P-BLOCK ELEMENT

NITROGEN FAMILY

GROUP-15 ELEMENTS (N, P, As, Sb, Bi)

Occurrence :

Nitrogen : Molecular nitrogen comprises 78% by volume of the atmosphere. It occurs as sodium nitrate, $NaNO_3$ (called Chile saltpetre) and potassium nitrate (Indian saltpetre).

Phosphorus :

(i) It is eleventh most abundant element in earth's crust occurs in minerals of the apatite family, $Ca_9(PO_4)_6$. $CaX_2(X = F, Cl \text{ or } OH)$ (e.g., fluorapatite $Ca_9(PO_4)_6 \cdot CaF_2$) and also found as chlorapatite $Ca_9(PO_4)_6 \cdot CaCl_2$).

(ii) Arsenic , antimony and bismuth are found mainly as sulphide minerals.

Electronic Configuration :

The valence shell electronic configuration of these elements is ns^2np^3.

Atomic and Ionic Radii :

Covalent radius : $N < P < As < Sb < Bi$

Ionisation Enthalpy :

$N > P > As > Sb > Bi$ (IE1 values)

Electronegativity :

$N > P > As > Sb = Bi$

Metallic Character

$$\underset{\text{None metal}}{N<P} \quad \underset{\text{Metalloid}}{As<} \quad \underset{\text{Metals}}{Sb<Bi}$$

Physical Properties :

(i) All the elements of this group are polyatomic. Dinitrogen is a diatomic gas while all others are solids.

(ii) Metallic character increases down the group.

(iii) The boiling points, in general, increase from top to bottom in the group but the melting point increases upto arsenic and then decreases upto bismuth.

(iv) Except nitrogen all the elements show allotropy.

P → exists in three allotropic form as white, red and black

As, Sb → exist as yellow and grey

Bi → exist as $\alpha, \beta, \gamma, \delta$ allotropic form

Catenation

The group 15 elements also show catenation property but to much smaller extent than carbon.

For example hydrazine (H2NNH2) has two N atoms bonded together HN3 has three N atoms.

HN_3 $\quad H-\ddot{N}=\overset{+}{N}=\ddot{N}:^{\ominus}$

• Among group 15 elements P has the maximum tendency for catenation forming cyclic as well as open chain compounds consisting of many phosphorous atoms.

P_2H_4 has two P atoms bonded together the lesser tendency of elements of group 15 to show catenation in compression to carbon is their low dissociation enthalpies.

$C-C$	353.3 kJ/mole
$N-N$	160.8 kJ/ mole
$P-P$	201.6 kJ/ mole
$As-As$	147.4 kJ/ mole

Chemical Properties :

Oxidation states and trends in chemical reactivity

(i) The common oxidation states of these elements are $-3, +3$ and $+5$.

(ii) The tendency to exhibit -3 oxidation state decreases down the group due to increase in size and metallic character. Bismuth hardly forms any compound in -3 oxidation state.

(iii) The stability of +5 oxidation state decreases down the group. The only well characterised Bi(V) compound is BiF_5.

(iv) The stability of +5 oxidation state decreases and that of +3 state increases (due to inert pair effect) down the group.

(v) Nitrogen exhibits $+1, +2$, +4 oxidation states also when it reacts with oxygen. Phosphorus also shows +1 and +4 oxidation states in some oxoacids.

(vi) In the case of nitrogen, all oxidation states from +1 to +4 tend to disproportionate in acid solution. For example,

(i) $3HNO_2 \rightarrow HNO_3 + H_2O + 2NO$

(vii) Similarly, in case of phosphorus nearly all intermediate oxidation states disproportionate into +5 and -3 both in alkali and acid.

(ii) $4H_3PO_3 \xrightarrow{\text{Heal}} 3H_3PO_4 + PH_3$

(viii) +3 oxidation state in case of arsenic, antimony and bismuth becomes increasingly stable with respect to disproportionation.

(ix) Nitrogen is restricted to a maximum covalency of 4 since only four (one *s* and three p) orbitals are available for bonding.

(x) The heavier elements have vacant d orbitals in the outermost shell which can be used for bonding 6 (covalency) and hence, expand their covalency as in PF_6^-.

Anomalous properties of nitrogen

(i) Nitrogen has unique ability to form $p_\pi - p_\pi$ multiple bonds with itself and with other elements having small size and high electronegativity (e.g., C, O).

(ii) Heavier elements of this group do not form pp-pp bonds as their atomic orbitals are so large and diffuse that they cannot have effective overlapping.

(iii) Nitrogen exists as a diatomic molecule with a triple bond (one *s* and two p) between the two atoms.

N_2 bond enthalpy (941.4 kJ mol^{-1}) is very high.

(iv) Phosphorus, arsenic and antimony form single bonds as P-P, As-As and Sb-Sb while bismuth forms metallic bonds in elemental state.

(i) Reactivity towards hydrogen:

$NH_3 > PH_3 > AsH_3 > SbH_3 \geq BiH_3$.

(ii) Reactivity towards oxygen: All these elements form two types of oxides: E_2O_3 and E_2O_5. Their acidic character decreases down the group. The oxides of the type E_2O_3 of nitrogen and phosphorus are purely acidic, that of arsenic and antimony amphoteric and those of bismuth predominantly basic.

(iii) Reactivity towards halogens: These elements react to form two series of halides: EX_3 and EX_5. In case of nitrogen, only NF3 is known to be stable. Trihalides except BiF_3 are predominantly covalent in nature.

(iv) Reactivity towards metals: All these elements react with metals to form their binary compounds exhibiting -3 oxidation state, such as, Ca3 N_2 (calcium nitride) Ca_3P_2 (calcium phosphide), Na_3As (sodium arsenide), Zn_3Sb_2 (zinc antimonide) and Mg_3Bi_2 (magnesium bismuthide).

DINITROGEN

Preparation :

(a) Commercial preparation :

Dinitrogen is produced commerciallyby the liquefaction and fractional distillation of air. Liquid dinitrogen (b.p. 77.2 K) distils out first leaving behind liquid oxygen (b.p. 90 K).

(b) Laboratory preparation :

(i) Dinitrogen is prepared by treating an aqueous solution of ammonium chloride with sodium nitrite.

$NH_4Cl(aq) + NaNO_2(aq) \rightarrow N_2(g) + 2H_2O(\ell) + NaCl(aq)$

Small amounts of NO and HNO_3 are also formed in this reaction; these impurities can be removed by passing the gas through aqueous sulphuric acid containing potassium dichromate.

(ii) Dinitrogen can also be obtained by the thermal decomposition of ammonium dichromate.

$(NH_4)2Cr_2O_7 \xrightarrow{Heat} N_2 + 4H_2O + Cr_2O_3$

Note : Very pure nitrogen can be obtained by the thermal decomposition of sodium or barium azide.

$Ba(N_3)_2 \xrightarrow{\Delta} Ba + 3\ N_2$

$2NaN_3 \xrightarrow{300°C} 2Na + 3\ N_2$

(c) Other preparation

$2NH_3 + 3NaOCl \longrightarrow N_2 + 3NaCl + 3H_2O$

$2NH_3 + 3Ca(OCl)_2 \longrightarrow 2\ N_2 + 3CaCl_2 + 6H_2O$

$8NH_3 + 3Br_2 \longrightarrow N_2 + 6NH_4Br$

$2NO + 2Cu \longrightarrow 2CuO + N_2$

(red, overheated) (Black)

Cl_2 passed into liquor NH_3

$3Cl_2 + 2NH_3 \longrightarrow N_2 + 6HCl$

$6NH_3 + 6HCl \longrightarrow 6NH_4Cl$

$3Cl_2 + 8NH_3 \longrightarrow N_2 + 6NH_4Cl$

In this method conc. of NH3 should not be lowered down beyond a particular limit.

$3Cl_2 + NH_3 \longrightarrow NCl_3 + 3HCl$

(Trimendously explosive)

Physical properties :

(i) Dinitrogen is a colourless, odourless, tasteless and non-toxic gas.

(ii) Nitrogen atom has two stable isotopes: ^{14}N and ^{15}N.

(iii) It has a very low solubility in water (23.2 cm^3 per litre of water at 273 K and 1 bar pressure)

(iv) Dinotrogen has low freezing and boiling points.

Chemical properties

Reaction with metal : At higher temperatures, it directly combines with some metals to form predominantly ionic nitrides and with non-metals, covalent nitrides. A few typical reactions are:

$$6Li + N_2 \xrightarrow{Heat} 2Li_3N$$
$$3Mg + N_2 \xrightarrow{Heat} Mg_3N_2$$

Reaction with metal : It combines with hydrogen at about 773 K in the presence of a catalyst (Haber's Process) to form ammonia:

$$N_2(g) + 3H_2(g) \overset{773k}{\rightleftharpoons} 2NH_3(g)$$

Dinitrogen combines with dioxygen only at very high temperature (at about 2000 K) to form nitric oxide, NO.

$$NO_2 + (g) \overset{Heat}{\rightleftharpoons} 2NO(g)$$

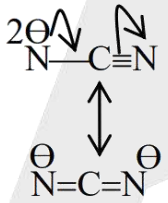
Absorption on calcium carbride

N_2 can be absorbed by calcium carbide at the temperature around 1000°C.

$$CaC_2 + N_2 \xrightarrow{1100°C} \underbrace{CaNCN + C}_{\text{nitrolim}}$$

It is a very good fertiliser.

Cyanamide ion



$$(Ca(NCN) + C) + 3H_2O \longrightarrow CaCO_3 + 2NH_3 + C$$

Slowly decomposes

$NH_2–CO–NH_2$ (Intermidiate fomed)

Ques. Why dinitrogen is inert at room temperature ?

Ans. Dinitrogen is inert at room temperature because of the high bond enthalpy of N ≡ N bond. Reactivity, however, increases rapidly with rise in temperature.

TYPES OF NITRIDE

Salt like or ionic : Li_3N, Na_3N, $K_3N(?), Ca_3N_2, Mg_3N_2, Be_3N_2$

Covalent : AlN, BN, $Si_3N_4, Ge_3N_4, Sn_3N_4$

Interstitial : $\underbrace{M = Sc, Ti, Zr, Hf, la}_{\text{HCP of FCC}}$

AMMONIA

Preparation :

(i) Ammonia is present in small quantities in air and soil where it is formed by the decay of nitrogenous organic matter e.g., urea.

$NH_2CONH_2 + 2H_2O \longrightarrow (NH_4)_2CO_3 \rightleftharpoons 2NH_3 + H_2O + CO_2$

(ii) Small scale preparation By the decomposition of ammonium salts when treated with caustic soda or calcium hydroxide.

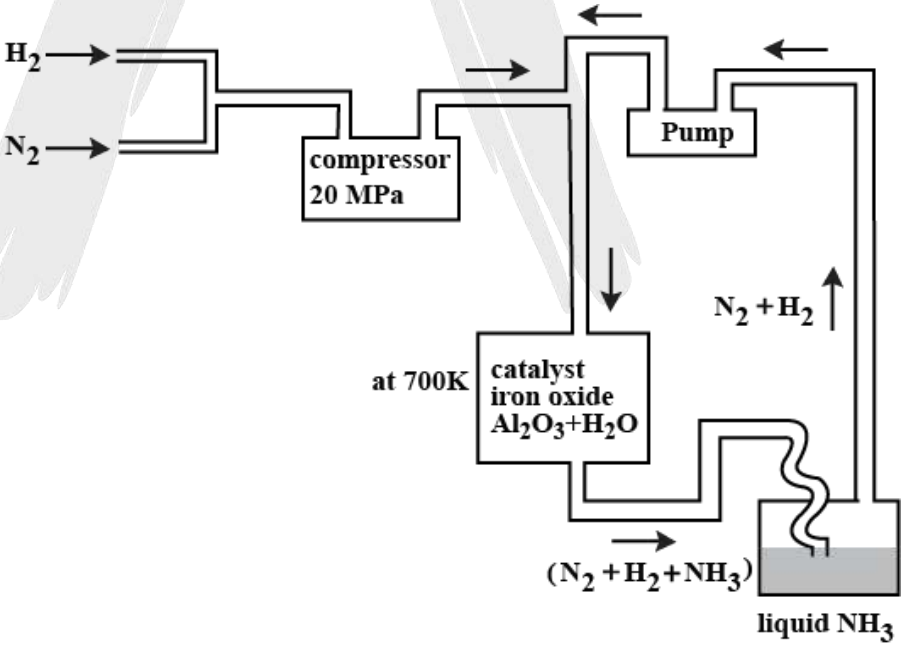
$2NH_4Cl + Ca(OH)_2 \rightarrow 2NH_3 + 2H_2O + CaCl_2$

$(NH_4)_2SO_4 + 2NaOH \rightarrow 2NH_3 + 2H_2O + Na_2SO_4$

(iii) Large scale manufacturing (Haber's Process)

$N2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g);\ D_fH^{\Theta} = -46.1\ kJ\ mol^{-1}$

- ❖ According to Le Chatelier's principle, high pressure and low temperature would favour the formation of ammonia.
- ❖ The optimum conditions for the production of ammonia are a pressure of 200×10^5 Pa (about 200 atm), a temperature of $\sim$ 700 K.
- ❖ Use of a catalyst such as iron oxide with small amounts of K_2O and Al_2O_3 to increase the rate of attainment of equilibrium.
- ❖ The flow chart for the production of ammonia is shown in figure. Earlier, iron was used as a catalyst with molybdenum as a promoter.



Manufacturing of Ammonia

Other prepration :

(i) Nitrate or nitrite reduction : $NO_3^-/NO_2^- + Zn$ or $Al + NaOH \longrightarrow NH_3 + [Zn(OH)_4]^{2-}$ or

$[Al(OH)_4]^-$

(ii) Metal nitride hydrolysis : $N^{3-} + 3H_2O \longrightarrow NH_3 \uparrow + 3OH^-$

Properties :

(i) Ammonia is a colourless gas with a pungent odour.

(ii) Its freezing and boiling points are 198.4 and 239.7 K respectively.

(iii) In the solid and liquid states, it is associated through hydrogen bonds.

(iv) Ammonia gas is highly soluble in water.

Basic character :

Its aqueous solution is weakly basic due to the formation of OH^- ions.

$NH_3(g) + H_2O(\ell) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

It forms ammonium salts with acids, e.g., NH_4Cl, $(NH_4)_2SO_4$, etc.

As a weak base, it precipitates the hydroxides (hydrated oxides in case of some metals) of many metals from their salt solutions.

For example,

$ZnSO_4(aq) + 2NH_4OH(aq) \longrightarrow Zn(OH)_2(s) + (NH_4)_2SO_4(aq)$

(White ppt)

$FeCl_3(aq) + NH_4OH(aq) \longrightarrow Fe_2O_3 \cdot xH_2O(s) + NH_4Cl(aq)$

(brown ppt)

Note -1: Other reactions

CH_3COOH is strong acid in liq. NH_3 while in water is weak acid.

$AcOH \rightleftharpoons Ac\overline{O} + H^+$

$4NH_3 + H^+ \longrightarrow NH_4^+$

$H_2O + H^+ \longrightarrow H_3O^+$

Basisity order $NH_3 > H_2O$

more solvation of H^+ in NH_3.

Note - 2 : Hydrolysis and Ammonolysis occurs is a same way.

$SiCl_4 + 4H_2O \longrightarrow 4HCl + Si(OH)_4 \xrightarrow{\Delta} SiO_2 + 2H_2O$

$SiCl_4 + 8NH_3 \longrightarrow 4NH_4Cl + Si(NH_2)_4 \xrightarrow{\Delta} Si_3N_4 + NH_3 \uparrow$

Rate of hydrolysis and Ammonolysis will be affected by the presence of HCl vapour & NH_4Cl vapour respectively.

Uses :

(i) Ammonia is used to produce various nitrogenous fertilisers.

(ii) In the manufacture of some inorganic nitrogen compounds, the most important one being

nitric acid.

(iii) Liquid ammonia is also used as a refrigerant.

OXIDES OF NITROGEN

Nitrogen forms a number of oxides in different oxidation states. The names, formulas, preparation and physical appearance of these oxides are given in Table.

Oxides of Nitrogen

Name	Formula	Oxidation state of nitrogen	Common Methods of Prepration	Physical Appearance and Chemical nature
Dinitrogen oxide [Nitrogen oxide]	N_2O	+1	$NH_4NO_3 \xrightarrow{Heat} N_2O + 2H_2O$	Colourless gas, neutral
Nitrogen monoxide [Nitrogen (II) oxide]	NO	+2	$2NaNO_2 + 2FeSO_4 + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 2NaHSO_4 + 2H_2O + 2NO$	Colourless gas, neutral
Dinitrogen trioxide [Nitrogen (III) oxide]	N_2O_3	+3	$2NO + N_2O_4 \xrightarrow{250\ K} 2\ N_2O_3$	Blue solid, acidic Blue liquid (−30°C)
Nitrogen dioxide [Nitrogen (IV) oxide]	NO_2	+4	$2\ Pb(NO_3)_2 \xrightarrow[673\ K]{} 4NO_2 + 2PbO + O_2$	Brown gas. Acidic
Nitrogen tetroxide [Nitrogen (IV) oxide]	N_2O_4	+4	$2NO_2 \underset{Heal}{\overset{Cool}{\rightleftharpoons}} N_2O_4$	Colourless solid / liquid, acidic
Nitrogen pentaoxide [Nitrogen (V) oxide]	N_2O_5	+5	$4HNO_3 + P_4O_{10} \rightarrow 4HPO_3 + 2\ N_2O_5$	Colourless solid, acidic

Preparations:

1. N_2O

(i) $NH_4NO_3 \longrightarrow N_2O + H_2O$

(ii) $Zn + HNO_3 \longrightarrow Zn(NO_3)_2 + N_2O + H_2O$

(dil.& cold)

2. NO

(i) $Cu + HNO_3(1:1) \longrightarrow Cu(NO_3)_2 + NO + H_2O$

hot

(ii) $KNO_3 + FeSO_4 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + K_2SO_4 + NO + H_2O$

$FeSO_4 + NO \longrightarrow FeSO_4 \cdot NO \xrightarrow{\Delta} FeSO_4 + NO^{\uparrow}$

(iii) Oswald process-Restricted oxidation of NH_3. Industrial process.

$4NH_3 + 5O_2 \xrightarrow[750°C,\ Pt\text{-}Cat]{6\ atm} 4NO + 6H_2O$

3. N_2O_3

(i) $HNO_3 + As_2O_3 \longrightarrow H_3AsO_4 + N_2O_3$

$$Cu + HNO_3(6M) \longrightarrow Cu(NO_3)_2 + \underbrace{NO + NO_2}_{\text{Cool}(-30°C)} \downarrow \text{Blue liq } (N_2O_3)$$

(ii)

4. NO_2

(i) $M(NO_3)_2 \xrightarrow{\Delta} MO + 2NO_2 + \frac{1}{2}O_2$

$M = Pb, Cu, Ba, Ca$

(ii) $(Cu, Pb, Ag) + HNO_3 \longrightarrow$ M-nitrate $+NO_2 + H_2O$

(hot & conc.)

N_2O_5

5. (i) $2HNO_3 + P_2O_5 \longrightarrow 2HPO_3 + N_2O_5$

(ii) $4AgNO_3 + 2Cl_2$ (dry gas) $\longrightarrow 4AgCl + 2\ N_2O_5 + O_2$

Properties:

(I) Decoposition Behaviour

(i) $N_2O \xrightarrow{500°C-900°C} 2\ N_2 + O_2$

(ii) $2NO \xrightarrow{800°C} 2\ N_2 + O_2$

(iii) $N_2O_3 \xrightarrow[\text{(Blue liq.) at } (-30°C)]{\text{Room temp.}} NO_2 + NO$

(iv) $2NO_2 \xrightarrow{620°C} 2NO + O_2$

$N_2O_4 \xrightarrow{11°C} 2NO_2$

(white solid) Brown gas at $(-11°C)$

(v) $N_2O_5 \xrightarrow{30°C} N_2O_5 \xrightarrow{40°C} 2NO_2 + \frac{1}{2}O_2$

Colourless yellow

Solid liq.

(II) Reaction with H2O&NaOH

H_2O NaOH

(i) N_2O : Fairly soluble in water and produces neutral solution

(ii) NO : Sparingly soluble in water and produces neutral soln.

(iii) N_2O_3: $2HNO_2$

Hence it is known as

$NaNO_2$ anhydride of HNO_2 $NaNO_2$

(iv) NO_2: $HNO_2 + HNO_3$

called as mixed anhydride $NaNO_2 + NaNO_3$

(v) N_2O_5: $2HNO_3$

called as anhydride of $NaNO_3$ HNO_3

Other properties:

$N_2O : 2N_2O \longrightarrow 2N_2 + O_2$ { Mixture contains 33% O_2 compared To 20% in air

Hence it is better supporter for combustion

$S + N_2O \longrightarrow SO_2 + N_2$

$P + N_2O \longrightarrow P_2O_5 + N_2$

$Mg + N_2O \longrightarrow MgO + N_2$

$Na + N_2O \longrightarrow Na_2O + N_2$

$Cu + N_2O \longrightarrow CuO + N_2$

$H_2 + N_2O \longrightarrow H_2O + N_2$

NOTE: -

(i) It burns : $NO + \frac{1}{2}O_2 \longrightarrow NO_2$

(ii) It supports combustion also for molten sulphur and hot phosphorous.

$S + 2NO \longrightarrow SO_2 + N_2$

$2P + 5NO \longrightarrow P_2O_5 + \frac{5}{2} N_2$

(iii) It is being absorbed by $FeSO_4$ solution.

(iv) It is having reducing property.

$KMnO_4 + NO + H_2SO_4 \longrightarrow K_2SO_4 + MnSO_4 + HNO_3 + H_2O$

(v) NO shows oxidising property also.

$SO_2 + 2NO + H_2O \longrightarrow H_2SO_4 + N_2O$

$H_2S + 2NO \longrightarrow H_2O + S\downarrow + N_2O$

$3SnCl_2 + 2NO + 6HCl \longrightarrow 3SnCl_4 + 2NH_2OH$

(Used for NH_2OH preparation)

(vi) NO combines with $X_2 (X_2 = Cl_2Br_2F_2)$ to produce NOX

$2NO + X_2 \longrightarrow 2NOX$

N_2O_3: No more properties.

(1) It is having oxidising property.

$S + NO_2 \longrightarrow SO_2 + NO$

$P + NO_2 \longrightarrow P_2O_5 + NO$

$C + NO_2 \longrightarrow CO_2 + NO$

$SO_2 + NO_2 + H_2O \longrightarrow H_2SO_4 + NO$

$H_2S + NO_2 \longrightarrow H_2O + S\downarrow + NO$

NO not formed : $2KI + 2NO_2 \longrightarrow I_2 + 2KNO_2$

(2) Reducing property of NO_2.

$KMnO_4 + NO_2 + H_2SO_4 \longrightarrow K_2SO_4 + MnSO_4 + HNO_3 + H_2O$

$O_3^0 + 2NO \rightarrow \underbrace{O_2^0}_{\text{not the reduction product of } O_3} + N_2O_5$

N_2O_5:

$I_2 + 5N_2O_5 \longrightarrow I_2O_5 + 10NO_2$

I_2O_5 is used for the estimation of CO

$I_2O_5 + 5CO \longrightarrow I_2 + 5CO_2$

$N_2O_5 + NaCl \longrightarrow NaNO_3 + NO_2Cl$

This likes proves that N2O5 is consisting of ion pair of NO_2^+ &NO_3^-

OXOACIDS OF NITROGEN

$H_2N_2O_2$ (hyponitrous acid), HNO_2 (nitrous acid) and HNO_3 (nitric acid). Amongst them HNO_3 is the most important.

NITROUS ACID (HNO_2)

Preparation

(a) M-nitrite $\xrightarrow[HClor_2SO_4]{\text{dilacid}} HNO_2$

(b) $N_2O_3 + H_2O \longrightarrow 2HNO_2$

Properties

(a) Oxidising property : Because of its easy oxidation to liberate nascent oxygen, it acts as a strong oxidant $2HNO_2 \longrightarrow H_2O + 2NO + (O)$

$2KI + 2HNO_2 + 2HCl \longrightarrow 2KCl + 2H_2O + 2NO + I_2$

$SnCl_2 + 2HNO_2 + 2HCl \longrightarrow SnCl_4 + 2NO + 2H_2O$

$SO_2 + 2HNO_2 \longrightarrow H_2SO_4 + 2NO$

$H_2S + 2HNO_2 \longrightarrow 2H_2O + S\downarrow + 2NO$

$2FeSO_4 + 2HNO_2 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + 2NO + 2H_2O$

(b) Reducing property : Nitrous acid also acts as a reducing agent as it can be oxidised into nitric acid.

$HNO_2 + (O) \longrightarrow HNO_3$

$2KMnO_4 + 5HNO_2 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 5HNO_3 + 3H_2O$

$K_2Cr_2O_7 + 3HNO_2 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 3HNO_3 + 4H_2O$

$H_2O_2 + HNO_2 \longrightarrow H_2O + HNO_3$

$HNO_2 + C_2H_5NH_2 \longrightarrow C_2H_5OH + N_2 + H_2OS$

$$HNO_2 + C_6H_5 - NH_2 \cdot HCl \xrightarrow{<5^\circ C} C_6H_5N = NCl + 2H_2O$$

Benzene diazonium chloride

NITRIC ACID

It was named aqua fortis (means strong water) by alchemists.

Preparation :

Laboratory Method : By heating KNO_3 or $NaNO_3$ and concentrated H_2SO_4 in a glass retort.

$KNO_3/NaNO_3 + H_2SO_4 \rightarrow KHSO_4/NaHSO_4 + HNO_3$

Large scale preparation (Ostwald's process) :

(i) This method is based upon catalytic oxidation of NH_3 by atmospheric oxygen.

$$4NH(g) + 5O_2(g) \xrightarrow[500\ K, 9\ bar]{Pt/Rh\text{-gauge catalyst}} 4NO(g) + 6H_2O(g)$$

(ii) Nitric oxide thus formed combines with oxygen giving NO_2.

$2NO(g)O_2(g) \rightleftharpoons 2NO(g)$

(iii) Nitrogen dioxide so formed, dissolves in water to give HNO_3.

$3NO_2(g) + H_2O(\ell) \longrightarrow 2HNO_3(aq) + NO(g)$

NO thus formed is recycled and the aqueous HNO_3 can be concentrated by distillation upto 68% by mass. Further concentration to 98% can be achieved by dehydration with concentrated H_2SO_4.

Birkel and Eyde Process or arc process

step 1 $N_2 + O_2 \xrightarrow{3000°C} \text{Electric Arc} - \text{heat}$

step 2 $NO + O_2 \longrightarrow NO_2$

step 3 $NO_2 + H_2O \longrightarrow HNO_2 + HNO_3$

step 4 $HNO_2 \longrightarrow HNO_3 + NO + H_2O$

Properties

Physical properties

(i) It is a colourless liquid (f.p. 231.4 K and b.p. 355.6 K).

(ii) Nitric acid usually acquires yellow or brown colour due to its decomposition by sunlight into NO_2.

$4HNO_3 \xrightarrow{\text{Sunlight}} 4NO_2 + 2H_2O + O_2$

The yellow or brown colour of the acid can be removed by warming it to $60 - 80$oC and bubbling dry air through it.

Chemical properties

Acidic character in aqueous solution, nitric acid behaves as a strong acid giving hydronium and nitrate ions.

$HNO_3(aq) + H_2O(\ell) \rightarrow H_3O^+(aq) + NO_3^-(aq)$

Oxidising nature: Nitric acid acts as a strong oxidising agent as it decomposes to give nascent oxygen easily.

$2HNO_3 \longrightarrow H_2O + 2NO_2 + O$

Or $2HNO_3 \longrightarrow H_2O + 2NO + 3O$

(i) Oxidation of non-metals : The nascent oxygen oxidises various non-metals to their corresponding oxyacids of highest oxidation state.

(1) Sulphur is oxidised to sulphuric acid

$S + 6HNO_3 \longrightarrow H_2SO_4 + 6NO_2 + 2H_2O$

conc.and hot

(2) Carbon is oxidised to carbonic acid

$C + 4HNO_3 \rightarrow H_2CO_3 + 4NO_2 + 2H_2O$

(3) Phosphorus is oxidised to orthophosphoric acid.

