MIND MAP

p - Block

Nitrogen Family

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

Electronic Configuration

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

Ionisation Enthalpy

N > P > As > Sb > Bi (IE_1 values)

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

Chemical Properties

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

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

Anomalous Properties of Nitrogen :-

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

Dinitrogen

Laboratory Preparation

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

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

Dinitrogen can also be obtained by the thermal decomposition of Ammonium Dichromate.

$$(NH_4)_2Cr_2O_7 \xrightarrow{Heat} N_2 + 4H_2O + Cr_2O_3$$

Reaction with Non-Metals

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

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

Ammonia

Preparation

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

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

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

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

Properties

Ammonia is a colourless gas with a pungent odour.

Its freezing and boiling points are 198.4 and 239.7 K respectively.

Nitrous Acid (HNO_2)

Preparation

(a) M−nitrite $\xrightarrow[HCl \text{ or } H_2SO_4]{\text{dil.acid}} HNO_2$

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

Properties

1. Oxidising Property

Because of its easy oxidation to liberate nascent oxygen, it acts as a strong oxidant

$2HNO_2 \longrightarrow H_2O + 2NO + [O]$

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

2. Reducing Property

Nitrous acid also acts as a reducing agent as it can be oxidised into nitric acid.

$HNO_2 + (O) \longrightarrow HNO_3$

$2KMnO_4 + 5HNO_2 + 3H_2SO_4 \downarrow$

$K_2SO_4 + 2MnSO_4 + 5HNO_3 + 3H_2O$

3. Physical Properties

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

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

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Laboratory Method

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

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

Large Scale Preparation (Ostwald's Process)

This method is based upon catalytic oxidation of NH_3 by atmospheric Oxygen.

$4NH_3(g) + 5O_2(g) \xrightarrow[500K, 9bar]{\text{Pt/Rh−gauge catalyst}} 4NO(g) + 6H_2O(g)$

(from air)

Chemical Properties

Oxidising Nature

Nitric acid acts as a strong oxidising agent as it decomposes to give nascent Oxygen easily.

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

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

(a) Sulphur is oxidised to sulphuric acid

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

Conc. and hot

(b) Carbon is oxidised to carbonic acid

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

Oxidation of Metalloids

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

Antimony is oxidised to antimonic acid

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

(conc. and hot)

Oxidation of Compounds

Ferrous sulphate is oxidised to ferric sulphate in presence of H_2SO_4

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

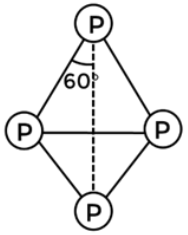
Iodine is liberated from KI.

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

Uses

The major use of nitric acid is in the manufacture of ammonium nitrate for fertilizers and other nitrates for use in explosives and pyrotechnics.

Allotropic Forms of Phosphorus



White Phosphorus

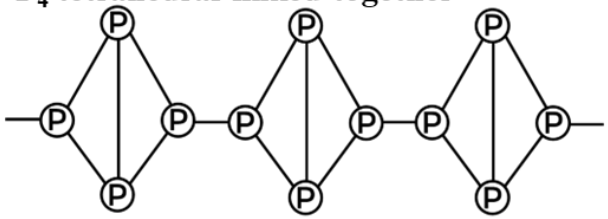
It dissolves in boiling NaOH solution in an inert atmosphere giving PH_3.

$P_4 + 3NaOH + 3H_2O \longrightarrow PH_3 + 3NaH_2PO_2$

(sodium hypophosphite)

Red Phosphorus

It is polymeric, consisting of chains of P_4 tetrahedral linked together



Red Phosphorus

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Black Phosphorus has two forms α-black Phosphorus and β-black Phosphorus.

α-black Phosphorus is formed when red Phosphorus is heated in a sealed tube at 803K.

Phosphine

Preparation

Phosphine is prepared by the reaction of Calcium phosphide with water or dilute HCl.

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

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

Properties

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

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

Uses

The spontaneous combustion of phosphine is technically used in Holme's signals.

Phosphorus Trichloride

Preparation

By passing dry Chlorine over heated white Phosphorus.

$P_4 + 6Cl_2 \longrightarrow 4PCl_3$

Properties

It is a colourless oily liquid.

Hydrolyses in the presence of moisture.

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

It reacts with organic compounds containing –OH group such as CH_3COOH, C_2H_5OH.

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

Phosphorus Pentachloride

Preparation

By the reaction of white Phosphorus with excess of dry Chlorine.

