox reaction).

(*iv*) Cyanogen $(CN)_2$ is called pseudohalogen while CN^-, CNO^- ions are called pseudohalide ions.

Q-20 Chlorine is used to purify drinking water. Excess of chlorine is harmful. The excess of chlorine is removed by treating with sulphur dioxide. Present a balanced equation for this redox change taking place in water.

Sol.

$$\overset{0}{Cl_2}(aq) + \overset{+4}{SO_2}(aq) + H_2O(l) \longrightarrow \overset{-1}{Cl^-}(aq) + \overset{+6\ 2-}{SO_4}(aq)$$

ON decreases by 1 per Cl atom

ON increases by 2 per S atom

Multiply Cl^- by 2 because in Cl_2, there are two chlorine atoms.

$$Cl_2(aq) + SO_2(aq) + H_2O(l) \rightarrow 2Cl^-(aq) + SO_4^{2-}(aq)$$

Balance first charge by adding $4H^+$ to RHS and then multiply H_2O by 2.

$$Cl_2(aq) + SO_2(aq) + 2H_2O(l) \longrightarrow 2Cl^-(aq) + SO_4^{2-} + 4H^+$$

This represents the balanced redox reaction.

Q-21 Refer to the periodic table given in your book and answer the following questions.

(*i*) Select the possible non-metals that can show disproportionation reaction.

(*ii*) Select three metals that can show disproportionation reaction.

Sol. (*i*) Phosphorus, chlorine and sulphur are the non-metals that can show disproportionation reaction.

(*a*) $P_4(s) + 3OH^-(aq) + 3H_2O(l) \longrightarrow PH_3(g) + 3H_2PO_2^-(aq)$

(*b*) $Cl_2(g) + 2OH^-(aq) \longrightarrow Cl^-(aq) + ClO^-(aq) + H_2O(l)$ (cold)

$3Cl_2(g) + 6OH^-(aq) \longrightarrow 5Cl^-(aq) + ClO_3^-(aq) + 3H_2O(l)$ (hot)

(*c*) $S_8(s) + 12OH^- \longrightarrow 4S^{2-}(aq) + 2S_2O_3^{2-}(aq) + 6H_2O(l)$

(*ii*) Manganese, copper, gallium and indium are the metals that can show disproportionation reaction.

(*a*) $2Mn^{3+}(aq) + 2H_2O(l) \longrightarrow \overset{4+}{MnO_2}(s) + Mn^{2+}(aq) + 4H^+$

(*b*) $2Cu^+(aq) \longrightarrow Cu^{2+}(aq) + \overset{0}{Cu}(s)$

(*c*) $3Ga^+(aq) \longrightarrow Ga^{3+}(aq) + 2\overset{0}{Ga}(s)$

(*d*) $3In^+(aq) \longrightarrow In^{3+}(aq) + 2\overset{0}{In}(s)$

Q-22 Copper dissolves in dilute nitric acid but not in dilute HCl. Explain.

Sol. Since, $E°$ of Cu^{2+}/Cu electrode (+ 0.34 V) is higher than that of H^+/H_2 electrode (0·0 V), therefore, H^+ ions cannot oxidise Cu to Cu^{2+} ions and hence, Cu does not dissolve in dil. HCl.

Q-23 Depict the galvanic cell in which the reaction,

$$Zn(s) + 2Ag^+(aq) \longrightarrow Zn^{2+}(aq) + 2Ag(s)$$

takes place, further show

(*i*) which of the electrode is negatively charged?

(*ii*) the carriers of the current in the cell.

(*iii*) individual reaction at each electrode.

Sol. The given redox reaction for the galvanic cell is

$$Zn(s) + 2Ag^+(aq) \longrightarrow Zn^{2+}(aq) + 2Ag(s)$$

At anode, Zn is oxidised to Zn^{2+} ions and at cathode, Ag^+ ions are reduced to Ag metal. Thus, galvanic cell for the above redox reaction may be depicted as $Zn \mid Zn^{2+}(aq) \parallel Ag^+(aq) \mid Ag$

(*i*) Zn electrode is negatively charged because of the oxidation of Zn to Zn^{2+} ions, electrons are accumulated on zinc electrode.

(*ii*) The ions carry current in the cell. Current flows from Ag electrode to Zn electrode. While electrons flow from Zn electrode to Ag electrode.

(*iii*) Individual reaction at each electrodes

Anode $Zn \longrightarrow Zn^{2+} + 2e^-$

Cathode $Ag^+(aq) + e^- \longrightarrow Ag(s)$

Q-24 ple 5. Suggest a scheme of classification of the following redox reactions.

(*i*) $N_2(g) + O_2(g) \longrightarrow 2NO\ (g)$

(*ii*) $2Pb(NO_3)_2(s) \longrightarrow 2PbO\ (s) + 2NO_2(g) + \frac{1}{2}O_2(g)$

(*iii*) $NaH(s) + H_2O\ (l) \longrightarrow NaOH\ (aq) + H_2(g)$

(*iv*) $2NO_2(g) + 2OH^-(aq) \longrightarrow NO_2^-(aq) + NO_3^-(aq) + H_2O(l)$

Solution (*i*) Since, the two molecules are combining to give a single product, so it is an example of combination reaction.

(*ii*) Since, the compound splits up into several simpler substances, out of which O_2 is in the elemental form, thus, it is classified as decomposition redox reaction.

(*iii*) $NaH(s) + H_2O(l) \longrightarrow NaOH(aq) + H_2(g)$

The ionic form of the reaction is $H^-(s) + H_2O(l) \longrightarrow OH^-(aq) + H_2(g)$

Here, H^- (hydride ion) displaces hydrogen from water molecule, so it is an example of displacement redox reaction.

Oxidation

(*iv*) $\overset{+4}{2NO_2}(g) + 2O\bar{H}\ (aq) \longrightarrow \overset{+3}{N}O_2^-\ (aq) + \overset{+5}{N}O_3(aq) + H_2^-O(l)$

Reduction

Since, in the above reaction, the same element undergoes oxidation as well as reduction, so it is an example of disproportionation reaction.

Q-25 Arrange the following metals in the order in which they displace each other from the solution of their salts. Al, Cu, Fe, Mg and Zn

Sol. $E^\circ_{Al^{3+}/Al} = -1.66\ V, E^\circ_{Cu^{2+}/Cu} = +0.34\ V,$

$$E^\circ_{Fe^{2+}/Fe} = -0.44\ V,\ E^\circ_{Mg^{2+}/Mg} = 2.36\ V$$

and $$E^\circ_{Zn^{2+}/Zn} = -0.76\ V$$

A metal with more negative value of E°_{red} is a stronger reducing agent than those which have less negative or positive value of E°_{red}. Therefore, Mg can displace all the given metals from their aqueous salt solutions. Al can displace all metals except Mg from their aqueous salt solutions. Zinc can displace Fe and Cu from their aqueous salt solutions and Fe can displace only Cu from its aqueous salt solution.

Hence, the order in which they can displace each other from the solution of their salts is as follows

Mg, Al, Zn, Fe, Cu

Q-26 *Write the net ionic equation for the reaction of potassium dichromate* (VI), $K_2Cr_2O_7$ *with sodium sulphite,* Na_2SO_3, *in an acid solution to give chromium* (III) *ion and the sulphate ion.*

Step 1 Following steps are involved in order to solve out such problems.

Writing skeleton ionic equation.

e.g., $Cr_2O_7^{2-}(aq) + SO_3^{2-}(aq) \longrightarrow Cr^{3+}(aq) + SO_4^{2-}(aq)$

Step 2 Assigning oxidation number to each element and balancing atoms other than H and O.

$$\overset{+6\ -2}{Cr_2O_7^{2-}}(aq) + \overset{+4\ -2}{SO_3^{2-}}(aq) \longrightarrow \overset{+3}{Cr^{3+}}(aq) + \overset{+6\ -2}{SO_4^{2-}}(aq)$$

Step 3 Finding change in oxidation number and equalise it

Change in ON = 6 − 4 = 2] × $\underline{3}$

$$\overset{+6\ -2}{Cr_2O_7^{2-}}(aq) + \underline{3}\overset{+4-2}{SO_3^{2-}}(aq) \longrightarrow \underline{2}\overset{+3}{Cr^{3+}}(aq) + \underline{3}\overset{+6-2}{SO_4^{2-}}(aq)$$

To balance number of Cr atoms

Change in ON = 6 − 3 = 3 per atom

or 3 × 2 = 6 net change (as two Cr atoms are involving)

To equalise the increase in oxidation state of S with decrease in oxidation state of Cr, we have to multiply it with 3, thus we have to also multiply SO_3^{2-} and SO_4^{2-} with 3.

Step 4 Balancing ionic charge

Since, the medium is acidic, so we can use only H^+ ions to balance the charge

$$Cr_2O_7^{2-}(aq) + 3SO_3^{2-}(aq) \longrightarrow 2Cr^{3+}(aq) + 3SO_4^{2-}(aq)$$
$$(-2) + (-2\times 3) \quad = \quad (2\times 3) + (-2\times 3)$$
$$-8 \qquad\qquad = 0$$

So, to balance −8 charge, we have to add $8H^+$ ions at the reactant side. Thus, the reaction becomes

$$Cr_2O_7^{2-}(aq) + 3SO_3^{2-}(aq) + 8H^+(aq) \longrightarrow 2Cr^{3+}(aq) + 3SO_4^{2-}(aq)$$

Step 5 Balancing of H and O atoms

Now count the total number of H atoms on both the sides and add H_2O molecule to equalise them.

In the above reaction, there are 8H atoms towards the reactant side, so in order to balance them, we add $4H_2O$ towards the product side.

$$Cr_2O_7^{2-}(aq) + 3SO_3^{2-}(aq) + 8H^+(aq) \longrightarrow 2Cr^{3+}(aq) + 3SO_4^{2-}(aq) + 4H_2O$$

Now, we check the number of O atoms. Since, the number of O atoms are already balanced, so the equation is a balanced chemical equation.

Q-27 Predict the products of electrolysis in each of the following.

(i) An aqueous solution of $AgNO_3$ with silver electrodes.

(ii) An aqueous solution of $AgNO_3$ with platinum electrodes.

(iii) A dilute solution of H_2SO_4 with platinum electrodes.

(iv) An aqueous solution of $CuCl_2$ with platinum electrodes.

- Higher the oxidation potential of an element, more readily it gets oxidised.
- In case of aqueous solution, H^+ and OH^- ions are also present, so compare the oxidation potential of the elements/ions with that of the H^+ and OH^- to decide the product.

Solution (i) An aqueous solution of $AgNO_3$ with silver electrodes.

Two oxidation and two reduction half reactions must be considered.

Oxidation (at anode)

(a) $Ag(s) \longrightarrow Ag^+(aq) + e^-; \quad E° = -0.80\ V$

(b) $2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-; \; E° = -1.23\ V$

Reduction (at cathode)

(c) $Ag^+(aq) + e^- \longrightarrow Ag(s); \quad E° = +0.80\ V$

(d) $2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq);$

$$E° = -0.83\ V$$

By $E°$ values of (a) and (b), it appears that at anode, silver of silver anode gets oxidised more readily because oxidation potential of Ag is greater than that of H_2O molecule. Similarly by $E°$ values of (c) and (d), it appears that at cathode, reduction potential of Ag^+ ions higher than that of H_2O molecules.

Therefore, on electrolysis of aqueous $AgNO_3$ solution with silver electrodes, Ag from silver anode dissolves while $Ag^+(aq)$ ions present in the solution gets reduced and deposited at cathode.

(ii) An aqueous solution of $AgNO_3$ with platinum electrodes. Platinum is an inert electrode so at anode oxidation of water takes place. As a result of this, O_2 is released at anode according to equation (b) {as in (i)}. At cathode reduction of Ag^+ ions takes place.

Therefore, on electrolysis of aqueous $AgNO_3$ solution with platinum electrodes, O_2 is released at anode and Ag^+ ions from solution gets deposited at cathode.

(iii) A dilute solution of H_2SO_4 with platinum electrodes.

$$H_2SO_4\ (aq) \rightleftharpoons 2H^+ + SO_4^{2-}$$

When current is passed, either H^+ ions or H_2O molecules are reduced at cathode.

$$2H^+(aq) + 2e^- \longrightarrow H_2(g);\ E° = 0.0\ V$$
$$2H_2O(aq) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq);$$
$$E° = -0.83\ V$$

At cathode, H^+ ions gets reduced first because reduction potential of H^+ ions is greater than H_2O molecules.

Similarly, on passing current either. SO_4^{2-} ions or H_2O molecules are oxidised at anode. SO_4^{2-} ions are resistant to oxidation and are not discharged at anode. So, at anode, H_2O moleules are oxidised to release O_2 gas.

$$2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-;$$
$$E° = -1.23\ V$$

Therefore, an electrolysis of an aqueous solution of H_2SO_4, only electrolysis of water occurs releasing H_2 at cathode and O_2 at anode.

(iv) An aqueous solution of $CuCl_2$ with platinum electrodes.

$$CuCl_2(aq) \rightleftharpoons Cu^{2+} + 2Cl^-(aq);$$

(ionisation of $CuCl_2$ in water)

Two oxidation and two reduction half reactions must be considered.

Oxidation (at anode)

(a) $2Cl^-(aq) \longrightarrow Cl_2(g) + 2e^-; E° = -1.36\ V$

(b) $2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-;$

$$E° = -1.23\ V$$

Reduction (at cathode)

(c) $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s);\ E° = +0.34\ V$

SARASWATI CHEMISTRY

Equilibrium

Q-1. A tank is full of water. Water is coming in as well as going out at same rate. What will happen to level of water in a tank ? What is name given to such state?

Sol. It will remain the same because rate of inflow is equal to rate of outflow. The state is called state of 'equilibrium'.

Q-2. Explain, why pure liquids and solids can be ignored while writing the equilibrium constant expression?

Sol. Molar concentration of a pure solid or liquid (if in excess) is constant (*i.e.*, independent of the amount present). That's why pure liquids and solids can be ignored while writing the equilibrium constant expression.

Q-3 The equilibrium constant expression for a gas reaction is,

$$K_c = \frac{[NH_3]^4 [O_2]^5}{[NO]^4 [H_2O]^6}$$

Write the balanced chemical equation corresponding to this expression.

Sol. The expression shows that $4NO$ and $6H_2O$ molecules are reactants and $4NH_3$ and $5O_2$ molecules are products. Thus, the balanced chemical equation is

$$4NO + 6H_2O \longrightarrow 4NH_3 + 5O_2$$

Q-4 Predict which of the following reaction will have appreciable concentration of reactants and products?

(*i*) $Cl_2(g) \rightleftharpoons 2Cl(g);\quad K_c = 5 \times 10^{-39}$

(*ii*) $Cl_2(g) + 2NO(g) \rightleftharpoons 2NOCl(g);\ K_c = 3.7 \times 10^{-8}$

(*iii*) $Cl_2(g) + 2NO_2(g) \rightleftharpoons 2NO_2Cl(g);\ K_c = 1.8$

Q-5. Write the conjugate acids for the following Bronsted bases NH_2^-, NH_3 and $HCOO^-$.

$\text{Base} + H^+ \rightleftharpoons \text{Conjugate acid}$

Sol. The conjugate acid should have one extra proton in each case and therefore the corresponding conjugate acid are NH_3, NH_4^+ and $HCOOH$ respectively.

Q-6. Which of the following are Lewis acids?

H_2O, BF_3, H^+, NH_4^+

Lewis acids have a tendency to accept electrons. Electron deficient or positively charged species have such tendency.

Sol. BF_3, H^+ and NH_4^+ act as Lewis acids.

Q-7 What will be the conjugate bases for the following Bronsted acids HF, H_2SO_4 and HCO_3^-?

$\text{Acid} \rightleftharpoons \text{Conjugate base} + H^+$

Sol. The conjugate bases should have one proton less in each case and therefore the corresponding conjugate bases are F^-, HSO_4^- and CO_3^{2-} respectively.

Q-8. What is K_c for the following equilibrium when the equilibrium concentration of each substance is $[SO_2] = 0.60\ M$, $[O_2] = 0.82\ M$ and $[SO_3] = 1.90\ M$?

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

Sol. Equilibrium constant,

$$K_c = \frac{[SO_3]^2}{[SO_2]^2 \cdot [O_2]} = \frac{(1.90\ M)^2}{(0.60\ M)^2\ (0.82\ M)}$$

$$\approx 12.23\ M^{-1}$$

Q-9 One mole of H_2O and one mole of CO are taken in 10 L vessel and heated to 725 K. At equilibrium, 40% of water (by mass) reacts with CO according to the equation,

$$H_2O(g) + CO(g) \rightleftharpoons H_2(g) + CO_2(g)$$

Calculate the equilibrium constant for the reaction.

Sol.

	$H_2O(g)$ +	$CO(g)$ $\rightleftharpoons$	$H_2(g)$ +	$CO_2(g)$
Initial conc.	1	1	0	0
Equili. conc.	$(1-x)$	$(1-x)$	x	x

H_2O reacted = 40% of 1 mole of H_2O = 0.4 mol

$\therefore \quad x = 0.4\ \text{mol}$

$(1 - x) = 1 - 0.4 = 0.6\ \text{mol}$

$$K_c = \frac{[H_2][CO_2]}{[H_2O][CO]} = \frac{0.4 \times 0.4}{0.6 \times 0.6} = 0.444$$

Q-10 A sample of pure PCl_5 was introduced into an evacuated vessel at 473 K. After equilibrium was attained, concentration of PCl_5 was found to be 0.5×10^{-1} mol L^{-1}. If value of K_c is 8.3×10^{-3}, what are the concentration of PCl_3 and Cl_2 at equilibrium ?

Sol. $$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

At equili. 0.5×10^{-1} M $\quad x \quad x$

$$\therefore \quad K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

$$8.3 \times 10^{-3} = \frac{x^2}{0.05} \text{ (because } [PCl_3] = [Cl_2])$$

or $$x^2 = 0.415 \times 10^{-3} = 4.15 \times 10^{-4}$$

$$x \approx 2.04 \times 10^{-2} \text{ mol L}^{-1}$$

Hence, $$[PCl_3] = [Cl_2] = 2.04 \times 10^{-2} \text{ mol L}^{-1}$$

Q-11. The value of K_c for the reaction, $3O_2(g) \rightleftharpoons 2O_3(g)$ is 2.0×10^{-50} at 25°C. If the equilibrium concentration of O_2 in air at 25°C is 1.6×10^{-2}, what is the concentration of O_3?

Sol. $3O_2(g) \rightleftharpoons 2O_3(g)$

$$K_c = \frac{[O_3]^2}{[O_2]^3}$$

or $$O_3 = \sqrt{K_c[O_2]^3}$$

$$[O_3] = 2.86 \times 10^{-28} \text{ mol L}^{-1}$$

Q-12 For the following equilibrium, $K_c = 6.3 \times 10^{14}$ at 1000 K

$$NO(g) + O_3(g) \rightleftharpoons NO_2(g) + O_2(g)$$

Both the forward and reverse reactions in the equilibrium are elementary bimolecular reactions. What is K_c for the reverse reaction?

Sol. For the reaction,

$$NO(g) + O_3(g) \rightleftharpoons NO_2(g) + O_2(g);$$

$$(K_c = 6.3 \times 10^{14} \text{ at } 1000 \text{ K})$$

$$K_c = \frac{[NO_2][O_2]}{[NO][O_3]} = 6.3 \times 10^{14} \quad \ldots\text{(i)}$$

For reverse reaction,

$$NO_2(g) + O_2(g) \rightleftharpoons NO(g) + O_3(g)$$

$$K_c' = \frac{[NO][O_3]}{[NO_2][O_2]} \quad \ldots\text{(ii)}$$

From Eqs. (i) and (ii), we get

$$K_c' = \frac{1}{K_c} = \frac{1}{6.3 \times 10^{14}}$$

$$= 1.587 \times 10^{-15}$$

Q-13. Neutral solutions have pH = 7 at 298 K. A sample of pure water is found to have pH < 7. Does it mean that it is acidic ? Explain.

Sol. pH < 7 for pure H_2O shows that water is at a temperature higher than 298 K. It is neutral at all temperatures. At higher temperature, H_2O dissociates more to give large concentrations of H^+ ions and OH^- ions. Hence, pH < 7. However, $[H^+] = [OH^-]$ at all temperatures.

Q-14 . Ionic product of water at 310 K is 2.7×10^{-14}. What is the pH of neutral water at this temperature?

Sol. $K_w = [H_3O^+] \cdot [OH^-] = 2.7 \times 10^{-14}$ at 310 K

$$H_2O + H_2O \rightleftharpoons [H_3O^+][OH^-]$$

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

Therefore, $$[H_3O^+] = \sqrt{2.7 \times 10^{-14}}$$

$$= 1.643 \times 10^{-7} \text{ M}$$

$$pH = -\log [H_3O^+] = -\log 1.643 \times 10^{-7}$$

$$pH = 7 + (-0.2156) = 6.7844$$

Q-15. The pH of a sample of vinegar is 3.76. Calculate the concentration of hydrogen ion in it.

Sol. $pH = -\log [H^+] = 3.76$

$$\log [H^+] = -3.76$$

[Before taking antilog add −1 in characteristic (− 3) and +1 in mantissa (0.76), *i.e.*, $-3.76 - 1 + 1 = \bar{4}.24$]

$$\log[H^+] = \bar{4}.24 \text{ or } [H^+] = \text{antilog } \bar{4}.24$$

$$[H^+] \text{ antilog}(3.76) = 1.738 \times 10^{-4} \text{ M}$$

Q-16. At 450 K, $K_p = 2.0 \times 10^{10}$/bar for the given reaction at equilibrium,

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

What is K_c at this temperature?

Sol. $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

$$\therefore \quad \Delta n_g = 2 - 3 = -1$$

$$K_c = \frac{K_p}{(RT)^{\Delta n_g}} = \frac{K_p}{(RT)^{-1}}$$

$$K_c = K_p \times RT$$

$$= 2.0 \times 10^{10} \times 0.0831 \times 450$$

$$= 7.479 \times 10^{11} \text{ L mol}^{-1}$$

Q-17 Following data is given for the reaction,

$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$;

$$\Delta_f H^\circ[CaO(s)] = -635.1\,kJmol^{-1}$$

$$\Delta_f H^\circ[CO_2(g)] = -393.5\,kJmol^{-1}$$

$$\Delta_f H^\circ[CaCO_3(s)] = -1206.9\,kJmol^{-1}$$

Predict the effect of temperature on the equilibrium constant of the above reaction.

Sol. $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

$$\Delta_f H^\circ = \Delta_f H^\circ[CaO(s)] + \Delta_f H^\circ[CO_2(g)] - \Delta_f H^\circ[CaCO_3(s)]$$

$$\Delta_f H^\circ = -635.1 + (-393.5) - (-1206.9)$$

$$= +178.3\ kJ\ mol^{-1}$$

Because ΔH value is positive, so the reaction is endothermic. Hence, according to Le-Chatelier's principle, reaction will proceed in forward direction on increasing temperature.

Q-18 The ionisation constant of HF, HCOOH and HCN at 298 K are 6.8×10^{-4}, 1.8×10^{-4} and 4.8×10^{-9} respectively. Calculate the ionisation constants of the corresponding conjugate base.

- To find K_b of a conjugate base, use the formula $K_a \cdot K_b = K_w = 1 \times 10^{-14}$.
- Conjugate bases of HF, HCOOH and HCN are F^-, $HCOO^-$ and CN^- respectively.

Sol. If K_a is the ionisation constant of a weak acid (HA) and K_b is the ionisation constant of its conjugate base (A^-) then $K_a \cdot K_b = K_w$

$$K_b\,(F^-) = \frac{K_w}{K_a\,(HF)} = \frac{1 \times 10^{-14}}{6.8 \times 10^{-4}}$$

$$= 1.47 \times 10^{-11}$$

$$K_b\,(HCOO^-) = \frac{K_w}{K_a\,(HCOOH)} = \frac{1 \times 10^{-14}}{1.8 \times 10^{-4}}$$

$$= 5.56 \times 10^{-11}$$

$$K_b\,(CN^-) = \frac{K_w}{K_a\,(HCN)} = \frac{1 \times 10^{-14}}{4.8 \times 10^{-9}} = 2.08 \times 10^{-6}$$

Q-19 The average concentration of SO_2 in atmosphere over a city on a certain day is 10 ppm, when the average temperature is 298 K. Given that the solubility of SO_2 in water at 298 K is 1.3653 mol/L and the pK_a of H_2SO_3 is 1.92, estimate the pH of acid rain on that day.

Sol. Amount of SO_2 in atmospheres = 10 ppm = $\frac{10}{10^6} = 10^{-5}$

Molar conc. of SO_2 in pressure of water

= amount of SO_2 × solubility of SO_2 in water

H_2SO_3 dissociates as $= 1.3653 \times 10^{-5}$

$$H_2SO_3 \rightleftharpoons H^+ + HSO_3^-$$

	H_2SO_3	H^+	HSO_3^-
Ini.	1.3653×10^{-5}	0	0
Molar conc. of equiv.	$(1.3653 \times 10^{-5} - x)$	x	x

$$K_a = \frac{x^2}{(1.3653 \times 10^{-5} - x)}$$

$$PK_a = 1.92$$

∴ $$-\log K_a = 1.92$$

or $$K_a = 1.2 \times 10^{-2}$$

Substituting $$1.2 \times 10^{-2} = \frac{x^2}{(1.3653 \times 10^{-5} - x)}$$

or $$x^2 = 1.2 \times 10^{-2}\,(1.3653 \times 10^{-5} - x)$$

On solving, we get

$$x = 1.3664 \times 10^{-5}$$

∴ $$pH = -\log(1.364 \times 10^{-5}) = 4.865$$

Q-20 The pH of 0.005 M codeine $(C_{18}H_{21}NO_3)$ solution is 9.95. Calculate its ionisation constant and pK_b.

- As codeine is a weak base, its ionisation constant is related to OH^- as
  $$K_b = \frac{[OH^-]^2}{[Codeine]}$$
- Calculate $[OH^-]$ from pOH with the help of the formula $pOH = -\log[OH^-]$
- $pK_b = -\log K_b$

Sol. $Codeine(C_{18}H_{21}NO_3) + H_2O \rightleftharpoons Codeine H^+ + OH^+$

$$pH = 9.95$$

∴ $$pOH = 14 - 9.95 = 4.05$$

Again, from $$pOH = -\log[OH^-]$$

$$\log[OH^-] = -4.05 = \bar{5}.95$$

$$[OH^-] = antilog\ \bar{5}.95 = 8.913 \times 10^{-5}$$

$$K_b = \frac{[codeine\ H^+]\ [OH^-]}{[codeine]} = \frac{[OH^-]^2}{[codeine]}$$

(because $[codeine\ H^+] = [OH^-]$)

$$K_b = \frac{(8.913 \times 10^{-5})^2}{0.005} = 1.588 \times 10^{-6}$$

From, $pK_b = -\log[K_b] = -\log[1.588\times 10^{-6}]$

$$pK_b = 6 + (-0.2009) = 5.7991$$
$$\approx 5.80$$

Q-21. It has been found that the pH of a 0.01 M solution of an organic acid is 4.15. Calculate the concentration of the anion, the ionisation constant of the acid and its pK_a.

- Organic acids are weak acids, so dissociate as $HA \rightleftharpoons H^+ + A^-$ and their K_a is calculated as, $K_a = \frac{[H^+][A^-]}{[HA]}$.
- To calculate K_a, $[H^+]$ and $[A^-]$ are required. Calculate $[H^+]$ by using the formula, $pH = -\log[H^+]$ and calculate $[A^-]$ by using the equation $HA \rightleftharpoons H^+ + A^-$.
- Then, calculate K_a by using the formula, $K_a = \frac{[H^+][A^-]}{[HA]}$.
- Calculate pK_a by using the formula $pK_a = -\log K_a$.

Sol.

$$HA \rightleftharpoons H^+ + A^-$$
$$pH = -\log[H^+] = 4.15$$
$$\log[H^+] = -4.15$$
$$\log[H^+] = \bar{5}.85 \text{ or } [H^+] = \text{antilog } \bar{5}.85$$
$$= 7.079\times 10^{-5}$$
$$[H^+] = [A^-] = 7.079\times 10^{-5}\ M$$

Thus,
$$K_a = \frac{[H^+][A^-]}{[HA]}$$
$$= \frac{(7.079\times 10^{-5})(7.079\times 10^{-5})}{0.01}$$
$$= 5011.22\times 10^{-10} = 5.0\times 10^{-7}$$

From,
$$pK_a = -\log K_a$$
$$= -\log[5.0\times 10^{-7}]$$
$$= -0.699 + 7 = 6.301$$

Q-22 The ionisation constant of acetic acid is 1.74×10^{-5}. Calculate the degree of dissociation of acetic acid in its 0.05 M solution. Calculate the concentration of acetate ion in the solution and its pH.

Sol.

$$\begin{array}{lcccc} & CH_3COOH + H_2O & \rightleftharpoons & CH_3COO^- & + H_3O^+ \\ \text{Initially} & C & & 0 & 0 \\ \text{At time } t & C-C\alpha & & C\alpha & C\alpha \end{array}$$

$$K_a = \frac{[CH_3COO^-]\ [H_3O^+]}{[CH_3COOH]}$$

$$[CH_3COO^-] = [H_3O^+]$$

$$\therefore\ [CH_3COO^-] = [H_3O^+] = \sqrt{K_a\cdot[CH_3COOH]}$$

Given, $K_a = 1.74\times 10^{-5}$, $[CH_3COOH] = 0.05$ M

$$\therefore\ [CH_3COO^-] = [H_3O^+] = \sqrt{1.74\times 10^{-5}\times 0.05}$$
$$[CH_3COO^-] = [H_3O^+] = \sqrt{17.4\times 10^{-6}\times 5.0\times 10^{-2}}$$
$$= 9.33\times 10^{-4}\ M$$

Again, from $[CH_3COO^-] = [H_3O^+] = C\cdot\alpha$

$$\text{Degree of dissociation, } \alpha = \frac{[H_3O^+]}{C}$$
$$= \frac{9.33\times 10^{-4}}{0.05} = 1.86\times 10^{-2}$$
$$pH = -\log[H_3O^+]$$
$$pH = -\log[9.33\times 10^{-4}]$$
$$4 - 0.9699 = 4 - 0.97 = 3.03$$

Q-23 The degree of ionisation of a 0.1 M bromoacetic acid solution is 0.132. Calculate the pH of the solution and the pK_a of bromoacetic acid.

- Find K_a by using the formula $K_a = C\cdot\alpha^2$ (for weak acid).
- Find pK_a by using the formula $pK_a = -\log K_a$.
- To find pH of the solution, find $[H_3O^+]$ concentration, by using the relation $[H_3O^+] = C\alpha$.

Sol.

$$\begin{array}{lcccc} & CH_2(Br)COOH + H_2O & \rightleftharpoons & CH_2(Br)COO^- & + H_3O^+ \\ \text{Initial conc.} & C & & 0 & 0 \\ \text{Equili. conc.} & C-C\alpha & & C\alpha & C\alpha \\ & C(1-\alpha) & & & \end{array}$$

$$K_a = \frac{[CH_2(Br)COO^-][H_3O^+]}{[CH_2(Br)COOH]}$$
$$= \frac{C\alpha\cdot C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)}$$
$$K_a = C\alpha^2 \qquad [\text{For weak acid } (1-\alpha)\approx 1]$$
$$K_a = 0.1\times(0.132)^2 = 0.00174$$
$$\approx 1.74\times 10^{-3}$$

From
$$pK_a = -\log K_a$$
$$pK_a = -\log[1.74\times 10^{-3}]$$
$$= -0.2405 + 3 = 2.7595$$

From $[H_3O^+] = C\alpha = 0.1\times 0.132 = 0.0132$

$$pH = -\log[H_3O^+]$$
$$\therefore\ pH = -\log[1.32\times 10^{-2}]$$
$$pH = -0.1206 + 2$$
$$= 1.8794 \approx 1.88$$

Q-24 Calculate the pH of the resultant mixtures

(*i*) 10 mL of 0.2 M $Ca(OH)_2$ + 25 mL of 0.1 M HCl

(*ii*) 10 mL of 0.01 M H_2SO_4 + 10 mL of 0.01 M $Ca(OH)_2$

(*iii*) 10 mL of 0.1 M H_2SO_4 + 10 mL of 0.1 M KOH

Sol. (*i*) Millimoles of base, $Ca(OH)_2 = M_1V_1$

$$= 2 \times 0.2 \times 10 = 4$$

Millimoles of acid, $HCl = M_2V_2 = 0.1 \times 25 = 2.5$

$$4 > 2.5$$

i.e., $M_1V_1 > M_2V_2$ hence, solution is basic.

$$\therefore \quad [OH^-] = \frac{M_1V_1 - M_2V_2}{V_1 + V_2}$$

$$= \frac{4 - 2.5}{10 + 25} = 0.043\text{ M}$$

$$\therefore \quad pOH = -\log[4.3 \times 10^{-2}]$$

$$= -0.6335 + 2 = 1.3665$$

$$pH = 14 - pOH$$

$$= 14 - 1.3665 = 12.6335 \approx 12.63$$

(*ii*) Millimoles of acid, $H_2SO_4 = M_1V_1$

$$= 2 \times 0.01 \times 10 = 0.2$$

Millimoles of base, $Ca(OH_2) = M_2V_2$

$$= 2 \times 0.01 \times 10 = 0.2$$

$M_1V_1 = M_2V_2$, hence solution is neutral.

$$\therefore \quad pH = 7$$

(*iii*) Millimoles of acid, $H_2SO_4 = M_1V_1 = 2 \times 0.1 \times 10 = 2$

Millimoles of base, $KOH = M_2V_2 = 0.1 \times 10 = 1$

$$2 > 1$$

i.e., $M_1V_1 > M_2V_2$

i.e., $M_1V_1 > M_2V_2$, hence solution is acidic,

$$[H^+] = \frac{M_1V_1 - M_2V_2}{V_1 + V_2}$$

$$= \frac{(0.2 \times 10) - (0.1 \times 10)}{10 + 10} = \frac{2 - 1}{20} = 0.05\text{ M}$$

$$pH = -\log[0.05] = -\log[5.0 \times 10^{-2}]$$

$$= 1.301 \approx 1.30$$

Q-25. The pH of 0.1M solution of cyanic acid (HCNO) is 2.34. Calculate the ionisation constant of the acid and its degree of ionisation in the solution.

As we have pH, find $[H_3O^+]$ to calculate K_a and α.

$$\alpha = \frac{[H_3O^+]}{C}$$

Sol. $HCNO + H_2O \rightleftharpoons H_3O^+ + CNO^-$

$$pH = -\log[H_3O^+] = 2.34$$

$$\log[H_3O^+] = -2.34 = \bar{3}.66$$

$$[H_3O^+] = \text{antilog } \bar{3}.66$$

$$= 4.571 \times 10^{-3}\text{ M}$$

Ionisation constant, $K_a = \dfrac{[H_3O^+][CNO^-]}{[HCNO]}$

$$= \frac{4.571 \times 10^{-3} \times 4.571 \times 10^{-3}}{0.1}$$

$$= 2.089 \times 10^{-4}$$

Degree of ionisation, $\alpha = \dfrac{[H_3O^+]}{C}$

$$\alpha = \frac{4.571 \times 10^{-3}}{0.1}$$

$$= 4.571 \times 10^{-2}$$

Q-26. The solubility of $Sr(OH)_2$ at 298 K is 19.23 g/L of solution. Calculate the concentrations of strontium and hydroxyl ions and the pH of the solution.

- First find concentration of $Sr(OH)_2$ solution in mol per litre as concentration is given in g/L.
- We have the $[OH^-]$, so find $[H^+]$ ion concentration with the help of $[H^+][OH^-] = 10^{-14}$.
- Find pH of the solution from $[H^+]$.

Sol. Solubility of $Sr(OH)_2 = 19.23$ g/L (at 298 K)

[Molar mass of $Sr(OH)_2 = 87.6 + 2(16 + 1)$

$$= 121.6\text{ g mol}^{-1}]$$

Molarity, $\quad M = \dfrac{19.23}{121.6 \times 1}$

$$M = 0.1581\text{ mol L}^{-1}$$

$$\underset{0.1581\text{ M}}{Sr(OH)_2} \longrightarrow \underset{0.1581\text{ M}}{Sr^{2+}} + \underset{2 \times 0.1581\text{ M}}{2OH^-}$$

Here, $\quad [Sr^{2+}] = 0.1581\text{ M}$

$$[OH^-] = 0.3162\text{ M}$$

From, $[H^+] \cdot [OH^-] = 10^{-14}$

$$[H^+] = \frac{10^{-14}}{0.3162} = 3.16 \times 10^{-14}$$

$$pH = -\log[H^+]$$

$$= -\log[3.16 \times 10^{-14}]$$

$$pH = -0.4997 + 14$$

$$= 13.5003 \approx 13.5$$

Q-27 If 0.561 g of KOH is dissolved in water to give 200 mL of solution at 298 K, calculate the concentrations of potassium, hydrogen and hydroxyl ions. What is its pH?

Sol. Molarity of KOH, $M = \dfrac{\text{mass of KOH (g)} \times 1000}{\text{molar mass (KOH)} \times \text{Volume of solution (in mL)}} \Rightarrow M = \dfrac{0.561 \times 1000}{56 \times 200}$

(Molar mass of $KOH = 39 + 16 + 1 = 56\ \text{g mol}^{-1}$) $\Rightarrow M = 0.05\ \text{mol L}^{-1}$

$$KOH \rightleftharpoons K^+ + OH^-$$

$\therefore$ $[K^+] = 0.05\ \text{M}$ and $[OH^-] = 0.05\ \text{M}$

From, $[H^+] \cdot [OH^-] = K_w = 1.0 \times 10^{-14}$

$$[H^+] = \frac{1.0 \times 10^{-14}}{0.05} = 20 \times 10^{-14}\ \text{M} = 2.0 \times 10^{-13}\ \text{M}$$

$$pH = -\log[H^+] = -\log[2.0 \times 10^{-13}] = -0.3010 + 13 = 12.7$$

Q-28 The ionisation constant of dimethylamine is 5.4×10^{-4}. Calculate its degree of ionisation in its 0.02 M solution. What percentage of dimethylamine is ionised if the solution is also 0.1 M in NaOH?

Sol. Given, K_b for dimethylamine $= 5.4 \times 10^{-4}$, C for dimethylamine $= 0.02\ \text{M}$

$$\alpha = \sqrt{K_b / C} = \sqrt{\frac{5.4 \times 10^{-4}}{0.02}} = 1.64 \times 10^{-1} = 0.164$$

In the presence of 0.1 M NaOH,

$$(CH_3)_2\dot{N}H + H_2O \rightleftharpoons (CH_3)_2\overset{+}{N}H_2 + OH^-$$

	$(CH_3)_2NH$	$(CH_3)_2\overset{+}{N}H_2$	OH^-
Initial conc.	0.02 M	0	0
Equili. conc.	$(0.02 - C\alpha)$	$C\alpha$	$C\alpha + 0.1$
	≈ 0.02		≈ 0.1 (0.1 from 0.1 M NaOH)

$$K_b = \frac{[(CH_3)_2\overset{+}{N}H_2]\,[OH^-]}{[(CH_3)_2NH]}$$

$$\therefore \quad 5.4 \times 10^{-4} = \frac{0.02\alpha \times 0.1}{0.02}$$

$$\alpha = \frac{5.4 \times 10^{-4} \times 0.02}{0.02 \times 0.1} = 54 \times 10^{-4} = 5.4 \times 10^{-3}$$

$$\alpha = 0.54\%$$

Q-29 For the reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, the partial pressures of N_2 and H_2 are 0.80 and 0.40 atmosphere respectively at equilibrium. The total pressure of the system is 2.80 atmosphere. What is K_p for the above reaction?

Sol. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

Given, at equilibrium, $p_{N_2} = 0.80$ atmosphere, $p_{H_2} = 0.40$ atmosphere

$$p_{N_2} + p_{H_2} + p_{NH_3} = 2.80\ \text{atmosphere}$$

$$\therefore \quad p_{NH_3} = 2.80 - (0.80 + 0.40) = 1.60\ \text{atmospheres}$$

From,

$$K_p = \frac{p^2_{NH_3}}{p_{N_2} \times p^3_{H_2}} = \frac{(1.60)^2}{0.80 \times (0.40)^3} = 50.0$$

Q-30 A sample of HI(g) is placed in flask at a pressure of 0.2 atm. At equilibrium, the partial pressure of HI(g) is 0.04 atm. What is K_p for the given equilibrium?

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

Sol.

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

	$2HI(g)$	$H_2(g)$	$I_2(g)$
Initial pressure	0.2 atm	0	0
Equili. pressure	0.04 atm	0.08 atm	0.08 atm

(Decrease in pressure of HI $= 0.2 - 0.04 = 0.16$ atm; so equilibrium pressure of H_2 is $\frac{0.16}{2} = 0.08$ atm, and for I_2 is $\frac{0.16}{2} = 0.08$ atm as two moles of HI on dissociation gives 1 mole H_2 and 1 mole I_2)

$$K_p = \frac{p_{H_2} \times p_{I_2}}{p_{HI}^2} = \frac{0.08 \times 0.08}{(0.04)^2} = 4.0$$

Q-31. Dihydrogen gas used in Haber's process is produced by reacting methane from natural gas with high temperature steam. The first stage of two stage reaction involves the formation of CO and H_2. In second stage, CO formed in first stage is reacted with more steam in water gas shift reaction,

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

If a reaction vessel at 400°C is charged with an equimolar mixture of CO and steam such that $p_{CO} = p_{H_2O} = 4.0$ bar, what will be the partial pressure of H_2 at equilibrium? $K_p = 10.1$ at 400°C.

Sol.

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

	$CO(g)$	$H_2O(g)$	$CO_2(g)$	$H_2(g)$
Initial pressure	4.0	4.0	0	0
At equili.	$(4.0 - p)$	$(4.0 - p)$	p	p

$$K_p = \frac{p_{CO_2} \cdot p_{H_2}}{p_{CO} \cdot p_{H_2O}} = \frac{p \cdot p}{(4-p)\cdot(4-p)}$$

$$10.1 = \frac{p^2}{(4-p)^2}$$

On solving, $p = \frac{12.71}{4.17} = 3.04$ bar

Hence, $p_{H_2} = 3.04$ bar

Q-32 The pH of 0.004 M hydrazine solution is 9.7. Calculate its ionisation constant K_b and pK_b.

Solution Hydrazine undergoes ionisation in the following manner.

$$NH_2NH_2 + H_2O \rightleftharpoons NH_2NH_3^+ + OH^-$$

$[H^+] = \text{antilog}(-\text{pH}) = \text{antilog}(-9.7) = 1.67 \times 10^{-10}$

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{1 \times 10^{-14}}{1.67 \times 10^{-10}} = 5.98 \times 10^{-5} = [NH_2NH_3^+]$$

$$K_b = \frac{[NH_2NH_3^+][OH^-]}{[NH_2NH_2]} = \frac{(5.98 \times 10^{-5})^2}{0.004} = 8.96 \times 10^{-7}$$

$$pK_b = -\log K_b = -\log(8.96 \times 10^{-7}) = 6.04$$

Q-33 Calculate the pH of 10^{-8} M HCl solution.

Solution $\text{pH} = -\log[\text{H}^+] = -\log 10^{-8} = 8$

But this is not true because an acidic solution cannot have pH greater than 7. In this condition, $[\text{H}^+]$ of water cannot be neglected.

Therefore, $[\text{H}^+]_{\text{total}} = [\text{H}^+]_{\text{HCl}} + [\text{H}^+]_{\text{H}_2\text{O}} = 10^{-8} + 10^{-7} = 10^{-8}(1+10) = 11 \times 10^{-8}$

Now from, $\text{pH} = -\log[\text{H}^+] = -\log(11 \times 10^{-8}) = -\log 11 - \log 10^{-8} = 6.958$

Q-34 What is meant by the conjugate acid-base pair? Find the conjugate acid/base for the following species.

$\text{HNO}_2, \text{CN}^-, \text{HClO}_4, \text{F}^-, \text{OH}^-, \text{CO}_3^{2-}$ and S^{2-}

$\text{Acid} - \text{H}^+ \longrightarrow$ Conjugate base

$\text{Base} + \text{H}^+ \longrightarrow$ Conjugate acid

Sol. An acid-base pair differ by a proton is known as conjugate acid-base pair.

Conjugate bases for $\text{HNO}_2, \text{HClO}_4$ and OH^- are NO_2^-, ClO_4^- and O^{2-} respectively conjugate acids, for $\text{CN}^-, \text{F}^-, \text{OH}^-, \text{CO}_3^{2-}$ and S^{2-} are HCN, HF, $\text{H}_2\text{O}, \text{HCO}_3^-$ and HS^- respectively.

Q-35 Classify the following species into Lewis acids and Lewis bases and show how these act as Lewis acid/base?

(*i*) OH^- (*ii*) F^-

(*iii*) H^+ (*iv*) BCl_3

Lewis acids have a tendency to accept electrons and Lewis bases have a tendency to donate electrons.

Sol. OH^- and F^- are electron rich species and can donate electron pair. Hence, these act as Lewis base.

$$:\ddot{\underset{\cdot\cdot}{\text{O}}}\text{H}^- + \text{H}^+ \longrightarrow \text{H}_2\text{O}$$

$$:\ddot{\underset{\cdot\cdot}{\text{F}}}:^- + \text{BF}_3 \longrightarrow [\text{BF}_4^-]$$

H^+ and BCl_3 are electron deficient species and can accept electron pair. Hence, these act as Lewis acid.

$$\text{H}_3\text{N}: + \text{H}^+ \longrightarrow \text{NH}_4^+$$

$$\text{H}_3\text{N}: + \text{BCl}_3 \longrightarrow \text{H}_3\text{N} \rightarrow \text{BCl}_3$$

Q-36 What is the maximum concentration of equimolar solutions of ferrous sulphate and sodium sulphide so that when mixed in equal volumes, there is no precipitation of iron sulphide? (For iron sulphide, $K_{sp} = 6.3 \times 10^{-18}$)

Sol. FeS is at the point of precipitation when

$$[\text{Fe}^{2+}][\text{S}^{2-}] = K_{sp}$$

$$[\text{Fe}^{2+}] = [\text{S}^{2-}] = \sqrt{K_{sp}} = \sqrt{6.3 \times 10^{-18}}$$

$$[\text{Fe}^{2+}] = [\text{S}^{2-}] = 2.51 \times 10^{-9}\ \text{M}$$

Since, equimolar solutions are to be mixed, hence on mixing concentration is halved. Thus, in original solution

$$[\text{FeSO}_4] = [\text{Na}_2\text{S}] = 2 \times 2.51 \times 10^{-9}$$

$$\text{M} = 5.02 \times 10^{-9}\text{M}$$

Q-37 What is the minimum volume of water required to dissolved 1g of calcium sulphate at 298 K? (For calcium sulphate, K_{sp} is 9.1×10^{-6}).

Sol. $\underset{s}{\text{CaSO}_4} \rightleftharpoons \underset{s}{\text{Ca}^{2+}} + \underset{s}{\text{SO}_4^{2-}}; K_{sp} = 9.1 \times 10^{-6}$

where s is the solubility of CaSO_4.

$$K_{sp} = [\text{Ca}^{2+}][\text{SO}_4^{2-}] = s \cdot s = s^2$$

$$s = \sqrt{K_{sp}} = \sqrt{9.1 \times 10^{-6}} \Rightarrow s = 3.017 \times 10^{-3}\ \text{M}$$

$\therefore$ Solubility of $\text{CaSO}_4 = 3.017 \times 10^{-3}\ \text{mol L}^{-1}$

$$= 3.017 \times 10^{-3} \times 136\ \text{g L}^{-1}$$

(Molar mass of $\text{CaSO}_4 = 136\ \text{g mol}^{-1}$)

$$= 410.3 \times 10^{-3}\ \text{gL}^{-1}$$

410.3×10^{-3} g CaSO_4 is dissolved in = 1 L.

$$\therefore\ 1\text{g CaSO}_4 \text{ is dissolved in} = \frac{1 \times 1}{410.3 \times 10^{-3}}$$

$$= 2.437\ \text{L}$$

Q-38 The concentration of sulphide ion in 0.1 M HCl solution saturated with hydrogen sulphide is 1.0×10^{-19} M. If 10 mL of this is added to 5 mL of 0.04 M solution of the following $\text{FeSO}_4, \text{MnCl}_2, \text{ZnCl}_2$ and CdCl_2, in which of these solutions precipitation will take place?

(Given, K_{sp} of FeS $= 6.3 \times 10^{-18}$,

K_{sp} of MnS $= 2.5 \times 10^{-13}$

K_{sp} of ZnS $= 1.6 \times 10^{-24}$, K_{sp} of CdS $= 8.0 \times 10^{-27}$)

For precipitation, ionic product > solubility product, so calculate ionic product of each salt and compare it with solubility product.

Sol. $[S^{2-}] = 1 \times 10^{-19}$ M

10 mL of S^{2-} is mixed with 5 mL of 0.04 M solution of different solutes so that final volume of solution is 15 mL.

$$\therefore \quad [S^{2-}]_{mix} = \frac{10 \times 10^{-19}}{15} = 6.67 \times 10^{-20} \text{ M}$$

$$[M^{2+}] = \frac{5 \times 0.04}{15} = 1.33 \times 10^{-2} \text{ M}$$

where, $[M^{2+}] = Fe^{2+}, Mn^{2+}, Zn^{2+}$ or Cd^{2+}

$$[M^{2+}][S^{2-}] = 1.33 \times 10^{-2} \times 6.67 \times 10^{-20}$$

i.e., ionic product of $[M^{2+}][S^{2-}] = 8.87 \times 10^{-22}$

Since, ionic product of $[M^{2+}][S^{2-}] > K_{sp}$ of ZnS and CdS.

So, these ($CdCl_2$ and $ZnCl_2$) are precipitated as CdS and ZnS.

Q-39 Equal volumes of 0.002 M solutions of sodium iodate and cupric chlorate are mixed together. Will it lead precipitation of copper iodate?

(For cupric iodate $K_{sp} = 7.4 \times 10^{-8}$)

- For precipitation, ionic product > K_{sp}, so first find concentration, (mol L^{-1}) of Cu^{2+} ions and IO_3^- ions in mixture and then ionic product of $[Cu^{2+}]$ and $[IO_3^-]$.
- If ionic product > K_{sp}, precipitation of $Cu(IO_3)_2$ will take place, otherwise not.

Sol. $2NaIO_3 + Cu(ClO_3)_2 \longrightarrow 2NaClO_3 + \underset{\text{Copper iodate}}{Cu(IO_3)_2}$

$$[Cu^{2+}]_{mix} = \frac{0.002}{2} = 0.001 \text{ M}$$

$$[IO_3^-]_{mix} = \frac{0.002}{2} = 0.001 \text{ M}$$

(Due to mixing of equal volumes, molar concentrations of each species is halved.)

$$Cu(IO_3)_2 \rightleftharpoons Cu^{2+} + 2IO_3^-$$

$Cu(IO_3)_2$ is precipitated if $[Cu^{2+}] \cdot [IO_3^-]^2 > K_{sp}$

$$[Cu^{2+}][IO_3^-]^2 = (1.0 \times 10^{-3}) \times (1.0 \times 10^{-3})^2$$

$$= 1 \times 10^{-9}$$

Ionic product < K_{sp}

$\therefore$ There will be no precipitation.

Q-40 The solubility product constant of Ag_2CrO_4 and AgBr are 1.1×10^{-12} and 5.0×10^{-13} respectively. Calculate the ratio of the molarities of their saturated solutions.

Sol. $\underset{s}{Ag_2CrO_4} \rightleftharpoons \underset{2s}{2Ag^+} + \underset{s}{CrO_4^{2-}}$; $K_{sp} = 1.1 \times 10^{-12}$

(Solubility of Ag_2CrO_4 is s mol L^{-1})

$$K_{sp} = [Ag^+]^2[CrO_4^{2-}]$$

$$K_{sp} = (2s)^2 \cdot s = 4s^3$$

or
$$s^3 = \frac{K_{sp}}{4} = \frac{1.1 \times 10^{-12}}{4}$$

$$= 0.275 \times 10^{-12}$$

$$s^3 = 2.75 \times 10^{-13}$$

$$3 \log s = \log 2.75 \times 10^{-13}$$

$$3 \log s = 0.4393 - 13 = -12.5607$$

$$\log s = \frac{-12.5607}{3} = -4.1869$$

$$= \bar{5}.8131$$

$$s = \text{antilog } \bar{5}.8131 = 6.503 \times 10^{-5} \text{ M}$$

Thus, solubility of $[Ag_2CrO_4] = 6.503 \times 10^{-5}$ M

$\underset{s}{AgBr} \rightleftharpoons \underset{s}{Ag^+} + \underset{s}{Br^-}$; $K_{sp} = 5.0 \times 10^{-13}$

(Solubility of AgBr is s mol L^{-1})

$$K_{sp} = [Ag^+][Br^-] = s \cdot s = s^2$$

or
$$s = \sqrt{K_{sp}} = \sqrt{5.0 \times 10^{-13}}$$

$$= \sqrt{50 \times 10^{-14}}$$

$$s = 7.07 \times 10^{-7} \text{ M}$$

Ratio of their solubilities

$$\frac{s(Ag_2CrO_4)}{s(AgBr)} = \frac{6.50 \times 10^{-5} \text{ M}}{7.07 \times 10^{-7} \text{ M}} = 91.93 \approx 92$$

Therefore, Ag_2CrO_4 is 92 times more soluble than AgBr.

Q-41 The ionisation constant of benzoic acid is 6.46×10^{-5} and K_{sp} for silver benzonate is 2.5×10^{-13}. How many times is silver benzoate more soluble in a buffer of pH 3.19 compared to its solubility in pure water?

Sol. $C_6H_5COOAg(s) \rightleftharpoons C_6H_5COO^- + Ag; K_1 = K_{sp}$

$$C_6H_5COO^- + H^+ \rightleftharpoons C_6H_5COOH; \quad K_2 = \frac{1}{K_a}$$

$$\underline{C_6H_5COOAg(s) + H^+ \rightleftharpoons C_6H_5COOH + Ag^+;}$$

$$K_3 = \frac{K_{sp}}{K_a}$$

$$\therefore \quad K_3 = \frac{[C_6H_5COOH][Ag^+]}{[H^+]}$$

$$= \frac{s \cdot s}{[H^+]} = \frac{s^2}{[H^+]} = \frac{K_{sp}}{K_a}$$

where, s is the solubility of C_6H_5COOAg.

In a buffer of pH = 3.19,

$$\log [H^+] = -3.19 = \bar{4}.81$$

$$\Rightarrow \quad [H^+] = \text{antilog } \bar{4}.81 = 6.46 \times 10^{-4}$$

$$\frac{s^2}{[H^+]} = \frac{K_{sp}}{K_a} \text{ or } S^2 = \frac{K_{sp} \times [H^+]}{K_a}$$

$$s = \sqrt{\frac{2.5 \times 10^{-13} \times 6.46 \times 10^{-4}}{6.46 \times 10^{-5}}}$$

$$s = \sqrt{2.5 \times 10^{-13} \times 10}$$

$$\Rightarrow \quad s = 1.6 \times 10^{-6} \text{ M} \qquad \text{(in buffer)}$$

In aqueous solution, solubility of C_6H_5COOAg

$$K_{sp} = [C_6H_5COO^-][Ag^+] = s \cdot s = s^2$$

$$s = \sqrt{K_{sp}} = \sqrt{2.5 \times 10^{-13}} = 5 \times 10^{-7} \text{ M}$$

$$\frac{s_{(C_6H_5COOAg)} \text{ in buffer}}{s_{(C_6H_5COOAg)} \text{ in aqueous solution}} = \frac{1.6 \times 10^{-6}}{5.0 \times 10^{-7}} = 3.2$$

C_6H_5COOAg is 3.2 times more soluble in buffer than in pure water.

Q-42. Calculate the degree of ionisation of 0.05 M acetic acid if its pK_a value is 4.74. How is the degree of dissociation affected when its solution also contains (*i*) 0.01 M (*ii*) 0.1 M in HCl?

- α is related to K_a as $\alpha = \sqrt{K_a / C}$, so first find K_a from pK_a as pK_a = − log (K_a) and then calculate α.
- To find α in the presence of 0.01 M HCl or 0.1 M HCl, calculate Cα for acetate ions by taking [H⁺] ion concentrations 0.01 M or 0.1 M.

Sol. $pK_a = -\log K_a$,

$\therefore \quad 4.74 = -\log K_a$

or $\quad K_a = \text{antilog } \bar{5}.26 = 1.82 \times 10^{-5}$

From, $\alpha = \sqrt{K_a / C}$

$$\alpha = \sqrt{\frac{1.82 \times 10^{-5}}{0.05}} = \sqrt{0.364 \times 10^{-3}} = \sqrt{3.64 \times 10^{-4}}$$

$$\alpha = 1.908 \times 10^{-2}$$

(*i*) In the presence of 0.01 M H⁺

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

	CH_3COOH	CH_3COO^-	H^+
Initial conc.	0.05 M	0	0
Equili. conc.	0.05 − Cα	Cα ≈ 0.05	(Cα + 0.01) ≈ 0.01

[CH_3COOH is a weak acid and HCl is a strong acid, so we can assume that (Cα + 0.01) ≈ 0.01]

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

$$\therefore \quad 1.82 \times 10^{-5} = \frac{C\alpha \times 0.01}{0.05}$$

$$\text{or} \quad C\alpha = \frac{1.82 \times 10^{-5} \times 0.05}{0.01}$$

$$\text{or} \quad 0.05 \times \alpha = 9.1 \times 10^{-5}$$

$$\therefore \quad \alpha = \frac{9.1 \times 10^{-5}}{0.05} = 1.82 \times 10^{-3}$$

(*ii*) In the presence of 0.1 M HCl

$$\text{Similarly,} \quad K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

$$1.82 \times 10^{-5} = \frac{C\alpha \times 0.1}{0.05}$$

$$([H^+] = (C\alpha + 0.1\text{ M}) \approx 0.1\text{ M})$$

(because 0.1 M HCl = 0.1 M H⁺ ions)

$$C\alpha = \frac{1.82 \times 10^{-5} \times 0.05}{0.1} = 0.91 \times 10^{-5}$$

$$\alpha = \frac{0.91 \times 10^{-5}}{0.05} = 1.82 \times 10^{-4}$$

In the presence of strong acid, dissociation of weak acid *i.e.*, CH_3COOH decreases due to common ion effect.

Q-43 What is the pH of 0.001 M aniline solution? The ionisation constant of aniline is 4.27×10^{-10}. Calculate the degree of ionisation of aniline in the solution. Also calculate the ionisation constant of the conjugate acid of aniline.

- Find [OH⁻] ion concentration by using the formula $[OH^-] = \sqrt{K_b C}$.
- To find pH of the solution first find pOH and then pH from pH + pOH = 14.
- Find α by using the formula $\alpha = \sqrt{K_b / C}$ (for weak base).
- Find K_a by using the formula $K_a \cdot K_b = K_w = 10^{-14}$.

Sol. $C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5NH_3^+ + OH^-$

$$K_b = \frac{[C_6H_5NH_3^+]\,[OH^-]}{[C_6H_5NH_2]}$$

$$= \frac{[OH^-]^2}{[C_6H_5NH_2]}$$

$$[OH^-] = \sqrt{K_b \cdot C} = \sqrt{4.27\times 10^{-10}\times 0.001}$$

$$[OH^-] = 6.534\times 10^{-7}$$

$$pOH = -\log[OH^-] = -\log[6.534\times 10^{-7}]$$

$$pOH = -0.8152 + 7 = 6.18$$

From, $pH + pOH = 14$

$$pH = 14 - 6.18 = 7.82$$

$$\begin{array}{lcccc} & C_6H_5NH_2 + H_2O & \rightleftharpoons & C_6H_5NH_3^+ & + OH^- \\ \text{Initial conc.} & C & & 0 & 0 \\ \text{Equili. conc.} & C - C\alpha & & C\alpha & C\alpha \end{array}$$

$$K_b = \frac{C\alpha \cdot C\alpha}{C(1-\alpha)} \quad [(1-\alpha)\approx 1 \text{ for weak base}]$$

$$K_b = C\alpha^2$$

or $\alpha = \sqrt{K_b / C}$

Degree of ionisation,

$$\alpha = \sqrt{\frac{4.27\times 10^{-10}}{0.001}} = 6.53\times 10^{-4}$$

K_a of conjugate acid of aniline,

$$K_a = \frac{K_w}{K_b} = \frac{10^{-14}}{4.27\times 10^{-10}}$$

$$= 2.34\times 10^{-5}$$

Q-44 The first ionisation constant of H_2S is 9.1×10^{-8}. Calculate the concentration of HS^- ion in its 0.1 M solution. How will this concentration be affected if the solution is 0.1 M in HCl also? If the second dissociation constant of H_2S is 1.2×10^{-13}, calculate the concentration of S^{2-} under both conditions.

- H_2S being a weak acid, dissociates as $H_2S + H_2O \rightleftharpoons H_3O^+ + HS^-$

  $\therefore \quad K_a = \frac{[H_3O^+]\,[HS^-]}{[H_2S]}$
- HCl being a strong acid dissociates completely, so calculate $[HS^-]$ in the presence of 0.1 M HCl by taking $[H^+]$ concentration as 0.1 M.
- Calculate $[S^{2-}]$ ion concentration by using the equation, $HS^- + H_2O \rightleftharpoons H_3O^+ + S^{2-}$
- Calculate $[S^{2-}]$ ion concentration in the presence of 0.1 M HCl.

Sol. (*i*) $H_2S + H_2O \rightleftharpoons H_3O^+ + HS^-$

$$K_{a_1} = \frac{[H_3O^+]\,[HS^-]}{[H_2S]}$$

$$[H_3O^+] = [HS^-] = \sqrt{K_{a_1}\cdot C}$$

$$= \sqrt{9.1\times 10^{-8}\times 0.1} = 9.54\times 10^{-5}\ M$$

(*ii*) In the presence of 0.1 M HCl

$$[H_3O^+] = 0.1\ M$$

$$K_{a_1} = \frac{[H_3O^+]\,[HS^-]}{[H_2S]}$$

$$9.1\times 10^{-8} = \frac{[0.1]\,[HS^-]}{[0.1]}$$

$$\Rightarrow \quad [HS^-] = 9.1\times 10^{-8}\ M$$

Hence, concentration of $[HS^-]$ is decreased in the presence of 0.1 M HCl due to commonion effect.

(*iii*) For second dissociation constant,

$HS^- + H_2O \rightleftharpoons H_3O^+ + S^{2-}$ (In absence of HCl)

$[HS^-]\,[H_3O^+] = 9.54\times 10^{-5}\ M$

Now, $$K_{a_2} = \frac{[H_3O^+]\,[S^{2-}]}{[HS^-]}$$

$$[H_3O^+] = [S^{2-}] = \sqrt{K_{a_2}\cdot C}$$

$$= \sqrt{1.2\times 10^{-13}\times 9.54\times 10^{-5}}$$

$$= 3.38\times 10^{-9} M$$

(*iv*) In the presence of 0.1 M HCl,

$$K_{a_2} = \frac{[H_3O^+]\,[S^{2-}]}{[HS^-]} = \frac{[0.1]\,[S^{2-}]}{[9.1\times 10^{-8}]}$$

$$[S^{2-}] = 1.092\times 10^{-19} M$$

Q-45 The ionisation constant of propanoic acid is 1.32×10^{-5}. Calculate the degree of ionisation of the acid in its 0.05 M solution and also its pH. What will be its degree of ionisation if the solution is 0.01 M in HCl also?

Sol.
$$\begin{array}{ccccc} CH_3CH_2COOH + H_2O & \rightleftharpoons & CH_3CH_2COO^- & + & H_3O^+; \\ \text{Propanoic acid} & & & & \\ (0.05 - C\alpha) & & C\alpha & & C\alpha \end{array}$$

From Ostwald's dilution law,

$$\alpha = \sqrt{K_a / C} = \sqrt{\frac{1.32\times 10^{-5}}{0.05}}$$

$$\alpha = 0.016248$$

$$[H_3O^+] = C\alpha = 0.05\times 0.016248$$

$$= 0.0008124 = 8.124\times 10^{-4}$$

From, $pH = -\log[H_3O^+] = -\log(8.124 \times 10^{-4})$

$$= 3.0902 \approx 3.09$$

When the solution contains 0.01 M HCl

$$K_a = \frac{[CH_3CH_2COO^-][H_3O^+]}{CH_3CH_2COOH}$$

$$1.32 \times 10^{-5} = \frac{C\alpha \times 0.01}{(0.05 - C\alpha)}$$

($[H_3O^+] = 0.01$ M from HCl. In the presence of 0.01 M HCl, dissociation of propanoic acid decreases).

$$C\alpha = \frac{1.32 \times 10^{-5} \times (0.05 - C\alpha)}{0.01}$$

$$= \frac{1.32 \times 10^{-5} \times 0.05}{0.01} \qquad [\text{as } (0.05 - C\alpha) \approx 0.05]$$

or $\quad 0.05 \times \alpha = 6.60 \times 10^{-5}$

$$\alpha = \frac{6.60 \times 10^{-5}}{0.05}$$

$$= 1.32 \times 10^{-3}$$

Q-46 The pH of milk, black coffee, tomato juice, lemon juice and egg white are 6.8, 5.0, 4.2, 2.2 and 7.8 respectively. Calculate the corresponding hydrogen ion concentration in each.

Sol. (*i*) pH of milk = 6.8

$$\log[H^+] = -6.8 = \bar{7}.20$$

$$[H^+] = \text{antilog } \bar{7}.20 = 1.585 \times 10^{-7} M$$

(*ii*) pH of black coffee = 5.0

$$\log[H^+] = -5.0$$

$$[H^+] = 10^{-5} M$$

(*iii*) pH of lemon juice = 2.2

$$\log[H^+] = -2.2 = \bar{3}.8$$

$$[H^+] = \text{antilog } \bar{3}.8 = 6.310 \times 10^{-3} M$$

(*iv*) pH of tomato juice = 4.2

$$\log[H^+] = -4.2 = \bar{5}.80$$

$$[H^+] = \text{antilog} \bar{5}.80 = 6.310 \times 10^{-5} M$$

(*v*) pH of egg white = 7.8

$$\log[H^+] = -7.8 = \bar{8}.20$$

$$[H^+] = \text{antilog } \bar{8}.20$$

$$= 1.585 \times 10^{-8} M$$

Q-47 Calculate the pH of the following solutions.

(*i*) 2 g of TlOH dissolved in water to give 2 L of solution.

(*ii*) 0.3 g of $Ca(OH)_2$ dissolved in water to give 500 mL solution.

(*iii*) 0.3 g of NaOH dissolved in water to give 200 mL of solution.

(*iv*) 1 mL of 13.6 M HCl is diluted with water to give 1 L of solution.

Sol. (*i*) Molecular mass of TlOH = $204 + 16 + 1 = 221 \text{ g mol}^{-1}$

Conc. in mol L^{-1} (molarity)

$$= \frac{\text{mass of TlOH (g)}}{\text{molar mass of TlOH} \times \text{volume of solution (L)}}$$

$$= \frac{2}{221 \times 2} = 0.00452 = 4.52 \times 10^{-3} M$$

$$pOH = -\log[OH^-]$$

$$= -\log[4.52 \times 10^{-3}] = 2.344$$

From, $\quad pH + pOH = 14$

$$pH = 14 - 2.334 = 11.656 \approx 11.66$$

(*ii*) Molecular mass of $Ca(OH)_2$

$$= 40 + [(16 + 1) \times 2] = 74 \text{ g mol}^{-1}$$

Molarity, M

$$= \frac{\text{mass of } Ca(OH)_2 (g) \times 1000}{\text{molar mass of } Ca(OH)_2 \times \text{volume of solution (mL)}}$$

$$M = \frac{0.3 \times 1000}{74 \times 500} = 0.0081$$

One mole of $Ca(OH)_2$ gives 2 moles of OH^-.

So, $\quad [OH^-] = 2 \times 0.0081 = 0.0162 M$

$$pOH = -\log[OH^-] = -\log[0.0162]$$

$$= 1.7905 \approx 1.79$$

From, $pH + pOH = 14$

or $\quad pH = 14 - 1.79 = 12.21$

Q-48 Reaction between N_2 and O_2 takes place as follows

$$2N_2(g) + O_2(g) \rightleftharpoons 2N_2O(g)$$

If a mixture of 0.482 mole N_2 and 0.933 mole O_2 is placed in a 10 L reaction vessel and allowed to form N_2O at a temperature for which $K_c = 2.0 \times 10^{-37}$, determine the composition of equilibrium mixture.

- Find the equilibrium concentrations of reactants and products in the given equation by assuming $2x$ mole of N_2 and x mole of O_2 are disappeared and $2x$ mole of N_2O are appeared.
- Find the value of x to determine the concentration of reaction mixture.

Sol.

	$2N_2(g)$ +	$O_2(g)$ $\rightleftharpoons$	$2N_2O(g)$
Initial conc.	0.482	0.933	0
Equilibrium conc.	$(0.482 - 2x)$	$(0.933 - x)$	$2x$
Active mass	$\left(\frac{0.482 - 2x}{10}\right)$	$\left(\frac{0.933 - x}{10}\right)$	$\left(\frac{2x}{10}\right)$

K_c is very very small, which means negligible amounts of N_2 and O_2 react.

$$[N_2]_{eq} = \frac{0.482-2x}{10} = \frac{0.482}{10} = 0.0482$$

Similarly, $[O_2]_{eq} = \frac{0.933-x}{10} = \frac{0.933}{10} = 0.0933$

$$K_c = \frac{[N_2O]^2}{[N_2]^2\,[O_2]}$$

$$= 2.0\times10^{-37}$$

$$= \frac{\left[\frac{4x^2}{100}\right]}{(0.0482)^2\,(0.0933)}$$

or $x^2 = 10.837\times10^{-40}$

or $x = 3.292\times10^{-20}$

$$[N_2O] = \frac{2x}{10} = \frac{2\times3.292\times10^{-20}}{10}$$

$$= 6.58\times10^{-21}\ \text{mol L}^{-1}$$

-49 At 700 K, equilibrium constant for the reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ is 54.8. If 0.5 mol L^{-1} of $HI(g)$ is present at equilibrium at 700 K, what are the concentration of $H_2(g)$ and $I_2(g)$ assuming that we initially started with $HI(g)$ and allowed it to reach equilibrium at 700 K?

As we started the reaction with HI, so equilibrium constant for the dissociation of HI ($2HI \rightleftharpoons H_2 + I_2$) is required. Thus, calculate equilibrium constant for backward reaction (K_c')$\left(K'_c = \frac{1}{K_c}\right)$ and then calculate $[H_2]$ and $[I_2]$.

Sol. $H_2(g) + I_2(g) \rightleftharpoons 2HI(g);\ K_c = 54.8$

$2HI(g) \rightleftharpoons H_2(g) + I_2(g);$

$$K'_c = \frac{1}{K_c} = \frac{1}{54.8}$$

again, $K'_c = \frac{[H_2]\,[I_2]}{[HI]^2} = \frac{1}{54.8}$

Given, $[HI] = 0.5\ \text{mol L}^{-1}$

According to equation, $[H_2] = [I_2] = [x]$

$$\frac{x.x}{[0.5]^2} = \frac{1}{54.8} \text{ or } x^2 = \frac{[0.5]^2}{54.8} = 0.00456$$

$$x = 0.0675\ \text{M}$$

Hence, $[H_2] = [I_2] = x = 0.0675$ M

Q-50 Bromine monochloride, BrCl decomposes into bromine and chlorine and reaches the equilibrium,

$$2BrCl(g) \rightleftharpoons Br_2(g) + Cl_2(g)$$

for which $K_c = 32$ at 500 K. If initially pure BrCl is present at a concentration of 3.3×10^{-3} mol L^{-1}, what is its molar concentration in the mixture at equilibrium?

- First, find equilibrium concentration for all reactants and products given in the equation by assuming x mole of BrCl decomposes.
- Find x by the expression of K_c and then find $[BrCl]_{equilibrium}$.

Sol.

$$\begin{array}{lccc} & 2BrCl(g) & \rightleftharpoons Br_2(g) & +Cl_2(g) \\ \text{Initial conc.} & 3.30\times10^{-3} & 0 & 0 \\ \text{Equili. conc.} & (3.30\times10^{-3}-x) & \frac{x}{2} & \frac{x}{2} \end{array}$$

$(K_c = 32 \text{ at } 500\text{ K})$

$$K_c = \frac{[Br_2]\,[Cl_2]}{[BrCl]^2} = \frac{\frac{x}{2}\times\frac{x}{2}}{(3.30\times10^{-3}-x)^2} = 32$$

or $x = \frac{0.03732}{12.312} = 3.032\times10^{-3}$ mol L^{-1}

$$[BrCl]_{eqm.} = (3.30\times10^{-3} - 3.032\times10^{-3})\ \text{mol L}^{-1}$$

$$= 2.68\times10^{-4}\ \text{mol L}^{-1}$$

Q-51 Find out the value of K_c for each of the following equilibria from the value of K_p

(i) $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$;

$K_p = 1.8\times10^{-2}$ at 500 K

(ii) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$;

$K_p = 167$ at 1073 K

First, find Δn_g by subtracting the moles of gaseous reactants from the moles of gaseous products for each equation, as K_p and K_c are related as $K_p = K_c\,(RT)^{\Delta n_g}$. Then, calculate K_c in each case.

Sol. (i) $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$;

$K_p = 1.8\times10^{-2}$ at 500 K

$\Delta n_g = n_P - n_R = 3 - 2 = 1$

$$K_c = \frac{K_p}{(RT)^{\Delta n_g}} = \frac{1.8\times10^{-2}}{0.0821\times500} = 4.38\times10^{-4}$$

(ii) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$;

$K_p = 167$ at 1073 K

$\Delta n_g = n_P - n_R = 1$

$$K_c = \frac{K_p}{(RT)^{\Delta n_g}} = \frac{167}{0.0821\times1073} = 1.89$$

Q-52 At 1127 K and 1 atm pressure, a gaseous mixture of CO and CO_2, in equilibrium with solid carbon has 90.55% CO by mass.

$$C(s) + CO_2(g) \rightleftharpoons 2CO(g)$$

Calculate K_c for this reaction at the above temperature.

- Since, the percentage by mass is given, so calculate the number of moles of CO and CO_2 to calculate their mole fractions.
- Then, calculate the partial pressures of CO and CO_2 by using the formula $p_A = x_A \cdot p_{total}$
- Calculate K_p by using the formula, $K_p = \frac{p^2_{CO}}{p_{CO_2}}$ and K_c by using the formula, $K_p = K_c (RT)^{\Delta n_g}$.

Sol. 90.55% CO by mass means 90.55 g CO and 9.45 g CO_2 are present in 100 g mixture.

