

Transition Elements

In periodic table the d block elements are placed between s block and p block elements. These are called transition elements because they show gradual degradation of periodic properties. The transition elements are mainly defined as those elements which either in atomic or ionic state contains partially filled d sub-shells.

It must be noted that the elements of group 12 (Zn, Cd and Hg) have completely filled d sub-shells in atomic as well as ionic form, so they do not truly represent transition elements. Moreover, they also do not exhibit general properties of transition elements like variable oxidation state, coloured compounds, formation of complex compounds etc. However, they are studied with transition elements just to maintain the status of periodic table. Further, it must be noted that the elements of group 3 (Sc, Y, La and Ac) differ in their properties from those of other transition elements (they are uniformly trivalent, diamagnetic and colourless).

General electronic configuration: $(n - 1) d^{1 \rightarrow 10} ns^{1 \rightarrow 2}$

Transition elements involve the filling of d sub-shell of penultimate shell. On the basis of the number of partially filled d sub-shell, d block elements are classified into four series (3d, 4d, 5d and 6d) series.

General Characteristic of d-Block Elements

Metallic Character

All transition elements are metallic in nature. They have tendency to form strong covalent bonds due to partially filled d sub-shell (except Zn, Cd, Hg) as well as strong metallic bond due to large number of electrons to be lost. Their melting and boiling points are very high (above 1000°C except Zn, Cd and Hg), they are very hard and brittle and have high densities.

Atomic Radii

Due to small screening effect of d sub-shell the atomic radius decreases with increase in atomic number. The size of transition of elements is small due to which their densities and ionization energies are high.

Oxidation State

During formation of compounds d orbital of inner shell can also participate in bonding so the transition elements exhibit variable oxidation state (except 3rd group and 12th group elements). The oxidation state of 3rd group elements (Sc, Y, La, Ac) is +3 whereas the oxidation state of 12th group (Zn, Cd, Hg) is +2 only. In lower oxidation states (+2, +3) the bonds formed are ionic, whereas in higher oxidation state the bonds formed are covalent. The highest possible oxidation state is +8 for transition elements.

Ionisation Energy

Ionisation energy of transition elements is in between those of s block and p block elements. Ionisation energy of transition elements in a particular series increases due to increase in nuclear charge. It must be kept in mind that the ionization energies of 5d elements is more than 3d and 4d elements because of very poor shielding of the nucleus by 4f electrons.

Complex formation

Transition metal ions have a great tendency to form complexes with other molecules or ions (which can donate electrons to form coordinate bonds) called ligands. This property of formation of complexes is due to vacant d orbitals (to accept electron pair) and high nuclear charge with small size, which facilitates the acceptance of electrons from the ligands.

The complexes of transition elements of small size are more stable as compared to those of large size element in a particular series with same

oxidation state. If the oxidation state is different, then the complex with more oxidation state of central metal will be more stable.

Colour

The d-orbitals in the transition metal ions and their complexes do not have same energies. Under the influence of anions or ligands, the d orbitals split into two sets. The energy difference of these two sets corresponds to visible region of spectrum. Due to the absorption of visible radiation for d-d transitions most of the compounds and complexes of transition elements are coloured. The colour will appear if the central metal contains partially filled d sub-shell. But if the d-subshell is completely filled, it will be colourless (eg. Cu^+ , Ag^+ , Sc^{3+} etc.).

Catalytic Properties

Transition metals and their compounds can absorb large number of substances at their surface, which reacts faster due to increased concentrations at surface (adsorption theory of catalysis). So they can catalyse many reactions.

Transition metals can form intermediate compounds with many substance due to variable oxidation states. So they provide new paths of lesser activation energies for several chemical reactions (activated complex theory). And so the rates of reaction will be increased by using these compounds as catalyst.

Magnetic Properties

Substances can be classified into two categories on the basis of magnetic behaviour. Some substances are slightly repelled by magnetic field, so they weigh less in magnetic field and are called diamagnetic substances. Second category of substances are attracted by magnetic field, so they weigh more in magnetic field and are called paramagnetic substances.

If all the electrons of the transition metal atom or its ion in compound are paired, the substances will be diamagnetic. And if any unpaired electron is present, the substances will be paramagnetic. Further paramagnetism increases with increase in number of unpaired electrons and is given by

$$m = \sqrt{n(n+2)} \text{ B.M.}$$

where n is number of unpaired electrons and B.M. is the unit of magnetic moment.

Reducing Character

The reduction potentials of transition elements (except Cu & Hg) are more than that of hydrogen electrodes, so they can liberate H₂ gas on treatment with acids. But sometimes transition elements other than Cu & Hg also does not displace hydrogen from acidic solutions due to formation of layer of inert oxides at their surface.

Formation of Alloys

One transition metal can replace another metal in crystal lattice due to similar size, resulting in the formation of alloys or solid solutions. These alloys have generally high melting points and are hard.

Interstitial Compounds

Transition metals can take up atoms of small size (H, C, N) in the voids of their lattice to form interstitial compounds, which have more tensile strength.

Inner Transition Elements

The f-block elements consists of two series of inner transition elements i.e. lanthanides and actinides. They are also called rare earth elements. Lanthanides involve the filling of 4f-orbitals while actinides involve the filling of 5f-orbitals in their atoms. These f-orbitals belong to the shell third from the outer shell. This factor accounts for some characteristic properties of these elements. The electronic configurations of the elements with fully filled (f^{14}) and half-filled (f^7) f-orbitals are relatively more stable. The extra stability of half-filled orbitals is seen in the elements europium ($4f^7, 6s^2$) and gadolinium ($4f^7 5d^1 6s^2$).

Lanthanides

The series of elements involving the filling of 4f orbitals is called actinide series. They follow La (57) and include element from atomic number 58 to 71. Except for gadolinium and lutetium which have a single electron in 5d orbitals the lanthanides do not have electrons in the 5d orbitals.

Physical and Chemical Properties of Lanthanides

Lanthanides are silvery white metals having low tensile strengths. They are good conductors of heat and electricity. Some of their physical properties are given below:

Density

Lanthanides have high densities ranging between 6.77 to 9.74 g cm^{-3} . The densities, in general, increase with increase in atomic number.

Melting point

Lanthanides have fairly high melting points. However, no definite trend is observed in melting and boiling points from La to Lu.

Ionisation energies

Lanthanides have fairly low ionization energies. The IE_1 and IE_2 values are quite comparable to those of alkaline earth metals particularly calcium.

Electropositive character

Lanthanides have high electropositive character due to low ionization energies.

Coloured Ions

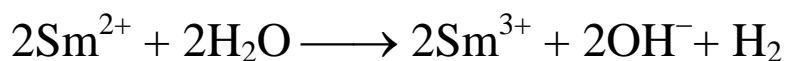
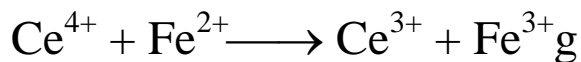
Many of the lanthanide ions are coloured in solid state as well as in solutions. The colour is attributed to f-f transition since they have partly filled f-orbitals.

Magnetic behaviour

The lanthanide ions (M^{3+}) generally show paramagnetism due to the unpaired electrons in f-orbitals.

Oxidation states

The lanthanides exhibit a principal oxidation state of +3. The +3 oxidation states in lanthanum, gadolinium and lutetium are especially stable because +3 ions of these elements have an empty, a half-filled and completely filled 4-f sub-shell respectively. Cerium and terbium also exhibit oxidation state of +4. Ce^{4+} has configuration $4f^0$ and Tb^{4+} has the configuration $4f^7$. Sm^{2+} ($4f^6$), Eu^{2+} ($4f^7$) and Yb^{2+} ($4f^{14}$) ions also exist in aqueous solutions. Although a few lanthanides exhibits oxidation states of +4 and +2, yet they have the tendency to attain the oxidation state of +3 because the +3 oxidation state is most stable state for all lanthanides. For example, Ce^{4+} is a good oxidizing agent while Sm^{2+} is a good reducing agent.



Lanthanide Contraction

The atomic radii and ionic radii of tripositive lanthanide ions (M^{3+}) show a steady and gradual decrease in moving from La to Lu. Although the atomic radii do show some irregularities but ionic radii decrease steadily from La to Lu. The steady decrease in the size of lanthanide ions (M^{3+}) with the increase in atomic number is called lanthanide contraction.

Cause of lanthanide contraction:

As the atomic number increases in lanthanide series, for every proton in the nucleus the extra electron goes to fill 4f orbitals. The 4f-electrons constitute inner shells and are rather ineffective in screening the nuclear charge. Thus, there is a gradual increase in the effective nuclear charge experienced by the outer electrons. Consequently, the attraction of the nucleus for the electrons in the outer most shell increase as the atomic number of lanthanides increases and the electron cloud shrinks. This result in gradual decrease in size of lanthanides with increase in atomic number.

Consequences of Lanthanide Contraction

(i) Similarity of second and third transition series:

The atomic radii of second row of transition elements are almost similar to those to the third row of transition elements. For example, among the elements of group 3, there is normal increase in size from Sc to Y to La. But after lanthanides the atomic radii from second to third transition series do not increase for group 4 and 5 etc.

Here the usual increase in size on moving down the group from second to third transition elements is cancelled by the decrease in size due to lanthanide contraction. Also as a result of lanthanide contraction the second and third rows of transition elements resemble each other more closely than do the first and second row.

(ii) Separation of lanthanides

Separation of lanthanides is also possible due to lanthanide contraction. All the lanthanides have quite similar properties and due to this reason they are difficult to be separated. However, because of lanthanide contraction their properties (such as ability to form complexes) vary slightly. This slight variation in properties is utilized in the separation of lanthanides by ion exchange methods.

(iii) Variation in basic strength of hydroxides:

The basic strength of hydroxide decreases from $\text{La}(\text{OH})_3$ to $\text{Lu}(\text{OH})_3$. Due to lanthanide contraction size of M^{3+} ions decreases and there is increase in the covalent character in $\text{M}-\text{OH}$ bond.