$2P + 10HNO_3 \rightarrow 2H_3PO_4 + 10NO_2 + 2H_2O$

conc. and hot

(4) Iodine is oxidised to iodic acid

$I_2 + 10HNO_3 \rightarrow 2HIO_3 + 10NO_2 + 4H_2O$

conc. and hot

(ii) Oxidation of metalloids

Metalloids like non-metals also form oxyacids of highest oxidation state.

(1) Arsenic is oxidised to arsenic acid

$2As + 10HNO_3 \rightarrow 2H_3AsO_4 + 10NO_2 + 2H_2O$

or $As + 5HNO_3 \rightarrow H_3AsO_4 + 5NO_2 + H_2O$

conc. and hot

(2) Antimony is oxidised to antimonic acid

$Sb + 5HNO_3 \rightarrow H_3SbO_4 + 5NO_2 + H_2O$

conc. and hot

(3) Tin is oxidised to meta-stannic acid.

$Sn + 2HNO_3 \rightarrow H_2SnO_3 + 4NO_2 + H_2O$

(iii) Oxidation of Compounds:

(1) Sulphur dioxide is oxidised to sulphuric acid

$SO_2 + 2HNO_3 \rightarrow H_2SO_4 + 2NO_2$

(2) Hydrogen sulphiode is oxidised to sulphur

$H_2S + 2HNO_3 \rightarrow 2NO_2 + 2H_2O + S$

(3) Ferrous sulphate is oxidised to ferric sulphate in presence of H_2SO_4

$6FeSO_4 + 3H_2SO_4 + 2HNO_3 \rightarrow 3Fe_2(SO_4)_3 + 2NO + 4H_2O$

(4) Iodine is liberated from KI.

$6KI + 8HNO_3 \rightarrow 6KNO_3 + 2NO + 3I_2 + 4H_2O$

(5) HBr, HI are oxidised to Br_2 and I_2, respectively.

$2HBr + 2HNO_3 \rightarrow Br_2 + 2NO_2 + 2H_2O$

Similarly, $2HI + 2HNO_3 \rightarrow I_2 + 2NO_2 + 2H_2O$

(6) Ferrous sulphide is oxidised to ferric sulphate

$FeS + HNO_3 \rightarrow Fe_2(SO_4)_3 + 8NO_2 + 4H_2O$

(7) Stannous chloride is oxidised to stannic chloride is presence of HCl.

$2HNO_3 + 14H \rightarrow NH_2OH + NH_3 + 5H_2O$

Hydroxylamine

$NH_3 + HNO_3 \rightarrow NH_4NO_3$

$7SnCl_2 + 14HCl + 3HNO_3 \rightarrow 7SnCl_4 + NH_2OH + NH_4NO_3 + 5H_2O$

(ii) Reaction with metal concentrated nitric acid is a strong oxidising agent and attacks most metals except noble metals such as gold and platinum.

Au & Pt dissolve in aqua regia a mixture of 25% conc. HNO3&75% conc. HCl.

Ex. $3Cu + 8HNO_3$ (dilute) $\rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$

$Cu + 4HNO_3$ (conc.) $\rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$

$4Zn + 10HNO_3$ (dilute) $\rightarrow 4Zn(NO_3)_2 + 5H_2O + N_2O$

$Zn + 4HNO_3$ (conc.) $\rightarrow Zn(NO_3)_2 + 2H_2O + 2NO_2$

Some metals (e.g., Cr, Al) do not dissolve in concentrated nitric acid because of the formation of a passive film of oxide on the surface.

Action on Proteins :

Nitric acid attacks proteins forming a yellow nitro compound called xanthoprotein. It, therefore, stains skin and renders wool yellow. This property is utilized for the test of proteins.

ALLOTROPIC FORMS OF PHOSPHORUS

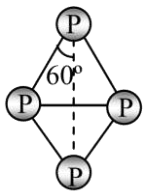
Phosphorus is found in many allotropic forms, the important ones being white, red and black.

White phosphorus dissolves in boiling NaOH solution in an inert atmosphere giving PH3.

$$P + 3NaOH + 3H_2O \longrightarrow PH + 3NaH_2PO_2$$

(Sodium hypophosphite)

It readily catches fire in air to give dense white fumes of P_4O_{10}.

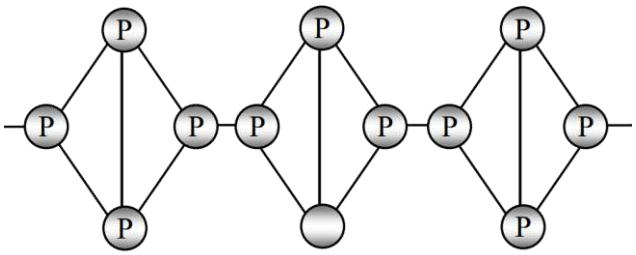


White Phosphorus

$$P_4 + 5O_2 \rightarrow P_4O_{10}$$

It consists of discrete tetrahedral P4 molecule as shown in Fig.

Red phosphorus : It is polymeric, consisting of chains of P_4 tetrahedra linked together in the manner as shown in Fig.



Red Phosphorus

Black phosphorus :

(i) It has two forms a-black phosphorus and β-black phosphorus.

(ii) α-Black phosphorus is formed when red phosphorus is heated in a sealed tube at 803 K.

(iii) It can be sublimed in air and has opaque monoclinic or rhombohedral crystals.

(iv) It does not oxidise in air. β-Black phosphorus is prepared by heating white phosphorus at 473 K under high pressure.

(v) It does not burn in air upto 673 K.

Comparison between White and Red Phosphorus

Property	White phosphorus	Red phosphorus
Physical state	Soft waxy solid.	Brittle powder.
Colour	White when pure. Attains yellow colour On standing.	Red.
Odour	Garlic	Odourless.
Solubility in water	Insoluble.	Insoluble.
Solubility in CS_2	Soluble	Insoluble.
Physiological action	Poisonous.	Non-poisonous.
Chemical activity	Very active.	Less active.
Stability	Unstable.	Stable
Phosphorescence	Glows in dark	Does not glow in dark.
Molecular formula	P_4	Complex polymer.

Prepration of white 'P'

(i) Bone ash or Apatite rock (Both have same formula) $\{Ca_3(PO_4)_2 + 3SiO_2 \xrightarrow{1200^\circ C} 3CaSiO_3 + P_2O_5$

$$2P_2O_5 + 10C \xrightarrow{1500^\circ C} P_4 + 10CO\uparrow$$

(Coke) White 'P'

(ii) $Ca_3(PO_4)_2 + 3H_2SO_4$ (conc.) $\longrightarrow 3CaSO_4 + 2H_3PO_4$

$$H_3PO_4 \xrightarrow[P^3H^\circ C]{-H_2O} HPO_3$$

meta phosphoric acid

$$12C + 4HPO_3 \xrightarrow{1000^\circ C} 2H_2\uparrow + 12CO\uparrow + P_4$$

Coke white 'P'

Reactions of 'P'

$P + H_2SO_4$ (hot & conc.) $\longrightarrow H_3PO_4 + SO_2 + H_2O$

$P + KIO_3 + H_2SO_4 \longrightarrow H_3PO_4 + I_2 + K_2SO_4$

Reaction with hot metal —

$3Na + P \longrightarrow Na_3P$

$3Mg + 2P \longrightarrow Mg_3P_2$

$3Ca + 2P \longrightarrow Ca_3P_2$

$2Cu + 2P \longrightarrow Cu_3P_2$

$Al + P \longrightarrow AlP$

$Ca_3P_2 + H_2O \longrightarrow M(OH)_n + PH_3$

or Mg_3P_2

or AlP

PHOSPHINE

Preparation

(i) Phosphine is prepared by the reaction of calcium phosphide with water or dilute HCl.

$Ca_3P_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2PH_3$

$Ca_3P_2 + 6HCl \rightarrow 3CaCl_2 + 2PH_3$

(ii) Laboratory prepration it is prepared by heating white phosphorus with concentrated NaOH solution in an inert atmosphere of CO_2.

$P_4 + 3NaOH + 3H_2O \longrightarrow PH + 3NaH_2PO_2$

(sodium hypophosphite)

Pure PH_3 is non inflammable but becomes inflammable owingto the presence of P_2H_4 or P_4 vapours. To purify it from the impurities, it is absorbed in HI to form phosphonium iodide (PH_4I) which on treating with KOH gives off phosphine.

Other preparation

$PH_4I + KOH \longrightarrow KI + PH_3 + H_2O$
$(PH_3 + HI)$
$2AlP + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + PH_3 \uparrow$ } Purest PH_3

$4PO_3 \xrightarrow{\Delta} PH_3 + 3H_3PO_4$

$2H_3PO_2 \xrightarrow{\Delta} PH_3 + 3H_3PO_4$

Phyiscal Properties :

(i) It is a colourless gas with rotten fish smell and is highly poisonous.

(ii) It explodes in contact with traces of oxidising agents like HNO_3, Cl_2 and Br_2 vapours.

(iii) It is slightly soluble in water but soluble in CS_2. The solution of PH_3 in water decomposes in presence of light giving red phosphorus and H_2.

Chemical Properties :

(i) It absorbed in copper sulphate or mercuric chloride solution, the corresponding phosphides are obtained.

$3CuSO_4 + 2PH_3 \rightarrow Cu_3P_2 + 3H_2SO_4$

$3HgCl_2 + 2PH_3 \rightarrow Hg_3P_2 + 6HCl$

Phosphine is weakly basic and like ammonia, gives phosphonium compounds with acids e.g.,

$PH_3 + HBr \rightarrow PH_4Br$

(ii) $PH_3 + O_2 \xrightarrow{150^\circ} P_2O_5 + H_2O$

(iii) $PH_3 + 3Cl_2 \longrightarrow PCl_3 + 3HCl$

(iv) $PH_3 + 4\,N_2O \xrightarrow[\text{sparking}]{\text{electrical}} H_3PO_4 + 4\,N_2$

(v) $PH_3 + 6AgNO_3 \longrightarrow [Ag_3P \cdot 3AgNOA_3 \downarrow] + H_3NO_3$

yellow ppt.

$Ag_3P \cdot 3AgNO_3 + 3H_2O \longrightarrow 6Ag \downarrow + 3HNO_3 + H3PO3$

Black ppt.

(vi) $PH_3 + 4HCHO + HCl \longrightarrow [P(CH_2OH)_4] + Cl^-$

white/colourless solid

which is used for making

fire-proof cotton fabrics

Note :

Like NH_3, PH_3 also can form addition product.

$CaCl_2 \cdot 8NH_3 Cu_2Cl_2 \cdot 2PH_3, AlCl_3 \cdot 2PH_3, SnCl_4 \cdot 2PH_3$

PH_3 can be absorbed by $Ca(OCl)Cl$.

$PH_3 + 3Ca(OCl)Cl + 3H_2O \longrightarrow PCl_3 + 3HCl + 3Ca(OH)_2$

$2NH_3 + 3Ca(OCl)Cl \longrightarrow N_2 + 3CaCl_2 + 3H_2O$

Uses :

(i) The spontaneous combustion of phosphine is technically used in Holme's signals. Containers containing calcium carbide and calcium phosphide are pierced and thrown in the sea when the gases evolved burn and serve as a signal.

(ii) It is also used in smoke screens.

PHOSPHORUS HALIDES

Phosphorus forms two types of halides, $PX_3 (X = F, Cl, Br, I)$ and $PX_5 (X = F, Cl, Br)$.

PHOSPHORUS TRICHLORIDE

Preparation

(i) By passing dry chlorine over heated white phosphorus.

$P_4 + 6Cl_2 \rightarrow 4PCl_3$

(ii) By the action of thionyl chloride with white phosphorus.

$P_4 + 8SOCl_2 \rightarrow 4PCl_3 + 4SO_2 + 2\ S_2Cl_2$

Properties

(i) It is a colourless oily liquid

(ii) Hydrolyses in the presence of moisture.

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

(iii) It reacts with organic compounds containing $-OH$ group such as CH3COOH, C2H5OH.

$3CH_3COOH + PCl_3 \rightarrow 3CH_3COCl + H_3PO_3$

$3C_2H_5OH + PCl_3 \rightarrow 3C_2H_5Cl + H_3PO_3$

PHOSPHORUS PENTACHLORIDE

Preparation

(i) By the reaction of white phosphorus with excess of dry chlorine.

$P_4 + 10Cl_2 \rightarrow 4PCl_5$

(ii) By the action of SO_2Cl_2 on phosphorus.

$P_4 + 10SO_2Cl_2 \rightarrow 4PCl_5 + 10SO_2$

Properties :

(i) PCl_5 is a yellowish white powder

(ii) It hydroslysis in moist air to $POCl_3$ and finally gets converted to phosphoric acid.

$PCl_5 + H_2O \rightarrow POCl_3 + 2HCl$

$POCl_3 + 3H_2O \rightarrow H_3PO_4 + 3HCl$

(iii) When heated, it sublimes but decomposes on stronger heating.

$PCl_5 \xrightarrow{heat} PCl_3 + Cl_2$

(iv) It reacts with organic compounds containing $-OH$ group converting them to chloro derivatives.

$C_2H_5OH + PCl_5 \rightarrow C_2H_5Cl + POCl_3 + HCl$

$CH_3COOH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl$

(v) Finely divided metals on heating with PCl5 give corresponding chlorides.

$2Ag + PCl_5 \rightarrow 2AgCl + PCl_3$

$Sn + 2PCl_5 \rightarrow SnCl_4 + 2PCl_3$

Uses :

It is used in the synthesis of some organic compounds, e.g., C_2H_5Cl, CH_3COCl.

OXIDES OF PHOSPHORUS

It forms three important oxides which exist in dimeric forms.

PHOSPHORUS TRIOXIDE (P_4O_6)

Preparation

Phosphorus trioxides is formed when phosphorus is burnt in a limited supply of air.

$P_4 + 3O_2$ (limited) $\longrightarrow P_4O_6$

Properties

(a) Heating in air : On heating in air, it forms phosphorus pentoxide.

$P_4O_6 + 2O_2 \longrightarrow P_4O_{10}$

Phosphorus (V) oxide

(b) Action of water : It dissolves in cold water to give phosphorus acid.

$P_4O_6 + 6H_2O$ (cold) $\longrightarrow 4H_3PO_3$

Phosphorus(V)acid

It is, therefore, considered as anhydride of phosphorus acid.

Note: With hot water, it gives phosphoric acid and inflammable phosphine.

PHOSPHORUS (V) OXIDE (P_4O_{10})

Preparation :

It is prepared by heating white phosphorus in excess of air.

$P_4 + 5O_2$ (excess) $\xrightarrow{\Delta} P_4O_{10}$

Properties

(a) It is snowy white solid.

(b) Action with water : It readily dissolves in cold water forming metaphosphoric acid.

$P_4O_{10} + 2H_2O(\text{ Cold }) \longrightarrow 4HPO_3$

Metaphosphoric acid.

With hot water it gives phosphoric acid.

$P_4O_{10} + 6H_2O(\text{Hot}) \longrightarrow 4H_3PO_4$

Phosphoric acid

(c) Dehydrating nature : Phosphorus pentoxide has strong affinity for water and, therefore, acts as a powerful dehydrating agent. It extracts water from many inorganic and organic compounds.

(d) P_4O_{10} is a very strong dehydrating agent and extracts water from many compounds including sulphuric acid and nitric acid.

$2HClO_4 \xrightarrow[-H_2O]{P_4O_{10}} Cl_2O7$

Chlorine (VII) oxide

$2CH_3CONH_2 \xrightarrow[-H_2O]{P_4O_{10}} CH_3CN$

Acetamide Methyl cyanide

Structure

(a) Its structure is similar to that of P_4O_6.

(b) In addition, each phosphorus atom forms a double bond with oxygen atom.

OXOACIDS OF PHOSPHORUS :

The important oxoacids of phosphorus with their formulae, methods of preparation and the presence of some characteristic bonds in their structures are given in a table.

Oxoacids of Phosphorus

Name	Formula	Oxidation State of Phosphorus	Characteristic Bonds and their number	Preparation
Hypophosphorus (Phosphinic)	H_3PO_2	+1	One P − OH Two P − H One P = O	White P_4 + alkali
Orthophosphorous (Phosphonic)	H_3PO_3	+3	Two P − OH One P − H One P = O	$P_2O_3 + H_2O$
Pyrophosphorous	$H_4P_2O_5$	+3	Two P − OH Two P − H Two P = O	$PCl_3 + H_3PO_3$

Hypophosphoric	$H_4P_2O_6$	+4	Four $P-OH$ Two $P=O$ One $P-OH$	Red P_4 + alkali
Orthophosphoric	H_3PO_4	+5	Three $P-OH$ One $P=P$	$P_4O_{10} + H_2O$
Pyrophosphoric	$H_4P_2O_7$	+5	Four $P-OH$ Two $P=H$ One $P-O-P$	Heat phosphoric acid
Metaphosphoric	$(HPO_3)_n$	+5	Three $P-OH$ Three $P=O$ Three $P-O-P$	Phosphorous acid $+Br_2$, heat in a sealed tube

Heating Effect :

$$H_3PO_2 \xrightarrow{140^\circ C} PH_3 + H_3PO_4$$

$$H_3PO_4 \xrightarrow[200^\circ C]{\text{gentle heat}} \underset{\text{Pyrophosphoric acid}}{H_4P_2O_7} \xrightarrow[320^\circ C]{\text{strong heat}} \underset{\text{metaphosphoric acid}}{(HPO_3)_n}$$

$$\text{orthophosphoric acid}$$

Graham salt

Graham's salt is the best known of these long chain polyphosphates, and is formed by quenching molten $NaPO_3$. Graham's salt is soluble in water. These solutions give precipitates with metal ions such as Pb^{2+} and Ag^{+}but not with Ca^{2+} and Mg^{2+}. Graham's salt is sold commercially under the trade name Calgon. In industry it is incorrectly called sodium hexametaphosphate crystallizing. It is widely used for softening water.

$$NaH_2PO_4 \xrightarrow{>240^\circ C} \underset{\text{Sodium trimetaphosphate}}{(NaPO_3)_3} \xrightarrow{625^\circ C} NaPO_3(\text{ liquid melt }) \xrightarrow[\text{cooling}]{\text{rapid}} \underset{\text{(Graham's salt) (glass)}}{(NaPO_3)_n}$$

OXYGEN FAMILY

GROUP 16 ELEMENTS (O, S, Se, Te, Po)

This is sometimes known as group of chalcogens.

Occurrence

Oxygen is the most abundant of all the elements on earth crust. Oxygen forms about 46.6% by mass of earth's crust. Dry air contains 20.946% oxygen by volume.

Electronic Configuration

ns^2np^4 is the general valence shell electronic configuration.

Atomic and Ionic Radii : Covalent radius : O < S < Se < Te

Ionisation Enthalpy : O > S > Se > Te > Po (IE1 values)

Electron Gain Enthalpy : S > Se > Te > Po > O

Electronegativity : O > S > Se > Te

Metallic Character : O < S < Se < Te < Po

Melting and Boiling points: M.P. : Te > Po > Se > S > O

B.P. : Te > Po > Se > S > O

Elemental State

Oxygen exist as diatomic molecular gas in this case there is $p\pi - p\pi$ overlap thus two O atoms form double bond $O = O$. The intermolecular forces in O_2 are weak VB forces. $\therefore$ O_2 exist as gas . On the other bond, other elements of family do not form stable $p\pi - p\pi$ bonds and do not exist as M2 molecules. Other atoms are linked by single bonds and form poly atomic complex molecules for eg.

$S - S8, Se - Se8$

Catenation

In this group only S has a strong tendency for catenation oxygen has this tendency to a limited extent.

$H_2O_2H - O - O - H$ (Poly oxides)
$H_2S_2H - S - S - H$ (Polysulphides or polysulphones)
$H_2S_3H - S - S - S - H$
$H_2S_4H - S - S - S - S - H$

Physical Properties

(i) Oxygen and sulphur are non-metals, selenium and tellurium metalloids, whereas polonium is a metal.

(ii) Polonium is radioactive and is short lived (Half-life 13.8 days).

(iii) All these elements exhibit allotropy.

Amongst tetrafluorides, SF_4 is a gas, SeF_4 a liquid and TeF_4 a solid. These fluorides have sp_3 d hybridisation and thus, have trigonal bipyramidal structures in which one of the equatorial positions is occupied by a lone pair of electrons. This geometry is also regarded as see-saw geometry. All elements except selenium form dichlorides and dibromides. These dihalides are formed by sp^3 hybridisation and thus, have tetrahedral structure. The well known monohalides

are dimeric in nature. Examples are S_2F_2, S_2Cl_2, S_2Br_2, Se_2Cl_2 and Se_2Br_2. These dimeric halides undergo disproportionation as given below : $2Se_2Cl_2 \rightarrow SeCl_4 + 3Se$

DIOXYGEN

(a) Laboratory method

(i) By heating oxygen containing salts such as chlorates, nitrates and permanganates.

$$2KClO_3 \xrightarrow[MnO_2]{Heat} 2KCl + 3O$$

(ii) By the thermal decomposition of the oxides of metals low in the electrochemical series and higher oxides of some metals.

$2Ag_2O(s) \rightarrow 4Ag(s) + O_2(g)$; $2Pb_3O_4(s) \rightarrow 6PbO(s) + O_2(g)$

$2HgO(s) \rightarrow 2Hg(\ell) + O_2(g)$; $2PbO_2(s) \rightarrow 2PbO(s) + O_2(g)$

(iii) Hydrogen peroxide is readily decomposed into water and dioxygen by catalysts such as finely divided metals and manganese dioxide.

$2H_2O_2(aq) \rightarrow 2H_2O(\ell) + O_2(g)$

(b) Large scale preparation : It can be prepared from water or air. Electrolysis of water leads to the release of hydrogen at the cathode and oxygen at the anode.

(c) Industrially method : Dioxygen is obtained from air by first removing carbon dioxide and water vapour and then, the remaining gases are liquefied and fractionally distilled to give dinitrogen and dioxygen.

Properties

(i) Dioxygen is a colourless and odourless gas.

(ii) Its solubility in water is to the extent of 3.08 cm^3 in 100 cm^3 water at 293 K which is just sufficient for the vital support of marine and aquatic life.

(iii) It liquefies at 90 K and freezes at 55 K.

(iv) Oxygen atom has three stable isotopes: ^{16}O, ^{17}O and ^{18}O. Molecular oxygen, O_2 is unique in being paramagnetic inspite of having even number of electrons.

(v) Dioxygen directly reacts with nearly all metals and non-metals except some metals (e.g., Au, Pt) and some noble gases. Some of the reactions of dioxygen with metals, non-metals and other compounds are as follows :

$2Ca + O_2 \rightarrow 2CaO$

$4Al + 3O_2 \rightarrow 2Al_2O_3$

$P_4 + 5O_2 \rightarrow P_4O_{10}$

$C + O_2 \rightarrow CO_2$

$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

Some compounds are catalytically oxidised. For example,

$2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3$

$4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$

Uses:

(i) It's importance in normal respiration and combustion processes, oxygen is used in oxyacetylene welding, in the manufacture of many metals, particularly steel.

(ii) Oxygen cylinders are widely used in hospitals, high altitude flying and in mountaineering.

(iii) The combustion of fuels, e.g., hydrazines in liquid oxygen, provides tremendous thrust in rockets.

SIMPLE OXIDES

A binary compound of oxygen with another element is called oxide. In many cases one element forms two or more oxides. The oxides vary widely in their nature and properties. Oxides can be simple (e.g., MgO, Al_2O_3) or mixed (Pb_3O_4, Fe_3O_4).

Types of simple oxide :

Acidic oxide : An oxide that combines with water to give an acid is termed acidic oxide (e.g., $SO_2, Cl_2O_7, CO_2, N_2O_5$).

$SO_2 + H_2O \rightarrow H_2SO_3$

As a general rule, only non-metal oxides are acidic but oxides of some metals in high oxidation state also have acidic character (e.g., Mn_2O_7, CrO_3, V_2O_5).

Basic oxide : The oxides which give a base with water are known as basic oxides (e.g., Na_2O, CaO, BaO). In general, metallic oxides are basic. For example, CaO combines with water to give $Ca(OH)_2$, a base.

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

Amphoteric oxide : Some metallic oxides exhibit a dual behaviour. They show characteristics of both acidic as well as basic oxides. Such oxides are known as amphoteric oxides.

$Al_2O_3(s) + 6HCl(aq) + 9H_2O(\ell) \rightarrow 2[Al(H_2O)_6]^{3+}(aq) + 6Cl^-(aq)$

$Al_2O_3(s) + 6NaOH(aq) + 3H_2O(\ell) \rightarrow 2Na_3[Al(OH)_6](aq)$

Neutral oxide: There are some oxides which are neither acidic nor basic. Such oxides are known as neutral oxides. Examples of neutral oxides are CO, NO and N_2O.

OZONE

Ozone is an allotropic form of oxygen.

Threats to ozone layer

(i) Experiments have shown that nitrogen oxides (particularly nitric oxide) combine very rapidly with ozone and there is, thus, the possibility that nitrogen oxides emitted from the exhaust systems of supersonic jet aeroplanes might be slowly depleting the concentration of the ozone layer in the upper atmosphere.

$NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$

(ii) Another threat to this ozone layer is probably posed by the use of freons which are used in aerosol sprays and as refrigerants.

Preparation

When a slow dry stream of oxygen is passed through a silent electrical discharge, conversion of oxygen to ozone (10%) occurs. The product is known as ozonised oxygen.

$3O_2 \rightarrow 2O_3\ \Delta H^-(298\ K) = +142\ kJ\ mol^{-1}$

Since the formation of ozone from oxygen is an endothermic process, it is necessary to use a silent electrical discharge in its preparation to prevent its decomposition. If concentration of ozone greater than 10 percent is required, a battery of ozonisers can be used, and pure ozone (b.p. 385 K) can be condensed in a vessel surrounded by liquid oxygen.

Note: $\left.\begin{matrix} 2\ F_2 + 2H_2O \longrightarrow 4HF + O_2 \\ F_2 + 3H_2O \longrightarrow 6HF + O_3 \end{matrix}\right]$ Ozonised $\Bigg]$ Is separated by passing into spiral tube cooled by liq. Oxygen air. Ozone condenses at $-112.4°C$. [b.p. of O_2 $-183°C$; b.p. of liq. Air is $-190°C$]

Properties

(i) Pure ozone is a pale blue gas, dark blue liquid and violet-black solid.

(ii) It is diamagnetic gas.

(iii) Ozone has a characteristic fishy smell and in small concentrations it is harmless.

Toxic effect :

(a) Toxic enough (more toxic than KCN). It's intense blue colour is due to the absorption of red light.

(b) However, if the concentration rises above about 100 parts per million, breathing becomes uncomfortable resulting in headache and nausea.

Oxidizing properties

It is one of best oxidising agent, in acid solution, its standard, reduction potential value is 2.07 V.

$O_3 + 2H^+ + 2e \longrightarrow O_2 + H_2O\ E° = +2.07\ V$

It is next to F_2. [above 2.07 V, only F_2, F_2O are there]

It is not really surprising, therefore, high concentrations of ozone can be dangerously explosive.

Due to the ease with which it liberates atoms of nascent oxygen ($O_3 \rightarrow O_2 + O$), it acts as a powerful oxidising agent. For example, it oxidises lead sulphide to lead sulphate and iodide ions to iodine.

$PbS(s) + 4O_3(g) \rightarrow PbSO_4(s) + 4O_2(g)$

$2I^-(aq) + H_2O(\ell) + O_3(g) \rightarrow 2OH^-(aq) + I_2(s) + O_2(g)$

(i) Metal Sulphides to Sulphates.