Number of moles of CO, $n_{CO} = \frac{90.55}{28} = 3.234$ mol

(Molar mass of CO = 28 g mol^{-1})

Number of moles of CO_2, $n_{CO_2} = \frac{9.45}{44} = 0.215$ mol

(Molar mass of CO_2 = 44 g mol^{-1})

Partial pressure of CO, $p_{CO} = x_{CO} \cdot p_{total}$

$$= \frac{3.234}{3.234 + 0.215} \times 1$$

$$p_{CO} = 0.938 \times 1 = 0.938 \text{ atm}$$

Similarly, $p_{CO_2} = x_{CO_2} \cdot p_{total}$

$$= \frac{0.215}{3.234 + 0.215} \times 1$$

$$p_{CO_2} = 0.062 \times 1 = 0.062 \text{ atm}$$

$$C(s) + CO_2(g) \rightleftharpoons 2CO(g)$$

$$K_p = \frac{p^2_{CO}}{p_{CO_2}} = \frac{(0.938)^2}{0.062} = 14.19$$

$$\Delta n_g = 2 - 1 = 1$$

$$K_p = K_c (RT)^{\Delta n_g}$$

$$K_c = \frac{K_p}{RT} \qquad (\Delta n_g = 1)$$

$$K_c = \frac{14.19}{0.0821 \times 1127} = 0.15336 \approx 0.153$$

Q-53 Equilibrium constant, K_c for the reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ at 500 K is 0.061. At a particular time, the analysis shows the composition of the reaction mixture is 3.0 mol L^{-1} N_2, 2.0 mol L^{-1} H_2 and 0.5 mol L^{-1} NH_3. Is the reaction at equilibrium? If not in, which direction does the reaction tend to proceed to reach equilibrium?

Sol. Plan Find Q_c and compare it with K_c. If $Q_c = K_c$, the reaction is in equilibrium, if $Q_c < K_c$, the reaction will go in forward direction and if $Q_c > K_c$, the reaction will go in backward direction.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g); K_c = 0.061 \text{ at } 500 \text{ K}$$

Given, $[N_2] = 3.0$ mol L^{-1}, $[H_2] = 2.0$ mol L^{-1}

and $[NH_3] = 0.5$ mol L^{-1} at time t

$$\text{So, } Q_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{[0.5]^2}{[3.0][2.0]^3} = 0.0104$$

Because $Q_c \neq K_c$, equilibrium has not been attained.

Because $Q_c < K_c$ (0.0104 < 0.061), the reaction will proceed from left to right, i.e., towards formation of more products.

Q-54 One of the reaction that takes place in producing steel from iron ore is the reduction of iron(II) oxide by carbon monoxide to give iron metal and CO_2.

$$FeO(s) + CO(g) \rightleftharpoons Fe(s) + CO_2(g);$$

$$K_p = 0.265 \text{ atm at } 1050 \text{ K}$$

What are the equilibrium partial pressures of CO and CO_2 at 1050 K if the initial partial pressures are: $p_{CO} = 1.4$ atm and $p_{CO_2} = 0.80$ atm?

- First find Q_p by the given initial partial pressures of [CO] and [CO_2].
- Compare Q_p and K_c to find the equilibrium partial pressure of [CO] and [CO_2].

Sol.

$$\begin{array}{lcccc} & FeO(s) + & CO(g) & \rightleftharpoons Fe(s) + & CO_2(g); \\ \text{Initial pressure} & & 1.4 \text{ atm} & & 0.80 \text{ atm} \end{array}$$

$(K_p = 0.265$ at 1050 K)

$$Q_p = \frac{p_{CO_2}}{p_{CO}} = \frac{0.80}{1.4} = 0.571 \quad [\text{ Fe and FeO are solids.}]$$

$Q_p > K_p$, the reaction will go in reverse direction. Due to this, pressure of CO_2 will decrease and that of CO will increase to attain equilibrium.

Suppose p is the decrease in pressure of CO_2 and p is the increase in pressure of CO. Hence, $p_{CO_2} = (0.80 - p)$ and $p_{CO} = (1.4 + p)$.

$$\text{Now, from} \quad K_p = \frac{p_{CO_2}}{p_{CO}}$$

$$0.265 = \frac{(0.80 - p)}{(1.4 + p)}$$

$$p = \frac{0.429}{1.265} = 0.339 \text{ atm}$$

Hence, at equilibrium,

$$p_{CO_2} = 0.80 - 0.339 = 0.461 \text{ atm}$$

and $$p_{CO} = 1.4 + 0.339 = 1.739 \text{ atm}$$

Q-55 • Does the number of moles of reaction products increase, decrease or remain same when each of the following equilibria is subjected to a decrease in pressure by increasing the volume?

(*i*) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

(*ii*) $CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s)$

(*iii*) $3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$

Sol. According to Le-Chatelier's principle, on decreasing pressure equilibrium shifts in that direction where pressure increases (*i.e.*, number of moles in gaseous state are more). Therefore, number of moles of reaction products in (a) increases (*ii*) decreases (*iii*) remains the same. (If $\Delta n_g = 0$, there is no effect of change in pressure).

Q-56 . (*i*) Describe the effect of

(*a*) addition of H_2

(*b*) addition of CH_3OH

(*c*) removal of CO

(*d*) removal of CH_3OH on the equilibrium of the reaction,

$$2H_2(g) + CO(g) \rightleftharpoons CH_3OH(g)$$

(*ii*) What happens to an equilibrium in a reversible reaction if a catalyst is added to it?

Sol. (*i*) $2H_2(g) + CO(g) \rightleftharpoons CH_3OH(g)$

According to Le-Chatelier's principle,

(*a*) addition of H_2 (increase in concentration of reactants) shifts the equilibrium in forward direction (more product is formed).

(*b*) addition of CH_3OH (increase in concentration of product) shifts the equilibrium in backward direction.

(*c*) removal of CO also shifts the equilibrium in backward direction.

(*d*) removal of CH_3OH shifts the equilibrium in forward direction.

(*ii*) When catalyst is added, the state of equilibrium is not disturbed but equilibrium is attained quickly. This is because the catalyst increases the rate of forward and backward reaction to the same extent.

Q-57 , Which of the following reactions will get affected by increasing the pressure? Also, mention whether change will cause the reaction to go into forward or backward direction.

(*i*) $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$

(*ii*) $CH_4(g) + 2S_2(g) \rightleftharpoons CS_2(g) + 2H_2S(g)$

(*iii*) $CO_2(g) + C(s) \rightleftharpoons 2CO(g)$

(*iv*) $2H_2(g) + CO(g) \rightleftharpoons CH_3OH(g)$

(*v*) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

(*vi*) $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$

According to Le-Chatelier's principle, increase in pressure shifts the equilibrium in the direction where pressure decreases (*i.e.*, number of moles are less). Furthermore, if $n_p \neq n_r$, the change in pressure affects the equilibrium.

Sol. (*i*) $n_p > n_r$, the reaction will go in backward direction.

(*ii*) $n_p = n_r$, the reaction will not be affected by increasing pressure.

(*iii*) $n_p > n_r$, the reaction will go in backward direction.

(*iv*) $n_p < n_r$, the reaction will go in forward direction.

(*v*) $n_p > n_r$, the reaction will go in backward direction.

(*vi*) $n_p > n_r$, the reaction will go in backward direction.

Q-58 • Determine the solubilities of silver chromate, barium chromate, ferric hydroxide, lead chloride and mercurous iodide at 298 K from their solubility product constants.

(*i*) [$K_{sp}(Ag_2CrO_4) = 1.1 \times 10^{-12}$,

(*ii*) $K_{sp}(BaCrO_4) = 1.2 \times 10^{-10}$,

(*iii*) $K_{sp}[Fe(OH)_3] = 1.0 \times 10^{-38}$,

(*iv*) $K_{sp}(PbCl_2) = 1.6 \times 10^{-5}$

(*v*) $K_{sp}(Hg_2I_2) = 4.5 \times 10^{-29}$]

Determine also the molarities of individual ions.

Sol. (*i*) $\underset{s}{Ag_2CrO_4} \rightleftharpoons \underset{2s}{2Ag^+} + \underset{s}{CrO_4^{2-}};\ K_{sp} = 1.1 \times 10^{-12}$

$$K_{sp} = [Ag^+]^2 \cdot [CrO_4^{2-}]$$

$$K_{sp} = [2s]^2 \cdot [s] = 4s^3,\ s^3 = \frac{K_{sp}}{4}$$

or $$s^3 = \frac{1.1 \times 10^{-12}}{4} = 0.275 \times 10^{-12}$$

On solving $s = 6.503 \times 10^{-5}$ M

$$[Ag^+] = 2s = 2 \times 6.503 \times 10^{-5}$$

$$= 13.006 \times 10^{-5} \approx 1.3 \times 10^{-4} \text{ M}$$

and $$[CrO_4^{2-}] = s = 6.503 \times 10^{-5} \text{ M}$$

(*ii*) $\underset{s}{BaCrO_4} \rightleftharpoons \underset{s}{Ba^{2+}} + \underset{s}{CrO_4^{2-}};\ K_{sp} = 1.2 \times 10^{-10}$

(Solubility of $BaCrO_4$ is s mol L^{-1})

$$K_{sp} = 1.2 \times 10^{-10} = [Ba^{2+}] \cdot [CrO_4^{2-}] = s^2$$

$$s = \sqrt{1.2 \times 10^{-10}} = 1.1 \times 10^{-5} \text{ M}$$

$$[Ba^{2+}] = [CrO_4^{2-}] = 1.1 \times 10^{-5} \text{ M}$$

(*iii*) $\underset{s}{Fe(OH)_3} \rightleftharpoons \underset{s}{Fe^{3+}} + \underset{3s}{3\,OH^-}; K_{sp} = 1.0 \times 10^{-38}$

(Solubility of $Fe(OH)_3$ is s mol L^{-1})

$$K_{sp} = [Fe^{3+}][OH^-]^3$$

$$K_{sp} = s \cdot (3s)^3 = 27s^4 \quad \text{or} \quad s^4 = \frac{K_{sp}}{27}$$

$$s^4 = \frac{1.0 \times 10^{-38}}{27} = 0.037 \times 10^{-38}$$

$$s = 1.387 \times 10^{-10},\ s \approx 1.39 \times 10^{-10}$$

$$[Fe^{3+}] = 1.39 \times 10^{-10}\ M$$

$$[OH^-] = 3s = 3 \times 1.39 \times 10^{-10} = 4.17 \times 10^{-10}\ M$$

(*iv*) $\underset{s}{PbCl_2} \rightleftharpoons \underset{s}{Pb^{2+}} + \underset{2s}{2\,Cl^-}; K_{sp} = 1.6 \times 10^{-5}$

(Solubility of $PbCl_2$ is s mol L^{-1})

$$K_{sp} = [Pb^{2+}][Cl^-]^2$$

$$K_{sp} = s \cdot (2s)^2 = 4s^3$$

$$s^3 = \frac{K_{sp}}{4} = \frac{1.6 \times 10^{-5}}{4} = 0.4 \times 10^{-5}$$

On solving $s = 1.585 \times 10^{-2} \approx 1.59 \times 10^{-2}$ M

$\therefore$ Solubility of $PbCl_2 = 1.59 \times 10^{-2}$ M

$$[Pb^{2+}] = 1.59 \times 10^{-2}\ M$$

$$[Cl^-] = 2 \times 1.59 \times 10^{-2}\ M = 3.18 \times 10^{-2}\ M$$

(*v*) $\underset{s}{Hg_2I_2} \rightleftharpoons \underset{s}{Hg_2^{2+}} + \underset{2s}{2I^-}; K_{sp} = 4.5 \times 10^{-29}$

(Solubility of Hg_2I_2 is s mol L^{-1})

$$K_{sp} = [Hg_2^{2+}][I^-]^2,\ K_{sp} = s \cdot (2s)^2 = 4s^3$$

$$s^3 = \frac{K_{sp}}{4} = \frac{4.5 \times 10^{-29}}{4} = 1.125 \times 10^{-29}$$

On solving $s = 2.241 \times 10^{-10}$ M

Solubility of $Hg_2I_2 = 2.241 \times 10^{-10}$ M

$$[Hg_2^{2+}] = 2.241 \times 10^{-10} M$$

$$[I^-] = 2 \times 2.241 \times 10^{-10}\ M$$

$$= 4.482 \times 10^{-10} M$$

Q-59 Nitric oxide reacts with Br_2 and gives nitrosyl bromide as per reaction given below

$$2NO(g) + Br_2(g) \rightleftharpoons 2NOBr(g)$$

When 0.087 mole of NO and 0.0437 mole of Br_2 are mixed in a closed container at constant temperature, 0.0518 mole of NOBr is obtained at equilibrium. Calculate the equilibrium amount of NO and Br_2.

Solution *In order to solve such problems, following steps are involved*

Step I Set up a balance sheet using symbols for the expected equilibrium amounts of reactants and products.

	$2NO$	+ Br_2	$\longrightarrow$ $2NOBr$	
Initial moles	0.087	0.0437	0	(as no reaction occur)
At equilibrium moles	$(0.087-2x)$	$(0.0437-x)$	$2x$	

[Remember ! multiply the value of x with the stoichiometric coefficient of the molecule].

Step II Compare with the given information

Given equilibrium moles of NOBr = 0.0518

$$\therefore \quad 2x = 0.0518 \quad \text{and} \quad x = \frac{0.0518}{2} = 0.0259$$

Step III Put the value of x to obtained equilibrium concentration of other species.

Moles of NO at equilibrium $= (0.087 - 2x)$

$$= 0.087 - 0.0518 = 0.0352 \text{ mol}$$

Moles of Br_2 at equilibrium $= (0.0437 - x)$

$$= 0.0437 - 0.0259 = 0.0178 \text{ mol}$$

Q-60 The value of K_p for the reaction,

$$CO_2\ (g) + C\ (s) \rightleftharpoons 2CO(g)$$

is 3.0 at 1000 K. If initially $p_{CO_2} = 0.48$ bar and $p_{CO} = 0$ bar and pure graphite is present, calculate the equilibrium partial pressures of CO and CO_2.

Solution For the reaction, let 'x' be the decrease in pressure of CO_2, then

	$CO_2(g)$ + $C(s)$ $\rightleftharpoons$	$2CO(g)$
Initial pressure	0.48 bar	0
At equilibrium	$(0.48 - x)$ bar	$2x$ bar

$$K_p = \frac{p^2_{CO}}{p_{CO_2}}$$

$$K_p = (2x)^2/(0.48 - x) = 3$$

$$4x^2 = 3\,(0.48 - x) \text{ or } 4x^2 + 3x - 1.44 = 0$$

$$a = 4, b = 3, c = -1.44$$

By applying $x = \dfrac{\left(-b \pm \sqrt{b^2 - 4ac}\right)}{2a}$

$$x = 2.66/8 = 0.33$$

The equilibrium partial pressures are,

$$p_{CO} = 2x = 2 \times 0.33 = 0.66 \text{ bar}$$

$$p_{CO_2} = 0.48 - x = 0.48 - 0.33 = 0.15 \text{ bar}$$

Q-61 The value of K_c for the reaction $2A \rightleftharpoons B + C$ is 2×10^{-3}. At a given time, the composition of reaction mixture is $[A] = [B] = [C] = 3 \times 10^{-4}$ M. In which direction the reaction well proceed?

Solution For the reaction the reaction quotient,

$$Q_c = [B]\,[C]\,/\,[A]^2$$

as $\quad [A] = [B] = [C] = 3\times10^{-4}\,\text{M}$

$$Q_c = (3\times10^{-4})\;(3\times10^{-4})/(3\times10^{-4})^2 = 1$$

As $Q_c > K_c$ so the reaction will proceed in the reverse direction.

Q-62 A mixture of 1.57 moles of N_2, 1.92 moles of H_2 and 8.13 moles of NH_3 is introduced into a 20 L reaction vessel at 500 K. At this temperature, the equilibrium constant, K_c for the reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ is 1.7×10^2. Predict the direction of the reaction.

Solution $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

$$Q_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

Given, $\quad [NH_3] = \frac{8.13}{20}\,\text{M} = 0.4065\,\text{M}$

$$[N_2] = \frac{1.57}{20}\,\text{M} = 0.0785\,\text{M};\; [H_2] = \frac{1.92}{20}\,\text{M} = 0.096\,\text{M}$$

$$Q_c = \frac{[0.4065\,\text{M}]^2}{[0.0785\,\text{M}][0.096\,\text{M}]^3} = 2.379\times10^3\;\text{M}^{-2}$$

$Q_c \neq K_c$, so the reaction mixture is not in equilibrium. $Q_c > K_c$, it indicates that the reaction will proceed in the direction of reactants.

Q-63 For the equilibrium,

$$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$$

the value of the equilibrium constant, K_c is 3.17×10^{-6} at 1069 K. Calculate the K_p for the reaction at this temperature?

Solution We Know that, $K_p = K_c\,(RT)^{\Delta n_g}$

For the above reaction,

$$\Delta n_g = (2+1) - 2 = 1$$

$$K_p = 3.75\times10^{-6}\,(0.0831\times1069)$$

$$K_p = 0.033\times10^{-2}$$

Q-64 Write the expression for the equilibrium constant, K_c for each of the following reactions.

(i) $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$
(ii) $2Cu(NO_3)_2(s) \rightleftharpoons 2CuO(s) + 4NO_2(g) + O_2(g)$
(iii) $CH_3COOC_2H_5(aq) + H_2O(l) \rightleftharpoons$
$CH_3COOH\,(aq) + C_2H_5OH(aq)$
(iv) $Fe^3(aq) + 3OH^-(aq) \rightleftharpoons Fe(OH)_3(s)$
(v) $I_2(s) + 5F_2(g) \rightleftharpoons 2IF_5(g)$

Solution (i) $K_c = \dfrac{[NO]^2[Cl_2]}{[NOCl]^2}$

(ii) $K_c = [NO_2]^4\,[O_2]$

(because molar concentrations of pure solids are constant)

(iii) $K_c = \dfrac{[CH_3COOH(aq)][C_2H_5OH(aq)]}{[CH_3COOC_2H_5(aq)]\,[H_2O(l)]}$

(iv) $K_c = \dfrac{1}{[Fe^{3+}(aq)]\cdot[OH^-(aq)]^3}$

because $\{Fe(OH)_3\;(s) = 1\}$

(v) $K_c = \dfrac{[IF_5]^2}{[F_2]^5}$ (because $[I_2(s) = 1]$)

Q-65 The ionisation constant of 0.05 M solution of phenol is 1.0×10^{-10}. What is the concentration of phenolate ion in 0.05 M solution of phenol. What will be its degree of ionisation if the solution is also 0.01 M in solution phenolate?

Solution The equation of the dissociation of phenol is as

$$C_6H_5OH \longrightarrow C_6H_5O^- + H^+(H_3O^+)$$

By Ostwald dilution law, $[C_6H_5O^-] = [H_3O^+]$

$$= \sqrt{K_a\cdot C} = \sqrt{1.10\times10^{-1}\times0.05} = 2.24\times10^{-6}\,\text{M}$$

When mixture contains 0.05 M phenol and 0.01 M phenolate ion (from sodium phenolate) then

$$K_a = \frac{[C_6H_5O^-][H_3O^+]}{[C_6H_5OH]}$$

$$1.0\times10^{-10} = \frac{[0.01]\times[H_3O^+]}{[0.05]}$$

$$[H_3O^+] = \frac{0.05\times1.0\times10^{-10}}{0.01} = 5\times10^{-10}\,\text{M}$$

$$[H_3O^+] = C\cdot\alpha = 5\times10^{-10}$$

or $\quad \alpha = \dfrac{5\times10^{-10}}{C}$

$$\alpha = \frac{5\times10^{-10}}{0.05} = 1\times10^{-8}$$

Q-66 The ionisation constant of HF is 3.2×10^{-4}. Calculate the degree of dissociation of HF in its 0.02 M solution. Calculate the concentration of all species present (H_3O^+, F^- and HF) in the solution and its pH.

Solution *Step* I HF is a Bronsted acid and water is a base here.

Step II The following proton transfer reactions are possible

(i) $HF + H_2O \rightleftharpoons H_3O^+ + F^-;\; K_a = 3.2\times10^{-4}$

(*ii*) $H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-; K_w = 1.0\times10^{-14}$

Step III As $K_a >> K_w$, [1] is the principle reaction.

Step IV	$HF + H_2O \rightleftharpoons$	H_3O^+	+ F^-
Initial conc. (M)	0.02	0	0
Change (M)	-0.02α	$+0.02$	$+0.02\alpha$
Equili. conc. (M)	$0.02-0.02\alpha$	0.02α	0.02α

Step V Equilibrium constant,

$$K_a = \frac{(0.02\alpha)^2}{(0.02-0.02\alpha)}$$

$$= \frac{0.02\alpha^2}{(1-\alpha)} = 3.2\times10^{-4}$$

or $\alpha^2 + 1.6\times10^{-2}\alpha - 1.6\times10^{-2} = 0$

using $x = \frac{-b\pm\sqrt{b^2-4ac}}{2a}$

we get $\alpha = +0.12$ and -0.12

The negative root is not acceptable and hence, $\alpha = 0.12$

Step VI $\therefore\ [H_3O^+] = [F^-] = C\alpha = 0.02\times0.12$

$$= 2.4\times10^{-3}\text{ M}$$

$$[HF] = C(1-\alpha) = 0.02(1-0.12)$$

$$= 17.6\times10^{-3}\text{ M}$$

Step VII $pH = -\log[H^+]$

$$= -\log(2.4\times10^{-3}) = 2.62$$

Q-67 The pH of 0.1 M monobasic acid is 4.50. Calculate the concentration of species H^+. A^- and HA at equilibrium. Also, determine the value of K_a and pK_a of the monobasic acid.

Solution

$$pH = -\log[H^+]$$

$\therefore$ $[H^+] = 1\times10^{-pH} = 1\times10^{-4.50} = 3.16\times10^{-5}$

Since, $[H^+] = [A^-] = 3.16\times10^{-5}$

and $K_a = [H^+][A^-]/[HA]$

$[HA]_{\text{equilibrium}} = 0.1-(3.16\times10^{-5})$

$$K_a = \frac{(3.16\times10^{-5})^2}{0.1}/0.1 = 1.0\times10^{-8}$$

$$pK_a = -\log(10^{-8}) = 8$$

Q-68 *The species H_2O, HCO_3^-, HSO_4^- and NH_3 can act both as Bronsted acids and bases. For each case give the corresponding conjugate acid and conjugate base.*

Solution A conjugate acid is obtained by adding a proton to the species and a conjugate base is obtained by removing a proton from the given species. *Thus, the corresponding conjugate acid and base for the given species are as follows*

Species	Conjugate acid	Conjugate base
H_2O	H_3O^+	OH^-
HCO_3^-	H_2CO_3	CO_3^{2-}
HSO_4^-	H_2SO_4	SO_4^{2-}
NH_3	NH_4^+	NH_2^-

Lewis Acids and Bases

According to this concept, a base is a substance that have a tendency to donate an electron pair to form a coordinate bond and an acid is a substance that accepts the electron pair donated by the Lewis base. Thus, a Lewis acid is an electrophile or electron deficient species. *e.g.*, $AlCl_3, Co^{3+}, Mg^{2+}$ etc., whereas a Lewis base is a nucleophile or electron rich species

e.g., H_2O, NH_3, OH^-, NO, CO etc.

According to Lewis, a general acid-base reaction can be expressed in the following manner.

$$A + :B \longrightarrow A \leftarrow B$$

$$\text{Acid} + \text{Base} \longrightarrow \text{Complex}$$

$$H^+ + :OH^- \longrightarrow H \leftarrow OH$$

$$BF_3 + :NH_3 \longrightarrow H_3N \rightarrow BF_3$$

It is also interesting to note that all Bronsted-Lowry bases also act as Lewis bases because of the presence of lone pairs on all the bases.

But all Bronsted Lowry acids do not behave as Lewis acids because of the absence of proton as in BF_3 which because of its electron deficiency acts as Lewis acid but not as Bronsted acid (due to the absence of proton).

Q-69 Calculate the molar solubility of $Ni(OH)_2$ in 0.10 M NaOH. The ionic product of $Ni(OH)_2$ is $2.0\ \times10^{-15}$.

Solution $Ni(OH)_2 \rightleftharpoons Ni^{2+} + 2OH^-$

S mol/L S mol/L $2S$ mol/L

$NaOH \longrightarrow Na^+ + OH^-$

0.10 M 0.10 M 0.10 M

$$[OH^-]_{\text{total}} = (2S+0.10)$$

$$K_{sp} = 2.0 \times 10^{-15} = [Ni^{2+}][OH^-]^2 = (S)(0.10 + 2S)^2$$

As K_{sp} is small, $2S << 0.10$, thus, $(0.10 + 2S) \approx 0.10$

$$\therefore \quad 2.0 \times 10^{-15} = S(0.10)^2 \Rightarrow S = 2.0 \times 10^{-13}\ M = [Ni^{2+}]$$

Q-70 (*i*) $K_p = 0.04$ atm at 899 K for the equilibrium shown below. What is the equilibrium concentration of C_2H_6 when it is placed in a flask at 4.0 atm pressure and allowed to come to equilibrium?

$$C_2H_6(g) \rightleftharpoons C_2H_4(g) + H_2(g)$$

(*ii*) At a certain temperature and total pressure of 10^5 Pa, iodine vapour contains 40% by volume of I atoms.

$$I_2(g) \rightleftharpoons 2I(g)$$

Calculate K_p for the equilibrium.

Sol. (*i*)

	$C_2H_6(g) \rightleftharpoons$	$C_2H_4(g)+$	$H_2(g)$
Initial pressure	4.0 atm	0	0
Equili. pressure	$(4.0 - p)$ atm	p	p

$$K_p = \frac{p_{C_2H_4} \cdot p_{H_2}}{p_{C_2H_6}} = \frac{p \times p}{4.0 - p}$$

$$0.04 = \frac{p^2}{4.0 - p} \quad \text{or} \quad 0.16 - 0.04p = p^2$$

$$p = -0.04 \pm \frac{\sqrt{0.0016 - 4(-0.16)}}{2}$$

$$p = \frac{-0.04 \pm 0.80}{2};\ p = 0.38 \qquad \text{(by taking positive value)}$$

Hence, $p_{C_2H_6} = 4.0 - 0.38 = 3.62$ atm

(*ii*) Given, $I_2(g) \rightleftharpoons 2I(g)$

Atoms in iodine vapours = 40% by volume

So, iodine vapours of I_2 molecules = 60% by volume

Partial pressure of iodine atoms, $p_I = \frac{40}{100} \times 10^5 = 0.40 \times 10^5$ Pa

Similarly, partial pressure of iodine molecule (I_2) $p_2 = \frac{60}{100} \times 10^5 = 0.60 \times 10^5$ Pa

According to equation, $K_p = \frac{p_I^2}{p_{I_2}} = \frac{(0.40 \times 10^5\ Pa)^2}{(0.60 \times 10^5\ Pa)} = 0.2666 \times 10^5\ Pa \approx 2.67 \times 10^4$ Pa

SARASWATI CHEMISTRY

Thermodynamics

Q-1 . Although heat is path function but heat absorbed by the system under certain specific conditions is independent of path. What are those conditions? Explain.

Sol. The two conditions under which heat becomes independent of path are

(*i*) when volume remains constant.

(*ii*) when pressure remains constant.

(*a*) At constant volume By first law of thermodynamics, $\Delta U = q + W$ or $q = \Delta U - W$. But $W = -p\Delta V$. Hence, $q = \Delta U + p\Delta V$. But as volume remains constant, $\Delta V = 0$.

$\therefore q_V = \Delta U$. But ΔU is state function. Hence, q_V is state function.

(*b*) At constant pressure $q_p = \Delta U + p\Delta V$.

But $\Delta U + p\Delta V = \Delta H$.

$\therefore q_p = \Delta H$. As ΔH is a state function, therefore, q_p is a state function.

Q-2 . Calculate the number of kJ of heat necessary to raise the temperature of 60.0 g of aluminium from 35°C to 55°C. Molar heat capacity of Al is 24 J mol^{-1} K^{-1}. Molar mass of Al = 27 g mol^{-1}

Sol. Given, mass of Al = 60.0 g

Molar mass of Al = 27 g mol^{-1}

Molar heat capacity, $C = 24\ J\ mol^{-1}\ K^{-1}$

$$\Delta T = 55°C - 35°C = 20°C \text{ or } 20K$$

Heat, $q = n \cdot C \cdot \Delta T$

$$q = \frac{60}{27} \times 24\ J\ mol^{-1}\ K^{-1} \times 20K \quad \left(n = \frac{60}{27}\ mol\right)$$

$$= 1066.66\ J = 1.067\ kJ$$

Q-3 . Determine the value of ΔH and ΔU for the reversible isothermal evaporation of 90.0 g of water at 100°C. Assume that water vapour behave as an ideal gas and heat of evaporation of water is 540 cal. ($R = 2.0$ cal mol^{-1} K^{-1})

Sol. $\Delta H = 90.0 \times 540 = 48600$ cal

$$\Delta H = \Delta U + p\Delta V = \Delta U + p(V_{vap.} - V_{liq.})$$

Volume of liquid is negligible as compared to volume of vapour.

$$\Delta H = \Delta U + pV_{vap.}$$

$$\Delta H = \Delta U + nRT \quad \text{or} \quad \Delta U = \Delta H - nRT$$

$$= 48600 - \frac{90}{18} \times 2 \times 373 \left(n = \frac{90}{18}\right)$$

$$= 48600 - 3730 = 44870 \text{ cal}$$

Q-4 10 moles of an ideal gas expand isothermally and reversibly from a pressure of 5 atm to 1 atm at 300 K. What is the largest mass that can be lifted through a height of 1 m by this expansion?

Sol. $W_{exp} = -2.303\, nRT \log\frac{p_1}{p_2} = -2.303\,(10 mol)$

$$\times (8.314\ JK^{-1} mol^{-1})(300\ K) \log\frac{5}{1} = -40.15 \times 10^3\ J$$

If M is the mass that can be lifted by this work through a height of 1 m, then work done = Mgh

$$40.15 \times 10^3\ J = M \times 9.81 \times m\,s^{-1} \times 1\ m$$

or $$M = \frac{40.15 \times 10^3\ kg\,m^2 s^{-2}}{9.81\ m\,s^{-2} \times 1\ m}$$

$$(\ J = kg\,m^2 s^{-2})$$

$$= 4092.76\ kg$$

Q-5 Calculate the enthalpy change on freezing of 1.0 mole of water at 10.0°C to ice at −10.0°C. $\Delta_{fus}H$ = 6.03 kJ mol^{-1} at 0°C.

$$C_p[H_2O(l)] = 75.3\ J\ mol^{-1}\ K^{-1};$$

$$C_p[H_2O(s)] = 36.8\ J\ mol^{-1}\ K^{-1}$$

- Conversion of 1 mole of water at 10°C to ice at −10°C involves the following steps
- 1 mol $H_2O(l)$ at 10°C $\longrightarrow$ 1 mol $H_2O(l)$ at 0°C
  $\Delta H_1 = C_{pH_2O(l)} \times \Delta T$
- 1 mol $H_2O(l)$ at 0°C $\longrightarrow$ 1 mol $H_2O(s)$ at 0°C
  $\Delta H_2 = \Delta H_{freezing}$
- 1 mol $H_2O(s)$ at 0°C $\longrightarrow$ 1 mol $H_2O(s)$ at 10°C
  $\Delta H_3 = C_{pH_2O(s)} \times \Delta T$;
- $\Delta T = 10$ K and we know that according to Hess's law, total enthalpy change, $\Delta H = H_1 + H_2 + H_3$ so first calculate $\Delta H_1, \Delta H_2, \Delta H_3$ and then ΔH.

Sol. Enthalpy change for the conversion of 1 mole liquid water at 10°C into 1 mole liquid water at 0°C,

$$\Delta H_1 = C_{pH_2O(l)} \times \Delta T = -75.3\ \text{J mol}^{-1}\ \text{K}^{-1} \times 10\text{K}$$
$$= -753\ \text{J mol}^{-1}$$

Enthalpy of fusion, $\Delta H_2 = \Delta H_{\text{freezing}} = -\Delta H_{\text{fusion}}$

$$= -6.03\ \text{kJ mol}^{-1}$$

Enthalpy change for the conversion of 1 mole of ice at 0°C to 1 mole of ice at 10°C,

$$\Delta H_3 = C_{pH_2O(s)} \times \Delta T$$
$$= -36.8\ \text{J mol}^{-1}\ \text{K}^{-1} \times 10\text{K} = -368\ \text{J mol}^{-1}$$
$$\Delta H_{\text{total}} = -(0.753 + 6 \cdot 03 - 0.368)\ \text{kJ mol}^{-1}$$
$$= -7.151\ \text{kJ mol}^{-1}$$

NOTE Heat is evolved in the process of cooling (freezing) so each step will have a negative sign with ΔH.

Q-6 . A swimmer coming out from a pool is covered with a film of water weighing about 18 g. How much heat must be supplied to evaporate this water at 298 K? Calculate the internal energy of vaporisation at 100°C ?

$$\Delta_{\text{vap}} H^{\ominus} \text{ for water at } 373\ \text{K} = 40.66\ \text{kJ mol}^{-1}$$

Solution The process of evaporation can be represented as

$$18\text{g } H_2O(l) \xrightarrow{\text{vaporisation}} 18\text{g } H_2O(g)$$

Number of moles in 18 g $H_2O(l) = \dfrac{18\text{g}}{18\text{g mol}^{-1}} = 1$ mol

and $\Delta_{\text{vap}} H^{\ominus}$ is the amount of heat required to vaporise 1 mole of a substance. Thus, 40.66 kJ mol^{-1} heat is required for evaporation of 18 g of water.

Further, we know that

$$\Delta_{\text{vap}} U = \Delta_{\text{vap}} H^{\ominus} - p\Delta V = \Delta_{\text{vap}} H^{\ominus} - \Delta_{n_g} RT$$

(assuming steam behaving as an ideal gas).

$$\therefore\ \Delta_{\text{vap}} U = 40.66\ \text{kJ mol}^{-1} - (1)(8.314\ \text{JK}^{-1}\ \text{mol}^{-1})$$
$$(373\ \text{K})(10^{-3})$$
$$\Delta_{\text{vap}} U^{\ominus} = 40.66\ \text{kJ mol}^{-1} - 3.10\ \text{kJ mol}^{-1} = 37.56\ \text{kJ mol}^{-1}$$

Q-7 . Enthalpies of formation of $CO(g)$, $CO_2(g)$, $N_2O(g)$ and $N_2O_4(g)$ are $-110, -393$, 81 and 9.7 kJ mol^{-1} respectively. Find the value of $\Delta_r H$ for the reaction.

$$N_2O_4(g) + 3CO(g) \longrightarrow N_2O(g) + 3CO_2(g)$$

Sol. Heat of reaction,

$$\Delta_r H^\circ = \Sigma \Delta_f H^\circ_{\text{products}} - \Sigma \Delta_f H^\circ_{\text{reactants}}$$
$$= [\Delta_f H^\circ(N_2O) + 3\Delta_f H^\circ(CO_2)]$$
$$- [\Delta_f H^\circ(N_2O_4) + 3\Delta_f H^\circ(CO)]$$
$$= [81 + (3 \times -393)] - [9.7 + (3 \times -110)]\ \text{kJ}$$
$$= -777.7\ \text{kJ} \approx -778\ \text{kJ}$$

Q-8 . Given that the enthalpy of formation of H_2O is -68 kcal/mol. Calculate the enthalpy of formation of OH^- ions.

Sol. For neutralisation reaction, we know that

$$H^+ + OH^- \longrightarrow H_2O;\ \Delta_r H^\circ = -13.7\ \text{kcal}$$
$$\therefore\ \Delta_r H^\circ = \Delta_f H^\circ(H_2O) - [\Delta_f H^\circ(H^+)$$
$$+ \Delta_f H^\circ(OH^-)]$$

i.e., $-13.7 = -68 - [0 + \Delta_f H^\circ(OH^-)]$

$$[\because \Delta_f H^\circ(H^+) = 0]$$

or $\quad \Delta_f H^\circ(OH^-) = -68 + 13.7$

$$= -54.3\ \text{kcal mol}^{-1}$$

Q-9 . Calculate the enthalpy change for the process

$$CCl_4(g) \longrightarrow C(g) + 4Cl(g)$$

and calculate the bond enthalpy of C—Cl in $CCl_4(g)$

$$\Delta_{\text{vap}} H^\circ(CCl_4) = 30.5\ \text{kJ mol}^{-1}$$
$$\Delta_f H^\circ(CCl_4) = -135.5\ \text{kJ mol}^{-1}$$
$$\Delta_a H^\circ(C) = 715.0\ \text{kJ mol}^{-1}$$

where, $\Delta_a H^\circ$ is enthalpy of atomisation,

$$\Delta_a H^\circ(Cl_2) = 242\ \text{kJ mol}^{-1}$$

Sol. Given,

(*i*) $CCl_4(l) \longrightarrow CCl_4(g);\ \Delta_{\text{vap}} H^\circ = +30.5\ \text{kJ mol}^{-1}$

(*ii*) $C(s) + 2Cl_2(g) \longrightarrow CCl_4(l);$

$$\Delta_f H^\circ = -135.5\ \text{kJ mol}^{-1}$$

(*iii*) $C(s) \longrightarrow C(g);\ \Delta_a H^\circ = 715.0\ \text{kJ mol}^{-1}$

(*iv*) $Cl_2(g) \longrightarrow 2Cl(g);\ \Delta_a H^\circ = 242\ \text{kJ mol}^{-1}$

Multiplying Eq. (iv) by 2, we get

(*v*) $2Cl_2(g) \longrightarrow 4Cl(g);\ \Delta_a H^\circ = 484.0\ \text{kJ mol}^{-1}$

Adding Eqs. (iii) and (v), we get

(*vi*) $C(s) + 2Cl_2(g) \longrightarrow C(g) + 4Cl(g);$

$$\Delta H = 1199\ \text{kJ mol}^{-1}$$

Reversing Eqs. (i) and (ii), we get

(*vii*) $CCl_4(g) \longrightarrow CCl_4(l);\ \Delta H = -30.5\ \text{kJ mol}^{-1}$

(*viii*) $CCl_4(l) \longrightarrow C(s) + 2Cl_2(g);\ \Delta H = +135.5\ \text{kJ mol}^{-1}$

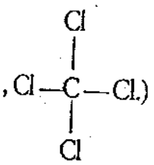
Adding Eqs. (vi), (vii) and (viii), we get

$$CCl_4(g) \longrightarrow C(g) + 4Cl(g);\ \Delta H = 1304\ \text{kJ mol}^{-1}$$

Bond enthalpy of C—Cl bond in

$$CCl_4 = \frac{1304}{4} = 326\text{ kJ mol}^{-1}$$

(There are four C—Cl bonds in CCl_4, Cl—C—Cl.)



$$\mathrm{Cl-\overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle Cl}{|}}{C}}-Cl}$$

Q-10. Water can be lifted into the water tank at the top of the house with the help of a pump. Then why is it not considered to be spontaneous?

Sol. A spontaneous process should occur continuously by itself after initiation. But this is not so in the given case because water will go up so long as the pump is working.

Q-11. Comment on the thermodynamic stability of $NO(g)$, given

$$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \rightarrow NO(g);\ \Delta_r H^\circ = 90\text{ kJ mol}^{-1}$$

$$NO(g) + \frac{1}{2}O_2(g) \rightarrow NO_2(g);\ \Delta_r H^\circ = -74\text{ kJ mol}^{-1}$$

Sol. $NO(g)$ is unstable because formation of NO is endothermic (energy is absorbed), but $NO_2(g)$ is formed because its formation is exothermic (energy is released). Therefore, unstable $NO(g)$ converts into stable $NO_2(g)$.

Q-12 For the reaction, $2Cl(g) \longrightarrow Cl_2(g)$, what are the signs of ΔH and ΔS ?

Sol. In the given reaction, a molecule of Cl_2 is formed from its two gaseous atoms and the energy is released with the formation of bond. Hence, ΔH is –ve. In this reaction, randomness (entropy) also decreases because 2 mole atoms of Cl have more randomness than one mole molecule of chlorine. Hence, ΔS is –ve.

Q-13. Under what condition, the heat evolved or absorbed in a reaction is equal to its free energy change?

Sol. As $\Delta G = \Delta H - T\Delta S$. Thus, $\Delta G = \Delta H$ only when either the reaction is carried out at 0 K or the reaction is not accompanied by any entropy change, *i.e.*, $\Delta S = 0$.

Q-14. For the reaction at 298 K, $2A + B \longrightarrow C$

$\Delta H = 400\text{ kJmol}^{-1}$ and $\Delta S = 0.2\text{ kJ K}^{-1}\text{ mol}^{-1}$

At what temperature will the reaction become spontaneous considering ΔH and ΔS to be constant over the temperature range?

For a reaction to be spontaneous, $\Delta G \le 0$. So, calculate the temperature at which $\Delta G = 0$ by using the relation, $\Delta G = \Delta H - T\Delta S$

Sol. Gibbs free energy,

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

$$0 = 400\text{ kJ mol}^{-1} - T \times 0.2\text{ kJK}^{-1}\text{mol}^{-1}$$

$$\text{Temperature, } T = \frac{400\text{ kJ mol}^{-1}}{0.2\text{ kJK}^{-1}\text{mol}^{-1}} = 2000\text{K}$$

Therefore, above 2000 K, the reaction will become spontaneous.

NOTE If $\Delta G < 0$, the process is spontaneous and if $\Delta G > 0$, the process is non-spontaneous.

Q-15. The equilibirum constant for a reaction is 10. What will be the value of ΔG°? $R = 8.314\text{ JK}^{-1}\text{mol}^{-1}$, $T = 300\text{K}$.

Sol. $\Delta G^\circ = -2.303\ RT \log K_c$

Given, $R = 8.314\text{ JK}^{-1}\text{mol}^{-1}$, $T = 300\text{K}$, $K_c = 10$

$$\Delta G^\circ = -2.303 \times 8.314\text{ JK}^{-1}\text{mol}^{-1} \times 300\text{K} \times \log 10$$

$(\log 10 = 1) = -5744.14\text{ J mol}^{-1}$

Q-16. Calculate the free energy change when 1 mole of NaCl is dissolved in water at 298 K. (Given, lattice energy of NaCl = $-777.8\text{ kJ mol}^{-1}$, hydration energy = $-774.1\text{ kJ mol}^{-1}$ and $\Delta S = 0.043\text{ kJ K}^{-1}\text{mol}^{-1}$ at 298 K).

Sol. ΔH = hydration energy – lattice energy

$$\Delta H = -774.1\text{kJ mol}^{-1} - (-777.8\text{ kJ mol}^{-1})$$

$$= 3.7\text{ kJ mol}^{-1}$$

$$\Delta G = \Delta H - T\Delta S = +3.7 - 298 \times 0.043 = +3.7 - 12.81$$

$$\Delta G = -9.11\text{ kJ mol}^{-1}$$

Q-17. For the reaction, $2A(g) + B(g) \longrightarrow 2D(g)$;

$\Delta U^\circ = -10.5$ kJ and $\Delta S^\circ = -44.1\text{JK}^{-1}$.

Calculate ΔG° for the reaction and predict whether the reaction may occur spontaneously.

$(R = 8.314 \times 10^{-3}\text{ kJ K}^{-1}\text{mol}^{-1}, T = 298\text{K})$

- We know that $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ so first find ΔH° by using the formula, $\Delta H = \Delta U + \Delta n_g RT$ and then ΔG° by putting the values of ΔH°, T and ΔS°.
- For a spontaneous reaction $\Delta G \le 0$.

Sol. $2A(g) + B(g) \longrightarrow 2D(g)$;

$$\Delta n_g = n_p - n_r = 2 - 3 = -1$$

$$\Delta H^\circ = \Delta U^\circ + \Delta n_g RT$$

$$\Delta H^\circ = -10.5\text{ kJ} + (-1 \times 8.314 \times 10^{-3}\text{ kJ K}^{-1}\text{mol}^{-1} \times 298\text{K})$$

$$= -12.977\text{ kJ mol}^{-1}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ;$$

$$\Delta G^\circ = 12.977\text{ kJ mol}^{-1} - (298\text{K} \times -44.1 \times 10^{-3}\text{ kJK}^{-1}\text{mol}^{-1})$$

$$= +0.1165\text{ kJmol}^{-1}$$

The reaction will no occur spontaneously because ΔG° is positive.

Q-18 Calculate the standard enthalpy of formation of $CH_3OH(l)$ from the following data

$$(i)\ CH_3OH(l) + \frac{3}{2}O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(l);\ \Delta_r H^\circ = -726\ \text{kJ mol}^{-1}$$

$$(ii)\ C_{(\text{graphite})} + O_2(g) \longrightarrow CO_2(g);\ \Delta_c H^\circ = -393\ \text{kJ mol}^{-1}$$

$$(iii)\ H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O\ (l);\ \Delta_f H^\circ = -286\ \text{kJ mol}^{-1}$$

Sol. Required reaction for the formation of methanol is as follows

$$C(s) + 2H_2(g) + \frac{1}{2}O_2(g) \longrightarrow CH_3OH(l);\ \Delta_f H^\circ = ?$$

Multiplying Eq. (iii) by 2

$$(i)\ 2H_2(g) + O_2(g) \longrightarrow 2H_2O\ (l);\ \Delta_f H^\circ = -572\ \text{kJ mol}^{-1}$$

Summing up the Eqs. (ii) and (iv), we get

$$(ii)\ C(s) + 2H_2(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l);\ \Delta_f H^\circ = -965\ \text{kJ mol}^{-1}$$

Reversing Eq. (i), we get

$$(iii)\ CO_2(g) + 2H_2O\ (g) \longrightarrow CH_3OH(l) + \frac{3}{2}O_2(g);\ \Delta_r H^\circ = +726\ \ \text{kJ mol}^{-1}$$

Adding Eqs. (v) and (vi) we get the required equation

$$C(s) + 2H_2(g) + \frac{1}{2}O_2(g) \longrightarrow CH_3OH(l);\ \Delta_f H^\circ = -965 + 726 = -239\ \text{kJ mol}^{-1}$$

Q-19 nple 13. For oxidation of iron, $4Fe(s) + 3O_2(g) \longrightarrow 2Fe_2O_3(s)$ entropy change is $-549.4\ \text{JK}^{-1}\text{mol}^{-1}$ at 298 K. Inspite of negative entropy change of this reaction, why is the reaction spontaneous? ($\Delta_r H^\ominus$ for this reaction is $-1648 \times 10^3\ \text{J mol}^{-1}$)

Solution The spontaneity of the reaction is decided by considering ΔS_{total} ($\Delta S_{\text{sys}} + \Delta S_{\text{surr}}$). At temperature T, entropy change of the surroundings.

$$\Delta S_{\text{surr}} = \frac{\Delta_r H^\ominus}{T}\ (\text{at constant pressure}) = -\frac{(-1648 \times 10^3\ \text{Jmol}^{-1})}{298\ \text{K}} = 5530\ \text{JK}^{-1}\text{mol}^{-1}$$

Thus, total entropy change for this reaction

$$\Delta S_{\text{total}} = 5530\ \text{JK}^{-1}\text{mol}^{-1} + (-549.4\ \text{JK}^{-1}\text{mol}^{-1}) = 4980.6\ \text{JK}^{-1}\text{mol}^{-1}$$

Positive value of ΔS_{total} shows that the above reaction is spontaneous.

Q-20 Why standard entropy of an elementary substance is not zero whereas standard enthalpy of formation is taken as zero?

Sol. A substance has a perfectly ordered arrangement of its constituent particles only at absolute zero. Hence, entropy is zero only at absolute zero. Enthalpy of formation is the heat change involed in the formation of one mole of the substance from its elements. An element formed from itself means no heat change, *i.e.*, $\Delta_f H^\circ = 0$.

Q-21 Air contains about 99% of N_2 and O_2 gases. Why do not they combine to form NO under the standard conditions? Standard Gibbs energy of formation of NO (g) is 86.7 kJ mol^{-1}.

Sol. For the combination of N_2 and O_2 to form NO, the standard Gibbs energy of formation,

$$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \longrightarrow NO(g)\ \text{is +ve}\ (+86.7\ \text{kJ mol}^{-1})$$

Therefore, this reaction is non-spontaneous under the standard conditions and hence N_2 and O_2 do not combine.

Q-22 A man takes a diet equivalent to 10000 kJ per day and does work, in expending his energy in all forms equivalent to 12500 kJ per day. What is change in internal energy per day? If the energy lost was stored as sucrose (1632 kJ per 100 g), how many days should it take to lose 2 kg of his weight? (Ignore water loss)

Sol. Energy taken by a man = 10000 kJ

Change in internal energy per day = 12500 − 10000 = 2500 kJ

The energy is lost by the man as he expands more energy than he takes

Now 100 g of sugar corresponds to energy = 1632 kJ loss in energy

$$2000 \text{ g of sugar corresponds to energy} = \frac{1632 \times 2000}{100} = 32640 \text{ kJ}$$

$$\therefore \text{ Number of days required to lose 2000 g of weight or 32640 kJ of energy} = \frac{32640}{2500} = 13 \text{ days}$$

Q-23 Calculate the entropy change in surroundings when 1.00 mole of $H_2O(l)$ is formed under standard conditions. $\Delta_f H^\circ = -286 \text{ kJ mol}^{-1}$.

Sol. Enthalpy change for the formation of 1 mole of $H_2O(l)$,

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l);$$

$$\Delta_f H^\circ = -286 \text{ kJ mol}^{-1}$$

Energy released in the above reaction, is absorbed by the surroundings.

It means $q_{surr} = +286 \text{ kJ mol}^{-1}$

$$\Delta S = \frac{q_{surr}}{T} = \frac{+286 \text{ kJ mol}^{-1}}{298 \text{K}}$$

$$= 0.9597 \text{ kJ K}^{-1}\text{mol}^{-1}$$

$$= 959.7 \text{ JK}^{-1}\text{mol}^{-1}.$$

Q-24 For an isolated system, $\Delta U = 0$, what will be ΔS?

Sol. For an isolated system, $\Delta U = 0$ and for a spontaneous process, total entropy change must be positive. For example, consider the diffusion of two gases *A* and *B* into each other in a closed container which is isolated from the surroundings.

The two gases *A* and *B* are separated by a movable partition. When partition is removed, the gases begin to diffuse into each other and the system becomes more disordered. It shows that $\Delta S > 0$ and $\Delta U = 0$ for this process.

Morever, $\Delta S = \frac{q_{rev}}{T} = \frac{\Delta H}{T}$

$$= \frac{\Delta U + p\Delta V}{T} = \frac{p\Delta V}{T} \qquad (\Delta U = 0)$$

i.e., $T\Delta S$ or $\Delta S > 0$

Q-25 Enthalpy of combustion of carbon to CO_2 is $-393.5 \text{ kJ mol}^{-1}$. Calculate the heat released upon formation of 35.2 g of CO_2 from carbon and dioxygen gas. (Molar mass of $CO_2 = 44 \text{ g mol}^{-1}$).

Sol. The reaction for the combustion of carbon into CO_2 is

$$C(s) + O_2(g) \longrightarrow \underset{44\,g}{CO_2(g)};\ \Delta H = -393.5 \text{ kJ mol}^{-1}$$

Heat released in the formation of 44 g CO_2 = 393.5 kJ

$$\therefore \text{ Heat released in the formation of } 35.2 \text{ g } CO_2 = \frac{393.5 \text{ kJ} \times 35.2 \text{ g}}{44 \text{ g}} = 314.8 \text{ kJ}$$

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SARASWATI CHEMISTRY

States of Matter

Q-1 . How much time would it take to distribute one Avogadro number of wheat grains if 10^{10} grains are distributed each second?

- $1 N_A = 6.022 \times 10^{23}$ where, N_A = Avogadro's number.
- Convert time into years

Sol. Time required $= \dfrac{\text{total grains}}{\text{grains distributed}} = \dfrac{6.022 \times 10^{23}}{10^{10}}$

$$= 6.022 \times 10^{13}\ \text{s} = \frac{6.022 \times 10^{13}}{365 \times 24 \times 60 \times 60}$$

$$= 1.909 \times 10^{6}\ \text{yr}$$

Q-2 . Explain why Boyle's law cannot be used to calculate the volume of a real gas when it is converted from its initial state to final state by an adiabatic expansion.

Sol. During adiabatic expansion, temperature is lowered and therefore, Boyle's law cannot be applied.

Q-3 Boyle's law states that at constant temperature, if pressure is increased on a gas, volume decreases and *vice-versa*. But when we fill air in a balloon, volume as well as pressure increase. Why?

Sol. The law is applicable only for a definite mass of the gas. As we fill air into the balloon, we are introducing more and more air into the balloon.

Thus, we are increasing the mass of air inside. Hence, the law is not applicable.

Q-4 What would be the SI unit for the quantity pV^2T^2/n?

Sol. $\dfrac{pV^2T^2}{n} = \dfrac{(\text{Nm}^{-2})\,(\text{m}^3)^2\,(\text{K})^2}{\text{mol}}$

$$= \text{Nm}^4\,\text{K}^2\,\text{mol}^{-1}$$

Q-5 In terms of Charles' law explain why −273°C is the lowest possible temperature?

Sol. According to Charles' law,

$$V_t = V_0\left[1 + \frac{t}{273}\right]$$

At $t = -273$°C,

$$V_t = V_0\left[1 - \frac{273}{273}\right] = 0$$

Thus, at −273°C, volume of a gas becomes zero and below this temperature the volume becomes negative, which is meaningless.

Q-6 . What will be the minimum pressure required to compress 500 dm^3 of air at 1 bar to 200 dm^3 at 30°C?

Apply Boyle's law $p_1V_1 = p_2V_2$ to calculate p_2 as temperature remains constant.

Sol. $p_1 = 1$ bar, $p_2 = ?$, $V_1 = 500\ \text{dm}^3$, $V_2 = 200\ \text{dm}^3$

$$p_1V_1 = p_2V_2 \text{ or } p_2 = \frac{p_1V_1}{V_2} = \frac{1\ \text{bar} \times 500\ \text{dm}^3}{200\ \text{dm}^3} = 2.5\ \text{bar}$$

Q-7 . A vessel of 120 mL capacity contains a certain amount of gas at 35°C and 1.2 bar pressure. The gas is transferred to another vessel of volume 180 mL, at 35°C. What would be its pressure?

Sol. Solve as Q. 2 [Ans. $p_2 = 0.8$ bar] $\dfrac{P_1V_1}{T_1} = \dfrac{P_2V_2}{T_2}$

Q-8 . A balloon filled with an ideal gas is taken from the surface of the sea deep to a depth of 100 m. What will be its volume in terms of its original volume?

Sol. Pressure at the surface = 76 cm = 76 × 13.6 cm Hg $h\rho g = h'\rho'g$

$$= 1033.6 \text{ cm of Hg} = 10.3 \text{ m of Hg}$$

$h_\omega = 16 \times 13.6$

∴ Pressure at 100 m depth = 100 + 10.3 m = 110.3 m

$h = 10.3$

Applying $p_1V_{1,(\text{At surface})} = p_2V_{2,(\text{At 100 m depth})}$

$$10.3 \times V = 110.3 \times V_2$$

or $V_2 = 0.093\ V = 9.3\%$ of V

$P_1V_1 \; P_2V_2$

$\dfrac{V_1}{V_2} = \dfrac{100+10.3}{10.3}$

Q-9 Calculate the number of electrons present in 1.4 g of dinitrogen gas.

- Convert the given mass into mole with the help of the formula, moles $= \dfrac{\text{mass}}{\text{molecular mass}}$
- 1 mole $= 6.022 \times 10^{23}$ molecule

Sol. $n_{N_2} = \dfrac{1.4}{28} = 0.05$ mol

$$1 \text{ mol} = 6.022 \times 10^{23} \text{ molecules}$$

$$0.05 \text{ mol} = 0.05 \times 6.022 \times 10^{23}$$

$$= 0.3011 \times 10^{23} \text{ molecules}$$

1 molecule of N_2 contains = 14 electrons

$\therefore$ 0.3011×10^{23} molecules will contain

$$= 0.3011 \times 10^{23} \times 14$$

$$= 4.2154 \times 10^{23} \text{ electrons}$$

Q-10 . Calculate the temperature of 4.0 moles of a gas occupying 5 dm^3 at 3.32 bar.
($R = 0.083 \text{ bar dm}^3 \text{ K}^{-1} \text{ mol}^{-1}$).

Sol. Apply ideal gas equation, $pV = nRT$

$$T = \frac{pV}{Rn} = \frac{3.32 \text{ bar} \times 5 \text{ dm}^3}{0.083 \text{ bar dm}^3 \text{ K}^{-1} \text{ mol}^{-1} \times 4 \text{ mol}}$$

$$T = 50 \text{ K}$$

Q-11 . 34.05 mL of phosphorus vapour weighs 0.0625 g at 546°C and 0.1 bar pressure. What is the molar mass of phosphorus?

Sol. $pV = nRT = \frac{mRT}{M}$

(m = mass of phosphorus (g) and
M = molar mass of phosphorus)

$$M = \frac{mRT}{pV}$$

$$M = \frac{0.0625 \text{ g} \times 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 819 \text{ K}}{0.1 \times 0.987 \text{ atm} \times 0.03405 \text{ L}}$$

$$M = 1250.4 \text{ g mol}^{-1}$$

Q-12 . Calculate the volume occupied by 8.8 g of CO_2 at 31.1°C and 1 bar pressure. $R = 0.083 \text{ bar L K}^{-1} \text{ mol}^{-1}$.

Sol. $pV = nRT$ or $pV = \frac{m}{M} RT$

Volume occupied by 8.8 g of CO_2,

$$V = \frac{mRT}{pM} = \frac{8.8 \text{ g} \times 0.083 \text{ bar L K}^{-1} \text{ mol}^{-1} \times 304.1 \text{ K}}{1 \text{ bar} \times 44 \text{ g mol}^{-1}}$$

$$V = 5.048 \text{ L}$$

Q-13 . Using the equation of state $pV = nRT$; show that at a given temperature, density of a gas is proportional to gas pressure p.

Sol. $pV = nRT$

$$pV = \frac{m}{M} RT \qquad \left\{ n = \frac{m}{M} = \frac{\text{mass of gas (g)}}{\text{molar mass of gas}} \right\}$$

or $$p = \frac{mRT}{VM} \text{ or } p = \frac{dRT}{M} \qquad \left(\text{Density, } d = \frac{m}{V} \right)$$

or $$d = \frac{pM}{RT};$$

If T = constant, $d \propto p$

Q-14 . At 0°C, the density of a certain oxide of a gas at 2 bar is same as that of dinitrogen at 5 bar. What is the molecular mass of the oxide?

Sol. Density, $d = \frac{Mp}{RT}$

When T and d are same and R is constant, then p_1M_1 (gaseous oxide) = p_2M_2 (nitrogen).

$2 \text{ bar} \times M_1 = 5 \text{ bar} \times 28 \text{ u}$ (Molar mass of N_2 = 28 u)

Q-15 A mixture of dihydrogen and dioxygen at one bar pressure contains 20% by weight of dihydrogen. Calculate the partial pressure of dihydrogen.

- To calculate the partial pressure, total pressure and mole fraction of hydrogen is required, so first calculate number of moles of H_2 and O_2 in the given mixture and mole fraction of hydrogen.
- Then, calculate p_{H_2} by using the formula $p_A = p_{total} \times x_A$

Sol. A mixture of H_2 and O_2 contains 20% by weight of H_2 means H_2 = 20 g and O_2 = 80 g

Moles of hydrogen, $n_{H_2} = \frac{20}{2} = 10 \text{ mol}$

Moles of oxygen, $n_{O_2} = \frac{80}{32} = 2.5 \text{ mol}$

Mole fraction of hydrogen,

$$x_{H_2} = \frac{n_{H_2}}{n_{H_2} + n_{O_2}} = \frac{10}{10 + 2.5} = 0.8$$

Partial pressure of H_2, $p_{H_2} = p_{total} \times x_{H_2}$

$$p_{H_2} = 1 \text{ bar} \times 0.8$$

$$p_{H_2} = 0.8 \text{ bar}$$

Q-16 A balloon is filled with hydrogen at room temperature. It will burst if pressure exceeds 0.2 bar. If at 1 bar pressure the gas occupies 2.27 L volume, upto what volume can the balloon be expanded?

Solution According to Boyle's law, $p_1V_1 = p_2V_2$

$$1 \text{ bar} \times 2.27 \text{ L} = 0.2 \text{ bar} \times V_2$$

or $$V_2 = \frac{1 \text{ bar} \times 2.27 \text{ L}}{0.2 \text{ bar}} = 11.35 \text{ L}$$

Since, balloon bursts at 0.2 bar pressure, the volume of balloon should be less than 11.35 L.

Q-17 The drain cleaner, Drainex contains small bits of aluminium which react with caustic soda to produce dihydrogen. What volume of dihydrogen at 20°C and 1 bar will be released when 0.15 g of aluminium reacts?

- To find the volume of dihydrogen, by using the equation $pV = nRT$, number of moles of hydrogen produced are required, so write a balanced chemical reaction between Al and NaOH and find the number of moles of H_2 produced from 0.15 g Al.
- Find V_{H_2} by using the relation $pV = nRT$.

Al H_2

·15 gm 28

NaOH

Sol. $2Al + 2NaOH + 2H_2O \longrightarrow 2NaAlO_2 + 3H_2$

2×27 g 3 mol

0.15 g $\dfrac{0.15 \times 3}{2 \times 27} = 0.00833$ mol

$2Al + NaOH \underset{+H_2O}{} \longrightarrow 2NaAlO_2 + 3H_2$

$pV = nRT$

$$V_{H_2} = \frac{0.00833 \text{ mol} \times 0.0821 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1} \times 293 \text{ K}}{1 \times 0.987 \text{ atm}}$$

($\because$ 1 bar = 0.987 atm)

$V_{H_2} = 0.203 = 203$ mL dm^3

$\boxed{54 \text{ gm of Al} \rightarrow 3 \text{ mol} \qquad \cdot 15 \rightarrow \dfrac{3 \times \cdot 15}{54}}$

$PV = nRT$

$1 \times V = \cdot 831 \times 293$

Q-18 Calculate the total pressure in a mixture of 8 g of dioxygen and 4 g of dihydrogen confined in a vessel of 1 dm^3 at 27°C. ($R = 0.083$ bar dm^3 K^{-1} mol^{-1})

To calculate the total pressure exerted by a mixture of gases first find total number of moles of gas and then apply the relation, $pV = nRT$.

Sol. Moles of O_2, $n_{O_2} = \dfrac{\text{mass}}{\text{mol. wt.}} = \dfrac{8}{32} = 0.25$ mol

[mol. wt. of $O_2 = 16 \times 2 = 32$]

Moles of H_2, $n_{H_2} = \dfrac{4}{2} = 2.0$ mol

[mol. wt. of $H_2 = 1 \times 2 = 2$]

Total number of moles $= 0.25 + 2.0$

$= 2.25$ mol

Pressure, $p = \dfrac{nRT}{V}$ $(n_1 + n_2)$

$$= \frac{2.25 \text{ mol} \times 0.083 \text{ bar dm}^3 \text{ K}^{-1} \text{mol}^{-1} \times 300 \text{ K}}{1 \text{ dm}^3}$$

$p = 56.025$ bar

Q-19. 2.9 g of a gas at 95°C occupied the same volume as 0.184 g of dihydrogen at 17°C, at the same pressure. What is the molar mass of the gas?

- Since, two gases are given write two separate equations (for unknown gas and for H_2) by using the relation, $pV = \dfrac{m}{M}RT$.
- To calculate the molar mass of unknown gas compare both the equations at the same volume and pressure.

Sol. Unknown gas; H_2 gas

$p_1V_1 = \dfrac{m_1RT_1}{M_1}$; $p_2V_2 = \dfrac{m_2RT_2}{M_2}$

$p_1V_1 = p_2V_2$

$\therefore \dfrac{m_1RT_1}{M_1} = \dfrac{m_2RT_2}{M_2}$

$$\frac{2.9 \text{ g} \times R \times 368 \text{ K}}{M_1} = \frac{0.184 \text{ g} \times R \times 290 \text{ K}}{2 \text{ g mol}^{-1}}$$

Molar mass of unknown gas,

$$M_1 = \frac{2.9 \text{ g} \times 368 \text{ K} \times 2 \text{ g mol}^{-1}}{0.184 \text{ g} \times 290 \text{ K}} = 40 \text{ g mol}^{-1}$$

Q-20. What will be the pressure exerted by a mixture of 3.2 g of methane and 4.4 g of carbon dioxide contained in a 9 dm^3 flask at 27°C?

Sol. Moles of CH_4, $n_{CH_4} = \dfrac{\text{mass of } CH_4}{\text{molar mass of } CH_4}$

$= \dfrac{3.2}{16} = 0.2$ mol

Similarly, moles of CO_2, $n_{CO_2} = \dfrac{4.4}{44} = 0.1$ mol

Total moles $= 0.2 + 0.1 = 0.3$ mol

$pV = nRT$

Pressure, $p = \dfrac{nRT}{V}$

$$= \frac{0.3 \text{ mol} \times 0.0821 \text{ dm}^3 \text{atm K}^{-1} \text{mol}^{-1} \times 300 \text{ K}}{9 \text{ dm}^3}$$

$= 0.821 \text{ atm} = 8.314 \times 10^4$ Pa

Q-21. What will be the pressure of the gaseous mixture when 0.5 L of H_2 at 0.8 bar and 2.0 L of dioxygen at 0.7 bar are introduced in a 1 L vessel at 27°

Sol. $pV = nRT$

Moles of H_2, $n_{H_2} = \frac{pV}{RT} = \frac{0.8 \times 0.5}{RT} = \frac{0.40}{RT}$

Similarly, moles of O_2, $n_{O_2} = \frac{pV}{RT} = \frac{0.7 \times 2}{RT} = \frac{1.4}{RT}$

Total number of moles $= \frac{0.40}{RT} + \frac{1.4}{RT} = \frac{1.8}{RT}$

Total pressure, $p_{\text{total}} = \frac{nRT}{V} = \frac{1.8 \times RT}{RT \times 1} = 1.8$ atm

Q-22 Pressure of 1 g of an ideal gas A at 27°C is found to be 2 bar. When 2 g of another ideal gas B is introduced in the same flask at same temperature, the pressure becomes 3 bar. Find a relationship between their molecular masses.

Sol. $pV = nRT$

For gas A, $\quad p_A V = n_A RT \quad$ ...(i)

Similarly for gas B, $\quad p_B V = n_B RT \quad$ ...(ii)

Number of moles of gas A; $n_A = \frac{1}{M_A}$

(M_A = molar mass of gas A)

Number of moles of gas B; $n_B = \frac{2}{M_B}$

(M_B = molar mass of gas B)

Pressure of gas A, $p_A = 2$ bar

Total pressure, $p_{\text{total}} = p_A + p_B = 3$ bar

Pressure of gas, $p_B = p_{\text{total}} - p_A = 3 - 2 = 1$ bar

V, R and T are same for both the gases.

Hence, from Eqs. (i) and (ii),

$$\frac{p_A}{p_B} = \frac{n_A}{n_B} = \frac{1 \times M_B}{M_A \times 2}$$

or $\quad \frac{M_B}{M_A} = \frac{2p_A}{p_B} = \frac{2 \times 2}{1}$ or $M_B = 4M_A$

Q-23 Density of a gas is found to be 5.46 g/dm^3 at 27°C and 2 bar pressure. What will be its density at STP?

STP mean at 1 bar and 273 K so compare the density at 27°C and 2 bar with the density at STP by using the relation $d = pM/RT$.

Sol. Density, $d = pM/RT$

For same gas at different temperatures and pressures

$$\frac{d_2}{d_1} = \frac{p_2 T_1}{p_1 T_2}$$

$$d_2 = \frac{p_2 T_1 d_1}{p_1 T_2} = \frac{1 \times 300 \times 5.46}{2 \times 273}$$

$$= 3 \text{ g dm}^{-3}$$

Q-24 On a ship sailing in pacific ocean where temperature is 23.4°C, a balloon is filled with 2 L air. What will be the volume of the balloon when the ship reaches Indian ocean, where temperature is 26.1°C?

Solution Given, $V_1 = 2\text{ L}; V_2 = ?$

$$T_2 = (26.1 + 273)\text{ K} = 299.1\text{ K}$$

$$T_1 = (23.4 + 273)\text{ K} = 296.4\text{ K}$$

According to Charles' law,

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \text{ or } V_2 = \frac{V_1 T_2}{T_1}$$

On substituting the corresponding values, we get

$$\Rightarrow \quad V_2 = \frac{2\text{ L} \times 299.1\text{ K}}{296.4\text{ K}}$$

$$= 2.018\text{ L}$$

Q-25 1500 mL flask contains 400 mg O_2 and 60 mg H_2 at 100°C. What is the total pressure in the flask?

Solution *Step* I Number of moles of O_2

$$= \frac{w}{m} = \frac{400 \times 10^{-3}}{32} = 0.0125$$

Number of moles of $H_2 = \frac{w}{m} = \frac{60 \times 10^{-3}}{2} = 0.03$

From $pV = nRT$, $p = \frac{nRT}{V}$

Partial pressure of $O_2 = \frac{0.0125 \times 0.0821 \times 373}{1500 \times 10^{-3}} = 0.255$ atm

Partial pressure of $H_2 = \frac{0.03 \times 0.0821 \times 373}{1500 \times 10^{-3}} = 0.612$ atm

Step II Total pressure $= 0.255 + 0.612 = 0.867$ atm

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Q-26. (*i*) Pay load is defined as the difference between the mass of displaced air and the mass of the balloon. Calculate the pay load when a balloon of radius 10 m, mass 100 kg is filled with helium at 1.66 bar at 27°C. (Density of air $= 1.2\ \text{kg m}^{-3}$ and $R = 0.083\ \text{bar dm}^3\ \text{K}^{-1}\ \text{mol}^{-1}$).

(*ii*) A mixture in which the mole ratio of H_2 and O_2 is 2 : 1, is used to prepare water by the reaction

$$2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(g)$$

The total pressure in the container is 0.8 atm at 20°C before the reaction. Calculate the final pressure at 120°C after reaction assuming 80% yield of water.

Sol. (*i*) Radius, $R_{\text{balloon}} = 10\ \text{m}$

$$V_{\text{balloon}} = \frac{4}{3}\pi r^3 = \frac{4}{3} \times \frac{22}{7} \times (10)^3 = 4190.476$$

✓ Pay load = $M_{air} -$ M_{balloon}.

$$V_{\text{balloon}} = V_{\text{displaced air (by balloon)}}$$

∴ Mass of displaced air $= V_{\text{displaced air}} \times$ density of air

$$m_{\text{displaced air}} = 4190.476\ \text{m}^3 \times 1.2\ \text{kg m}^{-3}$$

$$m = 5028.57\ \text{kg}$$

$M_{air} \Rightarrow d = \frac{M}{V}$

$1.2 = \frac{M}{\frac{4}{3}\pi r^3}$

Mass of He filled in balloon, $m_{\text{He}} = \dfrac{pVM}{RT}\left(pV = \dfrac{mRT}{M}\right)$

$$m_{\text{He}} = \frac{1.66\ \text{bar} \times 4190.476 \times 10^3\ \text{dm}^3 \times 4 \times 10^{-3}\ \text{kg mol}^{-1}}{0.083\ \text{bar dm}^3\ \text{K}^{-1}\ \text{mol}^{-1} \times 300\ \text{K}}$$

$$m_{\text{He}} = 1117.46\ \text{kg}$$

$MB = 100 + W_{He}$

$PV = nRT$

$1.6 \times \frac{4}{3}\pi R^3 = \frac{W \times 8.314 \times 300}{4 \times 10^{-3}}$

Total mass of filled balloon, m_{balloon} = mass of balloon + mass of He filled in the balloon

$$m_{\text{balloon}} = 100\ \text{kg} + 1117.46\ \text{kg} = 1217.46\ \text{kg}$$ ✓

Pay load = mass of displaced air − mass of balloon

$$= 5028.57\ \text{kg} - 1217.46\ \text{kg} = 3811.11\ \text{kg}$$

(*ii*)

	$2\,H_2(g)$	$+\ O_2(g) \longrightarrow$	$2\,H_2O(g)$
Initial moles	2	1	0
Moles at equiv.	$2 - 1.6$ $= 0.4$	$1 - 0.8$ $= 0.2$	1.6

$P = \frac{mRT}{M}$

$m = \frac{MPV}{RT}$

Total moles after reaction $= 0.4 + 0.2 + 1.6 = 2.2$

Let the initial pressure at 20° C $= p_1$

Pressure at 120° C $= p_2$

According to Gay-Lussac's law

$$\frac{p_1}{p_2} = \frac{T_1}{T_2} \quad \text{or} \quad \frac{0.8}{p_2} = \frac{293}{393} \quad \text{or} \quad p_2 = \frac{0.8 \times 393}{293} = 1.073\ \text{atm}$$

Now, $\dfrac{\text{initial moles}}{\text{moles after equiv.}} = \dfrac{\text{initial pressure}}{\text{pressure after equiv.}}$

$$\frac{3}{2.2} = \frac{1.073}{p_{\text{equiv.}}}$$

or $$p_{\text{equiv.}} = \frac{1.073 \times 2.2}{3} = 0.787\ \text{atm}$$

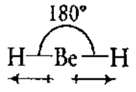
$\frac{P_1 V_1}{n_1} = \frac{P_2 V_2}{n_2}$

SARASWATI CHEMISTRY

Chemical Bonding *and* Molecular Structure

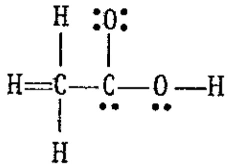
Q-1 Explain why BeH_2 molecule has a zero dipole moment although the Be—H bonds are polar?

Sol. BeH_2 molecule is linear. The two equal bond dipoles point in opposite directions and cancel the effect of each other. That's why its dipole moment is zero.

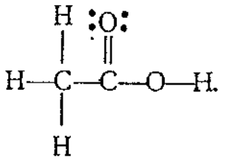


BeH_2 molecule, $\mu = 0$

Q-2 The skeletal structure of CH_3COOH as shown below is correct, but some of the bonds are shown incorrectly. Write the correct Lewis structure for acetic acid.



Sol. The correct Lewis structure for acetic acid is



Q-3 How do you express the bond strength in terms of bond order?

Sol. With increase in bond order, bond enthalpy increases. Therefore, greater the bond order, higher is the bond strength, *i.e.*, bond strength ∝ bond order.

Q-4 Why is NaCl harder than sodium metal?

Sol. This is because in NaCl, there is strong ionic bond between Na^+ and Cl^- whereas in Na metal, there is weak metallic bond.

Q-5 Write Lewis dot symbols for atoms of the following elements Mg, Na, B, O, N, Br.

Sol.

${}_{12}Mg = 2, 8, 2$	Lewis symbol = $\ddot{\text{M}}\text{g}$
${}_{11}Na = 2, 8, 1$	Lewis symbol = $\dot{\text{N}}\text{a}$
${}_{5}B = 2,3$	Lewis symbol = $\cdot\dot{\text{B}}\cdot$
${}_{8}O = 2, 6$	Lewis symbol = $\colon\ddot{\text{O}}\colon$
${}_{35}Br = 2, 8, 18, 7$	Lewis symbol = $\cdot\underset{\cdot\cdot}{\ddot{\text{Br}}}\colon$

Q-6 Write the Lewis structure for the following atoms and ions: S and S^{2-}; Al and Al^{3+}; H and H^-

Sol.