(iv) Chemical reactivity:

Many lanthanides react with carbon to form salt-like carbides and with hydrogen to give salt-like hydrides. Lanthanides react with oxygen and sulphur to form oxides (M_2O_3) and sulphides (M_2S_3) respectively. Cerium gives CeO_2 . The M_2O_3 oxides react with water to form insoluble hydroxides. Oxides and hydroxides on reaction with CO_2 gives carbonates, $\text{M}_2(\text{CO}_3)_3$. Lanthanide compounds are generally ionic. These compounds are generally coloured and exhibits paramagnetism. These elements occur together in nature because of their great chemical similarity and are difficult to separate. However, because of lanthanide contraction they do exhibit slight variation in their properties and this becomes the basis of their separation by ion-exchange methods.

Actinides

The series of elements involving the filling of 5f orbitals is called actinide series. They follow Ac(89) and include element from Th(90) to Lw(103). The chemistry of actinides is more complicated due to the existence of greater range of oxidation states for these metals. Moreover, all these metals are radioactive and therefore, their accessibility for laboratory investigations is limited. The elements beyond uranium are all man-made elements and are made by nuclear-chemical methods.

Physical and Chemical properties of Actinides

Oxidation states

The common oxidation state of these elements is +3. However, they also exhibit oxidation state of +4, +5, +6.

Physical appearance

Actinides are silvery white metals. They get tarnished when exposed to the attack of alkalis.

Density

All the actinides except thorium and americium have high densities.

Colour

The actinide ions in general are coloured. The appearance of colour depends upon the number of 5f-electrons. The ions containing $5f^0$ and $5f^7$ configuration are colourless. While those having 2 to 6 electrons in 5f-shell are coloured.

$U^{3+} (5f^3)$: Red, $Np^{3+} (5f^4)$: Bluish, $Pu^{3+} (5f^6)$: Blue, $Am^{3+} (5f^6)$: Pink

Ionisation energies

Ionisation energy values of actinides are low.

Electropositive character

All the known actinide metals are highly electropositive. They resemble lanthanide series in this respect.

Melting and boiling points

They have high melting point and boiling points. They do not follow regular gradation of melting or boiling point with increase in atomic number.

Magnetic properties

The actinides are paramagnetic due to the presence of unpaired electrons.

Radioactive nature

All the actinides are radioactive in nature.

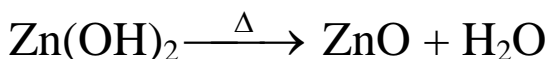
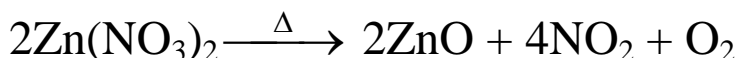
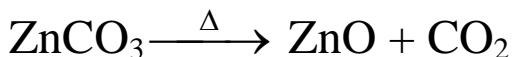
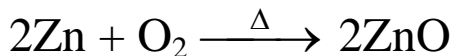
Actinide contraction

The size of atom/cation decrease regularly along the actinide series. The steady decrease in ionic radii with increase in atomic number is referred to as actinide contraction. This is due to poor shielding of 5f-electrons.

Zinc Compounds

Zinc Oxide (Zinc-White Or Philosopher's Wool)

Preparation



Very pure zinc oxide is prepared by mixing a solution of zinc sulphate with sodium carbonate. The precipitated basic zinc carbonate on heating gives pure zinc oxide.

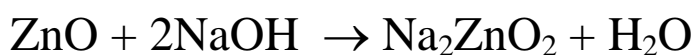
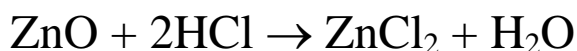
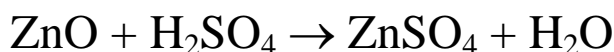


White ppt



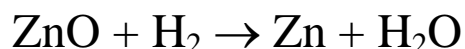
Properties

- (i) It is a white powder. It becomes yellow on heating and again turns white on cooling.
- (ii) It is very light. It is insoluble in water. It sublimes at 400°C.
- (iii) It is an amphoteric oxide and dissolves readily in acids forming corresponding zinc salts and alkalies forming zincates.

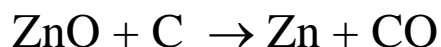


Sodium zincate

(iv) When heated in hydrogen above 400°C, it is reduced to metal.



It is also reduced by carbon into zinc.

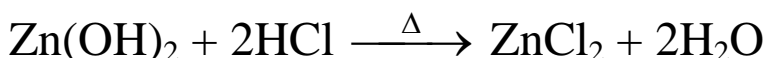
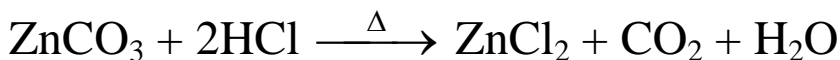
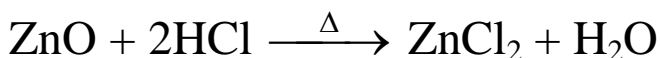


(v) When zinc oxide is heated with cobalt nitrate, a green mass is formed due to formation of cobalt zincate, which is known as Rinmann's green.

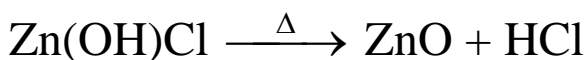
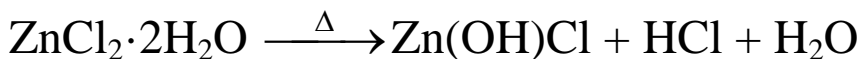


Zinc Chloride, $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$

Preparation



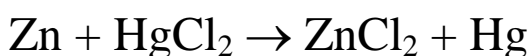
Anhydrous zinc chloride cannot be obtained by heating crystals of hydrated zinc chloride as hydrolysis occurs and basic chloride (zinc hydroxy chloride) is formed which on further heating gives zinc oxide.



The anhydrous zinc chloride is obtained by heating zinc in the atmosphere of dry chlorine or dry HCl gas.

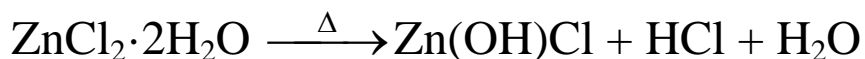


This can also be formed by distilling zinc powder with mercuric chloride.



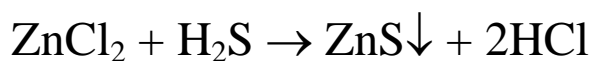
Properties

- (i) Anhydrous zinc chloride is a white solid, deliquescent and soluble in water. It melts at 660°C and boils at 730°C.
- (ii) Hydrated zinc chloride on heating forms zinc hydroxy chloride or zinc oxychloride.



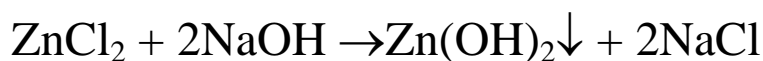
Zinc oxychloride

- (iii) When H_2S is passed through the solution, a white precipitate of zinc sulphide is formed.

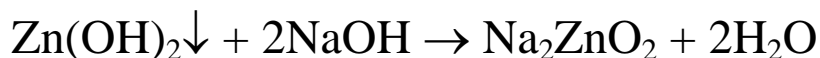


White ppt

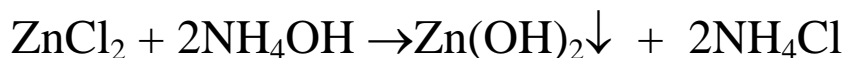
- (iv) When NaOH is added, a white precipitate of zinc hydroxide appears which dissolves in excess of sodium hydroxide forming sodium zincate.



White ppt



- (v) On adding NH_4OH solution, a white precipitate of zinc hydroxide appears which dissolves in excess of ammonia forming a complex salt.



White ppt



Tetramminezinc(II) chloride

d and f Block Elements

- (vi) When the solution of zinc chloride is treated with a solution of sodium carbonate, a white precipitate of basic zinc carbonate is formed.



Basic zinc carbonate

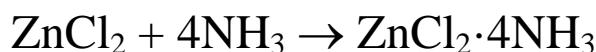
White ppt

But when a solution of sodium bicarbonate is used, a white precipitate of normal zinc carbonate is formed.



White ppt

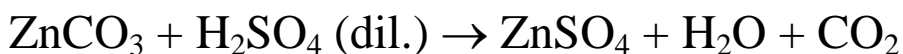
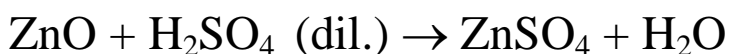
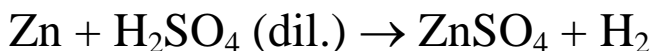
- (vii) Anhydrous zinc chloride absorbs ammonia gas and forms an addition compound.



- (viii) Its syrupy solution dissolves cellulose. Its syrupy solution when mixed with zinc oxide (ZnO) sets to a hard mass forming an oxychloride, $\text{ZnCl}_2 \cdot 3\text{ZnO}$.

Zinc Sulphate (White Vitriol) $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$

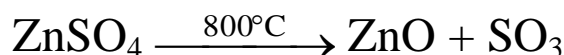
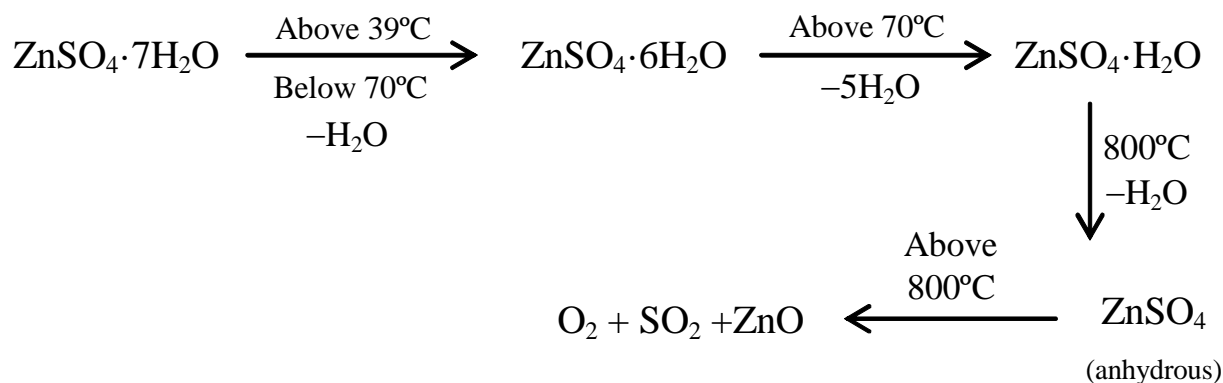
Preparation



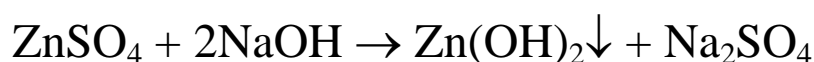
Properties

- (i) It is a colourless, crystalline solid. It is an efflorescent substance. It is freely soluble in water.
- (ii) On heating, the following changes occur.