$P_4 + 10Cl_2 \longrightarrow 4PCl_5$

Properties

It hydrolysis in moist air to $POCl_3$ and finally gets converted to phosphoric acid.

$PCl_5 + H_2O \longrightarrow POCl_3 + 2HCl$

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

Finely divided metals on heating with PCl5 give corresponding chlorides.

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

Uses

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

Iodine is liberated from KI.

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

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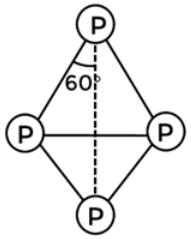

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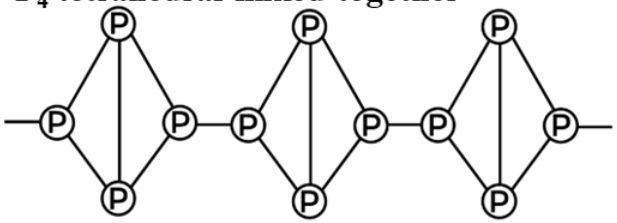

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Types of Simple Oxide

Simple oxides can be classified on the basis of their acidic, basic or amphoteric character.

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).

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.

Amphoteric Oxide

Some metallic oxides exhibit a dual behaviour.

They show characteristics of both acidic as well as basic oxides. Al_2O_3 reacts with acids as well as alkalies.

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,H_2O NO and N_2O.

Ozone

Threats To Ozone Layer

(i) Experiments have shown that nitrogen oxides (particularly nitric oxide) combine very rapidly with ozone.

There is 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.

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

Preparation

$$3O_2(g) \longrightarrow 2O_3$$

$$\Delta H^- (298\ K) = +142\ kJ\ mol^{-1}$$

Properties

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

(ii) It is diamagnetic gas.

Toxic Effect

(a) Toxic enough (more toxic than KCN).

It's intense blue colour is due to the absorption of red light.

Oxidizing Properties

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

$$O_3 + 2H^+ + 2e \longrightarrow O_2 + H_2O$$

$$E^\circ = +2.07\ V$$

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

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

Allotropic Forms of Sulphur

The stable form at room temperature is Rhombic Sulphur ,which transforms to Monoclinic Sulphur when heated above 369 K.

$$\alpha\text{—Sulphur} \underset{<369\ K}{\overset{>369\ K}{\rightleftharpoons}} \beta\text{—Sulphur}$$

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 dissolve to some extent in Benzene, Alcohol and Ether.

(iv) It is readily soluble in CS_2.

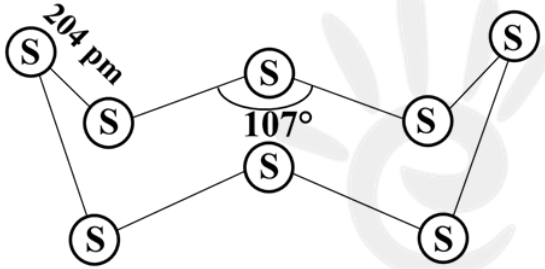
Monoclinic Sulphur (β - Sulphur)

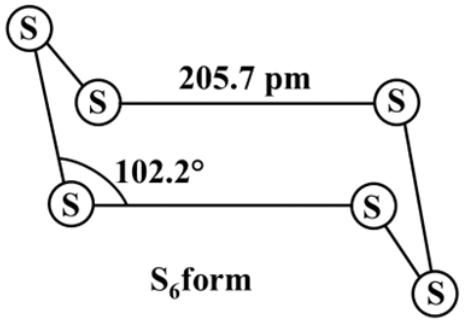
(i) Its m.p. is 393 K and specific gravity 1.98.

(ii) It is soluble in CS_2.

(iii) This form of Sulphur is prepared by melting rhombic sulphur in a dish and cooling ,till crust is formed. Two holes are made in the crust and the remaining liquid poured out.

Structure of α and β Sulphur





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Sulphur Dioxide

Laboratory Method

By treating a sulphite with dilute Sulphuric acid.

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

Properties

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

(ii)It is highly soluble in water.

(iii)Acidic character Sulphur dioxide, when passed through water, forms a solution of Sulphurous acid.

$$SO_2(g) + Cl_2 \xrightarrow[\text{of Charcoal}]{\text{In Presence}} SO_2Cl_2(\ell)$$

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

Reducing Properties

When moist, Sulphur dioxide behaves as a reducing agent.

$$2Fe^{3+} + SO_2 + 2H_2O \longrightarrow 2Fe^{2+} + So_4^{2-} + 4H^+$$

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

Hydrogen Sulphide (H_2S)

Preparation

By the action of dil. HCl or H_2SO_4 on Iron Pyrites.

