**MANGANESE**

Atomic number 25;

Electronic configuration: 1s22s22p63s23p63d54s2

Possible oxidation states +2, 1s22s22p63s23p63d5

 +3, 1s22s2 2p63s23p63d4

+4, 1s22s22p63s23p63d3

+6, 1s22s22p63s23p63d1

+7, 1s22s22p63s23p6

 **Chemical properties**

1. Strongly heated manganese combines with oxygen to form a mixed oxide.

3Mn(s) + 2O2(g)  Mn3O4(s)

1. Strongly heated manganese reacts with steam forming manganese (II) hydroxide and hydrogen gas.

Mn(s) + 2H2O(g)  Mn(OH)2(s) + H2(g)

1. Reaction with mineral acids

Manganese slowly dissolves in H2SO4 and HCl all which are dilute with evolution of hydrogen gas.

Mn(s) + 2HCl(aq) MnCl2(aq) + H2(g)

Mn(s) + H2SO4(aq) MnSO4(aq) + H2(g)

1. ***Reaction with nitrogen***

Strongly heated manganese combines with nitrogen to from manganese nitride.

3Mn(s) + N2(g) Mn3N2(s)

 **COMPOUNDS OF MANGANESE**

1. *When oxidation state is +2*

 Mn2+ ion in water forms **faint pink** solution due to [Mn(H2O)4]2+

1. **Manganese (II) oxide:**

It is a grey green solid formed by heating manganese II carbonate or manganese II nitrate in absence of oxygen

MnCO3(S) heat MnO(S) +CO2(g)

2Mn(NO3)2(S) heat MnO(s)g) + NO2(g)

 Manganese (II) oxide can also be prepared by heating manganese II oxalate

MnC2 O4(S) heat MnO(S) + CO(g) + CO2(g)

1. **Manganese (II) Hydroxide**

Manganese II hydroxide can be prepared by reacting aqueous alkali solution with manganese II ion solution

Mn2+(aq)+2OH(aq)  Mn (OH)2(s)

**Observation**

A white precipitate insoluble in excess and on standing immediately turns brown.

4Mn(OH)2(s) + O2(g) 2Mn2O3.2H2O(s)

 Brown ppt

1. Manganese (II) sulphates manganese (II) carbonate and manganese (II) chloride are all pink in colour and contain water of crystallization.
2. **When oxidation state is +3**

Manganese (III) compounds are relatively un common because Mn+3 is unstable in aqueous solution it undergoes disproportionation

e.g 2Mn3+(aq) + 2H2O(l) Mn2+(aq) + MnO2(s) + 4H+(aq)

 (i) **Manganese (III) oxide.**

Manganese (III) oxide can be prepared by oxidation of manganese (II) hydroxide in the presence of water.

 4Mn(OH)2(s) + O2(g) 2Mn2O3.2H2O(s)

It can also be prepared by heating manganese (IV) oxide in ammonia gas to form steam and nitrogen gas.

 6MnO2(s) + 2NH3(g) 3Mn2O3(s) + 3H2O(g) + N2(g)

Manganese III oxide is a basic oxide and brown in colour.

1. **When oxidation state is +4**

The most important oxide is Manganese (iv) oxide which is black in colour.

It can be prepared be heating manganese II nitrate in air.

Mn(NO3)2(s) heat MnO2(aq) +2NO2(g)

* Manganese (iv) oxide is also a powerful oxidizing agent. When reacted with hot concentrated HCl a yellowish green gas, chlorine is coloured.

MnO2(s) +4HCl(l) MnCl2(aq) +2H2O(l) +Cl2(g)

* Action of manganese (iv) oxide on oxalate ion

Manganese iv oxide in the presence of an acid acts as an oxidizing agent

 MnO2(s) + 4H+(aq) + 2e Mn2+(aq) + 2H2O(l)

 C2O42-(aq) 2CO2(g) + 2e

**Overall eqn:**MnO2(s) + 4H+(aq) + C2O42-(aq) Mn2+(aq) + 2H2O(l) + 2CO2(g)

**Qn.** *State what would be observed when acidified manganese (iv) oxide is added to the oxalate solution and write equation for reaction that took place.*

Effervescence of a colourless gas and a black solid deposits is given out.

* *Action of heat on manganese iv oxide*

When manganese IV oxide is strongly heated, it liberates oxygen gas.

 3MnO2(s) heat Mn3O4(s) + O2(g)

* *Uses of Manganese IV oxide*

It is used as a catalyst in decomposition of hydrogen peroxide to form water and oxygen gas.

1. **When oxidation is +6**

Compounds of this oxidation state are manganese (VI) ion (MnO42-) and Manganese (VI) oxide ie MnO3.