${}_{16}S = 2, 8, 6$	Lewis symbol = $\colon\ddot{\text{S}}\colon$
$S^{2-} = (16 + 2)$ electrons	Lewis symbol = $\left[\colon\underset{\cdot\cdot}{\ddot{\text{S}}}\colon\right]^{2-}$
${}_{13}Al = 2, 8, 3$	Lewis symbol = $\text{Al}\,.$
$Al^{3+} = (13 - 3) = 10$ electrons	Lewis symbol = $[\ddot{\text{Al}}]^{3+}$
${}_{1}H = 1$	Lewis symbol = $\dot{\text{H}}$
$H^- = (1 + 1) = 2$ electrons	Lewis symbol = $[\ddot{\text{H}}]^-$

Q-7 Use Lewis symbols to show electron transfer between the following atoms to form cations and anions.

(*i*) K and S (*ii*) Ca and O (*iii*) Al and N

Metals lose electrons to complete their octet while non-metals gain electrons to complete octet. So, write the Lewis symbol *i.e.*, symbols with valence electrons to show the transfer of electron from metal to non-metal.

Sol. (*i*)
$$2\underset{2,8,8,1}{\text{K}^{\bullet}} + \underset{2,8,6}{\colon\!\underset{\cdot\cdot}{\ddot{\text{S}}}\colon} \longrightarrow 2\text{K}^+\left[\colon\underset{\cdot\cdot}{\ddot{\text{S}}}\colon\right]^{2-};K_2S$$

(*ii*)
$$\underset{2,8,8,2}{\text{Ca}\colon} + \underset{2,6}{\underset{\cdot\cdot}{\ddot{\text{O}}}\colon} \longrightarrow \text{Ca}^{2+}\left[\colon\underset{\cdot\cdot}{\ddot{\text{O}}}\colon\right]^{2-};\text{CaO}$$

Q-8 Arrange the bonds in order of increasing ionic character in the molecules; LiF, K_2O, N_2, SO_2 and ClF_3.

Sol. Ionic character ∝ lattice energy

$$\propto \frac{1}{\text{size of ion}} \propto \text{charge on ion,}$$

A non-polar molecule like N_2 has almost negligible ionic character.

∴ The order of ionic character is

$$N_2 < SO_2 < ClF_3 < K_2O < LiF$$

Q-9 Define electronegativity. How does it differ from electron gain enthalpy?

Sol. Electronegativity of an element is the tendency of its atom to attract the shared pair of electrons towards itself in a covalent bond. Electron gain enthalpy of an element may be defined as the energy released when a neutral isolated gaseous atom accepts an extra electron to form the gaseous negative ion, *i.e.*, anion.

$$\underset{\text{Neutral gaseous atom}}{X(g)} + e^- \longrightarrow \underset{\text{Anion}}{X^-(g)}\ ;\ \Delta H = \Delta_{eg} H$$

Greater the amount of energy released in the above process, higher is the electron gain enthalpy of the element.

Electronegativity differs from electron gain enthalpy because electronegativity is a property of an atom in the bonded state while electron gain enthalpy relates to atoms in their isolated gaseous states. [For details see chapter 3]

Q-10 Write the significance/applications of dipole moment.

Sol. *The applications of dipole moment are*

(*i*) The dipole moment helps to predict whether a molecule is polar or non-polar. As $\mu = q \times d$, greater is the magnitude of dipole moment, higher will be the polarity of the bond. For non-polar molecules, the dipole moment is zero.

(*ii*) The percentage of ionic character can be calculated as

$$\text{Percentage of ionic character} = \frac{\mu_{\text{observed}}}{\mu_{\text{ionic}}} \times 100$$

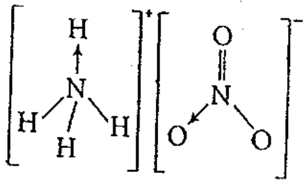
(*iii*) Symmetrical molecules have zero dipole moment although they have two or more polar bonds. (In determination of symmetry).

(*iv*) It helps to distinguish between *cis*-and *trans*-isomers. Usually *cis*-isomer has higher dipole moment than *trans*-isomer.

(*v*) It helps to distinguish between *ortho*, *meta* and *para*-isomers. Dipole moment of *para*-isomer is zero. Dipole moment of *ortho*-isomer is greater than that of *meta*-isomer.

Q-11 Indicate the type of bonds present in NH_4NO_3 and state the mode of hybridisation of two N-atoms in it.

Sol.



NH_4^+ ion contains covalent and dative bonds. (It is formed by donation of lone pair of electrons on N in NH_3 to H^+ ion). NO_3^- ion also contains covalent and dative bonds. Bond between NH_4^+ and NO_3^- ions is ionic.

N of NH_4^+ ion is sp^3 hybridised and is tetrahedral.

N of NO_3^- ion is sp^2 hybridised and is planar.

Q-12 Apart from tetrahedral geometry, another possible geometry for CH_4 is square planar with the four H-atoms at the corners of the square and the C atom at its centre. Explain, why CH_4 is not square planar?

Sol. Electronic configuration of carbon

In ground state ${}_6C$—$1s^2, 2s^2, 2p_x^1, 2p_y^1$

In excited state $1s^2, 2s^1, 2p_x^1, 2p_y^1, 2p_z^1$

sp^3-hybridised

In CH_4 molecule, carbon is sp^3 hybridised, so it is tetrahedral in shape. For square planar, dsp^2 hybridisation is required which is not possible in carbon due to the absence of *d*-orbitals. Furthermore according to VSEPR theory, the four bonded electron pairs around carbon atom arranged themselves in a regular tetrahedral geometry.

For tetahedral structure, the bond angle is 109°,28′ while is square planar structure, the bond angle is 90°. Therefore in tetrahedral structure repulsions between bonded electron pairs is less than that of the square planar.

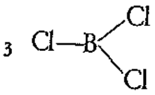
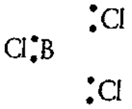
Q-13 Discuss the shape of the following molecules using VSEPR model

$BeCl_2$, BCl_3, $SiCl_4$, AsF_5, H_2S, PH_3

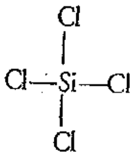
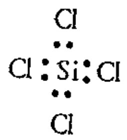
Sol. According to VSEPR theory, the shape of a molecule depends upon the number of valence shell electron pairs (bonded or non-bonded) around the central atom. Pairs of electrons in the valence shell repel each other. The order of their repulsions is as follows

$$lp - lp > lp - bp > bp - bp$$

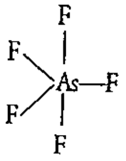
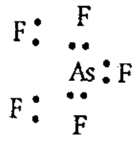
(*i*) $BeCl_2$ Cl$\mathbf{:}$Be$\mathbf{:}$Cl, The central atom Be has only 2 valence electrons which are bonded to Cl, so there are only 2 bond pairs and no lone pairs. It is of the type AB_2 and hence, the shape is linear.

(*ii*) BCl_3  or 

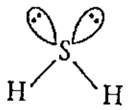
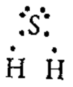
The central atom B has only 3 valence electrons which are bonded with three Cl atoms, so it contains only 3 bond pairs and no lone pair. It is of the type AB_3 and hence, the shape is trigonal planar.

(*iii*) $SiCl_4$  or 

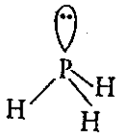
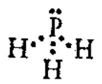
Similarly, the central atom Si has only 4 bond pairs and no lone pair. It is of the type AB_4 and hence, the shape is tetrahedral.

(*iv*) AsF_5  or 

The central atom As has only 5 bond pairs and no lone pair. It is of the type AB_5 and hence, the shape is trigonal bipyramidal.

(*v*) H_2S  or 

The central atom S has 6 valence electrons. Out of these only two are used in bond formation with two H-atoms while four (two pairs) remains as non-bonding electrons (*i.e.,* lone pairs). So, it contains 2 bond pairs and 2 lone pairs. It is of the type AB_2E_2 and hence, the shape is bent or V-shaped.

(*vi*) PH_3  or 

The central atom P has 5 valence electrons. Out of which three are utilised in bonding with H atoms and one pair remains as lone pair. So, it contains 3 bond pairs and one lone pair. It is of the type AB_3E and hence the shape is pyramidal.

Q-14 It is possible to isolate compounds containing the O_2^+ cation, the O_2^- (superoxide) anion, or the O_2^{2-} (peroxide) anion. By considering their molecular orbital energy level diagrams, place these ions in order of increasing O—O bond length.

To predict the relative values of the bond lengths, first calculate the bond orders for the different ions. Use the molecular orbital configuration to calculate bond order.

Solution O_2^+ $(8+8-1=15)=$

$$\sigma 1s^2, \overset{*}{\sigma}1s^2, \sigma 2s^2, \overset{*}{\sigma}2s^2, \sigma 2p_z^2, \pi 2p_x^2 \approx \pi 2p_y^2, \overset{*}{\pi}2p_x^1$$

$$\therefore \quad \text{Bond order} = \frac{N_b - N_a}{2} = \frac{10-5}{2} = 2.5$$

O_2^- $(8+8+1=17)=$

$$\sigma 1s^2, \overset{*}{\sigma}1s^2, \sigma 2s^2, \overset{*}{\sigma}2s^2, \sigma 2p_z^2, \pi 2p_x^2$$

$$\approx \pi 2p_y^2, \overset{*}{\pi}_x 2p_x^2 \approx \overset{*}{\pi}2p_y^1$$

$$BO = \frac{10-7}{2} = 1.5$$

O_2^{2-} $(8+8+2=18) = \sigma 1s^2, \overset{*}{\sigma}1s^2, \sigma 2s^2,$
$\overset{*}{\sigma}2s^2, \sigma 2p_z^2, \pi 2p_x^2 \approx \pi 2p_y^2\, \overset{*}{\pi}2p_x^2 \approx \overset{*}{\pi}2p_y^2$

$$BO = \frac{10-8}{2} = 1$$

$$\therefore \quad \text{Bond length} \propto \frac{1}{\text{Bond order (BO)}}$$

$\therefore$ The order of increasing bond length is $O_2^+ < O_2^- < O_2^{2-}$.

Q-15 Write the significance of a plus and a minus sign shown in representing the orbitals.

Sol. Orbitals are represented by wave functions. A plus sign in an orbital represents a positive wave function and a minus sign represents a negative wave function. Combination of two wave function having similar sign gave bonding molecular orbitals while that having opposite sign gave antibonding molecular orbitals.

Q-16 . Use molecular orbital theory to explain why the Be_2 molecule does not exist?

Sol. Electronic configuration of Be_2 molecule $(4+4=8), \sigma 1s^2, \overset{*}{\sigma}1s^2, \sigma 2s^2, \overset{*}{\sigma}2s^2$

$$\text{Bond order} = \frac{1}{2}[N_b - N_a] = \frac{1}{2}(4-4) = 0$$

Since bond order is zero, so Be_2 does not exist.

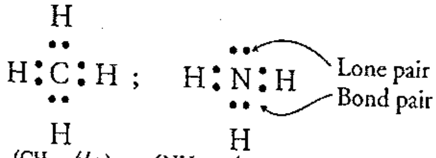
Q-17 Account for the following.

The experimentally determined N—F bond length in NF_3 is greater than the sum of the single covalent radii of N and F.

Sol. This is because both N and F are small and hence, have high electron density. So, they repel the bond pairs thereby making the N—F bond length larger.

Q-18 What do you understand by bond pairs and lone pairs of electrons? Illustrate by giving one example of each type.

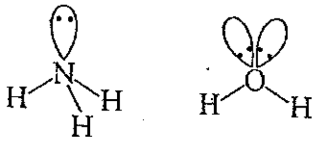
Sol. Covalent bond is formed by mutual sharing of electrons. The shared pair of electrons present between the bonded atoms are called bond pairs of electrons and unshared pair (non-bonding) electrons are called the lone pairs of electrons. *e.g.*, ammonia, NH_3 contains 3 bond pairs and 1 lone pair of electrons, whereas CH_4 contains only 4 bond pairs.



(CH_4–4*bp*) (NH_3–1*lp* and 3*bp*)

Q Although geometries of NH_3 and H_2O molecules are distorted tetrahedral, bond angle in water is less than that of ammonia. Discuss.

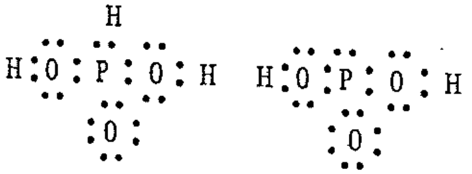
Sol.



NH_3 $bp = 3$ $lp = 1$ H_2O $bp = 2$ $lp = 2$

In H_2O molecule, there is lone pair-lone pair repulsion due the presence of two lone pairs of electrons while in NH_3 molecule there found only lone pair-bond pair repulsion. According to VSEPR theory, the former one is more stronger and hence, the bond angle in water is less than that of ammonia (NH_3).

Q-20 H_3PO_3 can be represented by structures 1 and 2 shown below. Can these two structures be taken as the canonical forms of the resonance hybrid representing H_3PO_3? If not give reasons for the same.



(1) (2)

Resonating structures or canonical forms differ only in the arrangement of electrons, but not in the positions of atoms.

Sol. No, these two structures cannot be taken as the canonical forms of the resonance hybrid because positions of the atoms have been changed.

Q-21 Describe the change in hybridisation (if any) of the Al atom in the following reaction.

$$AlCl_3 + Cl^- \longrightarrow AlCl_4^-$$

Sol. Electronic configuration of Al

In ground state ${}_{13}Al = 1s^2, 2s^2, 2p^6, 3s^2, 3p_x^1$

In excited state $= 1s^2, 2s^2, 2p^6, 3s^1, 3p_x^1, 3p_y^1$

In the formation of $AlCl_3$, Al undergoes sp^2 hybridisation and it is trigonal planar in shape. While in the formation of $AlCl_4^-$, Al undergoes sp^3 hybridisation.

It means empty $3p_z$ orbital also involved in hybridisation. Thus, the shape of $AlCl_4^-$ ion is tetrahedral.

Q-22. Is there any change in the hybridisation of B and N atoms as a result of the reaction?

$$BF_3 + NH_3 \longrightarrow F_3B \cdot NH_3$$

Find the number of lone pairs and bond pairs on the central atom to find hybridisation.

Sol. In BF_3, there are 3 bond pairs 0 lone pair, so boron is sp^2 hybridised and in NH_3, there are 3 bond pairs and 1 lone pair, so nitrogen is sp^3 hybridised. After the reaction hybridisation of boron changes to sp^3 but hybridisation of nitrogen remains the same because N shares its lone pair with electron deficient B.

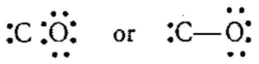
Q-23 *Write the Lewis dot structure of CO molecule.*

Solution

Step 1 The valence shell configurations of carbon and oxygen atoms are $2s^2\,2p^2$ and $2s^2\,2p^4$, respectively, Therefore, the valence electrons available are $4 + 6 = 10$.

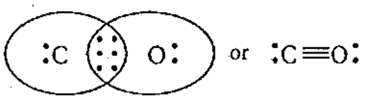
Step 2 The skeletal structure of CO can be written as C O.

Step 3 Join C and O by a single bond (one shared electron pair) and complete the octet on O, the remaining two electrons are the lone pair of C.



(The molecule contains only 2 atoms, so step 4 is not required whereas we can consider C as the central atom because of its less electronegativity).

Step 4 Still the octet on carbon is incomplete so we have to resort to multiple bonding (in this case a triple bond) between C and O atoms which satisfies the octet rule condition for both the atoms.



SARASWATI CHEMISTRY

Classification of Elements and Periodicity in Properties

Q-1 What is the basic theme of organisation in the periodic table?

Sol. The basic theme of organisation in the periodic table is to simplify and systematise the study of physical and chemical properties of all the elements and their innumerable compounds.

Q-2 Which properties of the elements depend on the electronic configuration of the atoms and which do not?

Sol. Chemical and many physical properties of the elements depend on the electronic configuration of the atoms, whereas the nuclear properties do not.

Q-3 Write the number designation of a group that has 2 electrons beyond a noble gas configuration. Write the number designation of a group with 12 electrons beyond a noble gas configuration.

Sol. The number designation of a group that has 2 electrons beyond a noble gas configuration will be 2 which means it will belong to group 2 of the periodic table. The number designation of a group with 12 electrons beyond a noble gas configuration will be 12, which means it will belong to the 12 group of the periodic table.

Q-4 Which element do you think would have been named by

(*i*) Lawrence Berkeley laboratory

(*ii*) Seaborg's group

Sol. (*i*) Lawrencium ($Z = 103$) and Berkelium ($Z = 97$)

(*ii*) Seaborgium ($Z = 106$)

Q-5 Would you expect the first ionisation enthalpies for two isotopes of the same element to be the same or different? Justify your answer.

Sol. First ionisation enthalpies of two isotopes of the same element are expected to be same because ionisation enthalpy depends upon the electronic configuration and effective nuclear charge. Isotopes of an element have same electronic configuration and thus, the same nuclear charge.

Q-6 Why do elements in the same group have similar physical and chemical properties?

Sol. Same group elements have similar valence shell electronic configuration therefore, have similar physical and chemical properties.

Q-7 In terms of electronic configuration, what the elements of a given period and a group have in common?

Sol. For elements in a period the number of shells is equal and for elements in a group the number of electrons in the outermost shell (valence shell) is the same.

Q-8 Write the atomic number of the element present in the third period and seventeenth group of the periodic table.

Sol. General configuration for 17th group elements is $ns^2\ np^5$. In the third period, the principal quantum number for valence shell is three, so the electronic configuration of valence shell for the given element is $3s^2, 3p^5$. Third period starts from atomic number, $Z = 11$ and end at $Z = 18$. Hence, the atomic number of the given element is $10 + 7 = 17$.

Q-9 How would you react to the statement that the electronegativity of N on Pauling scale is 3.0 in all the nitrogen compounds?

Sol. The statement that electronegativity of N on Pauling scale is 3.0 in all the nitrogen compounds is wrong because electronegativity of any given element is not constant. It varies depending on the element to which it is bound.

It increases as the oxidation state of the element increases or percentage of *s*-character of hybrid orbital increases.

Q-10 What is the basic difference between the terms electron gain enthalpy and electronegativity?

Sol. Electron gain enthalpy is the tendency of an isolated gaseous atom to accept an extra electron to form a gaseous anion while electronegativity is the tendency of an atom of an element to attract the shared pair of electrons towards itself in a covalent bond. Unlike electron gain enthalpy, electronegativity is not a measurable quantity.

Q-11 Predict the periods and blocks to which each of the following elements belong?

(*i*) $_{13}\text{Al}$ (*ii*) $_{24}\text{Cr}$ (*iii*) $_{29}\text{Cu}$ (*iv*) $_{11}\text{Na}$

Write electronic configuration and then predict period and block.

Sol. (*i*) $_{13}\text{Al} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^1$

[Third period and *p*-block]

(*ii*) $_{24}\text{Cr} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1, 3d^5$

[Fourth period and *d*-block]

(*iii*) $_{29}\text{Cu} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1, 3d^{10}$

[Fourth period and *d*-block]

(*iv*) $_{11}\text{Na} = 1s^2, 2s^2, 2p^6, 3s^1$

[Third period and *s*-block]

Q-12 An element *X* belongs to the third period of the *p*-block elements. It has 4 electrons in the outermost shell. Name the element.

Sol. The outer configuration of the element is $3s^2\ 3p^2$. Thus, the complete configuration is $1s^2, 2s^2\ 2p^6, 3s^2\ 3p^2$. So the atomic number is $2 + 8 + 4 = 14$. Hence, the element is silicon.

Q-13 In terms of period and group where would you locate the element with $Z = 114$?

First write electronic configuration of the given element. Highest value of *n* shows the period of element and group number = 10 + number of electrons in *ns* and *np* shells.

Sol. $_{114}Z = {}_{86}[\text{Rn}]\ 7s^2, 5f^{14}, 6d^{10}, 7p^2$

In the periodic table, the element with $Z = 114$ is located in *p*-block (as last electron enters in *p*-subshell).

Period-7th (as $n = 7$ for valence shell)

Group-14th (for *p*-block elements, group number $= 10 +$ number of electrons in valence shell).

Q-14 (*i*) How do the electronic configurations of the elements with $Z = 107-109$ differ from one another?

(*ii*) Rn ($Z = 86$) is the last noble gas discovered. Predict what will be the atomic number of the next noble gas to be discovered. Write its symbol.

Sol. (*i*) Element with $Z = 107$ has five, $Z = 108$ has six while $Z = 109$ has seven $6d$-electrons. Thus, these elements differ in the number of electrons in the $6d$-subshell.

(*ii*) 118, Uuo

Q-15 On the basis of quantum numbers, justify that sixth period of the periodic table should have 32 elements.

Sol. In the modern periodic table, each period starts with the filling of a new principal energy level. Sixth period begins with filling of principal quantum number, $n = 6$.

According to aufbau principle, in the ground state of the atoms, the orbitals are filled in order of their increasing energies. Therefore, in sixth period, electrons enter in $6s, 4f, 5d$ and $6p$ subshells. Total 16 orbitals $(2 + 7 + 5 + 3$ respectively) are present in these subshells.

According to Pauli's exclusion principle, each orbital can accomodate maximum two electrons, therefore 16 orbitals can have 32 electrons and hence, 6th period have 32 elements.

Q-16. How many elements can be accommodated in the present set up of the long form of the periodic table? Explain.

Sol. In the present set up of the long form of the periodic table, we have seven periods (*i.e.*, principal quantum number, $n = 7$) and four blocks (*s*, *p*, *d* and *f*-block elements).

Therefore, the maximum number of elements which can be accommodated in the present set up of the long form of the periodic table in accordance with aufbau principle is

$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10},$

$5p^6, 6s^2, 4f^{14}, 5d^{10}, 6p^6, 7s^2, 5f^{14}, 6d^{10}, 7p^6 = 118.$

Q-17 What is the basic difference in approach between the Mendeleev's periodic law and the modern periodic law?

Sol. Mendeleev's periodic law It states that the properties of the elements are a periodic function of their atomic weights.

Modern periodic law It states that the properties of the elements are a periodic function of their atomic numbers. thus, change in the base of classification of elements from atomic weight to atomic number is the basic difference between Mendeleev's periodic law and the modern periodic law.

Q-18. Which important property did Mendeleev use to classify the elements in his periodic table and did he stick to that?

Sol. Mendeleev used atomic weight as the basis of classification of elements in the periodic table. He arranged 63 elements known at that time in the periodic table on the basis of the order of their increasing atomic weight. At some places he ignored the increasing order of atomic weights to place the elements having similar properties together.

Q-19 Consider the following species

$$N^{3-}, O^{2-}, F^-, Na^+, Mg^{2+} \text{ and } Al^{3+}$$

(*i*) What is common in them?

(*ii*) Arrange them in the order of increasing ionic radii.

Sol. (*i*) All the given species have same number of electrons ($10e^-$). Therefore, all are isoelectronic.

(*ii*) The ionic radii of isoelectronic species decreases with increase in atomic number (as magnitude of the nuclear charge increases with increase in atomic number).

Therefore, their ionic radii increase in the order

$$\begin{array}{llllll} Al^{3+} & < Mg^{2+} & < Na^+ & < F^- & < O^{2-} & < N^{3-} \\ Z=13 & 12 & 11 & 9 & 8 & 7 \end{array}$$

Q-20 The first ionisation enthalpy values (in kJ mol^{-1}) of group 13 elements are

B	Al	Ga	In	Tl
801	577	579	558	589

How would you explain this deviation from the general trend?

Sol. In general, on moving down the group (13th group) from B to Al, the ionisation enthalpy decreases with increase in atomic size and screening effect as expected. But IE_1 of Ga is slightly higher (only 2 kJ mol^{-1}) than IE_1 of Al. It is due to imperfect shielding of the valence electrons by 3*d*-electrons. As a result of this, effective nuclear charge in Ga is slightly more than that of Al. That's why $(IE_1)\,\Delta_i H_1$ of Ga is slightly more than that of Al.

On moving from In to Tl, $\Delta_i H_1$ of Tl is larger than that of In. It is due to the fact that effective nuclear charge outweighs the shielding effect of all the electrons present in 4*f* and 5*d*-electrons.

Q-21 What do you understand by isoelectronic species? Name a species that will be isoelectronic with each of the following atoms or ions.

(*i*) F^- (*ii*) Ar

(*iii*) Mg^{2+} (*iv*) Rb^+

Sol. Isoelectronic species have the same number of electrons but different nuclear charges. In case of isoelectronic species as the nuclear charge increases, their size decreases.

(*i*) F^- has 10 electrons (9 + 1).

(*ii*) Ar has 18 electrons.

(*iii*) Mg^{2+} has 10 electrons (12–2) and

(*iv*) Rb^+ has 36 electrons (37–1).

N^{3-}, O^{2-}, Ne, Na^+ and Al^{3+} are some species which are isoelectronic with F^- and Mg^{2+}.

$P^{3-}, S^{2-}, Cl^-, K^+$ and Ca^{2+} are some species which are isoelectronic to Ar.

Similarly, Br^-, Kr and Sr^{2+} are isoelectronic with Rb^+.

Q-22 Among the second period elements the actual ionisation enthalpies are in the order

$$Li < B < Be < C < O < N < F < Ne$$

Explain why

(*i*) Be has higher $\Delta_i H$ than B?

(*ii*) O has lower $\Delta_i H$ than N and F?

Sol. (*i*) Be has higher $\Delta_i H$ (ionisation enthalpy) than boron. In both the cases, the electron to be removed belongs to the same principal shell. In ${}_4Be = (1s^2, 2s^2)$, it is 2*s*-electron while in boron ${}_5B = (1s^2, 2s^2, 2p^1)$ it is 2*p*-electron.

The penetration of a 2*s*-electron to the nucleus is more than that of a 2*p*-electron. It means 2*s*-electrons are more strongly attracted by the nucleus than 2*p*-electrons.

Therefore, higher amount of energy is required to remove a 2*s*-electron than a 2*p*-electron. Hence, Be has higher $\Delta_i H$ than B.

(*ii*) O has lower $\Delta_i H$ than N and F.

$${}_7N = 1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^1$$

$${}_8O = 1s^2, 2s^2, 2p_x^2, 2p_y^1, 2p_z^1$$

$${}_9F = 1s^2, 2s^2, 2p_x^2, 2p_y^2, 2p_z^1$$

Across a period ionisation enthalpy increases as we move from left to right due to decrease in atomic size.

But $\Delta_i H$ of nitrogen is greater than oxygen. It is becasue of the more stable electronic configuration (exactly half-filled orbitals are more stable) of nitrogen, so it is difficult to remove an electron from nitrogen than from oxygen. That's why oxygen has lower ionisation enthalpy than nitrogen and fluorine.

Q-23 Give the name and atomic number of the inert gas atom in which the total number of d-electrons is equal to the difference in numbers of total p and s electrons.

Sol. The first inert gas which contains d electrons is krypton. Its atomic number is 36 and its electronic configuration is $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^6$

Total number of d-electrons $= 10$

Total number of p-electrons $= 6 + 6 + 6 = 18$

Total number of s-electrons $= 2 + 2 + 2 + 2 = 8$

$\therefore$ Difference in total number of p and s electrons

$$= 18 - 8 = 10$$

Thus, the inert gas is krypton.

Q-24 Can an element with atomic number 126, if discovered, be accommodated in the present set up of the long form of periodic table?

Sol. No, the maximum number of elements which can be accommodated in the present set up of the long form of the periodic table is 118. Thereafter, filling of $8s$-orbital shall begin which will accommodate only two electrons. After $8s$-orbitals, the filling of $5g$-orbitals will begin. Since we do not have any provision for g-block elements in the present set up of the long form of periodic table, therefore, an element with atomic number 126, if discovered, cannot be accommodated in the present set up of the long form of periodic table.

25 How would you explain the fact that the first ionisation enthalpy of sodium is lower than that of magnesium but its second ionisation enthalpy is higher than that of magnesium?

ol. First ionisation enthalpy of sodium ($Na = 1s^2, 2s^2, 2p^6, 3s^1$) is lower than that of magnesium ($Mg = 1s^2, 2s^2\ 2p^6, 3s^2$) because the electron to be removed in both the cases is from $3s$-orbital but the nuclear charge is lower in the Na than that of magnesium $\left(\text{IE} \propto \dfrac{1}{\text{atomic size}}\right)$.

After the removal of first electron Na^+ acquires inert gas (Ne) configuration ($Na^+ = 1s^2, 2s^2, 2p^6$) and hence, removal of second electron from sodium is difficult. While in case of magnesium, after the removal of first electron, the electronic configuration of Mg^+ is $1s^2, 2s^2, 2p^6, 3s^1$.

In this case, $3s^1$ electron is easy to remove in comparison to remove an electron from inert gas configuration. Therefore, IE_2 of Na is higher than that of Mg.

Q-26 Use the periodic table to answer the following questions.

(*i*) Identify an element with five electrons in the outer subshell.

(*ii*) Identify an element that would tend to lose two electrons.

(*iii*) Identify an element that would tend to gain two electrons.

(*iv*) Identify the group having metal, non-metal, liquid as well as gas at the room temperature.

Sol. (*i*) General electronic configuration of elements having five electrons in the outer sub shell is $ns^2\ np^5$. This configuration belongs to halogen family, *i.e.*, F, Cl, Br, I, At.

(*ii*) Elements of second group are known as alkaline earth metals (Mg, Cs, Sr, Ba, etc). Their general electronic configuration for valence shell is ns^2. These elements form dipositive cations by the lose of two electrons easily.

(*iii*) 16th group elements such as O, S, Se, etc., have a tendency to accept two electrons because by the gain of two electrons they attain noble gas configuration. Their general electronic configuration for valence shell is ns^2np^4.

(*iv*) Group 1 or 17 of the periodic table contains metal, non-metal, liquid as well as gas at the room temperature, *e.g.*, H_2 is a non-metal and in gaseous state at room temperature. All other elements of this group are metals. Cs is a liquid metal. Similarly, Br_2 is a liquid non-metal while other elements of this group are gaseous non-metals. Iodine can form I^+ so it has some what metallic properties.

Q-27 Energy of an electron in the ground state of the hydroge atom is -2.18×10^{-18} J. Calculate the ionisation enthalpy atomic hydrogen in terms of J mol^{-1}.

Sol. Ionisation energy is the amount of energy required to remove th electron from the ground state (E_1) to infinity (E_∞).

$$E_1 = -2.18 \times 10^{-18}\ \text{J};\ E_\infty = 0;$$

$$\Delta E = E_\infty - E_1$$

$$= 0 - (-2.18 \times 10^{-18}\ \text{J})$$

$$= 2.18 \times 10^{-18}\ \text{J}$$

Ionisation enthalpy per hydrogen atom $= 2.18 \times 10^{-18}$ J

$\therefore$ Ionisation enthalpy per mole of hydrogen atoms

$$= 2.18 \times 10^{-18} \times 6.022 \times 10^{23}$$

$$= 13.12 \times 10^5\ \text{J mol}^{-1}$$

Q-28. Assign the position of the element having outer electronic configuration.

(*i*) $ns^2\, np^4$ for $n = 3$

(*ii*) $(n-1)\, d^2\, ns^2$ for $n = 4$ and

(*iii*) $(n-2)\, f^7\, (n-1)\, d^1\, ns^2$ for $n = 6$, in the periodic table.

Sol. (*i*) $ns^2\, np^4$ for $n=3$

$n=3$ means element belongs to third period. Since, last electron enters in the *p*-orbital, it belongs to *p*-block. For *p*-block elements, the group number $=10+$ valence shell electrons $=10+(2+4)=16$. Hence, the element belongs to 16th group.

(*ii*) $(n-1)\, d^2\, ns^2$ for $n=4$

$n=4$ means the element belongs to fourth period. Since, last electron enters in *d*-orbital, the given element belongs to *d*-block. For *d*-block elements, group number = number of *d*-electrons + number of *ns* electrons $= 2+2=4$

Hence, the element belongs to 4th group.

(*iii*) $(n-2)\, f^7\, (n-1)\, d^1\, ns^2$ for $n=6$

$n=6$ means, the element belongs to sixth period. Since, last electron enters in *f*-orbital, the given element belongs to *f*-block and all *f*-block elements are the members of third group. Hence, the element belongs to third group.

Q-29 Which of the following pairs of elements would have a more negative electron gain enthalpy?

(*i*) O or F (*ii*) F or Cl

Sol. (*i*) Oxygen and fluorine both belong to second period. Electron gain enthalpy generally becomes more negative across a period as we move from left to right. On moving from oxygen to fluorine, the effective nuclear charge increases and atomic size decreases with increase in atomic number. Due to this, forces of attraction of the nucleus increases for the incoming electron. That's why electron gain enthalpy becomes more negative for fluorine than that of oxygen. Furthermore fluorine attain stable gas configuration by picking up an electron.

$$\underset{2,7}{\mathrm{F}(g)} + e^- \longrightarrow \underset{2,8}{\mathrm{F}^-(g)}$$

Therefore, electron gain enthalpy of fluorine is much more negative (-328 kJ mol^{-1}) than that of oxygen (-141 kJ mol^{-1}).

(*ii*) Within a group, electron gain enthalpy becomes less negative down a group. But electron gain enthalpy of chlorine is more negative (-349 kJ mol^{-1}) than that of the fluorine (-328 kJ mol^{-1}). This is due to small size of fluorine as the electron-electron repulsions in relatively compact $2p$-orbital is greater than that in the larger $3p$-orbital and hence, the incoming electron feels greater repulsion in fluorine than in the chlorine. That's why chlorine have more negative electron gain enthalpy than that of fluorine.

Q-30. The first ionisation enthalpy ($\Delta_i H$) values of the third period elements, Na, Mg and Si are respectively 496, 737 and 786 kJ mol^{-1}. Predict whether the first $\Delta_i H$ value for Al will be more close to 575 or 760 kJ mol^{-1}? Justify your answer.

Solution We know that the first ionisation enthalpy generally increases from left to right along a period but the ionisation enthalpy of elements of group 2 (*i.e.*, Mg) is higher than that of the corresponding element of group 13 (*i.e.*, Al) due to the more penetrating power and less shielding of *ns*-electron. Thus, the correct order of ionisation enthalpy is

$$\mathrm{Na} < \mathrm{Al} < \mathrm{Mg} < \mathrm{Si}$$

We know $496 < ? < 737 < 786$

∴ The ionisation enthalpy of Al must be lower than that of the Mg, so its value will be close to 575. (Which is less than 737)

Q-31. Using the periodic table, predict the formulae of compounds which might be formed by the following pairs of elements; (*i*) silicon and bromine (*ii*) aluminium and sulphur.

Solution (*i*) Silicon (Si) being a member of group 14 have four valence electrons, *i.e.*, its valency is 4. Bromine is a member of halogen family and hence, its valence is 1. When these combine, the formula of the compound formed would be $\overset{4}{\text{Si}} \times \overset{1}{\text{Br}}$ or $SiBr_4$.

(*ii*) Aluminium being a member of group 13 contains three valence electrons so its valency is 3. Sulphur, on the other hands, belongs to group 16 and has 6 valence electrons, so its valency is $8-6=2$. When these combine, the formula of the compound formed would be = $\overset{3}{\text{Al}} \times \overset{2}{\text{S}}$ or Al_2S_3.

Q-32. The first $(\Delta_i H_1)$ and the second $(\Delta_i H_2)$ ionisation enthalpies (in kJ mol^{-1}) and the $(\Delta_{eg}H)$ electron gain enthalpy (in kJ mol^{-1}) of a few elements are given below

Elements	ΔH_1	ΔH_2	$\Delta_{eg}H$
I	520	7300	−60
II	419	3051	−48
III	1681	3374	−328
IV	1008	1846	−295
V	2372	5251	+48
VI	738	1451	−40

Which of the above elements is likely to be

(*i*) the least reactive element?

(*ii*) the most reactive metal?

(*iii*) the most reactive non-metal?

(*iv*) the least reactive non-metal?

(*v*) the metal which can form a stable binary halide of the formula $MX_2 (X = \text{halogen})$?

(*vi*) the metal which can form a predominantly stable covalent halide of the formula MX $(X = \text{halogen})$?

Sol. (*i*) The least reactive element is element (V) because it has highest $\Delta_i H_1$ (first ionisation enthalpy) and positive electron gain enthalpy $(\Delta_{eg}H)$. The element (V) is an inert gas because inert gases have positive electron gain enthalpy. The given values for element (V) match with He.

(*ii*) The most reactive metal is element (II) because it has the least $\Delta_i H_1$ (first ionisation enthalpy) and low negative electron gain enthalpy $(\Delta_{eg}H)$. The given values for element II match with K.

(*iii*) The most reactive non-metal is element (III) because it has high $\Delta_i H_1$ (first ionisation enthalpy) and a very high negative electron gain enthalpy $(\Delta_{eg}H)$. The given values for element III match with F.

(*iv*) The least reactive non-metal is element (IV). The element (IV) has not so high $\Delta_i H_1$ but it has high negative electron gain enthalpy $(\Delta_{eg}H)$. The given values for element (IV) match with (I).

(*v*) The metal which can form a stable binary halide of the formula MX_2 is element (VI). Element (VI) is alkaline earth metal because it has low $\Delta_i H_1$ but higher than that of alkali metals. Moreover, the difference between $\Delta_i H_1$ and $\Delta_i H_2$ is very less. The given values for element (VI) match with Mg.

(*vi*) Element (I) has low $\Delta_i H_1$ but a very high $\Delta_i H_2$. It has less negative electron gain enthalpy. So, element (I) is alkali metal. The given values for element (I) match with Li. Lithium forms predominantly stable covalent halide of the formula MX.

Q-33. Predict the formulae of the stable binary compounds that would be formed by the combination of the following pairs of elements.

(*i*) Lithium and oxygen

(*ii*) Magnesium and nitrogen

(*iii*) Aluminium and iodine

(*iv*) Silicon and oxygen

(*v*) Phosphorus and fluorine

(*vi*) Element 71 and fluorine

Sol.

	Element	Group number	Electrons in valence shell	Valency	Formulae of binary compound
(i)	Lithium	Group 1	1	1	Li_2O
	Oxygen	Group 16	6	$8 - 6 = 2$	
(ii)	Magnesium	Group 2	2	2	Mg_3N_2
	Nitrogen	Group 15	5	$8 - 5 = 3$	
(iii)	Aluminium	Group 13	3	3	AlI_3
	Iodine	Group 17	7	$8 - 7 = 1$	
(iv)	Silicon	Group 14	4	4	SiO_2
	Oxygen	Group 16	6	$8 - 6 = 2$	
(v)	Phosphorus	Group 15	5	3 or 5	PF_3 or PF_5
	Fluorine	Group 17	7	$8 - 7 = 1$	
(vi)	Element 71, (Lutetium)	Group 3	3	3	LuF_3
	Fluorine	Group 17	7	$8 - 7 = 1$	

Q-34 Which of the following will have the most negative electron gain enthalpy and which the least negative? (P, S, Cl, F) Explain your answer.

Solution As, we know the negative value of electron gain enthalpy increases along a period and decreases on moving down the group but the elements of second period like F have lesser electron gain enthalpy than the corresponding element of third period. This is because of the smaller size and hence greater repulsion in case of F as compared to Cl. Thus, the order of electron gain enthalpy is P < S < F < Cl. *i.e.*, the electron gain enthalpy is most negative for chlorine and less negative for phosphorus.

Q-35 Which of the following species will have the largest and the smallest size? Mg, Mg^{2+}, Al, Al^{3+}.

Solution Mg and Al belongs to same period (*i.e.*, third period) and along a period atomic radii decreases. Thus, the order of size of Mg and Al is

$$Al < Mg$$

Further, the size of a cation is always smaller than its parent atom and in case of isoelectronic species, size decreases as the nuclear charge increases.

Thus, the size of $Mg^{2+} > Al^{3+}$

$\therefore$ The correct order of size is $Al^{3+} < Al < Mg^{2+} < Mg$.

Thus, Mg is the largest atom and Al^{3+} is the smallest ion.

SARASWATI CHEMISTRY

Structure of Atom

Structure of Atom !!

Q-1 The magnitude of charge on the electron is 4.8×10^{-10} esu. What is the charge on the nucleus of a helium atom?

Sol. Helium nucleus contains 2 protons and charge of a proton is same as that of an electron. Therefore, the charge on the nucleus of a helium atom is $(+2) \times 4.8 \times 10^{-10} = +9.6 \times 10^{-10}$ esu.

Q-2 What is the difference between atomic mass and mass number?

Sol. Mass number is a whole number because it is the sum of number of protons and number of neutrons whereas atomic mass is fractional because it is the average relative mass of its atom as compared with mass of an atom of C–12 isotope taken as 12.

Q-3 Neutrons can be found in all atomic nuclei except in one case. Which is this atomic nucleus and what does it consist of ?

Sol. In case of hydrogen atom, there is no neutron. It consists of only one proton.

Q-4 In Millikan's experiment, static electric charge on the oil drops has been obtained by shining X-rays. If the static electric charge on the oil drop is -1.282×10^{-18} C, calculate the number of electrons present on it.

Sol. Number of electrons, $n = \dfrac{\text{total charge in oil drop}}{\text{charge on 1 electron}} = \dfrac{-1.282 \times 10^{-18}\,\text{C}}{-1.6022 \times 10^{-19}\,\text{C}} = 0.800 \times 10 = 8.0$ electrons

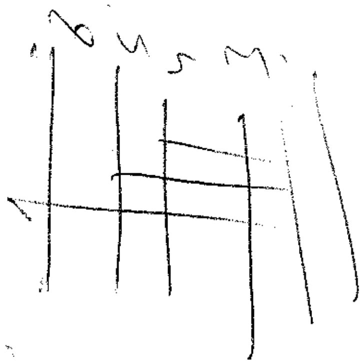
∴ Mass of 1 mole of electrons

$$= 9.11 \times 10^{-31} \times 6.022 \times 10^{23}$$
$$= 54.86 \times 10^{-8}$$
$$= 5.486 \times 10^{-7}\ \text{kg}$$

Charge on 1 electron $= 1.602 \times 10^{-19}$C

∴ Charge on 1 mole of electrons

$$= 1.602 \times 10^{-19} \times 6.022 \times 10^{23}$$
$$= 9.647 \times 10^{4}\,\text{C}$$



Q-5 Arrange the following type of radiations in increasing order of frequency.

(*i*) Radiation from microwave oven
(*ii*) Amber light from traffic signal
(*iii*) Radiation from FM radio
(*iv*) Cosmic rays from outer space and
(*v*) X-rays

Sol. The order of frequency is radiation from FM radio < microwaves < amber colour < X-rays < cosmic rays.

Q-6 What is the maximum number of emission lines when the excited electron of a H-atom in $n = 6$ drops to the ground state?

Sol. Number of lines produced when electron from n th shell drops to ground state $= \dfrac{n(n-1)}{2}$

When $n = 6$, number of lines produced

$$= \frac{6(6-1)}{2} = \frac{6 \times 5}{2} = 15$$

Q-7 Explain why the uncertainty principle is significant only for the motion of subatomic particles but is negligible for the macroscopic objects?

Sol. The energy of photon is sufficient to disturb a subatomic particle so that there is uncertainty in the measurement of position and momentum of the subatomic particle. However, the energy is insufficient to disturb a macroscopic object.

Q-8 Calculate the wavelength of an electron moving with velocity of 2.05×10^7 ms^{-1}.

Sol. We know that mass of an electron,

$$m = 9.11 \times 10^{-31} \text{ kg},$$

$$\text{Applying, } \lambda = \frac{h}{mv} = 3.5 \times 10^{-11} \text{ m}$$

Q-9 Dual behaviour of matter proposed by de-Broglie led to the discovery of electron microscope often used for the highly magnified images of biological molecules and other type of materials. If the velocity of the electron in this microscope is 1.6×10^6 ms^{-1}, calculate de-Broglie wavelength associated with this electron.

Sol. Using de-Broglie wavelength, $\lambda = \frac{h}{mv}$ we get

$$\lambda = 455 \text{ pm}$$

Q-10 Similar to electron diffraction, neutron diffraction microscope is also used for the determination of the structure of molecules. If the wavelength used here is 800 pm, calculate the characteristic velocity associated with the neutron (mass of neutron = 1.675×10^{-27} kg).

Sol. Wavelength, $\lambda = \frac{h}{mv}$

or
$$v = \frac{6.626 \times 10^{-34} \text{ kg m}^2\text{s}^{-1}}{1.675 \times 10^{-27} \text{ kg} \times 800 \times 10^{-12} \text{ m}}$$

$$= 0.494 \times 10^3 \text{ ms}^{-1} = 4.94 \times 10^2 \text{ ms}^{-1}$$

Q-11 Nitrogen laser produces a radiation at a wavelength of 337.1 nm. If the number of photons emitted is 5.6×10^{24}, calculate the power of this laser.

If n photons are emitted by a laser, the total energy of the photons emitted is equal to the power of the laser.

Sol. Energy of 1 photon, $E = \frac{hc}{\lambda}$

$$= \frac{6.626 \times 10^{-34} \text{ Js} \times 3.0 \times 10^8 \text{ ms}^{-1}}{337.1 \times 10^{-9} \text{ m}} \quad (1 \text{ nm} = 10^{-9} \text{ m})$$

$$= 0.05896 \times 10^{-17} \text{ J}$$

Energy of 5.6×10^{24} photons

$$= 0.05896 \times 10^{-17} \times 5.6 \times 10^{24} \text{ J}$$

$$= 0.3302 \times 10^7 \text{ J} = 3.302 \times 10^6 \text{ J}$$

Q-12 The velocity associated with a proton moving in a potential difference of 1000 V is 4.37×10^5 ms^{-1}. If the hockey ball of mass 0.1 kg is moving with this velocity, calculate the wavelength associated with this velocity.

Sol. Wavelength associated with the velocity of hockey ball

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34} \text{ kg m}^2\text{s}^{-1}}{0.1 \text{ kg} \times 4.37 \times 10^5 \text{ m s}^{-1}}$$

$$= 15.16 \times 10^{-39} \text{ m} = 1.516 \times 10^{-38} \text{ m}$$

Q-13 Calculate the wavelength, frequency and wave number of a light wave whose period is 2.0×10^{-10} s.

Sol. Frequency, $\nu = \frac{1}{\text{time period}} = \frac{1}{2.0 \times 10^{-10} \text{s}} = 5 \times 10^9 \text{s}^{-1}$

$$\text{Wavelength, } \lambda = \frac{c}{\nu} = \frac{3.0 \times 10^8 \text{ ms}^{-1}}{5 \times 10^9 \text{ s}^{-1}}$$

$$= 0.6 \times 10^{-1} \text{ m}$$

$$= 6.0 \times 10^{-2} \text{ m}$$

$$\text{Wave number, } \bar{\nu} = \frac{1}{\lambda} = \frac{1}{6.0 \times 10^{-2} \text{ m}}$$

$$= 16.66 \text{ m}^{-1}$$

Q-14 Calculate the wavelength of the spectral line obtained in the spectrum of Li^{2+} ion when the transition takes place between two levels whose sum is 4 and the difference is 2.

Sol. Suppose the transition takes place between levels n_1 and n_2.

Then, $n_1 + n_2 = 4$ and $n_2 - n_1 = 2$

Solving these equations, we get $n_1 = 1, n_2 = 3$

$$\therefore \quad \frac{1}{\lambda} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)Z^2$$

For Li^{2+}, $Z = 3$

$$\therefore \quad \frac{1}{\lambda} = 109677 \text{ cm}^{-1}\left(\frac{1}{1^2} - \frac{1}{3^2}\right) \times 3^2$$

$$= 109677 \times \left(\frac{1}{1} - \frac{1}{9}\right) \times 9 \text{ cm}^{-1}$$

$$= 109677 \times 8 \text{ cm}^{-1}$$

$$\text{or} \quad \lambda = \frac{1}{109677 \times 8 \text{ cm}^{-1}} = 1.14 \times 10^{-6} \text{ cm}$$

Q-15 Emission transitions in the Paschen series end at orbit $n = 3$ and start from orbit n and can be represented as $\nu = 3.29 \times 10^{15}\ (\text{Hz})\left[\frac{1}{3^2} - \frac{1}{n^2}\right]$. Calculate the value of n if the transition is observed at 1285 nm. Find the region of the spectrum.

Sol. Given, frequency, $\nu = \frac{c}{\lambda} = 3.29 \times 10^{15}\ \text{Hz}\left(\frac{1}{3^2} - \frac{1}{n^2}\right)$

$$\nu = \frac{3.0 \times 10^8 \text{ ms}^{-1}}{1285 \times 10^{-9} \text{ m}} = 3.29 \times 10^{15}\ \text{Hz}\left(\frac{1}{9} - \frac{1}{n^2}\right)$$

$$\frac{3.0 \times 10^8 \text{ ms}^{-1}}{1285 \times 10^{-9} \text{ m} \times 3.29 \times 10^{15} \text{ Hz}} = \left(\frac{1}{9} - \frac{1}{n^2}\right)$$

$$\frac{1}{n^2} = 0.1111 - 0.0709$$

$$\Rightarrow \quad n^2 = 25 \quad \text{or } n = 5$$

$\therefore$ The electrons jump from $n = 5$ to $n = 3$ *i.e.*, the transitions occurs in Paschen series and lies in infrared region.

Moreover, the radiation 1285 nm lies in the infrared region.

Q-16 The electron energy in hydrogen atom is given by $E_n = (-2.18 \times 10^{-18})/n^2 \text{J}$. Calculate the energy required to remove an electron completely from the $n = 2$ orbit. What is the longest wavelength of light in cm that can be used to cause this transition?

Sol. Energy required to shift an electron from $n = 2$ to $n = \infty$.

$$\Delta E = E_\infty - E_2 = 0 - \left(-\frac{2.18 \times 10^{-18} \text{ J atom}^{-1}}{2^2}\right)$$

$$= 5.45 \times 10^{-19} \text{ J atom}^{-1}$$

Wavelength, $\lambda = \frac{hc}{\Delta E} = 3.647 \times 10^{-5}$ cm

Q-17 How much energy is required to ionise a H-atom if the electron occupies $n = 5$ orbit? Compare your answer with the ionisation enthalpy of H-atom (energy required to remove the electron from $n = 1$ orbit).

Sol. Energy change, $\Delta E = E_f - E_i$

$$\Delta E = 2.18 \times 10^{18} \text{ J}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

When $n_i = 5$ and $n_f = \infty$,

$$\Delta E = 2.18 \times 10^{-18} \text{J}\left(\frac{1}{5^2} - \frac{1}{\infty}\right) = 0.0872 \times 10^{-18} \text{ J}$$

When $n_i = 1$ and $n_f = \infty$,

$$\Delta E' = 2.18 \times 10^{-18} \text{J}\left(\frac{1}{1^2} - \frac{1}{\infty}\right)$$

$$\Delta E' = 2.18 \times 10^{-18} \text{ J}.$$

$$\frac{\Delta E'}{\Delta E} = \frac{2.18 \times 10^{-18}}{0.0872 \times 10^{-18}} = 25$$

Hence, energy required to remove an electron from first orbit is 25 times than that required to remove an electron from fifth orbit.

Q-18 What is the energy in joules, required to shift the electron of the hydrogen atom from the first Bohr orbit to the fifth Bohr orbit and what is the wavelength of the light emitted when the electron returns to the ground state? The ground state electron energy is -2.18×10^{-11}erg.

Sol. $\Delta E = E_5 - E_1 = 2.18 \times 10^{-11}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$ erg

$(n_i = 1 \text{ and } n_f = 5)$

$$\Delta E = 2.18 \times 10^{-11}\left(\frac{1}{1^2} - \frac{1}{5^2}\right) \text{erg}$$

$$\Delta E = 2.18 \times 10^{-11} \times \frac{24}{25} = 2.0928 \times 10^{-11} \text{ erg}$$

$$= 2.0928 \times 10^{-18} \text{ J} \qquad (1 \text{ erg} = 10^{-7} \text{ J})$$

When electron returns to ground state, it emits energy equals to ΔE hence,

$$\Delta E = \frac{hc}{\lambda}$$

$$\text{or} \quad \lambda = \frac{hc}{\Delta E} = \frac{6.626 \times 10^{-34} \text{ Js} \times 3.0 \times 10^8 \text{ ms}^{-1}}{2.0928 \times 10^{-18} \text{ J}}$$

$$= 9.498 \times 10^{-8} \text{ m} = 949.8 \times 10^{-10} \text{ m} = 949.8 \text{ Å}$$

Q-19 The angular momentum of an electron in Bohr's orbit of H-atom is 3.02×10^{-34} kgm^{2}s^{-1}. Calculate the wavelength of the spectral line emitted when the electron jumps from this level to the next lower level.

Sol. Angular momentum (mvr)

$$= n\frac{h}{2\pi} = 3.02\times 10^{-34}\ \text{kgm}^2\text{s}^{-1}$$

$$n = 3.02\times 10^{-34}\times\frac{2\pi}{h} = \frac{3.02\times 10^{-34}\times 2\times 3.14}{6.3\times 10^{-34}} = 3$$

When the electron jumps from $n=3$ to $n=2$, the wavelength of spectral line,

$$\frac{1}{\lambda} = 109677\left(\frac{1}{n_2^2}-\frac{1}{n_1^2}\right) = 109677\left(\frac{1}{2^2}-\frac{1}{3^2}\right)$$

$$\frac{1}{\lambda} = 109677\times\frac{5}{36} = 15232.9\ \text{cm}^{-1}$$

$$\lambda = \frac{1}{15232.9\ \text{cm}^{-1}} = 6.56\times 10^{-5}\ \text{cm}^{-1}$$

Q-20 In H-atom, the energy of electron in the nth orbit is given as $E_n = -\frac{13.6}{n^2}$ eV.

Show that $E_{(n+1)} - E_n = \frac{13.6\times 2}{n^3}$ eV for large values of n.

Sol. $E_{(n+1)} - E_n = -\frac{13.6}{(n+1)^2} - \left(-\frac{13.6}{n^2}\right)$

$$= 13.6\left[\frac{1}{n^2}-\frac{1}{(n+1)^2}\right] = 13.6\times\frac{(n+1)^2-n^2}{n^2(n+1)^2}$$

$$= \frac{13.6\times(2n+1)}{n^2(n+1)^2} = \frac{13.6\times 2n}{n^2(n+1)^2}+\frac{13.6}{n^2(n+1)^2}$$

$$= \frac{13.6\times 2}{n(n+1)^2}+\frac{13.6}{n^2(n+1)^2}$$

As n is large, $n+1 \simeq n$.

Hence, $E_{(n+1)} - E_n = \frac{13.6\times 2}{n\times n^2}+\frac{13.6}{n^2\times n^2} = \frac{13.6\times 2}{n^3}$

(Neglecting second term because n^4 is very large.)

Q-21 Using s, p, d notations, describe the orbital with the following quantum numbers.

(i) $n=1, l=0$ (ii) $n=3, l=1$

(iii) $n=4, l=2$ (iv) $n=4, l=3$.

n represents the main shell and 0, 1, 2, 3, ... values of l represent the s, p, d, f ... orbitals respectively.

Sol.

	n	l	Subshell notation
(i)	1	0	$1s$
(ii)	3	1	$3p$
(iii)	4	2	$4d$
(iv)	4	3	$4f$

Q-22 An atom of an element contains 29 electrons and 35 neutrons. Deduce

(i) the number of protons

(ii) the electronic configuration of the element.

Sol. (i) For a neutral atom,

Number of electrons = number of protons

29 electrons = 29 protons.

(ii) $_{29}Z = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$

(The element is copper.)

Q-23 The unpaired electrons in Al and Si are present in $3p$-orbital. Which electrons will experience more effective nuclear charge from the nucleus?

Sol. $_{13}\text{Al} = 1s^2, 2s^2, 2p^6, 3s^2\ 3p^1$

$_{14}\text{Si} = 1s^2, 2s^2, 2p^6, 3s^2\ 3p^2$

Si (+ 4) has greater nuclear charge than aluminium (+ 3). Hence, $3p$ unpaired electrons of Si experience greater effective nuclear charge than Al.

Q-24 The quantum numbers of six electrons are given below. Arrange them in order of increasing energies. If any of these combination(s) has/have the same energy lists :

(i) $n=4, l=2, m_l=-2, m_s=-\frac{1}{2}$ 6

(ii) $n=3, l=2, m_l=1, m_s=+\frac{1}{2}$ 5

(iii) $n=4, l=1, m_l=0, m_s=+\frac{1}{2}$ 5

(iv) $n=3, l=2, m_l=-2, m_s=-\frac{1}{2}$ 5

(v) $n=3, l=1, m_l=-1, m_s=+\frac{1}{2}$ 4

(vi) $n=4, l=1, m_l=0, m_s=+\frac{1}{2}$ 5

Quantum number	Subshell notation	$n+l$
(i) $n=4, l=2, m_l=-2, m_s=-\frac{1}{2}$	$4d$	$4+2=6$
(ii) $n=3, l=2, m_l=1, m_s=+\frac{1}{2}$	$3d$	$3+2=5$
(iii) $n=4, l=1, m_l=0, m_s=+\frac{1}{2}$	$4p$	$4+1=5$
(iv) $n=3, l=2, m_l=-2, m_s=-\frac{1}{2}$	$3d$	$3+2=5$
(v) $n=3, l=1, m_l=-1, m_s=+\frac{1}{2}$	$3p$	$3+1=4$
(vi) $n=4, l=1, m_l=0, m_s=+\frac{1}{2}$	$4p$	$4+1=5$

Q-25 Which of the following sets of orbitals are degenerate and why?

(*i*) 1*s*, 2*s* and 3*s* in Mg atom.

(*ii*) $2p_x$, $2p_y$ and $2p_z$ in C atom.

(*iii*) 3*s*, $3p_x$ and 3*d* orbitals in H atom.

Sol. (*i*) 1*s*, 2*s* and 3*s* orbitals in Mg atom are not degenerate because these have different values of *n*.

(*ii*) $2p_x$, $2p_y$ and $2p_z$ orbitals in C atom are degenerate because these belong to same subshell.

(*iii*) 3*s*, $3p_x$ and 3*d* orbitals in H atom are degenerate because for H atom, the subshells having same value of *n* have same energies.

Q-26 Explain, giving reasons which of the following sets of quantum numbers are not possible?

(*i*) $n=0, l=0, m_l=0, m_s=+1/2$

(*ii*) $n=1, l=0, m_l=0, m_s=-\frac{1}{2}$

(*iii*) $n=1, l=1, m_l=0, m_s=+\frac{1}{2}$

(*iv*) $n=2, l=1, m_l=0, m_s=-\frac{1}{2}$

(*v*) $n=3, l=3, m_l=-3, m_s=+\frac{1}{2}$

(*vi*) $n=3, l=1, m_l=0, m_s=+\frac{1}{2}$

- *n* always be a positive integer.
- $n \neq l$

Sol. (*i*) is not possible as $n \neq 0$

(*ii*) is possible (1*s*)

(*iii*) is not possible because if $n=1$, $l=0$ only ($l \neq 1$)

(*iv*) is possible (2*p*)

(*v*) is not possible because if $n=3$, $l=0$, 1 and 2 ($l \neq 3$)

(*vi*) is possible (3*p*)

Q-27 If the diameter of a carbon atom is 0.15 nm, calculate the number of carbon atoms which can be placed side by side in a straight line across length of scale of length 20 cm long.

Sol. Diameter of a carbon atom = 0.15 nm = 0.15×10^{-9} m

Length along which atoms are to be placed = 20 cm = 0.2 m

Number of carbon atom which can be placed in the given length

$$=\frac{0.2\text{m}}{0.15\times10^{-9}\text{m}}=\frac{0.2\times10^{9}}{0.15\text{ m}}$$

$$=1.33\times10^{9}\text{ atoms}$$

5. 2×10^{8} atoms of carbon are arranged side by side. Calculate the radius of carbon atom if the length of this arrangement is 2.4 cm.

Sol Total length = 2.4 cm

Number of carbon atoms along the length = 2×10^{8}

∴ Diameter of 1 carbon atom

$$=\frac{2.4\text{ cm}}{2\times10^{8}}=1.2\times10^{-8}$$

$$\text{Radius of 1 carbon atom}=\frac{d}{2}=\frac{1.2\times10^{-8}\text{ cm}}{2\times10^{8}}$$

$$=0.060\text{ cm}$$

Q-28 The diameter of zinc atom is 2.6 Å. Calculate (*i*) radius of zinc atom in pm and (*ii*) number of atoms present in a length of 1.6 cm if the zinc atoms are arranged side by side lengthwise.

Sol. (*i*) Diameter of Zn atom = 2.6 Å = 2.6×10^{-10} m

$$\text{Radius of Zn atom}=\frac{2.6\times10^{-10}\text{ m}}{2}=130\text{ pm}$$

(*ii*) Given, length = 1.6 cm = 1.6×10^{-2} m

Number of Zn atoms in 1.6×10^{-2} m

$$=\frac{1.6\times10^{-2}\text{ m}}{2.6\times10^{-10}\text{ m}}=6.154\times10^{7}\text{ atoms}$$

Q-29 In Rutherford's experiment, generally the thin foil of heavy atoms, like gold, platinum, etc., have been used to be bombarded by the α-particles. If the thin foil of light atoms like aluminium, etc., is used, what difference would be observed from the above results?

Sol. Heavy atoms such as gold, platinum have heavy nucleus. Heavy nucleus contains large amount of positive charge. When a beam of a α-particles is shot at a thin gold foil, most of them pass through without much effect.

Some however, are deflected back or by small angles due to enormous repulsive force of heavy nucleus. If light aluminium foil is used, the number of α-particles deflected back or those deflected by small angles will be negligible.

Q-30 Symbols $^{79}_{35}Br$ and ^{79}Br can be written, whereas symbols $^{35}_{79}Br$ and ^{35}Br are not acceptable. Answer briefly.

Sol. The composition of any atom can be represented by using the normal element symbol (X) with superscript on the left hand side as the mass number (A) and subscript (Z) on the left hand side as the atomic number, *i.e.*, $^{A}_{Z}X$. Hence, the symbols $^{35}_{79}Br$ and ^{35}Br are not acceptable.

NOTE Atomic number is always written as subscript and mass number as superscript. However, both of these can be written on left or right side of the symbol.

Q-31 Calculate the approximate charge in coulomb and approximate mass in kilogram of the nucleus of lithium-7 isotope.

Sol. Nucleus of Li atom has 3 protons and 4 neutrons. Charge on one proton = 1.60×10^{-19} Coulombs.

$\therefore$ Charge on 3 protons (*i.e.*, charge on nucleus)

$$= 3 \times 1.60 \times 10^{-19} C$$
$$= 4.80 \times 10^{-19}\ C$$

Mass of proton $\approx$ mass of neutron $\approx 1.67 \times 10^{-27}$ kg

$\therefore$ Mass of nucleus $= 7 \times 1.67 \times 10^{-27}$ kg

$$= 11.69 \times 10^{-27}\ kg$$

Q-32 An element with mass number 81 contains 31.7% more neutrons as compared to protons. Assign the atomic symbol.

Sol. We know that mass number of the element,

$$A = p + n = 81 \qquad ...(i)$$

Let the number of protons, $p = x$

Then, number of neutrons,

$$n = x + \frac{31.7}{100}x = 1.317x$$

(As number of neutrons are 31.7% more than the protons.)

Hence, from Eq. (i)

$$x + 1.317x = 81$$

or $$2.317x = 81$$

or $$x = \frac{81}{2.317} = 34.958 \approx 35$$

Therefore, number of protons = 35 and the symbol is $^{81}_{35}Br$.

(Number of protons = Atomic number)

Q-33 Write the complete symbol for the atom with the given atomic number (Z) and atomic mass (A).

(*i*) $Z = 17, A = 35$ (*ii*) $Z = 92, A = 233$

(*iii*) $Z = 4, A = 9$

See the symbols of atoms having atomic number 17, 92 and 4 respectively in the periodic table as the atomic number is a fundamental property of an element, *i.e.*, certain for each element.

Sol. (*i*) $^{35}_{17}Cl$ (*ii*) $^{233}_{92}U$ (*iii*) $^{9}_{4}Be$

Q-34 Give the number of electrons in the species H_2^+, H_2 and O_2^+.

- Count the total number of electrons by adding electrons present in each atom of a molecule.
- Then remove or add electrons according to charge (positive or negative) to count the electrons in an ion.

Sol.

$$H_2 = {}_1H + {}_1H = 1 + 1 = 2e^-$$
$$H_2^+ = 2 - 1 = 1e^-$$
$$O_2 = {}_8O + {}_8O = 8 + 8 = 16e^-$$
$$O_2^+ = 16 - 1 = 15e^-$$

Q-35 An ion with mass number 56 contains 3 units of positive charge and 30.4% more neutrons than the electrons. Assign the symbol to this ion.

Sol. Let the number of electrons in an ion $= x$

$\therefore$ Number of neutrons $= x + \frac{30.4}{100}x = 1.304x$

(Number of neutrons are 30.4% more than the number of electrons).

In the netural atom, number of electrons $= x + 3$

(The ion carries + 3 charge)

So, number of protons $= x + 3$

we know that, mass number $= n + p$

$$= 1.304x + x + 3 = 56$$

Q-36 Which of the following are isoelectronic species, *i.e.*, those having the same number of electrons? $Na^+, K^+, Mg^{2+}, Ca^{2+}, S^{2-}$, Ar

Sol. Isoelectronic species have the same number of electrons but different atomic numbers.(Number of positive charge shows the number of electrons lost and number of negative charges shows number of electrons gained by an atom. Calculation of number of electrons have been shown below.

$${}_{11}Na^+ = 11 - 1 = 10e^-, \quad {}_{19}K^+ = 19 - 1 = 18e^-,$$
$${}_{12}Mg^{2+} = 12 - 2 = 10e^-, \quad {}_{20}Ca^{2+} = 20 - 2 = 18e^-,$$
$${}_{16}S^{2-} = 16 + 2 = 18e^-, \quad {}_{18}Ar = 18e^-$$

Hence, isoelectronic species are

(*i*) Na^+ and Mg^{2+} (*ii*) K^+, Ca^{2+}, S^{2-} and Ar

Q-37 Prove that density of the nucleus is constant.

Sol. Radius of the nucleus $= 1.33 \times 10^{-11} \times A^{1/3}$ m

Density of nucleus $= \frac{\text{mass}}{\text{volume}}$ A → No. of proton + neutron

$$= \frac{A \times 1.66 \times 10^{-27}\ kg}{\frac{4}{3} \times \pi \times (1.33 \times 10^{-11} \times A^{1/3})^3}$$

$$= \frac{1.66 \times 10^{-27} \times 3}{4 \times 3.14 \times (1.33 \times 10^{-11})^3}\ kg/m^3$$

= constant

1 e~

Thus, density of nucleus is constant, independent of the element under consideration.

Q-38 The ejection of the photoelectron from the silver metal in the photoelectric effect experiment can be stopped by applying the voltage of 0.35 V when the radiation of 256.7 nm is used. Calculate the work function for silver metal.

Sol. Energy of incident radiation, $h\nu = h\nu_0 + \text{KE}$ K. Energy

1 electron volt
u that energy
which is req. to move
1 electron in pot diff of 1 volt
and num 1.6×10⁻¹⁹ J
= 1 electron volt

$$E = h\nu = \frac{hc}{\lambda} = \frac{6.626\times10^{-34}\ \text{Js}\times3.0\times10^{8}\ \text{ms}^{-1}}{256.7\times10^{-9}\ \text{m}}$$

$$= 7.74\times10^{-19}\ \text{J} = \frac{7.74\times10^{-19}\ \text{eV}}{1.602\times10^{-19}}$$

$$= 4.83\ \text{eV}$$

Applied potential gives kinetic energy to the electron, *i.e.*,

$$\text{eV}_0 = \frac{1}{2}mv_{\text{max}}^2 = \text{KE}$$

$$= \frac{1}{2}mv_{\text{max}}^2 = 1.6\times10^{-19}\times0.35$$

$$= 0.56\times10^{19}\ \text{J} = 0.35\ \text{eV}$$

$\therefore$ KE = 0.35 eV

Work function, W_0 or

$$h\nu_0 = h\nu - \text{KE} = 4.83\ \text{eV} - 0.35\ \text{eV} = 4.48\ \text{eV}$$

Q-39 The longest wavelength doublet absorption transition is observed at 589 and 589.6 nm. Calculate the frequency of each transition and energy difference between two excited states.

Sol. (*i*) Given, wavelength

$$\lambda_1 = 589\ \text{nm} = 589\times10^{-9}\ \text{m}$$

$$\lambda_2 = 589.6\ \text{nm} = 589.6\times10^{-9}\ \text{m}$$

Frequency of wavelength 589 nm

$$\nu_1 = \frac{c}{\lambda_1} = \frac{3.0\times10^{8}\ \text{ms}^{-1}}{589\times10^{-9}\ \text{m}}$$

$$= 5.093\times10^{14}\ \text{s}^{-1}$$

Frequency of wavelength 589.6 nm

$$\nu_2 = \frac{c}{\lambda_2} = \frac{3.0\times10^{8}\ \text{ms}^{-1}}{589.6\times10^{-9}\ \text{m}}$$

$$= 5.088\times10^{14}\ \text{s}^{-1}$$

(*ii*) Energy difference between two excited states,

$$\Delta E = h\nu_1 - h\nu_2 = h(\nu_1 - \nu_2)$$

$$\Delta E = 6.626\times10^{-34}\ \text{Js}\ (5.093\times10^{14}\ \text{s}^{-1} - 5.088\times10^{14}\ \text{s}^{-1})$$

$$\Delta E = 6.626\times10^{-34}\ \text{Js}\times0.005\times10^{14}\ \text{s}^{-1}$$

$$\Delta E = 3.31\times10^{-22}\ \text{J}$$

3. Neon gas is generally used in sign boards. If it emits strongly at 616 nm, calculate

(*i*) the frequency of emission.

(*ii*) distance travelled by this radiation is 30 s.

(*iii*) energy of quantum.

(*iv*) number of quanta present if it produces 2 J of energy.

Sol. (*i*) Frequency, $\nu = \frac{c}{\lambda}$

$$\nu = \frac{3.0\times10^{8}\ \text{ms}^{-1}}{616\times10^{-9}\ \text{m}} = 4.870\times10^{14}\ \text{s}^{-1}$$

(*ii*) Distance travelled = speed × time

$$= 3.0\times10^{8}\ \text{ms}^{-1}\times30\ \text{s}$$

$$= 9.0\times10^{9}\ \text{m}$$

(*iii*) Energy of quantum (or photon),

$$E = h\nu = 6.626\times10^{-34}\ \text{J s}\times4.870\times10^{14}\ \text{s}^{-1}$$

$$= 32.268\times10^{-20}\ \text{J}$$

(*iv*) Number of quanta present

$$= \frac{\text{total energy produced}}{\text{energy of 1 quanta}}$$

$$= \frac{2\ \text{J}}{32.27\times10^{-20}\ \text{J}} \approx 6.2\times10^{18}\ \text{quanta}$$

Q-40. If the photon of the wavelength 150 pm strikes an atom and one of its inner bound electrons is ejected out with a velocity of $1.5\times10^{7}\ \text{m s}^{-1}$, calculate the energy with which it is bound to the nucleus.

- The energy ($h\nu_0$) with which an electron is bound to the nucleus is calculated by using the formula $h\nu = h\nu_0 + \text{KE}$, so first find $h\nu$ of incident radiation and KE of electron by using the formula $\text{KE} = \frac{1}{2}mv^2$.
- Then substitute the values of $h\nu$ and KE to find $h\nu_0$ (*i.e.*, energy with which electron is bound to the nucleus).

Sol. Energy of incident radiation $h\nu = h\nu_0 + \frac{1}{2}mv^2$

$$E = h\nu = \frac{hc}{\lambda} = \frac{6.626\times10^{-34}\ \text{Js}\times3.0\times10^{8}\ \text{ms}^{-1}}{150\times10^{-12}\ \text{m}}$$

$$(1\ \text{pm} = 10^{-12}\ \text{m})$$

$$E = 13.25\times10^{-16}\ \text{J}$$

$$\text{KE of ejected electron} = \frac{1}{2}mv^2$$

$$= \frac{1}{2}\times9.11\times10^{-31}\ \text{kg}\times(1.5\times10^{7}\ \text{ms}^{-1})^2$$

$KE = 1.025 \times 10^{-16}$ J

$$W_0 = h\nu_0 = h\nu - \frac{1}{2}mv^2$$

$$= 13.25 \times 10^{-16}\text{ J} - 1.025 \times 10^{-16}\text{ J}$$

$$= 12.225 \times 10^{-16}\text{ J}$$

$$= \frac{12.225 \times 10^{-16}}{1.602 \times 10^{-19}}\text{ eV}$$

$$= 7.63 \times 10^3\text{ eV}$$

Q-41 The Vividh Bharati Station of All India Radio, Delhi, Broadcasts on a frequency of 1368 kHz (kilohertz). Calculate the wavelength of the electromagnetic radiation emitted by transmitter. Which part of the electromagnetic spectrum does it belong to?

Sol. Frequency, $\nu = \frac{c}{\lambda}$

$$1368 \times 10^3\text{ Hz} = \frac{3 \times 10^8\text{ ms}^{-1}}{\lambda}$$

or $$\lambda = \frac{3 \times 10^8\text{ m s}^{-1}}{1368 \times 10^3\text{ Hz}}$$

$$= 219.3\text{ m, radiowave}$$

Q-42 Yellow light emitted from a sodium lamp has a wavelengh (λ) of 580 nm. Calculate the frquency (ν) and wave number ($\bar{\nu}$) of the yellow light.

Sol. Frequency, $\nu = \frac{c}{\lambda}$

$$1\text{ nm} = 10^{-9}\text{ m}$$

$$\therefore \quad 580\text{ nm} = 580 \times 10^{-9}\text{ m}$$

$$= 580 \times 10^{-7}\text{ cm}$$

$$\nu = \frac{3.0 \times 10^8\text{ ms}^{-1}}{580 \times 10^{-9}\text{ m}} = 5.17 \times 10^{14}\text{ s}^{-1}$$

(Velocity of light = $3 \times 10^8\text{ ms}^{-1}$)

Wave number, $$\bar{\nu} = \frac{1}{\lambda} = \frac{1}{580 \times 10^{-7}\text{ cm}}$$

$$= 1.724 \times 10^4\text{ cm}^{-1}$$

Q-43 • What is the number of photons of light with a wavelength of 4000 pm that provide 1 J of energy?