$MS + 4O_3 \longrightarrow MSO_4 + 4O_2[M = Pb, Cu, Zn, Cd]$

(ii) $2HX + O_3 \longrightarrow X_2 + H_2O + O_2[X = Cl, Br, I]$

(iii) $NaNO_2 + O_3 \longrightarrow NaNO_3 + O_2$

$Na_2SO_3 + O_3 \longrightarrow Na_2SO_4 + O_2$

$Na_2AsO_3 + O_3 \longrightarrow Na_2AsO_4 + O_2$

(iv) Moist S, P, As + O_3 ⇒

$S + H_2O + 3O_3 \longrightarrow H_2SO_4 + 3O_2$

$2P + 3H_2O + 5O_3 \longrightarrow 2H_3PO_4 + 5O_2$

$2As + 3H_2O + 5O_3 \longrightarrow 2H_3AsO_4 + 5O_2$

(v) Moist $I_2 \longrightarrow HIO_3$ whereas dry iodine $\longrightarrow I_4O_9$ (yellow)

$I_2 + 5O_3 + H_2O \longrightarrow 2HIO_3 + 5O_2$

$2I_2 + 9O_3 \longrightarrow I_4O_9 + 9O_2$

(vi) $2\,K_2MnO_4 + O_3 + H_2O \longrightarrow 2KMnO_4 + 2KOH + O_2$

$2\,K_4[Fe(CN)_6] + O_3 + H_2O \longrightarrow 2\,K_3[Fe(CN)_6] + 2KOH + O_2$

$2FeSO_4 + O_3 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + O_2 + H_2O$

(vii) (a) 2KI (acidified) $+O_3 + 2HCl \longrightarrow I_2 + 2KCl + H_2O + O_2$

(b) 2KI (neutral) $+O_3 + H_2O \longrightarrow \underbrace{I_2 + 2KOH}_{KI+KOI} + O_2$ } O_3 *is estimated by this reaction*

$2KI + KOI + 2HCl \longrightarrow 2KCl + I_2 + H_2O$ }

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

alk. $\begin{Bmatrix} KI + 3O_3 \longrightarrow KIO_3 + 3O_2 \\ KI + 4O_3 \longrightarrow KIO_4 + 4O_2 \end{Bmatrix}$

(viii) Hg loses its fluidity (tailing of Hg)

$2Hg + O_3 \longrightarrow Hg_2O + O_2$

similarly $2Ag + O_3 \longrightarrow Ag_2O + O_2$

Brown

(ix) $BaO_2 + O_3 \rightarrow BaO + 2O_2$

$H_2O_2 + O_3 \longrightarrow H_2O + 2O_2$

$Na_2O_2 + O_3 + H_2O \longrightarrow 2NaOH + 2O_2$

(x) $2KOH + 5O_3 \longrightarrow 2KO_3 + 5O_2 + H_2O$

In all above reaction O_3 gives up O_2 but some reactions are there which consumes all O-atom.

(i) $3SO_2 + O_3 \longrightarrow 3SO_3$

(ii) $3SnCl_2 + 6HCl + O_3 \longrightarrow 3SnCl_4 + 3H_2O$

Uses :

(i) Sterilising water

(ii) Detection of position of the double bond in the unsaturated compound.

(iii) It is used as a germicide, disinfectant and for sterilising water.

(iv) It is also used for bleaching oils, ivory, flour, starch, etc.

(v) It acts as an oxidising agent in the manufacture of potassium permanganate.

Ques. Ozone is thermodynamically unstable with respect to oxygen. Explain ?

Sol. Because its decomposition into oxygen results in the liberation of heat (ΔH is negative) and an increase in entropy (ΔS is positive). These two effects reinforce each other, resulting in large negative Gibbs energy change (ΔG) for its conversion into oxygen.

HYDROGEN PEROXIDE (H_2O_2)

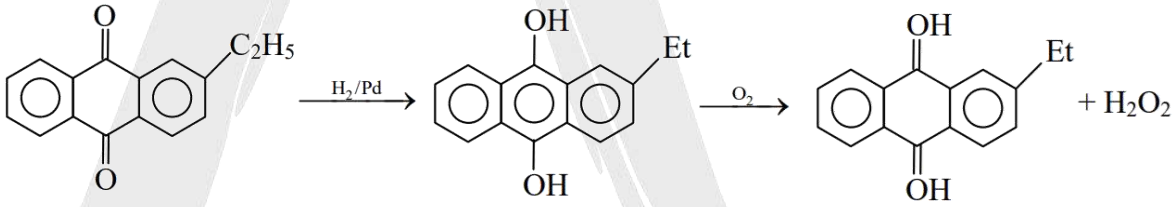
Method of preparation:

(i) $Na_2O_2 + H_2O$ (ice cold water) $\longrightarrow 2NaOH + H_2O_2$

(ii) $BaO_2 + H_2So_4 \longrightarrow BaSO_4 + H_2O_2$

Instead of H_2SO_4, H_3PO_4 is added now-a-days because H_2SO_4 catalyses the decomposition of H_2O_2 whereas H_3PO_4 favours to restore it.

$3BaO_2 + 2H_3PO_4 \rightarrow Ba_3(PO_4)_2 + 3H_2O_2$ and $Ba_3(PO_4)_2 + 3H_2SO_4 \rightarrow 3BaSO_4 + 2H_3PO_4$ (reused again)

(iii) 

Properties:

(i) Colourless, odourless liquid (b.p. 152°)

(ii) Acidic nature: $H_2O_2 + 2NaOH \longrightarrow Na_2O_2 + H_2O$

$H_2O_2 + Na_2CO_3 \longrightarrow Na_2O_2 + CO_2 + H_2O$

(iii) It is oxidant as well as reductant.

$H_2O_2 + 2H^+ + 2e \rightarrow 2H_2O$ [reaction in acidic medium]

$H_2O_2 + 2e \rightarrow 2OH^-$[rxn^n in alkali medium]

Oxidising Properties:

(i) $PbS + 4H_2O_2 \longrightarrow PbSO_4 + 4H_2O$ (Used in washing of oil painting)

(ii) $NaNO_2 + H_2O_2 \longrightarrow NaNO_3 + H_2O$

$Na_2SO_3 + H_2O_2 \longrightarrow Na_2SO_4 + H_2O$

$2KI + H_2O_2 \longrightarrow 2KOH + I_2$

$H_2S + H_2O_2 \longrightarrow S\downarrow + 2H_2O$

$H_2SO_4 + 2FeSO_4 + H_2O_2 \longrightarrow Fe_2(SO_4)_3 + 2H_2O$

$2\,K_4[Fe(CN)_6] + H_2O_2 + H_2SO_4 \longrightarrow 2\,K_3[Fe(CN)_6] + K_2SO_4 + 2H_2O$

Reducing properties:

(a) $Ag_2O + H_2O_2 \longrightarrow 2Ag + H_2O + O_2$

(b) $O_3 + H_2O_2 \longrightarrow H_2O + 2O_2$

(c) $MnO_2 + H_2O_2 + H_2SO_4 \rightarrow MnSO_4 + 2H_2O + O_2$

(d) $PbO_2 + H_2O_2 \rightarrow PbO + H_2O + O_2$

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

$PbO_2 + H_2O_2 \longrightarrow PbO + H_2O + O_2$

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

$Pb_3O_4 + H_2O_2 + 6HNO_3 \longrightarrow 3\,Pb(NO_3)_2 + 4H_2O + O_2$

(f) $X_2 + H_2O_2 \longrightarrow 2HX + O_2 [X = Cl, Br]$

(g) $2[Fe(CN)_6]^{3-} + 2OH^- + H_2O_2 \longrightarrow 2[Fe(CN)_6]^{4-} + 2H_2O + O_2$

(h) $NaOCl + H_2O_2 \longrightarrow NaCl + H_2O + O_2$

(i) $NaIO_4 + H_2O_2 \longrightarrow NaIO_3 + H_2O + O_2$

Uses : (i) As a rocket propellant:

$NH_2 \cdot NH_2 + 2H_2O_2 \longrightarrow N_2 + 4H_2O$ [highly exothermic and large increase in volume]

(ii) In detection of Cr^{+3}, Ti^{+4} etc.

$Ti(SO_4)_2 + H_2O_2 + 2H_2O \longrightarrow H_2TiO_4 + 2H_2SO_4$

Yellow or orange

Pertitanic acid

ALLOTROPIC FORMS OF SULPHUR

$$\alpha - \text{ sulphur} \underset{3696\text{ K}}{\overset{>36\text{ K}}{\rightleftharpoons}} \beta - \text{ sulphur}$$

At 369 K both the forms are stable. This temperature is called transition temperature.

Rhombic sulphur (α-sulphur)

(i) This allotrope is yellow in colour, m.p. 385.8 K and specific gravity 2.06 .

(ii) Rhombic sulphur crystals are formed on evaporating the solution of roll sulphur in CS_2.

(iii) It is insoluble in water but dissolves to some extent in benzene, alcohol and ether.

(iv) It is readily soluble in CS_2.

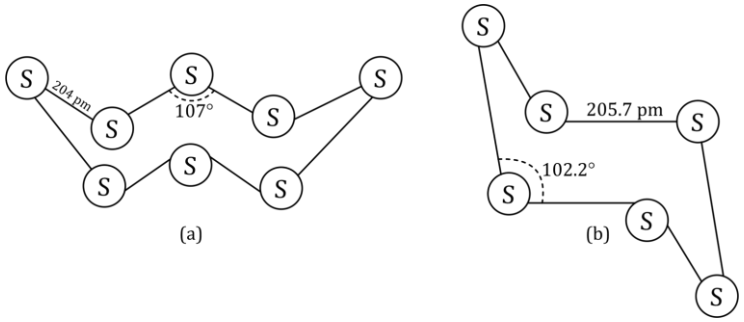
Monoclinic sulphur (β-sulphur)

(i) Its m.p. is 393 K and specific gravity 1.98.

(ii) It is soluble in CS_2.

Structure of α and β sulphur

Both rhombic and monoclinic sulphur have S_8 molecules. These S_8 molecules are packed to give different crystal structures. The S_8 ring in both the forms is puckered and has a crown shape.



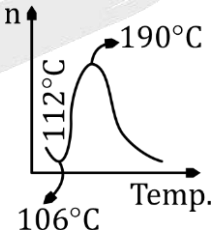
S_8 ring in rhombic sulphur S_6 form

Several other modifications of sulphur containing 6-20 sulphur atoms per ring have been synthesized in the last two decades. In cyclo- S_6, the ring adopts the chair form. At elevated temperatures ($\sim$ 1000 K), S_2 is the dominant species and is paramagnetic like O_2.

Note: Viscosity of 'S' with temperature : m.p. of ' S' $\longrightarrow$ 112.8°C.

> 112.8°C to 160°C $\Rightarrow$ slow decreases due to S_8 rings slip and roll over one another easily.

> 160°C, increases sharply due to breaking of S_8 rings into chains and polymerses into large size chain.



Amorphous forms are

(i) Plastic sulphur (ii) Milk of sulphur (iii) Colloidal sulphur

SULPHUR DIOXIDE

Preparation

Sulphur dioxide is formed together with a little (6-8%) sulphur trioxide when sulphur is burnt in air or oxygen:

$S(s) + O_2(g) \rightarrow SO_2(g)$

laboratory method by treating a sulphite with dilute sulphuric acid.

$SO_3^{2-}(aq) + 2H^+(aq) \rightarrow H_2O(\ell) + SO_2(g)$

other preparation :

$Cu + 2H_2SO_4$ (conc.) $\longrightarrow CuSO_4 + 2H_2O + SO_2$

$Hg + H_2SO_4 \longrightarrow HgSO_4 + H_2O + SO_2$

$2Ag + H_2SO_4 \longrightarrow Ag_2SO_4 + H_2O + SO_2$

$S + 2H_2SO_4 \longrightarrow 3SO_2 + 2H_2O$

$(\text{Charcoal}^{C} + 2H_2SO_4 \longrightarrow CO_2 + 2SO_2 + 2H_2O$

$NaHSO_3 + H_2SO_4 \longrightarrow NaHSO_4 + H_2O + SO_2$

Industrial method, by-product of the roasting of sulphide ores.

$4FeS_2(s) + 11O_2(g) \rightarrow 2Fe_2O_3(s) + 8SO_2(g)$

The gas after drying is liquefied under pressure and stored in steel cylinders.

Properties

(i) Sulphur dioxide is a colourless gas with pungent smell.

(ii) It is highly soluble in water.

(iii) It liquefies at room temperature under a pressure of two atmospheres and boils at 263 K.

(iv) Acdic character sulphur dioxide, when passed through water, forms a solution of sulphurous acid.

$SO_2(g) + H_2O(\ell) \rightleftharpoons H_2SO_3(aq)$

It reacts readily with sodium hydroxide solution, forming sodium sulphite, which then reacts with more sulphur dioxide to form sodium hydrogen sulphite.

$2NaOH + SO_2 \rightarrow Na_2SO_3 + H_2O$

$Na_2SO_3 + H_2O + SO_2 \rightarrow 2NaHSO_3$

$$SO_2(g) + Cl_2 \xrightarrow[\text{of charcoal}]{\text{in presence}} SO_2Cl_2(\ell)$$

$$SO_2(g) + O_2(g) \overset{V_2O_5}{\longrightarrow} 2SO_3(g)$$

Reducing properties

When moist, sulphur dioxide behaves as a reducing agent.

$2Fe^{3+} + SO_2 + 2H_2O \rightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+$

$5SO_2 + 2MnO_4^- + 2H_2O \rightarrow 5SO_4^{2-} + 4H^+ + 2Mn^{2+}$

Bonding in SO_2 : The molecule of SO_2 is angular. It is a resonance hybrid of the two canonical forms:

Uses:

(i) It is used refining petroleum and sugar

(ii) It is used in bleaching wool and silk

(iii) It is used as an anti-chlor, disinfectant and preservative. Sulphuric acid, sodium hydrogen sulphite and calcium hydrogen sulphite (industrial chemicals) are manufactured from sulphur dioxide. Liquid SO_2 is used as a solvent to dissolve a number of organic and inorganic chemicals.

HYDROGEN SULPHIDE (H_2S) SULPHURATED HYDROGEN

Preparation

By the action of dil. HCl or H_2SO_4 on iron pyrites.

$FeS + H_2SO_4 \longrightarrow FeSO_4 + H_2S \uparrow$

Properties

(a) It burn in air with blue flame

$2H_2S + O_2 \longrightarrow 2H_2O + S$

If the air supply is in excess

$2H_2S + 3O_2 \longrightarrow 2H_2O + 2SO_2$

(b) It is a mild acid.

$H_2S \longrightarrow H^+ + SH^-$

$SH^- \longrightarrow H^+ + S^{-2}$

(c) It act as a reducing agent. It reduces halogen into corresponding hydroacid.

$H_2S + X_2 \longrightarrow 2HX + S$

Tests of H_2S

(a) Unpleasant odour resembling that of rotten eggs.

(b) It turns lead acetate into paper black

$(CH_3COO)_2Pb + H_2S \longrightarrow \underset{\text{Black}}{PbS\downarrow} + 2CH_3COOH$

Uses

(a) It is mainly employed in salt analysis for the detection of cation.

(b) Reducing agent for $H_2SO_4, KMnO_4, K_2Cr_2O_7, O_3, H_2O_2, FeCl_3$

Note: Drying agent for this gas : fused $CaCl_2, Al_2O_3$ (dehydrated) P_2O_5 etc.

But not H_2SO_4, because

$H_2SO_4 + H_2S \longrightarrow 2H_2O + SO_2 + S$

SULPHURIC ACID

Industrial Manufacturing (Contact process)

Steps involved :

(i) Burning of sulphur or sulphide ores in air to generate SO_2.

(ii) Conversion of SO_2 to SO_3 by the reaction with oxygen in the presence of a catalyst (V_2O_5) :

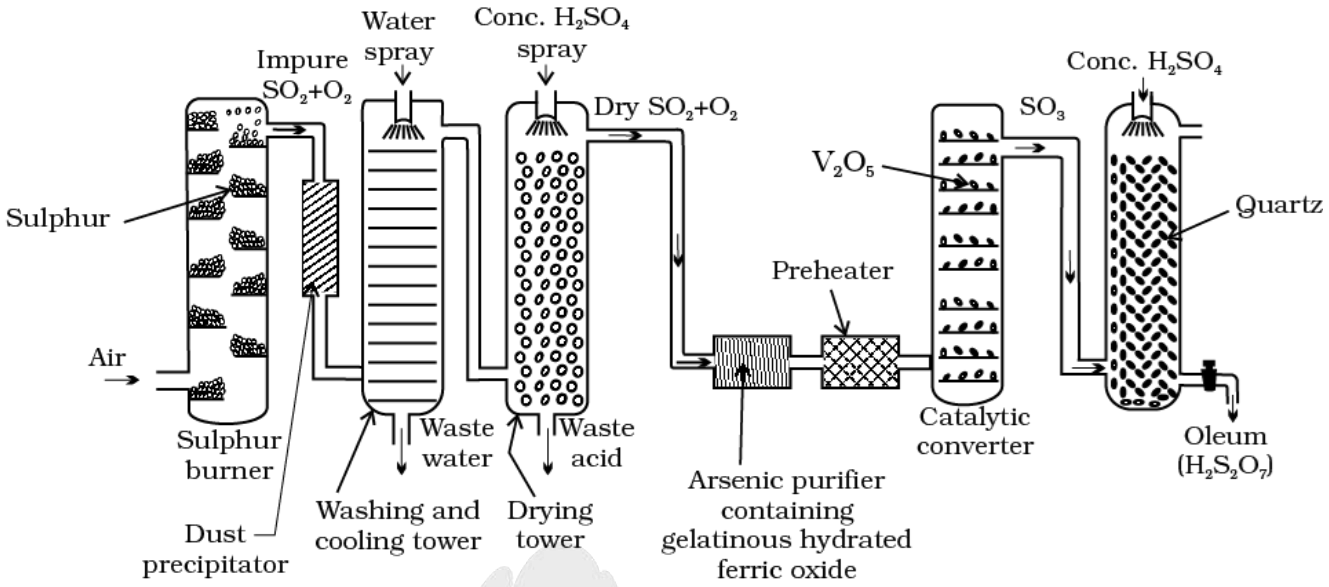
The key step in the manufacture of H_2SO_4 is the catalytic oxidation of SO_2 with O_2 to give SO_3 in the presence of V_2O_5 (catalyst).

$2SO_2(g) + O_2(g) \overset{V_2O_5}{\longrightarrow} 2SO_3(g) \Delta_rH^\Theta = -196.6 \text{ kJ mol}^1$

The reaction is exothermic, reversible and the forward reaction leads to a decrease in volume.

(iii) The SO_3 gas from the catalytic converter is absorbed in concentrated H_2SO_4 to produce oleum. Dilution of oleum with water gives H_2SO_4 of the desired concentration.

$SO_3 + H_2SO_4 \rightarrow \underset{\text{(Oleum)}}{H_2S_2O_7}$



FLOW DIAGRAM FOR THE MANUFACTURE OF SULPHURIC ACID

The sulphuric acid obtained by Contact process is 96 – 98% pure.

P_2O_5 is stronger dehydrating agent than H_2SO_4: $H_2SO_4 + P_2O_5 \longrightarrow 2HPO_3 + SO_3$

Properties

(i) Sulphuric acid is a colourless, dense, oily liquid with a specific gravity of 1.84 at 298 K.

(ii) The acid freezes at 283 K and boils at 611 K.

(iii) It dissolves in water.

Chemical properties

The chemical reactions of sulphuric acid are as a result of the following characteristics:

(1) Acidic character :

In aqueous solution, sulphuric acid ionises in two steps.

$H_2SO_4(aq) + H_2O(\ell) \rightarrow H_3O^+(aq) + HSO_4^-(aq): K_{a_1} =$ Very large ($K_{a1} > 10$)

$HSO_4^-(aq) + H_2O(\ell) \rightarrow H_3O^+(aq) + SO_4^{2-}(aq); K_{a_2} = 1.2 \times 10^{-2}$

(2) Dehydrating Propert :

Concentrated sulphuric acid is a strong dehydrating agent.

$C_{12}H_{22}O_{11} \xrightarrow[\text{Conc.}]{H_2SO_4} 12C + 11H_2O$

$C_6H_{12}O_6 \xrightarrow[-6H_2O]{H_2SO_4} 6C$

$(COOH)_2 \xrightarrow[-H_2O]{H_2SO_4} CO + CO_2$

$HCO_2H \xrightarrow[-H_2O]{} CO$

(3) Oxidizing Nature :

Hot concentrated sulphuric acid is a moderately strong oxidising agent. In this respect, it is intermediate between phosphoric and nitric acids.

$Cu + 2H_2SO_4$ (conc.) $\rightarrow CuSO_4 + SO_2 + 2H_2O$

$HBr/HI + H_2SO_4$ (conc.) $\rightarrow Br_2/I_2 + SO_2 + H_2O$

$3\,S + 2H_2SO_4$ (conc.) $\rightarrow 3SO_2 + 2H_2O$

$C + 2H_2SO_4$ (conc.) $\rightarrow CO_2 + 2SO_2 + 2H_2O$

$2P + 5H_2SO_4$ (conc.) $\rightarrow H_3PO_4 + 5SO_2$

H_2SO_4&SO_3:

$\overbrace{SO_2 + Cl_2}^{\text{Both gas}} \longrightarrow SO_2Cl_2$

$H_2SO_4 + 2PCl_5 \longrightarrow SO_2Cl_2 + 2POCl_3 + 2HCl$

SO_2Cl_2 → good chlorinating agent

Uses:

(i) petroleum refining

(ii) manufacture of pigments, paints and dyestuff intermediates

(iii) detergent industry

(iv) metallurgical applications (e.g., cleansing metals before enameling, electroplating and galvanising

(v) storage batteries

(vi) in the manufacture of nitrocellulose products and

(vii) as a laboratory reagent.

SODIUM THIOSULPHATE

Prep^n:

(i) Na_2SO_3 sol^n. + S (powder) $\xrightarrow{\text{boiling}}$ $Na_2S_2O_3$ $\xrightarrow{\text{eapporation}}$ monoclinic crystal

$Na_2SO_4 + 4C \xrightarrow{\text{roasting}} Na_2S +$

(ii) Salt cake Coke → SO_2 passed into it → $Na_2S_2O_3$ $[3SO_2 + 2Na_2S \longrightarrow 2Na_2S_2O_3 + S]$

(iii) $6NaOH + 4\,S \longrightarrow Na_2S_2O_3 + 2Na_2S + 3H_2O$

$3Ca(OH)_2 + 12\,S \longrightarrow CaS_2O_3 + 2CaS_5 + 3H_2O$

(iv) $Na_2SO_3 + Na_2S + I_2 \longrightarrow Na_2S_2O_3 + 2NaI$

Props:

(i) $4Na_2S_2O_3 \xrightarrow{\Delta} Na_2S_5 + 3Na_2SO_4$

(ii) $Na_2S_2O_3 + 2H^+ \longrightarrow H_2S_2O_3 \xrightarrow{\Delta} H_2O + SO_2 + S\downarrow$ (White turbidity)

Reaction:

(i) $Na_2S_2O_3 + I_2 \longrightarrow S_4O_6^{2-} + 2I^-$

$+Cl - \text{ water} \longrightarrow SO_4^{2-} + S + 2HCl$

$+Br2 - \text{ water} \longrightarrow SO_4^{2-} + S + 2HBr$

$+4OI^- + 2OH^- \longrightarrow 2SO_4^{2-} + 4I^- + H_2O$

$+4Cl_2 + 5H_2O \longrightarrow Na_2SO_4 + 8HCl + H_2SO_4$

HALOGEN FAMILY

GROUP 17 ELEMENTS (F, Cl, Br, I, At)

Electronic Configuration

The electronic configuration of outermost shell 17th group element is (ns^2np^5).

Atomic and ionic radii : $F < Cl < Br < I$

Ionisation Enthalpy : $F > Cl > Br > I$

Electron Gain Enthalpy: $Cl > F > Br > I$

Electronegativity : $F > Cl > Br > I$

Physical Properties

(i) Their melting and boiling points steadily increase with atomic number.

(ii) All halogens are coloured. For example, F_2 has yellow gas, Cl_2 greenish yellow gas, Br_2 red liquid and I_2 violet coloured solid.

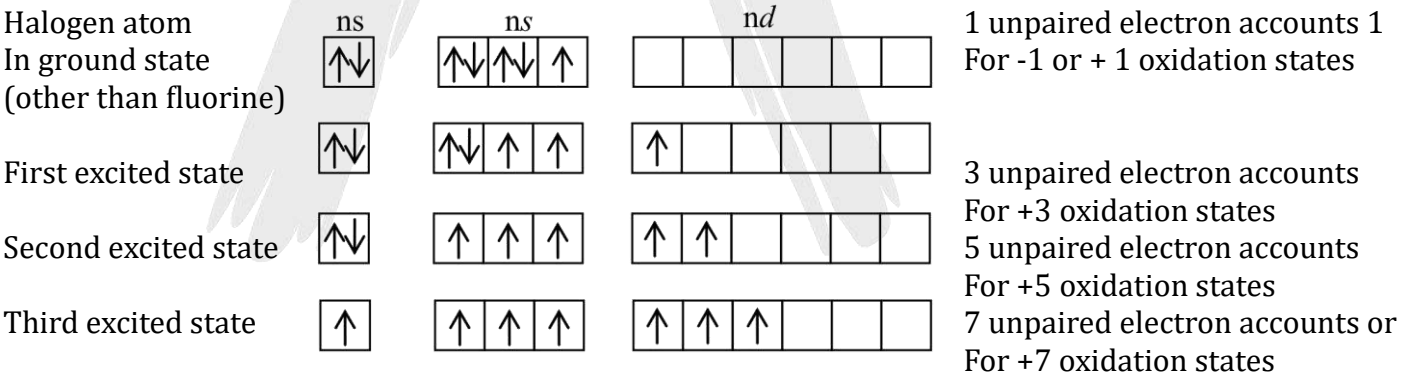
(iii) Fluorine and chlorine react with water. Bromine and iodine are only sparingly soluble in water but are soluble in various organic solvents such as chloroform, carbon tetrachloride, carbon disulphide and hydrocarbons to give coloured solutions.

(iv) Bond energy order; $Cl_2 > Br_2 > F_2 > I_2$

Chemical Properties

Oxidation states :

(i) All the halogens exhibit -1 oxidation state. However, chlorine, bromine and iodine exhibit +1, +3, +5 and +7 oxidation states also as explained below:



(ii) The higher oxidation states of chlorine, bromine and iodine are realised mainly when the halogens are in combination with the small and highly electronegative fluorine and oxygen atoms. e.g., in interhalogens, oxides and oxoacids.

(iii) The oxidation states of +4 and +6 occur in the oxides and oxoacids of chlorine and bromine.

(iv) The fluorine atom has no d orbitals in its valence shell and therefore cannot expand its octet. Being the most electronegative, it exhibits only -1 oxidation state.

Chemical reactivity

(i) All the halogens are highly reactive.

(ii) They react with metals and non-metals to form halides and the reactivity of the halogens decreases down the group. i.e. the order is $F_2 > Cl_2 > Br_2 > I_2$

(iii) The ready acceptance of an electron is the reason for the strong oxidising nature of halogens. F_2 is the strongest oxidising halogen and it oxidises other halide ions in solution or even in the solid phase.

In general, a halogen oxidises halide ions of higher atomic number.

$F_2 + 2X^- \rightarrow 2\ F^- + X_2 (X = Cl, Br \text{ or } I)$

$Cl_2 + 2X^- \rightarrow 2Cl^- + X_2 (X = Br \text{ or } I)$

$Br_2 + 2I^- \rightarrow 2Br^- + I_2$

(1) Reactivity towards water

$2\ F_2(g) + H_2O(l) \rightarrow 4H^+(aq) + 4\ F^-(aq) + O_2(g)$

$X_2(g) + H2O(l) \rightarrow HX(aq) + HOX(aq)$

(where X = Cl or Br)

$4I(aq) + 4H^+(aq) + O_2(g) \rightarrow 2I_2(s) + 2H_2O(l)$

(2) Reactivity towards hydrogen :

They all react with hydrogen to give hydrogen halides but affinity for hydrogen decreases from fluorine to iodine.

(i) The acidic strength order : $HF < HCl < HBr < HI$

(ii) The stability order of these halides : $H - F > H - Cl > H - Br > H - I$.

(3) Reactivity towards oxygen :

(i) Halogens form many oxides with oxygen but most of them are unstable. Fluorine forms two oxides OF_2 and $O_2\ F_2$. However, only OF_2 is thermally stable at 298 K. These oxides are essentially oxygen fluorides because of the higher electronegativity of fluorine than oxygen. Both are strong fluorinating agents. $O_2\ F_2$ oxidises plutonium to PuF_6 and the reaction is used in removing plutonium as PuF_6 from spent nuclear fuel.