Manganese (VI) ion can be prepared by heating a mixture of sodium hydroxide, manganese (IV) oxide and oxygen

2MnO2(s) +4NaOH (aq) +O2 2Na2MnO4 (aq) +2H2O (l)

 Overall ionic eqn, 2MnO2(s)+2OH(aq) +O2(aq) MnO42-(aq) +2H2O(l)

 Black

* Manganese (vi) ion in acidic medium undergoes disproportion reaction

3MnO42-(aq) +4H+ (aq) MnO2(S) +2MnO4-(aq) +2H2O (l)

 Green black purple

3MnO42-(aq)+2H2O(aq) MnO2(S)+2MnO4-(aq) +4OH(aq)

 Green black purple

 *Observation*: the dark green solution turns purple with black solid deposit

 Structure of manganese (vi) ion (MnO42-)

 

1. **When oxidation state is +7**

The main compounds are sodium permanganate and potassium permanganate

* They are purple in solution and in solid form.
* They act as oxidizing agents.

*Reasons why MnO4- is not primary standard solution.*

* It is highly contaminated with manganese (iv) oxide
* It slowly undergoes disproportionation reaction in alkali or acidic solution

*Potassium permanganate as oxidizing agent*

The best acid for acidifying KMnO4 is dilute H2SO4 not HNO3 or HCl. Potassium permanganate oxidizes chloride to chlorine and itself is reduced to Mn2+(aq).

MnO-4 (aq) + 8H+ (g) +5e Mn2+ (aq) +4H2O (l) x2

2Cl-(g) Cl2 (g) +2e x5

*Overall eqn*: 2MnO-4(aq) + 10Cl-(aq) +16H+(q) 2Mn2+(aq) 8H2O(l) +5Cl2(g)

HNO3 is a powerful oxidizing, it interferes with the properties of KMnO4

* Acidified KMnO4 slightly dissociates in acidic medium to form manganese IV oxide and oxygen gas

4MnO4- (aq) +4H+ (aq) 4MnO2(S) +3O2(g) +2H2O(l)

* Potassium permanganate slightly dissociates in neutral solution to form manganese IV oxide.

3e + MnO4- (aq) +2H2O(s) MnO2(s) +4OH (aq)

**OXIDIZING PROPERTIES OF MnO4-**

1. **Reaction with oxalate**: (Na2C2O4, K2C2O4,H2C2O4)

Observation: The purple colour of acidified potassium permaganet turns colouless with release of colourless gas

MnO4-(aq)+ 8H+(g) + 5e Mn2+(aq) +4H2O(l)

C2O42-(aq) 2CO2 (g) +2e

 *Overall equation:* 2MnO4-(aq) +16H+ 5C2O2-4(aq) 2Mn2+(aq)8H2O2+10CO2(g)

1. **Reaction with iron II ion**

1st eqn, MnO4-(aq) + 8H+(aq) + 5e Mn2+(aq) + 4H2O(l)

2nd eqn, Fe2+(aq) Fe3+(aq) + e

 *Overall eqn*, MnO4-(aq) + 8H+(aq) + 5Fe2+(aq) Mn2+(aq) + 5Fe3+(aq) + 4H2O(l)

*Observation.*

The purple colour of acidified KMnO4 turns colourless. The green colour of iron II ion solution turns brown.

1. **Reaction with hydrogen peroxide**

H2O2 (aq) 2H+(aq) + O2(g) + 2e

*Overall eqn.* 2MnO4-(aq) + 6H+ (aq) + 5H2O (aq) 2Mn2+(aq) + 8H2O(l) + 5O2(g)

*Observation.*

The purple colour of acidified KMnO4- turns colourless.

1. **Reaction with potassium iodide.**

 2I-(aq) I2(aq) + -2e

 *Overall eqn;* 2MnO4-(aq) + 16H+(aq) + 10I-(aq) 2Mn2+(aq) + 8H2O(l) + 5I2(s)

 *Observation:*

 The purple colour of MnO4- turns class with brown solid deposits.

1. **Reaction with Sn2+ ion**

 Sn2+(aq) Sn4+(aq) + 2e(aq)

 *Overall eqn;* 2MnO4-(aq) + 16H+(aq) + 5Sn2+(aq) 2Mn2+(aq) + 8H2O(l) + 5Sn4+(aq)

**Test for Mn2+ ion**

1. *Dilute NaOH solution.*

 A white ppt insoluble in excess, immediately turns brown.

 Mn2+(aq) + 2OH(aq) Mn(OH)2(s)

 4Mn(OH)2(s) + O2(g) 2Mn2O3.4H2O(l)

 Brown ppt

1. *Dilute ammonia solution;*

A white ppt insoluble in excess, rapidly turns brown.

Mn2+(aq) + 2OH(aq) Mn(OH)2(s)

4Mn(OH)2(s) + O2(g) 2Mn2O3.4H2O(s)

 *Confirmatory test for Mn2+*

1. Conc HNO3 and PbO2, then heat

2Mn2+(aq) + 5PbO2(s) + 4H+(aq) 2MnO4-(aq) + 2H2O(l) + 5Pb2+(aq)

 Purple

1. *Conc HNO3 and sodium bismuthate then heat*

*Observation*; purple colouration.

2Mn2+(aq) + 5NaBiO3(aq) 2MnO4-(aq) + 5Na+ + 5Bi3+(aq) + 7H2O(l)