- Number of photons is calculated by dividing total energy by energy of 1 photon, so first calculate the energy of 1 photon by applying, $E = \frac{hc}{\lambda}$
- Then, calculate the number of photons by using the formula

$$N = \frac{\text{total energy}}{\text{energy of one photon}}$$

Sol. Energy, $$\frac{hc}{\lambda} = \frac{6.626 \times 10^{-34}\text{ Js} \times 3.0 \times \text{ms}^{-1}}{4000 \times 10^{-12}\text{ m}}$$

$(1\text{ pm} = 10^{-12}\text{ m})$

$$= 4.9695 \times 10^{-17}\text{ J}$$

Number of photons,

$$N = \frac{1\text{ J}}{4.9695 \times 10^{-17}\text{ J}}$$

$$= 2.0122 \times 10^{16}\text{ photons}$$

Q-44. A 25 watt bulb emits monochromatic yellow light of wavelength 0.57 μm. Calculate the rate of emission of quanta per second.

Sol. 25 watt = 25 Js^{-1} (watt = Js^{-1})

Solve as Q. 5.

[Ans. number of photons = 7.169×10^{19} photons]

Q-45 • Electromagnetic radiation of wavelength 242 nm is just sufficient to ionise the sodium atom. Calculate the ionisation energy of sodium in kJ mol^{-1}.

Sol. Energy, $E = h\nu = \frac{hc}{\lambda}$

$$= \frac{6.626 \times 10^{-34}\text{ Js} \times 3.0 \times 10^8\text{ ms}^{-1}}{242 \times 10^{-9}\text{ m}}$$

$$E = 0.0821 \times 10^{-17}\text{ J/atom}$$

This energy is sufficient for ionisation of one Na atom, so it is the ionisation energy of Na.

$$E = 6.02 \times 10^{23} \times 0.0821 \times 10^{-17}\text{ J/mol}$$

$$E = 4.945 \times 10^5\text{ J/mol}$$

$$= 4.945 \times 10^2\text{ kJ/mol}$$

Q-46 The mass of an electron is 9.1×10^{-31} kg. If its KE (kinetic energy) is 3×10^{-25} J then calculate its velocity.

Sol. $KE = \frac{1}{2}mv^2$

or $$v = \left(\frac{2\text{ KE}}{m}\right)^{1/2} = \left(\frac{2 \times 3 \times 10^{-25}\text{ kg m}^2\text{s}^{-2}}{9.1 \times 10^{-31}\text{ kg}}\right)^{1/2}$$

$$= 8.12 \times 10^2\text{ ms}^{-1}$$

Q-47 The work function (W_0) of some metals is listed below. Count the number of metals which will show photoelectric effect when light of 300 nm wavelength falls on the metal.

Metal	Li	Na	K	Mg	Cu	Ag	Fe	Pt	W
W_0 (eV)	2.4	2.3	2.2	3.7	4.8	4.3	4.7	6.3	4.75

Sol. Given that wavelength is

$$\lambda = 300 \text{ nm} = 3\times10^{-7}\text{ m}$$

Therefore, energy is

$$E = h\nu = \frac{hc}{\lambda} = \frac{6.6\times10^{-34}\times3\times10^{8}}{3\times10^{-7}\times1.6\times10^{-19}} = 4.1\text{ eV}$$

For a metal to show photoelectric effect, its work function has to be less than or equal to 4.1 eV So, the number of metals having work function less than 4.1 eV is 4, *i.e.*, Li, Na, K and Mg.

Q-48 Electrons are emitted with zero velocity from a metal surface when it is exposed to radiation of wavelength 6800 Å. Calculate threshold frequency (ν_0) and work function (W_0) of the metal.

Sol. Threshold wavelength,

$$\lambda_0 = 6800\text{ Å} = 6800\times10^{-10}\text{ m}$$

Threshold frequency,

$$\nu_0 = \frac{c}{\lambda_0} = \frac{3.0\times10^{8}\text{ ms}^{-1}}{6800\times10^{-10}\text{ m}} = 4.41\times10^{14}\text{ s}^{-1}$$

Work function, $W_0 = h\nu_0$

$$= 6.626\times10^{-34}\text{ Js}\times4.41\times10^{14}\text{ s}^{-1}$$

$$= 2.922\times10^{-19}\text{ J}$$

Q-49 What transition in the hydrogen spectrum would have the same wavelength as the Balmer transition $n = 4$ to $n = 2$ of He^+ spectrum?

Sol. Wave number, $\bar{\nu} = RZ^2\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)$ and $\bar{\nu} = \frac{1}{\lambda}$

For He^+ spectrum (for Balmer transition)

$$\bar{\nu} = R\times(2)^2\left(\frac{1}{2^2}-\frac{1}{4^2}\right)$$

$$\bar{\nu} = R\times4\times\frac{3}{16} = \frac{3}{4}R \qquad \text{...(i)}$$

For H-spectrum, $\bar{\nu} = R\times1^2\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)$ ...(ii)

$$\frac{3}{4}R = R\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right) \Rightarrow \frac{3}{4} = \frac{1}{n_1^2}-\frac{1}{n_2^2}$$

Hence, $n_1 = 1$ and $n_2 = 2$. In H-spectrum, the transition from $n = 2$ to $n = 1$ have same wavelength as the Balmer transition from $n = 3$ to $n = 2$ of He^+ spectrum.

Q-50 What is the wavelength of light emitted when the electron in a hydrogen atom undergoes transition from an energy level with $n = 4$ to an energy level with $n = 2$?

Sol.

$$\frac{1}{\lambda} = 109677\left(\frac{1}{2^2}-\frac{1}{4^2}\right)\text{cm}^{-1}$$

or $\lambda = 486$ nm

The colour corresponding to this wavelength is blue.

Q-51 Lifetimes of the molecules in the excited states are often measured by using pulsed radiation source of duration nearly in the nanosecond range. If the radiation source has the duration of 2 ns and the number of photons emitted during the pulse source is 2.5×10^{15}, calculate the energy of the source.

Sol. Frequency, $\nu = \frac{1}{\text{Period}} = \frac{1}{2\text{ ns}} = \frac{1}{2\times10^{-9}\text{s}}$

$$= 0.5\times10^{9}\text{s}^{-1}$$

Energy of the source = Energy of 1 photon × number of photons produced

$$E_{source} = h\nu\times N$$

$$= 6.626\times10^{-34}\text{ Js}\times0.5\times10^{9}\text{s}^{-1}\times2.5\times10^{15}$$

$$= 8.28\times10^{-10}\text{J}$$

Q-52 The ionisation energy of H-atom (in the ground state) is x kJ. Find the energy required for an electron to jump from second to third energy level.

Sol. Energy in second energy level, $E_2 = -\frac{x}{2^2} = -\frac{x}{4}$

Energy in third energy level,

$I.E = E_\infty - E_1$

$x = 0 - \left(-\frac{kz^2}{n^2}\right)$

$x = k$

$$E_3 = -\frac{x}{3^2} = -\frac{x}{9}$$

$$E_3 - E_2 = -\frac{x}{9}+\frac{x}{4} = \frac{5x}{36}$$

Q-53 Calculate the energy required for the process

$$He^+(g) \longrightarrow He^{2+}(g) + e^-$$

The ionisation energy for the H-atom in the ground state is 2.18×10^{-18} J atom^{-1}.

Sol. Energy of electron in unielectron atomic system,

$$E_n = \frac{-2\pi^2 mZ^2e^4}{n^2h^2}$$

For H-atom, ionisation energy (IE) $= E_\infty - E_1$

$$IE = 0 - \left(-\frac{2\pi^2 me^4 1^2}{1^2h^2}\right)$$

(where, $Z = 1$ and $n = 1$ for H-atom)

$$IE = 2.18\times10^{-18}\text{ J atom}^{-1}$$

For He^+, $IE = E_\infty - E_1 = 0 - \left(\frac{-2\pi^2 me^2 2^2}{1^2(h^2)}\right)$

$$= 4 \times \frac{2\pi^2 me^4}{h^2} = 4 \times 2.18 \times 10^{-18}\ \text{J atom}^{-1}$$

$$= 8.72 \times 10^{-18}\ \text{J atom}^{-1}$$

∴ The energy required for the process

$He^+ \longrightarrow He^{2+} + e^-$ is $8.72 \times 10^{-18}\ \text{J atom}^{-1}$

Q-54 (*i*) The energy associated with the first orbit in the hydrogen atom is $-2.18 \times 10^{-18}\ \text{J atom}^{-1}$. What is the energy associated with the fifth orbit?

(*ii*) Calculate the radius of Bohr's fifth orbit for hydrogen atom.

Sol. (*i*) Energy in *n*th orbit, $E_n = \frac{-2.18 \times 10^{-18}}{n^2}$ J

Energy in fifth orbit,

$$E_5 = \frac{-2.18 \times 10^{-18}}{5^2}\ \text{J} = -8.72 \times 10^{-20}\ \text{J}$$

(*ii*) For H-atom, radius of *n* th orbit, $r_n = 0.529 \times n^2$ Å

∴ Radius of 5th Bohr orbit,

$$r_5 = 0.529 \times 5^2 = 13.225\ \text{Å} = 1.3225\ \text{nm}$$

Q-55 If the velocity of the electron in Bohr's first orbit is $2.19 \times 10^6\ \text{ms}^{-1}$, calculate the de-Broglie wavelength associated with it.

Solution We know that, mass of electron

$$= 9.11 \times 10^{-31}\ \text{kg}$$

$$h = 6.626 \times 10^{-34}\ \text{J s}$$

Wavelength, $\lambda = \frac{h}{mv}$

$$= \frac{6.626 \times 10^{-34}\ \text{kg m}^2\text{s}^{-1}}{9.11 \times 10^{-31}\ \text{kg} \times 2.19 \times 10^6 \times \text{ms}^{-1}}$$

$$\lambda = 3.32 \times 10^{-10}\ \text{m} = 332\ \text{pm}$$

Q-56 Show that the circumference of the Bohr orbit for the hydrogen atom in an integral multiple of the de-Broglie wavelength associated with the electron revolving around the orbit.

Solution According to Bohr model for H-atom, the angular momentum of an electron in a given stationary state,

$$mvr = \frac{nh}{2\pi} \quad \text{or} \quad 2\pi r = \frac{nh}{mv}$$

From de-Broglie equation wavelength, $\lambda = \frac{h}{mv}$

Hence, $2\pi r = n\lambda$

Therefore, the circumference ($2\pi r$) of the Bohr orbit for H-atom is an integral multiple of de-Broglie wavelength. (Here n = number of waves in *n*th orbit).

Q-57 A golf ball has a mass of 40 g and a speed of 45 m/s. If the speed can be measured within accuracy of 2%, calculate the uncertainty in the position.

Solution Uncertainty in velocity $\Delta v = \frac{45 \times 2}{100} = 0.9\ \text{ms}^{-1}$

From Heisenberg's principle,

$$\Delta x = \frac{h}{4\pi m \cdot \Delta v} = \frac{6.6 \times 10^{-34}\ \text{kg m}^2\text{s}^{-1}}{4 \times 3.14 \times 40 \times 10^{-3}\ \text{kg} \times 0.9}$$

$$= 1.46 \times 10^{-33}\ \text{m}$$

Q-58 If the position of the electron is measured within an accuracy of ±0.002 nm, calculate the uncertainty in the momentum of the electron. Suppose the momentum of the electron is $\frac{h}{4\pi_m \times 0.05\ \text{nm}}$, is there any problem in defining this value.

Solution $\Delta x = 0.002\ \text{nm} = 2.00 \times 10^{-12}\ \text{m}$

From Heisenberg's uncertainty principle,

$$\Delta x \times \Delta P \geq \frac{h}{4\pi}$$

$$\Delta P = \frac{h}{4\pi \Delta x} = \frac{6.626 \times 10^{-34}\ \text{kg m}^2\text{s}^{-1}}{4 \times 3.14 \times 2.00 \times 10^{-12}\ \text{m}}$$

$$\Delta P = 2.638 \times 10^{-23}\ \text{kg m s}^{-1}$$

Actual momentum $= \frac{h}{4\pi \times 0.05\ \text{nm}}$

$$= 1.055 \times 10^{-24}\ \text{kg m s}^{-1}$$

It cannot be defined as the actual value of momentum is smaller than uncertainty.

4 8 12 16

3 6 9

2 4 6 8

1 2 3 4

SARASWATI CHEMISTRY

Some Basic Concepts of Chemistry

Q-1 Suppose a length had been reported to be 31.24 cm. What is the minimum uncertainty implied in this measurement?

Sol. The minimum uncertainty implies in this measurement is ± 0.01 cm.

Q-2 If the speed of light is $3.0 \times 10^8\ \text{m s}^{-1}$, calculate the distance covered by light in 2.00 ns.

Sol. $2.00\ \text{ns} = 2.00 \times 10^{-9}\,\text{s} \qquad (1\ \text{ns} = 10^{-9}\ \text{s})$

Distance covered = speed × time

$$= 3.0 \times 10^8\ \text{m s}^{-1} \times 2.00 \times 10^{-9}\ \text{s} = 0.6\ \text{m}$$

Q-3 What is the difference between 5.0 g and 5.00 g?

Sol. Though the two values seem to be equivalent but scientifically they are different. 5.0 g has two significant figures and hence, its precision is 0.1 part in 5, *i.e.*, 20 ppt. 5.00 has three significant figures and hence, its precision is 0.01 parts in 5 , *i.e.*, 2 ppt. Hence, 5.00 g is more precise measurement than 5.0 g.

Q-4 Why is the law of Gay Lussac's not obeyed if any reactant or product is not a gas?

Sol. If any reactant or product is a liquid or solid, the volume occupied by them is extremely small as compared to the gas and hence, the law is not obeyed.

Q-5 How can you prove that red oxide of copper is not an element?

Sol. On heating red oxide of copper in the presence of hydrogen, its mass decreases and it forms shining metallic copper which is chemically different from the original compound.

$$Cu_2O + H_2 \longrightarrow 2Cu + H_2O$$

Q-6 If 2 L of N_2 is mixed with 2 L of H_2 at a constant temperature and pressure, then what will be the volume of NH_3 formed ?

Sol. $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$

1 L of N_2 reacts with 3 L of H_2.

2 L of N_2 will react with 6 L of H_2 but we have only 2 L of H_2, therefore, H_2 is the limiting reactant.

3 L of H_2 gives 2 L of NH_3.

$$\therefore \quad 2\ \text{L of } H_2 \text{ gives} = \frac{2}{3} \times 2 = \frac{4}{3} = 1.33\ \text{L of } NH_3$$

Q-7 What is the SI unit of mass? How is it defined?

Sol. SI unit of mass is kilogram (kg). It is equal to the mass of international prototype of the kilogram.

Q-8 Match the following with their multiples.

	Prefixes	Multiples
(i)	micro	10^6
(ii)	deca	10^9
(iii)	mega	10^{-6}
(iv)	giga	10^{-15}
(v)	femto	10

Sol. Micro $= 10^{-6}$, deca $= 10$, mega $= 10^6$, giga $= 10^9$ and femto $= 10^{-15}$.

Q-9 Pressure is determined as force per unit area of the surface. The SI unit of pressure, pascal is as shown below.

$$1\ \text{Pa} = 1\ \text{N m}^{-2}$$

If the mass of air at sea level is $1034\ \text{g cm}^{-2}$, calculate the pressure in pascal.

Sol. Pressure is the force or weight per unit area.

$$\text{Pressure} = \frac{1034\ \text{g} \times 9.8\ \text{ms}^{-2}}{\text{cm}^2}$$

$$= \frac{1034\ \text{kg} \times 100 \times 100 \times 9.8\ \text{m s}^{-2}}{1000\ \text{m}^2}$$

$$= 101332.0\ \text{N m}^{-2} \qquad (1\text{N} = 1\ \text{kg m s}^{-2})$$

$$= 1.01332 \times 10^5\ \text{Pa}$$

Q-10 Round up the following up to three significant figures.

(*i*) 34.216 (*ii*) 10.4107
(*iii*) 0.04597 (*iv*) 2808

To round up a number, left the last digit as such, if the digit next to it is less than 5 and increase it by 1, if the next digit is greater than 5.

Sol. (*i*) 34.2 (*ii*) 10.4 (*iii*) 0.0460 (*iv*) 2810

Q-11 If ten volume of dihydrogen gas react with five volume of dioxygen gas, how many volume of water vapour would be produced?

Sol. $2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$
$\quad 2V \quad\quad 1V \quad\quad\quad 2V$

According to Gay Lussac's law of gaseous volumes, 2 volume of dihydrogen react with 1 volume of O_2 to produce 2 volume of water vapour. Therefore, 10 volume of dihydrogen on reaction with 5 volume of dioxygen will produce 10 volume of water vapour.

Q-12 Calculate the atomic mass (average) of chlorine using the following data.

Isotope	% natural abundance	Molar mass
^{35}Cl	75.77	34.9689
^{37}Cl	24.23	36.9659

Sol. Average atomic mass is the sum of the products of fractional abundances (f_i) of the isotopes and their corresponding mass number (A_i).

Average atomic mass,

$$\overline{A} = \Sigma f_i \cdot A_i = f_1 \times A_1 + f_2 \times A_2 + \ldots\ldots$$

Average atomic mass,

$$\overline{A} = 0.7577 \times 34.9689 + 0.2423 \times 36.9659$$
$$= 26.4959 + 8.9568 = 35.4527$$

Q-13 What is the molecular mass of a substance each molecule of which contains 9 atoms of carbon, 13 atoms of hydrogen and 2.33×10^{-23} g other component?

Sol. Mass of 9 atoms of carbon $= 9 \times 12$ amu $= 108$ u

Mass of 13 atoms of hydrogen $= 13 \times 1$ amu $= 13$ u

Mass of 2.33×10^{-23} g of other component

$$= (1\text{ u}) \times \frac{(2.33 \times 10^{-23}\text{ g})}{(1.66 \times 10^{-24}\text{ g})}$$
$$= 14.04\text{ u}$$

Molecular mass of the substance

$$= (108 + 13 + 14.04)\text{ u} = 135.04\text{ u}$$

Q-14 Chlorophyll, the green colouring matter of plants contains 2.68% magnesium by weight. Calculate the number of magnesium atoms in 2.00 g of chlorophyll (Atomic mass of Mg = 24).

Sol. Mass of chlorophyll = 2.0 g

Percentage of Mg = 2.68 g

$$\text{Mass of Mg in 2.0 g of chlorophyll} = \frac{2.68 \times 2.0}{100} = 0.054\text{ g}$$

6.022×10^{23} atoms of magnesium = 24 g

$\therefore$ 24 g of Mg contains 6.022×10^{23} atoms

$$\therefore\ 0.054\text{ g of Mg contains } \frac{6.022 \times 10^{23}}{24} \times 0.054$$
$$= 1.3 \times 10^{21}\text{ atoms}$$

Q-15 Calculate the number of moles in the following masses

(*i*) 1.46 metric ton of Al (1 metric ton $= 10^3$ kg)

(*ii*) 7.9 mg of Ca

Sol. (*i*) 1.46 metric ton of Al $= 1.46 \times 10^3 \times 10^3$ g of Al

$$= 1.46 \times 10^6\text{ g}$$

Atomic mass of Al = 27

$$\text{Moles of Al} = \frac{\text{mass of Al}}{\text{atomic mass}} = \frac{1.46 \times 10^6}{27}$$
$$= 5.41 \times 10^4\text{ mol}$$

(*ii*) 7.9 mg of Ca $= 7.9 \times 10^{-3}$ g of Ca

Atomic mass of Ca = 40.1

$$\text{Moles of Ca} = \frac{\text{mass of Ca}}{\text{atomic mass}} = \frac{7.9 \times 10^{-3}}{40.1}$$
$$= 1.97 \times 10^{-4}\text{ mol}$$

Q-16 How much copper can be obtained from 100 g of copper sulphate ($CuSO_4$)?

Sol. Molar mass of $CuSO_4 = 63.54 + 32.06 + (4 \times 16)$

$$= 159.6\text{ g mol}^{-1}$$

159.6 g $CuSO_4$ contains 63.54 g Cu

$$1\text{ g } CuSO_4 \text{ will contain } \frac{63.54}{159.6}\text{ g Cu}$$

$$\therefore 100\text{ g } CuSO_4 \text{ will contain } \frac{63.54 \times 100}{159.6} = 39.81\text{ g Cu}$$

Q-17 How are 0.50 mole Na_2CO_3 and 0.50 M Na_2CO_3 different?

Sol. Molar mass of $Na_2CO_3 = (2 \times 22.99) + 12.01 + (3 \times 16)$

$$= 105.99 \approx 106\text{ g mol}^{-1}$$

0.50 mole $Na_2CO_3 = 0.50 \times 106 = 53$ g Na_2CO_3

0.50 M Na_2CO_3 means 53 g Na_2CO_3 is present in 1 L of the solution.

Q-18 In three moles of ethane (C_2H_6), calculate the following.

(*i*) Number of moles of carbons atoms.

(*ii*) Number of moles of hydrogen atoms.

(*iii*) Number of molecules of ethane.

Sol. (*i*) 1 mole of C_2H_6 contains 2 moles of carbon atoms.

$\therefore$ Number of moles of carbon atoms in 3 moles of

$$C_2H_6 = 2 \times 3 = 6.$$

(*ii*) 1 mole of C_2H_6 contains 6 moles of hydrogen atoms.

$\therefore$ Number of moles of hydrogen atoms in 3 moles of

$$C_2H_6 = 3 \times 6 = 18.$$

(*iii*) 1 mole of C_2H_6 contains 6.022×10^{23} molecules of ethane.

$\therefore$ Number of ethane molecules in 3 moles of

$$C_2H_6 = 3 \times 6.023 \times 10^{23}$$

$$= 1.8069 \times 10^{24}$$

Q-19 The average molar mass of a mixture of methane (CH_4) and ethane (C_2H_4) present in the ratio of $a : b$ is found to be 20.0 g mol^{-1}. If the ratio were reversed, what would be the molar mass of the mixture?

Sol. Molar mass of $CH_4 = 16 \text{ g mol}^{-1}$

Molar mass of $C_2H_4 = 28 \text{ g mol}^{-1}$

When they are present in the $a : b$, their average molar

$$\text{mass} = \frac{a \times 16 + b \times 28}{a + b} = 20 \text{ g mol}^{-1} \quad \text{(Given)}$$

i.e., $16a + 28b = 20(a + b)$

or $4a + 7b = 5(a + b)$

or $a = 2b$

or $\frac{a}{b} = \frac{2}{1} = 2:1$

If the ratio is reversed, now the ratio

$$a : b = 1 : 2$$

$$\therefore \text{ Average molar mass} = \frac{1 \times 16 + 2 \times 28}{1 + 2}$$

$$= 24 \text{ g mol}^{-1}$$

Q-20 If the density of methanol is 0.793 kg L^{-1}, what is its volume needed for making 2.5 L of its 0.25 M solution?

Sol. Given, $d = 0.793 \text{ kg L}^{-1} = 0.793 \times 10^3 \text{ g L}^{-1}$

Final volume, $V_2 = 2.5$ L

Final molarity, $M_2 = 0.25$ M

Molarity of initial solution $M_1 = ?$

Initial volume $V_1 = ?$

Molar mass of methanol,

$$CH_3OH = (1 \times 12.01) + (4 \times 1.0079) + 16.00$$

$$= 32.0416 \approx 32 \text{ g mol}^{-1}$$

$$\text{Molarity} = \frac{0.793 \times 10^3 \text{ g L}^{-1}}{32 \text{ g mol}^{-1}} = 24.781 \text{ mol L}^{-1}$$

$$M_1V_1 = M_2V_2$$

$$24.781 \times V_1 = 0.25 \times 2.5$$

$$V_1 = \frac{0.25 \times 2.5}{24.781} = 0.02522 \text{ L}$$

$$= 25.22 \text{ mL}$$

Q-21 Calculate the concentration of nitric acid in mol per litre in a sample which has a density 1.41gmL^{-1} and the mass per cent of nitric acid in it being 69%.

- We know that molarity $= \frac{w \times 1000}{m \times V}$ so in order to calculate molarity,we require mass and molar mass of solute and volume of the solution. To calculate mass convert mass per cent into gram.
- Calculate, molar mass of nitric acid by adding atomic masses of different atoms and volume of solution by using the formula, $d = \frac{m}{V}$.
- Now put these values in the formula of molarity.

Sol. $\text{Molarity} = \frac{w \times 1000}{m \times \text{volume of solution (mL)}}$

Given, $d = 1.41 \text{g mL}^{-1}$, mass % of HNO_3 = 69%

69% HNO_3 means 100 g of its solution contains 69 g HNO_3 (nitric acid).

Hence, mass of HNO_3 (solute) = 69 g

Molar mass of nitric acid,

$$HNO_3 = 1.0079 + 14.0067 + (3 \times 16.00)$$

$$= 63.0146 \text{ g mol}^{-1}$$

$$\text{Density, } d = \frac{m}{V} \text{ or } V = \frac{m}{d} = \frac{100 \text{ g}}{1.41 \text{ g mL}^{-1}}$$

$$\text{Molarity} = \frac{w \times 1000}{m \times \text{volume of solution (mL)}}$$

$$= \frac{69 \times 1000 \times 1.41}{63.0146 \times 100}$$

$$= 15.44 \text{ M}$$

Q-22 Chlorine is prepared in the laboratory by treating manganese dioxide (MnO_2) with aqueous hydrochloric acid according to the reaction,

$$4\,HCl(aq) + MnO_2(s) \longrightarrow 2H_2O\,(l) + MnCl_2(aq) + Cl_2(g)$$

How many gram of HCl reacts with 5.0 g of manganese dioxide?

Sol. $$\underset{4 \times 36.5}{4HCl\,(aq)} + \underset{87\text{ g}}{MnO_2(s)} \longrightarrow 2H_2O\,(l) + MnCl_2\,(aq) + Cl_2(g)$$

According to the balanced chemical equation,

87 g of MnO_2 reacts with 4×36.5 g HCl

5 g of MnO_2 will react with

$$\frac{4 \times 36.5 \times 5}{87} = 8.39 \text{ g HCl}$$

Q-23 . Calculate the molecular mass of the following.

(*i*) H_2O (*ii*) CO_2 (*iii*) CH_4

Sol. (*i*) Molecular mass of $H_2O = 2 \times$ atomic mass of hydrogen $+ 1 \times$ atomic mass of oxygen

$$= 2 \times 1.0079 \text{ u} + 1 \times 16.00 \text{ u} = 18.0158 \text{ u}$$

(*ii*) Molecular mass of $CO_2 = 1 \times$ atomic mass of carbon $+ 2 \times$ atomic mass of oxygen

$$= 1 \times 12.01 \text{ u} + 2 \times 16.00 \text{ u} = 44.01 \text{ u}$$

(*iii*) Molecular mass of $CH_4 = 1 \times$ atomic mass of carbon

$+ 4 \times$ atomic mass of hydrogen

$$= 1 \times 12.01 \text{ u} + 4 \times 1.0079 \text{ u}$$

$$= 16.0416$$

Q-24 Calculate molecular mass of glucose ($C_6H_{12}O_6$) molecule.

Or

A black dot used as a full stop at end of a sentence has a mass of about one attogram. Assuming that the dot is made up of carbon, calculate the approximate number of carbon atoms present in the dot ?

Sol. Molecular mass of glucose ($C_6H_{12}O_6$) $= 6\,(12.011 \text{ u}) + 12\,(1.008 \text{ u}) + 6\,(16.00 \text{ u})$

$$= (72.066 \text{ u}) + (12.096 \text{ u}) + (96.00 \text{ u})$$

$$= 180.162 \text{ u}$$

Or

Mass of carbon in the dot = 1 attogram $= 10^{-18}$ g

Gram atomic mass of carbon = 12 g, *i.e.*, 12 g of carbon contains 6.022×10^{23} atoms of carbon.

$\therefore$ 10^{-18} g of carbon will contain carbon atoms $= \dfrac{6.022 \times 10^{23}}{12} \times 10^{-18}$

$$= 5.02 \times 10^{4} \text{ atoms}$$

Q-25 Calculate the amount of carbon dioxide that could be produced when

(*i*) 1 mole of carbon is burnt in air.

(*ii*) 1 mole of carbon is burnt in 16 g of dioxygen.

(*iii*) 2 moles of carbon are burnt in 16 g of dioxygen.

Sol. $\underset{1\text{ mol}}{C(s)} + \underset{\substack{1\text{ mol}\\32\text{ g}}}{O_2(g)} \longrightarrow \underset{\substack{1\text{ mol}\\44\text{ g}}}{CO_2(g)}$

(*i*) According to the equation when 1 mole of carbon is burnt completely, CO_2 produced is 44 g.

(*ii*) 1 mole of carbon requires 32 g dioxygen from the reaction. But we have only 16 g dioxygen. Hence, dioxygen is the limiting reagent. So, the amount of CO_2 produced by 16 g dioxygen is 22 g.

(*iii*) In this case again, dioxygen is the limiting reagent. 16 g dioxygen can react only with 0.5 mole of carbon and produce 22 g CO_2.

Q-26 Dinitrogen and dihydrogen react with each other to produce ammonia according to the following chemical equation, $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$.

(*i*) Calculate the mass of ammonia produced if 2.00×10^3 g dinitrogen reacts with 1.00×10^3 g of dihydrogen.

(*ii*) Will any of the two reactants remain unreacted?

(*iii*) If yes, which one and what would be its mass?

Sol. (i) $\underset{\substack{1\text{ mol}\\28\text{ g}}}{N_2(g)} + \underset{\substack{3\text{ mol}\\6\text{ g}}}{3H_2(g)} \longrightarrow \underset{\substack{2\text{ mol}\\34\text{ g}}}{2NH_3(g)}$

28 g N_2 reacts with 6 g H_2.

$\therefore$ 1 g N_2 will react with $\frac{6}{28}$ g H_2.

$\therefore$ 2000 g N_2 will react with $\frac{2000 \times 6}{28} = 428.57$ g H_2

Hence, N_2 is the limiting reagent and H_2 is in excess. N_2 limits the amount of ammonia produced.

28 g N_2 produces 34 g NH_3

and 1 g N_2 produces $\frac{34}{28}$ g NH_3

$\therefore$ 2000 g N_2 will produce $\frac{34}{28} \times 2000 = 2428.57$ g NH_3

(*ii*) H_2 is in excess so it will remain unreacted.

(*iii*) Amount of H_2 remain unreacted

$$= 1000 - 428.57 = 571.43 \text{ g}$$

Q-27, Describe what you need to do in the laboratory to test (*i*) the law of conservation of mass, (*ii*) the law of definite proportion and (*iii*) the law of multiple proportions.

Sol. (*i*) To test the law of conservation of mass, a reaction would have to be carried out in which the mass of the reactants and the mass of the products are weighed and shown to be the same.

(*ii*) The law of definite proportions could be shown by demonstrating that no matter how a compound is obtained, the reactants remain at the same proportions by mass. This can be done by decomposing a compound and showing that the masses of the elements present are always in the same ratio.

(*iii*) To test the law of multiple proportions, two different compounds made up of the same elements would have to be decomposed. If the mass of one of the elements is kept constant the masses of other elements combining with that of the element in different samples would have to be in the small whole number ratio.

Q-28 10 mL of H_2 combine with 5 mL of O_2 to form water. When 200 mL of H_2 at STP is passed over heated CuO, the CuO loses 0.144 g of its weight. Does the above data correspond to the law of constant composition?

Sol. In the second experiment 0.144 g weight is lost from CuO. This is due to the reduction of CuO into Cu. In other words, 0.144 g oxygen combined with 200 mL H_2.

32 g oxygen occupies 22400 mL volume at STP.

$\therefore$ 0.144 g oxygen will occupy $= 22400 \times \frac{0.144}{32} = 100.8$ mL O_2

It means the ratio of H_2 and O_2 in water is 200 : 100.8 = 2 : 1. The same ratio is in first case (10 : 5 or 2 : 1). Thus, the law of constant composition is proved.

Q-29 A 0.005 cm thick coating of copper is deposited on a plate of 0.5 m^2 total area. Calculate the number of copper atoms deposited on the plate (density of copper = 7.2 g cm^{-3}, atomic mass = 63.5).

Sol. Area of plate $= 0.5 \text{ m}^2 = 0.5 \times 10^4 \text{ cm}^2$

Thickness of coating = 0.005 cm

Volume of copper deposited $= 0.5 \times 10^4 \times 0.005 = 25 \text{ cm}^3$

Mass of copper deposited $= 25 \times 7.2 = 180$ g

Now, 63.5 g of copper contains atoms $= 6.022 \times 10^{23}$

$\therefore$ 180 g of copper will contain atoms $= \frac{6.022 \times 10^{23}}{63.5} \times 180 = 1.71 \times 10^{24}$ atoms

Q-30 How many significant figures should be present in the answer of the following calculations?

(*i*) $\dfrac{0.02856 \times 298.15 \times 0.112}{0.5785}$ (*ii*) 5×5.364 (*iii*) $0.0125 + 0.7864 + 0.0215$

Solution

(*i*) Least precise number of the calculation is 0.112.

Number of significant figures in the answer = Number of significant figures in the least precise number = 3.

(*ii*) Least precise number of calculation = 5.364.

Number of significant figures in the answer = Number of significant figures in 5.364 = 4.

(*iii*) Since, the least number of decimal places in each term is four, the number of significant figures in the answer is also 4.

Q-31 Calculate the number of atoms in each of the following.

(*i*) 52 mole of Ar

(*ii*) 52 u of He

(*iii*) 52 g of He

Solution (*i*) 1 mole of Ar contains 6.022×10^{23} atoms

∴ 52 moles of Ar will contain $6.022 \times 10^{23} \times 52$

$= 3.13 \times 10^{25}$ atoms

(*ii*) 4 u of He = 1 atom

∴ 52 u of He $= \dfrac{1}{4} \times 52 = 13$ atoms

(*iii*) 4 g of He contains 6.022×10^{23} atoms

52 g of He will contain $\dfrac{6.022 \times 10^{23} \times 52}{4}$

$= 7.83 \times 10^{24}$ atoms

Q-32 Boron occurs in nature in the form of two isotopes having atomic mass 10 and 11. What are the percentage abundances of two isotopes in a sample of boron having average atomic mass 10.8?

Solution Let the % abundance of ^{10}B isotope = x

Then % abundance of ^{11}B isotope = $100 - x$

The average atomic mass $= \dfrac{x \times 10 + (100 - x) \times 11}{100}$

But, average atomic mass = 10.8

$$\therefore \quad \frac{x \times 10 + (100 - x) \times 11}{100} = 10.8$$

or $10x + 1100 - 11x = 10.8 \times 100$

or $-x = -1100 + 1080$

or $x = 20$

Thus, percentage abundance,

$^{10}B = 20, \ ^{11}B = 80$

Q-33 Calculate the number of moles in the following.

(*i*) 7.85 g of iron (*ii*) 4.68 mg of silicon

(*iii*) 65.6 μg of carbon

Solution (*i*) Moles of iron $= \dfrac{\text{mass of iron}}{\text{atomic mass}}$

$= \dfrac{7.85}{55.8} = 0.141$ mol

(*ii*) Moles of silicon $= \dfrac{\text{mass of silicon}}{\text{atomic mass}} = \dfrac{4.68 \times 10^{-3}}{28.1}$

$= 1.66 \times 10^{-4}$ mol

(*iii*) Moles of carbon $= \dfrac{\text{mass of carbon}}{\text{atomic mass}}$

$= \dfrac{65.6 \times 10^{-6}}{12}$

$= 5.47 \times 10^{-6}$ mol

Q-34 The cost of table salt (NaCl) and table sugar ($C_{12}H_{22}O_{11}$) is ₹2 per kg and ₹6 per kg, respectively. Calculate their costs per mol.

Solution One mole of NaCl = 58.5 g

Cost of NaCl per mol $= \dfrac{2}{1000} \times 58.5 =$ ₹0.117

= 11.7 paise or 12 paise

One mole of sugar ($C_{12}H_{22}O_{11}$) = 342 g

Cost of sugar per mol $= \dfrac{6}{1000} \times 342 =$ ₹2.05

Q-35 Two oxides of a metal contain 27.6% and 30.0% of oxygen respectively. If the formula of the first oxide is M_3O_4, find that of the second.

Sol. In the first oxide, oxygen = 27.6

Metal = 100 − 27.6 = 72.4 parts by mass.

As the formula of the oxide is M_3O_4, it means

72.4 parts by mass of metal = 3 atoms of metal and

4 atoms of oxygen = 27.6 parts by mass.

In the second oxide, oxygen = 30.0 parts by mass and

metal = 100 − 30 = 70 parts by mass.

But 72.4 parts by mass of metal = 3 atoms of metal.

$$\therefore \text{ 70 parts by mass of metal} = \frac{3}{72.4} \times 70 \text{ atoms of metal}$$

$$= 2.90 \text{ atoms of metal}$$

Also, 27.6 part by mass of oxygen = 4 atoms of oxygen.

$$\therefore \text{ 30 part by mass of oxygen} = \frac{4}{27.6} \times 30 \text{ atoms of oxygen}$$

$$= 4.35 \text{ atoms of oxygen.}$$

Hence, ratio of M : O in the second oxide

$$= 2.90 : 4.35 = 1 : 1.5 \text{ or } 2 : 3$$

∴ Formula of the other metal oxide is M_2O_3.

Q-36 In a reaction, $A + B_2 \longrightarrow AB_2$ identify the limiting reagent if any in the following reaction mixtures

(*i*) 300 atoms of A + 200 molecules of B

(*ii*) 2 moles of A + 3 moles of B

(*iii*) 100 atoms of A + 100 molecules of B

(*iv*) 5 moles of A + 2.5 moles of B

(*v*) 2.5 moles of A + 5 moles of B

Solution The given equation shows that 1 mole of A reacts with 1 mole of B_2 and 1 atom of A reacts with 1 molecule of B_2

(*i*) B is the limiting reagent because 200 molecules of B_2 will react with 200 atoms of A and 100 atoms of A will be left in excess.

(*ii*) A is the limiting reagent because 2 moles of A will react with 2 moles of B and 1 moles of B will be left in excess.

(*iii*) Both will react completely because it is stoichiometric mixture. No limiting reagent.

(*iv*) 2.5 moles of B will react with 2.5 moles of A, hence B is the limiting reagent.

(*v*) 2.5 moles of A will react with 2.5 moles of B. Hence A is the limiting reagent.

Q-37 (*i*) A sample of drinking water was found to be severely contaminated with chloroform, $CHCl_3$, supposed to be carcinogenic in nature. The level of contamination was 15 ppm (by mass).

(*a*) Express this in per cent by mass.

(*b*) Determine the molarity of chloroform in the water sample.

(*ii*) Calculate the molarity of a solution of ethanol in water in which the mole fraction of ethanol is 0.040.

Sol. (*i*) (*a*) 15 ppm means 15 parts in one million $(10)^6$ parts.

$$\text{Therefore, \% by mass} = \frac{15 \times 100}{10^6} = 1.5 \times 10^{-3}\%$$

(*b*) Molar mass of $CHCl_3$ = 119 g mol^{-1}

$1.5 \times 10^{-3}\%$ means 1.5×10^{-3} g chloroform is present in 100 g sample.

$$\text{Molarity, } M = \frac{w \times 1000}{m \times \text{volume of sample}}$$

(For water, density = 1 g cm^{-3}, so mass = volume)

$$M = \frac{1.5 \times 10^{-3} \times 1000}{119 \times 100} = 1.26 \times 10^{-4} \text{ M}$$

(*ii*) Molarity is defined as the moles of solute (ethanol) in 1L of the solution.

1L of ethanol solution (as it is diluted) = 1L of water

$$\text{Number of moles of } H_2O = \frac{1000 \text{ g}}{18} = 55.55 \text{ mol}$$

$$x_{H_2O} = 1 - x_{C_2H_5OH},$$

$$x_{H_2O} = 1 - 0.040 = 0.96$$

$$x_{H_2O} = \frac{n_{H_2O}}{n_{H_2O} + n_{C_2H_5OH}}$$

$$0.96 = \frac{55.55}{55.55 + n_{C_2H_5OH}}$$

$$\text{or} \quad n_{C_2H_5OH} = \frac{2.222}{0.96} = 2.3145 \text{ mol}$$

Q-38 The following data are obtained when dinitrogen and dioxygen react together to form different compounds.

	Mass of dinitrogen	Mass of dioxygen
(i)	14 g	16 g
(ii)	14 g	32 g
(iii)	28 g	32 g
(iv)	28 g	80 g

(*i*) Which law of chemical combination is obeyed by the above experimental data? Give statement.

(*ii*) Fill in the blanks in the following conversion.

(*a*) 1 km = ... mm = ... pm

(*b*) 1 mg = ... kg = ... ng

(*c*) 1 mL = ... L = ... dm^3

Sol. (*i*) On fixing the mass of dinitrogen as 28 g, the masses of dioxygen combined are 32, 64, 32 and 80 in the given four oxides. These are in the simple whole number ratio *i.e.*, 2 : 4 : 2 : 5. Hence, the given data obey the law of multiple proportions.

Law of multiple proportions Refer to text.

(*ii*) (*a*) $1\text{ km} = 1\text{ km}\times\frac{1000\text{ m}}{1\text{ km}}\times\frac{100\text{ cm}}{1\text{ m}}\times\frac{10\text{ mm}}{1\text{ cm}}$

$= 10^6\text{ mm}$.

$1\text{ km} = 1\text{ km}\times\frac{1000\text{ m}}{1\text{ km}}\times\frac{1\text{pm}}{10^{-12}\text{ m}} = 10^{15}\text{ pm}$

$\therefore 1\text{ km} = 10^6\text{ mm} = 10^{15}\text{ pm}$

(*b*) $1\text{ mg} = 1\text{ mg}\times\frac{1\text{g}}{1000\text{ mg}}\times\frac{1\text{ kg}}{1000\text{ g}} = 10^{-6}\text{kg}$

$1\text{ mg} = 1\text{ mg}\times\frac{1\text{ g}}{1000\text{ mg}}\times\frac{1\text{ ng}}{10^{-9}\text{ g}} = 10^6\text{ng}$

$\therefore 1\text{ mg} = 10^{-6}\text{ kg} = 10^6\text{ng}$

(*c*) $1\text{ mL} = 1\text{ mL}\times\frac{1\text{ L}}{1000\text{ mL}} = 10^{-3}\text{L}$

$1\text{ mL} = 1\text{ cm}^3 = 1\text{ cm}^3\times\frac{1\text{ dm}\times 1\text{ dm}\times 1\text{ dm}}{10\text{ cm}\times 10\text{ cm}\times 10\text{ cm}}$

$= 10^{-3}\text{ dm}^3$

$\therefore \quad 1\text{ mL} = 10^{-3}\text{L} = 10^{-3}\text{dm}^3$

Q-39 A welding fuel gas contains carbon and hydrogen only. Burning a small sample of it in oxygen gives 3.38 g carbon dioxide, 0.690 g of water and no other products. A volume 10.0 L (measured at STP) of this welding gas is found to weigh 11.6 g. Calculate (*i*) empirical formula (*ii*) molar mass of the gas and (*iii*) molecular formula.

Sol. (*i*) $44\text{ g }CO_2 = 12\text{ g carbon}$

$3.38\text{ g }CO_2 = \frac{12}{44}\times 3.38\text{ g} = 0.9218\text{ g carbon}$

$18\text{ g }H_2O = 2\text{ g hydrogen}$

$0.690\text{ g }H_2O = \frac{2}{18}\times 0.690\text{ g} = 0.0767\text{ g hydrogen}$

Total mass of compound = 0.9218 + 0.0767 = 0.9985 g (because compound contains only carbon and hydrogen)

$\%\text{ of C in the compound} = \frac{0.9218}{0.9985}\times 100 = 92.32$

$\%\text{ of H in the compound} = \frac{0.0767}{0.9985}\times 100 = 7.68$

Calculation for Empirical Formula

Element	Per cent by mass	Atomic mass	Relative number of moles of elements	Simplest molar ratio
C	92.32	12	$\frac{92.32}{12} = 7.69$	$\frac{7.69}{7.68} = 1$
H	7.68	1	$\frac{7.68}{1} = 7.68$	$\frac{7.69}{7.68} = 1$

Hence, empirical formula = CH

(*ii*) Calculation for molar mass of the gas

10.0 L of the given gas at STP weigh = 11.6 g

$\therefore$ 22.4 L of the given gas at STP will weigh

$= \frac{11.6\times 22.4}{10} = 25.984\text{ g}$

Molar mass = $25.984 \approx 26\text{ g mol}^{-1}$.

(*iii*) Empirical formula mass (CH) = 12 + 1 = 13

$\therefore \quad n = \frac{\text{molecular mass}}{\text{empirical formula mass}}$

$= \frac{26}{13} = 2$

Hence, molecular formula

$= n\times CH = 2\times CH = C_2H_2$

Q-40 A compound made up of two elements *A* and *B* has *A* = 70%, *B* = 30%. Their relative number of moles in the compound are 1.25 and 1.88. Calculate

(*i*) atomic masses of the elements *A* and *B*

(*ii*) molecular formula of the compound, if its molecular mass is found to be 160.

Sol. Relative number of moles of an element $= \frac{\%\text{ of the element}}{\text{atomic mass}}$

or atomic mass $= \frac{\%\text{ of element}}{\text{relative number of moles}}$

$\therefore \quad \text{Atomic mass of } A = \frac{70}{1.25} = 56$

and $\quad \text{Atomic mass of } B = \frac{30}{1.88} = 16$

Calculation of Empirical Formula

Element	Relative number of moles	Simplest molar ratio	Simplest whole number molar rati
A	1.25	$\frac{1.25}{1.25} = 1$	2
B	1.88	$\frac{1.88}{1.25} = 1.5$	3

$\therefore$ Empirical formula = A_2B_3

Calculation of molecular formula

Empirical formula mass = $2\times 56 + 3\times 16 = 160$

$$n = \frac{\text{molecular mass}}{\text{empirical formula mass}} = \frac{160}{160} = 1$$

$\therefore \quad$ Molecular formula = A_2B_3

NCERT

EXEMPLAR

QUESTIONS

SARASWATI CHEMISTRY

Environmental Chemistry

Q-1 Which of the following statements about photochemical smog is wrong?

(a) It has high concentration of oxidising agents
(b) It has low concentration of oxidising agent
(c) It can be controlled by controlling the release of NO_2, hydrocarbons, ozone etc
(d) Plantation of some plants like pinus helps in controlling photochemical smog

Ans. *(b)* Photochemical smog or Los Angles smog was first observed in Los Angles in 1950. It is formed due to photochemical reactions taking place when air contain NO_2 and hydrocarbons.

The concentrations of O_3, PAN, $RCHO$ and R_2CO builds up in the atmosphere. These compounds produce irritation in the eyes. Photochemical smog has high concentration of oxidants such as O_3, organic oxidant etc.

Q-2 Acid rain is known to contain some acids. Name these acids and where from they come in rain?

Ans. Acid rain contains H_2CO_3, HNO_3 and H_2SO_4. H_2CO_3 is formed by the dissolution of CO_2 of the air in which the water vapour present.

$$CO_2 + H_2O \longrightarrow H_2CO_3$$

Forest fire and lightning are the natural source of nitric oxide (NO). Nitrogen oxides are also produced by combustion engines, aircraft, furnaces, incinerators, industrial plants.

Nitric oxide slowly reacts with atmospheric air and produce NO_2. NO_2 dissolves in water to form HNO_3.

$$3NO_2 + H_2O \rightleftharpoons 2HNO_3 + NO$$

Sulphur oxides are produced by the burning of fossil fuels and in extraction of metals from their sulphide ores etc. Sulphur dioxide also produces sulphuric acid in the similar way.

$$SO_2 + O_2 + H_2O \xrightarrow[\text{Metal oxide}]{\text{Soot particles}} H_2SO_4 + [O]$$

Q-3 Ozone is a toxic gas and is a strong oxidising agent even then its presence in the stratosphere is very important. Explain what would happen if ozone from this region is completely removed?

Ans. The ozone layer in the stratosphere is a natural feature of the earth's environment. The ozone layer exists between 20 to 35 km above the earth surface layer. This layer protects the earth from the harmful effects of the ultraviolet radiation of the sun.

A depletion of ozone layer is considered as a serious threat to all forms of life on the earth. A 5% decrease in ozone concentration could increases the incidence of skin cancer by 20%. Ultraviolet radiation is also the factor for disease of eye, including cataract formation.

It can cause genetic mutations and destroy crops and other forms of vegetation. Aquatic animals and aquatic plants are generally affected by UV-radiation.

Q-4 On the basis of chemical reactions involved, explain how do chlorofluorocarbons cause thinning of ozone layer in stratosphere?

Ans. Chlorofluorocarbons are introduced into the atmosphere from aerosol sprays in which they function as propellants and from refrigerating equipments in which they act as coolants. It is also used as solvents.

It has very long life and stay in atmosphere for years and ultimately reach the upper layer of atmosphere (stratosphere) where it decompose in presence of UV-radiation of the sun. On account of decomposition, it forms chlorine atom or free radicals.

$$CF_2Cl_2 \xrightarrow{hv} {}^{\bullet}CF_2Cl + Cl^{\bullet}$$

The active chlorine atoms then destroy the ozone layer.

$$Cl^{\bullet} + O_3 \longrightarrow ClO^{\bullet} + O_2$$
$$ClO^{\bullet} + O \longrightarrow Cl^{\bullet} + O_2$$

It has been found that one molecule of chlorofluorocarbon can destroy one thousand ozone molecules in the stratosphere.

Q-5 What is the importance of measuring BOD of a water body?

Ans. Biological Oxygen Demand (BOD) is the measure of level of pollution caused by organic biodegradable material. These biodegradable materials are decomposed by microorganism (bacteria) consuming dissolved oxygen.

Low value of BOD indicates that water contains less biodegradable material.

Q-6 From where does ozone come in the photochemical smog?

Ans. Sunlight cause photochemical decomposition of NO_2 into NO and O.

$$NO_2 \xrightarrow{hv} NO + [O]$$

Atomic oxygen is a highly reactive species. It combines with diatomic oxygen and forms ozone.

$$O_2 + O + M \longrightarrow O_3 + M$$

where, M is inert gas such as nitrogen. This, O_3 is formed during the formation of smog.

Q-7 Some time ago formation of polar stratospheric clouds was reported over Antarctica. Why were these formed? What happens when such clouds break up by warmth of sunlight?

Ans. In summer season, nitrogen dioxide and methane react with chlorine monoxide and chlorine atoms forming chlorine sinks, preventing much ozone depletion, whereas in winter, special type of clouds called polar stratospheric clouds are formed over Antarctica.

These polar stratospheric clouds provide surface on which chlorine nitrate gets hydrolysed to form hypochlorous acid. It also reacts with hydrogen chloride to give molecular chlorine.

$$ClO^{\bullet}(g) + NO_2(g) \longrightarrow \underset{\text{Chlorine nitrate}}{ClONO_2(g)}$$
$$Cl^{\bullet}(g) + CH_4(g) \longrightarrow {}^{\bullet}CH_3(g) + HCl(g)$$
$$ClONO_2(g) + H_2O(g) \xrightarrow{\text{Hydrolysis}} HOCl(g) + HNO_3(g)$$
$$ClONO_2(g) + HCl(g) \longrightarrow Cl_2(g) + HNO_3(g)$$

When sunlight returns to the Antarctica in the spring, the sun's warmth breaks up the clouds and HOCl, Cl_2 are photolysed by sunlight.

$$HOCl(g) \xrightarrow{hv} O^{\bullet}H(g) + Cl^{\bullet}(g)$$
$$Cl_2(g) \xrightarrow{hv} 2Cl^{\bullet}(g)$$

The chlorine radicals thus formed, initiate the chain reaction for ozone depletion.

SARASWATI CHEMISTRY

Hydrocarbons

Q. 1 Arrange the following in decreasing order of their boiling points.

A. *n* –butane

B. 2-methylbutane

C. *n* –pentane

D. 2, 2-dimethylpropane

(a) $A > B > C > D$

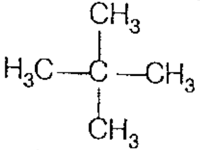
(b) $B > C > D > A$

(c) $D > C > B > A$

(d) $C > B > D > A$

Ans. ***(d)*** As the number of carbon atom increases, boiling point increases.
Boiling point decreases with branching

2, 2 -dimethyl propane,



$H_3C-C(CH_3)_2-CH_3$

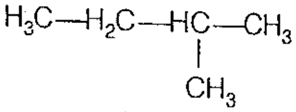
b.pt = 282.5K

***n* – pentane,**

$H_3C-CH_2-CH_2-CH_2-CH_3$

b.pt = 309.1 K

2-methyl butane



$H_3C-H_2C-HC(CH_3)-CH_3$

b.pt = 301 K

***n*-butane**

$H_3C-H_2C-CH_2-CH_3$

b.pt = 273 K

(4 carbon atoms with no branching)

Q. 2 Arrange the halogens F_2, Cl_2, Br_2, I_2, in order of their increasing reactivity with alkanes.

(a) $I_2 < Br_2 < Cl_2 < F_2$

(b) $Br_2 < Cl_2 < F_2 < I_2$

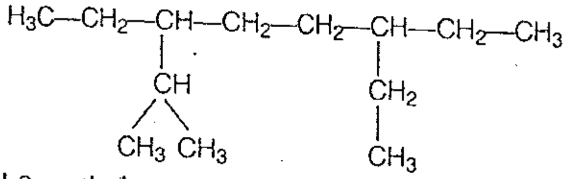
(c) $F_2 < Cl_2 < Br_2 < I_2$

(d) $Br_2 < I_2 < Cl_2 < F_2$

Ans. ***(a)*** Rate of reaction of alkanes with halogens is $F_2 > Cl_2 > Br_2 > I_2$

Alkane react with F_2 is vigorously and with I_2 the reaction is too slow that it requires a catalyst. It is because of high electronegativity of fluorine. Reactivity decreases with decrease in electronegativity and electronegativity decreases down the group

Q-3 The correct IUPAC name of the following alkane is



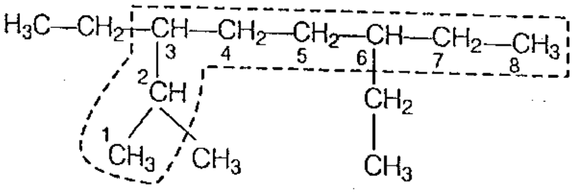
(a) 3,6-diethyl-2-methyloctane

(b) 5-isopropyl -3-ethyloctane

(c) 3-ethyl-5-isopropyloctane

(d) 3-isopropyl-6-ethyloctane

Ans. ***(a)*** The correct IUPAC name is



Longest chain - 8C atom alkane = octane
Branch on 2, 3, 6 follows lowest sum rule.
Branch of 2 – C – methyl; 3, 6, C atom-ethyl.
Ethyl comes alphabetically before methyl.
Hence, 3,6-diethyl 2-methyl octane.

Q-4 Arrange the following hydrogen halides in order of their decreasing reactivity with propene.

(a) $HCl > HBr > HI$
(b) $HBr > HI > HCl$
(c) $HI > HBr > HCl$
(d) $HCl > HI > HBr$

Ans. ***(c)*** Bond energy of HI is 296.8 kJ/mol, HBr is 36.7 kJ/mol and HCl is 430.5 kJ/mol. Hence, $HI > HBr > HCl$ is the order of reactivity with propene.

Q-5 Arrange the following carbanions in order of their decreasing stability.

A. $H_3C—C\equiv C^-$
B. $H-C\equiv C^-$
C. $H_3C—\bar{C}H_2$

(a) $A > B > C$
(b) $B > A > C$
(c) $C > B > A$
(d) $C > A > B$

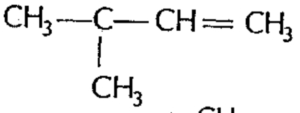
Ans. ***(b)*** $+I$-effect decreases the stability of carbon anion. Since, (CH_3) group has $+I$-effect, therefore, it intensifies the negative charge and hence destabilises (A) relative to (B). *sp* hybridised carbanion is more stabilised than sp^3

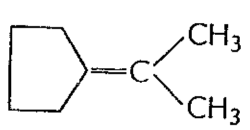
$$\underset{(B)^{sp}}{CH\equiv C^-} > \underset{(A)^{sp}}{CH_3—C\equiv C^-} > \underset{(C)\quad sp^3}{CH_3—CH_2}$$

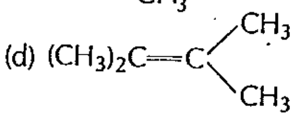
Hence, $B > A > C$

Q-6 Which of the following alkenes on ozonolysis give a mixture of ketones only?

(a) $CH_3—CH=CH—CH_3$

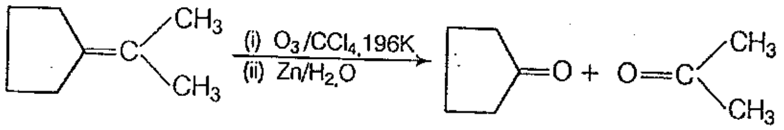
(b) 
$CH_3—\underset{\underset{CH_3}{|}}{C}—CH=CH_3$

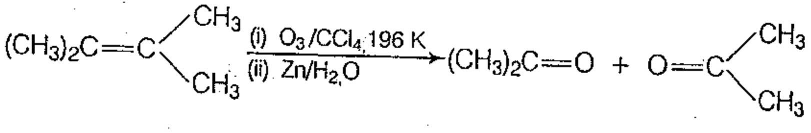
(c) 

(d) 
$(CH_3)_2C=C(CH_3)_2$

Ans. ***(c, d)***

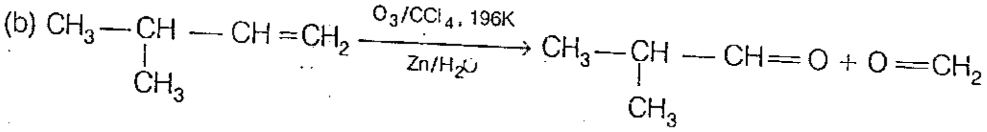
Alkenes which have two substituents on each carbon atom of the double bond, give mixture of ketones on ozonolysis. Thus, option (c) and (d) give mixture of ketones.

(c) 

(d) 

On the other hand, alkenes (a) and (b) give a mixture of two aldehydes.

(a) $CH_3CH{=}CH{-}CH_3 \xrightarrow[Zn/H_2O]{O_3/CCl_4,\ 196K} CH_3CH{=}O + O{=}CHCH_3$



(b) $CH_3{-}\underset{CH_3}{\underset{|}{C}H}{-}CH{=}CH_2 \xrightarrow[Zn/H_2O]{O_3/CCl_4,\ 196K} CH_3{-}\underset{CH_3}{\underset{|}{C}H}{-}CH{=}O + O{=}CH_2$

Q-7 For an electrophilic substitution reaction, the presence of a halogen atom in the benzene ring ....

(a) deactivates the ring by inductive effect

(b) deactivates the ring by reasonance

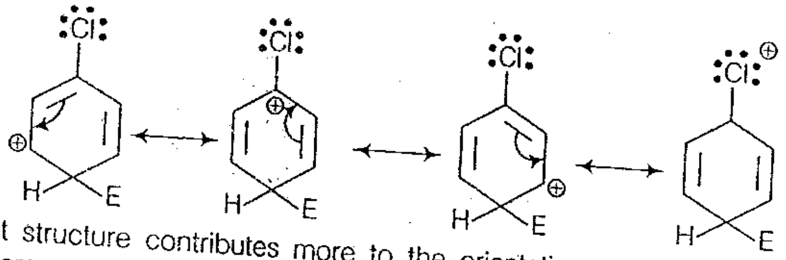
(c) increases the charge density at *ortho* and *para* position relative to *meta* position by resonance.

(d) directs the incoming electrophile to *meta* position by increasing the charge density relative to *ortho* and *para* position.

Ans. *(a, c)*

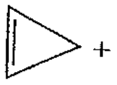
For an electrophilic substitution reaction, the presence of halogen atom in the benzene ring deactivates the ring by inductive effect and increases the charge density at *ortho* and *para* position relative to *meta* position by resonance.

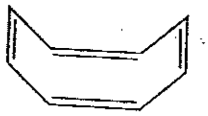
When chlorine is attached to benzene ring, chlorine being more electronegative pulls the electron *i.e.,–I*-effect. The electron cloud of benzene is less dense. Chlorine makes aryl halide, moderately deactivating group. But due to resonance the electron density on *ortho* and *para* position is greater than in *meta* position.

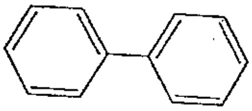


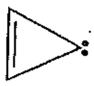
The last structure contributes more to the orientation and hence halogen are o-and p-directors.

Q-8 Four structures are given in options (a) to (d). Examine them and select the aromatic structures.

(a)


(b)


(c)


(d)


Ans. *(a, c)* Aromaticity requires following condition

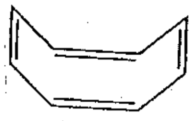
(i) planarity

(ii) complete delocalisation of π electrons in the ring .

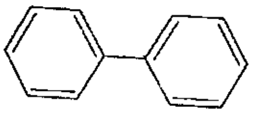
(iii) presence of $(4n + 2)\pi$ electrons in the ring.

(a)

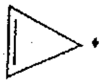

planar
π electrons = 2
$n = 0$

(b)


π electrons = 8
n= not integer
n= not planar

(c)


planar
π electrons
$(4n + 2)$= 6
in each ring
$n = 1$

(d)


π planar
n= not integer

Q-9 In an electrophilic substitution reaction of nitrobenzene, the presence of nitro group..........

(a) deactivates the ring by inductive effect

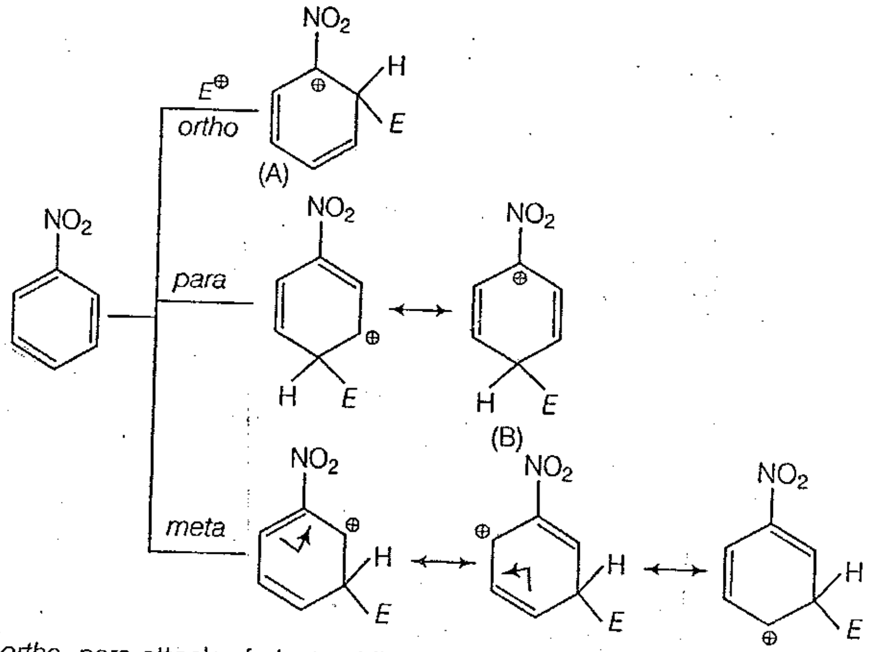
(b) activates the ring by inductive effect

(c) decreases the charge density at *ortho* and *para* position of the ring relative to *meta* position by resonance

(d) increases the charge density at *meta* position relative to the *ortho* and *para* positions of the ring by resonance

Ans. ***(a, c)***

Nitro group by virtue of $-I$-effect withdraw electrons from the ring and increase the charge and destabilises carbocation.



In *ortho, para*-attack of electrophile on nitrobenzene, we are getting two structures *(A)* and *(B)* in which positive charge is appearing on the carbon atom directly attached to the nitro group.

As nitro group is electron withdrawing by nature, it decreases the stability of such product and hence meta attack is more feasible when electron withdrawing substituents are attached.

Q-10 Rotation around carbon-carbon single bond of ethane is not completely free. Justify the statement.

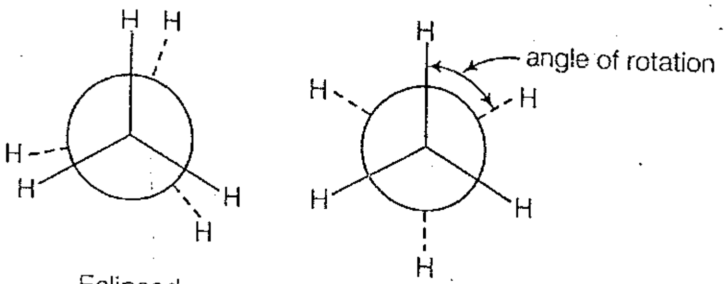
The infinite number of momentary arrangements of the atoms in space which result through rotation about a single bond are called conformations.

In ethane, if one carbon atom is kept stationary and other rotated around C — C axis, we have eclipsed, skew and staggered conformation.

Ans. Alkanes can have infinite number of conformations by rotation around C—C single bonds. This rotation around a C—C single bond is hindered by a small energy barrier of 1-20 kJ mol⁻ due to weak repulsive interaction between the adjacent bonds. such a type of repulsive interaction is called torsional strain. In staggered form of ethane, the electron cloud of carbon hydrogen bonds are far apart.

Hence, minimum repulsive force. In eclipsed electron cloud of carbon-hydrogen become close resulting in increase in electron cloud repulsion. This repulsion affects stablity of a conformer.

In all the conformations of ethane the staggered form has least torsional strain and the eclipsed form has the maximum torsional strain. Hence, rotation around C—C bond in ethtane is not completely free.

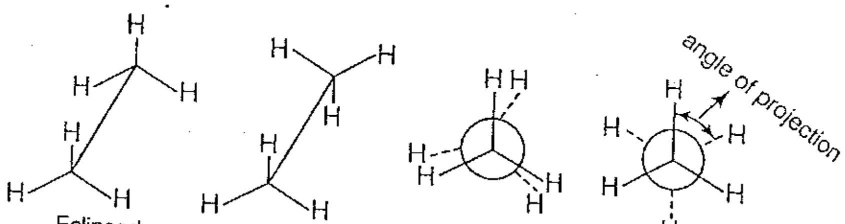


Eclipsed　　Staggered

Newman's projection of ethane

Q-11 Draw Newman and Sawhorse projections for the eclipsed and staggered conformations of ethane. Which of these conformations is more stable and why ?

Ans.



Eclipsed　Staggered

Sawhorse projections of ethane

Eclipsed　Staggered

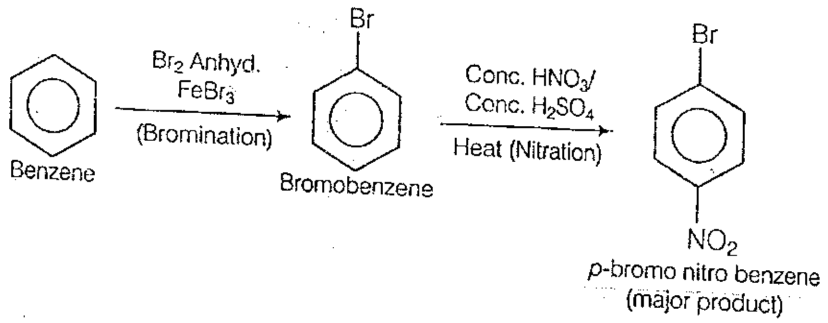
Newman projections of ethane

Staggered form of ethane is more stable than the eclipsed conformation, by about 12.55 kJ/mol. This is because any two hydrogen atoms on adjacent carbon atoms of staggered conformation are maximum apart while in eclipsed conformation, they cover or eclipse each other in space. Thus, in staggered form, there is minimum repulsive forces, minimum energy and maximum stability of the molecule.

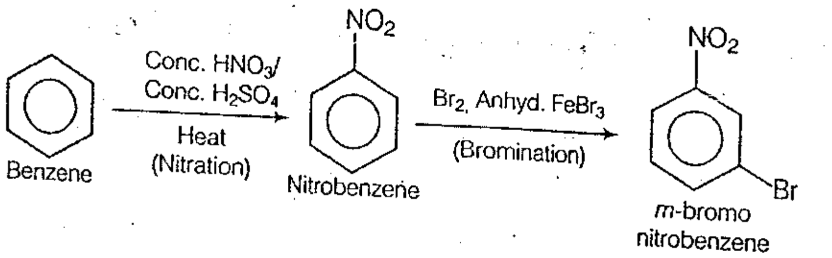
Q-12 How will you convert benzene into (a) *p*-nitrobromobenzene (b) *m*-nitrobromobenzene

Ans. Halogens attached to benzene ring is *ortho and para* directing where as nitro group is *meta* directing.

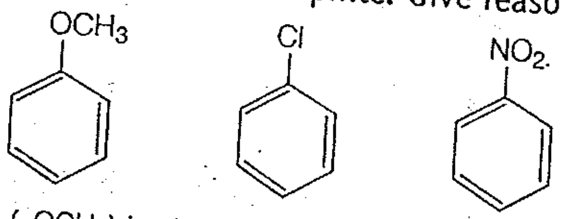
(a)



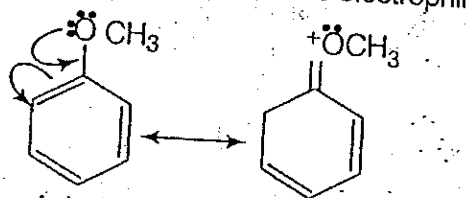
(b)



Q-13 Arrange the following set of compounds in the order of their decreasing relative reactivity with an electrophile. Give reason.

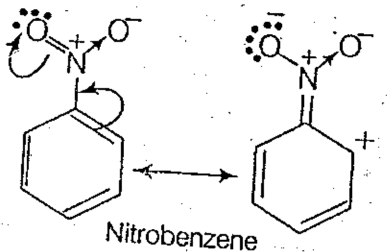


Ans. The methoxy group ($-OCH_3$) is electron releasing group. It increases the electron density in benzene nucleus due to resonance effect (+ *R*-effect). Hence, it makes anisole more reactive than benzene towards electrophile.



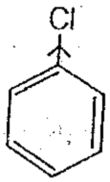
Anisol

(+ *R*-effect)



Nitrobenzene

(−*R* and −*I*-effect)

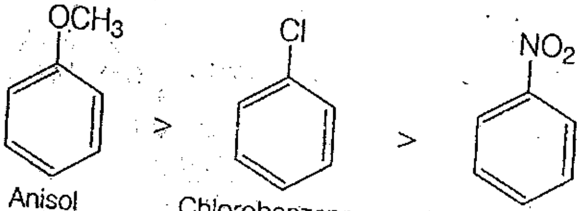


Chlorobenzene

(−*I*-effect)

In case of alkyl halides, halogens are moderately deactivating because of their strong − *I* effect. Thus, overall electron density on benzene ring decreases. It makes further substitution difficult.

− NO_2 group is electron withdrawing group. It decreases the electron density in benzene nucleus due to its strong - *R* - effect and strong − *I*-effect. Hence, it makes nitrobenzene less reactive. Therefore, overall reactivity of these three compounds towards electrophiles decreases in the following order



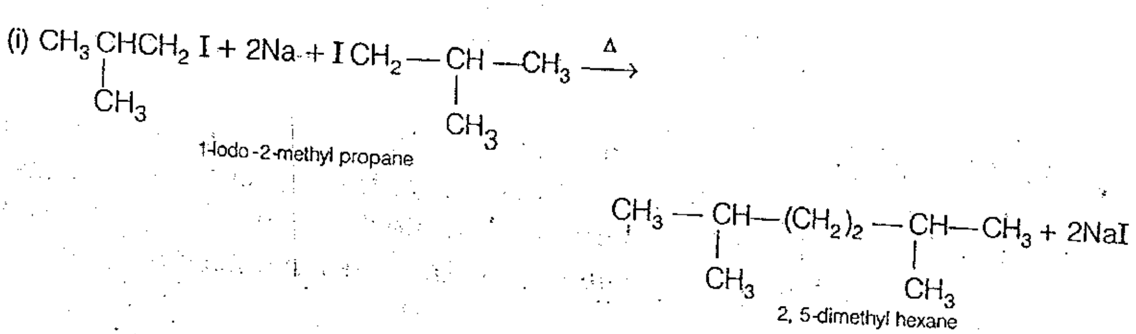
Anisol Chlorobenzene Nitrobenzene

Q-14 Write the structures and names of products obtained in the reactions of sodium with a mixture of 1-iodo-2-methylpropane and 2-iodopropane.

This question is based upon Wurtz reaction. Wurtz reaction represent that two alkyl groups can be coupled by reacting alkyl halide with

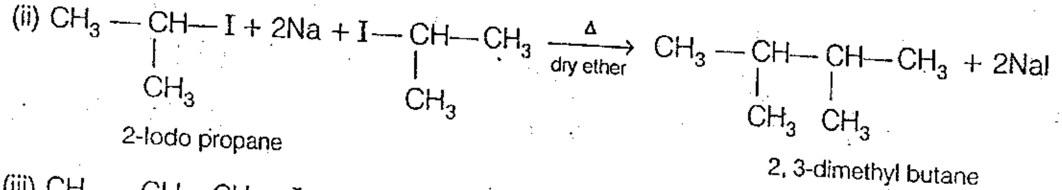
$$2RX + 2Na \xrightarrow[\text{dry ether}]{\Delta} R-R+2NaX$$

Ans. (i)



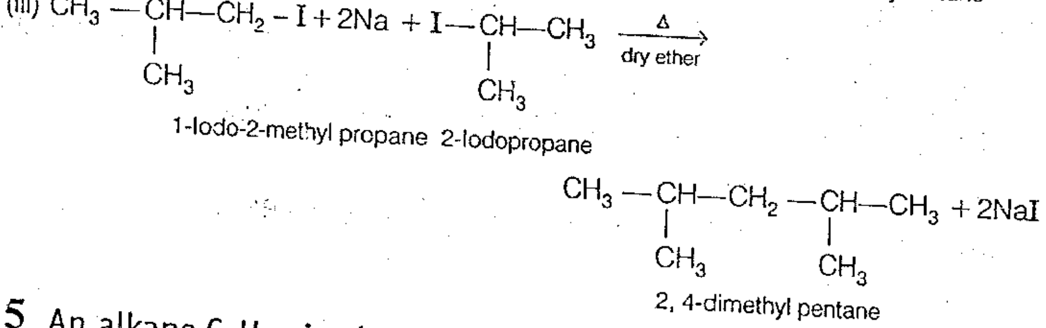
$$\underset{\text{1-Iodo-2-methyl propane}}{CH_3\underset{CH_3}{\underset{|}{C}}HCH_2I} + 2Na + ICH_2-\underset{CH_3}{\underset{|}{CH}}-CH_3 \xrightarrow{\Delta} \underset{\text{2, 5-dimethyl hexane}}{CH_3-\underset{CH_3}{\underset{|}{CH}}-(CH_2)_2-\underset{CH_3}{\underset{|}{CH}}-CH_3} + 2NaI$$

(ii)



$$\underset{\text{2-Iodo propane}}{CH_3-\underset{CH_3}{\underset{|}{CH}}-I} + 2Na + I-\underset{CH_3}{\underset{|}{CH}}-CH_3 \xrightarrow[\text{dry ether}]{\Delta} \underset{\text{2, 3-dimethyl butane}}{CH_3-\underset{CH_3}{\underset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}-CH_3} + 2NaI$$

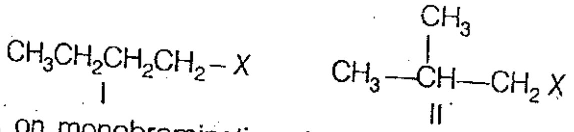
(iii)



$$\underset{\text{1-Iodo-2-methyl propane}}{CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-I} + 2Na + \underset{\text{2-Iodopropane}}{I-\underset{CH_3}{\underset{|}{CH}}-CH_3} \xrightarrow[\text{dry ether}]{\Delta} \underset{\text{2, 4-dimethyl pentane}}{CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_3} + 2NaI$$

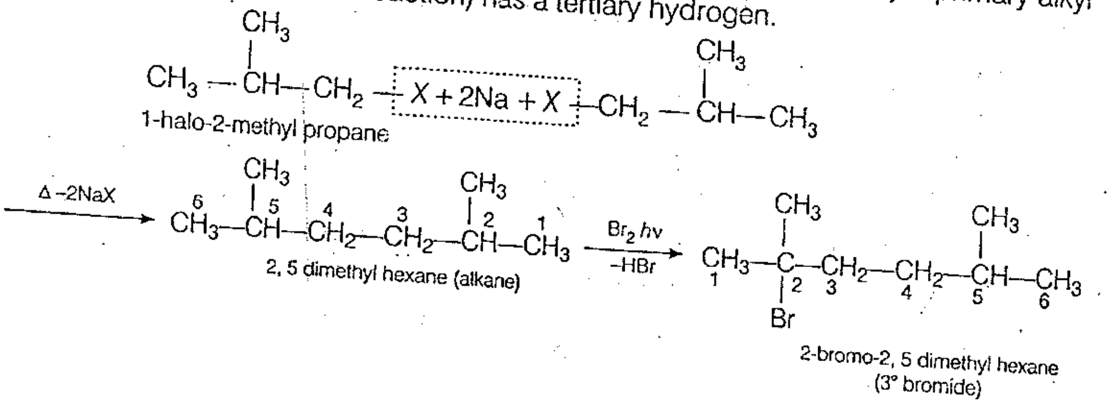
Q-15 An alkane C_8H_{18} is obtained as the only product on subjecting a primary alkyl halide to Wurtz reaction. On monobromination this alkane yields a single isomer of a tertiary bromide. Write the structure of alkane and the tertiary bromide.