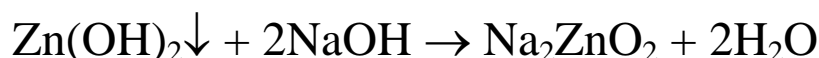
d and f Block Elements



- (iii) When sodium hydroxide is added to the solution of zinc sulphate, a white precipitate of zinc hydroxide appears which dissolves in excess of NaOH forming sodium zincate.



White ppt



- (iv) When sodium carbonate solution is added to the solution of zinc sulphate, a white precipitate of basic zinc carbonate is formed.



White ppt

However, when the solution of sodium bicarbonate is added, normal zinc carbonate is formed.



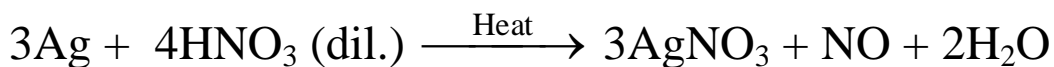
White ppt

- (v) With alkali metal sulphates and $(\text{NH}_4)_2\text{SO}_4$, it forms double sulphates such as $\text{K}_2\text{SO}_4 \cdot \text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$.

Silver Compounds

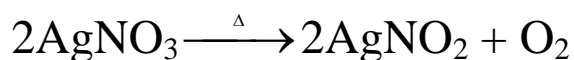
Silver Nitrate (Lunar Caustic), AgNO_3

Preparation

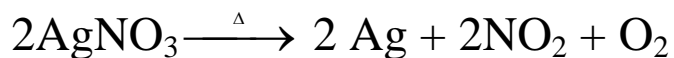


Properties

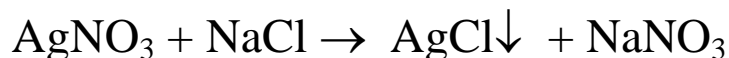
- (i) It is a colourless crystalline compound, soluble in water and alcohol. It melts at 212°C .
- (ii) In contact with organic substances, it blackens due to decomposition into metallic silver. Thus, it leaves black stain when comes in contact with skin and clothes. It produces burning sensation like caustic and leaves a blackish–white stain (moon like colour) on skin and thus called as *Lunar caustic*. It is decomposed by light also and therefore stored in coloured bottles.
- (iii) On heating above its melting point, it decomposes to silver nitrite and oxygen.



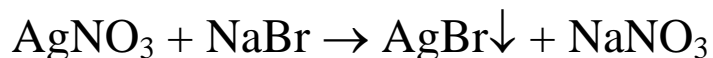
When heated in a red hot tube, it decomposes to metallic silver.



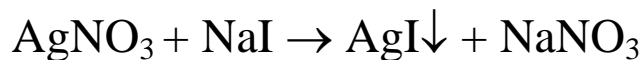
- (iv) Solutions of halides, phosphates, sulphides, chromates, thiocyanates, sulphates and thiosulphates, all give a precipitate of the corresponding silver salt with silver nitrate solution.



White ppt

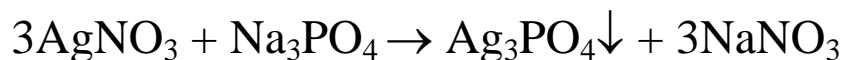


Pale yellow ppt

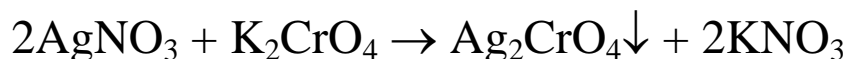


d and f Block Elements

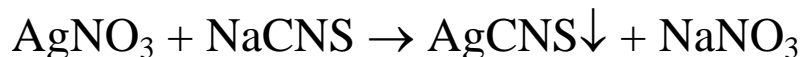
Yellow ppt



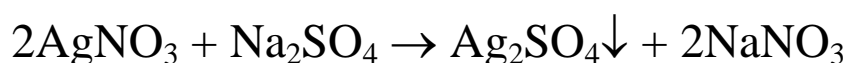
Yellow ppt



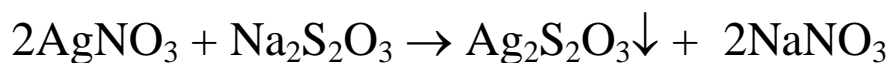
Brick red ppt



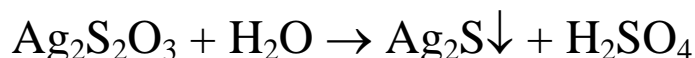
White ppt



White ppt



White ppt



Black ppt

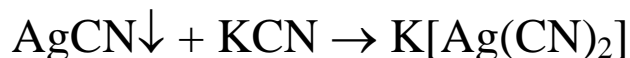
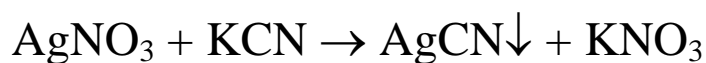
(v) Solid AgNO_3 absorbs ammonia gas with the formation of an addition compound, $\text{AgNO}_3 \cdot 3\text{NH}_3$.

(vi) When treated with a solution of NaOH , it forms precipitate of silver oxide. Originally, it has brown colour but turns black when dried.



Brown ppt

(vii) When KCN is added to silver nitrate, a white precipitate of silver cyanide appears which dissolves in excess of KCN forming a complex salt, potassium argentocyanide.

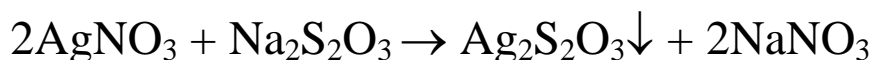


d and f Block Elements

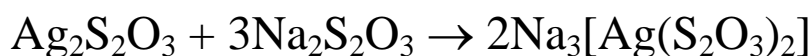
White ppt

Potassium argentocyanide

- (viii) When sodium thiosulphate is added to silver nitrate, a white precipitate of silver thiosulphate appears. This precipitate, however, dissolves in excess of sodium thiosulphate forming a complex salt.

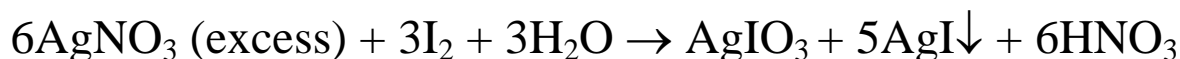


White ppt



Sodium argentothiosulphate

- (ix) AgNO_3 reacts with iodine in two ways:

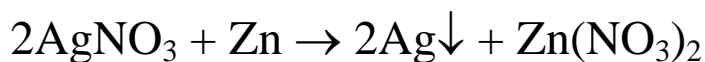
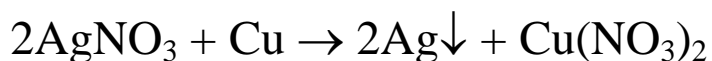


Yellow ppt

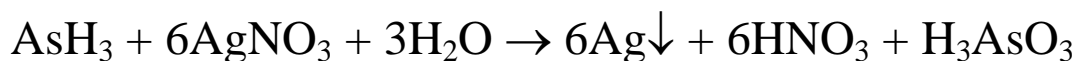
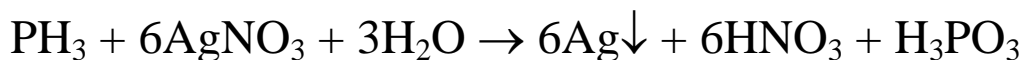


Yellow ppt

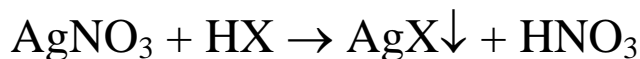
- (x) Silver is readily displaced from an aqueous silver nitrate solution by the base metals, particularly, if the solution is somewhat acidic.



- (xi) Phosphine, arsine and stibine all precipitate silver from silver nitrate solution.



- (xii) All halogen acids, except HF, precipitate silver halides from aqueous solution of AgNO_3 . [Silver fluoride (AgF) is soluble in water].



d and f Block Elements

(xiii) When NH_4OH is added to silver nitrate solution, a brown precipitate of silver oxide appears which dissolves in excess of ammonia forming a complex salt.

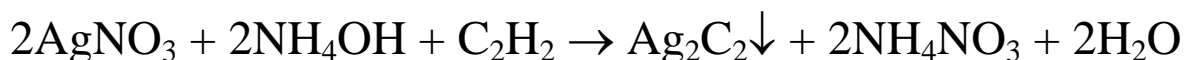


Brown ppt



The ammonical solution of AgNO_3 gives the following reaction:

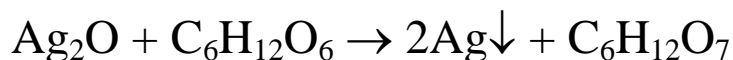
(a) It reacts with acetylene to form white precipitate of silver acetylide.



Silver acetylide

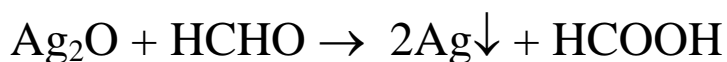
White ppt

(b) It converts glucose to gluconic acid.



Silver mirror

(c) It oxidises formaldehyde to formic acid.



Silver mirror

Silver Oxide, (Ag₂O)

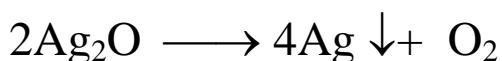
Preparation



Brown ppt

Properties

It is brownish powder insoluble in water and thermally unstable. It decomposes to silver and oxygen.

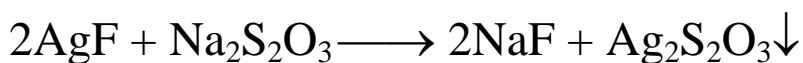


Ag₂O is soluble in aqueous ammonia.