(ii) Chlorine, bromine and iodine form oxides in which the oxidation states of these halogens range from +1 to +7 .

(iii) A combination of kinetic and thermodynamic factors lead to the generally decreasing order of stability of oxides formed by halogens, $I > Cl > Br$.

(iv) The higher oxides of halogens tend to be more stable than the lower ones.

(v) Chlorine oxides, Cl_2O, ClO_2, Cl_2O_6 and Cl_2O_7 are highly reactive oxidising agents and tend to explode. ClO_2 is used as a bleaching agent for paper pulp and textiles and in water treatment.

(vi) The bromine oxides, Br_2O, BrO_2, BrO_3 are the least stable halogen oxides (middle row anomally) and exist only at low temperatures. They are very powerful oxidising agents.

(vii) The iodine oxides, I_2O_4, I_2O_5, I_2O_7 are insoluble solids and decompose on heating. I_2O_5 is a very good oxidising agent and is used in the estimation of carbon monoxide.

(4) Reactivity towards metals :

Halogens react with metals to form metal halides.

$Mg(s) + Br_2(l) \rightarrow MgBr_2(s)$

The ionic character of the halides decreases in the order $MF > MCl > MBr > MI$ where M is monovalent metal.

FLUORINE

Method of Prep^{n} :

Moissan process : [By electrolysis of KHF_2 (which is obtained from CaF_2)]

$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$

$HF + KF \longrightarrow KHF_2$ { KF decreases the m.p.of the mix. depending upon the composition. }

$KHF_2 \xrightarrow{\text{Electrolysis}} H_2$ (at cathode) $+ F_2$ (at anode)

CHLORINE

Preparation

(i) By electrolysis of aq. NaCl :

$2NaCl + 2H_2O \longrightarrow 2NaOH + \underbrace{H_2}_{\text{at cathode}} + \underbrace{Cl_2}_{\text{(anode)}}$

$\underset{\text{(Malten)}}{2NaCl} \xrightarrow{\text{Electrolysis}} \underset{\text{(cathode)}}{2Na} + \underset{\text{(anode)}}{Cl_2}$

(ii) By heating manganese dioxide with concentrated hydrochloric acid.

$MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$

However, a mixture of common salt and concentrated H_2SO_4 is used in place of HCl.

$4NaCl + MnO_2 + 4H_2SO_4 \rightarrow MnCl_2 + 4NaHSO_4 + 2H_2O + Cl_2$

(iii) By the action of HCl on potassium permanganate.

$2KMnO_4 + 16HCl \rightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$

MANUFACTURE OF CHLORINE

(i) Deacon's process : By oxidation of hydrogen chloride gas by atmospheric oxygen in the presence of $CuCl_2$ (catalyst) at 723 K.

$4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$

(ii) Electrolytic process : Chlorine is obtained by the electrolysis of brine (concentrated NaCl solution).

Chlorine is liberated at anode. It is also obtained as a by-product in many chemical industries.

Properties

(i) It is a greenish yellow gas with pungent and suffocating odour.

(ii) It is soluble in water. Chlorine reacts with a number of metals and non-metals to form chlorides.

$2Al + 3Cl_2 \rightarrow 2AlCl_3$; $P_4 + 6Cl_2 \rightarrow 4PCl_3$

$2Na + Cl_2 \rightarrow 2NaCl$; $S_8 + 4Cl_2 \rightarrow 4\ S_2Cl_2$

$2Fe + 3Cl_2 \rightarrow 2FeCl_3$;

Reaction with hydrogen

It has great affinity for hydrogen. It reacts with compounds containing hydrogen to form HCl.

$H_2 + Cl_2 \rightarrow 2HCl$

$H_2S + Cl_2 \rightarrow 2HCl + S$

$C_{10}H_{16} + 8Cl_2 \rightarrow 16HCl + 10C$

Reaction with amonia

With excess ammonia, chlorine gives nitrogen and ammonium chloride whereas with excess chlorine,

nitrogen trichloride (explosive) is formed.

$8NH_3 + 3Cl_2 \rightarrow 6NH_4Cl + N_2$; (excess) $NH_3 + 3Cl_2 \rightarrow NCl_3 + 3HCl$ (excess)

Reaction with alkalies

$2NaOH + Cl_2 \rightarrow NaCl + NaOCl + H_2O$

(cold and dilute)

$6NaOH + 3Cl_2 \rightarrow 5NaCl + NaClO_3 + 3H_2O$

(hot and conc.)

$5X^- + XO_3^- + 6H^+ \longrightarrow 3X_2 + 3H_2O$

$[X = Cl, Br, I]$

Reaction with slaked lime

With dry slaked lime it gives bleaching powder.

$2Ca(OH)_2 + 2Cl_2 \rightarrow Ca(OCl_2) + CaCl_2 + 2H_2O$

The composition of bleaching powder is $Ca(\mathbf{OCl})_2 \cdot CaCl_2 \cdot \mathbf{Ca(OH)_2 \cdot 2H_2O}$.

Note : Chlorine water on standing loses its yellow colour due to the formation of HCl and HOCl.

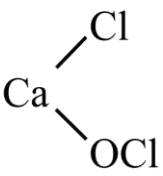
Hypochlorous acid (HOCl) so formed, gives nascent oxygen which is responsible for oxidising and bleaching properties of chlorine.

It is a powerful bleaching agent; bleaching action is due to oxidation.

$Cl_2 + H_2O \rightarrow 2HCl + O$

Coloured substance $+ O \rightarrow$ Colourless substance

Uses: It is used (i) for bleaching woodpulp (required for the manufacture of paper and rayon), bleaching cotton and textiles, (ii) in the extraction of gold and platinum (iii) in the manufacture of dyes, drugs and organic compounds such as CCl_4, $CHCl_3$, DDT, refrigerants, etc. (iv) in sterilising drinking water and (v) preparation of poisonous gases such as phosgene ($COCl_2$), tear gas (CCl_3NO_2), mustard gas ($ClCH_2CH_2SCH_2CH_2Cl$).

Bleaching Powder : 

Prep^{n}. $Cl_2(g) + \underset{\text{Slaked lime}}{Ca(OH)_2} \xrightarrow{40^\circ C} Ca(OCl)Cl + H_2O$

(a) On long standing it undergoes

(i) auto oxiation $6Ca(OCl)Cl \longrightarrow Ca(ClO_3)_2 + 5CaCl_2$

(ii) $2Ca(OCl)Cl \xrightarrow[\text{Cat.}]{CoCl_2} 2CaCl_2 + O_2$

(iii) $Ca(OCl)Cl + H2O \longrightarrow Ca(OH)_2 + Cl_2$

Oxidising Prop.:

$CaOCl_2 + H_2S \longrightarrow S + CaCl_2 + H_2O$

$CaOCl_2 + 2FeSO_4 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + CaCl_2 + H_2O$

$CaOCl_2 + KNO_2 \longrightarrow CaCl_2 + KNO_3$

$3CaOCl_2 + 2NH_3 \longrightarrow 3CaCl_2 + 3H_2O + N_2$

$CaOCl_2 + 2KI + 2HCl \longrightarrow CaCl_2 + 2KCl + H_2O + I_2$

$CaOCl_2 + 2KI + 2AcOH \longrightarrow CaCl_2 + 2KOAc + H_2O + I_2$

$CaOCl_2 + Na_3AsO_3 \longrightarrow Na_3AsO_4 + CaCl_2$

Reaction with acid:

$CaOCl_2 + 2HCl \longrightarrow CaCl_2 + H_2O + Cl_2$; $Ca(OCl)Cl + H_2SO_4 \longrightarrow CaSO_4 + H_2O + Cl_2$

$Ca(OCl)Cl + CO2 \longrightarrow CaCO_3 + Cl_2$

Note: ClO_2 does not dimerise because odd e' undergoes delocalisation (in its own vaccant 3 d-orbital)

$Cl_2O_4(Cl.ClO_4)$ is not the dimer of ClO_2. Actually it is Cl-perchlorate.

HYDROGEN CHLORIDE

Preparation

Laboratory method: it is prepared by heating sodium chloride with concentrated sulphuric acid.

$NaCl + H_2SO_4 \xrightarrow{420\ K} NaHSO_4 + HCl$

$NaHSO_4 + NaCl \xrightarrow{823\ K} Na_2SO_4 + HCl$

HCl gas can be dried by passing through concentrated sulphuric acid.

Properties

(i) It is a colourless and pungent smelling gas.

(ii) It is easily liquefied to a colourless liquid (b.p.189 K) and freezes to a white crystalline solid (f.p. 159 K).

(iii) It is extremely soluble in water

(iv) Acidic character : It ionises as follows

$HCl(g) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq) K_a = 10^7$

Its aqueous solution is called hydrochloric acid. High value of dissociation constant (Ka) indicates that it is a strong acid in water. It reacts with NH_3 and gives white fumes of NH_4Cl.

$NH_3 + HCl \rightarrow NH_4Cl$

Note: Aqua regia

When three parts of concentrated HCl and one part of concentrated HNO3 are mixed, aqua regia is formed which is used for dissolving noble metals, e.g., gold, platinum.

$Au + 4H^+ + NO_3^- + 4Cl^- \rightarrow AuCl_4^- + NO + 2H_2O$

$3Pt + 16H^+ + 4NO_3^- + 18Cl^- \rightarrow 3PtCl_6^{2-} + 4NO + 8H_2O$

Reaction with salts

Hydrochloric acid decomposes salts of weaker acids, e.g., carbonates, hydrogencarbonates, sulphites, etc.

$Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$

$NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2$

$Na_2SO_3 + 2HCl \rightarrow 2NaCl + H_2O + SO_2$

Uses: (i) It is used in the manufacture of chlorine, NH_4Cl and glucose (from corn starch)

(ii) It is used for extracting glue from bones and purifying bone black

(iii) It is used in medicine and as a laboratory reagent.

(iv) It bleaches vegetable or organic matter in the presence of moisture. Bleaching effect of chlorine is permanent.

INTERHALOGEN COMPOUNDS

When two different halogens react with each other, interhalogen compounds are formed. They can be assigned general compositions as XX', XX'_3, XX_5' and XX'_7 where X is halogen of larger size and X′ of smaller size and X is more electropositive than X′.

Preparation

The interhalogen compounds can be prepared by the direct combination or by the action of halogen on lower interhalogen compounds. The product formed depends upon some specific conditions, Fore.g.,

$\underset{\text{(equal volume)}}{Cl_2 + F_2} \xrightarrow{473K} 2ClF$; $I_2 + 3Cl_2 \longrightarrow 2ICl_3$

$Cl_2 + \underset{\text{(excess)}}{3F_2} \xrightarrow{573K} 2ClF_3$; $\underset{\text{(diluted with water)}}{Br_2 + 3F_2} \longrightarrow 2BrF_3$

$\underset{\text{(equimolar)}}{I_2 + Cl_2} \longrightarrow 2ICl$; $Br_2 + \underset{\text{(excess)}}{5F_2} \longrightarrow 2BrF_5$

Properties

(i) These are all covalent molecules and are diamagnetic in nature.

(ii) They are volatile solids or liquids at 298 K except ClF which is a gas.

(iii) Their physical properties are intermediate between those of constituent halogens except that their m.p. and b.p. are a little higher than expected.

(iv) Their chemical reactions can be compared with the individual halogens. In general, interhalogen compounds are more reactive than halogens (except fluorine). This is because $X - X'$ bond in interhalogens is weaker than $X - X$ bond in halogens except $F - F$ bond.

(v) All these undergo hydrolysis giving halide ion derived from the smaller halogen and a hypohalite (when XX'), halite (when XX'_3), halate (when XX'_5) and perhalate (when XX'_7) anion derived from the larger halogen.

$$XX' + H_2O \rightarrow HX' + HOX$$

PSEUDO HALOGEN

There are univalent ion consisting of two or more atoms of which at least one is N, that have properties similar to those of the halide ions. E.g.

(i) Na-salts are soluble in water but Ag-salts are insoluble in water.

(ii) H-compounds are acids like HX.

(iii) Some anions can be oxidised to give molecules X_2.

Anions :	**Acids**	**Dimer**
CN^-	HCN	$(CN)_2$
SCN^-	HSCN(thiocyanic acid)	$(SCN)_2$
$SeCN^-$		$(SeCN)_2$
OCN^-	HOCN	(cyanic acid)
NCN^{2-}(Bivalent)	H_2NCN (cyanamide)	
ONC^-	HONC (Fulminic acid)	
N_3^-	HN_3 (Hydrazoic acid)	

CN^{Θ} shows maximum similarities with Cl^-, Br^-, I^-

(i) forms HCN

(ii) forms $(CN)_2$

(iii) AgCN, $Pb(CN)_2$, are insoluble

(iv) Interpseudo halogen compounds ClCN, BrCN, ICN can be formed

(v) AgCN is insoluble in H_2O but soluble in NH_3

(vi) forms large no.of complex.e.g.

$[Cu(CN)_4]^{3-}$&$[CuCl_4]^{-3}$

$[Co(CN)_6]^{-3}$&$[CoCl_6]^{-3}$

NOBLE GASES FAMILY
GROUP 18 ELEMENTS (He, Ne, Ar, Kr, Xe, Rn)

Occurrence

(i) All the noble gases except radon occur in the atmosphere.
Relative abundance : Ar is highest (Ne, Kr, He, Rn)
(ii) Their atmospheric abundance in dry air is ~ 1% by volume of which argon is the major constituent.
(iii) Helium and sometimes neon are found in minerals of radioactive origin e.g., pitchblende, monazite, cleveite.
(iv) The main commercial source of helium is natural gas.
(v) Xenon and radon are the rarest elements of the group.
(vi) Radon is obtained as a decay product of ^{226}Ra.

$$^{226}_{88}\text{Ra} \rightarrow {}^{222}_{86}\text{Rn} + {}^{4}_{2}\text{He}$$

(vii) He liquid can exist in two forms. I-form when changes to II-form at λ-point temperature many physical properties change abruptly.

e.g.

(i) Sp. heat changes by a factor of 10
(ii) Thermal conductivity increases by 10^6 and it becomes 800 times faster than Cu
(iii) It shows zero resistance
(iv) It can flow up the sides of the vessel

Electronic Configuration

General electronic configuration of 18 group element is ns^2np^6 except helium which has 1 s^2.

Ionisation Enthalpy

He > Ne > Ar > Kr > Xe > Rn(I. E. order)

Atomic Radii

He < Ne < Ar < Kr < Xe < Rn (atomic radius order)

Electron Gain Enthalpy

They have large positive values of electron gain enthalpy due to stable electronic configurations, and there for have no tendency to accept the electron

Melting point and boiling point

He < Ne < Ar < Kr < Xe < Rn (Melting point order)

↓

(−269°C)

B.P. order : He < Ne < Ar < Kr < Xe < Rn (Boiling point order)

Density order :

He < Ne < Ar < Kr < Xe < Rn (Density order)

Physical properties :

(i) All the noble gases are monoatomic.

(ii) They are colourless, odourless and tasteless.

(iii) They are sparingly soluble in water.

(iv) They have very low melting and boiling points because the only type of interatomic interaction in these elements is weak dispersion forces.

(v) Helium has the lowest boiling point (4.2 K) of any known substance.

(vi) It has an unusual property of diffusing through most commonly used laboratory materials such as rubber, glass or plastics.

Chemical Properties

In general, noble gases are least reactive. Their inertness to chemical reactivity is attributed to the following reasons:

(i) The noble gases except helium ($1s^2$) have completely filled ns^2np^6 electronic configuration in their valence shell.

(ii) They have high ionisation enthalpy and more positive electron gain enthalpy.

Note: The reactivity of noble gases has been investigated occasionally, In March 1962, Neil Bartlett, then at the University of British Columbia, observed the reaction of a noble gas. First, he prepared a red compound which is formulated as $O_2{}^{+}PtF_6{}^{-}$. He, then realised that the first ionisation enthalpy of molecular oxygen ($1175 kJmol^{-1}$) was almost identical with that of xenon ($1170\ kJ\ mol^{-1}$). He made efforts to prepare same type of compound with Xe and was successful in preparing another red colour compound $Xe^{+}PtF_6^{-}$ by mixing PtF_6 and xenon. After this discovery, a number of xenon compounds mainly with most electronegative elements like fluorine and oxygen, have been synthesised. The compounds of krypton are fewer. Only the difluoride (KrF_2) has been studied in detail. Compounds of radon have not been isolated but only identified (e.g., RnF_2) by radiotracer technique. No true compounds of Ar, Ne or He are yet known.

FLUORINEDES OF XENON

Preparation

$$Xe(g) + \underset{\text{(xenoninexcess)}}{F_2(g)} \xrightarrow{673\ K,1\ bar} XeF_2(s)$$

$$Xe(g) + 2\ F_2(g) \xrightarrow{873\ K,7bar} XeF_4(s)$$

(1:5 ratio)

$$Xe(g) + 3\ F_2(g) \xrightarrow{573\ K,60-70bar} XeF_6(s)$$

(1:20ratio)

$$XeF_4 + O_2F_2 \xrightarrow{143\ K} XeF_6 + O_2$$

Physical properties

XeF_2, XeF_4 and XeF_6 are colourless crystalline solids and sublime readily at 298 K.

Chemical properties

(i) Hydrolysis:

$$2XeF_2(s) + 2H_2O(l) \rightarrow 2Xe(g) + 4HF(aq) + O_2(g)$$

$$6XeF_4 + 12H_2O \rightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$$

$$XeF_6 + 3H_2O \rightarrow XeO_3 + 6HF$$

Partial hydrolysis of XeF_6 gives oxyfluorides, $XeOF_4$ and XeO_2F_2.

$XeF_6 + H_2O \rightarrow XeOF_4 + 2HF$

$XeF_6 + 2H_2O \rightarrow XeO_2F \rightarrow +4HF$

Note : Hydrolysis in alkaline medium

$2XeF_2 + 4OH^- \longrightarrow 2Xe + 4F^- + 2H_2O + O_2$

$XeF_6 + 7OH^- \longrightarrow \underset{\text{Xenate ion}}{HXeO_4^-} + 3H_2O + 6F^-$

$2HXeO_4^- + 2OH^- \longrightarrow XeO_6^{4} \downarrow + Xe + 2H_2O + O_2$

(ii) As fluorinating agents: They are powerful fluorinating agents.

$2SF_4 + XeF4 \longrightarrow 2SF_6 + Xe$

$Pt + XeF_4 \longrightarrow PtF_4 + Xe$

(iii) As fluoride donar

$XeF_2 + MF_5 \longrightarrow [XeF]^+[MF_6]^- \ (M = As, Sb, P)$

$XeF_6 + BF_3 \longrightarrow [XeF_5]^+[BF_4^-]$

$XeF_6 + HF \longrightarrow [XeF_5]^+[HF_2]^-$

(iv) As Fluoride acceptor

$XeF_6 + MF \longrightarrow M^+[XeF_7]^-(M = Na, K, Rb, Cs)$

$2Cs^+[XeF_7]^- \xrightarrow[50°C]{\Delta} XeF_6 + Cs_2[XeF_8]$

$XeF_4 + MF \longrightarrow M^+ + XeF_5^-$

(alkali metals fluoride)

(v) Reaction with SiO_2

SiO_2 also converts XeF_6 into $XeOF_4$

$2XeF_6 + SiO_2 \longrightarrow SiF_4 \uparrow + \underset{\text{violet}}{2XeOF_4}$

Similarly, $XeO_3 + XeOF_4 \longrightarrow 2XeO_2F_2 \mid XeO_3 + 2XeF_6 \longrightarrow 3XeOF_4$

(vi) Oxdizing properties

H_2 reduces Xe - fluorides to Xe

$XeF_2 + H_2 \longrightarrow Xe + 2HF$ and so on

Xe - fluorides oxidise Cl^- to Cl_2 and I^- to I_2

$XeF_2 + 2HCl \longrightarrow 2HF + Xe + Cl_2$

$XeF_4 + 4KI \longrightarrow 4KF + Xe + 2I_2$

Uses of helium :

(i) He a non-inflammable and light gas. Hence, it is used in filling balloons for meteorological observations.

(ii) It is also used in gas-cooled nuclear reactors.

(iii) It is used in cryoscopy to obtain the very low temperature required for superconductor and laser

(b.p. 4.2 K) finds use as cryogenic agent for carrying out various experiments at low temperatures.

(iv) It is used to produce and sustain powerful superconducting magnets which form an essential part of modern NMR spectrometers and Magnetic Resonance Imaging (MRI) systems for clinical diagnosis.

(v) It is used as a diluent for oxygen in modern diving apparatus because of its very low solubility in blood. He is used in preference to N_2 to dil. O_2 in the gas cylinders used by divers. This is because N_2 is quite soluble in blood, so a sudden change in pressure causes degassing and gives bubbles of N_2 in the blood. This causes the painful condition called bends. He is slightly soluble so the risk of bends is reduced.

USES OF NEON :

(i) Ne is used in discharge tubes and fluorescent bulbs for advertisement display purposes.

(ii) Neon bulbs are used in botanical gardens and in green houses.

USES OF ARGON :

(i) Argon is used mainly to provide an inert atmosphere in high temperature metallurgical processes (arc welding of metals or alloys) and for filling electric bulbs.

(ii) It is also used in the laboratory for handling substances that are air-sensitive.

USES OF XENON AND KRYPTON :

There are no significant uses of Xenon and Krypton. They are used in light bulbs designed for special purposes.

SOLVED EXAMPLE

1. Though nitrogen exhibits +5 oxidation state, it does not form pentahalide. Give reason.

Sol. Nitrogen with n = 2, has s and p orbitals only. It does not have d orbitals to expand its covalency beyond four. That is why it does not form pentahalide.

2. PH_3 has lower boiling point than NH_3. Why?

Sol. Unlike NH_3, PH_3 molecules are not associated through hydrogen bonding in liquid state. That is why the boiling point of PH_3 is lower than NH_3.

3. Write the reaction of thermal decomposition of sodium azide.

Sol. Thermal decomposition of sodium azide gives dinitrogen gas.

$2NaN_3 \rightarrow 2Na + 3\ N_2$

4. Why does NH_3 act as a Lewis base ?

Sol. Nitrogen atom in NH_3 has one lone pair of electrons which is available for donation. Therefore, it acts as a Lewis base.

5. NH_3 can't be dried by H_2SO_4, P_2O_5 and anh. $CaCl_2$

Sol. because : $2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$

$H_2O + NH_3 + P_2O_5 \longrightarrow (NH_4)_3PO_4$

$CaCl_2 + 8NH_3 \longrightarrow \underset{\text{forms adduct}}{CaCl_2 \cdot 8NH_3}$

Quick lime is used for this purpose

$$CaO + H_2O \longrightarrow \left.\begin{matrix} Ca(OH)_2\ \text{(base)} \\ NH_3\ \text{(base)} \end{matrix}\right\} \text{Hence no interaction}$$

6. Why does NO_2 dimerise ?

Sol. NO_2 contains odd number of valence electrons. It behaves as a typical odd molecule. On dimerisation, it is converted to stable N_2O_4 molecule with even number of electrons.

7. In what way can it be proved that PH_3 is basic in nature?

Sol. PH_3 reacts with acids like HI to form PH_4I which shows that it is basic in nature.

$PH_3 + HI \rightarrow PH_4I$

Due to lone pair on phosphorus atom, PH_3 is acting as a Lewis base in the above reaction.

8. Why does PCl_3 fume in moisture ?

Sol. PCl_3 hydrolyses in the presence of moisture giving fumes of HCl.

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

9. Are all the five bonds in PCl_5 molecule equivalent? Justify your answer.

Sol. PCl_5 has a trigonal bipyramidal structure and the three equitorial $P-Cl$ bonds are equivalent, while the two axial bonds are different and longer than equitorial bonds.

10. How do you account for the reducing behaviour of H_3PO_2 on the basis of its structure?

Sol. In H_3PO_2, two H atoms are bonded directly to P atom which imparts reducing character to the acid.

11. Elements of Group 16 generally show lower value of first ionisation enthalpy compared to the corresponding periods of group 15 . Why?

Sol. Due to extra stable half-filled p orbitals electronic configurations of Group 15 elements, larger amount of energy is required to remove electrons compared to Group 16 elements.

12. H_2 S is less acidic than H_2Te. Why?

Sol. Due to the decrease in bond $(E-H)$ dissociation enthalpy down the group, acidic character increases.

13. Which form of sulphur shows paramagnetic behaviour ?

Sol. In vapour state sulphur partly exists as S_2 molecule which has two unpaired electrons in the antibonding π^* orbitals like O_2 and, hence, exhibits paramagnetism.

14. What happens when

(i) Concentrated H_2SO_4 is added to calcium fluoride

(ii) SO_3 is passed through water?

Sol. (i) It forms hydrogen fluoride

$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2HF$

(ii) It dissolves SO_3 to give H_2SO_4.

$SO_3 + H_2O \rightarrow H_2SO_4$

15. Halogens have maximum negative electron gain enthalpy in the respective periods of the periodic table. Why?

Sol. Halogens have the smallest size in their respective periods and therefore high effective nuclear charge.

As a consequence, they readily accept one electron to acquire noble gas electronic configuration.

16. Although electron gain enthalpy of fluorine is less negative as compared to chlorine, fluorine is a stronger oxidising agent than chlorine. Why?

Sol. It is due to

(i) low enthalpy of dissociation of F-F bond

(ii) high hydration enthalpy of F^-

17. Fluorine exhibits only -1 oxidation state whereas other halogens exhibit +1, +3, +5 and +7 oxidation states also. Explain.

Sol. Fluorine is the most electronegative element and cannot exhibit any positive oxidation state. Other halogens have d orbitals and therefore, can expand their octets and show +1, +3, +5 and +7 oxidation states also.

18. Write the balanced chemical equation for the reaction of Cl2 with hot and concentrated NaOH. Is this reaction a disproportionation reaction? Justify.

Sol. $3Cl_2 + 6NaOH \rightarrow 5NaCl + NaClO_3 + 3H_2O$

Yes, chlorine from zero oxidation state is changed to -1 and +5 oxidation states.

19. CaF_2 used in HF prep ^{n}. must be free from SiO_2. Explain.

Ans. $CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + HF$

If SiO_2 present as impurity

$4HF + SiO_2 \longrightarrow SiF_4 + 2H_2O$ } Hence presence of one molecule SiO_2

$SiF_4 + 2HF \longrightarrow H_2[SiF_6]$ } Consume 6 molecule of HF

HF can not be stored in glass vessel due to same reason.

20. When HCl reacts with finely powdered iron, it forms ferrous chloride and not ferric chloride. Why?

Sol. Its reaction with iron produces H_2.

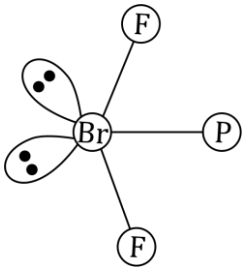
$Fe + 2HCl \rightarrow FeCl_2 + H_2$

Liberation of hydrogen prevents the formation of ferric chloride.

21. Discuss the molecular shape of BrF_3 on the basis of VSEPR theory.

Sol. The central atom Br has seven electrons in the valence shell. Three of these will form electronpair bonds with three fluorine atoms leaving behind four electrons. Thus, there are three bond pairs and two lone pairs. According to VSEPR theory, these will occupy the corners of a trigonal bipyramid.

The two lone pairs will occupy the equatorial positions to minimise lone pair-lone pair and the bond pair-lone pair repulsions which are greater than the bond pair-bond pair repulsions. In addition, the axial fluorine atoms will be bent towards the equitorial fluorine in order to minimize the lone-pair-lone pair repulsions. The shape would be that of a slightly bent ' T '.



22. Why are the elements of Group 18 known as noble gases ?

Sol. The elements present in Group 18 have their valence shell orbitals completely filled and, therefore, react with a few elements only under certain conditions. Therefore, they are now known as noble gases.

23. Noble gases have very low boiling points. Why?

Sol. Noble gases being monoatomic have no interatomic forces except weak dispersion forces and therefore, they are liquefied at very low temperatures. Hence, they have low boiling points.

24. Does the hydrolysis of XeF_6 lead to a redox reaction?

Sol. No, the products of hydrolysis are $XeOF_4$ and XeO_2 F_2 where the oxidation states of all the elements remain the same as it was in the reacting state.