Ans. From Wurtz reaction of an alkyl halide gives an alkane with double the number of carbon atoms present in the alkyl halide. Here, Wurtz reaction of a primary alkyl halide gives an alkane (C_8H_{18}), therefore, the alkyl halide must contain four carbon atoms. Now the two possible primary alkyl halides having four corbon atoms each are I and II.



$$\underset{\text{I}}{CH_3CH_2CH_2CH_2-X} \qquad \underset{\text{II}}{CH_3-\overset{CH_3}{\overset{|}{CH}}-CH_2X}$$

Since, alkane C_8H_{18} on monobromination yields a single isomer of tertiary alkyl halide, therefore, the alkane must contain tertiary hydrogen. This is possible, only if primary alkyl halide (which undergoes Wurtz reaction) has a tertiary hydrogen.

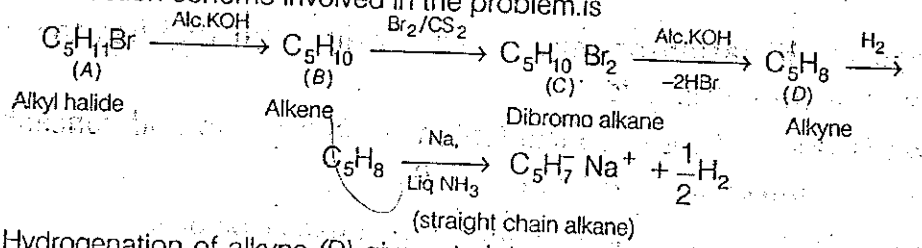


$$\underset{\text{1-halo-2-methyl propane}}{CH_3-\overset{CH_3}{\overset{|}{CH}}-CH_2-X} + 2Na + X-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_3$$

$$\xrightarrow{\Delta\ -2NaX} \underset{\text{2, 5 dimethyl hexane (alkane)}}{\overset{6}{CH_3}-\overset{CH_3}{\overset{|\,5}{CH}}-\overset{4}{CH_2}-\overset{3}{CH_2}-\overset{CH_3}{\overset{|\,2}{CH}}-\overset{1}{CH_3}} \xrightarrow[-HBr]{Br_2\,hv} \underset{\text{2-bromo-2, 5 dimethyl hexane (3° bromide)}}{\underset{1}{CH_3}-\overset{CH_3}{\underset{Br}{\overset{|}{\underset{|\,2}{C}}}}-\underset{3}{CH_2}-\underset{4}{CH_2}-\overset{CH_3}{\overset{|}{\underset{5}{CH}}}-\underset{6}{CH_3}}$$

Q-16 An alkyl halide C_5H_{11} *(A)* reacts with ethanolic KOH to give an alkene *'B'*, which reacts with Br_2 to give a compound *'C'*, which on dehydrobromination gives an alkyne *'D'*. On treatment with sodium metal in liquid ammonia, one mole of *'D'* gives one mole of the sodium salt of *'D'* and half a mole of hydrogen gas. Complete hydrogenation of *'D'* yields a straight chain alkane. Identify *A, B, C* and *D*. Give the reactions involved.

Ans. The reaction scheme involved in the problem is

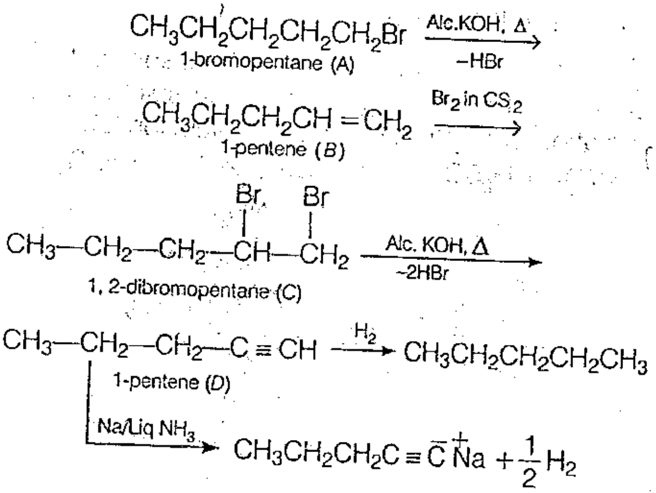


$$\underset{\substack{(A)\\ \text{Alkyl halide}}}{C_5H_{11}Br} \xrightarrow{\text{Alc.KOH}} \underset{\substack{(B)\\ \text{Alkene}}}{C_5H_{10}} \xrightarrow{Br_2/CS_2} \underset{\substack{(C)\\ \text{Dibromo alkane}}}{C_5H_{10}Br_2} \xrightarrow[-2HBr]{\text{Alc.KOH}} \underset{\substack{(D)\\ \text{Alkyne}}}{C_5H_8} \xrightarrow{H_2}$$

$$C_5H_8 \xrightarrow[\text{Liq NH}_3]{\text{Na,}} C_5H_7^-\,Na^+ + \frac{1}{2}H_2$$

(straight chain alkane)

Hydrogenation of alkyne *(D)* gives straight chain alkane hence all the compounds *(A)*, *(B)*, *(C)* and *(D)* must be straight chain compounds. Alkyne *(D)* form sodium salt which proves that it is terminal alkyne. Involved reactions are as follows



$$\underset{\text{1-bromopentane (A)}}{CH_3CH_2CH_2CH_2CH_2Br} \xrightarrow[-HBr]{\text{Alc.KOH, }\Delta}$$

$$\underset{\text{1-pentene }(B)}{CH_3CH_2CH_2CH=CH_2} \xrightarrow{Br_2\text{ in }CS_2}$$

$$\underset{\text{1, 2-dibromopentane (C)}}{CH_3-CH_2-CH_2-\overset{\overset{Br}{|}}{CH}-\overset{\overset{Br}{|}}{CH_2}} \xrightarrow[-2HBr]{\text{Alc. KOH, }\Delta}$$

$$\underset{\text{1-pentene }(D)}{CH_3-CH_2-CH_2-C\equiv CH} \xrightarrow{H_2} CH_3CH_2CH_2CH_2CH_3$$

$$\xrightarrow{\text{Na/Liq NH}_3} CH_3CH_2CH_2C\equiv\overset{-}{C}\overset{+}{Na} + \frac{1}{2}H_2$$

It is important point that alkyl halide *(A)* can not be 2-bromopentane because dehydrobromination of *(A)* would have given 2-pentene as the major product in accordance with Markownikoff's rule.

Q- 17 896 mL vapour of a hydrocarbon *'A'* having carbon 87.80% and hydrogen 12.19% weighs 3.28 g at STP. Hydrogenation of *'A'* gives 2-methylpentane. Also *'A'* on hydration in the presence of H_2SO_4 and $HgSO_4$ gives a ketone *'B'* having molecular formula $C_6H_{12}O$. The ketone *'B'* gives a positive iodoform test. Find the structure of *'A'* and give the reactions involved.

Ans. To determine the molecular mass of hydrocarbon (A) 896 mL vapour of C_xH_y (A) weighs 3.28 g at STP

22700 mL vapour of C_xH_y *(A)* weighs $\frac{328 \times 22700}{896}$ g/mol at STP

$$= 83.1 \text{ g/mol}$$

Hence, molecular mass of $C_xH_y(A) = 83.1\text{ g mol}^{-1}$. To determine the empirical formula of hydrocarbon *(A)*.

Element	%	Atomic mass	Relative ratio	Relative no. of atoms	Simplest ratio
C	87.8	12	7.31	1	3
H	12.19	1	12.19	1.66	$4.98 \approx 5$

Thus, Empirical formula of *A* is C_3H_5.

∴ Empirical formula mass = 36 + 5 = 41.

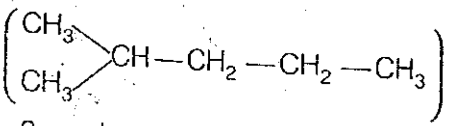
$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} = \frac{83.1}{41} = 2.02 \approx 2$$

Molecular mass is double of empirical formula mass.

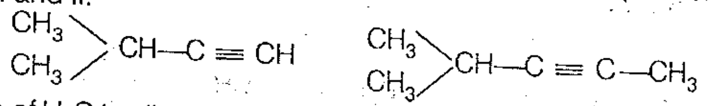
∴ Molecular formula is C_6H_{10}

To determine the structure of compounds (*A*) and (*B*)

$$\underset{(A)}{C_6H_{10}} \longrightarrow \text{2-methyl pentane}$$

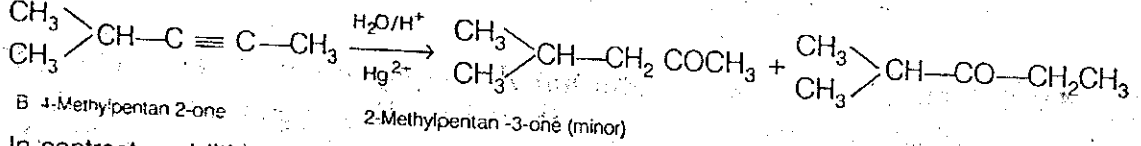


Hence, hydrogenation of hydrocarbon (A) requires 2 moles of hydrogen to form 2-methylpentane. Therefore, hydrocarbon(A) is an alkyne having five carbon atoms in a staight chain and a methyl substituent at position 2. Thus, the possible structures for the alkyne (*A*) are I and II.

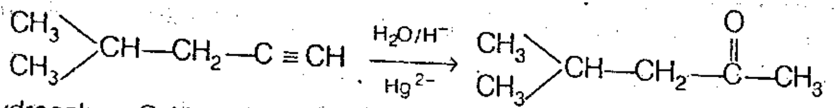


Since, addition of H_2O to alkyne (*A*) in presence of Hg^{2+}, give a ketone which gives positive iodoform test, therefore, ketone (*B*) must be a methyl ketone, *i.e.*, it must contain a $COCH_3$ group.

Now addition of H_2O to alkyne (II) should give a mixture of two ketones in which 2- methyl pentan -3 one (minor) and 4-methylpentan -2-one ketone (B) (which shows +ve iodoform test) predominates.



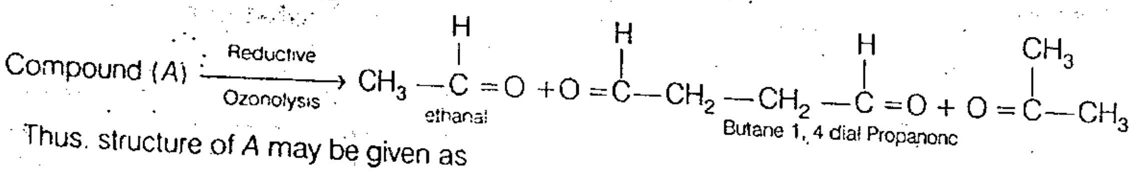
In contrast, addition of H_2O to alkyne (I) will give only one ketone, *i.e.*, 4- methylpentan-2-one which gives iodoform test.



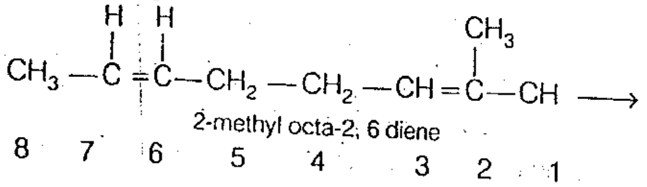
Thus, hydrocabon C_xH_y (*A*) is 4-methylpent –1–yne. 4- methylpentan -2 one (gives + ve iodoform test)

Q-18 An unsaturated hydrocarbon *'A'* adds two molecules of H_2 and on reductive ozonolysis gives butane-1, 4-dial, ethanal and propanone. Give the structure of *'A'*, write its IUPAC name and explain the reactions involved.

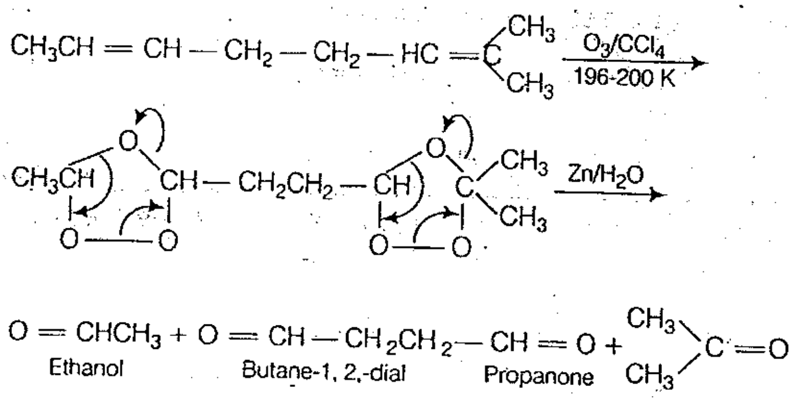
Ans. The scheme of reaction is



Thus, structure of *A* may be given as



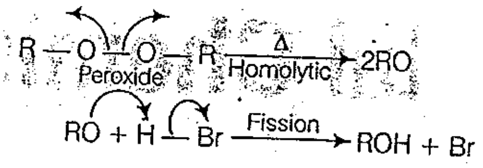
The reactions involved in the question·



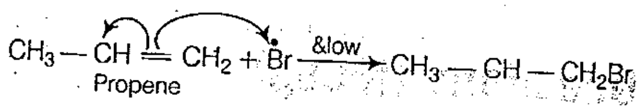
Q-19 In the presence of peroxide addition of HBr to propene takes place according to anti Markownikoff's rule but peroxide effect is not seen in the case of HCl and HI. Explain.

Ans. $\underset{\text{propene}}{CH_3-CH=CH_2} + HBr \xrightarrow{\text{Peroxide}} \underset{n\text{-propyl bromide}}{CH_3-CH_2CH_2Br}$

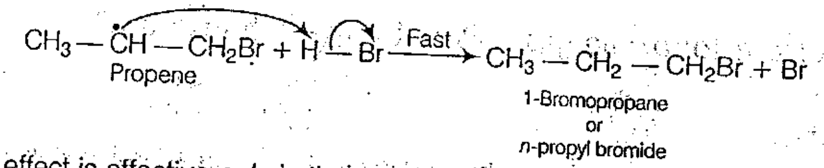
The mechanism of the reaction is



Step I



Step II



Peroxide effect is effective only in the case of HBr and not seen in the case of HCl and HI. This is due to the following reasons.

(i) H — Cl bond (103 kcal/mol) is stronger than H — Br bond (87 kcal/mol)

H — Cl bond is not decomposed by the peroxide free radical whereas the H — I bond is weaker (71 kcal/mol) form iodine free radicals.

(ii) Iodine free radical (I°) formed as H — I bond is weaker but iodine free radicals readily combine with each other to form iodine molecules rather attacking the double bond.

Organic Chemistry : Some Basic Principles and Techniques

Q-1 What is the correct order of decreasing stability of the following cations?

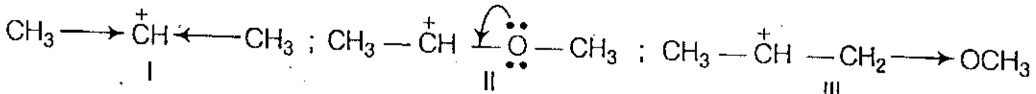
$CH_3-\overset{\oplus}{C}H-CH_3$ I

$CH_3-\overset{\oplus}{C}H-OCH_3$ II

$CH_3-\overset{\oplus}{C}H-CH_2-OCH_3$ III

(a) II > I > III (b) II > III > I (c) III > I > II (d) I > II > III

Ans. *(a)* *Stability of the given cations can be understood by the following structures*



Weak + *I*-effect of the two methyl groups stabilises carbocation (I)

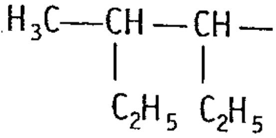
Strong + *R*-effect of $-OCH_3$ group stabilises carbocation (II)

$-I$-effect of $-OCH_3$ group destabilises the carbocation (III)

Hence, the stability of carbocation decreases

II > I > III

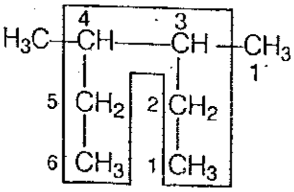
Q-2 Correct IUPAC name for



$H_3C-\underset{C_2H_5}{\underset{|}{CH}}-\underset{C_2H_5}{\underset{|}{CH}}-CH_3$ is ....

(a) 2-ethyl-3-methylpentane
(b) 3, 4-dimethylhexane
(c) 2-*sec*-butylbutane
(d) 2, 3-dimethylbutane

Ans. *(b)*



3, 4-dimethylhexane

Q-3 In which of the following compounds the carbon marked with asterisk is expected to have greatest positive charge?

(a) $^*CH_3-CH_2-Cl$
(b) $^*CH_3-CH_2-Mg^+Cl^-$
(c) $^*CH_3-CH_2-Br$
(d) $^*CH_3-CH_2-CH_3$

When a more electronegative atom is attached to carbon, the shared pair of electron moves towards more electronegative atom. Carbon has less electron density and gains partial positive charge.

Ans. *(a)* Electronegativity of Cl, Br, C and Mg follows the order Cl > Br > C > Mg

$^{*}CH_3 \rightarrow CH_2 \rightarrow Cl$ (−*I*-effect)

$^{*}CH_3 \leftarrow CH_2 \leftarrow Mg^{+}Cl^{-}$

$^{*}CH_3 \rightarrow CH_2 \rightarrow Br$ (−*I*-effect)

$^{*}CH_3—CH_2—CH_3$ (+ *I*-effect)

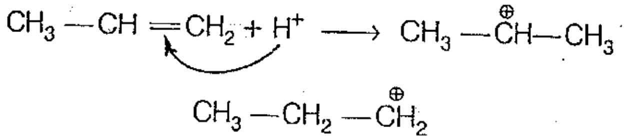
−*I* effect of Cl > Br.

Hence, $CH_3—CH_2—Cl$ has the greatest positive charge.

Q-4 Electrophilic addition reactions proceed in two steps. The first step involves the addition of an electrophile. Name the type of intermediate formed in the first step of the following addition reaction.
$H_3C—HC = CH_2 + H^+ \longrightarrow ?$

(a) 2° carbanion
(b) 1° carbocation
(c) 2° carbocation
(d) 1° carbanion

Ans. *(c)* When electrophile attacks $CH_3—CH = CH_2$ delocalisation of electrons can take place, in two possible ways



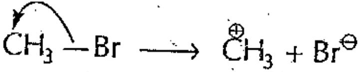
$CH_3—CH = CH_2 + H^+ \longrightarrow CH_3—\overset{\oplus}{C}H—CH_3$ (2° carbocation)

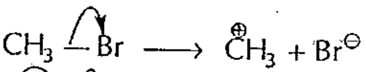
$CH_3—CH_2—\overset{\oplus}{C}H_2$ (1° carbocation)

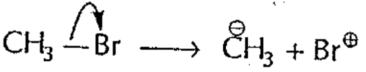
As 2° carbocation is more stable than 1° carbocation thus first addition is more feasible.

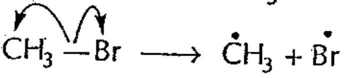
Note *Stability of carbocations is the basis of Markownikoff's rule.*

Q-5 Covalent bond can undergo fission in two different ways. The correct representation involving a heterolytic fission of $CH_3—Br$ is

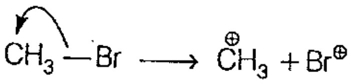
(a) 
$CH_3—Br \longrightarrow \overset{\oplus}{C}H_3 + Br^{\ominus}$

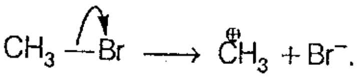
(b) 
$CH_3—Br \longrightarrow \overset{\oplus}{C}H_3 + Br^{\ominus}$

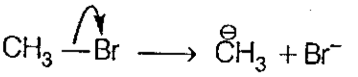
(c) 
$CH_3—Br \longrightarrow \overset{\ominus}{C}H_3 + Br^{\oplus}$

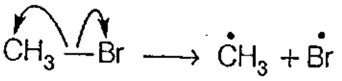
(d) 
$CH_3—Br \longrightarrow \dot{C}H_3 + \dot{B}r$

Ans. *(b)* Arrow denotes the direction of movement of electrons

(a) 
$CH_3—Br \longrightarrow \overset{\oplus}{C}H_3 + Br^{\oplus}$

(b) 
$CH_3—Br \longrightarrow \overset{\oplus}{C}H_3 + Br^{-}$.

(c) 
$CH_3—Br \longrightarrow \overset{\ominus}{C}H_3 + Br^{-}$

(d) 
$CH_3—Br \longrightarrow \dot{C}H_3 + \dot{B}r$ (homolytic)

Since, Br is more electronegative than carbon, hence heterolytic fission occurs in such a way that CH_3 gets the positive charge and Br gets the negative charge. Thus, option (b) is correct.

Q-6 Which of the following compounds contain all the carbon atoms in the same hybridisation state?

(a) $H—C \equiv C—C \equiv C—H$
(b) $CH_3—C \equiv C—CH_3$
(c) $CH_2 = C = CH_2$
(d) $CH_2 = CH—CH = CH_2$

Ans. *(a, d)*

Hybridisation of carbon atoms in different compounds is shown below

(a) $\underset{sp}{HC} \equiv \underset{sp}{C} - \underset{sp}{C} \equiv \underset{sp}{CH}$

(b) $\underset{sp^3}{CH_3} - \underset{sp}{C} \equiv \underset{sp}{C} - \underset{sp^3}{CH_3}$

(c) $\underset{sp^2}{CH_2} = \underset{sp}{C} = \underset{sp^2}{CH_2}$

(d) $\underset{sp^2}{CH_2} = \underset{sp^2}{CH} - \underset{sp^2}{CH} = \underset{sp^2}{CH_2}$

In options (a) and (d), all carbon atoms are in same hybridisation state *i.e.*, in *sp* and sp^2 hybridisation respectively.

Q-7 Electrophiles are electron seeking species. Which of the following groups contain only electrophiles?

(a) BF_3, NH_3, H_2O

(b) $AlCl_3$, SO_3, NO_2^+

(c) NO_2^+, CH_3^+, $CH_3-C^+{=}O$

(d) $C_2H_5^-$, $\dot{C}_2H_5$, $C_2H_5^+$

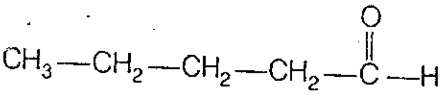
Electrophiles are electron deficient species. Hence, they are generally Lewis acids or ions with positive charge.

Ans. *(b, c)*

All $AlCl_3$, SO_3 (Lewis acids), NO_2^+, CH_3^+, $CH_3-\overset{+}{C}=O$ are electron deficient species. Hence, these are electrophiles.

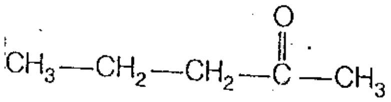
Direction (Q. Nos. 19-20) *Consider the following four compounds.*

(I)



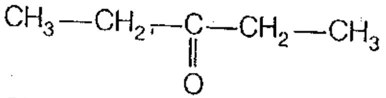
$CH_3-CH_2-CH_2-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-H$

(II)



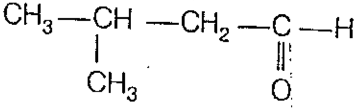
$CH_3-CH_2-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$

(III)



$CH_3-CH_2-\underset{\underset{\displaystyle O}{\|}}{C}-CH_2-CH_3$

(IV)



$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_2-\underset{\underset{\displaystyle O}{\|}}{C}-H$

Q-8 Nucleophile is a species that should have

(a) a pair of electrons to donate

(b) positive charge

(c) negative charge

(d) electron deficient species

Ans. *(a, c)*

Nucleophile (nucleus-loving) is a chemical species that donates an electron pair to an electrophile (electron-loving). Hence, a nucleophile should have either a negative charge or an electron pair to donate. Thus, option (a) and (c) are correct.

Q-9 Hyperconjugation involves delocalisation of ....

(a) electrons of carbon-hydrogen σ bond of an alkyl group directly attached to an atom of unsaturated system.

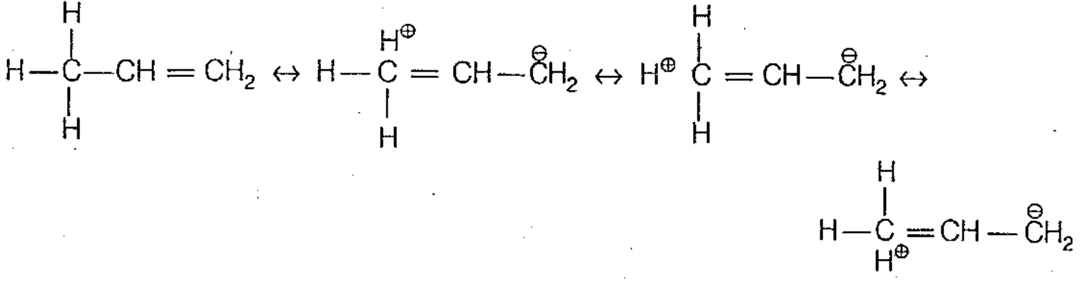
(b) electrons of carbon-hydrogen σ bond of alkyl group directly attached to the positively charged carbon atom.

(c) π-electrons of carbon-carbon bond

(d) lone pair of electrons.

Ans. *(a, b)*

Hyperconjugation is the delocalisation of sigma electron also known as sigma-pi conjugation. Presence of $\alpha-H$ with respect to double bond, triple bond or carbon containing positive charge (in carbonium ion) or unpaired electron (in free radical) is a condition for hyperconjugation.



Q-10 For testing halogens in an organic compound with $AgNO_3$ solution, sodium extract (Lassaigne's test) is acidified with dilute HNO_3. What will happen if a student acidifies the extract with dilute H_2SO_4 in place of dilute HNO_3?

Nitrogen, sulphur, halogens and phosphorous present in an organic compound are detected by Lassaigne's test. The elements in compound are converted from covalent to ionic form fused with sodium metal.

Ans. On adding dilute H_2SO_4 for testing halogens in an organic compound with $AgNO_3$, white precipitate of Ag_2SO_4 is formed. This will interfere with the test of chlorine and this Ag_2SO_4 may be mistaken for white precipitate of chlorine as AgCl. Hence, dilute HNO_3 is used instead of dilute H_2SO_4.

Q-11 Explain, how is the electronegativity of carbon atoms related to their state of hybridisation in an organic compound?

Ans. Electronegativity of carbon atom, also depends on the hybridisation of the carbon atom. Since, *s*-electrons are more strongly attracted by the nucleus than *p*-electrons, thus, electronegativity increases with increase in *s*-character of the hybridised orbital *i.e.*,

$$\xrightarrow{\text{25\%} \quad \text{33.3\%} \quad \text{50\%}}$$
$$sp^3 < sp^2 < sp \quad \text{Hybridisation}$$

$$\xrightarrow[\text{Increasing order of electronegativity}]{\text{Increasing order of \% } s\text{-character}}$$

Thus, *sp*-hybridised carbon is the most electronegative carbon.

Q-12 Match the terms mentioned in Column I with the terms in Column II.

Column I		Column II	
A.	Carbocation	1.	Cyclohexane and 1-hexene
B.	Nucleophile	2.	Conjugation of electrons of C—Hσ bond with empty *p*-orbital present at adjacent positively charged carbon
C.	Hyperconjugation	3.	sp^2 hybridised carbon with empty *p*-orbital
D.	Isomers	4.	Ethyne
E.	*sp*-hybridisation	5.	Species that can receive a pair of electrons
F.	Electrophile	6.	Species that can supply a pair of electrons.

Ans. A. → (3) B. → (6) C. → (2) D. → (1) E. → (4) F. → (5)

Column I	Column II	Explanation
A. Carbocation	sp^2-hybridised carbon with empty *p*-orbital	H_3C^+ is carbocation. Loss of e^- makes its *p*-orbitals empty (sp^2-hybridised carbon)
B. Nucleophile	Species that can supply a pair of electron	Nucleus loving *i.e.*, having negative charge or excess of electrons
C. Hyperconjugation	Conjugation of electrons of C—H σ bond with empty *p*-orbital present at adjacent positively charged carbon	
D. Isomers	Cyclohexane and 1-hexene	Same molecular formula but different structures
E. *sp*-hybridisation	Ethyne	$HC \equiv CH$ (*sp*-hybridisation)
F. Electrophile	Species that receive a pair of electron	Electron loving *i.e.*, positive charge or lack of electrons

Q-13 Give three points of differences between inductive effect and resonance effect.

Ans. *Difference between inductive effect and resonance effect is as follows*

Inductive effect	Resonance effect
Inductive effect involves σ – electrons displacement and occurs only in saturated compounds.	It involves π – electrons or lone pair of electrons and occurs only in unsaturated and conjugated system.
Inductive effect can move upto 3 – carbon atoms.	It is applicable all along the length of conjugated system.
In inductive effect, there is a slight displacement of electrons and thus only partial positive and negative charges appear.	In resonance effect, there is complete transfer of electrons and thus full positive and negative charges appear.

The *p*-Block Elements

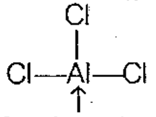
Q-1 Which of the following is a Lewis acid?

(a) $AlCl_3$ (b) $MgCl_2$ (c) $CaCl_2$ (d) $BaCl_2$

Lewis acid represent those substances in which octet remains incomplete act as electron acceptors.

Ans. ***(a)*** Alkaline earth metals form ionic chloride whereas aluminium chloride is covalent. Despite of sharing electrons with chlorine, the octet of aluminium is incomplete. To complete the octet, it needs electrons and thus, acts as a Lewis acid.

$_{13}Al = 2, 8, 3$ and $_{17}Cl = 2, 8, 7$



$$Cl-\overset{\overset{\Large Cl}{|}}{\underset{\uparrow}{Al}}-Cl$$

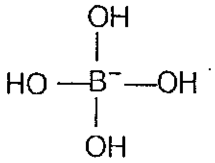
Octet incomplete

Q-2 The geometry of a complex species can be understood from the knowledge of type of hybridisation of orbitals of central atom. The hybridisation of orbitals of central atom in $[B(OH_4)]^-$ and the geometry of the complex are respectively

(a) sp^3, tetrahedral (b) sp^3, square planar
(c) sp^3d^2, octahedral (d) dsp^2, square planar

Hybridisation and geometry of a complex can be found by counting number of bond pairs and lone pairs present in a central atom.

Ans. ***(a)*** Structure of $B(OH)_4^-$ is



$$HO-\underset{\underset{\large OH}{|}}{\overset{\overset{\large OH}{|}}{B^-}}-OH$$

4 bond pair + 0 lone pair

Hybridisation — sp^3

Geometry — Tetrahedral

Q-3 Boric acid is an acid because its molecule

(a) contains replaceable H^+ ion
(b) gives up a proton
(c) accepts OH^- from water releasing proton
(d) combines with proton from water molecule

Ans. (c) Lewis acids are substances whose octet is incomplete and accepts electrons.

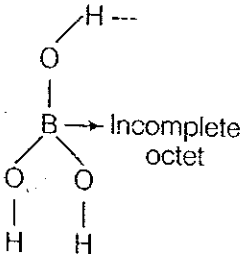
Boric acid is a monobasic weak acid. It does not liberate H^+ ion but accepts electrons from OH^- ion *i.e.*, behaves as Lewis acid.

$$H_3BO_3 + H_2O \longrightarrow B(OH)_4^- + H^+$$

or,

$$B(OH)_3 + 2H_2O \longrightarrow [B(OH)_4]^- + H_3O^+$$

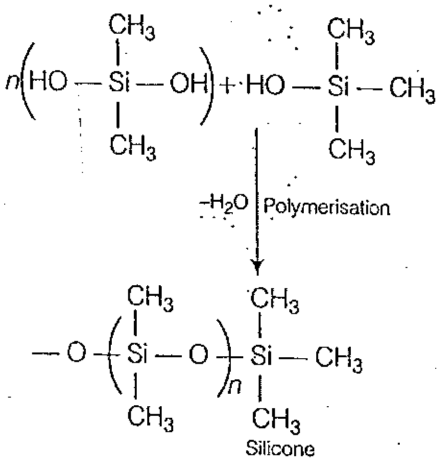
The structure of H_3BO_3 is as shown below, where the octet of boron in H_3BO_3 is incomplete.



Q-4 Silicon has a strong tendency to form polymers like silicones. The chain length of silicone polymer can be controlled by adding

(a) $MeSiCl_3$ (b) Me_2SiCl_2 (c) Me_3SiCl (d) Me_4Si

Ans. (c) Silicon has a strong tendency to form polymers like silicones. The chain length of silicon polymer can be controlled by adding Me_3SiCl which block the ends as shown below



Q-5 Ionisation enthalpy ($\Delta_i H$ kJ mol^{-1}) for the elements of group 13 follows the order

(a) $B > Al > Ga > In > Tl$ (b) $B < Al < Ga < In < Tl$

(c) $B < Al > Ga < In > Tl$ (d) $B > Al < Ga > In < Tl$

Ionisation enthalpy ($\Delta_i H$) is the energy required to remove a valence electron. On moving down the group 13, there is decrease in first ionisation enthalpy due to an increase in atomic size and screening effect.

Ans. (d) On moving from B to Al, all the ionisation enthalpies decreases as expected and this decrease is due to an increase in atomic size and shielding effect.

On moving from Al to Ga, the ionisation enthalpy increases slightly, because on moving from Al to Ga, both nuclear charge and shielding effect increase but due to poor shielding by *d*-electron in Ga, effective nuclear charge on valence electron increases resulting in *d*-block contraction, that's why ionisation enthalpies increase.

On moving from Ga to In, again there is slight decrease in ionisation enthalpies due to increased shielding effect by additional ten 4*d* electrons, which outweighs the effect of increased nuclear charge.

On moving from In to Tl, ionisation enthalpies show the increase again because fourteen 4*f* electrons shield valence electron poorely (order of shielding effect $s > p > d > f$) and so effective nuclear charge increases, consequently ionisation enthalpies increase.

Q-6 In the structure of diborane,

(a) All hydrogen atoms lie in one plane and boron atoms lie in a plane perpendicular to this plane

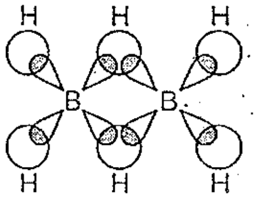
(b) 2 boron atoms and 4 terminal hydrogen atoms lie in the same plane and 2 bridging hydrogen atoms lie in the perpendicular plane

(c) 4 bridging hydrogen atoms and boron atoms lie in one plane and two terminal hydrogen atoms lie in a plane perpendicular to this plane

(d) All the atoms are in the same plane

Ans. *(b)* Boron is trivalent, we would expect a simple hydride BH_3. However BH_3 is not stable. The boron possess incomplete octet and BH_3 dimerises to form B_2H_6 molecule with covalent and three centre 2-electron bond. The simplest boron hydride is diborane B_2H_6.

As seen from the structure drawn, 6 electrons are required for the formation of conventional covalent bond structure by B-atom, whereas in diborane, there are 12 valence electrons, three from each boron atoms and six from the six hydrogen atoms. The geometry of B_2H_6 can be represented as



Bonding in diborane

The four terminal hydrogen atoms and two boron atoms lie one plane. Above and below the plane, there are two bridging hydrogen atoms. Each boron atom forms four bonds even though it has only three electrons. The terminal B—H bonds are regular bonds but the bridge B—H bonds are different.

Each bridge hydrogen is bonded to the two boron atoms only by sharing of two electrons. Such covalent bond is called three centre electron pair bond or a multi centre bond or banana bond.

Q-7 A compound *X*, of boron reacts with NH_3 on heating to give another compound *Y* which is called inorganic benzene. The compound *X* can be prepared by treating BF_3 with lithium aluminium hydride. The compounds *X* and *Y* are represented by the formulas.

(a) B_2H_6, $B_3N_3H_6$ (b) B_2O_3, $B_3N_3H_6$ (c) BF_3, $B_3N_3H_6$ (d) $B_3N_3H_6$, B_2H_6

Ans. *(a)* (i) Reaction of ammonia with diborane gives initially $B_2H_6 \cdot 2NH_3$ which is fermulated as $[B H_2(NH_3)_2]+ [BH_4]$ further heating gives borazine, $B_3N_3H_6$ also called borazole.

$$\underset{\substack{\text{Diborane}\\(X)}}{3B_2H_6} + 6NH_3 \xrightarrow{473\text{ K}} \underset{\substack{\text{Borazole}\\(Y)}}{2B_3N_3H_6} + 12H_2$$

Borazole has cyclic structure and is isoelectronic and isosteric with benzene and thus called inorganic benzene or triborine triammine or borazine.

(ii) Diborane can be prepared by the reduction of BF_3 with lithium aluminium hydride in diethyl ether.

$$4BF_3 + 3LiAlH_4 \longrightarrow \underset{(X)}{2B_2H_6} + 3AlF_3 + 3LiF$$

Q-8 The reason for small radius of Ga compared to Al is ....

(a) poor screening effect of *d* and *f*-orbitals

(b) increase in nuclear charge

(c) presence of higher orbitals

(d) higher atomic number

Ans. *(a, b)*

On moving down the group from Al to Ga, atomic radius decrease (exception) due to poor shielding by *d*-electrons. On moving from Al to Ga, shielding effect in *d*-electrons is unable to compensate increased nuclear charge.

Hence, successive increase of atomic radius as expected is not observed.

Q-9 Me_3SiCl is used during polymerisation of organo silicones because

(a) chain length of organo silicone polymers can be controlled by adding Me_3SiCl

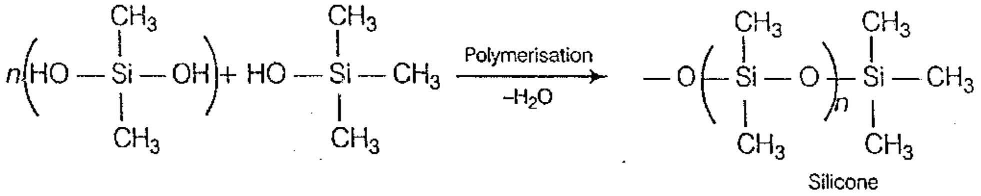
(b) Me_3SiCl blocks the end terminal of silicone polymer

(c) Me_3SiCl improves the quality and yield of the polymer

(d) Me_3SiCl acts as a catalyst during polymerisation

Ans. *(a, b)*

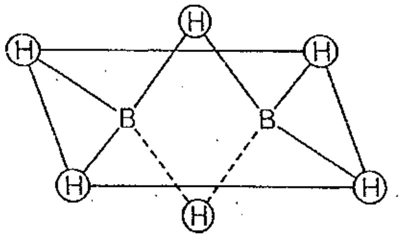
The chain length of the polymer can be controlled by adding $(CH_3)_3$ SiCl which blocks the ends as shown below



$$n\left(HO-\underset{CH_3}{\overset{CH_3}{Si}}-OH\right) + HO-\underset{CH_3}{\overset{CH_3}{Si}}-CH_3 \xrightarrow[-H_2O]{\text{Polymerisation}} -O\left(-\underset{CH_3}{\overset{CH_3}{Si}}-O-\right)_n\underset{CH_3}{\overset{CH_3}{Si}}-CH_3$$

Silicone

Q-10 Which of the following statements are correct? Answer on the basis of given figure.



(a) The two bridged hydrogen atoms and the two boron atoms lie in one plane

(b) Out of six B—H bonds two bonds can be described in terms of 3 centre 2 electron bonds

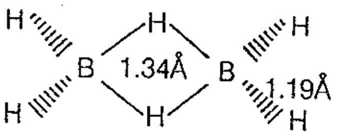
(c) Out of six B— H bonds four B— H bonds can be described in terms of 3 centre 2 electron bonds

(d) The four terminal B— H bonds are two centre-two electron regular bonds

Ans. *(a, b, d)*

The bonding and structure of the boranes are of great interest. They are different from all other hydrides as they are electron deficient.

In diborane, there are 12 valene electrons, three from each B-atom and six from H-atoms. Electron structure shown in figure.



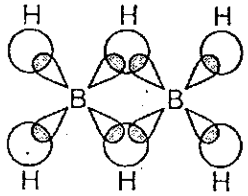
The two bridging H-atoms are in a plane perpendicular to the rest of the molecule and prevent rotation between the two B-atoms.

The terminal B—H distances are the same as the bond lengths measured in non-electron deficient compounds. These are assumed to be normal covalent bonds, with two electrons shared between two atoms. We can describe these bonds are two centre two electron bond (2c—2e).

Obviously, they are abnormal bonds as the two bridges involve only one electron each from one of the boron atoms and hydrogen atoms, making a total of four electrons.

According to molecular orbital theory, each B-atom uses sp^3-hybrid orbitals for bonding. Out of the four sp^3-hybrid orbitals on each B-atom, one is with out an electron shown in broken lines.

The terminal B—H bonds are normal 2 centre—2 electron bonds but the two bridge bonds are 3 centre—2 electron bonds. The 3 - centre—2 electron bridge bonds are also called banana bonds.

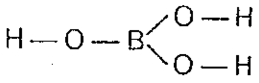


Bonding in diborane

Q-11 Explain the nature of boric acid as a Lewis acid in water.

Ans. Orthoboric acid is less soluble in cold water but highly soluble in hot water. It is a monobasic acid. It does not liberate H^+ ion but accepts OH^- from water, behaving as a Lewis acid.

$$H_3BO_3 + H_2O \longrightarrow B(OH)_4^- + H^+$$

The structure of H_3BO_3 is 

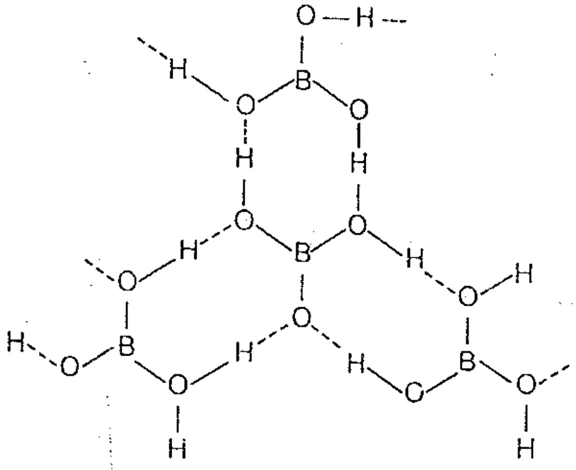
$$H-O-B\begin{matrix}\diagup O-H \\ \diagdown O-H\end{matrix}$$

Octet of boron remains incomplete. Oxygen atom contains lone pair of electrons in water molecule. Hence, instead of donating proton (H^+), boric acid accepts OH^- from water forming $B(OH)_4^-$ to complete octet.

Since, electron acceptor substance behaves as Lewis acid, therefore, boric acid acts as a Lewis acid in water.

Q-12 Draw the structure of boric acid showing hydrogen bonding. Which species is present in water ? What is the hybridisation of boron in this species ?

Ans. Orthoboric acid H_3BO_3, in solid state possesses a layer structure made up of $B(OH)_3$ units forming hexagonal rings of H-bonding as given below



Each H-atom acts as a bridge between two oxygen atoms of different BO_3^{3-} units.

Boric acid when dissolved in water, acts as Lewis acid forming $B(OH)_4^-$

$$H_3BO_3 + H_2O \longrightarrow B(OH)_4^- + H^+$$

The hybridisation of boron in $B(OH)_4^-$ is sp^3.

Q-13 Give reasons for the following

(a) CCl_4 is immiscible in water, whereas $SiCl_4$ is easily hydrolysed.

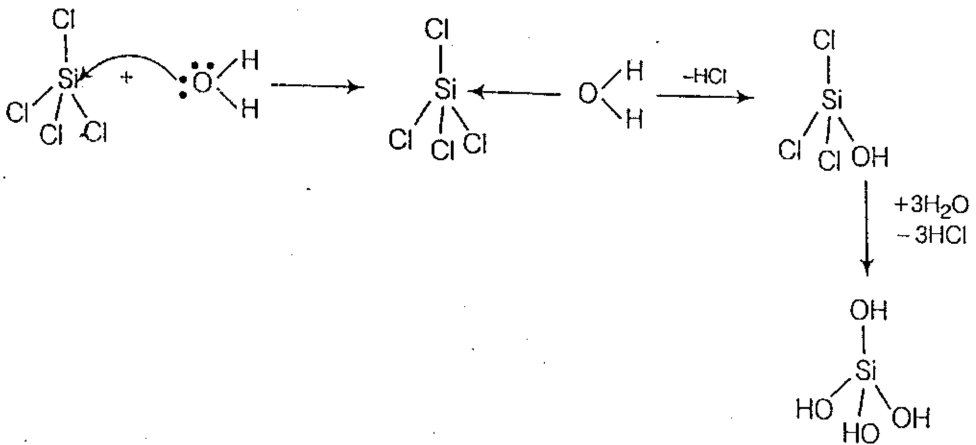
(b) Carbon has a strong tendency for catenation compared to silicon.

Ans. (a) Carbon tetrachloride (CCl_4) is a covalent compound while H_2O is a polar compound. CCl_4 does not form H-bond with water molecule. Hence, it is immiscible in water.

Further more, CCl_4 is not hydrolysed by water because of the absence of *d*-orbitals in carbon while $SiCl_4$ is readily hydrolysed by water.

$$SiCl_4 + 4H_2O \longrightarrow \underset{\text{Silicic acid}}{Si(OH)_4} + 4HCl$$

The hydrolysis of $SiCl_4$ occurs due to coordination of OH^- with empty 3*d* orbitals in silicon atom of $SiCl_4$ molecule.



(b) Carbon atoms have the tendency to link with one another through covalent bonds to form chains and rings. This property is called **catenation**. This is because C—C bonds are very strong.

Down the group, the size increases and electronegativity decreases and thereby, tendency to show catenation decreases. Thus, carbon has a strong tendency for catenation as compared to silicon.

Q-14 Explain the following.

(a) CO_2 is a gas whereas SiO_2 is a solid.

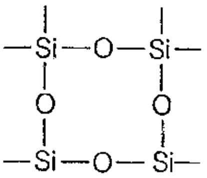
(b) Silicon forms SiF_6^{2-} ion whereas corresponding fluoro compound of carbon is not known.

Ans. (a) CO_2 has a linear structure. Its dipole moment is zero. It is believed that CO_2 molecule is a resonance hybrid has the following structures.

$$O{=}C{=}O \leftrightarrow {}^{-}O-C\equiv O^{+} \leftrightarrow O^{+}\equiv C-O^{-}$$

The CO_2 molecules are held together by weak van der Waals' forces and thus, it exists as gas. In SiO_2, due to large electronegative difference between Si and O, the Si—O bonds have considerable ionic nature.

Therefore, silica has three dimensional network like structure in which Si-atom is tetrahedrally bonded to four oxygen atoms and each oxygen atom is bonded to two silicon atoms by covalent bonds.



There is no discrete SiO_2 molecule. It is a network solid with octahedral coordination.

(b) In silicon, vacant 3*d* orbitals are available due to which it can accomodate electrons from 6 fluorine atoms, thereby forming SiF_6^{2-} ion. However, in case of C only $2p^2$ filled orbitals are available thus, it cannot expand their covalency more than 4. Thus, CCl_6^{2} is not known.

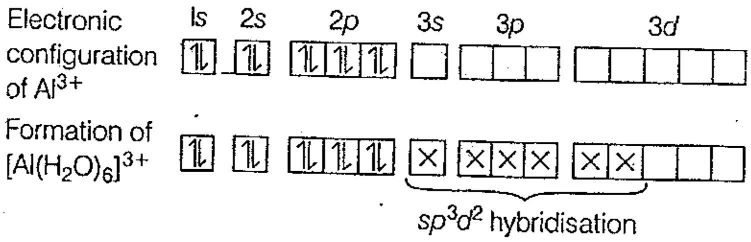
Q-15 When BCl_3 is treated with water, it hydrolyses and forms $[B[OH]_4]^-$ only whereas $AlCl_3$ in acidified aqueous solution forms $[Al[H_2O]_6]^{3+}$ ion. Explain what is the hybridisation of boron and aluminium in these species?

Ans. In trivalent state, most of the compounds being covalent are hydrolysed in water, *e.g.*, BCl_3 on hydrolysis in water form $[B(OH)_4]^-$ species, the hybridisation state of B is sp^3.

$$BCl + 3H_2O \longrightarrow B(OH)_3 + 3HCl$$
$$B(OH)_3 + H_2O \longrightarrow [B(OH)_4]^- + H^+$$

$AlCl_3$ in acidified aqueous solution form octahedral $[Al(H_2O)_6]^{3+}$ ion. In this complex, the 3*d* orbitals of Al are involved and the hybridisation state of Al is sp^3d^2

$$AlCl_3 + H_2O \xrightarrow{HCl} [Al(H_2O)_6]^{3+} + 3Cl^- \ (aq)$$



Q-16 Explain the following.

(a) Gallium has higher ionisation enthalpy than aluminium.

(b) Boron does not exist as B^{3+} ion.

(c) Aluminium forms $[AlF_6]^{3-}$ ion but boron does not form $[BF_6]^{3-}$ ion.

(d) PbX_2 is more stable than PbX_4.

(e) Pb^{4+} acts as an oxidising agent but Sn^{2+} acts as a reducing agent.

(f) Electron gain enthalpy of chlorine is more negative as compared to fluorine.

(g) $Tl(NO_3)_3$ acts as an oxidising agent.

(h) Carbon shows catenation property but lead does not.

(i) BF_3 does not hydrolyse.

(j) Why does the element silicon, not form a graphite like structure whereas carbon does?

Ans. (a) In gallium, due to poor shielding of valence electrons by the intervening 3*d* electrons. The nuclear charge becomes effective, thus, atomic radius decreases and hence, the ionisation enthalpy of gallium is higher than that of aluminium.

(b) Due to small size of boron, the sum of its first three ionisation enthalpies is very high. This prevent it to form +3 ions and force it to form only covalent compound. That's why boron does not exist as B^{3+} ion.

(c) Aluminium forms $[AlF_6]^{3-}$ ion because of the presence of vacant *d*-orbitals so it can expand its coordination number from 4 to 6. In this complex, Al undergoes sp^3d^2 hybridisation.

On the other hand, boron does not form $[BF_6]^{3-}$ ion, because of the unavailability of *d*-orbitals as it cannot expand its coordination number beyond four. Hence, it can form $[BF_4]^-$ ion (sp^3 hybridisation).

(d) Due to inert pair effect, Pb in +2 oxidation state is more stable than in +4 oxidation state hence PbX_2 is more stable than PbX_4.

(e) Due to inert pair effect, tendency to form +2 ions increases down the group, hence Pb^{2+} is more stable than Pb^{4+}. That's why Pb^{4+} acts as an oxidising agent while Sn^{2+} is less stable than Sn^{4+} and hence Sn^{2+} acts as a reducing agent.

$$\underset{\text{Reducing agent}}{Sn^{2+}} \longrightarrow Sn^{4+} + 2e^-$$

$$\underset{\text{Oxidising agent}}{Pb^{4+}} + 2e^- \longrightarrow Pb^{2+}$$

(f) Electron gain enthalpy of Cl is more negative than electron gain enthalpy of fluorine because when an electron is added to F, the added electron goes to the smaller $n = 2$ quantum level and suffers significant repulsion from other electrons present in this level.

Q- 17. Match the species given in Column I with the hybridisation given in Column II.

	Column I		Column II
A.	Boron in $[B(OH_4)]^-$	1.	sp^2
B.	Aluminium in $[Al(H_2O)_6]^{3+}$	2.	sp^3
C.	Boron in B_2H_6	3.	sp^3d^2
D.	Carbon in buckminster fullerene		
E.	Silicon in SiO_4^{4-}		
F.	Germanium in $[GeCl_6]^{2-}$		

Ans. A. → (2)   B. → (3)   C. → (2)   D. → (1)   E. → (2)   F. → (3)

A. Boron in $[B(OH)_4]^-$ sp^3 hybridised.

B. Aluminium in $[Al(H_2O)_6]^{3+}$ sp^3d^2 hybridised.

C. Boron in B_2H_6 sp^3 hybridised.

D. Carbon in Buckminsterfullerene sp^2 hybridised.

E. Silicon in SiO_4^{4-} sp^3 hybridised.

F. Germanium in $[GeCl_6]^{2-}$ sp^3d^2 hybridised.

Q-18 Account for the following observations.

(a) $AlCl_3$ is a Lewis acid.

(b) Though fluorine is more electronegative than chlorine yet BF_3 is a weaker Lewis acid than CI_3.

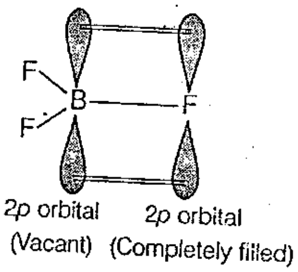
(c) PbO_2 is a stronger oxidising agent than SnO_2.

(d) The +1 oxidation state of thallium is more stable than its+3 state.

Ans. (a) In $AlCl_3$, Al has only six electrons in its valence shell. It is an electron deficient species. Therefore, it acts as a Lewis acid (electron acceptor).

(b) In BF_3 boron has a vacant 2*p*-orbital and fluorine has one 2*p*-completely filled unutilised orbital. Both of these orbitals belong to same energy level therefore, they can overlap effectively and form $p\pi$—$p\pi$ bond. This type of bond formation is known as back bonding.

While back bonding is not possible in BCl_3, because there is no effective overlapping between the 2*p*-orbital of boron and 3*p*-orbital of chlorine. Therefore, electron deficiency of B is higher in BCl_3 than that of BF_3. That's why BF_3 is a weaker Lewis acid than BCl_3.

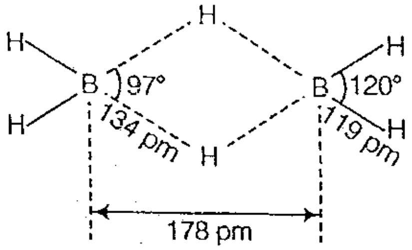


(c) In PbO_2 and SnO_2, both lead and tin are present in + 4 oxidation state. But due to stronger inert pair effect, Pb^{2+} ion is more stable than Sn^{2+}ion. In other words, Pb^{4+} ions *i.e.*, PbO_4 is more easily reduced to Pb^{2+} ions than Sn^{4+} ions reduced to Sn^{2+} ions. Thus, PbO_2 acts as a stronger oxidising agent than SnO_2.

(d) Tl^+ is more stable than Tl^{3+} because of inert pair effect.

Q-19 Boron fluoride exists as BF_3 but boron hydride doesn't exist as BH_3. Give reason. In which form does it exist ? Explain its structure.

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



Structure of diborane

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

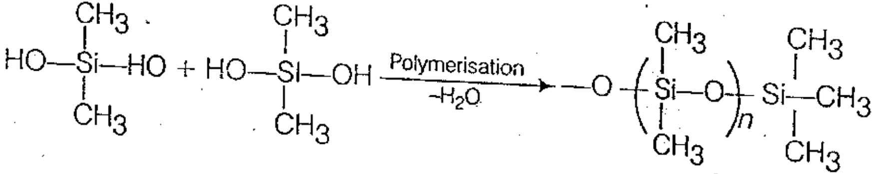
In B_2H_6, four terminal hydrogen atoms and two boron atoms lie in one plane. Above and below this plane there are two bridging H–atoms. The four terminal B—H bonds are regular while the two bridge (B—H—B) bonds are three centre- two electron bonds.

Q-20 (a) What are silicones? State the uses of silicones.

(b) What are boranes ? Give chemical equation for the preparation of diborane.

Ans. (a) Silicones are a group of organosilicon polymers, which have (R_2SiO) as a repeating unit. These may be linear silicones, cyclic silicones and cross-linked silicones. These are prepared by the hydrolysis of alkyl or aryl derivatives of $SiCl_4$ like $RSiCl_3$, R_2SiCl_2 and R_3SiCl and polymerisation of alkyl or aryl hydroxy derivatives obtained by hydrolysis.

$$2CH_3Cl + Si \xrightarrow[570\text{ K}]{\text{Cu powder}} (CH_3)_2SiCl_2 \xrightarrow[+2H_2O,-2HCl]{\text{Hydrolysis}} (CH_3)_2Si(OH)_2$$



$$HO-Si(CH_3)_2-HO + HO-Si(CH_3)_2-OH \xrightarrow[-H_2O]{\text{Polymerisation}} -O\left(-Si(CH_3)_2-O-\right)_n Si(CH_3)_3$$

Silicone

Uses

These are used as sealant, greases, electrical insulators and for water proofing of fabrics. These are also used in surgical and cosmetic plants.

(b) Boron forms a number of covalent hydrides with general formulae $B_n H_{n+4}$ and $B_n H_{n+6}$. These are called boranes. B_2H_6 and B_4H_{10} are the representative compounds of the two series respectively.

Preparation of Diborane

It is prepared by treating boron trifluoride with $LiAlH_4$ in diethyl ether.

$$4BF_3 + 3LiAlH_4 \longrightarrow 2B_2H_6 + 3LiF + 3AlF_3$$

On industrial scale it is prepared by the reaction of BF_3 with sodium hydride.

$$2BF_3 + 6NaH \xrightarrow{450\text{ K}} B_2H_6 + 6NaF$$

The s-Block Elements

SARASWATI CHEMISTRY

Q-1 Metal carbonates decompose on heating to give metal oxide and carbon dioxide. Which of the metal carbonates is most stable thermally?

(a) $MgCO_3$ (b) $CaCO_3$ (c) $SrCO_3$ (d) $BaCO_3$

All the alkaline earth metals form carbonates having general formula MCO_3. *These carbonates decompose on heating to form metal oxide and carbon dioxide.*

$$MCO_3 \rightleftharpoons 1\ MO + CO_2 \qquad [M = Be, Mg, Ca, Sr, Ba]$$

Thermal stability of carbonates increases with increase in atomic number, i.e., on moving down the group

$$BeCO_3 < MgCO_3 < CaCO_3 < SrCO_3 < BaCO_3.$$

Ans. ***(d)*** $BaCO_3$ is thermally most stable because of the small size of resulting oxide ion. With the increase in atomic number, the size of the metal ion, the stability of the metal ion decreases and, hence that of carbonate increases (maximum in case of $BaCO_3$).

Therefore, the increasing size of cation destabilizes the oxides and hence does not favour the decomposition of heavier alkaline earth metal carbonates like $BaCO_3$.

Q-2 The solubility of metal halides depends on their nature, lattice enthalpy and hydration enthalpy of the individual ions. Amongst fluorides of alkali metals, the lowest solubility of LiF in water is due to

(a) ionic nature of lithium fluoride
(b) high lattice enthalpy
(c) high hydration enthalpy for lithium ion
(d) low ionisation enthalpy of lithium atom

Ans. ***(b)*** Solubilities of alkali metal halides in water can be explained in terms of lattice enthalpy and hydration enthalpy. Lower lattice enthalpies and higher hydration enthalpies favour dissolution.

Among fluorides, the order of solubility is $LiF < NaF < KF < RbF < CsF$. Low solubility of LiF is due to very high lattice energy. On moving down in the group LiF to CsF, solubility increases because lattice energy decreases.

Except LiF, other halides of lithium are highly soluble in water.

Q-3 In the synthesis of sodium carbonate, the recovery of ammonia is done by treating NH_4Cl with $Ca(OH)_2$. The by-product obtained in this process is

(a) $CaCl_2$ (b) NaCl (c) NaOH (d) $NaHCO_3$

Ans. ***(a)*** Sodium carbonate is synthesised by Solvay ammonia soda process.

The reactions involved are

$$NH_3 + H_2O + CO_2 \longrightarrow \underset{\text{Ammonium bicarbonate}}{NH_4HCO_3}$$

$$NaCl + NH_4HCO_3 \longrightarrow \underset{\text{Sodium bicarbonate}}{NaHCO_3} \downarrow + NH_4Cl$$

$$2NaHCO_3 \xrightarrow{\Delta} \underset{\text{Sodium carbonate}}{Na_2CO_3} + H_2O + CO_2$$

NH_3 is recovered from NH_4HCO_3 and NH_4Cl formed during the reaction.

$$NH_4HCO_3 \xrightarrow{\text{Heat}} NH_3 + H_2O + CO_2$$

$$\underset{\text{Ammonium chloride}}{2NH_4Cl} + Ca(OH)_2 \longrightarrow \underset{\text{Ammonia}}{2NH_3} + \underset{\text{Calcium chloride}}{CaCl_2} + 2H_2O$$

Q-4 **When sodium is dissolved in liquid ammonia, a solution of deep blue colour is obtained. The colour of the solution is due to**

(a) ammoniated electron

(b) sodium ion

(c) sodium amide

(d) ammoniated sodium ion

Ans. ***(a)*** All alkali metal dissolve in liquid NH_3 giving highly conducting deep blue solution.

$$Na + (x+y)\,NH_3 \longrightarrow \underset{\text{Ammoniated cation}}{[Na\,(NH_3)x]^+} + \underset{\text{Ammoniated electron}}{e(NH_3)_y^-}$$

When light fall on these solutions, the ammoniated electrons excite in higher energy level by absorbing red wavelengths and so transmitted light is blue.

Q-5 **By adding gypsum to cement**

(a) setting time of cement becomes less

(b) setting time of cement increases

(c) colour of cement becomes light

(d) shining surface is obtained

Ans. ***(b)*** Raw materials for cement-limestone, clay, gypsum. Cement is a dirty greyish heavy powder containing calcium aluminates and silicates.

Gypsum ($CaSO_4 \cdot 5H_2O$) is added to the components to increase the setting time of cement so that it gets sufficiently hardened. Setting of cement is an exothermic process and involves hydration of calcium aluminates and silicates.

Q-6 **How do you account for the strong reducing power of lithium in aqueous solution?**

Ans. Strong reducing power of lithium in aqueous solution can be understood in terms of electrode potential. Electrode potential is a measure of the tendency of an element to lose electrons in the aqueous solution. It mainly depends upon the following three factors *i.e.,*

(i) $Li\,(s) \xrightarrow[\text{Enthalpy}]{\text{Sublimation}} Li\,(g)$

(ii) $Li\,(g) \xrightarrow[\text{Enthalpy}]{\text{Ionisation}} Li^+(g) + e^-$

(iii) $Li^+\,(g) + aq \longrightarrow Li^+\,(aq) +$ enthalpy of hydration

With the small size of its ion, lithium has the highest hydration enthalpy. However, ionisation enthalpy of Li is highest among alkali metals but hydration enthalpy predominates over ionisation enthalpy.

Therefore, lithium is the strongest reducing agent in aqueous solution mainly because of its high enthalpy of hydration.

Q-7 **Lithium resembles magnesium in some of its properties. Mention two such properties and give reasons for this resemblance.**

Ans. Lithium resembles with magnesium as its charge size ratio is closer to Mg. Its resemblance with Mg is known as diagonal relationship.

Generally, the periodic properties show either increasing or decreasing trend along the group and *vice-versa* along the period which brought the diagonally situated elements to closer value.

$$\begin{tikzcd} \text{Period} & \text{Group I} & \text{Group II} \\ 2 & \mathrm{Li} \arrow[dr] & \mathrm{Be} \\ 3 & \mathrm{Na} & \mathrm{Mg} \end{tikzcd}$$

Following characteristics can be noted

(i) Due to covalent nature, chlorides of Li and Mg are deliquescent and soluble in alcohol and pyridine.

(ii) Carbonates of Li and Mg decompose on heating and liberate CO_2

$$Li_2CO_3 \longrightarrow Li_2O + CO_2$$
$$MgCO_3 \longrightarrow MgO + CO_2$$

Q-8 Name an element from group 2 which forms an amphoteric oxide and a water soluble sulphate.

Ans. An element from group 2 which forms an amphoteric oxide and a water soluble sulphate is beryllium.

Beryllium forms oxides of formula BeO. All other alkaline earth metal oxides are basic in nature. BeO is amphoteric in nature *i.e.,* it reacts with acids and bases both.

$$Al_2O_3 + 2NaOH \longrightarrow 2NaAlO_2 + H_2O$$
$$Al_2O_3 + 6HCl \longrightarrow 2AlCl_3 + 3H_2O$$

Sulphate of beryllium is a white solid which crystallises as hydrated salts ($BeSO_4 \cdot 4H_2O$).

$BeSO_4$ is fairly soluble in water due to highest hydration energy in the group (small size).

For $BeSO_4$, hydration energy is more than lattice energy and so, they are readily soluble.

Q-9 Discuss the trend of the following

(i) Thermal stability of carbonates of Group 2 elements.

(ii) The solubility and the nature of oxides of Group 2 elements.

Ans. (i) All the alkaline earth melals form carbonates (MCO_3). All these carbonates decompose on heating to give CO_2 and metal oxide. The thermal stability of these carbonates increases down the group *i.e.,* from Be to Ba.

$$BeCO_3 < MgCO_3 < CaCO_3 < SCO_3 < BaCO_3$$

$BeCO_3$ is unstable to the extent that it is stable only in atmosphere of CO_2. These carbonates however show reversible decomposition in closed container.

$$BeCO_3 \rightleftharpoons BeO + CO_2$$

Hence, more is the stability of oxide formed, less will be stability of carbonates. Stability of oxides decreases down the group is beryllium oxide *i.e.,* high stable making $BeCO_3$ unstable.

(ii) All the alkaline earth metals form oxides of formula *MO*. The oxides are very stable due to high lattice energy and are used as refractory material.

Except BeO (predominantly covalent) all other oxides are ionic and their lattice energy decreases as the size of cation increases.

Q-10 Why are $BeSO_4$ and $MgSO_4$ readily soluble in water while $CaSO_4$, $SrSO_4$ and $BaSO_4$ are insoluble?

Ans. The lattice energy of alkaline earth metal sulphates is almost constant due to large size of sulphate ion. Thus, their solubility is decided by hydration energy which decreases on moving down the group.

The greater hydration enthalpies of Be^{2+} and Mg^{2+} ions overcome the lattice enthalpy factor and therefore, their sulphates are soluble in water.

However, hydration enthalpy is low for Ca^{2+}, Sr^{2+} ions and cannot overcome the lattice energy factor. Hence, these are insoluble.

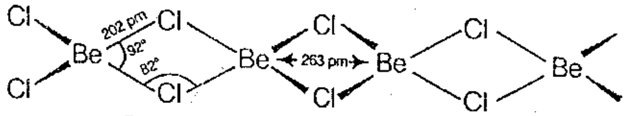
Q-11 Why do beryllium and magnesium not impart colour to the flame in the flame test?

Ans. All alkaline earth metals (except Be and Mg) impart a characteristic colour to the Bunsen flame. The different colours arise due to different energies required for electronic excitation and de-excitation.

Be and Mg atoms due to their small size, bind their electrons more strongly (because of higher effective nuclear charge). Hence, require high excitation energy and are not excited by the energy of the flame with the result that no flame colour is shown by them.

Q-12 What is the structure of $BeCl_2$ molecule in gaseous and solid state?

Ans. Beryllium chloride has different structures in solid and vapour state. In solid state, it exists in the form of polymeric chain structure in which each Be-atom is surrounded by four chlorine atoms having two of the chlorine atoms covalently bonded while the other two by coordinate bonds. The resulting bridge structure contains infinite chains.

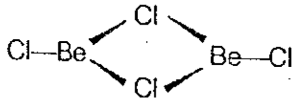


Structure of $BeCl_2$ in solid state

In vapour state, above 1200 K, it exists as a monomer having linear structure and zero dipole moment. But below 1200 K, it exists as dimer structure even in vapour state.

Cl—Be—Cl

Above 1200 K
Monomer



Below 1200 K
Dimer

Q-13 When a metal of group 1 was dissolved in liquid ammonia, the following observations were obtained

(a) Blue solution was obtained initially.

(b) On concentrating the solution, blue colour changed to bronze colour. How do you account for the blue colour of the solution? Give the name of the product formed on keeping the solution for some time.

Ans. (a) The reaction that takes place when alkali metal is dissolved in liquid ammonia is

$$M + (x + y)\,NH_3 \longrightarrow [M\,(NH_3)_x]^+ + [(NH_{3)y}]^-e$$

The blue colour of the solution is due to the presence of ammoniated electron which absorb energy in the visible region of light and thus, impart blue colour to the solution.

(b) In concentrated solution, the blue colour changes to bronze colour due to the formation of metal ion clusters. The blue solution on keeping for some time liberate hydrogen slowly with the formation of amide.

$$\underset{\text{Ammoniacal}}{M^+ + e^-} + NH_3 \longrightarrow \underset{\text{Amide}}{MNH_2} + \frac{1}{2}H_2$$

Q-14 The stability of peroxide and superoxide of alkali metals increase as we go down to group. Explain giving reason.

Ans. The stability of peroxide or superoxide increases as the size of metal ion increases *i.e.*,

$$KO_2 < RbO_2 < CsO_2$$

The reactivity of alkali metals toward oxygen to form different oxides is due to strong positive field around each alkali metal cation. Li^+ is the smallest, it does not allow O^{2-} ion to react with O_2 further. Na^+ is larger than Li, its positive field is weaker than Li^+. It cannot prevent the conversion of O^{2-} into O_2^{2-}.

The largest K^+, Rb^+ and Cs^+ ions permit O_2^{2-} ion to react with O_2 forming superoxide ion O_2^-.

$$\underset{\text{Oxide}}{O_2^{2-}} \xrightarrow{\frac{1}{2}O_2} \underset{\text{Peroxide}}{O^{2-}} \xrightarrow{O_2} \underset{\text{Superoxide}}{2O_2^-}$$

Futhermore, increased stability of the peroxide or superoxide with increase in the size of metal ion is due to the stabilisation of large anions by larger cations through lattice energy effect.

Q-15 When water is added to compound (*A*) of calcium, solution of compound (*B*) is formed. When carbon dioxide is passed into the solution, it turns milky due to the formation of compound (*C*). If excess of carbon dioxide is passed into the solution milkiness disappears due to the formation of compound (*D*). Identify the compounds *A*, *B*, *C* and *D*. Explain why the milkiness disappears in the last step.

Ans. Appearance of milkiness on passing CO_2 in the solution of compound *B* indicates that compound *B* is lime water and compound *C* is $CaCO_3$. Since, compound *B* is obtained by adding H_2O to compound *A*, therefore, compound *A* is quicklime, CaO.

The reactions are as follows

(i)
$$\underset{\substack{\text{Calcium}\\ \text{oxide}\\ (A)}}{CaO} + H_2O \longrightarrow \underset{\substack{\text{Lime water}\\ (B)}}{Ca(OH)_2}$$

(ii)
$$\underset{(B)}{Ca(OH)_2} + CO_2 \longrightarrow \underset{\substack{\text{Calcium carbonate}\\ \text{(Milkiness)}}}{CaCO_3} + \underset{(C)}{H_2O}$$

(iii) When excess of CO_2 is passed, milkiness disappears due to the formation of soluble calcium bicarbonate (*D*).

$$\underset{\substack{\text{Milkiness}\\ (C)}}{CaCO_3} + CO_2 + H_2O \longrightarrow \underset{\substack{\text{Calcium bicarbonate}\\ \text{(Soluble in } H_2O)\\ (D)}}{Ca(HCO_3)_2}$$

Q-16 Lithium hydride can be used to prepare other useful hydrides. Beryllium hydride is one of them. Suggest a route for the preparation of beryllium hydride starting from lithium hydride. Write chemical equations involved in the process.

Ans. BeH_2 can be prepared from the corresponding halides by the reduction with complex alkali metal hydrides such as lithium aluminium hydride $LiAlH_4$.

$$8LiH + Al_2Cl_6 \longrightarrow 2LiAlH_4 + 6LiCl$$
$$2BeCl_2 + LiAlH_4 \longrightarrow 2BeH_2 + LiCl + AlCl_3$$

Hydrogen

Q-1 Metal hydrides are ionic, covalent or molecular in nature. Among LiH, NaH, KH, RbH, CsH, the correct order of increasing ionic character is

(a) LiH > NaH > CsH > KH > RbH
(b) LiH < NaH < KH < RbH < CsH
(c) RbH > CsH > NaH > KH > LiH
(d) NaH > CsH > RbH > LiH > KH

Ans. ***(b)*** Metal hydrides are ionic, covalent or molecular in nature. Ionic character increases as the size of the atom increases or the electronegativity of the atom decreases. The correct order of increasing ionic character is

LiH < NaH < KH < RbH < CsH

Q-2 Consider the reactions

(i) $H_2O_2 + 2HI \longrightarrow I_2 + 2H_2O$

(ii) $HOCl + H_2O_2 \longrightarrow H_3O^+ + Cl^- + O_2$

Which of the following statements is correct about H_2O_2 with reference to these reactions? Hydrogen peroxide is ....

(a) an oxidising agent in both (i) and (ii)
(b) an oxidising agent in (i) and reducing agent in (ii)
(c) a reducing agent in (i) and oxidising agent in (ii)
(d) a reducing agent in both (i) and (ii)

(i) Reducing agents are those substance (atoms, ions or molecules) which can readily lose electrons to other substance.