Silver Thiosulphate, Ag₂S₂O₃

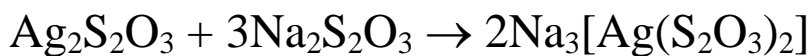
Preparation

Addition of more than the equivalent amount of sodium thiosulphate to a solution of silver acetate or fluoride, when a white precipitate of silver thiosulphate is formed.

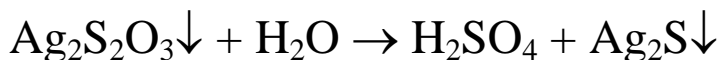
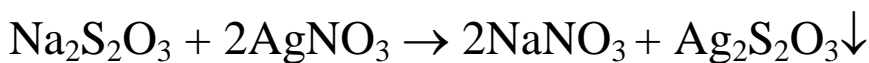


Properties

It forms needle-like crystals. It dissolves in excess of sodium thiosulphate solution producing a complex.



Silver thiosulphate is decomposed by water giving play of colour test, changing from white to black through yellow and brown, when silver nitrate solution is mixed with dilute sodium thiosulphate solution.



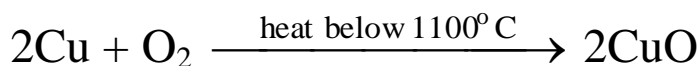
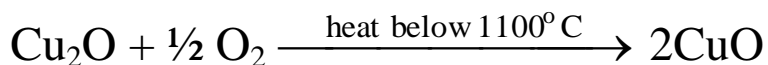
Copper Compounds

Cupric Oxide, CuO (Black Oxide of Copper)

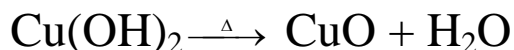
Preparation

It is prepared by the following methods.

- (i) By heating Cu₂O in air or by heating copper for a long time in air. The temperature should not exceed above 1100°C.



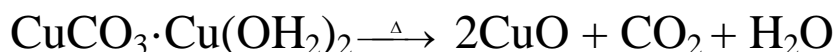
- (ii) By heating cupric hydroxide also, cupric oxide can be obtained.



- (iii) By heating copper nitrate also, cupric oxide can be obtained.

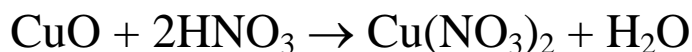
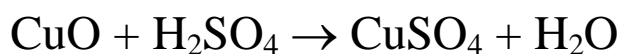
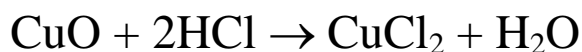


- (iv) On commercial scale, it is obtained by heating malachite, which is found in nature.



Properties

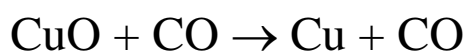
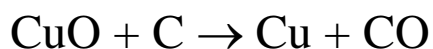
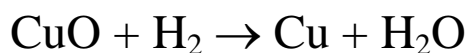
- (i) It is a black powdery substance and is stable towards moderate heating.
- (ii) The oxide is insoluble in water but dissolves in acids forming corresponding salts.



- (iii) When heated to 1100–1200°C, it is converted into cuprous oxide with evolution of oxygen.



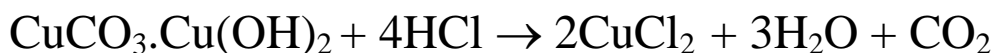
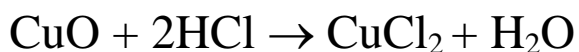
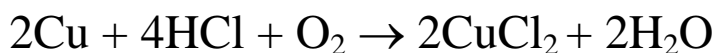
- (iv) It is reduced to metallic copper by reducing agents such as hydrogen, carbon and carbon monoxide.



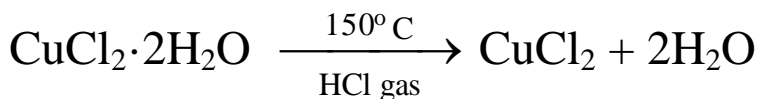
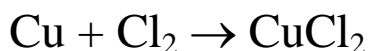
Cupric Chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$)

Preparation

- (i) The metal or cupric oxide or cupric hydroxide or copper carbonate is dissolved in concentrated HCl. The resulting solution on crystallization gives green crystals of hydrated cupric chloride.



- (ii) Anhydrous cupric chloride is obtained as a dark brown mass when copper metal is heated in excess of chlorine gas or by heating hydrated cupric chloride in HCl gas at 150°C.

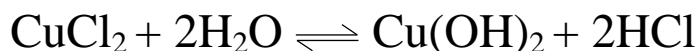


Properties

- (i) It is a deliquescent compound and is readily soluble in water. The dilute solution is blue but the concentrated solution is green. It

changes to yellow when concentrated HCl is added. The blue colour is due to complex cation $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ and yellow colour is due to the complex anion $[\text{CuCl}_4]^{2-}$ and green when both are present.

The aqueous solution is acidic due to hydrolysis of Cu^{2+} .



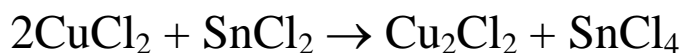
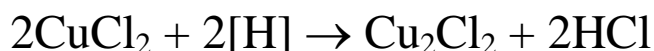
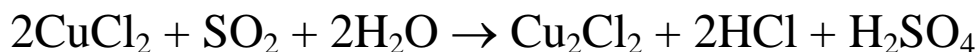
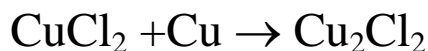
(iii) The anhydrous salt on heating forms Cu_2Cl_2 and Cl_2 .



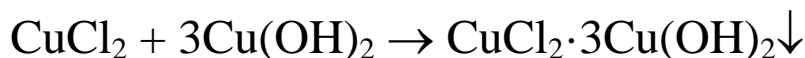
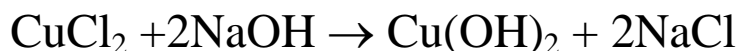
While the hydrated salt on strong heating gives CuO , Cu_2Cl_2 , HCl and Cl_2 .



(iv) It is readily reduced to Cu_2Cl_2 by copper turnings or SO_2 gas or nascent hydrogen (obtained by the action of HCl on Zn) or SnCl_2 .

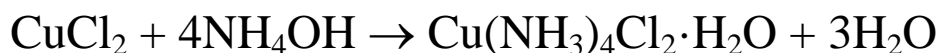


(v) A pale blue precipitate of basic cupric chloride, $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$ is obtained when NaOH is added.



Blue ppt

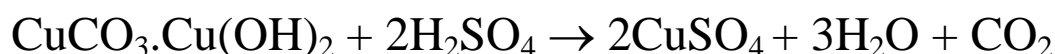
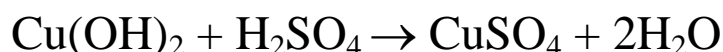
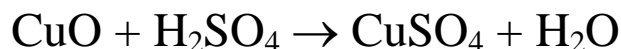
It dissolves in ammonium hydroxide forming a deep blue solution. On evaporating this solution, deep-blue crystals of tetramminecupric chloride are obtained.



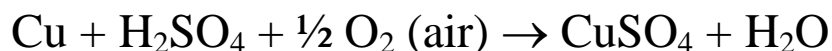
Copper Sulphate (Blue Vitriol) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

Preparation

- (i) Copper sulphate is prepared in the laboratory by dissolving cupric oxide or hydroxide or carbonate in dilute sulphuric acid. The solution is evaporated and crystallized.



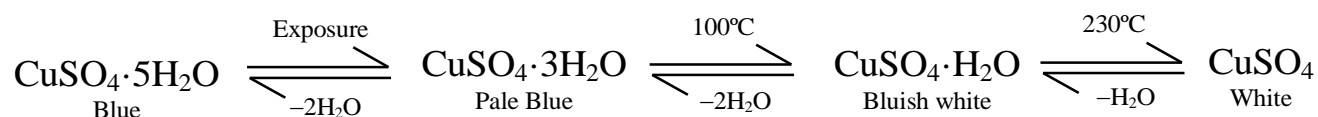
- (ii) On a commercial scale, it is prepared from scrap copper. The scrap copper is placed in a perforated lead bucket, which is dipped into hot dilute sulphuric acid. Air is blown through the acid. Copper sulphate is crystallized from the solution.



Properties

- (i) It is a blue crystalline compound and is fairly soluble in water.
- (ii) Heating effect

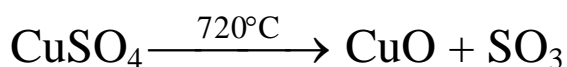
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ crystals effloresce on exposure to air and are converted into a pale blue powder, $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$. When heated to 100°C , bluish white monohydrate $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ is formed. The monohydrate loses the last molecule of water at 230°C giving the anhydrous salt of CuSO_4 , which is white.



Anhydrous copper sulphate (white) regains its blue colour when moistened with a drop of water (test of water).

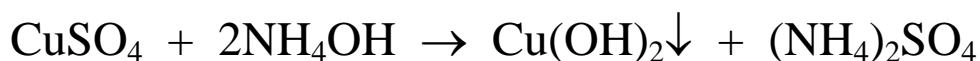
d and f Block Elements

If the anhydrous salt is heated at 720°C, it decomposes into cupric oxide and sulphur trioxide.

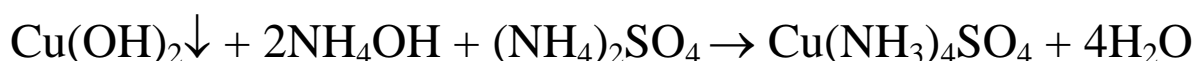


(iii) Action of NH_4OH

With ammonia solution, it forms the soluble blue complex. First it forms a precipitate of $\text{Cu}(\text{OH})_2$ which dissolves in excess of ammonia solution.



Blue ppt

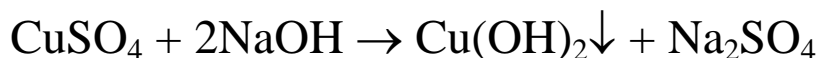


Tetramminecupric sulphate

The complex is known as Schweitzer's reagent, which is used for dissolving cellulose in the manufacture of artificial silk.

(iv) Action of alkalies

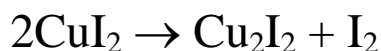
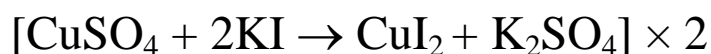
With alkalies, CuSO_4 forms a pale blue precipitate of copper hydroxide.