25. Standard electrode potential values, E^{Θ} 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.

Sol. Standard electrode potential values for two half cell reactions suggest that aluminium has high tendency to make $Al^{3+}(aq)$ ions, whereas Tl^{3+} is not only unstable in solution but is a powerful oxidizing agent also. Thus $Tl^{+}$is more stable in solution than Tl^{3+}. Aluminium being able to form +3 ions easily, is more electropositive than thallium.

26. White fumes appear around the bottle of anhydrous aluminium chloride. Give reason.

Sol. Anhydrous aluminium chloride is partially hydrolysed with atmospheric moisture to liberate HCl gas. Moist HCl appears white in colour.

27. Boron is unable to form BF_6^{3-} ion. Explain.

Sol. Due to non-availability of d orbitals, boron is unable to expand its octet. Therefore, the maximum covalence of boron cannot exceed 4 .

28. Why is boric acid considered as a weak acid?

Sol. Because it is not able to release H^{+}ions on its own. It receives OH^{-}ions from water molecule to complete its octet and in turn releases H^{+}ions.

29. Select the member(s) of group 14 that (i) forms the most acidic dioxide, (ii) is commonly found in +2 oxidation state, (iii) used as semiconductor.

Sol. (i) carbon
(ii) lead
(iii) silicon and germanium

30. $[SiF_6]^{2-}$ is known whereas $[SiCl_6]^{2-}$ not. Give possible reasons.

Sol. The main reasons are :

(i) six large chloride ions cannot be accommodated around Si^{4+} due to limitation of its size.

(ii) interaction between lone pair of chloride ion and Si^{4+} is not very strong.

31. Diamond is covalent, yet it has high melting point. Why?

Sol. Diamond has a three-dimensional network involving strong C − C bonds, which are very difficult to break and, in turn has high melting point.

32. SiH_4 is more reactive than CH_4. Explain

Reasons

(i) $Si^{\delta+} - H^{\delta-}$ in $C^{\delta-} - H^{\delta+}$

C - more electronegative than H

Si less electronegative than H

So bond polarity is reversed when Nu^- attacks, it faces repulsion in C but not in Si

(ii) Silicon is having vacant d orbital which is not in case of carbon

(iii) Silicon is larger in size compared to C. By which the incoming Nu^- doesn't face any steric hindrance to attack at Si whereas CH_4 is tightly held from all sides.

EXERCISE-I

Only one option is correct :

1. PH_3(Phosphine) when passed in aqueous solution of $CuSO_4$ it produce -

(A) Blue precipitate of $Cu(OH)_2$

(B) dark blue solution of $[Cu(PH_3)_4]SO_4$

(C) Black precipitate of Cu_3P_2

(D) Colorless solution of $[Cu(H_2O)_4]^+$

2. $H_3PO_2 \xrightarrow{\Delta} (X) + PH_3$; is

(A) Dehydration reaction

(B) Oxidation reaction

(C) Disproportionation reaction

(D) Dephosphorelation reaction

3. Which of the following species is not a pseudohalide?

(A) CNO^- (B) $RCOO^-$ (C) OCN^- (D) N_3^-

4. An orange solid (X) on heating, gives a colourless gas (Y) and a only green residue (Z). Gas (Y) on treatement with Mg, produces a white solid substance

(A) $Mg_3\ N_2$ (B) MgO (C) Mg_2O_3 (D) $MgCl_2$

5. Conc. HNO3 is yellow coloured liquid due to

(A) dissolution of NO in conc. HNO3

(B) dissolution of NO2 in conc. HNO3

(C) dissolution of N2O in conc. HNO3

(D) dissolution of N2O3 in conc. HNO3

6. A gas at low temperature does not react with the most of compounds. It is almost inert and is used to create inert atmosphere in bulbs. The combustion of this gas is exceptionally an endothermic reaction. Based on the given information, we can conclude that the gas is

(A) oxygen (B) nitrogen (C) carbon mono-oxide (D) hydrogen

7. When chlorine gas is passed through an aqueous solution of a potassium halide in the presence of chloroform, a voilet colouration is obtained. On passing more of chlorine water, the voilet colour is disappeared and solution becomes colourless. This test confirms the presence of in aqueous solution.

(A) chlorine (B) fluorine (C) bromine (D) iodine

8. $H_3PO_2 \xrightarrow{140^\circ C} A \xrightarrow{220^\circ C} B \xrightarrow{320^\circ C}$

Compound (C) is

(A) H_2PO_3 (B) H_3PO_3 (C) $(HPO_3)_n$ (D) $H_4P_2O_7$

9. An explosive compound (A) reacts with water to produce NH4OH and HOCl. Then, the compound (A), is

(A) TNG (B) NCl_3 (C) PCl_3 (D) HNO_3

10. An inorganic compound (A) made of two most occuring elements into the earth crust, having a polymeric tetra-headral network structure. With carbon, compound (A) produces a poisonous gas (B) which is the most stable diatomic molecule. Compounds (A) and (B) will be

(A) SiO_2, CO_2 (B) SiO_2, CO (C) SiC, CO (D) $SiO_2,\ N_2$

11. A sulphate of a metal (A) on heating evolves two gases (B) and (C) and an oxide (D). Gas (B) turns $K_2Cr_2O_7$ paper green while gas (C) forms a trimer in which there is no $S-S$ bond. Compound (D) with HCI, forms a Lewis acid (E) which exists as a dimer. Compounds (A), (B), (C), (D) and (E) are respectively

(A) $FeSO_4, SO_2, SO_3, Fe_2O_3, FeCl_3$ (B) $Al_2(SO_4)_3, SO_2, SO_3, Al_2O_3, FeCl_3$

(C) $FeS, SO_2, SO_3, FeSO_4, FeCl_3$ (D) $FeS, SO_2, SO_3, Fe_2(PO_4)_3, FeCl_2$

12. A tetra-atomic molecule (A) on reaction with nitrogen(I)oxide, produces two substances (B) and (C). (B) is a dehydrating agent in its monomeric form while substance (C) is a diatomic gas which shows almost inert behaviour. The substances (A) and (B) and (C) respectively will be

(A) $P_4, P_4O_{10},\ N_2$ (B) $P_4,\ N_2O_5,\ N_2$ (C) P_4, P_2O_3, Ar (D) P_4, P_2O_3, H_2

13. First compound of inert gases was prepared by scientist Neil Barthlete in 1962. This compound is

(A) $XePtF_6$ (B) XeO_3 (C) XeF_6 (D) $XeOF_4$

14. Carbongene has X% of CO_2 and is used as an antidote for poisoning of Y. Then, X and Y are

(A) $X = 95\%$ and Y = lead poisoning (B) $X = 5\%$ and Y = CO poisoning

(C) $X = 30\%$ and Y = CO2 poisoning (D) $X = 45\%$ and Y = CO poisoning

15. The correct order of acidic strength of oxides of nitrogen is

(A) $NO < NO_2 < N_2O < N_2O_3 < N_2O_5$

(B) $N_2O < NO < N_2O_3 < N_2O_4 < N_2O_5$

(C) $NO < N_2O < N_2O_3 < N_2O_5 < N_2O_4$

(D) $NO < N_2O < N_2O_5 < N_2O_3 < N_2O_4$

16. $H_3BO_3 \xrightarrow{T_1} X \xrightarrow{T_2} Y \xrightarrow{\text{redhot}} B_2O_3$

If $T_1 < T_2$ then X and Y respectively are

(A) X = Metaboric acid and Y = Tetraboric acid

(B) X = Tetraboric acid and Y = Metaboric acid

(C) X = Borax and Y = Metaboric acid

(D) X = Tetraboric acid and Y = Borax

17. When conc. H_2SO_4 was treated with $K_4[Fe(CN)_6]$, CO gas was evolved. By mistake, somebody used dilute H_2SO_4 instead of conc. H_2SO_4 then the gas evolved was
(A) CO (B) HCN (C) N_2 (D) CO_2

18. An inorganic white crystalline compound (A) has a rock salt structure. (A) on reaction with conc. H_2SO_4 and MnO_2, evolves a pungent smelling, greenish-yellow gas (B). Compound (A) gives white ppt. of (C) with $AgNO_3$ solution. Compounds (A), (B) and (C) will be respectively
(A) NaCl, Cl_2, Agcl (B) NaBr, Br_2, NaBr
(C) NaCl, Cl_2, Ag_2SO_4 (D) Na_zCO_3, CO_2, Ag_2CO_3

19. $$RCl \xrightarrow[Si]{Cu-powder} R_2SiCl_2 \xrightarrow{H_2O} R_2Si(OH)_2 \xrightarrow{condensation} A$$
Compound (A) is
(A) a linear silicone (B) a chlorosilane
(C) a linear silane (D) a network silane

20. When oxalic acid reacts with cone. H_2SO_4, two gases produced are of neutral and acidic in nature respectively. Potassium hydroxide absorbs one of the two gases. The product formed during this absorption and the gas which gets absorbed are respectively
(A) K_2CO_3 and CO_2 (B) $KHCO_3$ and CO_2
(C) K_2CO_3 and CO (D) $KHCO_3$ and CO

21. Conc. H_2SO_4 cannot be used to prepare HBr from NaBr because it
(A) reacts slowly with NaBr (B) oxidises HBr
(C) reduces HBr (D) disproportionates HBr

22. Ammonia can be dried by
(A) conc. H_2SO_4 (B) P_4O_{10} (C) CaO (D) anhydrous $CaCl_2$

23. When chlorine reacts with a gas X, an explosive inorganic compound Y is formed. Then X and Y will be
(A) X = O_2 and Y = NCl_3 (B) X = NH_3 and Y = NCl_3
(C) X = O_2 and Y = NH_4Cl (D) X = NH_3 and Y = NH_4Cl

24. $HNO_3 + P_4O_{10} \longrightarrow HPO_3 + A$; the product A is
(A) N_2O (B) N_2O_3 (C) NO_2 (D) N_2O_5

25. Which of the following is the correct order of acidic strength?
(A) $Cl_2O_7 > SO_3 > P_4O_{10}$ (B) $CO_2 > N_2O_5 > SO_3$
(C) $Na_2O > MgO > Al_2O_3$ (D) $K_2O > CaO > MgO$

26. $Ca + C_2 \longrightarrow CaC_2 \xrightarrow{N_2} A$
Compound (A) is used as a/an

(A) fertilizer (B) dehydrating agent

(C) oxidising agent (D) reducing agent

27. A gas which exists in three allotropic forms a, b and g is

(A) SO_2 (B) SO_3 (C) CO_2 (D) NH_3

28. A red coloured mixed oxide (X) on treatment with cone. HNO3 gives a compound (Y). (Y) with HCl, produces a chloride compound (Z) which can also be produced by treating (X) with cone. HCl.

Compounds (X), (Y), and (Z) will be

(A) $Mn_3O_4, MnO_2, MnCl_2$ (B) $Pb_3O_4, PbO_2, PbCl_2$

(C) $Fe_3O_4, Fe_2O_3, FeCl_2$ (D) $Fe_3O_4, Fe_2O_3, FeCl_3$

29. One mole of calcium phosphide on reaction with excess of water gives

(A) one mole of phosphine (B) two moles of phosphoric acid

(C) two moles of phosphine (D) one mole of phosphorus penta-oxide

30. $NaH_2PO_4 \xrightarrow{>240^\circ C} (NaPO_3)_3 \xrightarrow{625^\circ C} NaPO_3$ (liquid melt) $\xrightarrow[\text{cooling}]{\text{rapid}}$ D (glass)

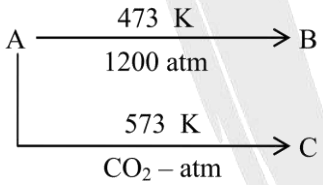
Sodium trimetaphosphate

Compound (D) is known as

(A) Microcosmic salt (B) Graham's salt

(C) Reimann's salt (D) Switzer's Salt

31. Three allotropes (A), (B) and (C) of phosphorous in the following change are respectively



(A) white, b-black, red (B) b-black, white, red

(C) red, b-black, white (D) red, violet, b-black

32. When an inorganic compound reacts with SO_2 in aqueous medium, produces (A). (A) on reaction with Na_2CO_3, gives compound (B) which with sulphur, gives a substance (C) used in photography.

Compound (C) is

(A) Na_2S (B) $Na_2S_2O_7$ (C) Na_2SO_4 (D) $Na_2S_2O_3$

33. $B(OH)_3 + NaOH \rightleftharpoons NaBO_2 + Na[B(OH)_4] + H_2O$

How can this reaction is made to proceed in forward direction?

(A) addition of cis 1,2 diol (B) addititon of borax

(C) addition of trans 1,2 diol (D) addition of Na_2HPO_4

34. Which is the compound responsible for the flickering light called will-o-the-wisp, some times seen in the Marsh.

(A) PH_3 (B) P_2H_4 (C) H_2S (D) $PH_3 + H_2S$

35. The gun powder is consisting of '_____ '+ sulphur + Charcoal what is the missing substance for gun powder

(A) $LiNO_3$ (B) NH_4NO_2 (C) KNO_3 (D) (A) and (B) mixture

36. An aqueous solution of borax is

(A) Neutral (B) Amphoteric (C) Basic (D) Acidic

37. Boric acid is polymeric due to

(A) Its acidic nature (B) The presence of hydrogen bonds

(C) Its monobasic nature (D) Its geometry

38. The type of hybridisation of boron in diborane is

(A) sp (B) sp^2 (C) sp^3 (D) dsp^2

39. Thermodynamically the most stable form of carbon is

(A) Diamond (B) Graphite (C) Fullerenes (D) Coal

40. Elements of group 14

(A) Exhibit oxidation state of +4 only

(B) Exhibit oxidation state of +2 and +4 only

(C) Form M^{2-} and M^{4+} ions

(D) Form M^{2+} and M^{4+} ions

41. $A + Br_2 \rightarrow N_2 + (B)$

$\downarrow$ NaOH

(A)

if A is a basic gas then identified (A) and (B)

(A) NH_3, NH_4Br (B) $NH_3,\ N_2O$ (C) $NH_3,\ N_2O_5$ (D) None of these

Question No. 50 to 55 (6 questions)

Questions given below consist of two statements each printed as Assertion (A) and Reason (R); while answering these questions you are required to choose any one of the following four responses:

(A) if both (A) and (R) are true and (R) is the correct explanation of (A)

(B) if both (A) and (R) are true but (*R*) is not correct explanation of (A)

(C) if (A) is true but (R) is false

(D) if (A) is false and (R) is true

42. Assertion: Borax bead test is applicable only to coloured salt.
Reason: In borax bead test, coloured salts are decomposed to give coloured metal meta borates.

43. Assertion: Aluminium and zinc metal evolve H_2 gas from NaOH solution
Reason: Several non-metals such as P, S, Cl, etc. yield a hydride instead of H_2 gas from NaOH

44. Assertion: Conc. H_2SO_4 cannot be used to prepare pure HBr from NaBr
Reason: It reacts slowly with NaBr.

45. Assertion: Oxygen is more electronegative than sulphur, yet H_2 S is acidic, while H_2O is neutral.
Reason: $H-S$ bond is weaker than $O-H$ bond.

46. Assertion: Chlorine gas disproportionates in hot & conc. NaOH solution.
Reason: NaCl and NaOCl are formed in the above reaction.

47. Assertion: Liquid IF_5 conducts electricity.
Reason: Liquid IF_5 self ionizes as, $2IF_5 \rightleftharpoons IF_4^+ + IF_6^-$

EXERCISE-II

One or more than one option may be correct :

1. When a compound X reacts with ozone in aqueous medium, a compound Y is produced. Ozone also reacts with Y and produces compound Z. Z acts as an oxidising agent, then X, Y and Z will be

(A) $X = HI, Y = I_2$ and $Z = HIO_3$ (B) $X = KI, Y = I_2$ and $Z = HIO_3$

(C) $X = KI, Y = I_2$ and $Z = HIO_4$ (D) $X = HI, Y = I_2$ and $Z = HIO_4$

2. Which of the following statements is/are correct regarding B_2H_6 ?

(A) banana bonds are longer but stronger than normal $B - H$ bonds

(B) B_2H_6 is also known as $3e - 2e$ compound

(C) the hybrid state of B in B_2H_6 is sp^3 while that of sp^2 in BH_3

(D) it cannot be prepared by reacting BF_3 with $LiBH_3$ in the presence of dry ether

3. Which of the following statements is/are correct regarding inter-halogen compounds of ABx types?

(A) x may be 1,3,5 and 7

(B) A is a more electronegative halogen than B

(C) FBr_3 cannot exit

(D) The interhalogens are generally more reactive than the halogens (except F_2) due to weaker A- X bonds compared to $X - X$ bond.

4. When an inorganic compound (X) having $3e - 2e$ as well as $2e - 2e$ bonds reacts with ammonia gas at a certain temperature, gives a compound (Y) iso-structural with benzene. Compound (X) with ammonia at a high temperature, produces a hard substance (Z). Then

(A) (X) is B_2H_6

(B) (Z) is known as inorganic graphite

(C) (Z) having structure similar to graphite

(D) (Z) having structure similar to (X)

5. Boric acid

(A) exists in polymeric form due to inter-molecular hydrogen bonding.

(B) is used in manufacturing of optical glasses.

(C) is a tri-basic acid

(D) with borax, it is used in the preparation of a buffer solution.

6. The correct statement(s) related to allotropes of carbon is/are

(A) graphite is the thermodynamically most stable allotrope of carbon and having a two dimensional sheet like structure of hexagonal rings of carbon (sp^2)

(B) diamond is the hardest allotrope of carbon and having a three dimensional network structure of C(sp^3)

(C) fullerene (C_{60}) is recently discovered non-crystalline allotrope of carbon having a footballlike structure.

(D) Vander Waal's force of attraction acts between the layers of graphite 6.14Å away from each other

7. $Al_2(SO_4)_3 + NH_4OH \longrightarrow X$, then

(A) X is a white coloured compound

(B) X is insoluble in excess of NH_4OH

(C) X is soluble in NaOH

(D) X cannot be used as an antacid

8. The species that undergo(es) disproportionation in an alkaline medium is/are

(A) Cl_2 (B) MnO_4^{2-} (C) P_4 (D) ClO_4^-

9. Select correct statement(s):

(A) Borax is used as a buffer

(B) 1M borax solution reacts with equal volumes of 2MHCl solution

(C) Titration of borax can be made using methyl orange as the indicator

(D) Coloured bead obtained in borax-bead test contains metaborate

10. Which of the following is / are correct for group 14 elements?

(A) The stability of dihalides are in the order CX2 < SiX2 < GeX2 < SnX2 < PbX2

(B) The ability to form pp-pp multiple bonds among themselves increases down the group

(C) The tendency for catenation decreases down the group

(D) They all form oxides with the formula MO2.

11. Zeolite is used in which of the following cases:

(A) Conversion of alcohols into gasoline

(B) Cracking of hydrocarbon

(C) Isomerisation of hydrocarbons

(D) Softning of hard water

12. Which of the following oxides are mixed oxide:

(A) PbO_2 (B) SnO_2 (C) Pb_2O_3 (D) Pb_3O_4

13. Which of the following oxide(s) gives brown ppt on reaction with conc. HNO_3 :

(A) PbO (B) SnO (C) Pb_2O_3 (D) Pb_3O_4

14. Which of the following reaction produces PH_3 :

(A) $Ca_3P_2 + H_2O \rightarrow$ (B) $P_4 + NaOH \rightarrow$

(C) $PH_4I + KOH \rightarrow$ (D) $H_3PO_2 \xrightarrow{\Delta}$

15. Which of the following element of chalcogen group can form MX_2 type of compound where $X = Cl$ and Br :

(A) O (B) S (C) Se (D) Te

16. $Ca_2\ B_6O_{11} + Na_2CO_3 \xrightarrow{\Delta} [X] + CaCO_3 + NaBO_2$ (Unbalanced equation)

Correct statement for [X]

(A) Structure of anion of crystalline (X) has one boron atom sp^3 hybridised and other three boron atoms sp^2 hybridised

(B) (X) with NaOH (aq.) gives a compound which on reaction with H_2O_2 in alkaline medium yields a compound used as brightner in soaps

(C) Hydrolysis of (X) with HCl or H_2SO_4 yields a compound which on reaction with HF gives fluoroboric acid

(D) [X] on heating with cobalt salt in oxidising flame gives blue coloured bead

17. (A) $+ 2C \frac{2000°Clo}{250°C}$ (B) $+ 2CO \uparrow$

(B) + Carbon $\frac{2000°Cto}{2500°C} \rightarrow$ (C)

If A is an example of $3-d$ silicate then select the correct statements about (C)

(A) Central atom of C is sp^3 hybridised

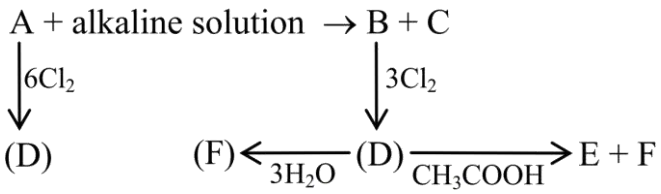
(B) (C) is non planar and all atoms are sp^3 hybridised

(C) C has diamond like structure, and it is colourless when impurity is present but yellow solid at room temperature

(D) (C) is silicon carbide (SiC) and it is not being affected by any acid except H_0PO_4

EXERCISE-III

Paragraph for Question No. 1 & 2



1. When D react with C_2H_5OH then product will be

(A) C_2H_5Cl, H_3PO_4 (B) C_2H_5Cl, H_3PO_3

(C) CH_3COCl, H_3PO_3 (D) Only H_3PO_3

2. B can be absorbed by :

(A) Ca(OCl)Cl (B) H_2S (C) Both (D) None

Paragraph for Question No. 3 to 6

$$HCOOH \xrightarrow[Conc.H_2SO_4]{373\ K} H_2O + (X)$$

$$C(s) + H_2O \xrightarrow{423-1273\ K} (X) + H_2(g)$$

3. Select the correct statement about (X)

(A) (X) is a colourless, odourless and almost water insoluble gas

(B) X is highly poisonous and burns with blue flame

(C) When (X) gas is passed through $PdCl_2$ solution giving rise to balck ppt

(D) All of these

4. Mixture of (X) gas $+H_2$ is called

(A) Water gas or synthesis gas

(B) Producer gas

(C) Methane gas

(D) None of these

5. In second reaction when air is used instead of steam a mixed of (X) gas and N2 is produced which is called

(A) Water gas (B) Synthesis gas (C) Producer gas (D) Carbon dioxide gas

6. Select the correct statement about (X)

(A) (X) gas is estimatate by I_2O_5 (B) Cu_2Cl_2 is absorber of (X) gas

(C) (X) gas is the purifying agent for Ni (D) All of these

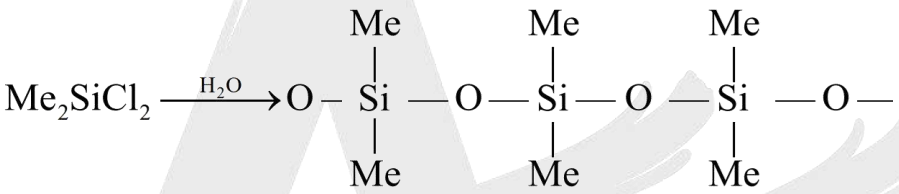
Paragraph for Question No. 7 & 8

Read the following write-ups and answer the questions at the end of it.

Silicons are synthetic polymers containing repreated R_2SiO units. Since, the empirical formula is that of a ketone (R_2CO), the name silicone has been given to these materials. Silicones can be made into oils, rubbery elastomers and resins. They find a variety of applications because of their chemical inertness, water repelling nature, heat-resistance and good electrical insulating property.

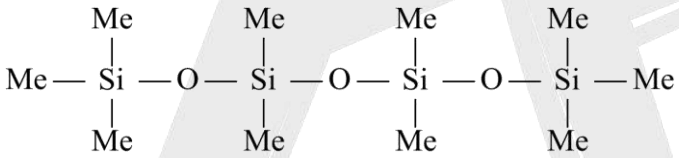
Commercial silicon polymers are usually methyl derivatives and to a lesser extent phenyl derivatives and are synthesised by the hydrolysis of

R_2SiCl_2[R = methyl (Me) or phenyl (ϕ)]

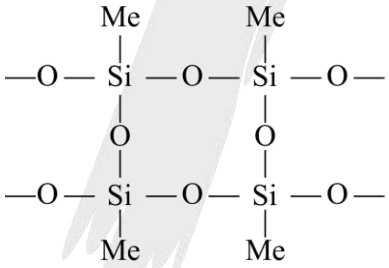


7. If we mix Me $MiCl_3$SithMe_2SiCl_2, we get silicones of the type:

(A)



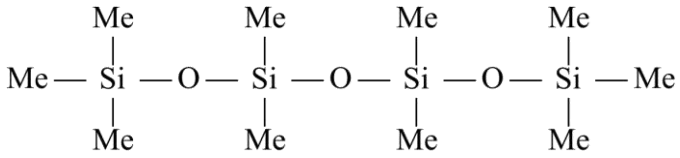
(B)

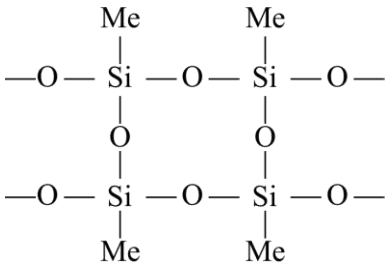


(C) both of the above

(D) none of the above

8. If we start with $MeSiCl_3$ as the starting material, silicones formed is:

(A) 

(B) 

(C) both of the above

(D) none of the above

Paragraph for Question No. 9 & 10

CO gas is absorbed by aqueous suspension of cuprous chloride forming the complex like $[CuCl(CO)(H_2O)_2]$.

9. Comment on the shape of the above complex.

(A) Tetrahedral (B) TBP (C) Square planar (D) Can not be predicted

10. Choose the correct statement regarding the above molecule

(A) Cl-atom is separated by equal angle from both of the water molecule

(B) Magnetic moment of the above complex is 1.73 B.M.

(C) There are two stereo isomer for the above complex.

(D) Both (A) and (C)

Paragraph for Question No. 11 to 12

There are some deposits of nitrates and phosphates in earth's crust. Nitrates are more soluble in water. Nitrates are difficult to reduce under the laboratory conditions but microbes do it easily. Ammonia forms large number of complexes with transition metal ions. Hybridization easily explains the ease of sigma donation capability of NH_3 and PH_3. Phosphine is a flammable gas and is prepared from white phosphorous.

11. Among the following, the correct statement is

(A) Phosphates have no biological significance in humans

(B) Between nitrates and phosphates, phosphates are less abundant in earth's crust

(C) Between nitrates and phosphates, nitrates are less abundant in earth's crust

(D) Oxidation of nitrates is possible in soil

12. White phosphorus on reaction with NaOH gives PH_3 as one of the products. This is a

(A) dimerization reaction

(B) disproportionation reaction

(C) condensation reaction

(D) precipitation reaction

13. Match List-I with List-II

List-I (Chemical reaction)

List-II (Name of process)

(I) $4NH_3 + 5O_2 \xrightarrow{800^\circ C/Pt} 4NO + 6H_2O$

(a) Contact process

(II) $4HCl + O_2 \xrightarrow{230^\circ C/CuCl_2} 2Cl_2 + 2H_2O$

(b) Ostwald's process

(III) $2SO_2 + O_2 \xrightarrow{450-500^\circ/V_2O_5} 2SO_3$

(c) Deacon's process

(IV) $2\ N_2 + 3H_2 \xrightarrow{Fe+Mo} 2NH_3$

(d) Haber's process

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

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

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

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

14.

Column-I	**Column-II**
(P) Dry ice	(1) Used as antidote for CO-poisoning
(Q) Carbongene	(2) Used as nonstick coating
(R) Carborundum	(3) Used as refrigerant
(S) Teflon	(4) Used as abrasive

Code:

	P	Q	R	S
(A)	4	1	3	2
(C)	3	1	4	2

	P	Q	R	S
(B)	4	2	1	3
(D)	1	4	3	2

15.