(ii) Oxidising agents are those substance (atoms, ions or molecules) which can readily accept electrons from other substance.

Ans. ***(b)***

Reduction

(i) $H_2O_2^{-1} + 2HI^{-1} \longrightarrow I_2^0 + 2H_2O^{-2}$

Oxidation

Thus, here H_2O_2 oxidises HI into I_2 hence, it behaves as oxidising agent.

Reduction

(ii) $HOCl^{+1} + H_2O_2^{-1} \longrightarrow H_3O^+ + Cl^- + H_2O_2^0$

Oxidation

Here, H_2O_2 reduces HOCl to Cl^{-1}, thus, it acts as reducing agent.

Q-3 Which of the following reactions increases production of dihydrogen from synthesis gas?

(a) $CH_4(g) + H_2O(g) \xrightarrow[Ni]{1270\,K} CO(g) + 3H_2(g)$

(b) $C(s) + H_2O(g) \xrightarrow{1270\,K} CO(g) + H_2(g)$

(c) $CO(g) + H_2O(g) \xrightarrow[\text{Catalyst}]{673\text{ K}} CO_2(g) + H_2(g)$

(d) $C_2H_6 + 2H_2O \xrightarrow[\text{Ni}]{1270\text{ K}} 2CO + 5H_2$

Ans. ***(c)*** The process of producing syn gas or synthesis gas from coal is called 'coal gasification'.

$$\underset{\text{Coal}}{C(s)} + \underset{\text{Steam}}{H_2O(g)} \xrightarrow[\text{Ni}]{1270\text{ K}} \underbrace{CO(g) + H_2(g)}_{\text{Syn gas}}$$

The production of hydrogen can be increased by reacting carbon monoxide of the syn gas with steam in the presence of iron chromate as a catalyst at 673 K.

$$CO(g) + H_2O(g) \xrightarrow{FeCrO_4,\ 673\text{ K}} CO_2(g) + H_2(g)$$

CO_2 is removed by scrubbing with a solution of sodium arsenite.

Q-4 Which of the following compounds is used for water softening?

(a) $Ca_3(PO_4)_2$ (b) Na_3PO_4 (c) $Na_6P_6O_{18}$ (d) Na_2HPO_4

Ans. ***(c)*** For water softening, sodium hexametaphosphate is used. The chemical formula is $Na_2[Na_4(PO_3)_6] = Na_6P_6O_{18}$. The trade name is calgon.

$$\underset{\text{(From hard water)}}{2CaCl_2} + \underset{\text{Sodium hexametaphosphate}}{Na_2[Na_4(PO_3)_6]} \rightarrow \underset{\text{Complex salt (soluble)}}{Na_2[Ca_2(PO_3)_6]} + 4NaCl$$

Q-5 Dihydrogen can be prepared on commercial scale by different methods. In its preparation by the action of steam on hydrocarbons, a mixture of CO and H_2 gas is formed. It is known as ....

(a) water gas (b) syn gas (c) producer gas (d) industrial gas

Ans. ***(a, b)***

Dihydrogen can be prepared on commercial scale by different methods. Reaction of steam on hydrocarbons or coke at high temperatures in the presence of catalyst yield hydrogen.

$$C_nH_{2n+2} + nH_2O + 2 \xrightarrow[\text{Ni}]{1270\text{ K}} nCO_2 + (2n+1)H_2$$

e.g.,

$$CH_4(g) + H_2O(g) \xrightarrow[\text{Ni}]{1270\text{ K}} CO(g) + 3H_2(g)$$

The mixture of CO and H_2 is called water gas. As this mixture of CO and H_2 is used for the synthesis of methanol and a number of hydrocarbons, it is also called synthesis gas or 'syn gas'.

Q-6 What are metallic/interstitial hydrides? How do they differ from molecular hydrides?

Ans. Metallic/interstitial hydrides are formed by many *d*-block and *f*-block elements. These hydrides conduct heat and electricity.

Unlike saline hydride, they are almost always non-stoichiometric, being deficient in hydrogen. *e.g.*, $LaH_{2.87}$, $YbH_{2.55}$, $TiH_{1.5-1.8}$, $ZrH_{1.3-1.75}$, $VH_{0.56}$, $NiH_{0.6-0.7}$, $PdH_{0.6-0.8}$ etc. In such hydrides, the law of constant composition does not hold good.

Comparision between molecular and metallic hydrides

Molecular hydrides	**Metallic hydrides**
These are mainly formed by *p*-block elements and some *s*-block elements (Be and Mg).	These are formed by group 3, 4, 5 (Sc, Ti, V, Y, Zr, Nb, La, Hf, Ta, Ac etc.,) 10, 11, 12 (Pd, Cu, Zn etc.,) and *f*-block elements (Ce, Eu, Yb, Th, U etc.)
Those are usually volatile compounds having low melting and boiling point.	These are hard, have a metallic lustre.
It conduct electricity.	These do not conduct electricity.

Q-7 Give reasons

(i) Lakes freeze from top towards bottom.

(ii) Ice floats on water.

Ans. (i) Density of ice is less than that of liquid water. During severe winter, the temperature of lake water keeps on decreasing. Since, cold water is heavier, therefore, it moves towards bottom of the lake and warm water from the bottom moves towards surface. This process continues. The density of water is maximum at 277 K.

Therefore, any further decrease in temperature of the surface water will decrease in density. The temperature of surface water keeps on decreasing and ultimately it freezes.

Thus, the ice layer at lower temperature floats over the water below it. Due to this, freezing of water into ice takes place continuously from top towards bottom.

(ii) Density of ice is less than that of liquid water, so it floats over water.

Q-8 Discuss briefly de-mineralisation of water by ion exchange resin.

Ans. Water which is free from all soluble minerals salts is called demineralised water. Demineralised water is obtained by passing water successively through a cation exchange and an anion exchange resins.

In cation exchanger, Ca^{2+}, Mg^{2+}, Na^+ and other cations present in water are removed by exchanging them with H^+ ions while in anion exchanger, Cl^-, HCO_3^-, SO_4^{2-}, etc., present in water are removed by exchanging them with OH^- ions.

$$\underset{\text{(Released in cation exchanger)}}{H^+} + \underset{\text{(Released in anion exchanger)}}{OH^-} \longrightarrow H_2O$$

Synthetic ion exchange resins are of two types.

Cation exchange resins contain large organic molecule with SO_3H group and are water soluble. It is changed to *R*Na by treating it with NaCl. The resin *R*Na exchanges Mg^{2+} and Ca^{2+} ions present in hard water to make the water soft.

$$2RNa(s) + M^{2+}(aq) \longrightarrow R_2M(s) + 2Na^+(aq) \quad (M = Ca^{2+} \text{ or } Mg^{2+})$$

The resin can be regenerated by passing NaCl (aqueous solution) in it.

Pure demineralised (deionised) water is obtained by passing water successively through a cation exchange and anion exchange resins. In the cation exchange process,

$$\underset{\substack{\text{(Cation exchange}\\ \text{resin in the } H^+ \text{ form)}}}{2RH(s)} + M^{2+}(aq) \rightleftharpoons MR_2(s) + 2H^+(aq)$$

H^+ exchanges for Ca^{2+}, Mg^{2+} and other cations present in water.

This process results in proton release and thus, makes the water acidic. In the anion exchange process

$$RNH_2(s) + H_2O(l) \rightleftharpoons R\overset{+}{N}H_3 \cdot OH^-(s)$$

$R\overset{+}{N}H_3 \cdot OH^-$ is substituted ammonium hydroxide anion exchange resin.

$$R\overset{+}{N}H_3 \cdot OH^-(s) + X^-(aq) \rightleftharpoons R\overset{+}{N}H_3 \cdot X^-(s) + OH^-(aq)$$

Q-9 Calculate the strength of 5 volumes H_2O_2 solution.

Ans. By definition, 5 volumes H_2O_2 solution means that 1 L of this H_2O_2 solution on decomposition produces 5 L of O_2 at STP.

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$
$$\underline{2 \times 34\text{ g} \longrightarrow 22.7\text{ L at STP}}$$

If 22.7 L O_2 at STP will be obtained from $H_2O_2 = 68$ g

$\therefore$ 5 L of O_2 at STP will be obtained from $H_2O_2 = \frac{68 \times 5}{22.7}$ g $= 14.98 = 15$ g

$\therefore$ Strength of H_2O_2 in 5 volume H_2O_2 solution $= 15\text{ g L}^{-1}$.

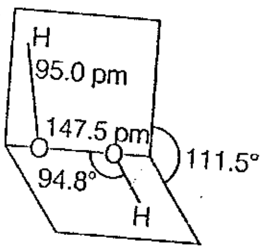
$\Rightarrow$ Percentage strength of H_2O_2 solution $= \frac{15}{1000} \times 100 = 1.5\%$

Therefore, strength of H_2O_2 in 5 volume H_2O_2 solution $= 15$ g/L $= 1.5\%\,H_2O_2$ solution.

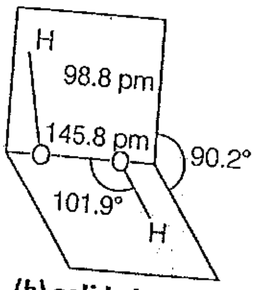
Q-10 (i) Draw the gas phase and solid phase structure of H_2O_2.

(ii) H_2O_2 is a better oxidising agent than water. Explain.

Ans. (i) H_2O_2 has a non-planar structure. *The molecular dimensions in the gas phase and solid phase are given below*



(a) gas phase



(b) solid phase

(a) H_2O_2 structure in gas phase, dihedral angle is 111.5°.

(b) H_2O_2 structure in solid phase at 110 K, dihedral angle is 90.2°.

(ii) H_2O_2 is better oxidising agent than water as discussed below

(a) H_2O_2 oxidises an acidified solution of KI to give I_2 which gives blue colour with starch solution but H_2O does not.

$$2KI + H_2SO_4 + H_2O_2$$
$$K_2SO_4 + 2H_2O + I_2$$

(b) H_2O_2 turns black PbS to white $PbSO_4$ but H_2O does not.

$$PdS + 4H_2O_2 \rightarrow PbSO_4 + 4H_2O.$$

Q-11 Explain why HCl is a gas and HF is a liquid?

Ans. F is smaller and more electronegative than Cl, so it forms stronger H-bonds as compared to Cl. As the consequence, more energy is needed to break the H-bonds in HF than HCl and hence the boiling point of HF is higher than that of HCl. That's why HF is liquid and HCl is a gas.

Q-12. Give reasons why hydrogen resembles alkali metals?

Ans. *Hydrogen resembles alkali metals, i.e.,* Li, Na, K, Rb, Cs *and* Fr *of* group I *of the periodic table in the following respects*

(i) Like alkali metals, hydrogen also contain one electron in its outermost (valence) shell and exhibit +1 oxidation state.

(ii) Like alkali metals, hydrogen also loses its only electron to form hydrogen ion, *i.e.*, H^+ (proton).

(iii) Like alkali metals, hydrogen combines with electronegative elements (non-metals) such as oxygen, halogens and sulphur forming their oxides, halides and sulphides respectively.

(iv) Like alkali metals, hydrogen also acts as a strong reducing agent.

Q-13. Why is water molecule polar?

Ans. Oxygen is more electronegative (EN=3.5) than hydrogen (EN = 2.1) hence, O — H bond is polar. In the water molecule, two polar O — H bonds are present which are held together at an angle of 104.5°. Due to the resultant of these two dipoles, water molecule is polar and has an dipole moment of 1.84 Debye.

Q-14 Why is hydrogen peroxide stored in wax lined bottles?

Ans. Hydrogen peroxide is decomposed by rough surfaces of glass, alkali oxides present in it and light to form H_2O and O_2.

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

To prevent this decomposition, hydrogen peroxide is usually stored in paraffin wax coated plastic or teflon bottles.

Q-15; Why does hard water not form lather with soap?

Ans. Hard water contains salts of calcium and magnesium ions. Hard water does not give lather with soap and forms scum/precipitate with soap. Soap containing sodium stearate ($C_{17}H_{35}COONa$) reacts with hard water to precipitate out as Ca/Mg stearate.

$$2C_{17}H_{35}COONa\,(aq) + M^{2+}\,(aq) \longrightarrow (C_{17}H_{35}COO)_2M \downarrow + 2Na^+\,(aq)$$

It is therefore, unsuitable for laundry. (where, *M* is Ca/Mg)

Q-16 (i) Give a method for the manufacture of hydrogen peroxide and explain the reactions involved therein.

(ii) Illustrate oxidising, reducing and acidic properties of hydrogen peroxide with equations.

Ans. (i) H_2O_2 is industrially manufactured by the auto-oxidation of 2alkylanthraquinols

$$\text{2-ethylanthraquinol} \underset{H_2/Pd}{\overset{O_2/(air)}{\rightleftharpoons}} H_2O_2 + \text{Oxidised product}$$

In this case, 1% H_2O_2 is formed. It is extracted with water and concentrated to ~ 30% (by mass) by distillation under reduced pressure. It can be further concentrated to ~ 85% by careful distillation under low pressure. The remaining water can be frozen out to obtain pure H_2O_2.

(ii) H_2O_2 acts as an oxidising as well as reducing agent in both acidic and alkaline media.
Following reactions are described below

(a) Oxidising action in acidic medium

$$2Fe^{2+}\ (aq) + 2H^+\ (aq) + H_2O_2\ (aq) \longrightarrow 2Fe^{3+}\ (aq) + 2H_2O\ (l)$$

$$PbS\ (s) + 4H_2O_2\ (aq) \longrightarrow PbSO_4\ (s) + 4H_2O\ (l)$$

(b) Reducing action in acidic medium

$$2MnO_4^- + 6H^+ + 5H_2O_2 \longrightarrow 2Mn^{2+} + 8H_2O + 5O_2$$

$$HOCl + H_2O_2 \longrightarrow H_3O^+ + Cl^- + O_2$$

(c) Oxidising action in basic medium

$$2Fe^{2+} + H_2O_2 \longrightarrow 2Fe^{3+} + 2OH^-$$

$$Mn^{2+} + H_2O_2 \longrightarrow Mn^{4+} + 2OH^-$$

(d) Reducing action in basic medium

$$I_2 + H_2O_2 + 2OH^- \longrightarrow 2I^- + 2H_2O + O_2$$

$$2MnO_4 + 3H_2O_2 \longrightarrow 2MnO_2 + 3O_2 + 2H_2O + 2OH^-$$

SARASWATI CHEMISTRY

Redox Reactions

Q-1 Which of the following arrangements represent increasing oxidation number of the central atom ?

(a) $CrO_2^-, ClO_3^-, CrO_4^{2-}, MnO_4^-$ (b) $ClO_3^-, CrO_4^{2-}, MnO_4^-, CrO_2^-$

(c) $CrO_2^-, ClO_3^-, MnO_4^-, CrO_4^{2-}$ (d) $CrO_4^{2-}, MnO_4^-, CrO_2^-, ClO_3^-$

Ans. *(a)* Writing the oxidation number (O.N.) of Cr, Cl and Mn on each species in the four set of ions, then,

(a) $\overset{+3}{Cr}O_2^-, \overset{+5}{Cl}O_3^-, \overset{+6}{Cr}O_4^{2-}, \overset{+7}{Mn}O_4^-$ (b) $\overset{+5}{Cl}O_3^-, \overset{+6}{Cr}O_4^{2-}, \overset{+7}{Mn}O_4^-, \overset{+3}{Cr}O_2^-$

(c) $\overset{+3}{Cr}O_2^-, \overset{+5}{Cl}O_3^-, \overset{+7}{Mn}O_4^-, \overset{+6}{Cr}O_4^{2-}$ (d) $\overset{+6}{Cr}O_4^{2-}, \overset{+7}{Mn}O_4^-, \overset{+3}{Cr}O_2^-, \overset{+5}{Cl}O_3^{3-}$

Only in the arrangement (a), the O.N. of central atom increases from left to right, therefore, option (a) is correct.

Q-2 The largest oxidation number exhibited by an element depends on its outer electronic configuration. With which of the following outer electronic configurations the element will exhibit largest oxidation number?

(a) $3d^1 4s^2$ (b) $3d^3 4s^2$ (c) $3d^5 4s^1$ (d) $3d^5 4s^2$

Ans. *(d)* Highest oxidation number of any transition element = $(n-1)d$ electrons + ns electrons. Therefore, large the number of electrons in the $3d$-orbitals, higher is the maximum oxidation number.

(a) $3d^1 4s^2 = 3$ (b) $3d^3 4s^2 = 3 + 2 = 5$

(c) $3d^5 4s^1 = 5 + 1 = 6$ and (d) $3d^5 4s^2 = 5 + 2 = 7$

Thus, option (d) is correct.

Q-3 Identify disproportionation reaction

(a) $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$

(b) $CH_4 + 4Cl_2 \longrightarrow CCl_4 + 4HCl$

(c) $2F_2 + 2OH^- \longrightarrow 2F^- + OF_2 + H_2O$

(d) $2NO_2 + 2OH^- \longrightarrow NO_2^- + NO_3^- + H_2O$

Ans. *(d)* Reactions in which the same substance is oxidised as well as reduced are called disproportionation reactions. Writing the O.N. of each element above its symbol in the given reactions

(a) $\overset{-4}{C}\overset{+1}{H}_4 + 2\overset{0}{O}_2 \longrightarrow \overset{+4}{C}\overset{-2}{O}_2 + 2\overset{+1}{H}_2\overset{-2}{O}$

(b) $\overset{-4}{C}\overset{+1}{H}_4 + 4\overset{0}{Cl}_2 \longrightarrow \overset{+4}{C}\overset{-1}{Cl}_4 + 4\overset{+1}{H}\overset{-1}{Cl}$

(c) $2\overset{0}{F}_2 + 2\overset{-2}{O}\overset{+1}{H} \longrightarrow 2\overset{-1}{F}^- + \overset{+2}{O}\overset{-1}{F}_2^- + \overset{+1}{H}_2\overset{-2}{O}$

(d) $2\overset{+4}{N}\overset{-2}{O}_2 + 2\overset{-2}{O}\overset{+1}{H}^- \longrightarrow \overset{+3}{N}\overset{-2}{O}_2^- + \overset{+5}{N}\overset{-2}{O}_3^- + \overset{+1}{H}_2\overset{-2}{O}$

Thus, in reaction (d), N is both oxidised as well as reduced since the O.N. of N increases from +4 in NO_2 to +5 in NO_3^- and decreases from +4 in NO_2 to +3 in NO_2^-.

Q-5 Which of the following elements does not show disproportionation tendency ?

(a) Cl (b) Br (c) F (d) I

Ans. ***(c)*** Being the most electronegative element, F can only be reduced and hence it always shows an oxidation number of –1. Further, due to the absence of *d*-orbitals it cannot be oxidised and hence it does not show positive oxidation numbers.

In other words, F cannot be oxidised as well as reduced simultaneously and hence does not show disproportionation reactions.

Q-6 Identify the correct statements with reference to the given reaction

$$P_4 + 3OH^- + 3H_2O \longrightarrow PH_3 + 3H_2PO_2^-$$

(a) Phosphorus is undergoing reduction only

(b) Phosphorus is undergoing oxidation only

(c) Phosphorus is undergoing oxidation as well as reduction

(d) Hydrogen is undergoing neither oxidation nor reduction

Ans. ***(c, d)***

Write the O.N. of each element above its symbol, then

$$\overset{0}{P_4} + 3\overset{-2}{O}\overset{+1}{H^-} + 3\overset{+1}{H_2}\overset{-2}{O} \rightarrow \overset{-3}{P}\overset{+1}{H_3} + 3\overset{+1}{H_2}\overset{+1}{P}O_2^-$$

In this reaction, O.N. of P increases from 0 in P_4 to +1 in $H_2PO_2^-$ and decreases to – 3 in PH_3, therefore, P undergoes both oxidation as well as reduction. Thus, options (a) and (b) are wrong and option (c) is correct.

Further, O.N. of H remains +1 in all the compounds, *i.e.*, H neither undergoes oxidation nor reduction. Thus, option (d) is correct.

Q-7 Which of the following electrodes will act as anodes, which connected to Standard Hydrogen Electrode ?

(a) Al/Al^{3+} $E^\ominus = -1.66$

(b) Fe/Fe^{2+} $E^\ominus = -0.44$

(c) Cu/Cu^{2+} $E^\ominus = +0.34$

(d) $F_2\,(g)/2F^-\,(aq)$ $E^\ominus = 02.87$

Ans. ***(a, b)***

All electrodes which have negative electrode potentials are stronger reducing agents than H_2 gas and hence acts as anodes when connected to standard hydrogen electrode. Thus, Al^{3+}/Al ($E^\ominus = -1.66$ V) and Fe^{2+}/Fe ($EE^\ominus = -0.44$ V) act as anode.

Q-8 The reaction $Cl_2(g) + 2OH^-(aq) \rightarrow ClO^-(aq) + Cl^-(aq) + H_2O(l)$ represents the process of bleaching. Identify and name the species that bleaches the substances due to its oxidising action.

Write the oxidation number of each element above its symbol. and then identify the bleaching reagent by observing the change in oxidation number.

Ans. $\overset{0}{Cl_2}(g) + 2\overset{-2}{O}\overset{+1}{H^-}(aq) \rightarrow \overset{+1}{Cl}\overset{-2}{O^-}(aq) + \overset{-1}{Cl^-}(aq) + \overset{+1}{H_2}\overset{-2}{O}(l)$

In this reaction, O.N. of Cl increases from 0 (in Cl_2) to 1 (in ClO^-) as well as decreases from 0 (in Cl_2) to –1 (in Cl^-). So, it acts both reducing as well as oxidising agent. This is an example of disproportionation reaction. In this reaction, ClO^- species bleaches the substances due to its oxidising action. [In hypochlorite ion (ClO^-) Cl can decrease its oxidation number from +1 to 0 or –1.]

Note *Disproportionation reactions are a special type of redox reactions. In which an element in one oxidation state is simultaneously oxidised and reduced.*

Q-9 MnO_4^{2-} undergoes disproportionation reaction in acidic medium but MnO_4^- does not. Give reason.

Ans. In MnO_4^{2-}, the oxidation number of Mn is +6. It can increase its oxidation number (to + 7) or decrease its oxidation number (to + 4, + 3, + 2, 0).
Hence, it undergoes disproportionation reaction in acidic medium.

$$3\overset{+6}{Mn}O_4^{2-} + 4H^+ \longrightarrow 3\overset{+7}{Mn}O_4^- + \overset{+4}{Mn}O_2 + 2H_2O$$

O.N. increases by 1 per atom (oxidation)

O.N. decreases by 2 per atom (reduction)

In MnO_4^-, Mn is in its highest oxidation state, *i.e.*, +7. It can only decrease its oxidation number. Hence, it cannot undergo disproportionation reaction.

Q-10 PbO and PbO_2 react with HCl according to following chemical equations

$$2PbO + 4HCl \longrightarrow 2PbCl_2 + 2H_2O$$
$$PbO_2 + 4HCl \longrightarrow PbCl_2 + Cl_2 + 2H_2O$$

Why do these compounds differ in their reactivity ?

Ans. *Writing the oxidation number of each element above its symbol in the following reactions*

(a) $$\underset{\text{Basic oxide}}{2\overset{+2}{Pb}\overset{-2}{O}} + \underset{\text{Acid}}{4\overset{+1}{H}\overset{-1}{Cl}} \longrightarrow 2\overset{+2}{Pb}\overset{-1}{Cl}_2 + 2\overset{+1}{H}_2\overset{-2}{O}$$

In this reaction, oxidation number of each element remains same hence, it is not a redox reaction. In fact, it is an example of **acid-base reaction.**

(b) $$\overset{+4}{Pb}\overset{-2}{O}_2 + 4\overset{+1}{H}\overset{-1}{Cl} \longrightarrow \overset{+2}{Pb}\overset{-1}{Cl}_2 + \overset{0}{Cl}_2 + 2\overset{+1}{H}_2\overset{-2}{O}$$

In PbO_2, Pb is in +4 oxidation state. Due to inert pair effect Pb in +2 oxidation state is more stable. So, Pb in +4 oxidation state (PbO_2) acts as an oxidising agent. It oxidises Cl^- to Cl_2 and itself gets reduced to Pb^{2+}.

$$\underset{\text{O.A.}}{\overset{+4}{Pb}\overset{-2}{O}_2} + \underset{\text{R.A.}}{4\overset{+1}{H}\overset{-1}{Cl}} \longrightarrow \overset{+2}{Pb}\overset{-1}{Cl}_2 + \overset{0}{Cl}_2 + 2\overset{+1}{H}_2\overset{-2}{O}$$

O.N. decreases by 2 per atom

O.N. increases by 1 per atom

Q-11 Write balanced chemical equation for the following reactions.

(a) Permanganate ion (MnO_4^-) reacts with sulphur dioxide gas in acidic medium to produce Mn^{2+} and hydrogen sulphate ion.
(Balance by ion electron method)

(b) Reaction of liquid hydrazine (N_2H_4) with chlorate ion (ClO_3^-) in basic medium produces nitric oxide gas and chloride ion in gaseous state.
(Balance by oxidation number method)

(c) Dichlorine heptaoxide (Cl_2O_7) in gaseous state combines with an aqueous solution of hydrogen peroxide in acidic medium to give chlorite ion (ClO_2^-) and oxygen gas.
(Balance by ion electron method)

Ans. (a) **Ion electron method** Write the skeleton equation for the given reaction.
$MnO_4^-\ (aq) + SO_2(g) \longrightarrow Mn^{2+}(aq) + HSO_4^-\ (aq)$

Find out the elements which undergo change in O.N.

O.N. of Mn decreases by 5

$$2\overset{+7}{Mn}O_4^-\ (aq) + \overset{+4}{S}O_2\ (g) \longrightarrow \overset{2+}{Mn}\ (aq) + H\overset{+6}{S}O_4^-\ (aq)$$

O.N. of Sincreases by 2

Divide the given skeleton into two half equations.

Reduction half equation : $MnO_4^-(aq) \longrightarrow Mn^{2+}(aq)$

Oxidation half equation : $SO_2(g) \longrightarrow HSO_4^-(aq)$

To balance reduction half equation

In acidic medium, balance H and O-atoms

$$MnO_4^-\ (aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + H_2O\ (l)$$

To balance the complete reaction

$$2MnO_4\ \ (aq) + 16H^+(aq) + 10e^- \longrightarrow Mn^{2+}(aq) + 8H_2O\ (l)$$

$$\underline{5SO_2\ \ (g) + 10\ H_2O(l) \longrightarrow 5HSO_4^-(aq) + 15H^+(aq) + 10e^-}$$

$$2MnO_4^-(aq) + 5SO_2(g) + 2H_2O(l) + H^+(aq) \rightarrow 2Mn^{2+}(aq)\ + 5HSO_4^-(aq)$$

(b) **Oxidation number method** Write the skeleton equation for the given reaction.

$$N_2H_4\ (l) + ClO_3^-(aq) \longrightarrow NO(g) + Cl^-\ (g)$$

O.N. increases by 4 per N-atom

$$\overset{-2}{N_2}H_4(l) + \overset{+5}{Cl}O_3^-\ (aq) \longrightarrow \overset{+2}{N}O\ (g) + \overset{-1}{Cl}\ {}^-(aq)$$

O.N. decreases by 6 per Cl-atom

Multiply NO by 2 because in N_2H_4 there are 2N atoms

$$N_2H_4(l) + ClO_3^-(aq) \longrightarrow 2NO(g) + Cl^-(aq)$$

Total increase in O.N. of N $= 2 \times 4 = 8$ ($8e^-$ lost)

Total decrease in O.N. of Cl $= 1 \times 6 = 6$ ($6e^-$ gain)

Therefore, to balance increase or decrease in O.N. multiply N_2H_4 by 3, 2NO by 3 and ClO_3^-, Cl^- by 4

$$3N_2H_4(l) + 4ClO_3^-(aq) \longrightarrow 6NO(g) + 4Cl^-(aq)$$

Balance O and H-atoms by adding $6H_2O$ to RHS

$$3N_2H_4(l)\ +\ 4ClO_3^-(aq) \longrightarrow 6NO(g)\ +\ 4Cl^-(aq)\ +\ 6H_2O(l)$$

(c) **Ion electron method** Write the skeleton equation for the given reaction.

$$Cl_2O_7(g)\ + H_2O_2(aq) \longrightarrow ClO_2^-(aq) + O_2(g)$$

Find out the elements which undergo a change in O.N.

O. N. of Cl decreases by 4 per Cl-atom

$$\overset{+7}{Cl_2}\overset{-7}{O_7}(g) + \overset{+1}{H_2}\overset{-1}{O_2}\ (aq) \longrightarrow \overset{+3}{Cl}\overset{-2}{O_2^-}(aq) + O_2\ (g)$$

O.N. of O increases by 1per O-atom

Divide the given skeleton equation into two half equations.

Reduction half equation : $Cl_2O_7 \longrightarrow ClO_2^-$

Oxidation half equation : $H_2O_2 \longrightarrow O_2$

To balance the reduction half equation

$$Cl_2O_7(g) + 6H^+(aq) + 8e^- \longrightarrow 2ClO_2^-(aq) + 3H_2O(l)$$

To balance the oxidation half equation

$$H_2O_2(aq) \longrightarrow O_2(g) + 2H^+ + 2e^-$$

To balance the complete reaction

$$Cl_2O_7\ (g) + 6H^+\ (aq) + 8e^- \longrightarrow 2ClO_2^-(aq) + 3H_2O\ (l)$$

$$4H_2O_2(aq) \longrightarrow 4O_2(g) + 8H^+\ (aq) + 8e^-$$

$$Cl_2O_7\ (g) + 4H_2O_2\ (aq) \longrightarrow 2ClO_2^-\ (aq) + 3H_2O\ (l) + 4O_2(g) + 2H^+ + (aq)$$

This represents the balanced redox reaction.

Q-12 Calculate the oxidation number of phosphorus in the following species.

(a) HPO_3^{2-} (b) PO_4^{3-}

Ans. (a) Suppose that the O.N. of P in HPO_3^{2-} be x.

Then, $1 + x + 3(-2) = -2$

or, $x + 1 - 6 = -2$

or, $x = +3$

(b) Suppose that the O.N. of P in PO_4^{3-} be x.

Then, $x + 4(-2) = -3$

or, $x - 8 = -3$

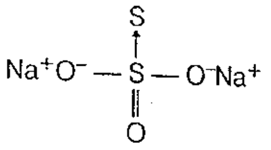
or, $x = +5$

Q-13 Calculate the oxidation number of each sulphur atom in the following compounds.

(a) $Na_2S_2O_3$ (b) $Na_2S_4O_6$ (c) Na_2SO_3 (d) Na_2SO_4

Ans. *The oxidation number of each sulphur atom in the following compounds are given below*

(a) **$Na_2S_2O_3$** Let us consider the structure of $Na_2S_2O_3$.



$$\mathrm{Na^+O^- - \underset{\overset{\|}{O}}{\overset{\overset{S}{\uparrow}}{S}} - O^-Na^+}$$

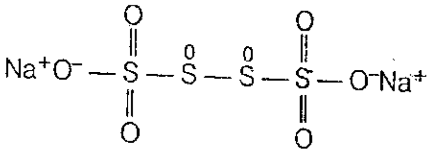
There is a coordinate bond between two sulphur atoms. The oxidation number of acceptor S-atom is –2. Let, the oxidation number of other S-atom be x.

$$\underbrace{2(+1)}_{\text{For Na}} + \underbrace{3 \times (-2)}_{\text{For O–atoms}} + x + \underbrace{1(-2)}_{\text{For coordinate S-atom}} = 0$$

$$x = +6$$

Therefore, the two sulphur atoms in $Na_2S_2O_3$ have –2 and +6 oxidation number.

(b) **$Na_2S_4O_6$** Let us consider the structure of $Na_2S_4O_6$.



$$\mathrm{Na^+O^- - \underset{\overset{\|}{O}}{\overset{\overset{O}{\|}}{S}} - \overset{0}{S} - \overset{0}{S} - \underset{\overset{\|}{O}}{\overset{\overset{O}{\|}}{S}} - O^-Na^+}$$

In this structure, two central sulphur atoms have zero oxidation number because electron pair forming the S—S bond remain in the centre. Let, the oxidation number of (remaining S-atoms) S-atom be x.

$$\underset{\text{For Na}}{2(+1)}+\underset{\text{For O}}{6(-2)}+2x+2(0)=0$$

$$2-12+2x=0 \text{ or } x=+\frac{10}{2}=+5$$

Therefore, the two central S-atoms have zero oxidation state and two terminal S-atoms have +5 oxidation state each.

(c) Na_2SO_3 Let the oxidation number of S in Na_2SO_3 be x.

$$2(+1)+x+3(-2)=0 \text{ or } x=+4$$

(d) Na_2SO_4 Let the oxidation number of S be x.

$$2(+1)+x+4(-2)=0 \text{ or } x=+6$$

Q-14 Balance the following equations by the oxidation number method.

(a) $Fe^{2+} + H^+ + Cr_2O_7^{-2} \longrightarrow Cr^{3+} + Fe^{3+} + H_2O$

(b) $I_2 + NO_3^- \longrightarrow NO_2 + IO_3^-$

(c) $I_2 + S_2O_3^{2-} \longrightarrow I^- + S_4O_6^{2-}$

(d) $MnO_2 + C_2O_4^{2-} \rightarrow Mn^{2+} + CO_2$

Ans. Oxidation number method

(a)

$$\overset{2+}{Fe^{2+}} + H^+ + \overset{+6}{Cr_2O_7^{2-}} \longrightarrow 2\overset{+3}{Cr^{3+}} + \overset{+3}{Fe^{3+}} + H_2O$$

O.N. decreases by 3 per Cr-atom
(3 × 2 = 6 e^- gain)

O.N. increases by 1 per Fe-atom (1 e^- lose)

(Multiply Cr^{3+} by 2 because there are 2Cr atoms in $Cr_2O_7^{2-}$ ion.).

Balance increase and decrease in oxidation number.

$$6Fe^{2+} + H^+ + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 6Fe^{3+} + H_2O$$

Balance charge by multiplying H^+ by 14.

$$6Fe^{2+} + 14H^+ + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 6Fe^{3+} + H_2O$$

Balance H and O-atoms by multiplying H_2O by 7.

$$6Fe^{2+} + 14H^+ + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

This represents a balanced redox reaction.

(b)

$$\overset{0}{I_2} + \overset{+5}{NO_3^-} \longrightarrow \overset{+4}{NO_2} + 2\overset{+5}{IO_3^-}$$

O.N. decreases by
1 per N-atom (1 e^- gain)

O.N. increases by 5 per I-atom
(2 × 5 electrons lose)

Balance increase and decrease in oxidation number

$$I_2 + 10NO_3^- \longrightarrow 10NO_2 + 2IO_3^-$$

Balance charge by writing $8H^+$ in LHS of the equation.

$$I_2 + 10NO_3^- + 8H^+ \longrightarrow 10NO_2 + 2IO_3^-$$

Balance H-atoms by writing $4H_2O$ in RHS of the equation.

$$I_2 + 10NO_3^- + 8H^+ \longrightarrow 10NO_2 + 2IO_3^- + 4H_2O$$

Oxygen atoms are automatically balanced.

This represents a balanced redox reaction.

(c)

$$\overset{0}{I_2} + 2\overset{+2}{S_2}O_3^{2-} \longrightarrow 2\overset{-1}{I^-} + \overset{2.5}{S_4}O_6^{2-}$$

O.N. decreases by 1 per I-atom (2 × 1 e^- gain)

O.N. increases by 0.5 per S-atom (4 × 0.5 = $2e^-$ lose)

(Multiply $S_2O_3^{2-}$ by 2 because there are 4 S-atoms in $S_4O_6^{2-}$ ion.)

Increase and decrease in oxidation number is already balanced. Charge and oxygen atoms are also balanced.

This represents a balanced redox reaction.

(d)

$$\overset{+4}{Mn}O_2 + \overset{+3}{C_2}O_4^{2-} \longrightarrow Mn^{2+} + 2\overset{+4}{C}O_2$$

O.N. decreases by 2 per Mn-atom (2 e^- gain)

O.N. increases by 1 per C-atom (2 × 1 = 2 e^- lose)

Increase and decrease in oxidation number is already balanced.

Add $4H^+$ towards LHS of the equation to balance charge.

$$MnO_2 + C_2O_4^{2-} + 4H^+ \longrightarrow Mn^{2+} + 2CO_2$$

Add $2H_2O$ towards RHS of the equation to balance H-atoms

$$MnO_2 + C_2O_4^{2-} + 4H^+ \longrightarrow Mn^{2+} + 2CO_2 + 2H_2O$$

This represents a balanced redox reaction.

Q-15 Identify the redox reaction out of the following reactions and identify the oxidising and reducing agents in them.

(a) $3HCl(aq) + HNO_3(aq) \longrightarrow Cl_2(g) + NOCl(g) + 2H_2O(l)$

(b) $HgCl_2(aq) + 2KI(aq) \longrightarrow HgI_2(s) + 2KCl(aq)$

(c) $Fe_2O_3(s) + 3CO(g) \xrightarrow{\Delta} 2Fe(s) + 3CO_2(g)$

(d) $PCl_3(l) + 3H_2O(l) \longrightarrow 3HCl(aq) + H_3PO_3(aq)$

(e) $4NH_3(aq) + 3O_2(g) \longrightarrow 2N_2(g) + 6H_2O(g)$

Ans. (a) Writing the O.N. on each atom above its symbol, then

$$3\overset{+1}{H}\overset{-1}{Cl}(aq) + \overset{+1}{H}\overset{+5}{N}\overset{-2}{O}_3(aq) \longrightarrow \overset{0}{Cl}_2(g) + \overset{+3}{N}\overset{-2}{O}\overset{-1}{Cl}(g) + 2\overset{+1}{H}_2\overset{-2}{O}(l)$$

Here, the O.N. of Cl increases from –1 in HCl to 0 in Cl_2, therefore, Cl^- is oxidised and hence HCl acts as the reducing agent.

The O.N. of N decreases from +5 in HNO_3 to +3 in NOCl, therefore, HNO_3 acts as the oxidising agent.

Thus, this reaction is a redox reaction.

(b) Writing the O.N. of each atom above its symbol, we have,

$$\overset{+2}{Hg}\overset{-1}{Cl}_2(aq) + 2\overset{+1}{K}\overset{-1}{I}(aq) \longrightarrow \overset{+2}{Hg}\overset{-1}{I}_2(s) + 2\overset{+1}{K}\overset{-1}{Cl^-}(aq)$$

Here, the O.N. of none of the atoms undergo a change, therefore, this reaction is not a redox reaction.

(c) $\overset{+3}{Fe}_2\overset{-2}{O}_3(s) + 3\overset{+2}{C}\overset{-2}{O}(g) \xrightarrow{\Delta} 2\overset{0}{Fe}(s) + 3\overset{+4}{C}\overset{-2}{O}_2(g)$

Here, O.N. of Fe decreases from +3 in Fe_2O_3 to 0 in Fe, therefore, Fe_2O_3 acts as an oxidising agent. Further, O.N. of C increases from +2 in CO to +4 in CO_2, therefore, CO acts as a reducing agent.

Thus, this reaction is an example of redox reaction.

(d) Writing the O.N. of each atom above its symbol, then

$$\overset{+3}{P}\overset{-1}{Cl_3}(l)+3\overset{+1}{H_2}\overset{-2}{O}(l) \rightarrow 3\overset{+1}{H}\overset{-1}{Cl}(aq)+\overset{+1}{H_3}\overset{+3}{P}\overset{-2}{O_3}(aq)$$

Here, O.N. of none of the atoms undergo a change, therefore, this reaction is not a redox reaction.

(e) Writing the O.N. of each atom above its symbol, then

$$4\overset{-3}{N}\overset{+1}{H_3}(aq)+3\overset{0}{O_2}(g) \longrightarrow 2\overset{0}{N_2}(g)+6\overset{+1}{H_2}\overset{-2}{O}(l)$$

Here, O.N. of N increases from –3 to 0 in N_2, therefore, NH_3 acts as a reducing agent. Further, O.N. of O decreases from 0 in O_2 to –2 in H_2O, therefore, O_2 acts as a oxidising agent. Thus, this reaction is a redox reaction.

Q-16 Balance the following ionic equations.

(a) $Cr_2O_7^{2-} + H^+ + I^- \longrightarrow Cr^{3+} + I_2 + H_2O$

(b) $Cr_2O_7^{2-} + Fe^{2+} + H^+ \longrightarrow Cr^{3+} + Fe^{3+} + H_2O$

(c) $MnO_4^- + SO_3^{2-} + H^+ \longrightarrow Mn^{2+} + SO_4^{2-} + H_2O$

(d) $MnO_4^- + H^+ + Br^- \longrightarrow Mn^{2+} + Br_2 + H_2O$

Ans. (a) Write the O. N. of all atoms above their respective symbols.

O. N. decreases by, 3 per Cr-atom

O.N. decreases by 3 per Cr-atom

$$\overset{+6}{Cr_2}\overset{-2}{O_7} + H^+ + I^- \longrightarrow \overset{+3}{Cr} + \overset{0}{I_2} + \overset{+1}{H_2}\overset{-2}{O}$$

O.N. increases by 1 per I-atom

Divide the given equation into two half reactions

Reduction half reaction : $Cr_2O_7 \rightarrow Cr^{3+}$

Oxidation half reaction : $I^- \rightarrow I_2$

To balance reduction half reaction.

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

To balance oxidation half reaction

$$2I^- \longrightarrow I_2 + 2e^-$$

To balance the reaction by electrons gained and lost

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

$$6I^- \longrightarrow 3I_2 + 6e^-$$

$$Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O$$

This gives the final balanced ionic equations.

(b) Write the skeletal equation of the given reaction

$$Cr_2O_7^{2-}(aq) + Fe^{2+}(aq) \longrightarrow Cr^{3+}(aq) + Fe^{3+}(aq)$$

Write the O. N. of all the elements above their respective symbols.

O.N. decreases by 3 per Cr-atom

$$\overset{+6\ -2}{Cr_2O_7}\ (aq) + Fe^{2+}(aq) \longrightarrow Cr^{3+}(aq) + Fe^{3+}\ (aq)$$

O.N. increases by 1 per Fe-atom

Divide the given equation into two half reactions

Oxidation half reaction : $Fe^{2+}(aq) \rightarrow Fe^{3+}(aq)$

reduction half reaction : $Cr_2O_7^{2-}(aq) \rightarrow Cr^{3+}(aq)$

To balance oxidation half reaction

$$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$$

To balance reduction half reaction

$$Cr_2O_7^{2-}(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq)$$

Balance charge by adding H^+ ions.

$$Cr_2O_7^{2-}(aq) + 14H^+\ (aq) + 6e^- \longrightarrow 2Cr^{3+}(aq)$$

Balance O atoms by adding H_2O molecules

$$Cr_2O_7^{2-}\ (aq) + 14H^+\ (aq) + 6e^- \longrightarrow 2Cr^{3+}\ (aq) + 7H_2O\ (l)$$

To balance the reaction

$$6Fe^{2+}(aq) \longrightarrow 6Fe^{3+}(aq) + 6e^-$$

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

$$Cr_2O_7^{2-}(aq) + 6Fe^{2+}(aq) + 14H^+(aq) \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l) + 6Fe^{3+}(aq)$$

(c) Write the O. N. of all atoms above their respective symbols.

O.N. decreases by 5 per Mn-atom

$$\overset{+7\ -2}{MnO_4^-} + \overset{+4\ -2}{SO_3^{2-}} \longrightarrow Mn^{2+} + \overset{+6\ -2}{SO_4^{2-}} + H_2O$$

O.N. increases by 2 per S-atom

Divide the skeleton equation into two half-reactions.

Reduction half reaction: $MnO_4^- \longrightarrow Mn^{2+}$

Oxidation half reaction : $SO_3^{2-} \longrightarrow SO_4^{2-}$

To balance reduction half reaction

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

To balance oxidation half reaction

$$SO_3^{2-} \longrightarrow SO_4^{2-} + 2e^-$$

Balance charge by adding H^+ ions.

$$SO_3^{2-} \longrightarrow SO_4^{2-} + 2H^+ + 2e^-$$

Balance O-atoms by adding H_2O molecules

$$SO_3^{2-} + H_2O \longrightarrow SO_4^{2-} + 2H^+ + 2e^-$$

To balance the reaction

$$2MnO_4^- + 16H^+ + 10e^- \longrightarrow 2Mn^{2+} + 8H_2O$$

$$5SO_3^{2-} + 5H_2O \longrightarrow 5SO_4^{2-} + 10H^+ + 10e^-$$

$$2MnO_4^- + 5SO_3^{2-} + 6H^+ \longrightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O$$

This represents the correct balanced redox equation.

(d) Write the O. N. of all the atoms above their respective symbols.

O.N. decreases by 5 per Mn-atom

$$\overset{+7-2}{MnO_4^-} + H^+ + Br^- \longrightarrow Mn^{2+} + \overset{0}{Br_2} + \overset{+2-1}{H_2O}$$

O.N. increases by 1 per Br-atom

Divide skeleton equation into two half reactions

Reduction half reaction $MnO_4^- \rightarrow Mn^{2+}$

Oxidation half reaction $Br^- \rightarrow Br_2$

To balance reduction half reaction

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

To balance oxidation half reaction

$$2Br^- \longrightarrow Br_2 + 2e^-$$

To balance the reaction

$$2MnO_4^- + 16H^+ + 10e^- \longrightarrow 2Mn^{2+} + 8H_2O$$

$$10Br^- \longrightarrow 5Br_2 + 10e^-$$

$$2MnO_4^- + 10Br^- + 16H^+ \longrightarrow 2Mn^{2+} + 5Br_2 + 8H_2O$$

This represents the correct balanced ionic equation.

Q- 17 Match Column I with Column II for the oxidation states of the central atoms.

	Column I		Column II
A.	$Cr_2O_7^{2-}$	1.	+3
B.	MnO_4^-	2.	+4
C	VO_3^-	3.	+5
D.	FeF_6^{3-}	5.	+6
		6.	+7

Ans. A. → (4) B. → (5) C. → (3) D. → (1)

Suppose that x be the oxidation states of central atoms.

A. Oxidation number of Cr in $Cr_2O_7^{2-}$

$$2x + 7(-2) = -2$$
$$2x - 14 = -2$$
$$2x = +12$$
$$x = +6$$

B. Oxidation number of Mn in MnO_4^-

$$x + 4(-2) = -1$$
$$x - 8 = -1$$
$$x = +7$$

C. Oxidation number of V in VO_3^-

$$x + 3(-2) = -1$$
$$x - 6 = -1$$
$$x = +5$$

D. Oxidation number of Fe in FeF_6^{3-}

$$x + 6(-1) = -3$$
$$x - 6 = -3$$

or

$$x = +3$$

Q-18 On the basis of standard electrode potential values, suggest which of the following reactions would take place? (Consult the book for $E^{\ominus}$ value)

(a) $Cu + Zn^{2+} \longrightarrow Cu^{2+} + Zn$
(b) $Mg + Fe^{2+} \longrightarrow Mg^{2+} + Fe$
(c) $Br_2 + 2Cl^- \longrightarrow Cl_2 + 2Br^-$
(d) $Fe + Cd^{2+} \longrightarrow Cd + Fe^{2+}$

Ans. As we know that,

$$E^\circ_{Cu^{2+}/Cu} = 0.34\ V,\ E^\circ_{Zn^{2+}/Zn} = -0.76\ V,$$
$$E^\circ_{Mg^{2+}/Mg} = -2.37\ V, E^\circ_{Fe^{2+}/Fe} = -0.74\ V,$$
$$E^\circ_{Br_2/Br^-} = +\ 1.08\ V, E^\circ_{Cl_2/Cl^-} = +1.36\ V$$
$$E^\circ_{Cd^{2+}/Cd} = -\ 0.44\ V$$

(a) $E^\circ_{Cu^{2+}/Cu} = +\ 0.34\ V$ and $E^\circ_{Zn^{2+}/Zn} = -0.76\ V$

$$Cu + Zn^{2+} \longrightarrow Cu^{2+} + Zn$$

In the given cell reaction, Cu is oxidised to Cu^{2+}, therefore, Cu^{2+}/Cu couple acts as anode and Zn^{2+} is reduced to Zn, therefore, Zn^{2+}/Zn couple acts as cathode.

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$
$$E^\circ_{cell} = -0.76 - (+0.34) = -1.10V$$

Negative value of E°_{cell} indicates that the reaction will not occur.

(b) $Mg + Fe^{2+} \longrightarrow Mg^{2+} + Fe$

$$E^\circ_{Mg^{2+}/Mg} = -2.37V \text{ and } E^\circ_{Fe^{2+}/Fe} = -0.74\ V$$

In the given cell reaction, Mg is oxidised to Mg^{2+} hence, Mg^{2+}/Mg couple acts as anode and Fe^{2+} is reduced to Fe hence, Fe^{2+}/Fe couple acts as cathode.

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$
$$E^\circ_{cell} = -0.74 - (-2.37) = +1.63V$$

Positive value of E°_{cell} 5 indicates that the reaction will occur.

(c)

$$Br_2 + 2Cl^- \longrightarrow Cl_2 + 2Br^-$$
$$E^\circ_{Br^-/Br_2} = +\ 1.08\ \ V \text{ and } E^\circ_{Cl^-/Cl_2} = +1.36\ \ V$$

In the given cell reaction, Cl^- is oxidised to Cl_2 hence, Cl^-/Cl_2 couple acts as anode and Br_2 is reduced to Br^- hence; Br^-/Br_2 couple acts as cathode.

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$
$$E^\circ_{cell} = +1.08 - (+\ 1.36) = -0.28\ V$$

Negative value of E°_{cell} indicates that the reaction will occur.

(d)

$$Fe + Cd^{2+} \longrightarrow Cd + Fe^{2+}$$
$$E^\circ_{Fe^{2+}/Fe} = -0.74\ V. \text{ and } E^\circ_{Cd^{2+}/Cd} = -0.44\ V$$

In the given cell reaction, Fe is oxidised to Fe^{2+} hence, Fe^{2+}/Fe couple acts as anode and Cd^{2+} is reduced to Cd hence, Cd^{2+}/Cd couple acts as cathode.

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$
$$E^\circ_{cell} = -0.44 - (-0.74) = +0.30\ V.$$

Positive value E°_{cell} indicates that the reaction will occur.

Q-19 **Why does fluorine not show disproportionation reaction?**

Ans. In a disproportionation reaction, the same species is simultaneously oxidised as well as reduced. Therefore, for such a redox reaction to occur, the reacting species must contain an element which has atleast three oxidation states.

The element, in reacting species, is present in an intermediate state while lower and higher oxidation states are available for reduction and oxidation to occur (respectively).

Fluorine is the strongest oxidising agent. It does not show positive oxidation state. That's why fluorine does not show disproportionation reaction.

Q-20 **Find out the oxidation number of chlorine in the following compounds and arrange them in increasing order of oxidation number of chlorine.**
$NaClO_4$, $NaClO_3$, NaClO, $KClO_2$, Cl_2O_7, ClO_3, Cl_2O, NaCl, Cl_2, ClO_2.
Which oxidation state is not present in any of the above compounds?

Ans. Suppose that the oxidation number of chlorine in these compounds be x.

O.N. of Cl in $NaClO_4$ $\therefore$ $+1 + x + 4(-2) = 0$ or, $x = +7$
O.N. of Cl in $NaClO_3$ $\therefore$ $+1 + x + 3(-2) = 0$ or, $x = +5$
O.N. of Cl in NaClO $\therefore$ $+1 + x + 1(-2) = 0$ or, $x = +1$
O.N. of Cl in $KClO_2$ $\therefore$ $+1 + x + 2(-2) = 0$ or, $x = +3$
O.N. of Cl in Cl_2O_7 $\therefore$ $+2x + 7(-2) = 0$ or, $x = +7$
O.N. of Cl in ClO_3 $\therefore$ $x + 3(-2) = 0$ or, $x = +6$
O.N. of Cl in Cl_2O $\therefore$ $2x + 1(-2) = 0$ or, $x = +1$
O. N. of Cl in NaCl $\therefore$ $+1 + x = 0$ or, $x = -1$
O. N. of Cl in Cl_2 $\therefore$ $2x = 0$ or, $x = 0$
O. N. of Cl in ClO_2 $\therefore$ $x + 2(-2) = 0$ or, $x = +4$

None of these compounds have an oxidation number of +2.

Increasing order of oxidation number of chlorine is : –1, 0, +1, +3, +4, +5, +6, +7

Therefore, the increasing order of oxidation number of Cl in compounds is

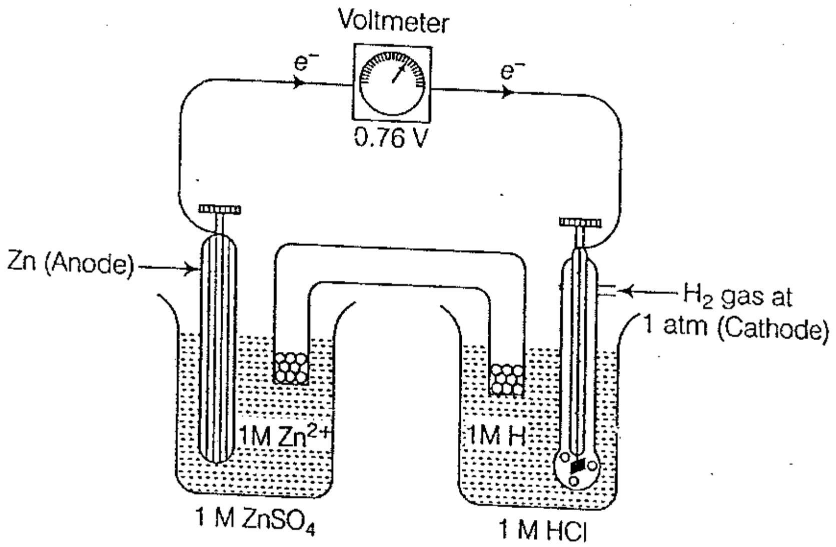
$$NaCl < Cl_2 < NaClO < KClO_2 < ClO_2 < NaClO_3 < ClO_3 < Cl_2O_7$$

Q-21 **Which method can be used to find out strength of reductant/oxidant in a solution? Explain with an example.**

Ans. Measure the electrode potential of the given species by connecting the redox couple of the given species with standard hydrogen electrode. If it is positive, the electrode of the given species acts as reductant and if it is negative, it acts as an oxidant.

Find the electrode potentials of the other given species in the same way, compare the values and determine their comparative strength as an reductant or oxidant.

e.g., measurement of standard electrode potential of Zn^{2+}/Zn electrode using SHE as a reference electrode.



The EMF of the cell comes out to be 0.76 V. (reading of voltmeter is 0.76V). Zn^{2+}/Zn couple acts as anode and SHE acts as cathode.

$$\therefore \quad E^\circ_{cell} = 0.76 = E^\circ_{cathode} - E^\circ_{anode}$$

$$0.76 = 0 - E^\circ_{anode}$$

$$E^\circ_{anode} = -0.76\text{ V}$$

$$E^\circ_{Zn^{2+}/Zn} = -0.76\text{V}.$$

SARASWATI CHEMISTRY

Equilibrium

Q. 1 We know that the relationship between K_c and K_p is

$$K_p = K_c\ (RT)^{\Delta n}$$

What would be the value of Δn for the reaction?

$$NH_4Cl(s) \rightleftharpoons NH_3(g) + HI(g)$$

(a) 1 (b) 0.5 (c) 1.5 (d) 2

Ans. ***(d)*** The relationship between K_p and K_c is

$$K_p = K_c\ (RT)^{\Delta n}$$

where, Δn = (number of moles of gaseous products) – (number of moles of gaseous reactants)

For the reaction,

$$NH_4Cl\ (s) \rightleftharpoons NH_3(g) + HCl\ (g)$$

$$\Delta n = 2 - 0 = 2$$

Q-2 Which of the following is not a general characteristic of equilibria involving physical processes?

(a) Equilibrium is possible only in a closed system at a given temperature

(b) All measurable properties of the system remain constant

(c) All the physical processes stop at equilibrium

(d) The opposing processes occur at the same rate and there is dynamic but stable condition

Q-3 PCl_5, PCl_3, and Cl_2 are at equilibrium at 500 K in a closed container and their concentrations are $0\cdot 8 \times 10^{-3}$ mol L^{-1}, 1.2×10^{-3} mol L^{-1} and 1.2×10^{-3} mol L^{-1}, respectively. The value of K_c for the reaction

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2\ (g)$$ will be

(a) 1.8×10^{3} mol L^{-1} (b) 1.8×10^{-3}

(c) 1.8×10^{-3} mol^{1} L (d) 0.55×10^{4}

Ans. ***(b)*** For the reaction, $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

At 500 K in a closed container, $[PCl_5] = 0.8 \times 10^{-3}$ mol L^{-1}

$[PCl_3] = 1.2 \times 10^{-3}$ mol L^{-1}

$[Cl_2] = 1.2 \times 10^{-3}$ mol L^{-1}

$$K_c = \frac{[PCl_3]\ [Cl_2]}{[PCl_5]} = \frac{(1.2 \times 10^{-3}) \times (1.2 \times 10^{-3})}{(0.8 \times 10^{-3})}$$

$$= 1.8 \times 10^{-3}$$

Q-4 K_{a_1}, K_{a_2} and K_{a_3} are the respective ionisation constants for the following reactions.

$$H_2S \rightleftharpoons H^+ + HS^-$$

$$HS^- \rightleftharpoons H^+ + S^{2-}$$

$$H_2S \rightleftharpoons 2H^+ + S^{2-}$$

The correct relationship between $K_{a_1}, K_{a_2}, K_{a_3}$ is

(a) $K_{a_3} = K_{a_1} \times K_{a_2}$ (b) $K_{a_3} = K_{a_1} + K_{a_2}$

(c) $K_{a_3} = K_{a_1} - K_{a_2}$ (d) $K_{a_3} = K_{a_1} / K_{a_2}$

To find out the correct relationship between three ionisation constants (K_{a_1}, K_{a_2} and K_{a_3}) this must be keep in mind that when two reactions are added, their equilibrium constants are multiplied.

Q-5 What will be the value of pH of 0.01 mol dm^{-3} CH_3COOH ($K_a = 1.74 \times 10^{-5}$)?

(a) 3.4 (b) 3.6 (c) 3.9 (d) 3.0

Ans. *(a)* Given that, $K_a = 1.74 \times 10^{-5}$

Concentration of $CH_3COOH = 0.01$ mol dm^{-3}

$$[H^+] = \sqrt{K_a \cdot C}$$
$$= \sqrt{1.74 \times 10^{-5} \times 0.01} = 4.17 \times 10^{-4}$$
$$pH = -\log [H^+]$$
$$= -\log (4.17 \times 10^{-4}) = 3.4$$

Q-6 K_a for CH_3COOH is 1.8×10^{-5} and K_b for NH_4OH is 1.8×10^{-5}. The pH of ammonium acetate will be

(a) 7.005 (b) 4.75 (c) 7.0 (d) Between 6 and 7

Ans. *(c)* Given that, K_a for $CH_3COOH = 1.8 \times 10^{-5}$

K_b for $NH_4OH = 1.8 \times 10^{-5}$

Ammonium acetate is a salt of weak acid and weak base. For such salts

$$pH = 7 + \frac{pK_a - pK_b}{2}$$
$$= 7 + \frac{[-\log 1.8 \times 10^{-5}] - [-\log 1.8 \times 10^{-5}]}{2}$$
$$= 7 + \frac{4.74 - 4.74}{2} = 7.00$$

Q-7 Which of the following options will be correct for the stage of half completion of the reaction $A \rightleftharpoons B$?

(a) $\Delta G^\ominus = 0$ (b) $\Delta G^\ominus > 0$ (c) $\Delta G^\ominus < 0$ (d) $\Delta G^\ominus = -RT \ln K$

Ans. *(a)* As we know that

$$\Delta G^\ominus = -RT \ln K$$

At the stage of half completion of the reaction,

$$A \rightleftharpoons B, [A] = [B]$$

Therefore, $K = 1.$

Thus, $\Delta G^\ominus = 0$

Q-8 On increasing the pressure, in which direction will the gas phase reaction proceed to re-establish equilibrium, is predicted by applying the Le-Chatelier's principle. Consider the reaction,

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Which of the following is correct, if the total pressure at which the equilibrium is established, is increased without changing the temperature?

(a) K will remain same

(b) K will decrease

(c) K will increase

(d) K will increase initially and decrease when pressure is very high

Ans. ***(a)*** In the reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

If the total pressure at which the equilibrium is established, is increased without changing the temperature, K will remain same. K changes only with change in temperature.

Q-9 At 500 K, equilibrium constant, K_c, for the following reaction is 5.

$$\frac{1}{2}H_2(g) + \frac{1}{2}I_2(g) \rightleftharpoons HI(g)$$

What would be the equilibrium constant K_c for the reaction?

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

(a) 0.04 (b) 0.4 (c) 25 (d) 2.5

Ans. ***(a)*** For the reaction, $\frac{1}{2}H_2(g) + \frac{1}{2}I_2(g) \rightleftharpoons HI(g)$

$$K_c = \frac{[HI]}{[H_2]^{1/2}[I_2]^{1/2}} = 5$$

Thus, for the reaction, $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$

$$K_{c_1} = \frac{[H_2][I_2]}{[HI]^2} = \left(\frac{1}{K_c}\right)^2 = \left(\frac{1}{5}\right)^2 = \frac{1}{25} = 0.04$$

Q-10 For the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, the value of K is 50 at 400 K and 1700 at 500 K. Which of the following option(s) is/are correct?

(a) The reaction is endothermic

(b) The reaction is exothermic

(c) If $NO_2(g)$ and $N_2O_4(g)$ are mixed at 400 K at partial pressures 20 bar and 2 bar respectively, more $N_2O_4(g)$ will be formed

(d) The entropy of the system increases

Ans. ***(a, c, d)***

For the reaction, $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

At 400 K, $K = 50$

At 500 K, $K = 1700$

(a) As the value of K increase with increase of temperature and $K = \frac{K_f}{K_b}$, this means that K_f increases, *i.e.*, forward reaction is favoured. Hence, reaction is endothermic.

(c) Since, number of moles of gaseous products are greater than the number of moles of gaseous reactants. Thus, higher pressure favours the backward reaction, *i.e.*, more $N_2O_4(g)$ will be obtained, if $P_{\text{product}} > P_{\text{reactant}}$.

(d) As reaction is accompanied by increase in the number of moles, entropy increases.

Q-11 The ionisation of hydrochloric acid in water is given below

$$HCl\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + Cl^-\ (aq)$$

Label two conjugate acid-base pairs in this ionisation.

Adds proton

Ans. $\underset{\text{Acid}}{HCl}\,(aq) + \underset{\text{Base}}{H_2O(l)} \rightleftharpoons \underset{\text{Conjugate acid}}{H_3O^+(aq)} + \underset{\text{Conjugate base}}{Cl^-(aq)}$

Lose proton

Note *If Bronsted acid is a strong acid then its conjugate base is a weak base and vice-versa. Generally, the conjugate acid has one extra proton and each conjugate base has one less proton.*

Q-12 Conjugate acid of a weak base is always stronger. What will be the decreasing order of basic strength of the following conjugate bases?

$$OH^-, RO^-\ CH_3COO^-, Cl^-$$

Ans. Conjugate acid of the given bases are H_2O, ROH, CH_3COOH and HCl. Order of their acidic strength is

$$HCl > CH_3COOH > H_2O > ROH$$

Hence, order of basic strength of their conjugate bases is

$$Cl^- < CH_3COO^- < OH^- < RO^-$$

Q-13 Arrange the following in increasing order of pH.

$$KNO_3(aq), CH_3COONa\ (aq)\ NH_4Cl\ (aq), C_6H_5COONH_4(aq)$$

Ans. (i) KNO_3 is a salt of strong acid (HNO_3) strong base (KOH), hence its aqueous solution is neutral; pH = 7.

(ii) CH_3COONa is a salt of weak acid (CH_3COOH) and strong base (NaOH), hence, its aqueous solution is basic; pH > 7.

(iii) NH_4Cl is a salt of strong acid (HCl) and weak base (NH_4OH) hence, its aqueous solution is acidic; pH < 7.

(iv) $C_6H_5COONH_4$ is a salt of weak acid, C_6H_5COOH and weak base, NH_4OH. But NH_4OH is slightly stronger than C_6H_5COOH. Hence, pH is slightly > 7.

Therefore, increasing order of pH of the given salts is,

$$NH_4Cl < C_6H_5COONH_4 > KNO_3 < CH_3COONa$$

Q-14 The value of K_c for the reaction $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$ is 1×10^{-4}. At a given time, the composition of reaction mixture is $[HI] = 2 \times 10^{-5}$ mol, $[H_2] = 1 \times 10^{-5}$ mol and $[I_2] = 1 \times 10^{-5}$ mol. In which direction will the reaction proceed?

Ans. Given that,

$$[HI] = 2 \times 10^{-5}\ \text{mol}$$
$$[H_2] = 1 \times 10^{-5}\ \text{mol}$$
$$[I_2] = 1 \times 10^{-5}\ \text{mol}$$

At a given time, the reaction quotient Q for the reaction will be given by the expression

$$Q = \frac{[H_2]\,[I_2]}{[HI]^2}$$

$$= \frac{1\times10^{-5}\times1\times10^{-5}}{(2\times10^{-5})^2} = \frac{1}{4}$$

$$= 0.25 = 2.5\times10^{-1}$$

As the value of reaction quotient is greater than the value of K_c, *i.e.*, 1×10^{-4} the reaction will proceed in the reverse reaction.

Q-15 On the basis of the equation pH = – log [H^+], the pH of 10^{-8} mol dm^{-3} solution of HCl should be 8. However, it is observed to be less than 7.0. Explain the reason.

Ans. Concentration 10^{-8} mol dm^{-3} indicates that the solution is very dilute. So, we cannot neglect the contribution of H_3O^+ ions produced from H_2O in the solution. Total $[H_3O^+] = 10^{-8} + 10^{-7}$ M. From this we get the value of pH close to 7 but less than 7 because the solution is acidic.

From calculation, it is found that pH of 10^{-8} mol dm^{-3} solution of HCl is equal to 6.96.

Q-16 pH of a solution of a strong acid is 5.0. What will be the pH of the solution obtained after diluting the given solution a 100 times?

Ans. Given that,

$$pH = 5$$

$$[H^+] = 10^{-5} \text{ mol L}^{-1}$$

On diluting the solution 100 times $[H^+] = \frac{10^{-5}}{100} = 10^{-7} \text{ mol L}^{-1}$

On calculating the pH using the equation pH = – log [H^+], value of pH comes out to be 7. It is not possible. This indicates that solution is very dilute.

Hence, Total H^+ ion concentration = H^+ ions from acid + H^+ ion from water

$$[H^+] = 10^{-7} + 10^{-7} = 2\times10^{-7} \text{ M}$$

$$pH = -\log[2\times10^{-7}]$$

$$pH = 7 - 0.3010 = 6.699$$

Q- 17 A sparingly soluble salt gets precipitated only when the product of concentration of its ions in the solution (Q_{sp}) becomes greater than its solubility product. If the solubility of $BaSO_4$ in water is 8×10^{-4} mol dm^{-3}. Calculate its solubility in 0.01 mol dm^{-3} of H_2SO_4.

Ans.

$$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$$

$$K_{sp} \text{ for } BaSO_4 = [Ba^{2+}][SO_4^{2-}] = s\times s = s^2$$

But $s = 8\times10^{-4} \text{ mol dm}^{-3}$

∴ $K_{sp} = (8\times10^{-4})^2 = 64\times10^{-8}$

In the presence of 0.01MH_2SO_4, the expression for K_{sp} will be

$$K_{sp} = [Ba^{2+}][SO_4^{2-}]$$

$$K_{sp} = (s).(s+0.01) \quad (0.01\text{ M } SO_4^{2-} \text{ ions from } 0.01\text{ M } H_2SO_4)$$

$$64\times10^{-8} = s\cdot(s+0.01)$$

$$s^2 + 0.01s - 64\times10^{-8} = 0$$

$$s = \frac{-0.01 \pm \sqrt{(0.01)^2 + (4\times64\times10^{-8})}}{2}$$

$$= \frac{-0.01 \pm \sqrt{10^{-4} + (256\times10^{-8})}}{2}$$

$$= \frac{-0.01 \pm \sqrt{10^{-4}(1 + 256 \times 10^{-4})}}{2}$$

$$= \frac{-0.01 \pm 10^{-2}\sqrt{1 + 0.0256}}{2} = \frac{10^{-2}(-1 \pm 1.012719)}{2}$$

$$= 5 \times 10^{-3}(-1 + 1.012719) = 6.4 \times 10^{-5} \text{ mol dm}^{-3}$$

Note *$s <<< 0.01$, so, $s + 0.01 \approx 0.01$ and $64 \times 10^{-8} = s \times 0.01$*

$$s = \frac{64 \times 10^{-8}}{0.01} = 6.4 \times 10^{-5}$$

Q-18 pH of 0.08 mol dm^{-3} HOCl solution is 2.85. Calculate its ionisation constant.

To solve this problem, we use two steps

Step I *Find out the concentration of hydrogen ion [H$^+$] through the formula* $-\text{pH} = \log [\text{H}^+]$

Step II *Afterward, calculate the K_a of HOCl which is weak monobasic acid by using the formula $K_a = \frac{[\text{H}^+]^2}{C}$. where, C is concentration of the solution*

Ans. pH of HOCl = 2.85

But, $-\text{pH} = \log [\text{H}^+]$

$\therefore$ $-2.85 = \log [\text{H}^+]$

$\Rightarrow$ $\bar{3}.15 = \log [\text{H}^+]$

$\Rightarrow$ $[\text{H}^+] = 1.413 \times 10^{-3}$

For weak monobasic acid $[\text{H}^+] = \sqrt{K_a \times C}$

$\Rightarrow$ $K_a = \frac{[\text{H}^+]^2}{C} = \frac{(1.413 \times 10^{-3})^2}{0.08}$

$= 24.957 \times 10^{-6} = 2.4957 \times 10^{-5}$

Q-19 Calculate the pH of a solution formed by mixing equal volumes of two solutions *A* and *B* of a strong acid having pH = 6 and pH = 4 respectively.

Ans. pH of solution $A = 6$. Hence, $[\text{H}^+] = 10^{-6}$ mol L^{-1}

pH of solution $B = 4$. Hence, $[\text{H}^+] = 10^{-4}$ mol L^{-1}

On mixing 1 L of each solution, molar concentration of total H$^+$ is halved.

Total, $[\text{H}^+] = \frac{10^{-6} + 10^{-4}}{2}$ mol L^{-1}

$[\text{H}^+] = \frac{1.01 \times 10^{-4}}{2} = 5.05 \times 10^{-5}$ mol L^{-1}

$[\text{H}^+] = 5.0 \times 10^{-5}$ mol L^{-1}.

$\text{pH} = -\log [\text{H}^+]$ $\Rightarrow$ $\text{pH} = -\log (5.0 \times 10^{-5})$

$\text{pH} = -[\log 5 + (-5 \log 10)]$ $\Rightarrow$ $\text{pH} = -\log 5 + 5$

$\text{pH} = 5 - \log 5 = 5 - 0.6990$ $\Rightarrow$ $\text{pH} = 4.3010 \approx 4.3$

Thus, the pH of resulting solution is 4.3.

Q-20. The solubility product of $Al(OH)_3$ is 2.7×10^{-11}. Calculate its solubility in $g\ L^{-1}$ and also find out pH of this solution. (Atomic mass of Al = 27 u)

Ans. Let S be the solubility of $Al(OH)_3$.

$$\underset{\substack{1 \\ 1-S}}{Al(OH)_3} \rightleftharpoons \underset{\substack{0 \\ S}}{Al^{3+}}(aq) + \underset{\substack{0 \\ 3S}}{3OH^-}(aq)$$

Concentration of species at $t = 0$

Concentration of various species at equilibrium

$$K_{sp} = [Al^{3+}][OH^-]^3 = (S)(3S)^3 = 27S^4$$

$$S^4 = \frac{K_{sp}}{27} = \frac{2.7 \times 10^{-11}}{27} = 1 \times 10^{-12}$$

$$S = 1 \times 10^{-3}\ mol\ L^{-1}$$

(i) **Solubility of $Al(OH)_3$**

Molar mass of $Al(OH)_3$ is 78 g. Therefore,

Solubility of $Al(OH)_3$ in $g\ L^{-1} = 1 \times 10^{-3} \times 78\ g\ L^{-1} = 78 \times 10^{-3}\ g\ L^{-1}$

$= 7.8 \times 10^{-2}\ g\ L^{-1}$

(ii) **pH of the solution** $\quad S = 1 \times 10^{-3}\ mol\ L^{-1}$

$$[OH^-] = 3S = 3 \times 1 \times 10^{-3} = 3 \times 10^{-3}$$

$$pOH = 3 - \log 3$$

$$pH = 14 - pOH = 11 + \log 3 = 11.4771$$

Q-21 Calculate the volume of water required to dissolve 0.1 g lead (II) chloride to get a saturated solution.

(K_{sp} of $PbCl_2 = 3.2 \times 10^{-8}$, atomic mass of Pb = 207u)

Ans. Suppose, solubility of $PbCl_2$ in water is $s\ mol\ L^{-1}$

$$\underset{(1-s)}{PbCl_2(s)} \rightleftharpoons \underset{s}{Pb^{2+}}(aq) + \underset{2s}{2Cl^-}(aq)$$

$$K_{sp} = [Pb^{2+}].[Cl^-]^2$$

$$K_{sp} = [s][2s]^2 = 4s^3$$

$$3.2 \times 10^{-8} = 4s^3$$

$$s^3 = \frac{3.2 \times 10^{-8}}{4} = 0.8 \times 10^{-8}$$

$$s^3 = 8.0 \times 10^{-9}$$

Solubility of $PbCl_2$, $s = 2 \times 10^{-3}\ mol\ L^{-1}$

Solubility of $PbCl_2$ in $gL^{-1} = 278 \times 2 \times 10^{-3} = 0.556\ g\ L^{-1}$

0.556 g of $PbCl_2$ dissolve in 1 L of water. $\quad$ ($\because$ Molar mass of $PbCl_2 = 207 + (2 \times 35.5) = 278$)

$\therefore$ 0.1 g of $PbCl_2$ will dissolve in $= \frac{1 \times 0.1}{0.556}$ L of water

$= 0.1798$ L

To make a saturated solution, dissolution of 0.1g $PbCl_2$ in 0.1798 L ≈ 0.2 L of water will be required.

Q-22 A reaction between ammonia and boron trifluoride is given below.

$$:NH_3 + BF_3 \longrightarrow H_3N:BF_3$$

Identify the acid and base in this reaction. Which theory explains it? What is the hybridisation of B and N in the reactants?

