**CHROMIUM**

Atomic number is 24

Electronic configuration 1s2 2s2 2p6 3s2 3p6 3d5 4s1

Possible oxidation state are +2, +3, +6

For Cr2+ 1s2 2s2 2p6 3s2 3p6 3d4  - Blue

 Cr3+ 1s2 2s2 2p6 3s2 3p6 3d3 - Green

 Cr6+ 1s2 2s2 2p6 3s2 3p6 - Orange

The most stable oxidation state is +3,

**Chemical properties of chromium**

1. Reaction with oxygen

Heated chromium combines with oxygen to form chromium III oxide which is green solid.

 4Cr(s) + 3O2(g) 2Cr2O3(s)

1. Reaction with dil HCl or dilute H2SO4

React slowly with chromium metal to form a blue solution of the corresponding salt.

Cr(s) + 2HCl(aq) CrCl2(aq) + H2(g)

Cr(s) + H2SO4(aq) CrSO4(aq) + H2(g)

The blue solution will immediately undergo oxidation reaction to form Cr3+insoluble which is green in colour.

 4Cr2+(aq) + 4H+(aq) + O2(g) 4Cr3+(aq) + 2H2O(l)

 4CrCl2(aq) + 4HCl(aq) + O2(g) 4CrCl3(aq) + 2H2O(l)

1. Reaction with hot conc sulphuric acid.

It oxidizes chromium to chromium III sulphate and itself is reduced to SO2 and water.

 2Cr(s) + 6H2SO4(l) Cr2(SO4)3(aq) + 3SO2(g) + 6H2O(l)

1. Reaction with chlorine gas.

Heated chromium directly combines with dry chlorine gas to form chromium III chloride.

 2Cr(s) + 3Cl2(g) 2CrCl3(s)

**COMPOUNDS OF CHROMIUM**

**When oxidation state is +2.**

Compounds of chromium in +2 oxidation state are blue in colour unstable in air and can easily be oxidized to chromium III ion.

 Cr2+(aq) Cr3+(aq) + e

Ways of preparing compounds of chromium II ion.

1. By adding zinc amalgam in acidified potassium dichromate.

 1 Cr2O72-(aq) + 14H+(aq) + 8e 2Cr2+(aq) + 7H2O(l)

 4 Zn(s) Zn2+ +2e

**Overall eqn**; Cr2O72-(aq) + 14H+(aq) + 4Zn(s)  2Cr2+(aq) + 7H2O(l) + 4Zn2+

**Question.**

Zinc dust was added to acidified potassium dichromate.

1. State what was observed and write the equation of the reaction that took place.

 *Zinc dissolves and orange colour of acidified potassium dichromate turns blue*.

Example of Cr2+ compounds Cr (OH)2, CrCl2, CrSO4 but all are unstable and can easily be oxidized to chromium III

**WHEN THE OXIDATION STATE IS +3**

This is the most stable oxidation state of chromium and in aqueous solution, it forms a complex ion that exists as [Cr (H2O)6]3+(aq) which is green in colour. Like Al3+ and iron (III), the aqueous solutions of Cr3+ has pH less than 7 and are acidic in nature.

*Acidity of* [Cr (H2O)6]3+(aq) and reaction with carbonate ions

In aqueous solution this complex ion readily undergoes hydrolysis due to the high charge density of the cation and produces hydroxonium ions in solution

[Cr (H2O)6]3+(aq) +3H2O (l) [Cr(H2O)3.3OH] (s) +3H3O+ (aq)

The resultant solution is acidic and if sodium carbonate is added to a solution of chromium (III) ions, effervescence of a colourless gas is also produced.

2H3O+ (aq) + CO32- (g) CO2 (g) + 3H2O (l)

Examples

1. **Chromium III oxide.**

It is green, ionic compound, prepared by heating chromium in air.

 4Cr(s) + 3O2(g)  2Cr2O3(s)

It can also be prepared by heating chromium III hydroxide.

 2Cr(OH)3(s) Cr2O3(s) + 3H2O(l)

By decomposing ammonium dichromate [(NH4)2 Cr2O7]

 (NH4)2Cr2O7(s) heat Cr2O3(s) + N2(g) + 4H2O(l)

Chromium III oxide is amphoteric oxide i.e reacts with both alkali solutions and acidic solutions.