Blue ppt

(v) Action of potassium iodide

First cupric iodide is formed, which decomposes to give white cuprous iodide and iodine.



(vi) Action of potassium cyanide

First cupric cyanide is formed which decomposes to give cuprous cyanide and cyanogen gas. Cuprous cyanide dissolves in excess of potassium cyanide to form a complex, potassium cuprocyanide $[\text{K}_3\text{Cu}(\text{CN})_4]$.

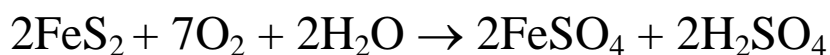


Iron Compounds

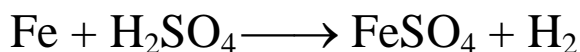
Ferrous Sulphate (Green Vitriol), $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$

Preparation

- (i) By the oxidation of pyrites under the action of water and atmospheric air.

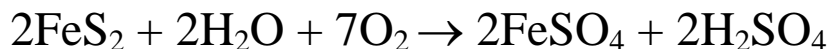


- (ii) It is obtained by dissolving scrap iron in dilute sulphuric acid.



The solution is crystallized by the addition of alcohol as ferrous sulphate is sparingly soluble in it.

- (iii) It can also be prepared in the laboratory from the Kipp's waste. Heating with a small quantity of iron fillings neutralizes the excess of sulphuric acid. The solution is then crystallised.
- (iv) Commercially, ferrous sulphate is obtained by the slow oxidation of iron pyrites in the presence of air and moisture. The pyrites are exposed to air in big heaps.



The free sulphuric acid is removed by the addition of scrap iron. On crystallization, green crystals are obtained.

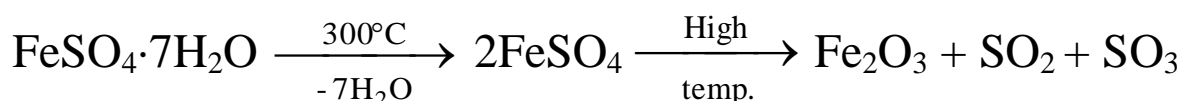
Properties

- (i) Hydrated ferrous sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) is a green crystalline compound. Due to atmospheric oxidation, the crystals acquire brownish–yellow colour due to formation of basic ferric sulphate.



Basic ferric sulphate

- (ii) Action of heat



Ferrous Ammonium Sulphate (Mohr's Salt)

$(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$

Preparation

The double salt is best prepared by making saturated solutions of pure ferrous sulphate and pure ammonium sulphate in air free distilled water at 40°C . Both the solutions are mixed and allowed to cool. Generally, few drops of sulphuric acid and a little iron wire are added before crystallisation so as to prevent oxidation of ferrous sulphate into ferric sulphate. The salt is obtained as pale green crystals.

Properties

It is pale green crystalline compound, which does not effloresce like ferrous sulphate. It is less readily oxidised in the solid state. It is, therefore, a better volumetric reagent in preference of ferrous sulphate. Chemically, it is similar to ferrous sulphate. All the chemical reactions

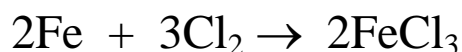
observed in the case of ferrous sulphate are given by ferrous ammonium sulphate.

Ferric Chloride (FeCl₃)

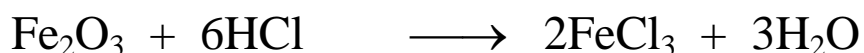
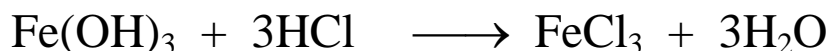
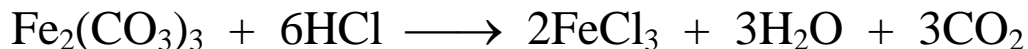
This is the most important ferric salt. It is known in anhydrous and hydrated forms. The hydrated form consists of six water molecules, FeCl₃.6H₂O.

Preparation

- (i) Anhydrous ferric chloride is obtained by passing dry chlorine gas over heated iron fillings. The vapours are condensed in a bottle attached to the outlet of the tube.



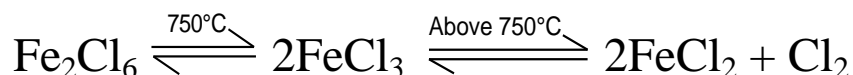
- (ii) Hydrated ferric chloride is obtained by the action of hydrochloric acid on ferric carbonate, ferric hydroxide or ferric oxide.



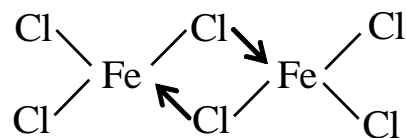
The solution on evaporation and cooling deposits yellow crystals of hydrated ferric chloride, FeCl₃.6H₂O.

Properties

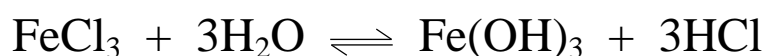
- (i) Anhydrous ferric chloride is a dark red deliquescent solid. It is sublimed at about 300°C and its vapour density corresponds to dimeric formula, Fe₂Cl₆. The dimer dissociates at high temperature to FeCl₃. The dissociation into FeCl₃ is complete at 750°C. Above this temperature, it breaks into ferrous chloride and chlorine.



- (ii) Anhydrous ferric chloride behaves as a covalent compound as it is soluble in non-polar solvents like ether, alcohol, etc. It is represented by chlorine bridge structure.

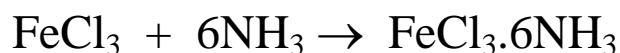


- (iii) It dissolves in water. The solution is acidic in nature due to its hydrolysis as shown below.



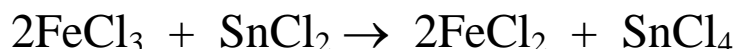
The solution is stabilised by the addition of hydrochloric acid to prevent hydrolysis.

- (iv) Anhydrous ferric chloride absorbs ammonia.

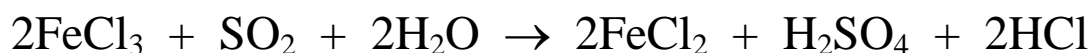


- (v) Ferric chloride acts as an oxidising agent.

- (a) It oxidises stannous chloride to stannic chloride.



- (b) It oxidises SO_2 to H_2SO_4 .



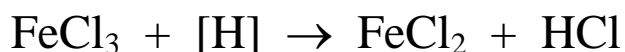
- (c) It oxidises H_2S to S



- (d) It liberates iodine from KI.

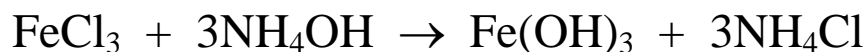


- (e) Nascent hydrogen reduces FeCl_3 into FeCl_2 .

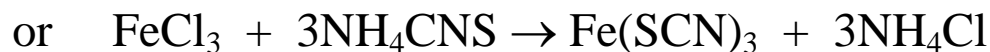


d and f Block Elements

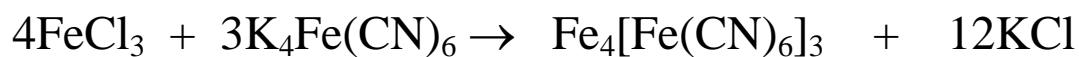
- (vi) When ammonium hydroxide is added to the solution of ferric chloride, a reddish-brown precipitate of ferric hydroxide is formed.



- (vii) When a solution of thiocyanate ions is added to ferric chloride solution, a deep red colouration is produced due to formation of a complex salt.



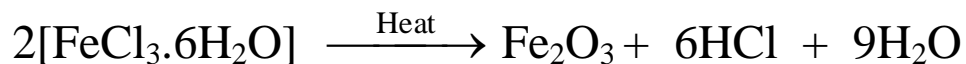
- (viii) Ferric chloride forms a complex, prussian blue with potassium ferrocyanide.



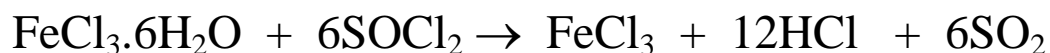
Prussian blue

(Ferri ferrocyanide)

- (ix) On heating hydrated ferric chloride $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, anhydrous ferric chloride is not obtained. It is changed to Fe_2O_3 with evolution of H_2O and HCl .



Hydrated ferric chloride may be dehydrated by heating with thionyl chloride.



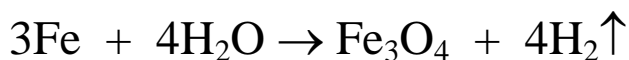
Ferrous Oxide

Preparation

Iron can burn in oxygen when heated, producing magnetic oxide of iron, Fe_3O_4 (an equimolar mixture of FeO and Fe_2O_3).

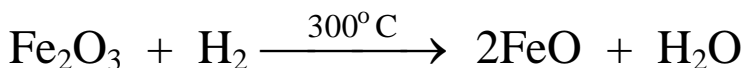


Pure iron has no action with pure water but steam, reacts with red-hot iron liberating hydrogen and forming Fe_3O_4 .



Ferrous oxide (FeO) can be found wherever there is iron exposed to the oxygen in the atmosphere.

The oxide is a black powder, formed by heating ferric oxide with hydrogen at 300°C or by heating ferrous oxalate in absence of air at $160^\circ\text{--}170^\circ\text{C}$.



Properties

- (i) Iron oxide is naturally black in colour and it appears as a solid crystalline substance at room temperature.
- (ii) Melting point of FeO is 1370°C and its density is 5.7 g/cm^3 .
- (iii) Iron oxide will decompose into its elements before boiling.
- (iv) It is oxidized in air with incandescence (pyrophoric).
- (v) It is sparingly soluble in water and as a basic oxide dissolves in dilute acids to give ferrous salts.

- (vi) Iron oxide is commonly used as a pigment for colouring all sorts of materials like paints, plastics and rubber. It is also used for the dye in tattoos.
- (vii) The iron and oxide ions in iron oxide are bonded with ionic bonds, making iron oxide a salt. There is a 1 : 1 ratio of iron ions to oxide ions and being a salt, iron oxide does not have individual molecules, but forms geometrical structure with all of the ions bonded by electrostatic forces.

Passivity of Iron

The inertness exhibited by metals under conditions when chemical activity is to be expected is called chemical passivity. The following are the common properties of iron.