Column-I **Compound**	**Column-II** **Correct statement for compounds given**
(P) $SnCl_2$	(1) Used in printing technology
(Q) Butter of tin	(2) Used for gilding purpose (in joining gold pieces)
(R) Mosaic gold	(3) Reducing agent
(S) Pink salt	(4) Mordant

Code:

	P	Q	R	S
(A)	4	3	2	1
(C)	2	1	3	4

	P	Q	R	S
(B)	3	4	2	1
(D)	1	3	4	2

16. **Column-I (Metal)**

(P) Fe

(Q) Cu

(R) Pb

(S) Sn

Column-II (Correct statements)

(1) Produces NO with 20%HNO_3

(2) Produces NH_4NO_3 with 6%HNO_3

(3) Produces NO_2 with 70%HNO_3

(4) Produces NH_4NO_3 with 20%HNO_3

Code:

	P	Q	R	S
(A)	2,1	1	3,4	2,3
(B)	2,3	1,3	1,3	2,3,4
(C)	1,3	1,2	3,4	2
(D)	1,4	2,3	1,3	1,4

17. **Column-I (Reactions)**

(P) $XeF_2 + PF_5 \rightarrow$

(Q) $XeF_4 + Pt \rightarrow$

(R) $XeF_4 + H_2O \rightarrow$

(S) $XeF_6 + CsF \rightarrow$

Column-II (Correct statements)

(1) Fluoride of Xe acts as fluoride acceptor

(2) Fluoride of Xe undergoes disproportion

(3) Fluoride of Xe acts as fluorinating agent

(4) Fluoride of Xe act as fluoride donor

Code:

	P	*Q*	*R*	*S*
(A)	4	2	3	1
(C)	4	3	2	1

	P	*Q*	*R*	*S*
(B)	3	2	1	4
(D)	3	4	2	1

18. **Column-I (Substances)**

(P) O_3

(Q) Bleaching powder

(R) H_2O_2

(S) HNO_3

Column-II (Can be prepared by)

(1) Acidification of BaO_2 with H_3PO_4

(2) Birkeland Eyde process

(3) Dry O_2 is passed through a silent electrical discharge

(4) Cl_2 gas is passed through slaked lime

Code:

	P	Q	R	S
(A)	3	4	1	2
(C)	2	1	3	4

	P	Q	R	S
(B)	1	3	4	2
(D)	4	1	2	3

EXERCISE-IV (JEE-MAINS)

1. Which products are expected from the disproportionation of hypochlorous acid: **[AIEEE-2002]**

(1) $HClO_3$ and Cl_2O (2) $HClO_2$ and $HClO$

(3) HCl and Cl_2O (4) HCl and $HClO_3$

2. Identify the incorrect statement among the following : **[AIEEE-2002]**

(1) Ozone reacts with SO_2 to give SO_3

(2) Silicon reacts with NaOH (aq.) in the presence of air to give Na_2SiO_3 and H_2O

(3) Cl_2 reacts with excess of NH_3 to give N_2 and HCl

(4) Br_2 reacts with hot and strong NaOH solution to given NaBr, $NaBrO_4$ and H_2O

3. Aluminium is industrially prepared by: **[AIEEE-2002]**

(1) Fused cryolite (2) Bauxite ore

(3) Alunite (4) Borax

4. For making good quality mirrors, plates of float glass are used. These are obtained by floating molten glass over a liquid metal which does not solidify before glass. The metal used can be : **[AIEEE-2003]**

(1) Sodium (2) Magnesium (3) Mercury (4) Tin

5. What may be expected when phosphine gas is mixed with chlorine gas: **[AIEEE-2003]**

(1) PCl_5 and HCl are formed and mixture cools down

(2) $PH_3 \cdot Cl_2$ is formed with warming up

(3) The mixture only cools down

(4) PCl_3 and HCl are formed and the mixture warms up

6. Graphite is a soft solid lubricant extremely difficult to melt. The reason for this anomalous behavour is that graphite : **[AIEEE-2003]**

(1) Has molecules of variable molecular masses like polymers

(2) Has carbon atoms arranged in large plated of rings of strongly bonded carbon atoms with weak interplate bonds

(3) Is a non crystalline substance

(4) Is an allotropic form of diamond

7. Concentrated hydrochloric acid when kept in open air sometimes produces a cloud of white fumes. This is due to : **[AIEEE-2003]**

(1) Strong affinity of HCl gas for moisture in air results in forming of droplets of liquid solution which appears like a cloudy smoke

(2) Due to strong affinity for water, conc. HCl pulls moisture of air towards self. The moisture forms droplets of water and hence the cloud

(3) Conc. HCl emits strongly smelling HCl gas all the time

(4) Oxygen in air reacts with emitted HCl gas to form a cloud of Cl_2 gas

8. Aluminium chloride exists as dimer, Al_2Cl_6 in solid state as well as in solution of non-polar solvents such as benzene. When dissolved in water, it gives- **[AIEEE-2004]**

(1) $Al^{3+} + 3Cl^-$ (2) $[Al(H_2O)_6]^{3+} + 3Cl^-$

(3) $[Al(OH)_6]^{3-} + 3HCl$ (4) $Al_2O_3 + 6HCl$

9. The soldiers of Napolean army while at Alps during freezing winter suffered a serious problem as regards to the tin buttons of their uniforms. White Metallic tin buttons get converted to grey powder.

This transformation is related to:- **[AIEEE-2004]**

(1) An interaction with water vapour contained in humid air

(2) A change in crystalline structure of tin

(3) A change in the partial pressure of O_2 in air

(4) An interaction with N_2 of air at low temperature

10. Which one of the following statements regarding helium is incorrect **[AIEEE-2004]**

(1) It is used to produce and sustain powerful superconducting magnets

(2) It is used as a cryogenic agent for carrying out experiments at low temperatures

(3) It is used to fill gas balloons instead of hydrogen because it is lighter then hydrogen and noninflammable

(4) It is used in gas-cooled nuclear reactors

11. The number of hydrogen atoms attached to phosphorus atom in hypophosphorous acid is : **[AIEEE-2005]**

(1) Zero (2) Two (3) One (4) Three

12. Heating an aqueous solution of aluminium chloride to dryness will give :- **[AIEEE-2005]**

(1) $AlCl_3$ (2) Al_2Cl_6 (3) Al_2O_3 (4) $Al(OH)Cl_2$

13. Which one of the following is the correct statement **[AIEEE-2005]**

(1) Boric acid is a protonic acid

(2) Beryllium exhibits coordination number of six

(3) Chlorides of both beryllium and aluminium have bridged chloride structures in solid phase

(4) $B_2H_6, 2NH_3$ is known as "inorganic benzene"

14. In silicon dioxide : **[AIEEE-2005]**

(1) Each silicon atom is surrounded by four oxygen atoms and each oxygen atom is bonded to two silicon atoms

(2) Each silicon atom is surrounded by two oxygen atoms and each oxygen atom is bonded to two silicon atoms

(3) Silicon atom is bonded to two oxygen atoms

(4) There are double bonds between silicon and oxygen atoms

15. Regular use of which of the following fertilizer increases the acidity of soil : **[AIEEE-2007]**

(1) Potassium nitrate (2) Urea

(3) Superphosphate of lime (4) Ammonium sulphate

16. The stability of dihalides of Si, Ge, Sn and Pb increases steadily in the sequence: **[AIEEE-2007]**

(1) $GeX_2 << SiX_2 << SnX_2 << PbX_2$ (2) $SiX_2 \ll GeX_2 \ll PbX_2 << SnX_2$

(3) $SiX_2 << GeX_2 \ll SnX_2 << PbX_2$ (4) $PbX_2 \ll SnX_2 \ll GeX_2 \ll SiX_2$

17. Among the following substituted silanes the one which will give rise to cross linked silicone polymer on hydrolysis is **[AIEEE-2008]**

(1) R_4Si (2) $RSiCl_3$ (3) R_2SiCl_2 (4) R_3SiCl

18. Which one of the following reactions of Xenon compounds is not feasible ? **[AIEEE-2009]**

(1) $2XeF_2 + 2H_2O \rightarrow 2Xe + 4HF + O_2$ (2) $XeF_6 + RbF \rightarrow Rb[XeF_7]$

(3) $XeO_3 + 6HF \rightarrow XeF_6 + 3H_2O$ (4) $3XeF_4 + 6H_2O \rightarrow 2Xe + XeO_3 + 12HF + 1.5O_2$

19. Which of the following statement is wrong ? **[AIEEE-2011]**

(1) Single N − N bond is weaker than the single P − P bond

(2) N_2O_4 has two resonance structures

(3) The stability of hydrides increases from NH_3 to BiH_3 in group 15 of the periodic table

(4) Nitrogen cannot form dp-pp bond

20. Which of the following statements regarding sulphur is incorrect? **[AIEEE-2011]**

(1) At 600°C the gas mainly consists of S_2 molceules

(2) The oxidation state of sulphur is never less than +4 in its compounds

(3) S_2 molecule is paramagnetic

(4) The vapour at 200°C consists mostly of S_8 rings

21. Boron cannot form which one of the following anions? **[AIEEE-2011]**

(1) $B(OH)_4^-$ (2) BO_2^- (3) BF_6^{3-} (4) BH_4^-

22. In view of the signs of $\Delta_r G^\circ$ for the following reactions

$PbO_2 + Pb \rightarrow 2PbO, \Delta_r G^\circ < 0$

$SnO_2 + Sn \rightarrow 2SnO, \Delta_r G^\circ > 0,$

Which oxidation states are more characteristic for lead and tin ? **[AIEEE-2011]**

(1) For lead +4 , for tin +2 (2) For lead +2 , for tin +2

(3) For lead +4 , for tin +4 (4) For lead +2 , for tin +4

23. The number of S − S bonds in SO_3, $S_2O_3^{2-}$, $S_2O_6^{2-}$ and $S_2O_8^{2-}$ respectively are :- **[Jee Main(Online)-2012]**

(1) 1,0,1,0 (2) 0,1,1,0 (3) 1,0,0,1 (4) 0,1,0,1

24. Which one of the following depletes ozone layer? **[Jee Main(Online)-2012]**

(1) NO and freons (2) SO_2 (3) CO (4) CO_2

25. In which of the following arrangements, the sequence is not strictly according to the property written against it ? **[Jee Main(Online)-2012]**

(1) $CO_2 < SiO_2 < SnO_2 < PbO_2$: increasing oxidising power

(2) B < C < O < N : increasing first ionisation enthalpy

(3) $NH_3 < PH_3 < AsH_3 < SbH_3$: increasing basic strength

(4) HF < HCl < HBr < HI : increasing acid strength

26. The formation of molecular complex $BF_3 - NH_3$ results in a change in hybridisation of boron :- **JEE(Main) Online-2012]**

(1) from sp_3 to sp_3 d
(2) from sp_2 to dsp_2
(3) from sp_3 to sp_2
(4) from sp_2 to sp_3

27. The catenation tendency of C, Si and Ge is in the order Ge < Si < C. The bond energies (in kJmol − 1) of C − C, Si − Si and Ge − Ge bonds are respectively: **[JEE(Main) Online-2013]**

(1) 348,260,297
(2) 348,297,260
(3) 297,348,260
(4) 260,297,348

28. The gas evolved on heating CaF_2 and SiO_2 with concentrated H_2SO_4, on hydrolysis gives a white gelatinous precipitate. The precipitate is: **[Jee Main(Online)-2014]**

(1) silica gel
(2) silicic acid
(3) hydrofluosilicic acid
(4) calciumfluorosilicate

29. Which of the following series correctly represents relations between the elements from X to Y ?

	X → Y	**[Jee Main(Online)-2014]**
(1)	$_{18}Ar \rightarrow {}_{54}Xe$	Noble character increases
(2)	$_3Li \rightarrow {}_{19}K$	Ionization enthalpy increases
(3)	$_6C \rightarrow {}_{32}Ge$	Atomic radii increases
(4)	$_9F \rightarrow {}_{35}Br$	Electron gain enthalpy with negative sign increases

30. Which of the following statements about the depletion of ozone layer is correct? **[Jee Main(Online)-2014]**

(1) The problem of ozone depletion is more serious at poles because ice crystals in the clouds over poles act as catalyst for photochemical reactions involving the decomposition of ozone by $Cl^-$and ClO^-radicals

(2) The problem of ozone depletion is less serious at poles because NO_2 solidifies and is not available for consuming ClO° radicals

(3) Oxides of nitrogen also do not react with ozone in stratosphere

(4) Freons, chlorofluorocarbons, are inert chemically, they do not react with ozone in stratosphere

31. Which of the following xenon-OXO compounds may not be obtained by hydrolysis of xenon fluorides ? **[Jee Main(Online)-2014]**

(1) XeO_2F_2 (2) XeO_3 (3) XeO_4 (4) $XeOF_4$

32. Hydrogen peroxide acts both as an oxidising and as a reducing agent depending upon the nature of the reacting species. In which of the following cases H_2O_2 acts as a reducing agent in acid medium ? **[Jee Main(Online)-2014]**

(1) MnO_4^- (2) SO_3^{2-} (3) KI (4) Cr_2O_7

33. Consider the reaction **[Jee Main(Online)-2014]**

$H_2SO_{3(aq)} + Sn^{4+}_{(aq)} + H_2O_{(n)} \rightarrow Sn^{2+}_{(aq)} + HSO^-_{4(aq)} + 3H^+_{(aq)}$

Which of the following statements is correct?

(1) H_2SO_3 is the reducing agent because it undergoes oxidation

(2) H_2SO_3 is the reducing agent because it undergoes reduction

(3) Sn^{4+} is the reducing agent because it undergoes oxidation

(4) Sn^{4+} is the oxidizing agent because it undergoes oxidation

34. In the following sets of reactants which two sets best exhibit the amphoteric character of $Al_2O_3 \cdot xH_2O$? **[JEE(Main) Online-2014]**

Set-1 : $Al_2O_3 \cdot xH_2O(s)$ and $OH^-(aq)$

Set-2 : $Al_2O_3 \cdot xH_2O(s)$ and $H_2O(\ell)$

Set-3 : $Al_2O_3 \cdot xH_2O(s)$ and $H^+(aq)$

Set-4 : $Al_2O_3 \cdot xH_2O(s)$ and NH_3 (aq)

(1) 1 and 2 (2) 2 and 4 (3) 1 and 3 (4) 3 and 4

35. Which of the following compounds has a P-P bond :- **[Jee Main(Online)-2015]**

(1) $H_4P_2O_5$ (2) $(HPO_3)_3$ (3) $H_4P_2O_7$ (4) $H_4P_2O_6$

36. Chlorine water on standing loses its colour and forms :- **[Jee Main(Online)-2015]**

(1) HCl and $HClO_2$ (2) HCl only

(3) HOCl and $HOCl_2$ (4) HCl and HOCl

37. Which among the following is the most reactive ? **[Jee Main-2015]**

(1) I_2 (2) IC_1 (3) Cl_2 (4) Br_2

38. Which one has the highest boiling point ? **[Jee Main-2015]**

(1) Kr (2) Xe (3) He (4) Ne

39. From the following statements regarding H_2O_2, choose the incorrect statement : **[Jee Main-2015]**

(1) It has to be stored in plastic or wax lined glass bottles in dark

(2) It has to be kept away from dust

(3) It can act only as an oxidizing agent

(4) It decomposes on exposure to light

40. The reaction of zinc with dilute and concentrated nitric acid, respectively produces : **[JEE Main-2016]**

(1) NO_2 and N_2O (2) N_2O and NO_2

(3) NO_2 and NO (4) NO and N_2O

41. The non-metal that does not exhibit positive oxidation state is : **[JEE Main-2016]**

(1) Oxygen (2) Fluorine (3) Iodine (4) Chlorine

42. Which intermolecular force is most responsible in allowing xenon gas to liquefy? **[JEE (Main) Online 2016]**

(1) Ionic (2) Instantaneous dipole-induced dipole

(3) Dipole – dipole (4) Ion – dipole

43. The following statements concern elements in the periodic table. Which of the following is true? **[JEE (Main) Online 2016]**

(1) The group 13 elements are all metals.

(2) For group 15 elements, the stability of +5 oxidation state increases down the group.

(3) All the elements in Group 17 are gases.

(4) Elements of group 16 have lower ionization enthalpy values compared to those of group 15 in the corresponding periods.

44. Assertion : Among the carbon allotropes, diamond is an insulator, whereas, graphite is a good conductor of electricity. **[JEE (Main) Online 2016]**

Reason : Hybridization of carbon in diamond and graphite are sp^3 and sp^2, respectively.

(1) Assertion is incorrect statement, but the reason is correct.

(2)Both assertion and reason are correct, and the reason is the correct explanation for the assertion.

(3) Both assertion and reason are incorrect.

(4) Both assertion and reson are correct, but the reason is not the correct explanation for the assertion.

45. Identify the incorrect statement : **[JEE (Main) Online 2016]**

(1) S_8 ring has a crown shape.

(2) The $S-S-S$ bond angles in the S_8 and S_6 rings are the same

(3) S_2 is paramagnetic like oxygen

(4) Rhombic and monoclinic sulphur have S_8 molecules.

46. The product obtained when chlorine reacts with cold and dilute aqueous NaOH are : **[JEE-Main 2017]**

(1) ClO^- and ClO_3^- (2) ClO_2^- and ClO_3^-

(3) Cl^- and ClO^- (4) Cl^- and ClO_2^-

47. In graphite and diamond, the percentage of p-characters of the hybrid orbitals in hybridisation are respectively : **[Main-2018(Online)]**

(1) 33 and 25 (2) 33 and 75 (3) 50 and 75 (4) 67 and 75

48. In the following sets of reactants which two sets best exhibit the amphoteric character of $Al_2O_3 \cdot xH_2O$? **[Main-2018(Online)]**

Set-1 : $Al_2O_3 \cdot xH_2O(s)$ and $OH^-(aq)$

Set-2 : $Al_2O_3 \cdot xH_2O(s)$ and $H_2O(\ell)$

Set-3 : $Al_2O_3 \cdot xH_2O(s)$ and $H^-(aq)$

Set-4 : $Al_2O_3 \cdot xH_2O(s)$ and $NH_3(aq)$

(1) 1 and 2 (2) 2 and 4 (3) 1 and 3 (4) 3 and 4

49. The compound that does not produce nitrogen gas by the thermal decomposition is **[Main-2018(Online)]**

(1) $(NH_4)_2SO_4$ (2) $Ba(N_3)_2$ (3) $(NH_4)_2Cr_2O_7$ (4) NH_4NO_2

50. Good reducing nature of H_3PO_2 is attributed to the presence of : **[Main-2019(Online)]**

(1) Two P-H bonds (2) One $P-OH$ bond

(3) One $P-H$ bond (4) Two P-OH bonds

51. Among the following reactions of hydrogen with halogens, the one that requires a catalyst is : **[Main-2019(Online)]**

(1) $H_2 + Br_2 \rightarrow 2HBr$ (2) $H_2 + F_2 \rightarrow 2HF$

(3) $H_2 + I_2 \rightarrow 2HI$ (4) $H_2 + Cl_2 \rightarrow 2HCl$

52. The pair that contains two $P-H$ bonds in each of the oxoacids is: **[Main-2019(Online)]**

(1) $H_4P_2O_5$ and H_3PO_3 (2) $H_4P_2O_5$ and $H_4P_2O_6$

(3) H_3PO_2 and $H_4P_2O_5$ (4) H_3PO_3 and H_3PO_2

53. Iodine reacts with concentrated HNO_3 to yield Y along with other products. The oxidation state of iodine in Y is : **[Main-2019(Online)]**

(1) 5 (2) 1 (3) 3 (4) 7

54. The element that does NOT show catenation is: **[Main-2019(Online)]**

(1) Si (2) Ge (3) Pb (4) Sn

55. Chlorine on reaction with hot and concentrated sodium hydroxide gives :

(1) ClO_3^- and ClO_2^- (2) Cl^- and ClO_2^-

(3) Cl^- and ClO^- (4) Cl^- and ClO_3^-

56. The element that shows greater ability to form $p-\pi p_\pi$ multiple bond, is: **[Main-2019(Online)]**

(1) Si (2) C (3) Sn (4) Ge

Topic – 1 : Group -15 Elements (Nitrogen Family)

57. White phosphorus reacts with thionyl chloride to give **[Main July 28, 2022 (II)]**

(A) PCl_5, SO_2 and S_2Cl_2

(B) PCl_3, SO_2 and S_2Cl_2

(C) PCl_3, SO_2 and Cl_2

(D) PCl_5, SO_2 and Cl_2

58. Which oxoacid of phosphorous has the highest number of oxygen atoms present in its chemical formula? **[Main July 27, 2022 (I)]**

(A) Pyrophosphorous acid

(B) Hypophosphoric acid

(C) Phosphoric acid

(D) Pyrophosphoric acid

59. $A \xrightarrow{573K} \text{Red phorus} \xrightarrow[\text{under pressure}]{\text{heat;803K}} B$

Red phosphorus is obtained by heating "A" at 573 K, and can be converted to "B" by heating at 803 K under pressure. A and B, respectively, are **[Main June 30, 2022 (I)]**

(A) β-black phosphorus and white phosphorus.

(B) white phosphorus and β-black phosphorus.

(C) α-black phosphorus and white phosphorus.

(D) white phosphorus and α-black phosphorus.

60. Phe oxoacid of phosphorus that is easily obtained from a reaction of alkali and white phosphorus and has two P − H bonds, is : **[Main June 29, 2022 (I)]**

(A) Phosphonic acid

(B) Phosphinic acid

(C) Pyrophosphorus acid

(D) Hypophosphoric acid

61. The number of non-ionisable protons present in the product B obtained from the following reaction is _____ . **[Main July 26, 2022 (II)]**

$C_2H_5OH + PCl_3 \rightarrow C_2H_5Cl + A$

$A + PCl_3 \rightarrow B$

62. Consider the following reactions : **[Main June 25, 2022 (II)]**

$PCl_3 + H_2O \longrightarrow A + HCl$

$A + H_2O \longrightarrow B + HCl$

number of ionisable protons present in the product B _____ .

63. Match **List-I** with **List –II** **[Main March 16, 2021]**

List-I	**List-II**
Name of oxo acid	**Oxidation state of ' P '**
(A) Hypophosphorous acid	(I) +5
(B) Orthophosphoric acid	(II) +4
(C) Hypophosphoric acid	(III) +3
(D) Orthophosphorous acid	(IV) +2
	(V) +1

Choose the correct answer from the options given below:

(A) (A)-(IV), (B)-(V), (C)-(II), (D)-(III) (B) (A)-(V), (B)-(IV), (C)-(II), (D)-(III)

(C) (A)-(V), (B)-(I), (C)-(II), (D)-(III) (D) (A)-(IV), (B)-(I), (C)-(II), (D)-(III)

64. Given below are two statements: **[Main June 28, 2022 (I)]**

Statement I: The pentavalent oxide of group- 15 element. E_2O_5 is less acidic than trivalent oxide. E_2O_3 of the same element.

Statement II : The acidic character of trivalent oxide of group 15 elements E_2O_3 decreases down the group. In light of the above statements choose most appropriate answer from the options given below:

(A) If both Statement -1 and Statement -2 are correct, and Statement -2 is the correct explanation of the Statement - 2.

(B) If both Statement -1 and Statement -2 are correct, but Statement -2 is not the correct explanation of the Statement - 1.

(C) If Statement - 1 is correct but Statement -2 is incorrect.

(D) If Statement -1 is incorrect but Statement - 2 is correct,

Topic – 2

Group – 16 Element (Oxygen Family)

65. Which of the following oxoacids of sulphur contains " S " in two different oxidation states?

[Main June 28, 2022 (II)]

(A) $H_2S_2O_3$ (B) $H_2S_2O_6$

(C) $H_2S_2O_7$ (D) $H_2S_2O_8$

66. Reaction of an inorganic sulphite X with dilute H_2SO_4 generates compound Y. Reaction of Y with NaOH gives X. Further, the reaction of X with Y and water affords compound Z. Y and Z, respectively, are:

[Main Sep. 06, 2020 (II)]

(A) SO_2 and Na_2SO_3 (C) SO_2 and $NaHSO_3$

(B) SO_3 and $NaHSO_3$ (D) S and Na_2SO_3

67. Copsider the following sulphure based oxoacids.

$H_2SO_3, H_2SO_4, H_2S_2O_8$ and $H_2S_2O_7$.

Amongst these oxoacids, the number of those with peroxo $(O-O)$ bond is

[Main July 29, 2022 (II)]

68. Among the following allotropic forms of sulphur, the number of allotropic forms, which will show paramagnetism is

[Main Feb. 24, 2021 (II)]

(A) α-sułphur (B) β-sulphur (C) S_2-form

Topic-3

Group – 17 Elements (Halogen Family)

69. Concentrated HNO_3 reacts with Iodine to give **[Main July 28, 2022 (II)]**

(A) HI, NO_2 and H_2O

(B) HIO_2, N_2O and H_2O

(C) HIO_3, NO_2 and H_2O

(D) HIO_4, N_2O and H_2O

70. The interhalogen compound formed from the reaction of bromine with excess of fluorine is a: **[Main July 25, 2022 (I)]**

(A) hypohalite

(B) halite

(C) perhalate

(D) halite

71. Which one of the following correctly represents the order of stability of oxides, X_2O; (X = halogen) ? **[Main Aug. 31, 2021 (II)]**

(A) Br > Cl > I

(B) Br > I > Cl

(C) Cl > I > Br

(D) I > Cl > Br

72. Arrange the following bonds according to their average bond energies in descending order: C – Cl, C – Br, C – F, C – I **[Main Jan. 08, 2020 (II)]**

(A) C – F > C – Cl > C – Br > C – I

(B) C – Br > C – I > C – C - > C – F

(C) C – I > C – Br > C – Cl > C – F

(D) C – Cl > C – Br > C – I > C – F

73. The number of interhalogens from the following having square pyramidal structure is : $ClF_3, IF_7, BrF_5, BrF_3, I_2Cl_6, IF_5, ClF, ClF_5$ **[Main July 28, 2022 (I)]**

74. The number of halogen/(s) forming halic (V) acid is **[Main Aug. 31, 2021 (I)]**

75. Chlorine reacts with hot and concentrated NaOH and produces compounds (X) and (Y). Compound (X) gives white precipitate with silver nitrate solution. The average bond order between Cl and O atoms in (Y) is _____ . **[Main Jan. 07, 2020 (I)]**

76. Given below are two statements: one is labelled as Assertion A and the other is labelled as Reason R. **[Main June 27, 2022 (II)]**

Assertion A : Flourine forms one oxoacid.

Reason R : Flourine has smallest size amongst all halogens and is highly electronegative.

Topic-4: Group-18 Element (Noble Gases)

77. Match List-I with List-II: **[Main July 25, 2022 (II)]**

List-I (Molecule)	**List-II (hybridization; shape)**
(A) XeO_3	(I) sp^3d; linear
(B) XeF_2	(II) sp^3; pyramidal
(C) $XeOF_4$	(III) sp^3d^3; distorted octahedra
(D) XeF_6	(IV) sp^3d^2; sqaure pyramidal

78. The reaction in which the hybridisation of the underlined atom is affected is : **[Main Sep. 04, 2020(II)]**

(A) $H_3\underline{P}O_2 \xrightarrow{\text{Disproportionation}}$

(B) $H_2\underline{S}O_4 + BaCl \xrightarrow{420K}$

(C) $\underline{N}H_3 \xrightarrow{H^+}$

(D) $\underline{Ne}F_4 + SbF_5 \longrightarrow$

79. Thesum of number of lone pairs of electrons present on the central atoms of XeO_3, $XeOF_4$ and XeF_6 is _____ . **[Main July 25, 2022 (II)]**

EXERCISE-V (JEE-ADVANCED)

(IIT JEE ASKED QUESTIONS)

Fill in the blanks

1. The hydrolysis of alkyl substituted chlorosilanes given..... **[1991]**

2. The hydrolysis of trialkychlorosilane R_3SiCl, yields ..... **[1994]**

3. One recently discovered allotrope of carbon (e.g., C_{60}) is commonly known as .... **[1994]**

True/False

4. Carbon tetrachloride burns in air when lighted to give phosgene. **[1983]**

5. Graphite is a better lubricant on the moon than on the earth. **[1987]**

6. All the $Al-Cl$ bonds in Al_2Cl_6 are equivalent. **[1989]**

7. Diamond is harder than graphite. **[1993]**

8. The basic nature of the hydroxides of group 13 (Gr. IIIB) decreases progressively down the group. **[1993]**

9. The tendency for catenation is much higher for C than for Si. **[1993]**

10. Complete and balance the following chemical equations - **[IIT-1998, 2 M]**

(i) $P_4O_{10} + PC_{15} \longrightarrow$

(ii) $SnCl_4 + C_2H_5Cl + Na \longrightarrow$

11. Work out the following using chemical equations **[IIT- 1998, 2M]**

"Chlorination of calcium hydroxide produces bleaching powder"

12. Hydrogen peroxide acts both as an oxidizing and as a reducing agent in alkaline solution towards certain first row transition metal ion. Illustrate both these properties of H_2O_2 using chemical equations - **[IIT- 1998, 4 M]**

13. In the contact process for industrial manufacture of sulphuric acid, some amount of sulphuric acid is used as a starting material. Explain briefly. What is the catalyst used in the oxidation of SO_2 ? **[IIT- 1998,4 M]**

14. Give reasons in one or two sentences for each of the following: **[1985]**

(i) Graphite is used as a solid lubricant,

(ii) Fluorine cannot be prepared from fluorieds by chemical oxidation.