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

Properties

(i) It is a colourless gas having an offensive smell of rotten eggs.

(ii)It burn in air with blue flame

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

(iii)If the air supply is in excess

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

(iv) It is a mild acid.

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

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

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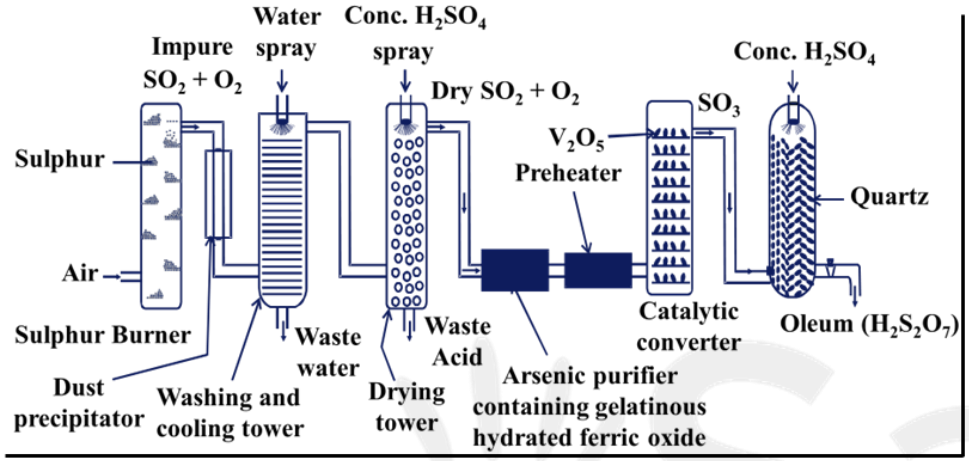
Sulphuric Acid
Industrial Manufacturing (Contact process)



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.

Chemical Properties

(a) Low volatility

(b) Strong acidic character

(c) Strong affinity for water

(d) Ability to act as an oxidizing agent.

Acidic Character

In aqueous solution, sulphuric acid ionises in two steps.

Acidic Character

$$H_2SO_4(aq) + H_2O(\ell) \longrightarrow H_3O^+(aq) + HSO_4^-(aq)$$

= Very large (K > 10)

$$HSO_4^-(aq) + H_2O(\ell) \longrightarrow H_3O^+(aq) + SO_4^{2-}(aq)$$

$K = 1.2 \times 10^{-2}$

Dehydrating Property

Concentrated sulphuric acid is a strong dehydrating agent.

Many wet gases can be dried by passing them through sulphuric acid, provided the gases do not react with the acid.

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

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

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

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

Oxidizing Nature

Hot concentrated Sulphuric acid is a moderately strong oxidising agent.

In this respect, it is intermediate between phosphoric and nitric acids.

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

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

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Uses

It is needed for the manufacture of hundreds of other compounds and also in many industrial processes.
The bulk of sulphuric acid produced is used in the manufacture of fertilisers

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).

Bond energy order

$Cl_2 > Br > F_2 > I_2$

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

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 $F_2 > Cl_2 > Br_2 > I_2$

Reactivity Towards Water

The relative oxidising power of halogens can further be illustrated by their reactions with water.

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

$$X_2(g) + H_2O(\ell) \longrightarrow HX(aq) + HOX(aq)$$

(where X = Cl or Br)

$$4I^-(aq) + 4H^+(aq) + O_2(g) \longrightarrow 2I_2(s) + 2H_2O(\ell)$$

Reason for the Anomalous Behaviour of Fluorine

The Anomalous behaviour of Fluorine is due to its small size, highest electronegativity, low F-F bond dissociation enthalpy, and non availability of d-orbitals in valence shell.

Reactivity Towards Oxygen

Halogens form many Oxides with Oxygen but most of them are unstable.

Fluorine forms two Oxides OF_2 and O_2F_2.

However, only OF_2 is thermally stable at 298 K.

Both are strong fluorinating agents.

O_2F_2 oxidises Plutonium to PuF_6 and the reaction is used in removing Plutonium as PuF_6 from spent nuclear fuel.

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.

Reactivity of Halogens towards other Halogens

Halogens combine amongst themselves to form a number of compounds known as interhalogens of the types XX', XX_3', XX_5' and XX_7'