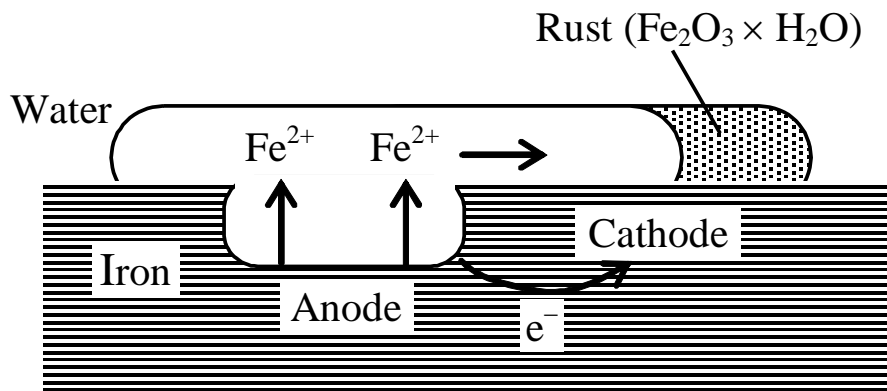
- (a) It evolves hydrogen gas, when made to react with dilute HCl or dilute H_2SO_4 .
- (b) It precipitates silver from silver nitrate solution and copper from copper sulphate solution.

But if a piece of iron is first dipped in concentrated nitric acid for sometime and then made to react with the above reagents, neither hydrogen is evolved nor silver or copper are precipitated. Thus, iron by treatment with concentrated nitric acid has lost its usual properties or it has been rendered inert or passive. Such behaviour is not only shown by iron but also by many other metals like Cr, Co, Ni, Al etc. This phenomenon is known as passivity and the chemical substances, which bring passivity, are called passivators.

Other oxidising agents can render iron passivelike chromic acid, KMnO_4 , concentrated H_2SO_4 etc. The passivity of the iron is believed to be due to formation of an extremely thin film (invisible) of oxide on the surface of iron. Passive iron can be made active by scratching or heating in a reducing atmosphere of H_2 or CO , or heating in HNO_3 upto 75°C .

Corrosion of Iron

Corrosion is defined as the gradual transformation of a metal into its combined state because of the reaction with the environment. Metals are usually extracted from their ores. Nature tries to convert them again into the ore form. The process, by which the metals have the tendency to go back to their combined state, is termed *corrosion*.



When iron is exposed to moist air, it is found to be covered with a reddish–brown coating, which can easily be detached. The reddish brown coating is called ‘rust’. Thus, the corrosion of iron or formation of the rust is called *rusting*. The composition of the rust is not certain but it mainly contains hydrated ferric oxide, $2Fe_2O_3 \cdot 3H_2O$, together with a small quantity of ferrous carbonate. The rust is formed by the action of water on iron in the presence of dissolved oxygen and carbon dioxide. It has been observed that impure iron is more prone to rusting.

The following are the favourable conditions for the rusting of iron

- (i) Presence of moisture
- (ii) Presence of a weakly acidic atmosphere
- (iii) Presence of impurity in the iron.

Various theories have been proposed to explain the phenomenon of rusting of iron but the most accepted theory is the modern electrochemical theory. When impure iron comes in contact with water containing dissolved

d and f Block Elements

carbon dioxide, a voltaic cell is set up. The iron and other impurities act as electrodes while water having dissolved oxygen and carbon dioxide acts as an electrolyte. Iron atoms pass into the solution as ferrous ions.

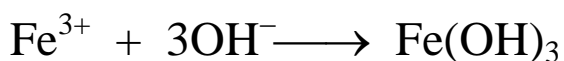


Iron, thus, acts as anode.

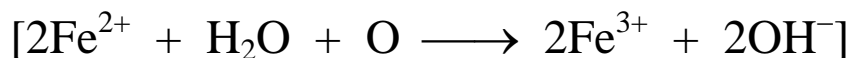
The impurities act as cathode. At the cathode, the electrons are used in forming hydroxyl ions.



In presence of dissolved oxygen, ferrous ions are oxidised to ferric ions, which combine with hydroxyl ions to form ferric hydroxide.



Rust



Corrosion or rusting is a surface phenomenon and thus, the protection of the surface prevents the corrosion. Iron can be protected from the rusting by use of following methods:

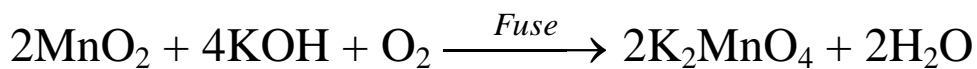
- (i) Applying paints, lacquers and enamels on the surface of iron.
- (ii) By forming a firm and coherent protective coating of ferrosferric oxide. This is done by passing steam over hot iron.
- (iii) By coating a thin film of zinc, tin, nickel, chromium, aluminium, etc.

Manganese Compounds

Potassium Permanganate (KMnO_4)

Preparation

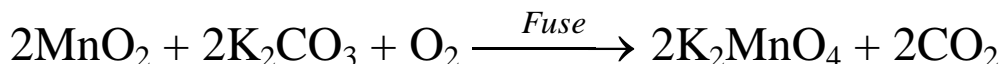
It is prepared by fusion of pyrolusite with KOH or K_2CO_3 and air. Instead of oxygen any other oxidising agent such as KNO_3 may also be used.



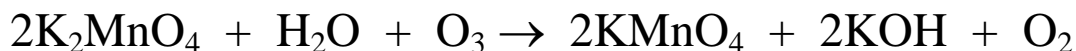
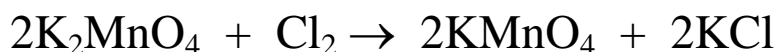
Pyrolusite

Potassium manganates

(Green)



The fused mass is extracted with water and current of Cl_2 or O_3 or CO_2 is passed so as to convert manganates into permanganate.



Potassium permanganate is manufactured by electrolytic oxidation of manganates in alkaline medium.

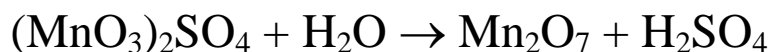
Properties

(i) KMnO_4 is a purple coloured crystalline compound. It is fairly soluble in water.

(ii) When heated alone or with an alkali, it decomposes evolving oxygen.



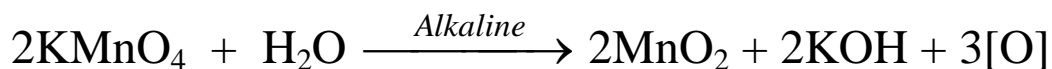
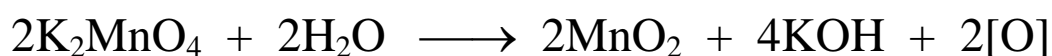
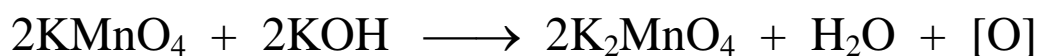
(iii) On treatment with concentrated H_2SO_4 , it forms manganese heptaoxide which decomposes explosively on heating.



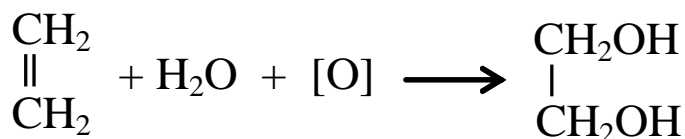
(iv) KMnO_4 acts as an oxidising agent in alkaline, neutral or acidic solutions.

(a) In alkaline solution

KMnO_4 is first reduced to manganate and then to insoluble manganese dioxide. Colour changes first from purple to green and finally becomes colourless. However, brownish precipitate is formed.



It oxidises ethylene to ethylene glycol.



In alkaline medium it is called Bayer's reagent.

(b) In neutral solution

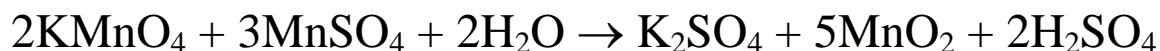
Brownish precipitate of MnO_2 is formed.



(i) H_2S is oxidised to sulphur



(ii) Manganese sulphate is oxidised to MnO_2

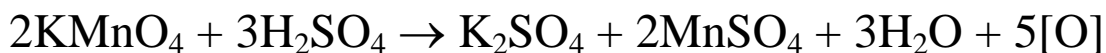


(iii) Sodium thiosulphate is oxidised to sulphate and sulphur



(c) In acidic solution (in presence of dilute H_2SO_4)

Manganous sulphate is formed. The solution becomes colourless.



(i) Ferrous salts are oxidised to ferric salts.



(ii) Iodide is evolved from potassium iodide.



(iii) $2\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 + 5\text{H}_2\text{S} \rightarrow \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 5\text{S} + 8\text{H}_2\text{O}$

(iv) $2\text{KMnO}_4 + 5\text{SO}_2 + 2\text{H}_2\text{O} \rightarrow \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 2\text{H}_2\text{SO}_4$

(v) $2\text{KMnO}_4 + 5\text{KNO}_2 + 3\text{H}_2\text{SO}_4 \rightarrow \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 5\text{KNO}_3 + 3\text{H}_2\text{O}$

(vi) $5\text{H}_2\text{C}_2\text{O}_4 + 2\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 \rightarrow \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 10\text{CO}_2 + 8\text{H}_2\text{O}$

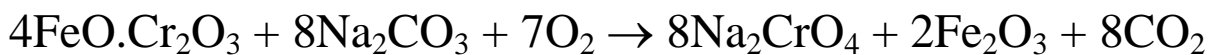
(vii) $2\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 + 10\text{HX} \rightarrow \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 8\text{H}_2\text{O} + 5\text{X}_2$

Chromium Compounds

Potassium Dichromate ($K_2Cr_2O_7$)

Manufacture

Chromite ore is heated with sodium carbonate in presence of air.



Chromite ore (from air)

Na_2CrO_4 is extracted with water, thereby leaving Fe_2O_3 (insoluble) behind and unconverted ore.



This solution is concentrated, when Na_2SO_4 crystallizes out. On further concentration, $Na_2Cr_2O_7$ crystals are obtained.

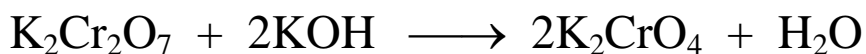
The hot saturated solution of $Na_2Cr_2O_7$ is mixed with KCl . $NaCl$ precipitates out from the hot solution, which is filtered off. On cooling the mother liquor, crystals of $K_2Cr_2O_7$ separates out.