15. Write balanced equations for : **[1990]**

(i) The preparation of crystalline silicon from $SiCl_4$

(ii) The preparation of phosphine from CaO and white phosphorus

(iii) The preparation of ammonium sulphate from gypsum, ammonia and carbon dioxide.

16. Anhydrous $AlCl_3$ is covalent. From the data given below, predict whether it would remain covalent or become ionic in aqueous solution. **[1997]**

Ionisation energy for Al $= 5137$ kJ mol^{-1}

$\Delta H_{hydration}$ for $Al^{3+} = -4665$ kJ mol^{-1}

$\Delta H_{hydration}$ for $Cl^- = -381$ kJ mol^{-1}

17. Aluminium sulphide gives a foul odour when it becomes damp. Write a balanced chemical equation for the reaction. **[1997]**

18. Draw the structure of a cyclic silicate, $(Si_3O_9)^{6-}$ with proper labelling - **[IIT-1998]**

19. Give reasons for the following in one or two sentences only. **[IIT- 1999]**

20. Give reason : **[IIT- 2000]**

Why elemental nitrogen exists as a diatomic molecule whereas elemental phosphorus is a tetra atomic molecule.

21. Give an exapmle of oxidation of one halide by another halogen. Explain the feasibility of the reaction. **[IIT- 2000]**

22. Compounds X on reduction with $LiAlH_4$ gives a hydride Y containing 21.72% hydrogen alongwith other products. The compound Y reacts with air explosively resulting in boron trioxide. Identify X and Y. Give balanced reactions involved in the formation of Y and its reaction with air Draw the structure of Y. **[IIT- 2001]**

23. Starting from $SiCl_4$, prepare the following in steps not exceeding the number given in parenthesis (reactions only) **[IIT- 2001]**

(i) Silicon (1)

(ii) Linear silicon containing methyl group only (4)

(iii) Na_2SiO_3 (3)

24. Write the balanced chemical equation for developing photographic films. **[IIT- 2001]**

25. Identify (X) in the following synthetic scheme and write their structures. **[IIT- 2001]**

$$Ba\overset{*}{C}O_3 + H_2SO_4 \longrightarrow X\ (gas)\ (C\ denotes\ C^{14})$$

26. Write the balanced equations for the reactions of the following compounds with water **[2002]**

(i) Al_4Cl_3 (ii) CaNCN (iii) BF_3 (iv) NCl_3 (v) XeF_3

27. Write the balanced equations for the reactions of the following compounds with water: **[IIT- 2002]**

(i) Al_4C_3 (ii) CaNCN (iii) BF_3 (iv) NCl_3 (v) XeF_4

28. Identify the following: **[IIT- 2003]**

$$Na_2CO_3\ (aq) \xrightarrow{SO_2} A \xrightarrow{Na_2CO_3} B \xrightarrow[\Delta]{\text{elemental S}} C \xrightarrow{I_2} D$$

Also mention the oxidation state of S in all the compounds.

29. Arrange the following oxides in the increasing order of Bronsted basicity. **[IIT- 2004]**

$Cl_2O_7, BaO, SO_3, CO_2, B_2O_3$

30. When zeolite, which is hydrated sodium aluminium silicate, is treated with hard water, the sodium ions are exchanged with : **[1990]**

(A) H^+ions (B) Ca^{2+} ions (C) $SO_4{}^{2-}$ ions (D) Mg^{2+} ions

31. Which of the following halides is least stable and has doubtful existence ? **[1996]**

(A) CCl_4 (B) GeI_4 (C) SnI_4 (D) PbI_4

32. The number of $P-O-P$ bonds in cyclic tetrametaphosphoric acid is - **[IIT-2000]**

(A) Zero (B) Two (C) Three (D) Four

33. The correct order of acidic strength is - **[IIT- 2000]**

(A) $Cl_2O_7 > SO_2 < P_4O_{10}$ (B) $CO_2 > N_2O_5 > SO_3$

(C) $Na_2O > MgO > Al_2O_3$ (D) $K_2O > CaO > MgO$

34. Amongst H_2O, H_2S, H_2Se and H_2Te, the one with the highest boiling point is - **[IIT- 2000]**

(A) H_2O because of hydrogen bonding

(B) H_2Te because of higher molecular weight

(C) H_2S because of hydrogen bonding

(D) H_2Se because of lower molecular weight.

35. Ammonia can be dried by - **[IIT- 2000]**

(A) Conc. H_2SO_4 (B) P_4O_{10} (C) CaO (D) Anhydrous $CaCl_2$

36. Which of the following are hydrolysed - **[REE 2000]**

(A) NCl_3 (B) BCl_3 (C) CCl_4 (D) $SiCl_4$

37. The set with correct order of acidity is - **[IIT- 2001]**

(A) $HClO < HClO_2 < HClO_3 < HClO_4$

(B) $HClO_4 < HClO_3 < HClO_2 < HClO$

(C) $HClO < HClO_4 < HClO_3 < HClO_2$

(D) $HClO_4 < HClO_2 < HClO_3 < HClO$

38. The reaction, $3ClO^-(aq) \longrightarrow ClO_3^-(aq) + 2Cl^-(aq)$ is an example of - **[IIT- 2001]**

(A) Oxidation reaction (B) reduction reaction

(C) Disproportionation reaction (D) Decomposition reaction

39. The number of S-S bonds in sulphur trioxide trimer, (S_3O_9) is - **[IIT- 2001]**

(A) Three (B) Two (C) One (D) Zero

40. Statement-I : Between $SiCl_4$ and CCl_4, only SiCl4 reacts with water **[IIT- 2001]**

Because :

Statement-II : $SiCl_4$ is ionic and CCl_4 is covalent

(A) If both assertion and reason are correct and reason is the corect explanation of the assertion

(B) If both assertion and reason are correct, but reason is not the correct explanation of the assertion

(C) If assertion is correct, but reason is incorrect

(D) If assertion is incorrect, but reason is correct.

41. Polyphosphates are used as water softening agents because they - **[IIT- 2002]**

(A) Form soluble complexes with anionic species

(B) Precipitate anionic species

(C) Form soluble complexes with cationic species

(D) Precipitate cationic species

42. Identify the correct order of solubility of Na_2 S, CuS, and ZnS in aqueous medium- **[IIT- 2002]**

(A) CuS > ZnS > Na_2 S (B) ZnS > Na_2 S > CuS

(C) Na_2 S > CuS > ZnS (D) Na_2 S > ZnS > CuS

43. Identify, the correct order of acidic strength of CO_2, CuO, CaO, H_2O – **[IIT- 2002]**

(A) CaO < CuO < H_2O < CO_2 (B) H_2O < CuO < CaO < CO_2

(C) CaO < H_2O < CuO < CO_2 (D) H_2O < CO_2 < CaO < CuO

44. H_3BO_3 is - **[IIT- 2002,3]**

(A) Monobasic acid and weak Lewis acid (B) Monobasic and weak Bronsted acid

(C) Monobasic and strong Lewis acid (D) Tribasic and weak Bronsted acid

45. When $I^-$is oxidised by MnO_4^-in alkaline medium, I^-converts into - **[IIT- 2003]**

(A) IO_3^- (B) I_2 (C) IO_4^- (D) IO^-

46. Column-I (Change) Column-II (Given change is done by) **[IIT- 2003]**

(A) $Bi^{3+} \longrightarrow (BiO)^+$ (P) Heat

(B) $[AlO_2]^- \longrightarrow Al(OH)_3$ (Q) Hydrolysis

(C) $SiO_4^{4-} \longrightarrow Si_2O_7^{6-}$ (R) Acidification

(D) $(B_4O_7^{2-}) \longrightarrow [B(OH)_3]$ (S) Dilution by water

47. $(Me)_2SiCl_2$ on hydrolysis will produce - **[IIT- 2003]**

(A) $(Me)_2Si(OH)_2$ (B) $(Me)_2Si = O$

(C) $[-O-(Me)_2Si-O-]_n$ (D) $Me_2SiCl\,(OH)$

48. Which is the most thermodynamically stable allotropic form of phosphorus? **[IIT- 2004]**

(A) Red (B) White (C) Black (D) Yellow

49. When PbO_2 reacts with conc. HNO_3 the gas evolved may be : **[IIT- 2004]**

(A) NO_2 (B) O_2 (C) N_2 (D) N_2O

50. Which of the following is not oxidised by O_3 ? **[IIT- 2005]**

(A) KI (B) $FeSO_4$ (C) $KMnO_4$ (D) K_2MnO_4

51. Which blue-liquid is obtained on reacting equimolar amounts of two gases at $-30°C$?

(A) N_2O (B) N_2O_3 (C) N_2O_4 (D) N_2O_5

[IIT- 2005]

52. $B(OH)_3 + NaOH \rightleftharpoons NaBO_2 + Na[B(OH)_4] + H_2O$ how can this reaction is made to proceed in forward direction? **[IIT- 2006]**

(A) Addition of cis 1, 2 diol (B) Addition of borax

(C) Addition of trans 1, 2 diol (D) Addition of Na_2HPO_4

53. Among the following, the paramagnetic compound is - **[IIT- 2007]**

(A) Na_2O_2 (B) O_3 (C) N_2O (D) KO_2

54. Statement-I : Boron always forms covalent bond **[IIT-2007]**

Because :

Statement-II : The small size of B^{3+} favours formation of covalent bond.

(A) Statement-I is True, Statement-II is Ture, Statement-II is a correct explanation for Statement-I

(B) Statement-I is Ture, Statement-II is Ture, Statement-II is not a correct explanation for Statement-II

(C) Statement-I is Ture, Statement-II is False

(D) Statement-I is False, Statement-II is Ture

55. Statement-I : In water, orthoboric acid behaves as a weak monobasic acid. **[IIT-2007]**
Statement-II : In water, orthoboric acid acts as a proton donor.
(A) Statement-I is True, Statement-II is Ture, Statement-II is a correct explanation for Statement-I
(B) Statement-I is Ture, Statement-II is Ture, Statement-II is not a correct explanation for Statement-II
(C) Statement-I is Ture, Statement-II is False
(D) Statement-I is False, Statement-II is Ture

Comprehension # 1 (Q. 56 to 58)

The noble gases have closed-shell electronic configuration and are monoatomic gases under normal conditions. The low boiling point of the lighter noble gases are due to weak dispersion forces between the atoms and the absence of other interatomic interactions. The direct reaction of xenon with fluorine leads to a series of compounds with oxidation number +2, +4 and +6 . XeF_4 reacts violently with water to give XeO_3. The compounds of xenon exhibit rich stereochemistry and their geometries can be deduced considering the total number of electron pairs in the valence shell. **[IIT- 2007]**

56. Argon is used in arc welding because of its -
(A) Low reactivity with metal
(B) Ability to lower the melting point of metal
(C) Flammability
(D) High calorific value

57. The structure of XeO_3 is -
(A) Linear (B) Planar (C) Pyramidal (D) T-shaped

58. XeF_4 and XeF_6 are expected to be -
(A) Oxidising agent
(B) Reducing agent
(C) Unreactive
(D) Strongly basic

Comprehension # 2 (Q.59 to 61)

There are some deposits of nitrates and phosphates in earth's crust. Nitrates are more soluble in water. Nitrates are difficult to reduce under the laboratory conditions but microbes do it easily. Ammonia forms large number of complexes with transition metal ions. Hybridization easily explains the ease of sigma donation capability of NH_3 and PH_3. Phosphine is a flammable gas and is prepared from white phosphorous. **[IIT- 2008]**

59. Among the following, the correct statement is :-

(A) Phosphates have no biological significance in humans

(B) Between nitrates and phosphates, phosphates are less abundant in earth's crust

(C) Between nitrates and phosphates, nitrates are less abundant in earth's crust

(D) Oxidation of nitrates is possible in soil

60. Among the following, the correct statement is :-

(A) Between NH_3 and PH_3, NH_3 is a better electron donor because the lone pair of electrons occupies spherical ' s ' orbital and is less directional

(B) Between NH_3 and PH_3, PH_3 is a better electron donor because the lone pair of electrons occupies sp^3 orbital and is more directional

(C) Between NH_3 and PH_3, NH_3 is a better electron donor because the lone pair of electrons occupies sp^3 orbital and is more directional

(D) Between NH_3 and PH_3. PH_3 is a better electron donor because the lone pair of electrons occupies spherical ' s ' orbital and is less directional.

61. White phosphorus on reaction with NaOH gives PH_3 as one of the products. This is a :-

(A) dimerization reaction (B) disproportionation reaction

(C) condensation reaction (D) precipitation reaction

62. The reaction of P_4 with *X* leads selectively to P_4O_6. The X is **[JEE 2009]**

(A) DryO_2 (B) A mixture of O_2, and N_2

(C) Moist O_2 (D) O_2 in the presence of aqueous NaOH

63. The reaction of white phosphorus with aqueous NaOH gives phosphine along with another phosphorus containing compound. The reaction type ; the oxidation states of phosphorus in phosphine and the other product are respectively **[JEE 2012]**

(A) redox reaction ; -3 and -5

(B) redox reaction ; +3 and +5

(C) disproportionation reaction ; -3 and +1

(D) disproportionation reaction ; -3 and +3

64. Bleaching powder contains a salt of an oxoacid as one of its components. The anhydride of that oxoacid is : **[JEE 2012]**

(A) Cl_2O (B) Cl_2O_7 (C) ClO_2 (D) Cl_2O_6

65. With respect to graphite and diamond, which of the statement(s) given below is (are) correct ?
(A) Graphite is harder than diamond. **[JEE 2012]**
(B) Graphite has higher electrical conductivity than diamond.
(C) Graphite has higher thermal conductivity than diamond.
(D) Graphite has higher C − C bond order than diamond.

66. Concentrated nitric acid, upon long standing, turns yellow-brown due to the formation of -
(A) NO (B) NO_2 (C) N_2O (D) N_2O_4
[JEE 2013]

67. The correct statement(s) about O_3 is(are) **[JEE 2013]**
(A) O − O bond lengths are equal
(B) Thermal decomposition of O_3 is endothermic
(C) O_3 is diamagnetic in nature
(D) O_3 has a bent structure

Comprehension # 3 (Q. 68 and 69)

The reaction of Cl_2 gas with cold dilute and hot concentrated NaOH in water give sodium salt of two (different) oxoacids of chlorine P and Q respectively. The Cl_2 gas reacts with SO_2 gas , in presence of charcoal to give a product R. R reacts with white phosphorous to give a compound S. On hydrolysis, *S* gives as oxoacid of phosphorous *T*.

68. R, S and T, respectively are - **[JEE 2013]**
(A) SO_2Cl_2, PCl_5 and H_3PO_4 (B) SO_2Cl_2, PCl_3 and H_3PO_3
(C) $SOCl_2$, PCl_3 and H_3PO_2 (D) SO_2Cl_2, PCl_5 and H_3PO_4

69. P and Q, respectively, are the sodium salts of -
(A) Hypochlorus and chloric acid (B) Hypochlorus and chlorus acid
(C) Chloric and perchloric acids (D) Chloric and hypochlorus acids

70. The unbalanced chemical reactions given in List-I show missing reagent or condition (?) which are provided in List-II. Match List-I with List-II and select the correct answer using the code given below the lists :A **[JEE 2013]**

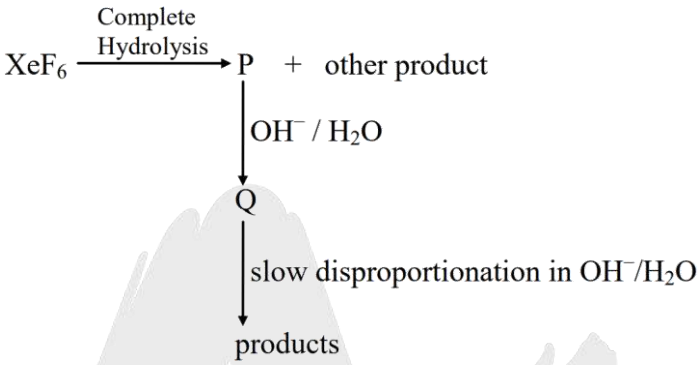
List-I	**List-II**
(P) $PbO_2 + H_2SO_4 \xrightarrow{?} PbSO_4 + O_2$ + other product	(1) NO
(Q) $Na_2S_2O_3 + H_2O \xrightarrow{?} NaHSO_4$ + other product	(2) I_2
(R) $N_2H_4 \xrightarrow{?} N_2$ + other product	(3) Warm
(S) $XeF_2 \xrightarrow{?} Xe$ + Other product	(4) Cl_2

Code:

	P	Q	R	S		P	Q	R	S
(A)	4	2	3	1	(B)	3	2	1	4
(C)	1	4	2	3	(D)	3	4	2	1

71. Under ambient conditions, the total number of gases released as products in the final step of the reaction scheme shown below is **[JEE Adv. 2014]**

(A) 0 (B) 1 (C) 2 (D) 3



72. The product formed in the reaction of $SOCl_2$ with white phosphorous is **[JEE Adv. 2014]**

(A) PCl_3 (B) SO_2Cl_2 (C) SCl_2 (D) $POCl_3$

73. The correct statements(s) for orthoboric acid is / are - **[JEE Adv. 2014]**

(A) It behaves as a weak acid in water due to self ionization

(B) Acidity of its aqueous solution increses upon addition of ethylene glycol

(C) It has a three dimensional structure due to hydrogen bonding.

(D) It is a weak electrolyte in water

74. The correct statement(s) regarding, (i) HClO, (ii) $HClO_2$, (iii) $HClO_3$ and (iv) $HClO_4$, is(are)

(A) The number of Cl = O bonds in (ii) and (iii) together is two **[JEE Adv. 2015]**

(B) The number of lone pairs of electrons on Cl in (ii) and (iii) together is three

(C) The hybridization of Cl in (iv) is sp^3

(D) Amongst (i) to (iv), the strongest acid is (i)

75. When O_2 is adsorbed on a metallic surface, electron transfer occurs from the metal to O_2. The TRUE, statement (s) regarding this adsorption is (are) **[JEE Adv. 2015]**

(A) O_2 is physisorbed (B) heat is released

(C) occupancy of π^*_{2p} of O_2 is increased (D) bond length of O_2 is increased

76. Under hydrolytic conditions, the compounds used for preparation of linear polymer and for chain termination, respectively, are **[JEE Adv. 2015]**

(A) CH_3SiCl_3 and $Si(CH_3)_4$ (B) $(CH_3)_2SiCl_2$ and $(CH_3)_3SiCl$

(C) $(CH_3)_2SiCl_2$ and CH_3SiCl_3 (D) $SiCl_4$ and $(CH_3)_3SiCl$

77. Three moles of B_2H_6 are completely reacted with methanol. The number of moles of boron containing product formed is - **[JEE Adv. 2015]**

78. The increasing order of atomic radii of the following group 13 elements is : [JEE Adv. 2016]

(A) Al < Ga < In < Tl (B) Ga < Al < In < Tl

(C) Al < In < Ga < Tl (D) Al < Ga < Tl < In

79. The crystalline form of borax has **[JEE Adv. 2016]**

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

(B) All boron atoms in the same plane

(C) Equal number of sp^2 and sp^3 hybridized boron atoms

(D) One terminal hydroxide per boron atom

80. The nitrogen containing compound produced in the reaction of HNO_3 with P_4O_{10}

(A) can also be prepared by reaction of P_4 and HNO_3 **[JEE Adv. 2016]**

(B) is diamagnetic

(C) contains one N − N bond

(D) reacts with Na metal producing a brown gas

PARAGRAPH Q.81 to 82

Upon heating $KClO_3$ in the presence of catalytic amount of MnO_2, a gas W is formed. Excess amount of W reacts with white phosphorus to give X. The reaction of X with pure HNO_3 gives Y and Z. **[JEE(Advanced) 2017]**

81. W and X are, respectively

(A) O_2 and P_4O_6 (B) O_3 and P_4O_{10} (C) O_3 and P_4O_6 (D) O_2 and P_4O_{10}

82. Y and Z are, respectively

(A) N_2O_4 and HPO_3 (B) N_2O_3 and H_3PO_4

(C) N_2O_5 and HPO_3 (D) N_2O_4 and H_3PO_3

83. The compound(s) which generate(s) N_2 gas upon thermal decomposition below 300°C is (are) **[JEE(Advanced) 2018]**

(A) NH_4NO_3 (B) $(NH_4)_2Cr_2O_7$ (C) $Ba(N_3)_2$ (D) Mg_3N_2

84. A tin chloride Q undergoes the following reactions (not balanced) **[JEE(Advanced) 2019]**

$Q + Cl^- \rightarrow X$

$Q + Me_3N \rightarrow Y$

$Q + CuCl_2 \rightarrow Z + CuCl$

X is a monoanion having pyramidal geometry. Both Y and Z are neutral compounds.

Choose the correct option(s)

(1) There is a coordinate bond in Y

(2) The central atom in Z has one lone pair of electrons

(3) The central atom in X is $sp3$ hybridized

(4) The oxidation state of the central atom in Z is +2

85. With reference to aqua regia, choose the correct options(s) **[JEE(Advanced) 2019]**

(1) Reaction of gold with aqua regia produces NO_2 in the absence of air

(2) Reaction of gold with aqua regia produces an anion having Au in +3 oxidation state

(3) Aqua regia is prepared by mixing conc. HCl and conc. HNO_3 in 3: 1(v/v) ratio

(4) The yellow colour of aqua regia is due to the presence of NOCl and Cl_2

86. The amount of water produced (in g) in the oxidation of 1 mole of rhombic sulphur by conc. HNO_3 to a compound with the highest oxidation state of sulphur is (Given data : Molar mass of water $= 18\ g\ mol^{-1}$) **[JEE(Advanced) 2019]**

87. At 143 K, the reaction of XeF_4 with O_2 F_2, produces a Xenon compound Y. The total number of lone pair(s) of electron present on the whole molecule of Y is **[JEE(Advanced) 2019]**

88. A colorless aqueous solution contains nitrates or two metals, X and Y. When it was added to an aqueous solution of NaCl, a white precipitate was formed. This precipitate was found to be partly soluble in hot water to give a residue P and a solution Q. The residue P was soluble in aq. NH_3 and also in excess sodium thiosulfate. The hot solution Q gave a yellow precipitate with KI. The metals X and Y, respectively, are. **[JEE(Advanced) 2020]**

(A) Ag and Pb (B) Ag and Cd (C) Cd and Pb (D) Cd and Zn

89. The correct statement(s) related to oxoacids of phosphorous is(are) **[JEE(Advanced) 2021]**

(A) Upon heating, H_3PO_3 undergoes disproportionation reaction to produce H_3PO_4 and PH_3.

(B) While H_3PO_3 can act as reducing agent, H_3PO_4 cannot.

(C) H_3PO_3 is a monobasic acid.

(D) The H atom of $P-H$ bond in H_3PO_3 is not ionizable in water.

90. Ozonolysis of ClO_2 produces an oxide of chlorine. The average oxidation state of chlorine in this oxide is. **[JEE(Advanced) 2021]**

91. Dissolving 1.24 g of white phosphorous in boiling NaOH solution in an inert atmosphere gives a gas Q. The amount of $CuSO_4$ (in g) required to completely consume the gas Q is_____.

[JEE(Advanced) 2022]

[Given: Atomic mass of $H = 1, O = 16, Na = 23, P = 31, S = 32, Cu = 63$]

92. The reaction of $HClO_3$ with HCl gives a paramagnetic gas, which upon reaction with O_3 produces. **[JEE(Advanced) 2022]**

(A) Cl_2O (B) ClO_2 (C) Cl_2O_6 (D) Cl_2O_7

93. Match the reactions (in the given stoichiometry of the reactants) in List-I with one of their products given in List-II and choose the correct option. **[JEE(Advanced) 2023]**

List-I	**List-II**
(P) $P_2O_3 + 3H_2O \rightarrow$	(1) $P(O)(OCH_3)Cl_2$
(Q) $P_4 + 3NaOH + 3H_2O \rightarrow$	(2) H_3PO_3
(R) $PCl_5 + CH_3COOH \rightarrow$	(3) PH_3
(S) $H_3PO_2 + 2H_2O + 4AgNO_3 \rightarrow$	(4) $POCl_3$
	(5) H_3PO_4

(A) $P \rightarrow 2; Q \rightarrow 3; R \rightarrow 1; S \rightarrow 5$ (B) $P \rightarrow 3; \rightarrow Q \rightarrow 5; R \rightarrow 4; \rightarrow 2$

(C) $P \rightarrow 5; Q \rightarrow 2; R \rightarrow 1; S \rightarrow 3$ (D) $P \rightarrow 2; Q \rightarrow 3; R \rightarrow 4; S \rightarrow 5$

94. Consider the following molecules: Br_3O_8, F_2O, $H_2S_4O_6$, $H_2S_5O_6$, and C_3O_2. Count the number of atoms existing in their zero oxidation state in each molecule. Their sum is

[JEE(Advanced) 2023]

ANSWER KEY

EXERCISE-I

1.	C	**2.**	C	**3.**	B	**4.**	A	**5.**	B	**6.**	B	**7.**	D
8.	C	**9.**	B	**10.**	B	**11.**	A	**12.**	A	**13.**	A	**14.**	B
15.	B	**16.**	A	**17.**	B	**18.**	A	**19.**	A	**20.**	A	**21.**	B
22.	C	**23.**	B	**24.**	D	**25.**	A	**26.**	A	**27.**	B	**28.**	B
29.	C	**30.**	B	**31.**	A	**32.**	D	**33.**	A	**34.**	B	**35.**	C
36.	C	**37.**	B	**38.**	C	**39.**	B	**40.**	D	**41.**	A	**42.**	A
43.	B	**44.**	C	**45.**	A	**46.**	C	**47.**	A				

EXERCISE-II

1.	A,B	**2.**	A,B,C	**3.**	A,C,D	**4.**	A,B,C	**5.**	A,B,D	**6.**	A,B
7.	A,B,C	**8.**	A,B,C	**9.**	A,B,C,D	**10.**	A, C,	**11.**	A,B,C,D		
12.	C,D	**13.**	C,D	**14.**	A,B,C,D	**15.**	A,B,D	**16.**	B,C,D		
17.	A,B,C,D										

EXERCISE-III

1.	B	**2.**	A	**3.**	D	**4.**	A	**5.**	C	**6.**	D	**7.**	A
8.	B	**9.**	A	**10.**	A	**11.**	C	**12.**	B	**13.**	B	**14.**	C
15.	B	**16.**	B	**17.**	C	**18.**	A						

EXERCISE-IV(JEE-MAIN)

1.	4	**2.**	4	**3.**	2	**4.**	3	**5.**	4	**6.**	2	**7.**	3
8.	2	**9.**	2	**10.**	3	**11.**	2	**12.**	3	**13.**	3	**14.**	1
15.	4	**16.**	3	**17.**	2	**18.**	3	**19.**	3	**20.**	2	**21.**	3
22.	4	**23.**	2	**24.**	1	**25.**	3	**26.**	4	**27.**	2	**28.**	2
29.	3	**30.**	1	**31.**	3	**32.**	1	**33.**	1	**34.**	3	**35.**	4
36.	4	**37.**	2	**38.**	2	**39.**	3	**40.**	2	**41.**	2	**42.**	2
43.	4	**44.**	4	**45.**	2	**46.**	3	**47.**	4	**48.**	3	**49.**	1
50.	1	**51.**	3	**52.**	3	**53.**	1	**54.**	3	**55.**	4	**56.**	2

Topic – 1

Group -15 Elements (Nitrogen Family)

57.	**B**	**58.**	**D**	**59.**	**D**	**60.**	**B**	**61.**	**2**	**62.**	**2**	**63.**	**C**
64.	**A**										

Topic – 2

Group – 16 Element (Oxygen Family)

65.	**A**	**66.**	**C**	**67.**	**1**	**68.**	**1**

Topic-3

Group – 17 Elements (Halogen Family)

69. C **70.** B **71.** D **72.** A **73.** 3 **74.** 3

75. 1.67 **76.** A

Topic-4

Group-18 Element (Noble Gases)

77. A **78.** D **79.** 3

EXERCISE-IV (JEE- ADVANCED)

Fill in the blanks

1. Silicones **2.** $R_3Si(OH)$ **3.** Buckminstre fullerene

True/False

4. F **5.** T **6.** *F* **7.** T **8.** *F* **9.** T

Subjective

10. (i) $P_4O_{10} + 6PCl_3 \longrightarrow 10POCl_3$

(ii) $SnCl_4 + 2C_2H_5Cl + 2Na \longrightarrow Na_2SnCl_6 + C_4H_{10}$

11. $3Ca(OH)_2 + 2Cl_2 \longrightarrow \underbrace{Ca(OCl)_2 + Ca(OH)_2CaCl_2 \cdot 2H_2O}$

Bleaching powder is a mixture of $CaOCl_2$

And hydrated basic calcium chloride.