Ans. Although BF_3 does not have a proton but acts as Lewis acid as it is an electron deficient compound. It reacts with NH_3 by accepting the lone pair of electrons from NH_3 and complete its octet. The reaction can be represented by

$$BF_3 + :NH_3 \longrightarrow BF_3 \leftarrow NH_3$$

Lewis electronic theory of acids and bases can explain it. Boron in BF_3 is sp^2 hybridised where N in NH_3 is sp^3 hybridised.

Q-23 Following data is given for the reaction $CaCO_3(s) \longrightarrow CaO(s) + CO_2\ (g)$

$$\Delta_f H^\ominus\ [CaO(s)] = -\ 635.1 kJ\ mol^{-1}$$

$$\Delta_f H^\ominus\ [CO_2(g)] = -\ 393.5 kJ\ mol^{-1}$$

$$\Delta_f H^\ominus\ [CaCO_3(s)] = -\ 1206.9 kJ\ mol^{-1}$$

Predict the effect of temperature on the equilibrium constant of the above reaction.

Ans. Given that,

$$\Delta_f H^\ominus\ [CaO(s)] = -\ 635.1 kJ\ mol^{-1}$$

$$\Delta_f H^\ominus\ [CO_2(g)] = -\ 393.5 kJ\ mol^{-1}$$

$$\Delta_f H^\ominus\ [CaCO_3(s)] = -\ 1206.9 kJ\ mol^{-1}$$

Q-24 For the reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

$$\text{Equilibrium constant, } K_c = \frac{[NH_3]^2}{[N_2]\ [H_2]^3}$$

Some reactions are written below in Column I and their equilibrium constants in terms of K_c are written in Column II. Match the following reactions with the corresponding equilibrium constant.

Column I (Reaction)	**Column II** (Equilibrium constant)
A. $2N_2(g) + 6H_2(g) \rightleftharpoons 4NH_3(g)$	1. $2K_c$
B. $2NH_3(g) \rightleftharpoons 2N_2(g) + 3H_2(g)$	2. $K_c^{1/2}$
C. $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$	3. $\frac{1}{K_c}$
	4. K_c^2

Ans. A. → (4) B. → (3) C. → (2)

For the reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

$$\text{Equilibrium constant } K_c = \frac{[NH_3]^2}{[N_2]\ [H_2]^3}$$

A. The given reaction $[2N_2(g) + 6H_2(g) \rightleftharpoons 4NH_3(g)]$ is twice the above reaction.
Hence, $K = K_c^2$

B. The reaction $[2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)]$ is reverse of the above reaction.
Hence, $K = \dfrac{1}{K_c}$

C. The reaction $\left[\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)\right]$ is half of the above reaction..
Hence, $K = \sqrt{K_c} = K_c^{\frac{1}{2}}$.

Q-25 Match standard free energy of the reaction with the corresponding equilibrium constant.

A. $\Delta G^\ominus > 0$	1. $K > 1$
B. $\Delta G^\ominus < 0$	2. $K = 1$
C. $\Delta G^\ominus = 0$	3. $K = 0$
	4. $K < 1$

Ans. A. → (4) B. → (1) C. → (2)

As we know that, $\Delta G^\ominus = -RT \ln K$

A. If $\Delta G^\ominus > 0$, *i.e.*, ΔG° is positive, then $\ln K$ is negative *i.e.*, $K < 1$.

B. If $\Delta G^\ominus < 0$, *i.e.*, ΔG° is negative then $\ln K$ is positive *i.e.*, $K > 1$.

C. If $\Delta G^\ominus = 0$, $\ln K = 0$, *i.e.*, $K = 1$.

Q-26 How can you predict the following stages of a reaction by comparing the value of K_c and Q_c?

(i) Net reaction proceeds in the forward direction.
(ii) Net reaction proceeds in the backward direction.
(iii) No net reaction occurs.

Ans. *Prediction of the following stages of a reaction by comparing the value of K_c and Q_c are*

(i) If $Q_c < K_c$, the reaction will proceed in the direction of the products (forward reaction).
(ii) If $Q_c > K_c$, the reaction will proceed in the direction of reactants (reverse reaction).
(iii) If $Q_c = K_c$, the reaction mixture is already at equilibrium.

Q-27 On the basis of Le-Chatelier principle explain how temperature and pressure can be adjusted to increase the yield of ammonia in the following reaction.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H = -\,92.38 \text{ kJ mol}^{-1}$$

What will be the effect of addition of argon to the above reaction mixture at constant volume?

Ans.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g); \ \Delta H = -\,92.38 \text{ kJ mol}^{-1}$$

It is an exothermic process as ΔH is negative.

Effect of temperature According to Le-Chatelier's principle, low temperature is favourable for high yield of ammonia, but practically very low temperatures slow down the reaction. So, optimum temperature 700 K is favourable in attainment of equilibrium.

Effect of pressure Similarly, high pressure about 200 atm is favourable for high yield of ammonia. On increasing pressure, reaction goes in the forward direction because the number of moles decreases in the forward direction.

Addition of argon At constant volume addition of argon does not affect the equilibrium because it does not change the partial pressures of the reactants or products involved in the reaction and the equilibrium remains undisturbed.

Q-28 A sparingly soluble salt having general formula $A_x^{p+} B_y^{q-}$ and molar solubility S is in equilibrium with its saturated solution. Derive a relationship between the solubility and solubility product for such salt.

Ans. A sparingly soluble salt having general formula $A_x^{p+} B_y^{q-}$. Its molar solubility is S mol L^{-1}.

Then,

$$A_x^{p+} B_y^{q-} \rightleftharpoons xA^{p+}(aq) + yB^{q-}(aq)$$

S moles of A_xB_y dissolve to give x moles of A^{P+} and y moles of B^{q-}.

Therefore, solubility product $(K_{sp}) = [A^{P+}]^x [B^{q-}]^y$

$$= [xS]^x [yS]^y$$
$$= x^x y^y S^{x+y}$$

Q-29 Write a relation between ΔG and Q and define the meaning of each term and answer the following.

(a) Why a reaction proceeds forward when $Q < K$ and no net reaction occurs when $Q = K$?

(b) Explain the effect of increase in pressure in terms of reaction quotient Q. For the reaction, $CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$

Ans. The relation between ΔG and Q is

$$\Delta G = \Delta G^{\ominus} + RT\ln Q$$

ΔG = change in free energy as the reaction proceeds.
$\Delta G^{\ominus}$ = standard free energy
Q = reaction quotient
R = gas constant
T = absolute temperature in K

(a) Since, $\Delta G^{\ominus} = -RT\ln K$

$\therefore$ $\Delta G = -RT\ln K + RT\ln Q$

$$\Delta G = RT\ln\frac{Q}{K}$$

If $Q < K$, ΔG will be negative and the reaction proceeds in the forward direction.
If $Q = K$, $\Delta G = 0$ reaction is in equilibrium and there is no net reaction.

(b)

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$

$$K_c = \frac{[CH_4]\,[H_2O]}{[CO]\,[H_2]^3}$$

On increasing pressure, volume decreases. If we doubled the pressure, volume will be halved but the molar concentrations will be doubled. Then,

$$Q_c = \frac{2[CH_4]\cdot 2[H_2O]}{2[CO]\,\{2[H_2]\}^3} = \frac{1}{4}\frac{[CH_4]\,[H_2O]}{[CO]\,[H_2]^3} = \frac{1}{4}K_c$$

Therefore, Q_c is less than K_c, so Q_c will tend to increase to re-establish equilibrium and the reaction will go in forward direction.

SARASWATI CHEMISTRY

Thermodynamics

Q-1 During complete combustion of one mole of butane, 2658 kJ of heat is released. The thermochemical reaction for above change is

(a) $2C_4H_{10}(g) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(l); \Delta_c H = -2658.0 \text{kJ mol}^{-1}$

(b) $C_4H_{10}(g) + \frac{13}{2}O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l); \Delta_c H = -1329.0 \text{kJ mol}^{-1}$

(c) $C_4H_{10}(g) + \frac{13}{2}O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l); \Delta_c H = -2658.0 \text{kJ mol}^{-1}$

(d) $C_4H_{10}(g) + \frac{13}{2}O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l); \Delta_c H = +2658.0 \text{kJ mol}^{-1}$

Ans. *(c)* Given that, the complete combustion of one mole of butane is represented by thermochemical reaction as

$$C_4H_{10}(g) + \frac{13}{2}O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l)$$

We have to take the combustion of one mole of C_4H_{10} and $\Delta_c H$ should be negative and have a value of 2658 kJ mol^{-1}.

Q-2 $\Delta_f U^\ominus$ of formation of $CH_4(g)$ at certain temperature is -393 kJ mol^{-1}. The value of $\Delta_f H^\ominus$ is

(a) zero

(b) $< \Delta_f U^\ominus$

(c) $> \Delta_f U^\ominus$

(d) equal to $\Delta_f U^\ominus$

Ans. *(b)* The reaction is $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

$$\Delta n_g = (n_p - n_r)_g = 1 - 3 = -2$$

$$\Delta_f H^{-\ominus} = \Delta_f U^\ominus + \Delta n_g RT$$

As $\Delta n_g = -2$

$\therefore$ $\Delta_f H^\ominus < \Delta_f U^\ominus$

Q-3 The pressure-volume work for an ideal gas can be calculated by using the expression $W = -\int_{V_i}^{V_f} p_{ex} dV$. The work can also be calculated from the pV-plot by using the area under the curve within the specified limits. When an ideal gas is compressed (a) reversibly or (b) irreversibly from volume V_i to V_f. Choose the correct option.

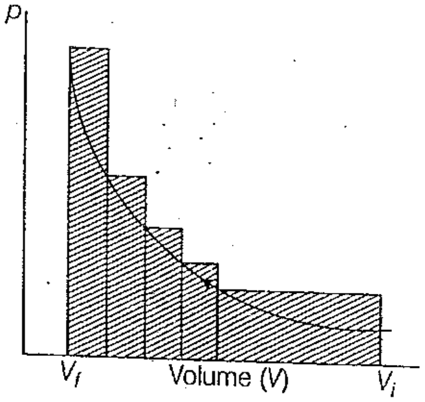
(a) W (reversible) $= W$ (irreversible)

(b) W (reversible) $< W$ (irreversible)

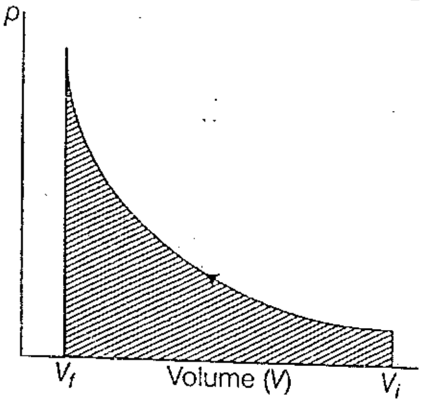
(c) W (reversible) $= W$ (irreversible)

(d) W (reversible) $= W$ (irreversible) $+ p_{ex} \cdot \Delta V$

Ans. ***(b)*** The correct option is W (reversible) $<$ W (irreversible). This is because area under the curve is always more in irreversible compression as can be seen from given figure.



pV-plot when pressure is not constant and changes in finite steps during compression from initial volume, V_i to final volume, V_f. Work done on the gas is represented by the shaded area.



PV-plot when pressure is not constant and changes in infinite steps (reversible conditions) during compression from initial volume, V_i to final volume, V_f. Work done on the gas is represented by the shaded area.

Q-4 On the basis of theromochemical equations (1), (2) and (3), find out which of the algebraic relationships given in options (a) to (d) is correct

1. C (graphite) + O_2 $(g) \rightarrow CO_2$ (g) ; $\Delta_r H = x$ kJ mol^{-1}
2. C (graphite) + $\frac{1}{2}$ O_2 $(g) \rightarrow CO$ (g) ; $\Delta_r H = y$ kJ mol^{-1}.
3. CO $(g) + \frac{1}{2} O_2$ $(g) \rightarrow CO_2$ (g) ; $\Delta_r H = z$ kJ mol^{-1}

(a) $z = x + y$ (b) $x = y - z$ (c) $x = y + z$ (d) $y = 2z - x$

Ans. ***(c)*** The algebraic relationships of the given reaction is
equation (a) – equation (b) = equation (c)

(a) C (graphite) + O_2 $(g) \rightarrow CO_2$ (g) ; $\Delta_r H = x$ kJ mol^{-1}

(b) C (graphite) + $\frac{1}{2}$ O_2 $(g) \rightarrow CO$ (g) ; $\Delta_r H = y$ kJ mol^{-1}

CO $(g) + \frac{1}{2}$ O_2 $(g) \rightarrow CO_2$ (g) ; $\Delta_r H = z$ kJ mol^{-1}

Hence, $x - y = z$ or $x = y + z$

Q-5 For an ideal gas, the work of reversible expansion under isothermal condition can be calculated by using the expression $W = -nRT \ln \frac{V_f}{V_i}$. A sample containing 1.0 mol of an ideal gas is expanded isothermally and reversible to ten times of its original volume, in two separate experiments. The expansion is carried out at 300 K and at 600 K respectively. Choose the correct option.

(a) Work done at 600 K is 20 times the work done at 300 K
(b) Work done at 300 K is twice the work done at 600 K
(c) Work done at 600 K is twice the work done at 300 K
(d) $\Delta U = 0$ in both cases

Ans. *(c, d)*

Given that, the work of reversible expansion under isothermal condition can be calculated by using the expression

$$W = -nRT\ln\frac{V_f}{V_i}$$

$$V_f = 10\ V_i$$
$$T_2 = 600\text{ K}$$
$$T_1 = 300\text{ K}$$

Putting these values in above expression

$$W_{600K} = 1 \times R \times 600\text{ K}\ln\frac{10}{1}$$

$$W_{300K} = 1 \times R \times 300\text{ K}\ln\frac{10}{1}$$

$$\text{Ratio} = \frac{W_{600K}}{W_{300K}} = \frac{1 \times R \times 600\text{ K}\ln\frac{10}{1}}{1 \times R \times 300\text{ K}\ln\frac{10}{1}} = \frac{600}{300} = 2$$

For isothermal expansion of ideal gases, $\Delta U = 0$. Since, temperature is constant this means there is no change in internal energy. Therefore, $\Delta U = 0$

Q-6 18.0 g of water completely vaporises at 100°C and 1 bar pressure and the enthalpy change in the process is 40.79 kJ mol^{-1}. What will be the enthalpy change for vaporising two moles of water under the same conditions? What is the standard enthalpy of vaporisation for water?

Ans. Given that, quantity of water = 18.0 g, pressure = 1 bar

As we know that, 18.0 gH_2O = 1 mole H_2O

Enthalpy change for vaporising 1 mole of H_2O = 40.79 kJ mol^{-1}

∴ Enthalpy change for vaporising 2 moles of $H_2O = 2 \times 40.79$ kJ = 81.358kJ

Standard enthalpy of vaporisation at 100°C and 1 bar pressure, $\Delta_{vap}H^\circ = +\ 40.79$ kJ mol^{-1}

Q-7 Use the following data to calculate $\Delta_{lattice}H^\ominus$ for NaBr. $\Delta_{sub}H^\ominus$ for sodium metal = 108.4 kJ mol^{-1}, ionisation enthalpy of sodium = 496 kJ mol^{-1}, electron gain enthalpy of bromine = −325 kJ mol^{-1}, bond dissociation enthalpy of bromine = 192 kJ mol^{-1}, $\Delta_f H^\ominus$ for NaBr(*s*) = − 360. 1 kJ mol^{-1}

This question is based upon the concept of Born-Haber cycle as well as Hess's law. Following steps are used to solve this problem.

(*i*) $Na(s) \rightarrow Na(g); \Delta_{sub}H^\ominus$

(*ii*) $Na(g) \rightarrow Na^+(g) + e^-(g); IE$

(*iii*) $\frac{1}{2}Br_2(g) \rightarrow Br(g); \Delta_{diss}H^\ominus$

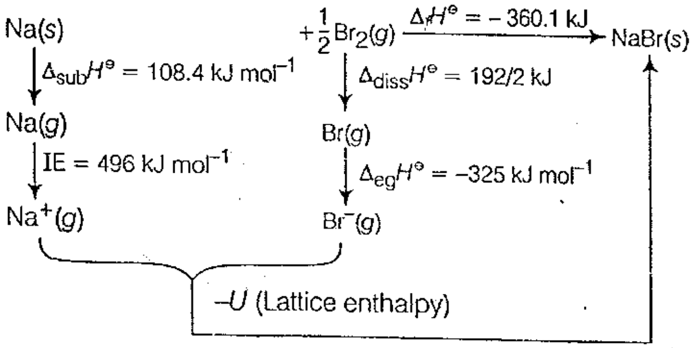
(*iv*) $Br(g) + e^-(g) \rightarrow Br^-(g); \Delta_{eg}H^\ominus$

(*v*) Applying Hess's law $\Delta_f H^\ominus = \Delta_{sub}H^\ominus + IE + \Delta_{diss}H^\ominus + \Delta_{eg}H^\ominus + U$

Ans. Given that, $\Delta_{sub}H^\ominus$ for Na metal = 108.4 kJ mol^{-1}

IE of Na = 496 kJ mol^{-1}, $\Delta_{eg}H^\ominus$ of Br = – 325 kJ mol^{-1}, $\Delta_{diss}H^\ominus$ of Br = 192 kJ mol^{-1}, $\Delta_f H^\ominus$ for NaBr = – 360.1 kJ mol^{-1}

Born-Haber cycle for the formation of NaBr is as



Q-8 The standard molar entropy of H_2O (*l*) is 70 JK^{-1} mol^{-1}. Will the standard molar entropy of $H_2O(s)$ be more, or less than 70 JK^{-1} mol^{-1}?

Ans. The standard molar entropy of H_2O (*l*) is 70 JK^{-1} mol^{-1}. The solid form of H_2O is ice. In ice, molecules of H_2O are less random than in liquid water.

Thus, molar entropy of H_2O (*s*) < molar entropy of H_2O (*l*). The standard molar entropy of H_2O (*s*) is less than 70 J K^{-1} mol^{-1}.

Q-9. Which quantity out of $\Delta_r G$ and $\Delta_r G^\ominus$ will be zero at equilibrium?

Ans. Gibbs energy for a reaction in which all reactants and products are in standard state. $\Delta_r G^\ominus$ is related to the equilibrium constant of the reaction as follows

$$\Delta_r G = \Delta_r G^\ominus + RT \ln K$$

At equilibrium,
$$0 = \Delta_r G^\circ + RT \ln K \qquad (\because \Delta_r G = 0)$$

or
$$\Delta_r G^\ominus = -RT \ln K$$

$$\Delta_r G^\ominus = 0 \text{ when } K = 1$$

For all other values of *K*, $\Delta_r G^\ominus$ will be non-zero.

Q-10 Although heat is a path function but heat absorbed by the system under certain specific conditions is independent of path. What are those conditions? Explain.

Ans. *The two conditions under which heat becomes independent of path are*

(i) when volume remains constant

(ii) when pressure remains constant

Explanation

(i) **At constant volume** By first law of thermodynamics, $\Delta U = q + W$ or $q = \Delta U - W$. But $W = -p\Delta V$ Hence, $q = \Delta U + p\Delta V$. But as volume remains constant $\Delta V = 0$

$\therefore q_V = \Delta V$ but ΔU is a state function.

Hence, q_V is a state function.

(ii) **At constant pressure** As we know, $q_p = \Delta U + p\Delta V$. But $\Delta U + p\Delta V = \Delta H$.

$\therefore q_p = \Delta H$. As ΔH is a state function therefore, q_p is a state function.

Q-11 Heat capacity (C_p) is an extensive property but specific heat (c) is intensive property. What will be the relation between C_p and c for 1 mole of water?

Ans. For water, molar heat capacity, $C_p = 18 \times$ Specific heat, c

$$C_p = 18 \times c \text{ Specific heat}$$

$$c = 4.18 \text{ Jg}^{-1}\text{K}^{-1} \qquad \text{(for water)}$$

Heat capacity,

$$C_p = 18 \times 4.18 \text{ JK}^{-1}\text{mol}^{-1}$$

$$= 75.3 \text{ JK}^{-1}\text{mol}^{-1}$$

Q-12 The difference between C_p and C_v can be derived using the empirical relation $H = U + pV$. Calculate the difference between C_p and C_v for 10 moles of an ideal gas.

Ans. Given that, C_v = heat capacity at constant volume,

C_p = heat capacity at constant pressure

Difference between C_p and C_v is equal to gas constant (R).

$$\therefore \quad C_p - C_v = nR \qquad \text{(where, } n = \text{no. of moles)}$$

$$= 10 \times 4.184 \text{ J}$$

$$= 41.84 \text{ J}$$

Q-13 The net enthalpy change of a reaction is the amount of energy required to break all the bonds in reactant molecules minus amount of energy required to form all the bonds in the product molecules. What will be the enthalpy change for the following reaction? $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$. Given that, bond energy of H_2, Br_2 and HBr is 435 kJ mol^{-1}, 192 kJ mol^{-1} and 368 kJ mol^{-1} respectively.

To, calculate the enthalpy change, use the following formula when the reactants, and products are in gas phase as

$$\Delta_r H^\ominus = \Sigma \text{ bond energy (reactants)} - \Sigma \text{ bond energy (products)}$$

Ans. Given that, bond energy of H_2 = 435 kJ mol^{-1}

bond energy of Br_2 = 192 kJ mol^{-1}

bond energy of HBr = 368 kJ mol^{-1}

For the reaction

$$H_2(g) + Br_2(g) \rightarrow 2HBr(g)$$

$$\Delta_r H^\ominus = \Sigma\text{BE (Reactants)} - \Sigma\text{BE (Products)}$$

$$= \text{BE }(H_2) + \text{BE}(Br_2) - 2\text{BE (HBr)}$$

$$= 435 + 192 - (2 \times 368) \text{ kJ mol}^{-1}$$

$$= -109 \text{ kJ mol}^{-1}$$

Q-14 The enthalpy of vaporisation of CCl_4 is 30.5 kJ mol^{-1}. Calculate the heat required for the vaporisation of 284 g of CCl_4 at constant pressure. (Molar mass of CCl_4 = 154 g mol^{-1})

Ans. Given that, 1 mol of CCl_4 = 154 g

$\Delta_{vap} H$ for 154 g CCl_4 = 30. 5 kJ

$\therefore$ $\Delta_{vap} H$ for 284 g $CCl_4 = \frac{30.5 \times 284}{154}$ kJ = 56. 25 kJ

Q-15: The enthalpy of reaction for the reaction

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l) \text{ is } \Delta_r H^\ominus = -572 \text{ kJ mol}^{-1}$$

What will be standard enthalpy of formation of H_2O (l)?

Ans. Given that,

$$2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(l),\ \Delta_r H^\circ = -572 \text{ kJ mol}^{-1}$$

Enthalpy of formation is the enthalpy change of the reaction when 1 mole of the compound is formed from its elements then

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l),\ \Delta_r H^\circ = ?$$

This can be obtained by dividing the given equation by 2.

Therefore, $\Delta_f H^\circ\ (H_2O) = -\frac{572 \text{ kJmol}^{-1}}{2} = -286 \text{ kJ mol}^{-1}$

Q-16 Represent the potential energy/enthalpy change in the following processes graphically.

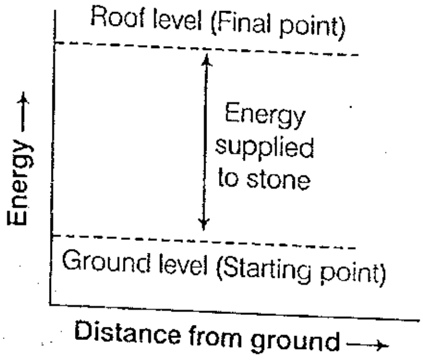
(a) Throwing a stone from the ground to roof.

(b) $\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \rightleftharpoons HCl(g)\ \Delta_r H^\ominus = -92.32 \text{ kJ mol}^{-1}$

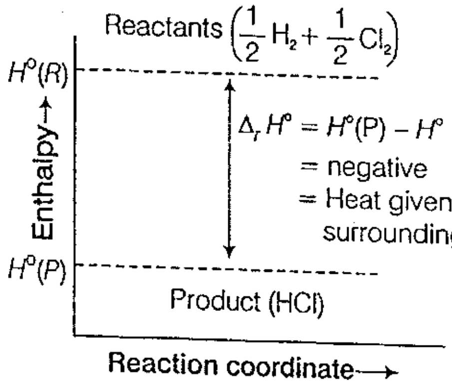
In which of the processes potential energy/enthalpy change is contributing factor to the spontaneity?

Ans. *Representation of potential energy/enthalpy change in the following processes*

(a) Throwing a stone from the ground to roof.

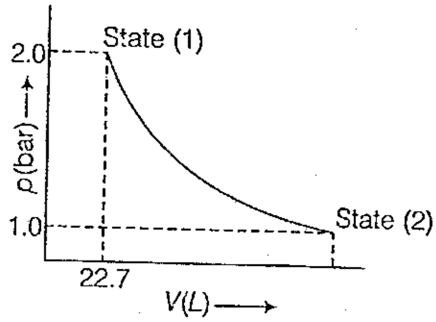


(b) $\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \rightleftharpoons HCl(g);\ \Delta_r H^\ominus = -92.32 \text{ kJ mol}^{-1}$



Energy increases in (a) and it decreases in (b) process. Hence, in process (b), enthalpy change is the contributing factor to the spontaneity.

Q- 17 1.0 mol of a monoatomic ideal gas is expanded from state (1) to state (2) as shown in figure. Calculate the work done for the expansion of gas from state (1) to state (2) at 298 K.



Ans. The given diagram represent that the process is carried out in infinite steps, hence it is isothermal reversible expansion of the ideal gas from pressure 2.0 atm to 1.0 atm 298 K.

$$W = -2.303\, nRT \log \frac{p_1}{p_2}$$

$$W = -2.303 \times 1 \text{ mol} \times 8.314 \text{ JK}^{-1}\text{mol}^{-1} \times 298 \text{ K} \log 2 \qquad \left(\because \frac{p_1}{p_2} = \frac{2}{1}\right)$$

$$W = -2.303 \times 1 \times 8.314 \times 298 \times 0.3010 \text{ J}$$
$$W = -1717.46 \text{ J}$$

Q-18 An ideal gas is allowed to expand against a constant pressure of 2 bar from 10 L to 50 L in one step. Calculate the amount of work done by the gas. If the same expansion were carried out reversibly, will the work done be higher or lower than the earlier case?
(Given that, 1 L bar = 100 J)

Ans. In the first case, as the expansion is against constant external pressure

$$W = -p_{ext}\,(V_2 - V_1) = -\,2 \text{bar} \times (50 - 10) \text{ L}$$
$$= -\,80 \text{ L bar} \qquad (1 \text{ L bar} = 100 \text{ J})$$
$$= -\,80 \times 100 \text{ J}$$
$$= -\,8 \text{ kJ}$$

If the given expansion was carried out reversibly, the internal pressure of the gas should be greater than the external pressure at every stage. Hence, the work done will be more.

Q-19 Derive the relationship between ΔH and ΔU for an ideal gas. Explain each term involved in the equation.

Ans. From the first law of thermodynamics, $q = \Delta U + p\Delta V$
If the process carried out at constant volume, $\Delta V = 0$
Hence, $q_v = \Delta U$
[Here, q_v = Heat absorbed at constant volume, ΔU = change in internal energy]
Similarly, $q_p = \Delta H$
Here, q_p = heat absorbed at constant pressure
ΔH = enthalpy change of the system.

Enthalpy change of a system is equal to the heat absorbed or evolved by the system at constant pressure.

As we know that at constant pressure, $\Delta H = \Delta U + p\Delta V$

where, ΔV is the change in volume.

This equation can be rewritten as $\Delta H = \Delta U + p(V_f - V_i) = \Delta U + (pV_f - pV_i)$ ...(i)

where, V_i = initial volume of the system V_f = final volume of the system

But for the ideal gases, $pV = nRT$

So that $pV_1 = n_1RT$

and $pV_2 = n_2RT$

where, n_1 = number of moles of the gaseous reactants

n_2 = number of moles of the gaseous products.

Substituting these values in Eq. (i), we get

$$\Delta H = \Delta U + (n_2RT - n_1RT)$$

$$\Delta H = \Delta U + (n_2 - n_1)RT$$

or

$$\Delta H = \Delta U + \Delta n_g RT$$

where, $\Delta n_g = n_2 - n_1$ is the difference between the number of moles of the gaseous products and gaseous reactants.

Putting the values of ΔH and ΔU we get

$$q_p = q_v + \Delta n_g RT$$

Note *Conditions under which $q_p = q_v$ or $\Delta H = \Delta U$*

(i) When reaction is carried out in a closed vessel so that volume remains constant i.e., $\Delta V = 0$

(ii) When reaction involves only solids or liquids or solutions but no gaseous reactant or product. This is because the volume changes of the solids and liquids during a chemical reaction are negligible.

(iii) When reaction involves gaseous reactants and products but their number of moles are equal (i.e., $n_p = n_r$) e.g.,

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$$

$$C(s) + O_2(g) \longrightarrow CO_2(g)$$

Since, q_p is different from q_v only in those reactions which involves gaseous reactants and products and (n_p) gaseous $\neq (n_r)$ gaseous.

Q-20 Extensive properties depend on the quantity of matter but intensive properties do not. Explain whether the following properties are extensive or intensive.

Mass, internal energy, pressure, heat capacity, molar heat capacity, density, mole fraction, specific heat, temperature and molarity.

Ans. **Extensive properties** Those properties whose value depends on the quantity or size of matter present in the system is known as extensive properties.

e.g., mass, internal energy, heat capacity.

Intensive properties Those properties which do not depend on the quantity or size of matter present are known as intensive properties. e.g., pressure, molar heat capacity, density, mole fraction, specific heat, temperature and molarity.

Mole fraction or molarity of a solution is same whether we take a small amount of the solution or large amount of the solution.

Ratio of two extensive properties is always intensive.

$$\frac{\text{Extensive}}{\text{Extensive}} = \text{Intensive}$$

So, mole fraction and molarity are intensive properties.

e.g.,

$$\text{mole fraction} = \frac{\text{Moles of the component}}{\text{Total no. of moles}} = \frac{\text{Extensive}}{\text{Extensive}}$$

and

$$\text{molarity} = \frac{\text{Mole}}{\text{Volume}} = \frac{\text{Extensive}}{\text{Extensive}}$$

Q. 51 Match the following.

List I	List II
A. Adiabatic process	1. Heat
B. Isolated system	2. At constant volume
C. Isothermal change	3. First law of thermodynamics
D. Path function	4. No exchange of energy and matter
E. State function	5. No transfer of heat
F. $\Delta U = q$	6. Constant temperature
G. Law of conservation of energy	7. Internal energy
H. Reversible process	8. $p_{ext=0}$
I. Free expansion	9. At constant pressure
J. $\Delta H = q$	10. Infinitely slow process which proceeds through a series of equilibrium states.
K. Intensive property	11. Entropy
L. Extensive property	12. Pressure
	13. Specific heat

Ans. A. → (5) B. → (4) C. → (6) D. → (1) E. → (7, 11, 12) F. → (2) G. → (3) H. → (10) I. → (8) J. → (9) K. → (1, 12, 13) L. → (7,11)

Q. 60 The lattice enthalpy of an ionic compound is the enthalpy when one mole of an ionic compound present in its gaseous state, dissociates into its ions. It is impossible to determine it directly by experiment. Suggest and explain an indirect method to measure lattice enthalpy of NaCl(s).

Ans. The lattice enthalpy of an ionic compound is the enthalpy change which occurs when one mole of an ionic compound dissociates into its ions in gaseous state. For the reaction

$$\mathrm{Na^+Cl^-}(s) \rightarrow \mathrm{Na^+}(g) + \mathrm{Cl^-}(g);\ \Delta_{\text{lattice}} H^\ominus = +\ 788\ \mathrm{k\,J\,mol^{-1}}$$

Since, it is impossible to determine lattice enthalpies directly by experiment, we use an indirect method where we construct an enthalpy diagram called a Born-Haber cycle.

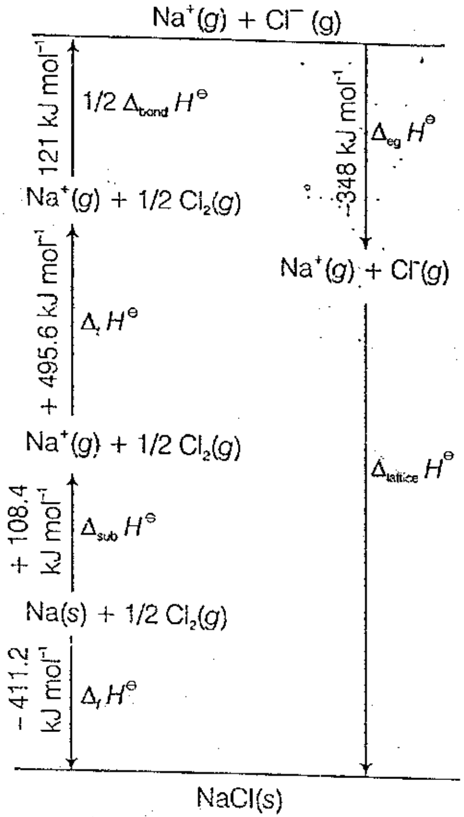
Let us now calculate the lattice enthalpy of Na^+Cl^- (s) by following steps given below

(i) $\mathrm{Na^+}\ (s) \rightarrow \mathrm{Na}(g)$; Sublimation of sodium metal, $\Delta_{\text{sub}} H^\ominus = 108.4\ \mathrm{kJ\,mol^{-1}}$

(ii) $\mathrm{Na}\ (g) \rightarrow \mathrm{Na^+}(g) + e^-\ (g)$; The ionisation of sodium atoms, ionisation enthalpy $\Delta_i H^\ominus = 496\ \mathrm{kJ\,mol^{-1}}$

(iii) $\frac{1}{2}\ \mathrm{Cl_2}\ (g) \rightarrow \mathrm{Cl}\ (g)$; The dissociation of chlorine, the reaction enthalpy is half the bond dissociation enthalpy $\frac{1}{2}\ \Delta_{\text{bond}} H^\ominus = 121\ \mathrm{kJ\,mol^{-1}}$.

(iv) $\mathrm{Cl}\ (g) + e^-(g) \rightarrow \mathrm{Cl^-}(g)$; electron gained by chlorine atoms. The electron gain enthalpy, $\Delta_{eg} H^\ominus = -\ 348.6\ \mathrm{kJ\,mol^{-1}}$



Enthalply diagram for lattice enthalpy of NaCl

(v) $Na^+(g)+Cl^-(g) \longrightarrow Na^+Cl^-(s)$

The sequence of steps is shown in given figure and is known as Born-Haber cycle. The importance of the cycle is that, the sum of the enthalpy changes round a cycle is zero.

Applying Hess's law, we get

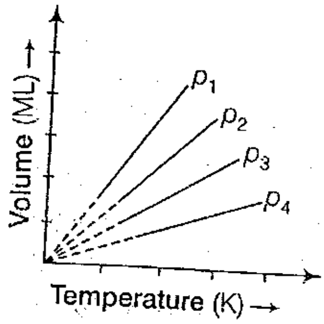
$$\Delta_{lattice}H^{\ominus} = 411.2 + 108.4 + 121 + 496 - 348.6$$

$$\Delta_{lattice}\ H^{\ominus} = +\ 788\ kJ$$

SARASWATI CHEMISTRY

States *of* Matter

Q-1 A plot of volume (V) *versus* temperature (T) for a gas at constant pressure is a straight line passing through the origin. The plots at different values of pressure are shown in figure. Which of the following order of pressure is correct for this gas?



(a) $p_1 > p_2 > p_3 > p_4$

(b) $p_1 = p_2 = p_3 = p_4$

(c) $p_1 < p_2 < p_3 < p_4$

(d) $p_1 < p_2 = p_3 < p_4$

Q-2 What is SI unit of viscosity coefficient (η) ?

(a) Pascal (b) Nsm^{-2} (c) km^{-2} s (d) Nm^{-2}

Ans. ***(b)*** The SI unit of viscosity coefficient (η) is Nm^{-2} s or Nsm^{-2}.

As we know that,
$$f = \eta A \frac{dv}{dx}$$
where,

f = force

η = viscosity coefficient

$\frac{dv}{dx}$ = velocity gradient

Substitute SI units of f = N, dx = m, A = m^2 and v = ms^{-1} in above equation, to get,

$$\eta = \frac{N \times m}{m^2 \times ms^{-1}} = Nm^{-2}s$$

Hence, the si unit of η=is nsm^{-2}

Q-3 If 1 g of each of the following gases are taken at STP, which of the gases will occupy (a) greatest volume and (b) smallest volume?

CO, H_2O, CH_4, NO

Ans. From Avogadro's law, we know that

Volume of 1 mole of the gas = graw molecular mass = 22.4 L at STP

Volume occupied by 28 g CO (1 mol CO) = 22.4 L at STP

($\because$ Molar mass of CO = 12+ 16 = 28 g mol^{-1})

$\therefore$ Volume occupied by 1 g CO = $\frac{22.4}{28}$ L at STP

Similarly, volume occupied by 1 g H_2O = $\frac{22.4}{18}$ L at STP

($\because$ Molar mass of H_2O = (2× 1) + 16 = 18 g mol^{-1})

Volume occupied by 1g $CH_4 = \frac{22.4}{16}$ L at STP

($\because$ Molar mass of $CH_4 = 12 + (4 \times 1) = 16\ g\ mol^{-1}$)

Volume occupied by 1g NO $= \frac{22.4}{30}$ L at STP

($\because$ Molar mass of NO $= 14 + 16 = 30\ g\ mol^{-1}$)

Thus, 1 g CH_4 will occupy maximum volume while 1 g of NO will occupy minimum volume at STP.

Q-4 Use the information and data given below to answer the questions (a) to (c),

Stronger intermolecular forces result in higher boiling point.

Strength of London forces increases with the number of electrons in the molecule.

Boiling point of HF, HCl, HBr and HI are 293 K, 189 K, 206 K and 238 K respectively.

(a) Which type of intermolecular forces are present in the molecules HF, HCl, HBr and HI?

(b) Looking at the trend of boiling points of HCl, HBr and HI, explain out of dipole-dipole interaction and London interaction, which one is predominant here.

(c) Why is boiling point of hydrogen fluoride highest while that of hydrogen chloride lowest? B ↑ [illegible]

Ans. From the information and data given in the question, we concluded that

(a) In HCl, HBr and HI, dipole-dipole and London forces are present because molecules possess permanent dipole. In HF dipole-dipole, London forces and hydrogen bonding are present.

(b) Electronegativity of chlorine, bromine and iodine decreases in the order are present

Cl> Br> I

Therefore, dipole moment should decrease from HCl to HI Thus, dipole-dipole interaction should decrease from HCl to HI. But boiling point increases on moving from HCl to HI. This means that London forces are predominant.

This is so because London forces increases as the number of electrons in a molecule increases and in this case number of electrons is increasing from HCl towards HI

(c) Hydrogen fluoride has highest dipole moment attributes due to highest electronegativity of fluorine as well as presence of hydrogen bonding in HF. Therefore, HF has highest boiling point.

Q-5 What will be the molar volume of nitrogen and argon at 273.15 K and 1 atm?

Ans. When temperature and pressure of a gas is 273.15 K (or 0 °C) and 1 atm (or 1 bar or 10^5 pascal), such conditions are called standard temperature and pressure conditions (STP). Under these conditions, the volume occupied by 1 mole of each and every gas is 22.4L. Hence, the moler volume of N_2 and Ar at 273.15 K and 1 atm is 22.4L.

Q-6 Compressibility factor, Z of a gas is given as $Z = \frac{pV}{nRT}$

(i) What is the value of Z for an ideal gas?

(ii) For real gas what will be the effect on value of Z above Boyle's temperature?

Ans. (i) For ideal gas, compressibility factor, $Z = 1$.

(ii) Above Boyle's temperature, real gases show positive deviation.

So,

$$Z > 1$$

Note *Following important points come out from the compressibility factor,* $Z = \frac{pV}{nRT}$.

(i) For ideal gas $Z = 1$ *at all temperatures and pressures because* $pV = nRT$.

(ii) At very low pressure all gases shown have $Z \simeq 1$ *and behave as ideal gas.*

(iii) At high pressure, all the gases have $Z > 1$ *These are more difficult to compress.*

(iv) At intermediate pressures most gases have $Z < 1$

Q-7 For real gases the relation between p, V and T is given by van der Waals' equation

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

where, 'a' and 'b' are van der Waals' constants, 'nb' is approximately equal to the total volume of the molecules of a gas. 'a' is the measure of magnitude of intermolecular attraction.

(i) Arrange the following gases in the increasing order of 'b'. Give reason.

$$O_2, CO_2, H_2, He$$

(ii) Arrange the following gases in the decreasing order of magnitude of 'a'. Give reason.

$$CH_4, O_2, H_2$$

Ans. (i) Molar volume occupied by the gas molecules $\propto$ size of the molecules and van der Waals' constant 'b' represents molar volume of the gas molecules. Hence, value of 'b' increases in the following order

$$H_2 < He < O_2 < CO_2$$

(ii) van der Waals' constant 'a' is the measure of magnitude of intermolecular attraction. The magnitude of intermolecular attractions increases with increase in size of electron cloud in a molecule. Hence, for the given gases magnitude of 'a' decreases in the following order

$$CH_4 > O_2 > H_2$$

Greater the size of electron cloud, greater is the polarisability of the molecule and greater is the dispersion forces or London forces.

Q-8 The relation between pressure exerted by an ideal gas (p_{ideal}) and observed pressure (p_{real}) is given by the equation,

$$p_{\text{ideal}} = p_{\text{real}} + \frac{an^2}{V^2}$$

(i) If pressure is taken in Nm^{-2}, number of moles in mol and volume in m^3, calculate the unit of 'a'.

(ii) What will be the unit of 'a' when pressure is in atmosphere and volume in dm^3?

Ans. Given that, $p_{\text{ideal}} = p_{\text{real}} + \frac{an^2}{V^2}$

(i) $a = \frac{pV^2}{n^2}$ If units of $p = Nm^{-2}$,

units of $V = m^3$, units of $n = mol$

then, units of $a = \frac{Nm^{-2}\ (m^3)^2}{(mol)^2} = Nm^4\ mol^{-2}$

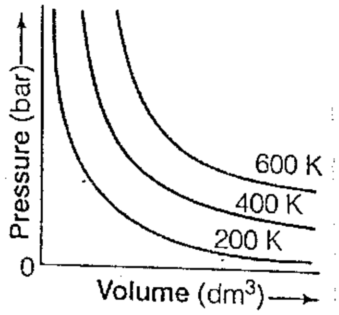
(ii) If units of $p = atm$, units of $V = dm^3$, units of $n = mol$

then, units of $a = \frac{pV^2}{n^2} = \frac{atm.\ (dm^3)^2}{(mol)^2} = atm\ dm^6\ mol^{-2}$

Q-9 The variation of pressure with volume of the gas at different temperatures can be graphically represented as shown in figure. On the basis of this graph answer the following questions.

(i) How will the volume of a gas change if its pressure is increased at constant temperature?

(ii) At a constant pressure, how will the volume of a gas change if the temperature is increased from 200 K to 400 K?

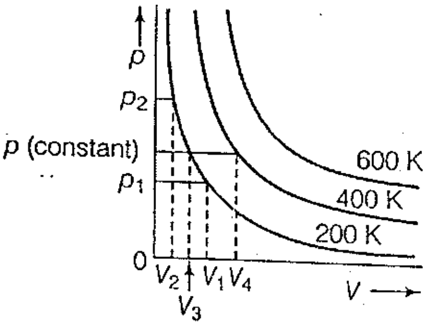


Ans. (i) In accordance to Boyle's law, pressure of a gas is inversly proportional to its volume if temperature is kept constant. Thus, the volume of a gas will decrease if the pressure on the gas is increased keeping the temperature constant. e.g., at 200 K when pressure increases from p_1 to p_2, volume of the gas decreases, $V_2 < V_1$.

(ii) In accordance to Iharles law, volume of a gas is directly proportional to its temperature if pressure is kept constant.

Thus, on increasing temperature, the volume of a gas will increase if pressure is kept constant.

At constant p when we increase the temperature from 200 K to 400 K, the volume of the gas increases, $V_4 > V_3$.



Q-10 Pressure *versus* volume graph for a real gas and an ideal gas are shown in figure. Answer the following questions on the basis of this graph.

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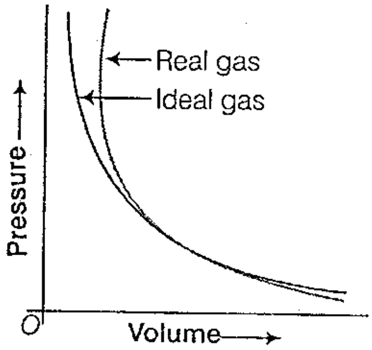


(i) Interpret the behaviour of real gas with respect to ideal gas at low pressure.

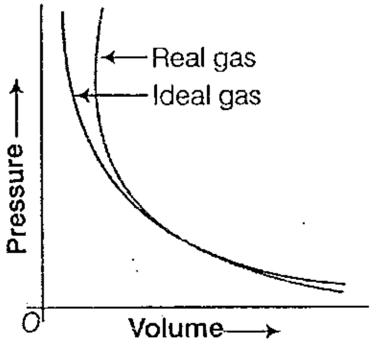
(ii) Interpret the behaviour of real gas with respect to ideal gas at high pressure.

(iii) Mark the pressure and volume by drawing a line at the point where real gas behaves as an ideal gas.

Ans. **(i)** At low pressure, the real gas shows very small deviation from ideal behaviour because the two curves almost coincide at low pressure.

(ii) At high pressure, the real gas show large deviations from ideal behaviour as the curves are far apart.

(iii) At point '*A*', both the curves intersect each other. At this point real gas behaves as an ideal gas. p_1 and V_1 are the pressure and volume which corresponds to this point *A*.



Q-11 Match the following gas laws with the equation representing them.

A.	Boyle's law	1.	$V \propto n$ at constant T and p
B.	Charle's law	2.	$p_{\text{Total}} = p_1 + p_2 + p_3 + \ldots$ at constant T, V
C.	Dalton's law	3.	$\dfrac{pV}{T} = \text{constant}$
D.	Avogadro's law	4.	$V \propto T$ at constant n and p
		5.	$p \propto \dfrac{1}{V}$ at constant n and T

Ans. A. → (5) B. → (4) C. → (2) D. → (1)

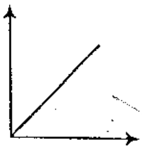
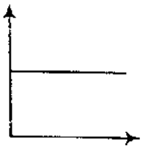
A. Boyle's law, $p \propto \frac{1}{V}$ at constant T and n.

B. Charle's law, $V \propto T$ at constant p and n.

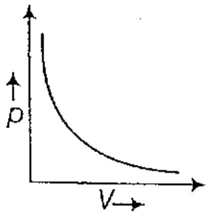
C. Dalton's law, $p_{\text{Total}} = p_1 + p_2 + p_3 + \ldots$ at constant T, V.

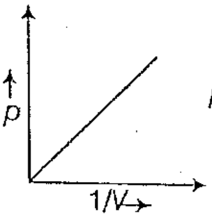
D. Avogadro's law, $V \propto n$ at constant T and p.

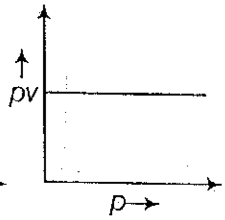
Q-12 Match the following graphs of ideal gas with their coordinates.

Graphical representation	X and Y coordinates
A. 	1. pV vs. V
B. 	2. p vs. V
C. 	3. p vs. $\frac{1}{V}$

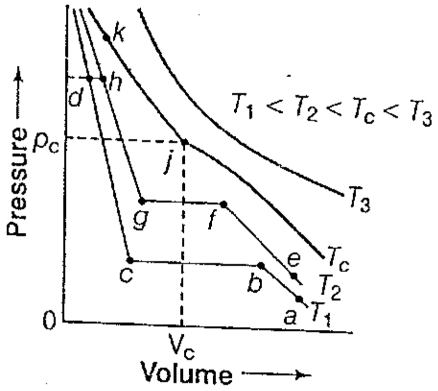
Ans. A. → (2) B. → (3) C. → (1)







Q-13 Isotherms of carbon dioxide at various temperatures are represented in figure. Answer the following questions based on this figure.



(i) In which state will CO_2 exist between the points a and b at temperature T_1?

(ii) At what point will CO_2 start liquefying when temperature is T_1?

(iii) At what point will CO_2 be completely liquefied when temperature is T_2?

(iv) Will condensation take place when the temperature is T_3?

(v) What portion of the isotherm at T_1 represent liquid and gaseous CO_2 at equilibrium?

Ans. (i) In gaseous state, CO_2 will exist between the points *a* and *b* at temperature T_1.

(ii) At point *b*, the plot becomes linear, this shows the phase transition, *i.e.*, liquification of CO_2 starts and at point *c*, it gets completely liquified.

(iii) Similarly, at temperature T_2, *g* is the point at which CO_2 will be completely liquified.

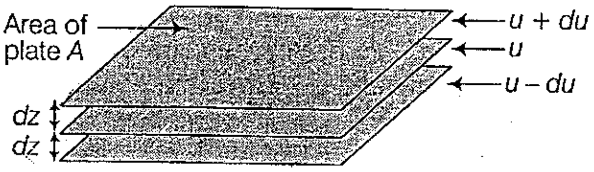
(iv) Condensation will not take place at T_3 temperature because $T_3 > T_c$ (critical temperature).

(v) Between *b* and *c*, liquid and gaseous CO_2 are in equilibrium.

Q-14 Explain the term 'laminar flow'. Is the velocity of molecules same in all the layers in laminar flow? Explain your answer.

Ans. When a liquid flows over a fixed surface, the layer of molecules in the immediate contact of surface is stationary. The velocity of the upper layers increases as the distance of layers from the fixed layer increases.

This type of flow in which there is a regular gradation of velocity in passing from one layer to the next is called laminar flow.



Gradation of velocity in the laminar flow

In laminar flow, the velocity of molecules is not same in all the layers because every layer offers some resistance or friction to the layer immediately below it.

SARASWATI CHEMISTRY

Chemical Bonding and Molecular Structure

Q-1 Which of the following statement is not correct from the view point of molecular orbital theory?

(a) Be_2 is not a stable molecule

(b) He_2 is not stable but He_2^+ is expected to exist.

(c) Bond strength of N_2 is maximum amongst the homonuclear diatomic molecules belonging to the second period.

(d) The order of energies of molecular orbitals in N_2 molecule is

$$\sigma 2s < \sigma^* 2s < \sigma 2p_z < (\pi 2p_x = \pi 2p_y) < (\pi^* 2p_x = \pi^* 2p_y) < \sigma^* 2p_z$$

Ans. *(d)* Existance of molecule, bonding nature and energy order of molecular orbitals can be explained on the basis of molecular orbital theory as follows

(i) Molecules having zero bond order never exists while molecular having non-zero bond order is either exists or expected to exist.

(ii) Higher the value of bond order, higher will be its bond strength.

Electrons present in bonding molecular orbital are known as bonding electrons (N_b) and electrons present on anti-bonding molecular orbital are known as anti-bonding electrons (N_a) and half of their difference is known as bond order *i.e.*,

(a) $Be_2\ (4 + 4 = 8) = \sigma 1s^2, \sigma^* 1s^2, \sigma 1s^2, \sigma^* 2s^2$

$$\text{Bond order (BO)} = \frac{1}{2}$$

[Number of bonding electrons (N_b) – Number of anti-bonding electrons N_a]

$$= \frac{4-4}{2} = 0$$

Here, bond order of Be_2 is zero. Thus, it does not exist.

(b) $He_2\ (2 + 2 = 4) = \sigma 1s^2, \sigma^* 1s^2$

$$BO = \frac{2-2}{2} = 0$$

$\therefore$ Here, bond order of Be_2 is zero. Hence, it does not exist.

$$He_2^+\ (2 + 2 - 1 = 3) = \sigma 1s^2, \sigma^* 1s^1$$

$$BO = \frac{2-1}{2} = 0.5$$

$\therefore$ Since, the bond order is not zero, this molecule is expected to exist.

(c) $N_2\ (7 + 7 = 14) = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_x^2 \approx \pi 2p_y^2, \sigma 2p_z^2$

$$BO = \frac{10-4}{2} = 3$$

Thus, dinitrogen (N_2) molecule contain triple bond and no any molecule of second period have more than double bond. Hence, bond strength of N_2 is maximum amongst the homonuclear diatomic molecules belonging to the second period.

(d) It is incorrect. The correct order of energies of molecular orbitals in N_2 molecule is

$$\sigma 2s < \sigma^* 2s < (\pi 2p_x = \pi 2p_y) < \sigma 2p_z < \pi^* 2p_x \approx \pi^* 2p_y < \sigma^* 2p_z$$

Q-2 Which of the following statements are not correct?

(a) NaCl being an ionic compound is a good conductor of electricity in the solid state

(b) In canonical structure there is a difference in the arrangement of atoms

(c) Hybrid orbitals form stronger bonds than pure orbitals

(d) VSEPR theory can explain the square planar geometry of XeF_4

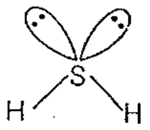
Ans. *(a, b)*

(a) NaCl is a bad conductor of electricity in solid due to the absence of free ions.

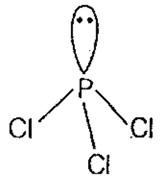
(b) Canonical structures differ in the arrangement of electrons, not in the arrangement of atoms.

Q-3 Explain the non-linear shape of H_2S and non-planar shape of PCl_3 using valence shell electron pair repulsion theory.

Ans. Central atom of H_2 is S. There are 6 electrons in its valence shell ($_{16}S = 2, 8, 6$). Two electrons are shared with two H-atoms and the remaining four electrons are present as two lone pairs.



Hence, total pairs of electrons are four (2 bond pairs and 2 lone pairs). Due to the presence of 2 lone pairs the shape becomes distorted tetrahedral or angular or bent (non-linear).

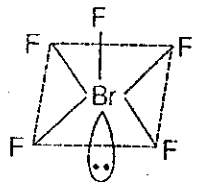


PCl_3–Central atom is phosphorus. There are 5 electrons in its valence shell ($_{15}P = 2, 8, 5$). Three electrons are shared with three Cl-atoms and the remaining two electrons are present as one lone pair.

Hence, total pairs of electrons are four (1 lone pair and 3 bond pairs). Due to the presence of one lone pair, the shape becomes pyramidal (non-planar).

Q-4 Explain the shape of BrF_5.

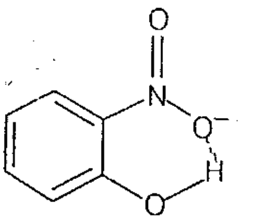
Ans. The central atom Br has seven electrons in the valence shell. Five of these will form bonds with five fluorine atoms and the remaining two electrons are present as one lone pair.



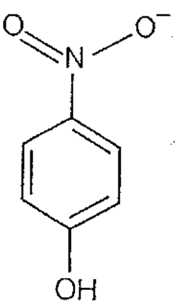
Hence, total pairs of electrons are six (5 bond pairs and 1 lone pair). To minimize repulsion between lone pairs and bond pairs, the shape becomes square pyramidal.

Q-5. Structures of molecules of two compounds are given below.

(I)



(II)



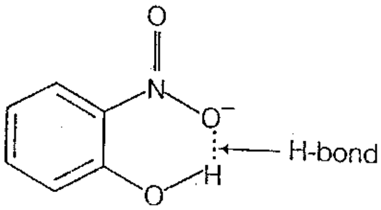
(a) Which of the two compounds will have intermolecular hydrogen bonding and which compound is expected to show intramolecular hydrogen bonding?

(b) The melting point of compound depends on, among other things, the extent of hydrogen bonding. On this basis explain which of the above two compounds will show higher melting point?

(c) Solubility of compounds in water depends on power to form hydrogen bonds with water. Which of the above compounds will form hydrogen bond with easily and be more soluble in it?

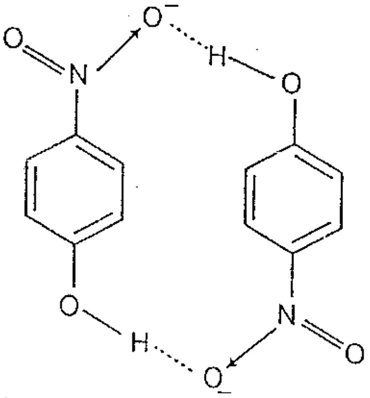
Ans. (a) Compound (I) will form intramolecular H-bonding. Intramolecular H-bonding is formed when H-atom, in between the two highly electronegative atoms, is present within the same molecule. In *ortho*-nitrophenol (compound I), H-atom is in between the two oxygen atoms.

(I)



Compound (II) forms intermolecular H-bonding. In *para*-nitrophenol (II) there is a gap between NO_2 and OH group. So, H-bond exists between H-atom of one molecule and O-atom of another molecule as depicted below.

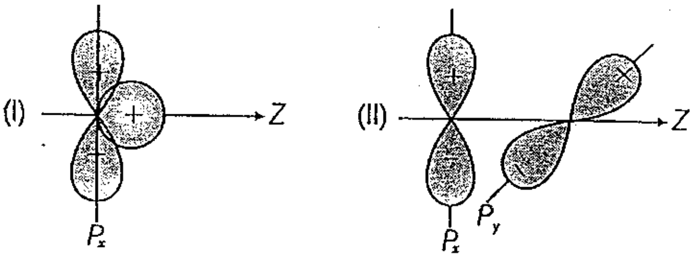
(II)



(b) Compound (II) will have higher melting point because large number of molecules are joined together by H-bonds.

(c) Due to intramolecular H-bonding, compound (I) is not able to form H-bond with water, so it is less soluble in water. While molecules of compound II form H-bonding with H_2O easily, so it is soluble in water.

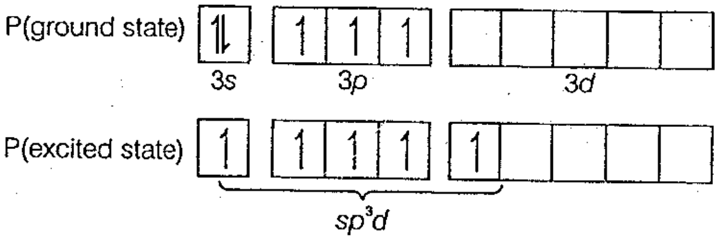
Q-6 Why does type of overlap given in the following figure not result in bond formation?

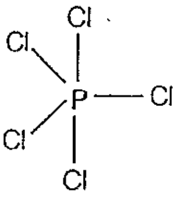


Ans. In the figure (I), area of ++ overlap is equal to +− overlap, so net overlap is zero, while in figure (II), there is no overlap due to different symmetry.

Q-7 Explain why PCl_5 is trigonal bipyramidal whereas IF_5 is square pyramidal.

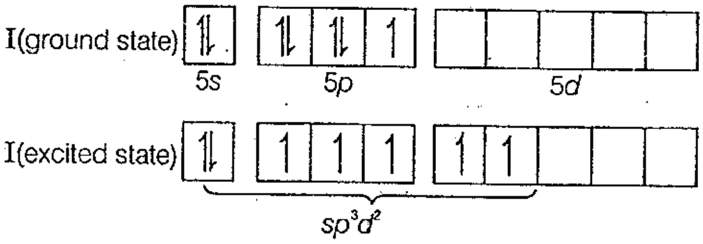
Ans. PCl_5–The ground state and the excited state outer electronic configurations of phosphorus ($Z = 15$) are represented below

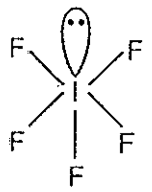




In PCl_5, P is sp^3d hybridised, therefore, its shape is trigonal bipyramidal.

IF_5–The ground state and the excited state outer electronic configurations of iodine ($Z = 53$) are represented below.





In IF_5, I is sp^3d^2 hybridised, therefore, shape of IF_5 is square pyramidal.

Q-8 The energy of $\sigma 2p_z$ molecular orbital is greater than $\pi 2p_x$ and $\pi 2p_y$ molecular orbitals in nitrogen molecule. Write the complete sequence of energy levels in the increasing order of energy in the molecule. Compare the relative stability and the magnetic behaviour of the following species.

$$N_2, N_2^+, N_2^-, N_2^{2+}$$

Ans. Electronic configuration of N-atom ($Z = 7$) is $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$. Total number of electrons present in N_2 molecule is 14, 7 from each N-atom. From the view of various rules for filling of molecular orbitals, the electronic configuration of N_2 molecule will be

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

Comparative study of the relative stability and the magnetic behaviour of the following species

(i) N_2 molecule $\sigma 1s^2, \sigma^* s^2, \sigma 2s^2, \sigma^* 2s^2, \pi p_x^2 \approx \pi 2p_y^2, \sigma 2p_z^2$

Here, $N_b = 10$, $N_a = 4$.

Hence, Bond order $= \frac{1}{2}(N_b - N_a) = \frac{1}{2}(10 - 4) = 3$

Hence, presence of no unpaired electron indicates it to be diamagnetic.

(ii) N_2^+ ions $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_x^2 \approx \pi 2p_y^2, \sigma 2p_z^1$

Here, $N_b = 9$, $N_a = 4$ so that BO $= \frac{1}{2}(9 - 4) = \frac{5}{2} = 2.5$

Further, as N_2^+ ion has one unpaired electron in the $\sigma(2p_2)$ orbital, therefore, it is paramagnetic in nature.

(iii) N_2^- ions $\sigma 1s^2, \sigma^* s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_x^2 \approx \pi 2p_y^2, \sigma 2p_z^2, \pi^* 2p_x^1$

Here, $N_b = 10$, $N_a = 5$ so that BO $= \frac{1}{2}(10 - 5) = \frac{5}{2} = 2.5$

Again, as it has one unpaired electron in the $\pi^*(2p_x)$ orbital, therefore, it is paramagnetic.

(iv) N_2^{2+} ions $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_x^2 \approx \pi 2p_y^2$

Here, $N_b = 8$, $N_a = 4$. Hence, BO $= \frac{1}{2}(8 - 4) = 2$

Presence of no unpaired electron indicates it to be diamagnetic in nature.

As bond dissociation energies are directly proportional to the bond orders, therefore, the dissociation energies of these molecular species in the order.

$$N_2 > N_2^- = N_2^+ > N_2^{2+}$$

As greater the bond dissociation energy, greater is the stability, the stability of these species is also in the above order.

Q-9 Give reason for the following.

(a) Covalent bonds are directional bonds while ionic bonds are non-directional.

(b) Water molecule has bent structure whereas carbon dioxide molecule is linear.

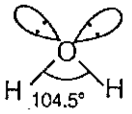
(c) Ethyne molecule is linear.

Ans. (a) A covalent bond is formed by the overlap of atomic orbitals. The direction of overlapping gives the direction of bond. In ionic bond, the electrostatic field of an ion is non-directional.

Each positive ion is surrounded by a number of anions in any direction depending upon its size and *vice-versa*. That's why covalent bonds are directional bonds while ionic bonds are non-directional.

(b) In H_2O, oxygen atom is sp^3 hybridised with two lone pairs. The four sp^3 hybridised orbitals acquire a tetrahedral geometry with two corners occupied by hydrogen atoms while other two by the lone pairs.

The bond angle is reduced to 104.5° from 109.5° due to greater repulsive forces between *lp* – *lp* and the molecule thus acquires a V-shape or bent structure (angular structure).



In CO_2 molecule, carbon atom is *sp*-hybridised. The two *sp* hybrid orbitals are oriented in opposite direction forming an angle of 180°.

$$\mathrm{O}\underset{\sigma}{\overset{\pi}{=\!=}}\mathrm{C}\underset{\sigma}{\overset{\pi}{=\!=}}\mathrm{O}$$

That's why H_2O molecule has bent structure whereas CO_2 molecule is linear.

(c) In ethyne molecule, both the carbon atoms are *sp* hybridised, having two unhybridised orbitals, *i.e.*, $2p_x$ and $2p_y$. The two *sp* hybrid orbitals of both the carbon atoms are oriented in opposite direction forming an angle of 180°.

$$\mathrm{H{-}C}\overset{\sigma}{\equiv}\mathrm{C{-}H}$$
$$2\pi\text{-bond}$$

That's why ethyne molecule is linear.

Q-10. What is an ionic bond? With two suitable examples the difference between an ionic and a covalent bond?

Ans. **Ionic bond** The bond formed, as a result of the electrostatic attraction between the positive and negative ions was termed as the electrovalent bond or ionic bond. *e.g.*, the formation of NaCl from sodium and chlorine can be explained as

$$\underset{[\mathrm{Ne}]3s^1}{\mathrm{Na}} \longrightarrow \underset{[\mathrm{Ne}]}{\mathrm{Na}^+} + e^-$$

$$\underset{[\mathrm{Ne}]3s^2 3p^5}{\mathrm{Cl}} + e \longrightarrow \underset{[\mathrm{Ne}]3s^2 3p^6 \text{ or } [\mathrm{Ar}]}{\mathrm{Cl}^-}$$

$$\mathrm{Na}^+ + \mathrm{Cl}^- \longrightarrow \mathrm{NaCl} \text{ or } \mathrm{Na}^+\mathrm{Cl}^-$$

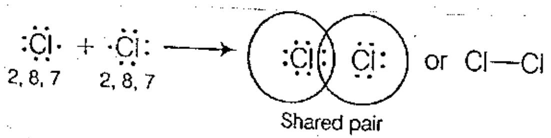
Similarly, the formation of CaF_2 may be shown as

$$\underset{[\mathrm{Ar}]4s^2}{\mathrm{Ca}} \longrightarrow \underset{[\mathrm{Ar}]}{\mathrm{Ca}^{2+}} + 2e^-$$

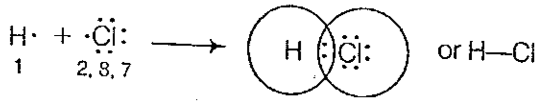
$$\underset{[\mathrm{He}]\,2s^2 2p^5}{\mathrm{F}} + e^- \longrightarrow \underset{[\mathrm{He}]\,2s^2 2p^6 \text{ or } [\mathrm{Ne}]}{\mathrm{F}^-}$$

$$\mathrm{Ca}^{2+} + 2\mathrm{F}^- \longrightarrow \mathrm{CaF}_2 \text{ or } \mathrm{Ca}^{2+}(\mathrm{F}^-)_2$$

Covalent bond The bond formed between the two atoms by mutual sharing of electrons between them is called covalent bond. *e.g.*, the formation of chlorine molecule can be explained as



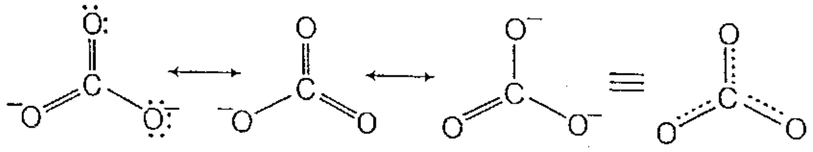
Similarly, in the formation of HCl



Q-11 All the C—O bonds in carbonate ion (CO_3^{2-}) are equal in length. Explain.

To explain the reason of equal in length of C—O bonds, it should keep in mind about the resonance. As a result of resonance, the bond length in a molecule become equal.

Ans. Carbonate ion (CO_3^{2-}) = 3 bond pair + 1 lone pair ⇒ trigonal planar



Due to resonance all C—O bond length are equal.

Q-12 What is meant by the term average bond enthalpy? Why is there difference in bond enthalpy of O—H bond in ethanol (C_2H_5OH) and water?

Ans. All the similar bonds in a molecule do not have the same bond enthalpies. *e.g.*, in H_2O(H — O — H) molecule after the breaking of first O—H bond, the second O—H bond undergoes some change because of changed chemical environment.

Therefore, in polyatomic molecules the term mean or average bond enthalpy is used. It is obtained by dividing total bond dissociation enthalpy by the number of bonds broken.

e.g.,

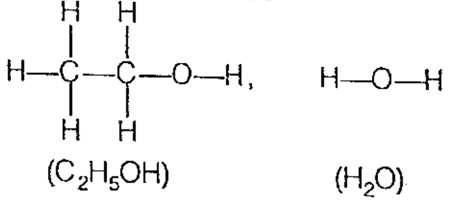
$$H_2O(g) \longrightarrow H(g) + OH(g);$$

$$\Delta_a H_1^\circ = 502 \text{ kJ mol}^{-1} \quad OH(g) \longrightarrow H + O(g);$$

$$\Delta_a H_2^\circ = 427 \text{ kJ mol}^{-1}$$

$$\text{Average O—H bond enthalpy} = \frac{502 + 427}{2} = 464.5 \text{ kJ mol}^{-1}$$

The bond enthalpies of O—H bond in C_2H_5OH and H_2O are different because of the different chemical (electronic) environment around oxygen atom.



Q-13 (a) Discuss the significance/applications of dipole moment.

(b) Represent diagrammatically the bond moments and the resultant dipole moment in CO_2, NF_3 and $CHCl_3$.

Ans. (a) *The applications of dipole moment are*

(i) The dipole moment helps to predict whether a molecule is polar or non-polar. As $\mu = q \times d$, greater is the magnitude of dipole moment, higher will be the polarity of the bond. For non-polar molecules, the dipole moment is zero.

(ii) *The percentage of ionic character can be calculated as*

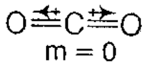
$$\text{Percentage of ionic character} = \frac{\mu_{\text{observed}}}{\mu_{\text{ionic}}} \times 100$$

(iii) Symmetrical molecules have zero dipole moment although they have two or more polar bonds (in determination of symmetry).

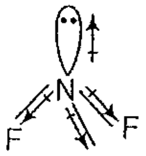
(iv) It helps to distinguish between *cis* and *trans* isomers. Usually *cis*-isomer has higher dipole moment than *trans* isomer.

(v) It helps to distinguish between *ortho*, *meta* and *para* isomers. Dipole moment of *para* isomer is zero. Dipole moment of ortho isomer is greater than that of *meta* isomer.

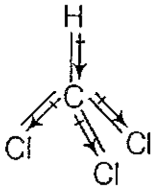
(b)



m = 0



m = 0.24 D



m = 1.03 D

Q-14. **Briefly describe the valence bond theory of covalent bond formation by taking an example of hydrogen. How can you interpret energy changes taking place in the formation of dihydrogen?**

Ans. Valence bond theory (VBT) was introduced by Heitler and London (1927) and developed further by Pauling and other. VBT is based on the knowledge of atomic orbitals, electronic configurations of elements, the overlap criteria of atomic orbitals, the hybridisation of atomic orbitals and the principles of variation and superposition.

Consider two hydrogen atoms *A* and *B* approaching each other having nuclei N_A and N_B and electrons present in them are represented by e_A and e_B. When the two atoms are at large distance from each other, there is no interaction between them.

As these two atoms approach each other, new attractive and repulsive forces begin to operate.

Attractive forces arise between

(i) nucleus of one atom and its own electron

i.e., $N_A - e_A$ and $N_B - e_B$

(ii) nucleus of one atom and electron of other atom

i.e., $N_A - e_B, N_B - e_A$

Similarly, repulsive forces arise between

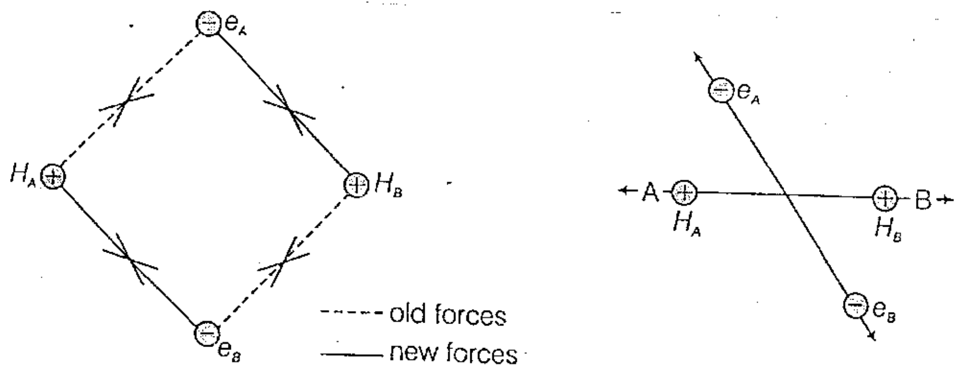
(i) electrons of two atoms like $e_A - e_B$

(ii) nuclei of two atoms like $N_A - N_B$

Attractive forces tend to bring the two atoms close to each other whereas repulsive forces tend to push them apart.

Experimentally, we have been found that the magnitude of new attractive force is more than the new repulsive forces. As a result two atoms approach each other and potential energy decreases.

Hence, a stage is reached where the net force of attraction balances the force of repulsion and system acquires minimum energy. At this stage, two H-atoms are said to be bonded together to form a stable molecule having the bond length of 74 pm.



Attractive forces

Repulsive forces

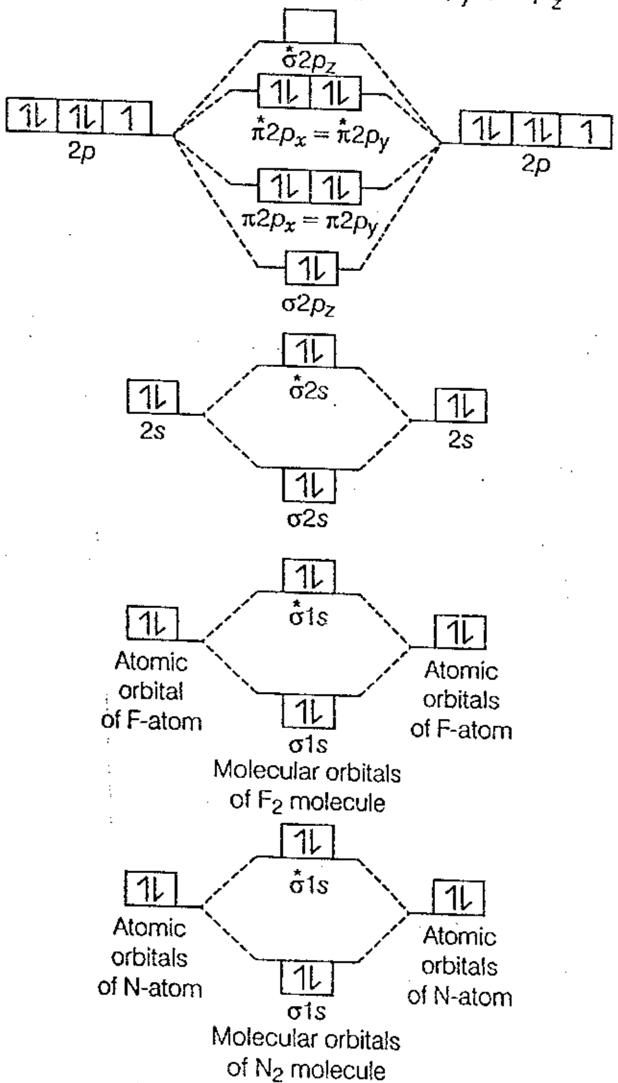
Forces of attraction and repulsion during the formation of H_2 molecule

Since, the energy gets released when the bond is formed between two hydrogen atoms, the hydrogen molecule is more stable than that of isolated hydrogen atoms.