Properties

It is orange-red coloured crystalline compound. It is moderately soluble in cold water but freely soluble in hot water. It melts at $398^\circ C$. On heating strongly, it decomposes liberating oxygen.



On heating with alkalis, it is converted to chromate, i.e. the colour changes from orange to yellow. On acidifying, yellow colour again changes to orange.



Orange

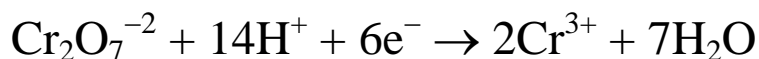
Yellow

d and f Block Elements

In alkaline solution, chromate ions are present while in acidic solution, dichromate ions are present. Potassium dichromate reacts with hydrochloric acid and evolves chlorine.



It acts as a powerful oxidising agent in acidic medium (dilute H_2SO_4).

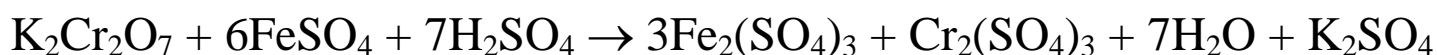


The oxidation state of Cr changes from +6 to +3. Some typical oxidation reactions are given below:

(i) Iodine is liberated from potassium iodide.



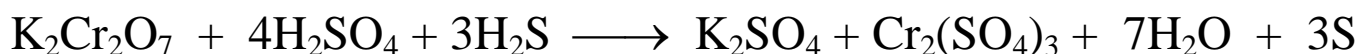
(ii) Ferrous salts are oxidised to ferric salts.



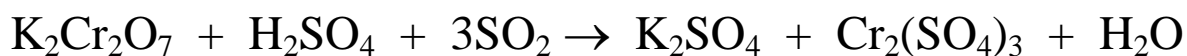
(iii) Sulphites are oxidised to sulphates



(iv) H_2S is oxidised to sulphur



(v) SO_2 is oxidised to H_2SO_4



When the solution is evaporated, chrome-alum is obtained.

(vi) It oxidises ethyl alcohol to acetaldehyde and acetaldehyde to acetic acid.



Ethyl alcohol Acetaldehyde Acetic acid

It also oxidises nitrites to nitrates, arsenites to arsenates, thiosulphate to sulphate and sulphur, HBr to Br₂, HI to I₂, etc.

Chromyl chloride test:

This is a test of chloride. When a mixture of a metal chloride and potassium dichromate is heated with concentration H₂SO₄, orange red vapours of chromyl chloride are evolved.



When chromyl chloride vapours are passed through NaOH solution, yellow coloured solution is obtained.



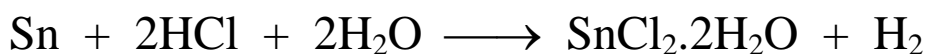
Yellow solution

Tin Compounds

Stannous Chloride, SnCl_2

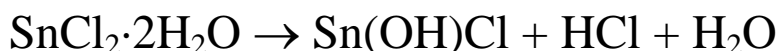
Preparation

Tin dissolved in hot concentrated hydrochloric acid yields $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ on concentrating and crystallization.



Properties

The hydrated salt on heating forms the oxychloride.

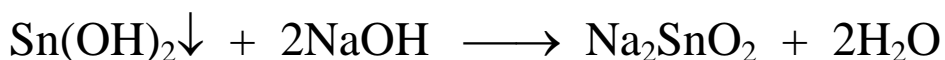
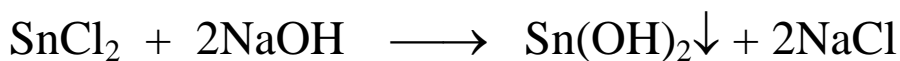


This hydrolysis can be prevented by the presence of excess HCl, with some pieces of tin added.

Aqueous and non-aqueous solutions of tin(II) salts are capable of acting as reducing agents, but they must be stored under an inert atmosphere because air oxidation is spontaneous and rapid.

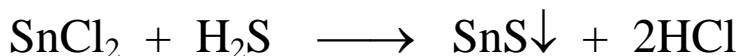


Stannous chloride reacts with NaOH forming a white precipitate of tin(II) hydroxide which dissolves in excess of NaOH forming sodium stannite.

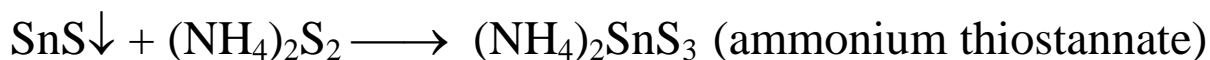


Sodium stannite

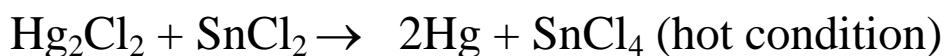
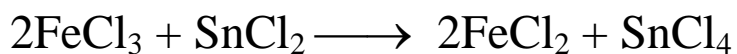
Sodium stannite is oxidised by atmospheric oxygen to form sodium stannate, Na_2SnO_3 . From a solution of stannous chloride, H_2S precipitates brown SnS , soluble in ammonium polysulphides.



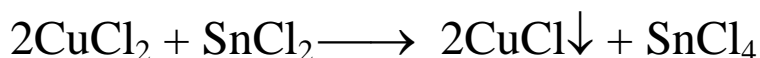
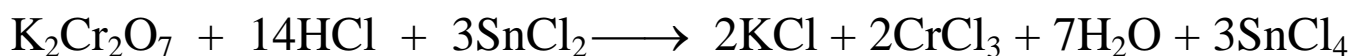
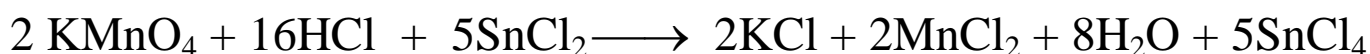
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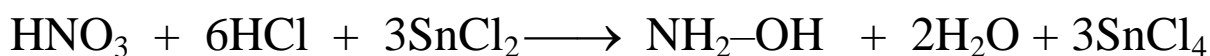
SnCl_2 is a powerful reducing agent, as the following reactions illustrate.



Grey

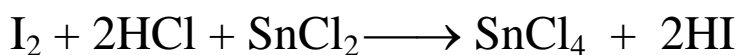
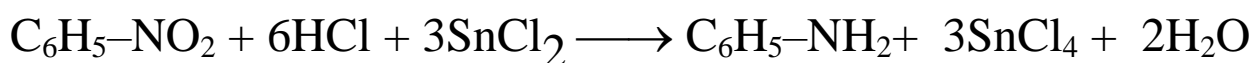


White ppt

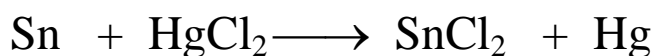
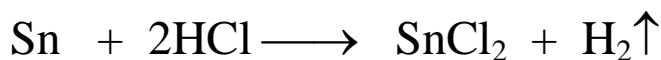


Hydroxylamine

Stannous chloride reduces nitro compounds to amino compounds and iodine to iodides.



Anhydrous stannous chloride, a glassy substance is prepared by heating tin in a stream of HCl or with mercuric chloride.



Excess

Anhydrous SnCl_2 forms a dimer (Sn_2Cl_4) in the vapour, dissolves in organic solvents and forms many addition compounds with NH_3 . e.g. $\text{SnCl}_2 \cdot 2\text{NH}_3$.

In aqueous and non-aqueous solutions Sn(II) forms trihalo complexes, such as $[\text{SnCl}_3]^-$, where the pyramidal structure indicates the presence of a stereochemically active lone pair. The $[\text{SnCl}_3]^-$ ion can serve as a soft donor to d-metal ions. One unusual example of this ability is the red cluster compound $\text{Pt}_3\text{Sn}_8\text{Cl}_{20}$, which is trigonal bipyramidal.

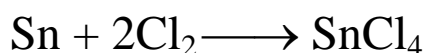
Uses:

As a reducing agent in the laboratory, as a mordant in dyeing and in the preparation of purple of Cassius.

Stannic Chloride, SnCl_4 (Butter of Tin)

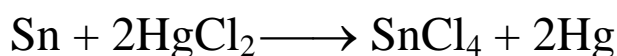
Preparation

Dry Cl_2 gas when passed over heated tin in a retort forms SnCl_4 .

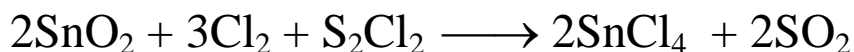


Liquid SnCl_4 is thus collected in a cooled receiver protected from moisture.

It is also made by heating Sn with excess of HgCl_2 .



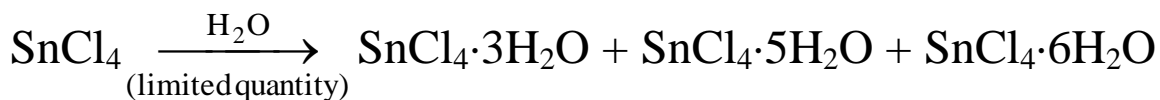
Another method of preparation is from heated SnO_2 by passing mixture of Cl_2 and S_2Cl_2 (sulphur monochloride) vapour over it.



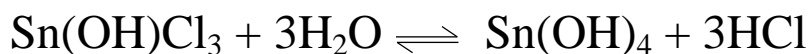
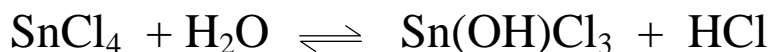
It is also obtained by the removal of tin from (i.e., detinning of) scrap tin plates by chlorine.

Properties

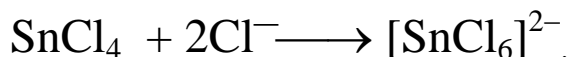
It is a colourless fuming liquid, soluble in organic solvents and volatile in nature. These properties indicate its covalent nature. It forms hydrates with a limited quantity of water but undergoes hydrolysis with excess of water.



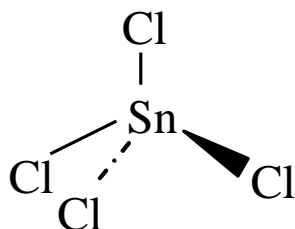
$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ is known as '*butter of tin*' or '*oxymuriate of tin*'. It is used as a mordant and also for weighing silk.