12. When H_2O_2 acts as oxidizing agent, therefore, following reaction takes place:

$H_2O_2 + 2e^- \longrightarrow 2OH^-$

while, regarding is action on reducing agent, the following reaction takes place :

$H_2O_2 + 2OH^- \longrightarrow O_2 + 2H_2O + 2e^-$

Oxidizing character:

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

Reducing character:

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

13. In $SO_3 + H_2O \longrightarrow H_2SO_4$ reaction, H_2SO_4 is obtained in misty form and reaction is explosive (highly exothermic). By adding H_2SO_4 the above reaction is prevented.

$H_2SO_4 + SO_3 \longrightarrow H_2\ S_2O_7$ (oleum)

$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$

The catalyst used is V_2O_5 and K_2O is used as promotor for the oxidation of SO_2 into SO_3.

14. (i) Graphite, hexagonal planes are held by weak van der Waals forces. Since these forces are overcome, one plane slides over the other. This explains the lubricating properties of graphite.

(ii) Fluoride has negative oxidation potential

$2F^- \longrightarrow F_2 + 2e^-, E_{OP} = -2.87$ volts

Hence, fluoride is the poorest reducing agent.

Hence, F_2 can't be prepared by oxidation of HF by even strong oxidising agents such as $KMnO_4, MnO_2$ etc.

15. (i) $\underset{\text{vapour}}{3SiCl_4} + \underset{\text{molten}}{4Al} \xrightarrow{\Delta} \underset{\text{volatilized}}{4AlCl_3} + 3Si$

(ii) $15CaO + 4P_4 \xrightarrow{\Delta} 5Ca_3P_2 + 3P_2O_5 \uparrow$

$[Ca_3P_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2PH_3 \uparrow] \times 5$

$15CaO + 4P_4 + 30H_2O \rightarrow 15CaO(OH)_2 + 3P_2O_5 \uparrow + 10PH_3 \uparrow$

(iii) $2NH_3 + CO_2 + H_2O \rightarrow (NH_4)_2CO_3$

$\underset{\text{gypsum}}{CaSO_4} + (NH_4)_2CO_3 \rightarrow CaCO_3 \downarrow (NH_4)_2SO_4$

$CaSO_4 + 2NH_3 + CO_2 + H_2O \rightarrow CaCO_3 \downarrow + (NH_4)_2SO_4$

16. Total hydration energy of Al^{3+} and $3Cl^-$ ions of $AlCl_3$

$(\Delta H_{\text{hydration}})$

$=$ (Hydration energy of $Al^{3+} + 3 \times$ hydration energy of Cl^-)

$= [-4665 + 3(-381)]kJmol^{-1} = 5808$ kJ mol^{-1}

This amount of energy is more than that required for the ionisation of Al into Al^{3+} (Ionisation energy of Al to Al^{3+}). Due to this reason, $AlCl_3$ becomes ionic in aqueous solution. In aqeous solution, it exists in ionic form as below :

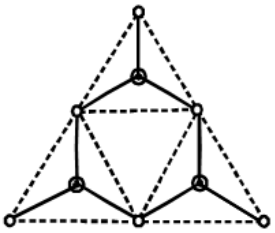
$AlCl_3 + 6H_2O \longrightarrow (Al(H_2O)_6^{3+} + 3Cl^-$

17. $Al_2S_3 + 6H_2O \rightarrow \underset{\text{foul odour}}{2Al(OH)3 \downarrow} + 3H_2S$

Foul odour, on damping of Al2 S3 is due to formation of H2 S gas.

18. In cyclic $(Si_3O_9)^{6-}$, three tetrahedral of SiO_4 are joined together by sharing of two oxygen atoms per tetrahedral.

Structure of $(Si_3O_9^{6-})$



In it dark circles (·) represent Si and open circles (O) represent oxygen atom or iron.

19. $BeCl_2$ is hydrolysed due to high polarising power and presence of vacant p-orbitals in Be atom. $\left(Be = 1\,s^2, 2\,s^2, 2p_x^1, 2p_y^0, 2p_z^0\right)$

20. In nitrogen, d-orbitals are not present, so in it the possiblity of intramolecular multiplicityy exists which leads to the completion of octet through π-bond between two nitrogen atoms. In phosphorus, d-orbitals are present, so in it due to large size of P, the $P-P$ bonds are longer and hence intramolecular multiplicity is ruled out. So, for the completion of octet, it forms the bonds with three other ' P ' atoms. Hence due to this reason it shows molecular formula as P_4.

21. $2I^-(aqueous) + Cl_2 \longrightarrow I_2 + 2Cl^-(aqueous)$

(i) $2I^-(aqueous) \longrightarrow I_2\,(s) + 2e^-$

(ii) $Cl_2(\,g) + 2e^- \longrightarrow 2Cl^-(aq)$

Thus, I^- is oxidised into I_2 by Cl_2 due to higher oxidised potential of Cl_2 than I_2

22. X: BCl_3

Y: B_2H_6

$4BCl_3 + 3LiAlH_4 \longrightarrow 3AlCl_3 + 3LiCl + 2\,B_2H_6$

X

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

Y

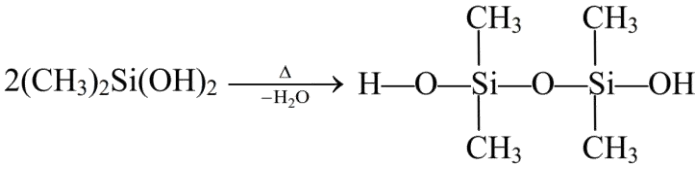
23. (i) $3SiCl_4 + 4Al \longrightarrow 3Si + 4AlCl_3$ (in one step)

(ii) $SiCl_4 + 2Mg \longrightarrow 2MgCl_2 + Si$

$Si + Cu \longrightarrow Si - Cu$

$2CH_3Cl + Si - Cu \longrightarrow (CH_3)_2SiCl_2 + Cu$

$(CH_3)_2SiCl_2 + 2H_2O \longrightarrow (CH_3)_2Si(OH)_2 + 2HCl$



(iii) $SiCl_4 + 4H_2O \longrightarrow Si(OH)_4 + 4HCl$

$Si(OH)_4 \longrightarrow SiO_2 + 2H_2O$

$SiO_2 + Na_2CO_3 \xrightarrow[1673\ K]{\Delta} Na_2SiO_3 + CO_2$

24. Unreacted AgBr is removed by hypo ($Na_2S_2O_3$)

$AgBr + 2Na_2S_2O_3 \longrightarrow Na_3[Ag(S_2O_3)_2] + NaBr$

25. $14CO_2$

26. (i) $Al_4Cl_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4 \uparrow$

(ii) $CaNCN + 3H_2O \longrightarrow CaCO_3 \downarrow + 2NH_3$

(iii) $4BF_3 + 3H_2O \longrightarrow \underset{\text{boric acid}}{H_3BO_3} + \underset{\text{foricacid}}{3HBF_4}$

(iv) $NCl_3 + 3H_2O \longrightarrow NH_3 + \underset{\text{hypochlorous acid}}{3HOCl}$

(v) $2XeF_4 + 3H_2O \longrightarrow Xe + \underset{\text{xenon trioxide}}{XeO_3} + F_2 + 6HCl$

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

(ii) $CaNCN + 3H_2O \longrightarrow CaCO_3 + 2NH_3$

(iii) $BF_3 + 3H_2O \longrightarrow H_3BO_3 + 3HF$

$3HF + 3BF_3 \longrightarrow 3HBF_4$

$4BF_3 + 3H_2O \longrightarrow H_3BO_3 + 3HBF_4$

28. Oxidation state

(A) : $NaHSO_3 + 4$

(B) : $Na_2SO_3 + 4$

(C) : $Na_2S_2O_3 + 2$

(D) : $Na_2S_4O_6 + 2.5$

29. $Cl_2O_7 < SO_3 < CO_2 < B_2O_3 < BaO$

objective

44. A **45.** A

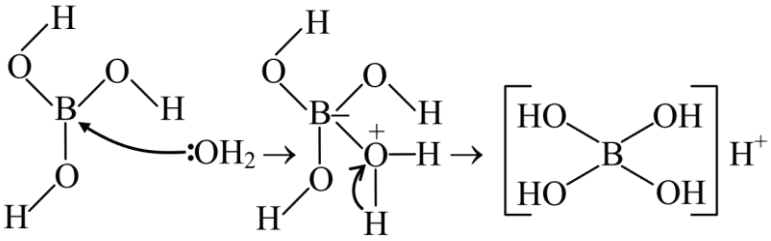
46. (A) → Q, S;; B) → R, S;; (C) → P; (D) → Q, R

47. C **48.** C **49.** B **50.** C **51.** B **52.** A **53.** D

54. A

Boron always forms covalent bond because boron requires very high energy of form B^{3+} and again B^{3+} due to its very small size having high polarising power thus cause greater polarisation and eventually significant covalent characteristics-Fajans rule.

55. C



Comprehension # 1 (Q. 56 to 58)

56. A **57.** C **58.** A

Comprehension # 2 (Q. 59 to 61)

59. C **60.** C **61.** B **62.** B **63.** C **64.** A **65.** B,D

66. B **67.** A,C,D

Comprehension # 3 (Q. 68 and 69)

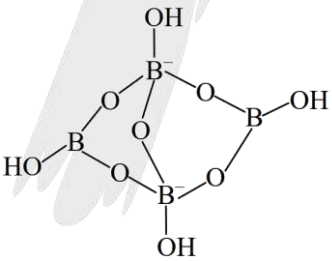
75. B, C, D **76.** B **77.** 6

78. B

Sol. The order of radius of 13^{th} group elements is Ga < Al < In < Tl.

Reason ⇒ Due to poor shielding effect of d-orbital, radius of Ga is smallar than Al.

79. (A, C, D)



(A) Having $[B_4O_5(OH)_4]^{2-}$ tetranuclear (boron) unit

(B) All boron atoms not in same plane

(C) Two boron are sp^2 hybridised and two boron are sp^3 hybridised

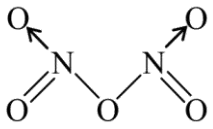
(D) One terminal hydroxide per boron atom is present.

80. B,D

Sol. $P_4O_{10} + 4HNO_3 \xrightarrow{\text{dehydration } HNO_3} \underset{\text{(requiredproduct)}}{4(HPO_3)} + 2\,N_2O_5$

(A) $P_4 + 20HNO_3 \rightarrow 4H_3PO_4 + 20NO_2 \uparrow + 4H_2O$

(B) N_2O_5 is diamagnetic in nature

(C) $N_2O_5 \rightarrow$ 

(D) $Na + N_2O_5 \rightarrow NaNO_3 + NO_2 \uparrow$

81.	D	**82.**	C	**83.**	B, C	**84.**	1,3	**85.**	2,3,4	**86.**	1	**87.**	19
88.	A	**89.**	A,B,D	**90.**	6	**91.**	2.38	**92.**	C	**93.**	D	**94.**	6

SOLUTION JEE MAINS

Topic – 1

Group -15 Elements (Nitrogen Family)

57. (B) When white phosphorous reacts with $SOCl_2$, it form phosphorous trichloride.

$$P_4 + 8SOCl_2 \rightarrow 4PCl_3 + 4SO_2 + 2\ S_2Cl_2$$

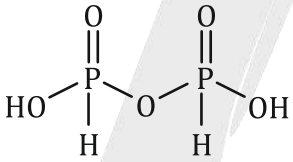
58. (D) Pyrophosphoric acid is $H_4P_2O_7$ with highest number of oxygen atoms.

59. (D) Red phosphrous is obtained by heating white phosphorous at 573 K in inert atmosphere.
When red phosphorous is heated in a sealed tube at 803 K, we get α-black phosphorous.
β-Black phosphorous is prepared by heating white phosphorous at 473 K under high pressure.

60. (B) $P_4 + 3NaOH + 3H_2O \rightarrow PH_3 + 3NaH_2PO_2$
The oxoacid formed in the product of above reaction is sodium salt of phosphinicacid.

61. $C_2H_2OH + PCl_3 \longrightarrow \underset{(A)}{C_2H_5Cl} + H_3PO_3$

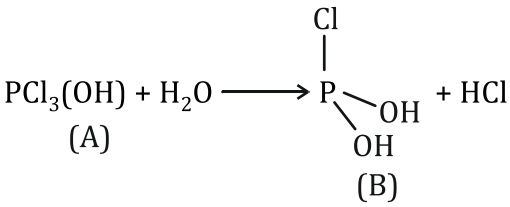
$\underset{(A)}{H_3PO_3} + PCl_3 \longrightarrow \underset{(B)}{H_4P_2O_5} + HCL$



(B)

Number of non-ionisable protons in 'B' are 2.

62. (2) $PCl_3 + H_2O \xrightarrow[\text{hydrolysis}]{\text{Partial}} \underset{(A)}{PCl_2(OH)} + HCl$



(B)

Number of ionisable protons in B = 2

63. **(C)**

Name of oxo acids	Oxidation state
Hypophosphorous acid (H_3PO_2)	+1
Orthophosphorous acid (H_3PO_3)	+3
Hypophosphoric acid ($H_4P_2O_6$)	+4
Orthophosphoric acid (H_3PO_4)	+5

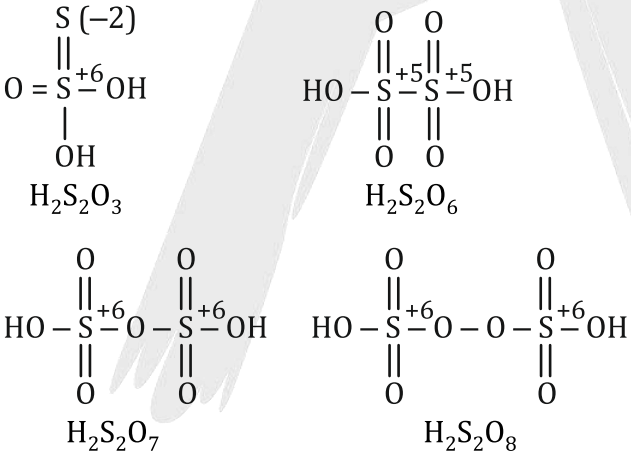
64. (A) As positive oxidation state increase, the acidic character increases.

Pentavalent oxides, E_2O_5 has E in +5 oxidation state. Trivalent oxides; E_2O_3 has E in +3 oxidation state. So, Acidic character $E_2O_5 > E_2O_3$ Down the group non-metallic/acidic character decreases.

Topic – 2

Group – 16 Element (Oxygen Family)

65. (A) Sulphur have a general tendency to form two double bond.



66. (c) $X = Na_2SO_3$

$$\underset{(X)}{SO_3^{2-}} + H_2SO_4 \rightarrow [H_2SO_3] \rightarrow H_2O + \underset{(Y)}{SO_2}$$

$$SO_2 + 2NaOH \rightarrow \underset{(X)}{Na_2SO_3} + H_2O$$

$$\underset{(X)}{Na_2SO_3} + \underset{(Y)}{SO_2} + H_2O \rightarrow \underset{(Z)}{2NaHSO_3}$$

67. If $(O.S)_{actual} > (O.S)_{actual}$ [Peroxy linkage]

$(O.S)_{actual} = (O.S)_{max}$[Oxy linkage]

$(O.S)_{actual} < (O.S)_{max}$[Non metal-non-metal bond]

Max O.S of sulphure $= +6$

For H_2SO_3

$x + 2 - 6 = 0 \Rightarrow x = +4$

For H_2SO_4

$x + 2 - 8 = 0 \Rightarrow x = +6$

For H_2SO_4

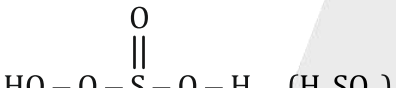
$x + 2 - 8 = 0 \Rightarrow x = +6$

For $H_2S_2O_8$

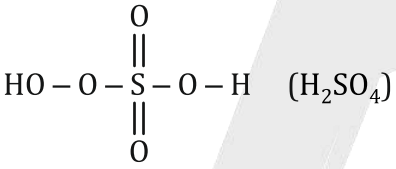
$2x + 2 - 16 = 0 \Rightarrow x = 7$

For $H_2S_2O_7$

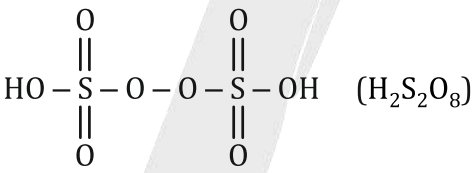
$2x + 2 - 14 = 0 \Rightarrow x = +6$



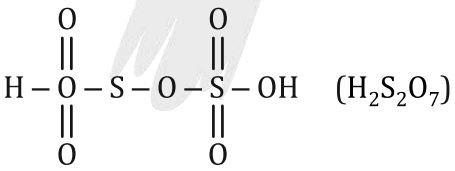
(H_2SO_3)



(H_2SO_4)



$(H_2S_2O_8)$



$(H_2S_2O_7)$

68. (1) α-sulphur and β-sulphur are diamagnetic. S_2-form is paramagnetic.

Topic-3

Group – 17 Elements (Halogen Family)

69. (C) The reaction involved is:

$I_2 + 10HNO_3$ (conc) $\rightarrow 2HIO_3 + 10NO_2 + 4H_2O$

70. (B) Br_2 + Excess $F_2 \rightarrow BrF_5$

[Hint: Due to high reactivity of BrF_5, it absorbs moisture from surrounding resulting into formation of $HBrO_3$]

71. (D) The stability of oxides of halogens decreases in the order I > Cl > Br

The stability of oxides of iodine is greater than those of chlorine and bromine. Iodine oxygen bond is stable due to greater polarity of the bond while the stability of the chlorine oxygen bond is due to multiple bond formation involving d-orbitals of the chlorine atom. Bromine being in between, lacks both these characteristics. Thus the stability of oxides of halogens decreases as mentioned above.

72. (A) Generally, bond energy $\propto \frac{1}{\text{Bond length}}$

So, bond energy order is : C-F > C − Cl > C − Br > C − I

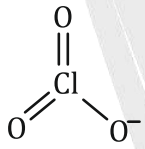
73. (3) AB_5 species have square pyramidal structures. Hence, BrF_5, IF_5 and ClF_5.

74. (3) The number of halogen forming halic (V) acid is 3. $HClO_3$, $HBrO_3$ and HIO_3 are those acids.

75. $\underset{\text{Hot \& conc.}}{3Cl_2} + 6NaOH \rightarrow 5\underset{(X)}{NaCl} + \underset{(Y)}{NaClO_3} + 3H_2O$

$\underset{(X)}{NaCl} + AgNO_3 \rightarrow \underset{\text{(white ppt.)}}{AgCl} + NaNO_3$

Average bond order between Cl and O



atom in $NaClO_3 = \frac{5}{3} = 1.67$

76. (A) Due to small size and high electronegativity of fluorine it can not expand its oxidation state and show only one oxoacid i.e., HOF

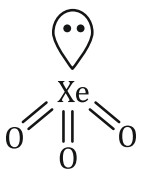
Topic-4

Group-18 Element (Noble Gases)

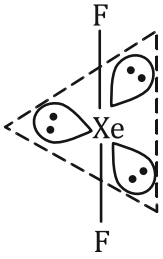
77. (3) S. N of Xe $= 4(3\ B \cdot P + 1\ell.P)$

(A) Steric number of Xe = 4 (3B.p. +11 .p.)

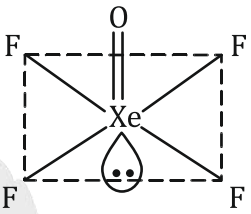
Hybridization = sp^3; shape = pyramidal geometry = tetrahedral



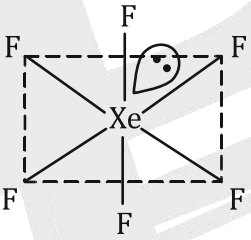
(B) Steric number of Xe = 5 (2B.p. +31. p.) Hybridization = sp^3d; shape = linear geometry = trigonal bipyramidal



(C) Steric number of Xe = 6 (5B.p. +11. p.) Hybridization = sp^3d^2; shape = square pyramidal geometry = octahedral



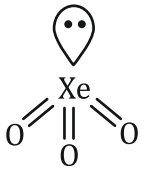
(D) Steric number of Xe = 7 (6B.P. +11. p.) Hybridization = sp^3d^3 Shape = distorted octahedral



78. (A) (a) $\underset{sp^3}{H_3\underline{P}O_2} \xrightarrow{\text{Disproportionation}} \underset{sp^3}{H_3\underline{P}O} + \underset{sp^3}{\underline{P}H_3}$ (B) $\underset{sp^3}{H_2\underline{S}O_4} + NaCl \xrightarrow{420K} \underset{sp^3}{Na_2\underline{S}O_4} + 2HCl$

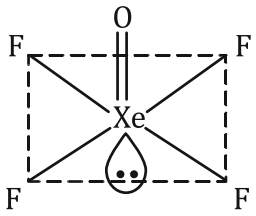
(C) $\underset{sp^3}{\underline{N}H_3} \xrightarrow{H^+} \underset{sp^3}{\underline{N}H_4^+}$ (D) $\underset{sp^3d^2}{\underline{Xe}F_4} + 5bF_5 \longrightarrow \underset{sp^3d}{[\underline{Xe}F]^+}[SbF_6]^-$

79. S. N of Xe = $4(3\ B.P + 1\ell.P)$



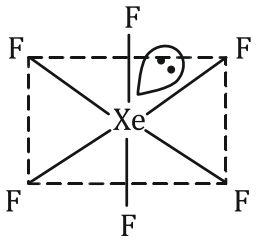
– One lone pair on central atom

S.N of Xe = 6(5B.P+1ℓ.P)



– One lone pair on central atom

S.N of Xe = 7 (6B.P+1ℓ.P)



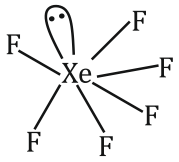
– One lone pair on central atom

Total lone pair = 1+1+1=3

SOLUTION JEE ADVANCED

86. (1) α-sulphur and β-sulphur are diamagnetic. S_2-form is paramagnetic.

87. $XeF_4 + O_2F_2 \rightarrow XeF_6 + O_2x$



Shape of XeF_6 is distorted octahedral contains one lone pair e^-s on central atom 3 lone pair e^-s on each F atom surrounded by Xe.

Total no. of lone pairs: $1 + 18 = 19$

88. (A) X: Ag, Y: Pb

$$AgNO_3 \xrightarrow{NaCl} AgCl\,(s);\ PbNO_3 \xrightarrow{NaCl} PbCl_2(s)$$

$$\underset{(P)}{AgCl(s)} + NH3(aq) \rightarrow \underset{\text{soluble}}{[Ag(NH_3)_2]^+}$$

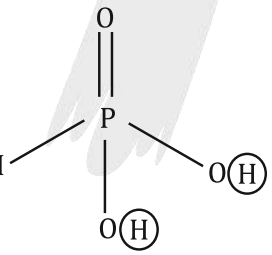
$$PbCl_2(s) + KI \longrightarrow PbI_2$$

(Q) yellow ppt.

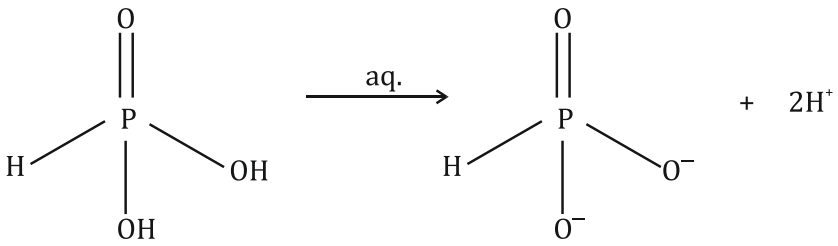
$$AgCl(s) + Na_2S_2O_3 \longrightarrow Na_3[Ag(S_2O_3)_2] + NaCl$$

89. (a) $4H_3PO_3 \xrightarrow{\Delta} 3H_3PO_4 + PH_3$ (correct)

(b) H_3PO_4 has "P" in its highest oxidation state, hence cannot act as a reducing agent (correct)

(c)  So, it is dibasic acid (incorrect)

(d) The hydrogen which is directly attached to phosphorous does not ionized in water.



90. $2ClO_2 + 2O_3 \rightarrow Cl_2O_6 + 2O_2$

$Cl_2O_6 \Rightarrow 2x + 6(-2) = 0$

91. (2.38) $P_4 + 3NaOH + 3H_2O$

(White phosphorous)

$\xrightarrow[\text{atmosphere}]{\text{Inert}} \underset{\text{phosphine}}{PH_3\uparrow} + 3NaH_2PO_2$

PH_3 : a non-inflammable gas in its Phosphine in water.

When PH_3 is absorbed in $CuSO_4$ solution cupric phosphide forms: $2PH_3 + 3CuSO_4 \longrightarrow CuP_2 + 3H_2SO_4$ 1 mol of $P_4 = 31 \times 4 = 124$ g

$\therefore$ 1.24 g of white phosphorous = 0.01 mol

$\therefore$ 0.01 mol°P_4 forms 0.01 mol°PH_3

No. of moles of $CuSO_4$ is required for complete consumption of 0.01 mol $= 0.01 \times \frac{3}{2} = 15 \times 10^{-3}$

M.W. of $CuSO_4 = 159$ g/mol

$\therefore$ Amount of $CuSO_4$ required $= 15 \times 10^{-3} \times 159 = 2.38$ g

92. (C) $2HClO_3 + 2HCl \longrightarrow \underset{\text{(paramegnetic)}}{2ClO_2} + Cl_2 + 2H_2O$

$2ClO_2 + 2O_3 \longrightarrow Cl_2O_6 + 2O_2$

93. Correct option is (D) **P → 2; Q → 3; R → 4; S → 5**

$P_2O_3 + H_2O \rightarrow H_3PO_3$

$P_4 + NaOH + H_2O \rightarrow PH_3 + NaH_2PO_2$

$PCl_5 + CH_3COOH \rightarrow CH_3\overset{\overset{O}{\|}}{C}—Cl + POCl_3 + HCl$

$H_3PO_2 + H_2O + AgNO_3 \rightarrow H_3PO_4 + HNO_3 + Ag\downarrow$

Hence :-

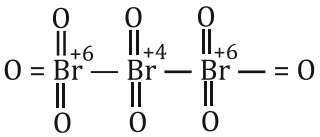
P → 2

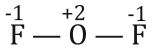
Q → 3

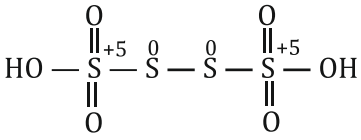
R → 4

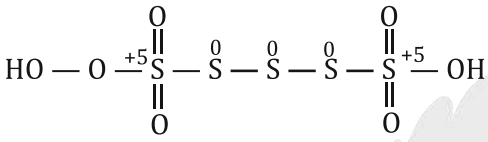
S → 5

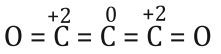
94.











Total atom with zero oxidation number state are 6 .