Q-15. Use the molecular orbital energy level diagram to show that N_2 would be expected to have a triple bond. F_2, a single bond and Ne_2, no bond.

Ans. **Formation of N_2 molecule** Electronic configuration of N- atom $_7N = 1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^1$

N_2 molecule = $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_x^{\ 2} \approx \pi 2p_y^{\ 2}, \sigma 2p_z^2$

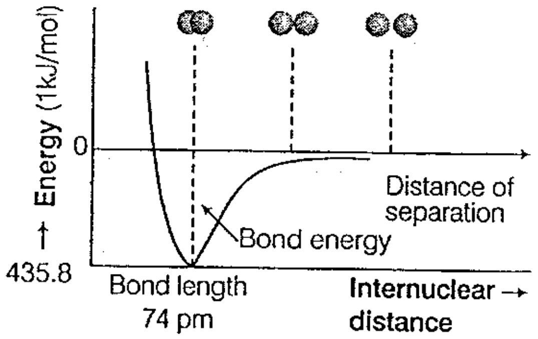


Bond order = $\frac{1}{2}[N_b - N_a] = \frac{1}{2}(10 - 4) = 3.$

Bond order value of 3 means that N_2 contains a triple bond.

The energy so released is called as bond enthalpy, which is corresponding to minimum in the curve depicted in the given figure. Conversely 435.8 kJ of energy is required to dissociate one mole of H_2 molecule.

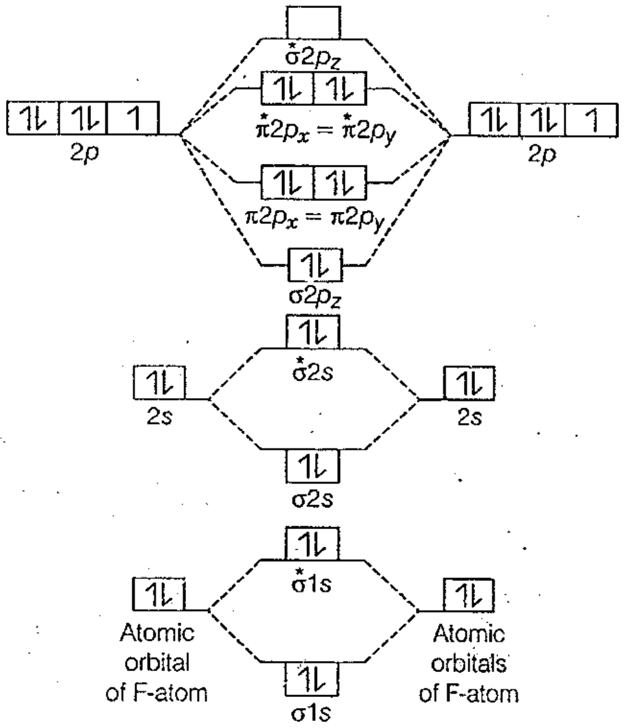
$$H_2(g) + 435.8\text{kJ mol}^{-1} \longrightarrow H(g) + H(g)$$



The potential energy curve for the formation of H_2 molecule as a function of internuclear distance of the H-atoms. The minimum in the curve corresponds to the most stable state or H_2.

Formation of F_2 molecule, ${}_9F = 1s^2, 2s^2, 2p_x^2, 2p_y^2, 2p_z^1$

F_2 molecule $= \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2 \approx \pi 2p_y^2, \pi^* 2p^2x \approx \pi^* 2p^2y$



Molecular orbitals of F_2 molecule

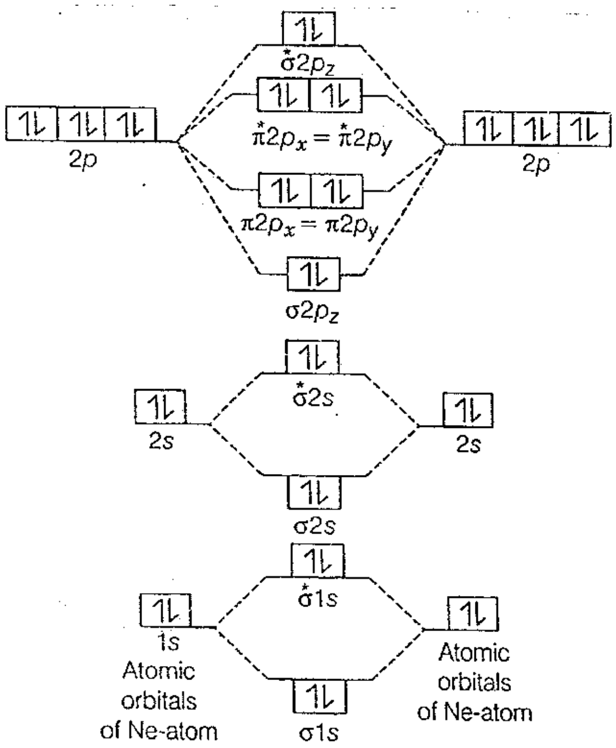
$$\text{Bond order} = \frac{1}{2}[N_b - N_a] = \frac{1}{2}(10 - 8) = 1$$

Bond order value 1 means that F_2 contains single bond.

Formation of Ne_2 molecule ${}_{10}Ne = 1s^2, 2s^2, 2p_x^2, 2p_y^2, 2p_z^2$

Ne_2molecule $= \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2 \approx \pi 2p_y^2, \pi^* 2p^2x$

$\approx \pi^* 2p^2y, \sigma^* 2p_z^2$



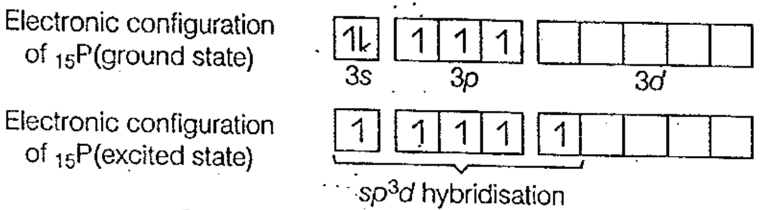
Molecular orbitals of Ne_2 molecule

Bond order $= \frac{1}{2}[N_b \; - N_a] = \frac{1}{2}(10 - 10) = 0$

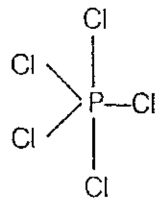
Bond order value zero means that there is no formation of bond between two Ne-atoms. Hence, Ne_2 molecule does not exist.

Q-16 Describe hybridisation in the case of PCl_5 and SF_6. The axial bonds are longer as compared to equatorial bonds in PCl_5 whereas in SF_6 both axial bonds and equatorial bonds have the same bond length. Explain.

Ans. Formation of PCl_5



In PCl_5, phosphorus is sp^3d hybridised to produce a set of five sp^3d hybrid orbitals which are directed towards the five corners of a trigonal bipyramidal. These five sp^3d hybrid orbitals overlap with singly occupied *p*-orbitals of Cl-atoms to form five P—Cl sigma bonds.



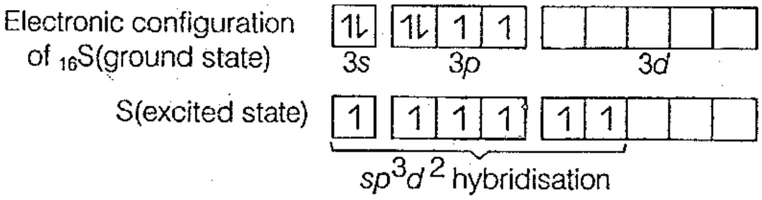
(Trigonal bipyramidal)

PCl_5

Three P—Cl bonds lie in one plane and make an angle of 120° with each other. These bonds are called equatorial bonds. The remaining two P—Cl bonds one lying above and other lying below the plane make an angle of 90° with the equatorial plane.

These bonds are called axial bonds. Axial bonds are slightly longer than equatorial bonds because axial bond pairs suffer more repulsive interaction from the equatorial bond pairs.

Formation of SF_6

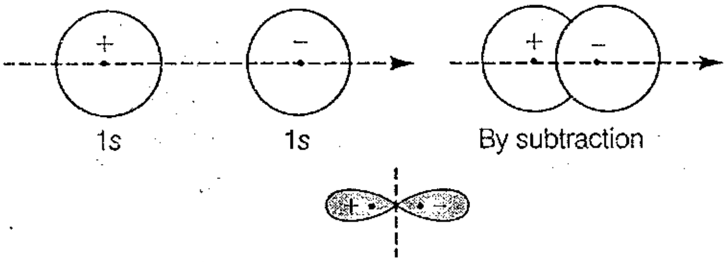


In SF_6, sulphur is sp^3d^2 hybridised to produce a set of six sp^3d^2 hybrid orbitals which are directed towards the six corners of a regular octahedron. These six sp^3d^2 hybrid orbitals overlap with singly occupied orbitals of fluorine atoms to form six S—F sigma bonds.
Thus, SF_6 molecule has a regular octahedral geometry and all S—F bonds have same bond length.

Q- 17 Which of the following molecular orbitals has maximum number of nodal planes?

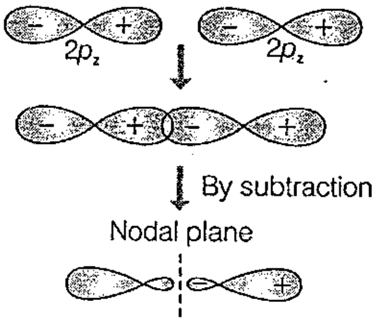
(a) $\sigma^* 1s$ (b) $\sigma^* 2p_z$
(c) $\pi 2p_x$ (d) $\pi^* 2p_y$

Ans. *(d)* Nodal plane are $\sigma^* 1s = 1, \sigma^* 2p_z = 1, \pi 2p_x = 1, \pi^* 2p_y = 2$

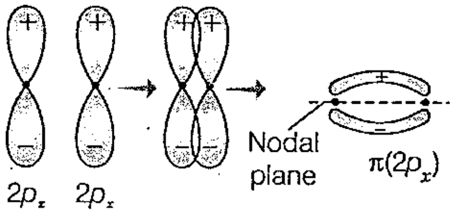


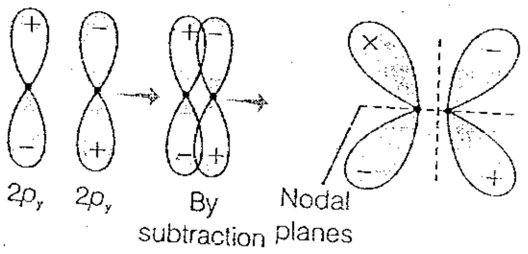
σ* (1s)
Anti-bonding molecular orbital

The molecular orbitals whose number of nodal planes are as



σ* ($2p_z$)





$\pi^*(2p_y)$

Q-18 Which of the following pair is expected to have the same bond order?

(a) O_2, N_2

(b) O_2^+, N_2^-

(c) O_2^-, N_2^+

(d) O_2^-; N_2^-

Ans. *(b)* On the basec of molecular orbetal therory we can calculate bond order of molecules ions as

$$BO = \frac{1}{2}(N_b - N_a)$$

Molecular orbital electronic configuration (MOEC) of N_2 is

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

Bond order of $N_2 = \frac{1}{2}(10-4) = 3$

MOEC of $N_2^+ = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_x^2 \simeq \pi 2p_y^2, \sigma 2p_2$

BO of $N_2^+ = \frac{1}{2}(9-4) = 2.5$

MOEC of $N_2^- = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_x^2 \simeq \pi 2p_y^2, \sigma 2p_z^2, \pi^* 2p_x^1 \simeq \pi^* 2p_y$

BO of $N_2^- = \frac{1}{2}(10-5) = 2.5$

MOEC of $O_2 = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2 \simeq \pi 2p_y^2, \pi^* 2p_x^1 \simeq \pi^* 2p_y^1$

BO of $O_2 = \frac{1}{2}(10-6) = 2$

MOEC of $O_2^- = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2 \simeq \pi 2p_y^2, \pi^* 2p_x^2 \simeq \pi^* 2p_y^1$

BO of $O_2^- = \frac{1}{2}(10-7) = 1.5$

MOEC of $O_2^+ = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2 \simeq \pi 2p_y^2, \pi^* 2p_x^2 \simeq \pi^* 2p_y$

BO of $O_2^+ = \frac{1}{2}(10-5) = 2.5$

(a) Bond order of O_2 and N_2 are 2 and 3, respectively.
(b) Bond order of both O_2^+ and N_2^- are 2.5.
(c) Bond order of O_2^- and N_2^+ are 1.5 and 2.5, respectively.
(d) Bond order of O_2^- and N_2^- are 1.5 and 2.5 respectively.

SARASWATI CHEMISTRY POINT

[CLASS - XI]

CHEMISTRY (THEORY)

[SAMPLE PAPER-I]

Time Allowed: 3 hrs **M.M.: 70**

General Instruction:

(i) All questions are compulsory
(ii) Marks for each question are indicated against it.
(iii) Question numbers 1 to 8 are very short answer questions and carry 1 marks each.
(iv) Question numbers 9 to 18 are short answer questions and carry 2 marks each.
(v) Question numbers 19 to 27 are also short answer questions and carry 3 marks each.
(vi) Question numbers 28 to 30 are long answer questions and carry 5 mark each.
(vii) Use log tables if necessary. Use of calculators is not allowed.

Q: 1. The following set of quantum number is not possible. Explain, Why?
$n = 2, l = 3, m = -3, m = +\frac{1}{2}$

Q: 2. Name a species which is isoelectronic with the following ions:
Mg^{2+}, N^{3-}, O^{2-}

Q: 3. For an isolated system $\Delta U = 0$, what will be ΔS?

Q: 4. Explain the structure of CO_2 in terms of resonance.

Q: 5. What are the conditions under which gases deviate from ideality.

Q: 6. Justify that the following reaction is a redox reaction:
$H_2O\,(s) + F_2\,(g) \rightarrow HF\,(g) + HOF\,(g)$

Q: 7. Write the IUPAC name of following:

$CH_2 = CH - C \equiv CH$

Q: 8. What is the oxidation state of K in KO_2?

Q: 9. Write balanced equation for the reaction between?

(a) Na_2O_2 and water

(b) Ca metal with HCl

Or

Describe the hybridization in case of PCl_5. Why are the axial bonds longer as compared to equatorial bonds?

Q: 10.(a) Use molecular orbital theory to explain why Be_2 molecular does not exist.

(b) Explain the formation of σ and π bonds in C_2H_4 with the help of diagram. Mention the hybrid state of two carbon atoms.

Q: 11. Calculate the mass of a photon with wavelength 3.6 Å. ($h = 6.26 \times 10^{-34}$ JS)

~~wave~~ $\lambda = \frac{h}{mc}$

$m = \frac{h}{\lambda c} = \frac{6.626 \times 10^{-34}}{3.6 \times 10^{-10} \times 3 \times 10^{8}} = \frac{\cancel{6.626 \times 10^{-34}}}{\cancel{108} \times 10^{-2}}$

5.08

~~5.379~~

~~5.4~~ /

5.08×10^{-32} kg

HNO_3

Q: 12. Predict the products of electrolysis of an aqueous solution of $AgNO_3$ with silver electrodes. Write reaction that occure at each electrode.

Cl^-

Cl^- is ~~more~~ ~~electronegative~~ electron donor

and (OH^-) comes after that

SO_4^{2-} OH^- | NO_3^-

Q: 13. Write all the reactions involved in the preparation of sodium carbonate from sodium chloride in Solvay process.

Q: 14. Complete the following equations:

(a) $Al + NaOH + H_2O \rightarrow$

(b) $H_3BO_3 \xrightarrow{\Delta} A \xrightarrow{\Delta} B$

Q: 15. A polluted water sample has been found to have 15 ppm $CHCl_3$ in it.

(a) Express this value in percent by mass

(b) Determine the molality of chloroform in the water sample.

Q: 16. An alkene 'A' on ozonolysis gives a mixture of ethanol and pentan-3-one. Write the structure and IUPAC name of A.

Q: 17. What is the basic principle involved in the following process:

(a) Partition chromatography

(b) Distillation under reduced pressure

Q: 18. **(a)** Explain why Be and Mg do not give colour to the flame whereas other alkaline earth metals do.

(b) Why alkali and alkaline earth metals cannot be prepared by chemical reduction methods?

Q: 19.(a) Calculate the concentration of nitric acid in moles per in a sample which has density 1.41 gmL^{-1} and the mass percent of HNO_3 in it being 69%.

(b) How many atoms are present in 48u of C?

Q: 20.(a) What are degenerate orbitals? Give Example.

(b) Show that the circumference of the Bohr's orbit for H atom is an integral multiple of de Broglie's wavelength associate with the electron revolving around the orbit.

Or

(a) Mention the difference between electromagnetic wave theory and Planck's quantum theory.

(b) How many electrons can have quantum number value $n = 4$, $m_s = ½$.

Q: 21.(a) Write the general outer electronic configuration of f-block elements.

(b) Predict the formula of a compound formed between silicon and oxygen.

(c)N has higher ionisation enthalpy than O and why?

Q: 22.(a) Calculate the total pressure in a mixture of 8 g O_2 and 4 g H_2 confined in a vessel of volume 1 dm³ at 27° C.(R = 0.083 bar $dm^{-3}\ K^{-1}\ mol^{-1}$).

(b) In terms of Charle's law explain why -273.15° C is the lowest possible temperature.

Q: 23.(a) The species H_2O and NH_3 can act both Bronsted acids and bronsted Bases. For each give the corresponding conjugate acid and conjugate base.

(b) What will be the pH of 0.002 M HCl?

Q: 24.(a) How the expression for Kp for the following reaction:

$CH_4\ (g) + H_2O\ (g) \rightleftharpoons CO\ (g) + 3H_2\ (g)$

(b) How will the value of Kp and compensation of equilibrium mixture be affected by:

(i) Increasing the pressure

(ii) Using a catalyst

Q: 25.(a) Out of NH_3, H_2O and HF Which would you expect to have highest magnitude of hydrogen bonding and why?

(b) Write chemical equation to justify that H_2O_2 can act as an oxidising agent as well as reducing agent.

Q: 26. Give reasons:

(a) Why CO is a poisonous gas?

(b) Lead (IV) chloride is highest unstable toward heat.

(c) Boric acid is not protic acid.

Q: 27. Explain the following terms:

(a) Ozone hole

(b)BOD

(c) Green chemistry

Q: 28.(a) Drive the relationship between Cp and Cv for an ideal gas.

(b) Given $N_2\,(g) + 3H_2\,(g) \rightarrow 2NH_3\,(g)$ $\Delta H = -92.4$ kJ/mol.

What is the standard enthalpy of formation of NH_3 gas?

(c) The equilibrium constant for a reaction is 10. What will be sign of ΔG? Will this reaction be spontaneous?

Or

(a) Compare the thermodynamic stabilities of NO and NO_2 from the following data:

$\frac{1}{2}N_2 + \frac{1}{2}O_2 \rightarrow NO\,(g)$ $\Delta_r H^{\circ} = 90$kj mol^{-1}

$NO\,(g) + \frac{1}{2}O_2 \rightarrow NO_2(g)$ $\Delta_r H^{\circ} = -74$kJmol^{-1}

(b) Write the Born Haber Cycle for the formation of $CaCl_2$ (s).

(c) For the reaction at 298 K : $2A + B \rightarrow C$

$\Delta H = 400\ kJ\ mol^{-1}$ and $\Delta S = 0.2\ kJK^{-1}\ mol^{-1}$

Determine the temperature at which the reaction would be spontaneous.

Q: 29.(a) Give the reactions involved in the estimation of N and Cl by Lassiagene's test.

(b) Explain the following with example:

(i) Electrophiles

(ii) Nucleophiles

(iii) Inductive effect

Or

(a) Explain why:

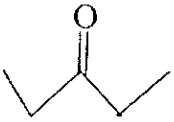
(i) $(CH_3)_3C^+$ is more stable than $CH_3CH_2^+$ and CH_2^+ is the least stable cation.

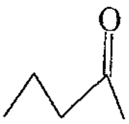
(ii) On adding $AgNO_3$ to CCl_4 Solution, white precipitate of AgCl is not obtained.

(iii) Nitric acid is added to sodium extract before adding $AgNO_3$ for testing halogens.

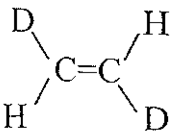
(b) What is the relationship between the numbers of the following pairs of structures?

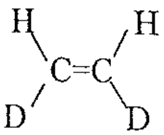
(1)





(2)





Q: 30.how will you convert:

- **(i)** Benzene to acetophenone
- **(ii)** Benzene to p-nitrophenone
- **(iii)**Ethanoic acid to methane

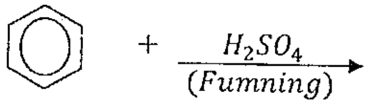
(b) Write IUPAC name of the product obtained by addition reaction of HBr to hex-1-ene in the presence of peroxide.

(c) Hydrogen atoms of ethyne are acidic in nature, why?

Or

(a) Complete the following:

(i)



(ii) $CaC_2 + H_3O \rightarrow$

(iii) $CH_2 = CH_2 + H_2O + O \xrightarrow[273\,K]{dil\,KMnO_2}$

SARASWATI CHEMISTRY POINT

[CLASS - XI]

CHEMISTRY (THEORY)

[SAMPLE PAPER-II]

Time Allowed: 3 hrs **M.M.: 70**

General Instruction:

(i) All questions are compulsory
(ii) Marks for each question are indicated against it.
(iii) Question numbers 1 to 8 are very short answer questions and carry 1 marks each.
(iv) Question numbers 9 to 18 are short answer questions and carry 2 marks each.
(v) Question numbers 19 to 27 are also short answer questions and carry 3 marks each.
(vi) Question numbers 28 to 30 are long answer questions and carry 5 mark each.
(vii) Use log tables if necessary. Use of calculators is not allowed.

Q: 1. Write the electronic configuration of Cu^+ (Z = 29).

Q: 2. State modern periodic law.

Q: 3. Give one example of intensive property.

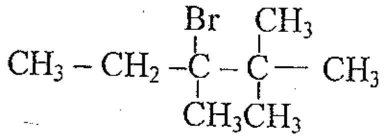
Q: 4. What would you observe when HCl gas is passed into the saturated solution of NaCl?

Q: 5. Calculate oxidation state of Mn in K_2MnO_4.

Q: 6. Draw the structure of $C_2H_5^+$.

Q: 7. Which reactive intermediate is formed when the covalent bond in CH_3- Li undergoes hetrolytic cleavage?

Q: 8. Pridict the alkene as a major product obtained by the dehydrohalogenation of:



$$CH_3-CH_2-\underset{CH_3}{\overset{Br}{C}}-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$$

Q: 9.A sample of NaOH weighing 0.38 g is dissolved in the water and solution is made 50.0 mL in a volumetric flask. Calculate the molarity of the resulting solution. (Molar mass of NaOH = 40 g mol^{-1})

Q: 10. Electromegnetic radiation of wavelength of 242 nm is just sufficient to ionise sodium atom. Calculate the ionization enthalpy of sodium in kJ/mol.

Q: 11. Draw the energy level diagram of molecular orbitals in N_2 molecule.

Q: 12. On the basic of kinetic theory of gases explain why:

(i) Gases exert pressure

(ii)The volume of fixed amount of gases constant pressure increase with the rise in temperature.

Q: 13.A student forget to add the reaction mixture to a flask at 27° C and placed on the flame and heated it to 477° C. What fraction of air has been expelled out?

Q: 14. State Le Chatelier principle. Predict the direction of the reaction:
$2SO_2 (g) + O_2 (g) \rightarrow 2SO_3(s)$
When noble gas is added to the reaction mixture at constant pressure.

Q: 15. Balance the following chemical equation in alkaline medium:
$I^- + MnO_4^- \rightarrow IO_3^- + MnO_2$

Q: 16. Contrast the action of heart on the following and explain your answer:
(i) Na_2CO_3 and $CaCO_3$
(ii)$Ca(NO_3)_2$ and $NaNO_3$

Q: 17. Write the chemical equation for the following reactions:
(i) Markownikov's rule
(ii) Friedel-Crafts reaction

Or

Explain the following technique of separation of organic compounds with suitable examples:

(i) Chromatography
(ii) Differential extraction

Q: 18.(a) Why is fusion of organic compound with sodium metal is essential before performing tests for detection of extra elements in the organic compounds?

(b) Write the chemistry involved in the test used for detection of nitrogen.

Q: 19. State Gay-Lussac's law combing volume of gas and Avogadro's law. Standard molar volume of any ideal gas is 22.7 L. Give the value of standard temperature and pressure.

Q: 20.(a) State Pauli's exclusion principle.

(b) Which rule will be disobeyed b the following electronic configurations?

(i) $2s^3$ **(ii)** $2s^2\,2p_x^2\;2p_y^1\;2p_z^0$

Q: 21. Account the following:

(i) Lionization enthalpy of nitrogen (Z = 7) is more than that of oxygen (Z = 8).

(ii) Electron gain enthalpy of chlorine (Z = 17) is more negative than that of fluorine (Z = 9).

(iii) Noble gases have high positive value of electron gain enthalpy.

Q: 22.(a) How many sigma (σ) and pi (π) bonds are there in $CH_2 = CH - CH \equiv CH$?s

(b) Using VSEPR model to predict the geometrical shapes of the following species:

(i) ClF_3 **(ii)** XeF_2

Q: 23.(a) If water molecules were linear instead of angular, Would water (H_2O) be a good solvent as it is? Why or why not?

(b) How is H_2O_2 prepared by hydrated barium peroxide? Show by chemical reactions that H_2O_2 acts both as oxidising and reducing agent.

Q: 24. Comment on each of the following observations:

(i) The mobilities of the alkali metal ions in aqueous solution are $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$.

(ii) Lithium is only alkali metal to form a nitride directly.

(iii) Alkaline earth metals are herder than alkali metals.

Or

What happened when?

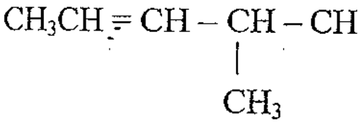
(i) Sodium metal is dropped in water.

(ii) Sodium metal is heated in free supply.

(iii) Sodium peroxide dissolved in water.

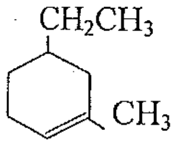
Q: 25. Write the IUPAC name of the following organic compounds:

(i)

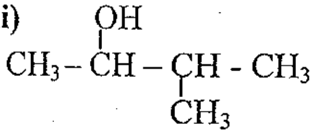


$CH_3CH=CH-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH$

(ii)



(iii)



$CH_3-\overset{\displaystyle OH}{\overset{|}{CH}}-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$

Q: 26. K_a for an acid (HA) is 5×10^{-6}. What is the pH of 0.2 M Solution of HA? Find also the molar concentration of A^-.

Q: 27. Write the use of green chemistry in the following day to day life processes of decreases in pollution:

(i) Dry cleaning of clothes
(ii) Bleaching of paper
(iii) Synthesis of chemicals

Q: 28.(a) Calculate $\Delta_r G^\ominus$ for conversation of oxygen to ozone:

$$3/2\ O_2(g) \rightarrow O_3 \text{ at } 298\ K$$

K_p for this conversation is 2.47×10^{-29}.

(b) State the second law of thermodynamics. How is Gibbs energy change is related with spontaneity of a process?

Or

(a) Define Gibbs energy.

(b) Predict the direction in which a reversible reaction will move when $\Delta G = +ve$

(c) Using the data given below, calculate the value of $\Delta_r G^{\oslash}$ and K_p for the following reaction at 298 K:

$3CH \equiv CH\ (g) \rightleftharpoons C_6H_6\ (g)$

Assuming ideal gas behaviour, $\Delta_j G^{\ominus}$ [$CH = CH\ (g)$] = 2.09×10^5 J mol^{-1}. $\Delta_j G^{\ominus}$ [C_6H_6 (g)] = 1.24×10^5 J mol^{-1} and R = 8.314 J K^{-1} mol^{-1}.

Q: 29.(a) Draw the structure of diborane.

(b) Define the term inter pair effect. Explain your answer with the help of lead chlorides.

(c)(i) Which is more ionic $SnCl_2$ or $SnCl_4$ and why?

(ii) PbO_2 is a strong oxidising agent. Assign a reason for this.

Or

a) Account for the following:

(i) $AlCl_3$ is a Lewis acid.

(ii) CO_2 is a gas while silicon dioxide is a solid.

(iii) Carbon shows catenation property but Pb does not.

b) Write the balanced chemical equation for the following reactions:

(i) $NaH + B_2H_6 \rightarrow$

(ii) $BF_3 + LiH \rightarrow$

Q: 30.(a) Make the following conversations:

(i) Propene to propanal

(ii)2-Beromopropane from propene

(b)A hydrocarbon 'A' Adds one mole of hydrogen in presence of Pt catalyst to from n-hexane. When 'A' is oxidised with hot $KMnO_4$ solution (alkaline), a single carboxylic acid containing three carbon atoms is isolated. Give the structure of 'A' and write chemical equation of reactions involved.

Or

a) Give on chemical test to distinguish the following pairs:

- **(i)** Ethene and Ethyne
- **(ii)** Ethane and Ethene

b) An alkene $C_{18}H_{16}$ on ozonolysis from ozonide which on hydrolysis with Zn dust from an aldehyde an pentan-2-one as products. Draw the structures of alkene and write the chemical reaction involved.

SARASWATI CHEMISTRY POINT

[CLASS - XI]

CHEMISTRY (THEORY)

[SAMPLE PAPER-III]

Time Allowed: 3 hrs **M.M.: 70**

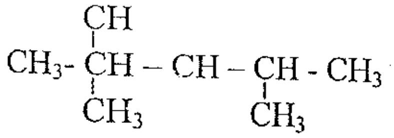
General Instruction:

(i) All questions are compulsory
(ii) Marks for each question are indicated against it.
(iii) Question numbers 1 to 8 are very short answer questions and carry 1 marks each.
(iv) Question numbers 9 to 18 are short answer questions and carry 2 marks each.
(v) Question numbers 19 to 27 are also short answer questions and carry 3 marks each.
(vi) Question numbers 28 to 30 are long answer questions and carry 5 mark each.
(vii) Use log tables if necessary. Use of calculators is not allowed.

Q: 1. Define Avogadro's Law.

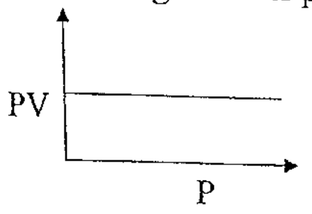
Q: 2. Write the electronic configuration of Cr (At. no. 24).

Q: 3. Give the IUPAC name of the following:



$$CH_3-\underset{CH_3}{\overset{CH}{CH}}-CH-\underset{CH_3}{CH}-CH_3$$

Q: 4. Which gas law is proved by the following graph?



Q: 5. The equilibrium constant of the following reaction is K_r.

$H_2 + I_2 \rightleftharpoons 2HI$

Predict the equilibrium constant of the reverse reaction.

Q: 6. Productof the sing of ΔS for the following reaction.

$CaCO_3\,(s) \xrightarrow{\Delta} CaCO\,(s) + CO_2\,(g)$

Q: 7. Can we store $CuSO_4$ in Zinc vessel?

Given: $E^\circ_{Cu^{2+}/Cu} = 0.34$ V;

$E^\circ_{Zn^{2+}/Zn} = -0.76$ V

Q: 8. How are 0.50 M Na_2CO_3 and 0.50 mol Na_2CO_3 different?

Q: 9. What do you understand by state functions? Neither q nor w is a state function but q + w is a state function. Explain.

Q: 10. **(a)** Draw the shape of B_2H_6 molecule. What is the hybridization of B-atoms.

(b) Why two different B-H bond lengths are observed for molecule?

Q: 11. Which of the following will have the most negative electron gain enthalpy and which will have the least value?
P, S, Cl, F.

Q: 12. Balance the following reaction in basic medium:
$Al + NO_3^- \rightarrow Al(OH)_4^- + NH_3$

Or

Predict the products of electrolysis in each of the following:
(i) An aqueous solution of $AgNO_3$ with silver electrodes.
(ii) A dilute solution of H_2SO_4 with Pi electrodes.

Q: 13. What happens when:
(i) Sodium metal is dropped in water.
(ii) $BaCl_3$ solution is added to sodium sulphate solution.

Q: 14. Which method of separation of components of a mixture should be used for the following mixtures:
(i) Mixture if o-and p-nitrophenol

(ii) A mixture containing two compounds with different solubilities in water.

Q: 15. There are four elements named A, B, C and D with atomic numbers z-1, z, z+1, z+2 respectively. B is a noble gas. Predict:

(i) Which element possesses the lowest first ionisation enthalpy?

(ii) Which element possesses the highest electronegativity?

Q: 16. Explain the following:

(i) NF_3 has lowest dipole moment than that of NH_3.

(ii) O_2 is paramagnetic is nature.

Q: 17. Complete the following reactions:

(i) $CH_3 - CH = CH_2 \xrightarrow[Peroxide]{HBr}$

(ii) $CH_3 - CH_2Br \xrightarrow[\Delta]{Alc.\ KOH}$

Q: 18.(a)Categorise the following as electrophile or nucleophile:
SO_3^-, OH_3^-
(b)Write the resonation structure of CH_3COO^-ion.

Q: 19.(a)Calculate the bond order of the following species and predict their magnetic behaviour:
N_2, N_2^-
(b)According to VSEPR theory,deduce the shape of XeF_4.

Q: 20.(a)Write Van der Waal's equation for 1 mole of a gas.
(b)Pressure of 1 g of an ideal gas at 27° C is found to be 2bar. When 2 g of another ideal gas B is introduced in the same flask at same temperature, the pressure become 3bar. Find a relationship between their molecular masses.

Or

(a) Calculate the temperature of 4.0 mol of a gas occupying $5 dm^3$ at 3.32bar. ($R = 0.083$ bar dm^3 K^{-1} mol^{-1}).

(b) The Van der Waal's constant of two gases A and B are:

Gas	a (atm L^2 mol^{-2})	b (L mol^{-1})
A	1.6	0.03
B	3.7	0.05

Which of the two gases is more easily liquefied?

Q: 21.(a) For an isolated system $\Delta U = 0$, what will be ΔS?

(b) Calculate the standard enthalpy of formation of CH_3OH (l) from the following data:

$CH_3OH (l) + \frac{3}{2} O_2 (g) \rightarrow CO_2 (g) + 2H_2O (g)$

$\Delta_r H^{\ominus} = -726$ kJ mol^{-1}

$C (g) + O_2 (g) \rightarrow CO_2 (g)$

$\Delta_r H^{\ominus} = -393$ kJ mol^{-1}

$H_2 (g) + \frac{1}{2} O_2 (g) \rightarrow H_2O (l)$

$\Delta_r H^0 = -286$ kJ mol^{-1}

Q: 22. Complete the following reactions:

(i) $PbS + H_2O_2 \rightarrow$
(ii) $K_4[Fe(CN)_6] + H_2SO_4 + H_2O_2 \rightarrow$
(iii) $KMnO_4 + H_2O_2 + H_2OS_4 \rightarrow$

Q: 23. Arrange the following in increasing order of property indicated against each:

(i) $BaSO_4$, $SrSO_4$, $CaSO_4$ (solubility in water)
(ii) Li^+, Na^+, K^+, Rb^+ (Ionic mobility)
(iii) LiCl, NaCl, KCl, RbCl (Ionic character)

Q: 24. Explain the following:

(i) Graphite is used as a lubricant.
(ii) $[SiF_6]^{2-}$ is known but $[SiCl_6]^{2-}$ is not.
(iii) Ga has smaller atomic radius than Al.

Q: 25. A welding fuel gas contains carbon and hydrogen only. Burning a small sample of it in oxygen gives 3.38 g CO_2. 0.690 g H_2O and no other products. A volume of 10.0 L (measured at STP) of this welding gas is found to weigh 11.6g. Calculate:

(i) Empirical formula of welding gas

(ii) Molar mass of the gas

(iii) Its molecular formula

Q: 26.(a) Why 3° Carbocation is more stable than 2° carbocation?

(b) 0.3780 g of an organic chlorocompound gave 0.5740 g of silver chloride in Carius estimation. Calculate the percentage of chlorine present in the compound. (at. Mass of Ag = 108u, at. Mass of Cl = 35.5u)

Q: 27.(a) What is the cause of acid rain?

(b) Define Eutrophication.

(c) What do you mean by green chemistry?

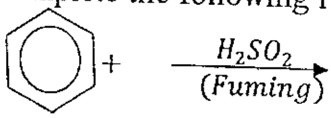
Q: 28.(a) Carry out the following conversation:

(i) Ethanoic acid to Methane

(ii) Benzene to Acetophenone

(b) Why is Wurtz reaction not preferred for preparation of alkanes having odd number of carbon atoms?

(c) Complete the following reaction:



(d) Give a chemical reaction test to distinguish between enthane and ethyne.

Or

(a) Give one example of:

- **(i)** Nucleophilic substitution reaction
- **(ii)** Electrophilic aromatic substitution

(b) Out of staggard and eclipsed conformation on n-butane, which is more stable and why?

(c) A hydrocarbon 'X' adds one mole of hydrogen in presence of Pi catalyst to form n-hexane. When 'X' is oxidised with $KMnO_4$. A single carbonxylic acid Y containing three carbon atoms is obtained identify X and Y.

Q: 29.(a) Hydrogen gas is obtained from the natural gas by the partial oxidation of natural gas by steam. The reaction is endothermic and can be represented as:

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$$

How will the composition of equilibrium mixture affected by:

(i) Increase in pressure

(ii) Increase in temperature

(iii) Using a catalyst

(b)Equal volume of 0.002 M solution of NaCl and $AgNO_3$ are mixed. Will it lead to the precipitation of AgCl? (K_{sp} of AgCl is 7.4×10^{-8})

Or

(a) Classify the following species as Lewis acid or Lewis base:

(i) OH^-

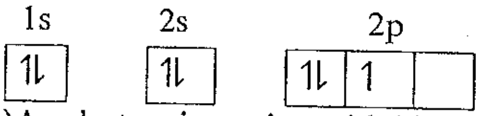
(ii) NH_4^+

(b) A solution of 0.2 M sodium nitric is basic in nature. Give reasons for this observation.

(c) A 0.2 M solution of formic acid is 3.2% ionised. What is its ionisation constant?

Q: 30.(a) List the quantum number(m and l) for electronic in electrons in 3d orbitals?

(b) Write the rule due to which the following electronic configuration for nitrogen is not possible:



(c) An electron is moving with kinetic energy of 2.275×10^{-25} J. Calculate its de Broglie wavelength. ($h = 6.626 \times 10^{-34}$ JS; $m_e = 9.1 \times 10^{-31}$ kg)

Or

(a) How many sub-shells are associated with n = 4?

(b) Give the boundary surface diagrams for the following orbitals:
$dx^2 - y^2$, dz^2

(c) Calculate the wavelength of a photo emitted during a transition from n = 5 state to the n = 2 state in the hydrogen atom. The ground state electron energy for H atom is 2.18×10^{-18} J/atom.

SARASWATI CHEMISTRY POINT

[CLASS - XI]

CHEMISTRY (THEORY)

[SAMPLE PAPER-IV]

Time Allowed: 3 hrs

M.M.: 70

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1. How many helium atoms are present in 52 u He? (1)

2. Write the electronic configuration of $_{26}Fe^{3+}$. (1)

3. Which of the following ion is unlikely to exist and why? (1)

4. Predict the hybridization of c in CH_4. (1)

5. What is the sign of ΔS for the following reaction?
$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$ (1)

6. Write the relation between the molar solubility (S) and K_{sp} for $Al_2S_3(s)$. (1)

7. What is the IUPAC name of $(CH_3)_3\,C\,CH_2C(CH_3)_2CH_3$ (1)

8. Complete the following reaction.
$CH_3CH = CH_2 \xrightarrow[\text{dark}]{\text{HCl}}$. (1)

9. Chlorophyll, the green colouring matter of plants responsible for photosynthesis contains 2.68 % of magnesium by mass. Calculate the number of magnesium atoms in 2.00g chlorophyll. (2)

10. The kinetic energy of a subatomic particle is 5.65×10^{-25} J. Calculate the frequency of the particle wave. ($h = 6.62 \times 10^{-34}$ Js) (2)

11. Give four points to distinguish between sigma & pi bonds. (2)

12. (a) How many antibonding electrons are present in O_2 molecule and how many are unpaired?

(b) Predict the hybridization of oxygen in H_3O^+. What is the shape of H_3O^+ ion? (2)

13. (a) At what temperature will the hydrogen molecules have the same kinetics energy as nitrogen molecules at 35°C?

(b) Under what condition, the real gas behaves ideally? (2)

14. Pressure of 1g of an ideal gas A at 27°C is found to be 2 bar. When 2g of another ideal gas B is introduced in the same flask at the same temperature, the pressure becomes 3 bar. Find the relationship between their molecular masses. (2)

15. Determine the solubility of barium sulphate in 0.05 M barium chloride solution. (Ksp of $BaSO_4 = 1.1 \times 10^{-10}$) (2)

16. Comment on each of the following observations:

(a) Lithium is the only alkali metal to form nitrides.

(b) $BeSO_4$ is soluble in water while $BaSO_4$ is insoluble. (2)

17. Why are boron halides and diborane referred to as 'electron deficient compounds'? (2)

18. Explain the following:

(i) Wurtz reaction

(ii) Markovnikov's rule. (2)

19. (i) Calculate the number of radial nodes in 3s.

(ii) State Hund's rule of maximum multiplicity.

(iii) What is the significance of y^2? (3)

20. Account for the following:

(i) First ionisation enthalpy of magnesium is greater than that of aluminium.

(ii) Lithium ad magnesium show similarity in their chemical properties.

(iii) Oxygen has a lower electron gain enthalpy that sulphur. (3)

21. One mole of H_2O and one mole of CO are taken in a 10L vessel and heated to 725 K. At equilibrium, 40% of water by mass reacts with CO according to the equation $H_2O(g) + CO(g) \rightleftharpoons H_2(g) + CO_2(g)$ Calculate the equilibrium constant for the reaction. (3)

22. (a) What is the oxidation state of sulphur in each compound?

$Na_2S_2O_3$, SO_4^{2-}

(b) Balance the following redox reaction:

$Cr_2O_7^{2-} + I^- + H^+ \rightarrow Cr^{3+} + I_2 + H_2O$ (3)

23. (a) What happens when ionic hydrides are treated with water?

(b) What happens when water reacts with cyanamide of calcium?

(c) How will you prepare H_2O_2 commercially? (3)

24. (a) Arrange the carbonates of group 2 in order of increasing thermal stability.

(b) Complete the following equation:

$NaHCO_3 \xrightarrow{\text{heat}}$

(c) Potassium forms KO_2, while Na forms Na_2O_2. Explain. (3)

25. (a) Give the structure of 2, 3-dibromo-3-ethylheptane.

(b) Write the IUPAC name of

(c) Why is $CH_3CHCH_2CH_2CH_3$ more stable carbocation than $CH_3CH_2C^+HCH_2CH_3$ (3)

26. What are electrophiles and nucleophiles? Give two examples of each. (3)

27. (a) What do you understand by Eutrophication? How does it threatens the development of fish?

(b) Name the two gases which cause greenhouse effect. (3)

28.(a) Write an equation when ethyne is passed through a red and hot tube.

(b) Write a short note on Friedel-Craft alkylation.

(c) Convert benzene into acetophenone.

(d) Complete the equation.

$$CH_3\,C \equiv CH \xrightarrow[H_gSO_4]{H_2O\ /\ H_2SO_4}$$

(e) Alkene (X) on oxidation gives propanoic acid and propanone. What is the structure and the IUPAC name of X? (5)

29. (a) Account for the following:

(i) CO_2 is a gas while SiO_2 is a solid at room temperature.

(ii) Aluminium sulphide gives a foul odour when it becomes damp.

(iii) Elemental silicon does not exist in graphite-like structure.

(b) What happens when aluminium is added to strong NaOH solution?

(c) C forms CF_4 but Si forms $(SiF_6)^{2-}$. Explain. (5)

30.(a) Define free energy.

(b) For the reaction

$Ag_2O(s) \rightleftharpoons 2Ag(s) + ½\ O_2g$

$\Delta H°_r = 40$ kJ/mol and $\Delta S°_r = +\ 110\ JK^{-1}\ mol^{-1}$

Calculate the temperature at which ΔG° becomes zero. What will be the sign of ΔG° above this temperature?

(c) Calculate the heat evolved in the following reaction:

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) - 2H_2O(l)$

Given:

$DH^\circ_f\, CH_4 = -72$ kJ/mol
$DH^\circ_f CO_2 = -393$ kJ/mol
$DH^\circ_f H2O = -286$ kJ/mol

(5)

SARASWATI CHEMISTRY POINT

[CLASS - XI]

CHEMISTRY (THEORY)

[SAMPLE PAPER-V]

Time Allowed: 3 hrs **M.M.: 70**

1. Write the structure of the product formed when propylene reacts with hydrogen bromide in the presence of organic peroxide. (1)

2. What is the effect of increasing temperature on the position of the following equilibrium: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + 92$ kJ. (1)

3. Write an equation relating DH and DU. (1)

4. Define molarity. (1)

5. State Heisenberg's uncertainty principle. (1)

6. Write the IUPAC name of the following compound:
$CH_3\,CH_2\,CH(OH)\,CH_2\,COOH$ (1)

7. Why is molecular nitrogen chemically unreactive? (1)

8. Why is Cl^- larger in size than Cl? (1)

9. The absolute isotope abundance ratio of chlorine $^{35}Cl/^{37}Cl$ is 3.1272. Calculate the atomic mass of chlorine. The mass of $^{35}Cl$and ^{37}Cl are 34.96885 and 36.96590u, respectively. (2)

10. Calculate the wavelength of the photon absorbed when e^- in a hydrogen atom jumps from its first excited state to the third excited states. (C = 3×10^8 m/s, h = 6.62×10^{-34} Js) (2)

11. Write the molecular orbital configuration of F_2. Calculate its bond order. (2)

12. Using orbital diagram, show the hybridization in ethene, C_2H_4. Molecule. (2)

13. 34.05 ml of phosphorous vapours weighs 0.0625 g at 546°C and 1 bar pressure. What is the molecular formula of phosphorous? (R = 0.083 L bar mol^{-1} K^{-1}) (2)

14. A mixture of hydrogen and oxygen at one bar pressure contains 20% (by weight) of hydrogen. Calculate the partial pressure of hydrogen. (2)

15. A gas absorbs 200 J of heat and expands its volume from 10 L to 20 L at 2 atm pressure. Calculate the change in internal energy. (2)

16. Write the structure of the major organic product formed in the following reactions:

(a) $CH_3-CH_2-CH_2-CH_2-Cl \xrightarrow[KOH]{hot \,\&\, alc.}$

(b) $CH_3-CH_2-CH_2-CH_2-OH \xrightarrow[170^\circ C]{H_2SO_4}$ (2)

17. How is boric acid prepared? What happens when boric acid is

(a) Added to water

(b) Strongly heated? (2)

18. What are carbides? How are they classified? Give two examples of each? (2)

19. (a) State Pauli exclusion principle.

(b) How man electrons in $_{17}Cl^-$ have $n + l$ value equals to 3?

(c) Draw the shape of 2s orbital. (3)

20. (a) Write the symbol and IUPAC name of an element with atomic number 129.

(b) Why is Li smaller in size than Na?

(c) Cl has higher e- gain enthalpy than F while F has higher Electronegativity than Cl Explain. (3)

21. Calculate the DG° for the following reaction at 27°C:

$3\,C_2H_2\,(g) \rightarrow C_6H_6\,(g)$

Given:

$\Delta G^\circ_f\, C_6H_6 = -\,7.5 \times 10^5\ J\ mol^{-1}$

$\Delta G^\circ_f\, C_2H_2 = -\,1.5 \times 10^5\ J\ mol^{-1}$

Also, predict whether we recommend this process on the commercial scale or not? (3)

22. (a) Balance the following redox reaction in basic medium:

$MnO_4^- + I^- \rightarrow MnO_2 + IO_3^-$

(b) Can we store $AgNO_3$ solution in a nickel container or not?

Given:

$E^\circ_{Ni_2^+/Ni} = -0.25$ V;

$E^\circ_{Ag^+/Ag} = +0.80$ V

(3)

23. (a) Name the two nuclear isomers of hydrogen. Which is more stable?

(b) Draw the structure of H_2O_2 in the gas phase.

(c) Why do we store H_2O_2 in black wax coated bottles?

(3)

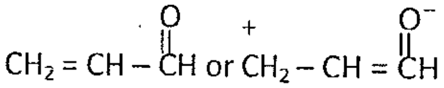
24. (a) Why can't we store sodium hydroxide in aluminium containers?

(b) $SiCl_4$ hydrolyse very readily whereas CCl_4 is inert towards water. Explain.

(c)State two anomalous behaviours of boron. (3)

25. (a) What do you understand by hyperconjugation? Using this explain why $(CH_3)_3C^+$ is more stable than $(CH_3)_2CH^+$.

(c) Which of the following structures is more stable and why?



$CH_2=CH-\overset{O}{\overset{\|}{C}}H$ or $\overset{+}{C}H_2-CH=\overset{O^-}{\overset{\|}{C}}H$ (3)

26. (a) Draw al possible alcohols with a molecular formula $C_4H_{10}O$. Also, write their IUPAC names.

(b) Draw the structure of 2-hydroxy but-3-enoic acid. (3)

27. (a) What are the harmful effects of carbon monoxide?
    (b) How are sulphur and nitrogen oxides produced in the atmosphere? What measures should we take to minimize their emission into the air? (3)

28. (a) The ph of a 0.05 M monobasic acid (HA) is 4.54. Calculate the concentration of the various species present at equilibrium.
    (b) State Le-Chatelier's principle. Discuss the effect of the following factor on the equilibrium: $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

$\Delta H° = -182$ kJ

(i) Increasing pressure
(ii) Increasing temperature
(iii) Addition of inert gas
(iv) Addition of a catalyst

(5)

29. (a) account for the following:

- (i) Solution of sodium in liquid ammonia gives a blue colour.
- (ii) $BeCO_3$ is stored in an atmosphere of CO_2.
- (iii) Lithium ion has least mobility in aqueous medium.

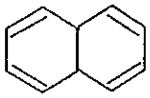
(b) How will you prepare sodium hydroxide commercially? Name the process. (5)

30. (a) Explain Friedel-Craft acetylation.

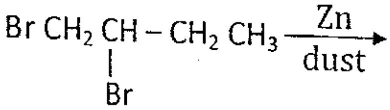
(b) How will you convert benzene into ethyl benzene?

(c) Which of the following compounds are aromatic and why?


,

,


(d) Complete the following equations:



$\mathrm{Br\,CH_2\,\underset{\underset{Br}{|}}{CH}-CH_2\,CH_3} \xrightarrow[\text{dust}]{\text{Zn}}$

(e) Alkane (A) with MW = 72 u gives only one mono chloro product on reaction with Cl_2 and sunlight. What is the structure and IUPAC name of (A)? (5)

SARASWATI CHEMISTRY POINT

[CLASS - XI]

CHEMISTRY (THEORY)

[SAMPLE PAPER-VI]

Time Allowed: 3 hrs **M.M. : 70**

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1. Predict the position of the elements in the periodic table satisfying the electronic configuration $(n-1)d^1 ns^2$ for $n = 4$. (1)

2. Define the term Avogadro's number. (1)

3. Why the change in enthalpy cannot the sole criterion for the spontaneity of a process? (1)

4. Arrange the following metal in the order in which they displace each other from the solution of their salts: Al, Cu, Fe, Mg and Zn. (1)

5. What are fullerenes? (1)

6. Define the term empirical formula and molecular formula. (1)

7. Calculate the number of protons, neutrons and electrons in 8035Br. (1)

8. Write the main features of the long form of periodic table. (1)

9. Write structural formulas of the following compounds:
   (i) 3, 4, 4, 5-Tetramethylheptane
   (ii) 2, 5-Dimethylhexane. (2)

10. 0.3780 g of an organic compound gave 0.5740 g of silver chloride in carius estimation. Calculate the percentage of chlorine present in the compound.

Or

In the estimation of sulphur by Carius method 0.468 g of an organic sulphur compound afforded 0.668 of barium sulphate. Find out the percentage of sulphur in the given compound. (2)

11. Diamond is covalent, yet it has high melting point. Why? (2)

12. Draw the structure of C_{60}, Buckminsterfullerene. Why is it called as Buckminsterfullerene? (2)

13. The enthalpy of formation of hypothetical CaCl (s) theoretically found to be – 188 kJ mol^{-1} and $\Delta_f H°$ for $CaCl_2$ (s) is -795 kJ mol^{-1}. Calculate the $\Delta_f H°$ for the disproportionation reaction. (2)

14. Density of a gas is found to be 5.46 g dm^{-3} at 27°C at 2 bar pressure. What will be its density at STP? (2)

15.What sorts of information can you draw from the following reaction?
$(CN)_2\ (g) + 2OH^-\ (aq) \rightarrow CN^-\ (aq) + CNO^-\ (aq) + H_2O(l)$ (2)

16. What are the harmful effects of photochemical smog and how can they be controlled? (2)

17. Calculate the molarity of a solution of ethanol in water in which the mole fraction of othanol is 0.040.0. (2)

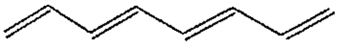
18. Give the significance of principal quantum number. (2)

19.(a) why does the benzene undergo electrophilic substitution reactions easily and nucleophilic substitutions with difficulty?

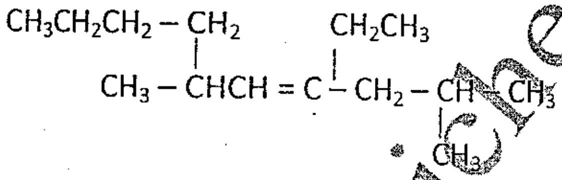
(b) Arrange the following compounds according to their increasing boiling points:
Hexane, heptanes, 2-Methylpentane, 2-2-Dimethylpentane

Or

Calculate number of sigma and pi bonds in the given structure:

(i) 

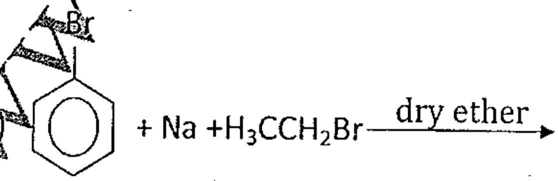
(ii) $CH_2=C(CH_2CH_2CH_3)_2$

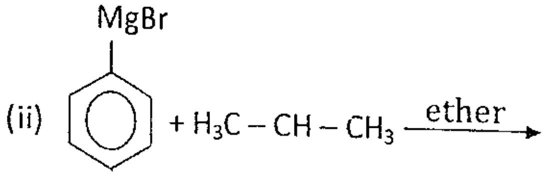
(iii) 

$$CH_3-\overset{\overset{CH_3CH_2CH_2-CH_2}{|}}{C}HCH=\overset{\overset{CH_2CH_3}{|}}{C}-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3$$

(3)

20. Complete the following reaction:

(i) 

(ii) 

(iii) $CH_3-C\equiv CH \xrightarrow[\text{Catalyst}]{873\text{ K}}$

(3)

21. Emission transitions in the Paschen series end at orbit $n = 3$ and start from orbit n and can be represented as $n = 3.2 \times 10^{15}$ Hz. Calculate the value of n if the transition is observed at 1285 nm. Find the region of the spectrum. (3)

22. What are the various factors due to which the ionisation enthalpy of the main group elements tends to decrease down a group? (3)

23. When metal (X) is treated with sodium hydroxide, a white precipitate (A) is obtained, which is soluble in excess of NaOH to give soluble complex (B)? Compound (A) is soluble in dilute HCl to form compound (C). The compound (A) when heated strongly gives (D), which is used to extract metal. Identify (X), (A), (B), (C) and (D). Write suitable equations to support their identities. (3)

24. Explain the following reactions:

(i) Silicon is heated with methyl chloride at high temperature in the presence of copper.

(ii) Silicon dioxide is treated with hydrogen fluoride.

(iii) Hydrated alumina is treated with aqueous NaOH solution. (3)

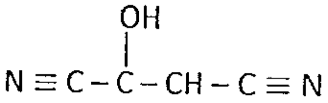
25. When an alkali metal dissolves in liquid ammonia the solution can acquire different colours. Explain the reason for this type of colour change. (3)

26. Discuss the principle and method of softening of hard water by synthetic ion-exchange resins. (3)

27. At 700 K, equilibrium constant for the reaction: $H_2 (g) + I_2 (g) \rightleftharpoons 2HI (g)$ is 54.8. If 0.5 mol L^{-1} of HI (g) is present at equilibrium at 700 K, what are the concentration of $H_2(g)$ and $I_2 (g)$ assuming that we initially started with HI (g) and allowed it to reach equilibrium at 700 K. (3)

28. (a) For each of the following compounds, write a condensed formula and also their bond line formula.

(i) $HOCH_2CH_2CH_2CH(CH_3)CH(CH_3)CH_3$

(ii) 
$N \equiv C-\overset{\overset{OH}{|}}{C}-CH-C \equiv N$

(b) Give the wedge and dash representation of CH_4.

(c) Arrange the following alkyl radicals in increasing order of their stability.

$\overset{+}{C}H_3, \overset{+}{C}H_2CH_3, \overset{+}{C}H(CH_3)_2, \overset{+}{C}(CH_3)_2$

OR

(a) Name the method used for the quantitative estimation of carbon and hydrogen in an organic compound.

(b) How can you confirm the purity of a compound?

(c) Structures and IUPAC names of some hydrocarbons are given below. Explain, why the names given in parentheses are incorrect? (5)

29. (a) Two litres of an ideal gas at a pressure of 1 atm expands isothermally into a vacuum until its total volume is 10 litres. How much heat is absorbed and how much work is done in the expansion.

(b) Derive a relationship between heat of reaction at constant pressure and constant volume e.g., $\Delta H = \Delta U + \Delta n_g RT$.

OR

(a) A swimmer coming out from a pool is covered with a film of water weighing about 18 g. How much heat must be supplied to evaporate this water at 298 K? Calculate the internal energy of Vapourisation at 100°c.

$\Delta_{vap}H^\circ$ for water at 373 K = 4066kJ mol^{-1}

(b) Derive a relationship between Cp and Cv for an ideal gas. (5)

30.(a) What is meant by the conjugate acid base pair? Find the conjugate acid/base for the following species:

(b) The ionisation constant of phenol is 1.0×10^{-10}. What is the concentration of phenolate ion in 0.05M solution of phenol? What will be its degree of ionization if the solution is also 0.01 M in sodium phenate.

OR

(a) The first ionisation constant of H_2S is $9.1 \times 10_{-8}$ and second dissociation constant of H_2S is 1.2×10^{-13}. Calculate the concentration of HS^- ion in its 0.1 M solution and how will this concentration be effected if the solution is 0.1 M in HCl also. Calculate the concentration of S^2.

(b) The ionisation constant of acetic acid is 1.74×10^{-5}. Calculate the degree of dissociation of acetic acid in its 0.05 M solution. Calculate the concentration of acetate ion in the solution and its pH.

(5)

SARASWATI CHEMISTRY POINT

[CLASS - XI]

CHEMISTRY (THEORY)

[SAMPLE PAPER-VII]

Time Allowed: 3 hrs **M.M.: 70**

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1. How many elements can be accommodated in the present set up of the long form of the periodic table? (1)

2. An aqueous solution of sodium carbonate gives alkaline tests. Why? (1)

3. What is the oxidation state of S in $Na_2S_2O_3$? (1)

4. What will be the pH of a 0.1 M ammonium acetate if $pK_a = pK_b = 4.74$? (1)

5. Write the conjugate acids of C_6H_5OH and NH_2NH_2. (1)

6. The equilibrium constant of a reaction at 27°C and 127°C are 1.52×10^{-4} and 1.26×10^{-2} respectively. Is the reaction exothermic or endothermic? (1)

7. The enthalpy change for the reaction: $2NH_3 (g) \rightarrow N_2 (g) + 3H_2 (g)$ is 92.2 kJ. What is the enthalpy of formation of ammonia? (1)

8. What would be the SI units for the quantity pV^2T^2/n? (1)

9. Give molecular electronic configuration of peroxide ion and oxygen molecule. Which of the two has larger bond length? (2)

10. How would you explain the fact that the first ionization enthalpy of sodium is lower than that of magnesium but its second ionization enthalpy is higher than that of magnesium? (2)

11. Calculate the wavelength of an electron having mass = 9.1×10^{-31} kg and kinetic energy $=3.0 \times 10^{25}$ J. (2)

12. If 20.0 g of $CaCO_3$ is treated with 20.0 of HCl, how many grams of CO_2 can be produced according to the reaction: $CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$ (2)

13. Explain the following:

(i) Liquids like acetone and ether are kept at cold places.

(ii) Hydrogen and helium are not liquefied at room temperature. (2)

14. For the water gas reaction:

$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$ the standard Gibbs energy for the reaction at 1000 K is $-8.1\ kJ\ mol^{-1}$. Calculate its equilibrium constant. (2)

15. What is Le Chatelier's principles. With the help of this explain: ice melts when pressure is applied on it? (2)

16. Calculate the strength in volumes of a solution containing 30.36 g/L of H_2O_2. (2)

17. Discuss the various reactions that occur in the solvay process. (2)

18. Give the basic difference between Duma's method and Kjeldahl's method for the estimation of nitrogen. (2)

19. Draw structures of cyclic and acylic isomers of molecular formula C_3H_6O. (3)

20. (a) Which of the two: $O_2N\ CH_2CH_2O^-$ or $CH_3CH_2O^-$ is expected to be more stable and why?

(b) Why alkyl groups act as electron donors when attached to a p-system.

(c) Which of the following carbocation is more stable:

(i) $(CH_3)_3\ CCH_2^+$

(ii) $CH_3C^+H_2CH_3$

(iii) $CH_3CH_2CH_2^+$

(3)

21. (a) How will you convert:

(i) Ethane to butane

(ii) Ethane to ethyne

(iii) Ethyne to methane

(b) What effect does branching of alkane change has on its boiling into.

(c) Draw cis and trans isomers of hex-2-ene. Which isomer will have higher boiling point?

(3)

22. (a) Write down the products of ozonolysis of 1, 2-Dimethylbenzene. How do the results support the Kekule structure of benzene?

(b) Why is benzene extra ordinarily stable though it contains three double bonds? (3)

23. Give the reasons:

(i) Aluminium wires are used to make transmission cables.

(ii) Diamond is used as an abrasive.

(iii) Aluminium utensils should not be kept in water overnight. (3)

24. Complete the following reactions:

(i) $Ca_3N_2\ (s) + H_2O\ (l) \longrightarrow$

(ii) $MnO_4^- + H^+ + H_2O_2 \longrightarrow$

(iii) $I_2 + H_2O_2 + OH^- \longrightarrow$ (3)

25. (a) The Mn^{3+} ion is unstable in solution and undergoes disproportionation to give Mn^{2+} MnO_2 and H^+ ion. Write a balance ionic equation for the reaction.
(b) Predict the product of electrolysis of an aqueous solution of $AgNO_3$ with Ag electrodes. (3)

26. (a) The wavelength of first spectral line in the Balmer series is 6561 Å. Calculate the wavelength of the second spectral line in Balmer series.
(b) How many electrons in a given atom can have the following quantum number values: n = 4, l = 2, m = 1 (3)

27. Commercially available sulphuric acid contains 93% acid by mass and has a density of $1.84\ g\ mL^{-1}$. Calculate (i) the molarity of the solution (ii) volume of concentrated acid required to prepare 2.5 L of 0.50 M H_2SO_4. (3)

28. (a) On the basis of VSEPR theory, explain the shapes of following:
H_2O and NH_3 molecules
(b) Draw resonance structures for SO_3 and CO_2 molecules.
(c) Which out of NH_3 and NF_3 has higher dipole moment and why? (5)

29. (a) What is solubility product? How is it different from ionic product.

(b) Calculate the molar solubility of $Ni(OH)_2$ in 0.10 M and NaOH. K_{sp} of $Ni(OH)_2 = 2.0 \times 10^{-15}$.

(c) What are acidic buffers? Give on example.

(d) Calculate the pH of 10^{-8} M HCl solution. (5)

30. (a) Assign structures for the following:

(i) An alkyne (X) has molecular formula C_5H_8. It reacts neither with sodamide nor with amoniacal cuprous chloride.

(ii) A hydrocarbon 'Y' decolourises bromine water. On ozonolysis it gives 3-Methyl butanal and formaldehyde. Give the name of the compound.

(iii) A hydrocarbon (Z) has molecular formula C_8H_{10}. It does not decolourise bromine water and is oxidised to benzoic acid on heating with $K_2Cr_2O_7$. It can also have three other isomers A, B and C. Write the structures of Z, A, B and C.

(b) What effect does branching of an alkane chain has on its boiling point?

(c) Draw cis and trans isomers of hex-2-ene. Which isomer will have higher boiling point?

(5)

SARASWATI CHEMISTRY POINT

[CLASS - XI]

CHEMISTRY (THEORY)

[SAMPLE PAPER-VIII]

Time Allowed: 3 hrs **M.M.: 70**

1. Write the mathematical expression for the First law of Thermodynamics? (1)

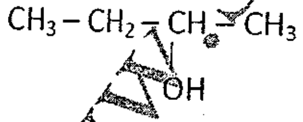
2. Write the corresponding conjugate acid and conjugate base for HCO_3^-? (1)

3. Arrange the following acids in the increasing order of their acidic strength.
   A – (pKa = 4.74)
   B – (pKa = 5.43)
   C – (pKa = 6.73)
   (1)

4. Pick out the cation which will have the highest and lowest hydration energy.
   Ca^{2+}, Mg^{2+}, Sr^{2+}
   (1)

5. Give the formula of 'inorganic benzene'. (1)

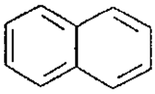
6. Give the number of a-carbons in the following molecules?

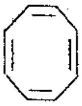


$CH_3-CH_2-\underset{OH}{\underset{|}{CH}}-CH_3$

(1)

7. Identify non-aromatic compound form the following:

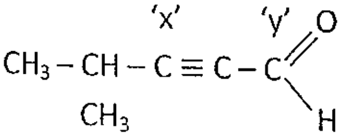
(a) 

(b) 

(c) 

(1)

8. Which hybrid orbitals are used by 'C' atoms labeled as 'x' and 'y'.



$$CH_3-\underset{CH_3}{\overset{'x'}{CH}}-C\equiv \overset{'y'}{C}-CHO$$

(1)

9. (a) Which out of NH_3 and NF_3 has high dipole moment and why?

(b) Distinguish between σ and π bonds in terms of extent of overlap and rotation along the internuclear axis.

(2)

10. (a) Give two properties to show similarity between Li and Mg.

(b) BaO in soluble but $BaSO_4$ is insoluble in water. Explain.

Or

(a) Give reason for anomalous behaviour of Li.

(b) Caesium and Potassium are used in photo electric effect. Explain? (2)

11. (a) What is inert pair effect?

(b) What is the effect of heat on orthoboric acid? (2)

12. Give the IUPAC name of the following:

(i) $CH_3\,CH_2\,CH(OH)\,CH_2\,COOH$

(ii) $(CH_3)_3\,C\,CH_2C(CH_3)_2CH_3$ (2)

13. (a) For an isolated system, $\Delta U = 0$, What will be ΔS?

(b) Given: $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)\ \Delta rH^\circ = -92.4\ kJ\ mol^{-1}$

What is standard enthalpy of formation of NH_3? (2)

SARASWATI CHEMISTRY POINT

14. The following reaction has attained equilibrium $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$ $\Delta H = -92\ kJ\ mol^{-1}$

What will happen if,

(a) Volume of the reaction vessel is suddenly reduced

(b) Partial pressure of H_2 is suddenly doubled? (2)

15. (a) Classify the following species as Lewis Acid & Lewis base

(i) BCl_3 (ii) F^-

(b) The ionisation constant of HCOOH is 1.8×10^{-4}. Calculate the ionisation constant of the corresponding conjugate base. (2)

16. Balance the following redox reaction in Acidic medium –

$H_2O_2\,(aq) + Fe_2^{+}\,(aq) \rightarrow Fe_3^{+}\,(aq) + H_2O(l)$ (2)

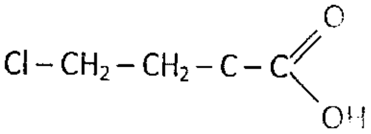
17. Balance the following redox reaction in Basic medium –

$MnO^-_4 (aq) + I^- (aq) \rightarrow MnO_2(s) + I_2(s)$

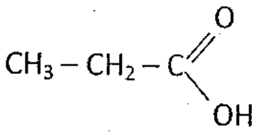
(2)

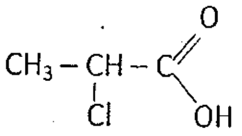
18. Arrange the following in the increasing order of the property mentioned:

(a) $CH_3 \overset{\oplus}{C}H_2, (CH_3)_3 \overset{\oplus}{C}, (CH_3)_2 \overset{\oplus}{C}H$ (stability)

(b) 

(Acidic strength)





(2)

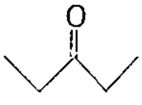
19. How will you convert (Give equations)
   (a) Ethyne to Benzene
   (b) Acetylene to Acetophenone
   (c) Methane Ethane

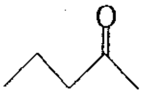
(3)

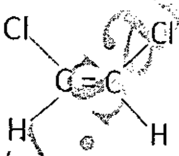
20. (a) Give the structure of 4-Methylcyclohexene
   (b) Explain metamerism with a suitable example.
   (c) Draw all the canonical forms of benzylic carbanion showing electron displacement by suitable arrows.

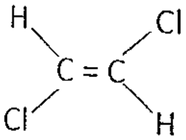
(3)

21. (a) C – C bond length in propene is little shorter (1.49 Å) than C – C bond length (1.54 Å) in ethane. Why?
   (b) Which type of isomerism is exhibited by the following pairs.

(i) 

and 

(ii) 

and 

(d) What is the minimum number of carbon atom that an alkane must contain to have chain isomers?

(3)

22. (a) Using Molecular orbital theory. Explain that O^-_2 molecule can exist and is paramagnetic. (At. No. =8)

(b) Draw the Lewis dot diagram of O_3 and find out the formal charge of each O atom.

(3)

23. (a) State Hess's law of constant heat summation.

(b) Calculate the change in Enthalpy for the reaction:

$H_2C \equiv CH_2 (g) + 3O_2 (g) \rightarrow 2\,CO_2(g) + 2H_2O(l)$

Given Bond energy:

(C – H) 414 kJ $mole^{-1}$, (O – O) 499 kJ $mole^{-1}$

(C = C) 619 kJ $mole^{-1}$, (C = O) 724 kJ mol^{-1}(2)

(O – H) 460 kJ mol_{-1}

(3)

24. (a) K_p for the reaction $2SO_2 (g) + O_2 (g) \rightleftharpoons 2SO_3 (g)$ is 16 at a certain temperature. Calculate the value of Kp at the same temperature for the reaction

$SO_3 (g) \rightleftharpoons SO_2 (g) + O_2 (g)$

(b) One mole of H_2O and one mole of CO are taken in a 10 litre vessel and heated to 725 k. At equilibrium, 40% of water (by mass) reacts with CO according to equation:

$H_2O (g) + CO (g) \rightleftharpoons H_2(g) + CO_2 (g)$

Calculate the equilibrium constant for the reaction.

(3)

25. (a) What will be the effect of the aqueous solution of the following salt on blue litmus paper.

(i) NH_4NO_3 (ii) NaCl

(b) Equal volume of 0.002 M solution of sodium iodate and cupric chlorate are mixed together. Will it lead to the precipitation of copper iodate?

Ksp $[Cu(IO_3)_2]$ = 7.4 ´10^{-8}.

(3)

26. (a) $Ka_2 << Ka_1$ for H_2SO_4. Why?

(c) Calculate the pH of the resultant mixture when 10 ml of 0.2 M $Ca(OH)_2$ is mixed with 25 ml of 0.1 M HCl.

Or

(a) NH_4Cl is added before adding NH4OH for the qualitative analysis of 3rd gp cation. Explain.

(b) The ionisation constant of phenol is 1×10^{-10}. What is the concentration of phenate ion in 0.05 M solution of Phenol? What will be the degree of ionization if solution is also 0.01 M I sodium phenate? (3)

27. (a) Give the mechanism of nitration of benzene.

(b) Write the following reactions:

(i) Friedal Craft Alkylation

(ii) Wurtz reaction (3)

28. (a) An Alkene 'A' gives 2-Methyl propanal and 2, 2-Dimethyl butanal on reductive ozonolysis. Identify 'A' and write the equation.

(b) Complete the following reaction:

(i) $CH_3 - CH = CH_2 + HBr \xrightarrow{\text{Peroxide}}$

(ii) $CH_3 - C = CH + H_2O \xrightarrow[\text{33 K}]{Hg^{2+}/H^+}$

(c) Terminal alkynes are acidic in nature. Explain.

Or

(a) Isopropyl alcohol on dehydration with conc. H_2SO_4 gave 'A' which on reaction with HBr in dark formed 'B' as major product. Identify 'A' and 'B' and give chemical equation.

(b) How would you distinguish between Propane and propene? Give equation.

(c) Benzene undergo electrophilic substitution reaction easily. Explain. (3)

29. (a) When an alkali metal dissolves in liquid NH_3, the solution can acquire different colors. Explain the reasons giving relevant equations.

(b) Give reasons:

(i) LiI is more soluble than KI in alcohol.

(ii) Be and Mg do not give colour to flame whereas other members give.

(iii) Li^+ forms oxide but Na^+ form peroxide and superoxide.

Or

(a) Write the balanced equation for the following:

(i) Lithium nitrate is strongly heated.

(ii) Sodium peroxide is dissolved in water.

(b) Give reasons for the following:

(i) First I.E. of alkaline earth metals are higher than those of the corresponding group I metals.

(ii) Li_2CO_3 decomposes at lower temperature whereas Na_2CO_3 at higher temperature.

(iii) Alkaline earth metals have higher M.P. than alkali metals. (5)

30. (a) What happens when:

(i) Silicon is heated with methyl chloride at high temperature is presence of Cu.

(ii) $SiCl_4$ is hydrolysed in water.

(b) Explain the following giving reasons:

(i) Boric acid is not a protic acid.

(ii) Boron is unable to form ion

(iii) Atomic radius of Gallium is less than Aluminium

Or

(a) Explain the structure of diborane.

(b) Give reasons for the following:

(i) $[SiF_6]^{2-}$ is known whereas $[CF_6]^{2-}$ not.

(ii) In group 14, there is considerable increased in covalent radius from C to Si but small increases from Si to Pb.

(iii) B – Cl bond has a dipole moment but BCl_3 has zero dipole moment. (5)

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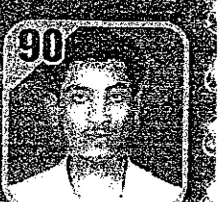
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