This hydrolytic reaction is slow, reversible and can be suppressed by HCl, with which the following reaction occurs:



Salts with this ion e.g. $(\text{NH}_4)_2\text{SnCl}_6$ are known as chlorostannates. Other addition compounds are obtained with NH_3 , PCl_5 etc., e.g. $\text{SnCl}_4 \cdot 4\text{NH}_3$. The structure of SnCl_4 is



The tetrachloride, bromide and iodide of tin are molecular compounds, but the tetrafluoride has a structure consistent with it being an ionic solid because the small F^- ion permits a six coordinate structure.

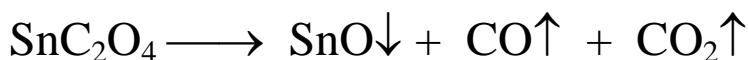
Uses

Butter of tin is used as a mordant and for weighing silk.

Tin(II) Oxide, SnO

Preparation

SnO is precipitated by boiling stannous chloride solution with sodium carbonate or by heating the hydroxide or oxalate in absence of air.



When freshly precipitated, the oxide has the composition $2\text{SnO} \cdot 2\text{H}_2\text{O}$.

Properties

It is usually an olive green powder, which gives greyish crystals in contact with water. When heated in air, it forms the dioxide. Both the oxide and hydrated oxide dissolve in acids forming stannous salts and in alkalies, forming stannites.

Uses

SnO acts as strong reducing agent.

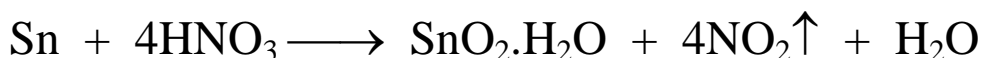
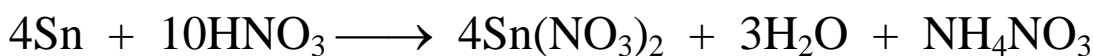


Tin(IV) Oxide, SnO₂

SnO₂ occurs in nature as tinstone or cassiterite.

Preparation

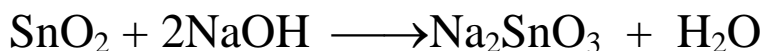
It is easily obtained by combustion of tin in air, by ignition of metastannic acid produced from the action of nitric acid on tin. Cold and dilute nitric acid reacts with tin forming stannous nitrate, while concentrated nitric acid attacks tin with the formation of hydrated stannic oxide.



(hydrated stannic oxide is also known as meta stannic acid)

Properties

It is a soft, white solid sparingly soluble in water and acids except concentrated sulphuric acid but readily soluble in fused alkalis to form stannate.



Uses

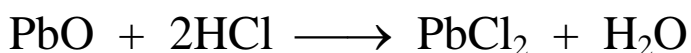
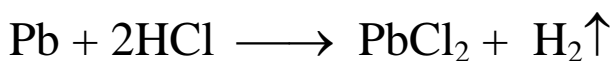
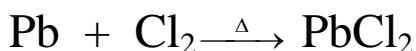
Tin dioxide is used as a polishing powder and the name “putty powder” and for making milky glass and white glazes for tiles and enamels.

Lead Compounds

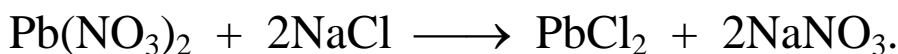
Lead Chloride, PbCl_2

Preparation

Prepared by slow direct combination or by the action of boiling concentrated HCl on lead (its oxide or carbonate).



The usual method of preparation is to precipitate PbCl_2 as a white crystalline precipitate by adding a soluble chloride to a lead salt solution.



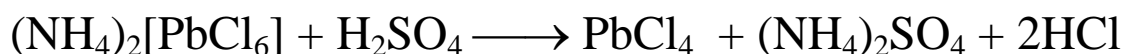
Properties

It is sparingly soluble in cold water but more soluble in hot water. In concentrated solutions of Cl^- ions, it dissolves forming complex ions, $[\text{PbCl}_3]^-$ and $[\text{PbCl}_4]^{2-}$.

Lead Tetrachloride, PbCl_4

Preparation

This is made by dissolving PbO_2 in ice-cold concentrated HCl . Concentrated H_2SO_4 decomposes ammonium chloroplumbate to yield PbCl_4 .

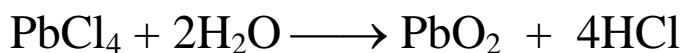


Properties

PbCl_4 is a yellow oily liquid. It is heavy and dissolves in organic solvents. It is a covalent and unstable compound, readily decomposes on heating.



It is easily hydrolysed by water and forms a double salt with NH_4Cl .



Lead tetrabromide and tetraiodide are unknown, so the dihalides dominate the halogen chemistry of lead.

Lead Monoxide, PbO

It naturally occurs as lead ochre (an of various fine earths or days that contain ferric oxide, red, yellow or brown pigment. The colour of this oxide is yellow or red depending on the mode of preparation.

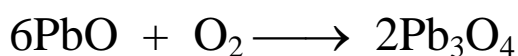
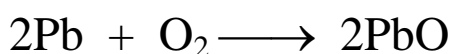
Preparation

When lead is gently heated in air, yellow powder is formed as the monoxide, called massicot. When heating is continued it melts and on cooling gives the reddish–yellow scales of litharge. These differ only in crystalline structure. The transition temperature being 558°C . Lead

monoxide can also be prepared by thermal decomposition of lead nitrate as well as lead carbonate..

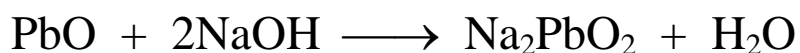
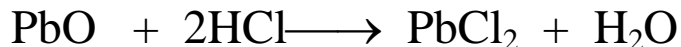


Dry air has no action on lead, but in moist air it tarnishes, forming a film of oxide first and finally basic carbonate, which protects it from further action. On heating in air or oxygen, it forms litharge, PbO. But prolonged heating gives red lead, Pb₃O₄.



Properties

- (i) At room temperature, it is a yellow amorphous powder that is insoluble in water but dissolves in acids as well as alkalies.



Thus, it behaves as an amphoteric oxide. The acidic properties being rather feeble.

- (ii) It is easily reduced to the metallic state by hydrogen, carbon or carbon monoxide.
- (iii) In the red form of PbO, the Pb(II) ions are four coordinate but the O²⁻ ions around the Pb(II) lie in a square.

Uses

Used in paints, in the vulcanisation of rubber and in the preparation of red lead and lead salts.

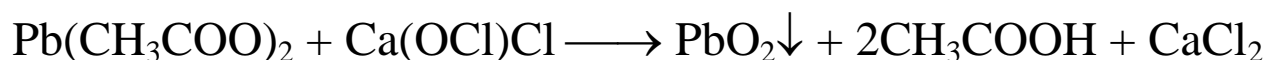
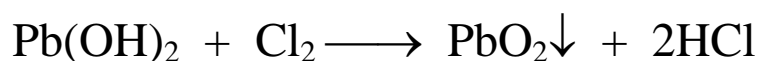
Lead Dioxide, PbO₂

Preparation

- (i) Action of cold concentrated nitric acid on red lead gives lead nitrate in solution while lead dioxide is thrown as a chocolate powder.

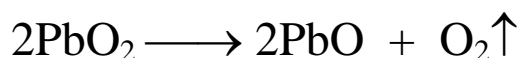


- (ii) Action of powerful oxidizing agents like chlorine, bromine or bleaching powder on alkaline lead salt solution.

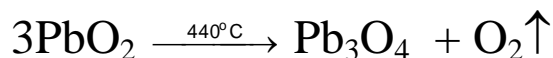


Properties

- (i) It is a chocolate coloured powder insoluble in water and dilute acids.
(ii) It liberates oxygen on gentle heating.



- (iii) At 440°C, it is converted into red lead, Pb₃O₄.



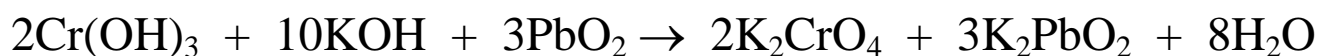
- (iv) PbO₂ is an amphoteric oxide.



- (v) It is a good oxidizing agent. It oxidizes manganous salts to pink permanganic acid when boiled in nitric acid solution.



- (vi) In alkaline medium, chromium hydroxide is oxidized to yellow chromate by PbO₂.



The maroon form of lead(IV) oxide, PbO_2 , crystallizes in the rutile structure. This oxide is a component of the cathode of a lead–acid battery.

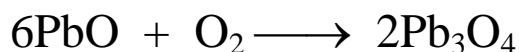
Uses

In the laboratory, lead dioxide finds application as an oxidizing agent. It is also used as the cathode in lead storage battery.

Red Lead, Pb_3O_4

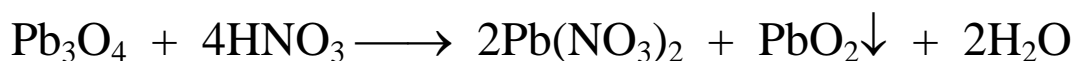
Preparation

Roasting of litharge in air at 450°C gives Pb_3O_4 (a bright red powder also called sindur).



Properties

- (i) Sparingly soluble in water but dissolves in dilute nitric acid.

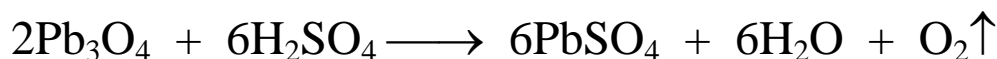


The above reaction indicates that red lead may be considered as plumbous ortho plumbate, $2\text{PbO}.\text{PbO}_2$.

- (ii) It turns dark when heated but restores the original colour on cooling. At about 550°C , it decomposes giving off oxygen.



- (iii) It reacts with concentrated HCl and sulphuric acid liberating chlorine and oxygen respectively.



Red lead, Pb_3O_4 contains $\text{Pb}(\text{IV})$ in an octahedral arrangement and $\text{Pb}(\text{II})$ in an irregular six coordinate environment. The assignment of different

d and f Block Elements

oxidation number to the lead in these two sites is based on the shorter Pb–O distance for the atom identified as Pb(IV).

Uses

Red lead, mixed with linseed oil is extensively used as a red paint and also for plumbing work.