 Cr2O3(s) + 6OH (aq) + 3H2O (l) 2[Cr(OH)6]3-(aq)

1. **Chromium III hydroxide:**

It is green precipitate prepared by reacting sodium hydroxide with Cr3+ ion solution.

**Note**: Little NaOH is required because Cr3+ hydroxide is soluble in excess sodium hydroxide.

 Cr3+(aq) + 3OH(aq) Cr2(OH)3(s)

 Green precipitate

Properties of chromium III hydroxide

It is amphoteric hydroxide

 Cr(OH)3(s) + 3OH(aq) [Cr(OH)6]3-(aq)

 Green solution

NB: When dilute ammonia solution is added to *green precipitate* of chromium III hydroxides it dissolves to form *pink or violet* solution.

When excess NaOH followed by H2O2 is added to Cr3+ solution a yellow solution is formed due to the formation of chromate.

 2Cr(OH)3(s) + 4OH(aq) + 3H2O2(aq) 2CrO4(aq) + 8H2O(l)

1. **Chromium III chloride**

Prepared by passing dry chlorine gas over heated chromium

2Cr(s) + 3Cl2(g) CrCl3(s)

*Hydrate Isomerism:*

Hydrate isomerism is where the isomers differ in the number of water molecules directly bonded to metal ion like Cr3+

*eg.* the hydrate CrCl3.6H2O has 3 isomeric salts.

|  |  |  |  |
| --- | --- | --- | --- |
| Isomer | Colour | Number of free chloride ion | Reaction with AgNO3 solution |
| [Cr(H2O)6]Cl3[Cr(H2O)5Cl]Cl2.H2O[Cr (H2O)4Cl2]Cl.2H2O | VioletLight GreenDark green | 321 | Ppts 3 moles of AgClPpts 2 moles of AgClPpts 1 mole of AgCl |

The isomers also show differences in conductivity of in aqueous solution due to the different number of conducting ions present. The violet isomer has 4 conducting ions and therefore has the highest conductivity. The light green has 3 conducting ions and the second most conducting while the dark green isomer has only two conducting species and is the least conducting.

**WHEN OXIDATION STATE IS +6**

Because of the high polarizing power/charge density of Cr6+ ion, it forms very many complexes than chromium, Cr3+ and Cr2+

Example of compounds include CrO3, CrO42-, Cr2O72-

1. **CrO3; (chromium VI oxide)**

Prepared by adding concentrated HCl or H2SO4 to potassium dichromate solution

Cr2O72-(aq) + 2H+ 2CrO3(s) + H2O(l)

* Is a dark solid/precipitate
* Structure of CrO3

 *Trigonal planar*

 Cr

* It is an acidic oxide, dissolves in water to form chromic acid.

CrO3(s) + H2O (l) H2CrO4 (aq)

* CrO3 dissolves in alkaline solution as NaOH to form chromate

CrO3(s) + 2OH (aq) CrO42-(aq) + H2O (l)

1. **Chromates,**

Chromates are prepared by adding dilute alkali solution (NaOH(aq)) to a dichromate solution.

Cr2O72-(aq) + 2OH (aq) 2CrO42-(aq) + H2O(l)

*Equation:* to show how to prepare potassium chromate;

 K2Cr2O7 (aq) + 2KOH (aq) 2K2CrO4(aq) + H2O

 Orange yellow

Structure of chromate;

 2-

 Cr

They are salts of chromic acid and are yellow in colour.

**Test for chromate ion.**

1. *Lead (II) Nitrate solution.*

Observation: yellow ppt is formed.

CrO42-(aq) + Pb2+(aq) PbCrO4(s)

 *Yellow ppt*

1. *Barium nitrate/barium chloride.*

Observation: A yellow ppt is formed.

 Ba2+(aq) + CrO42-(aq) BaCrO4(s)

 yellow

1. *Silver nitrate solution.*

Observation: A brick red ppt is formed.

 2Ag+(aq) + CrO42-(aq) Ag2CrO4(s)

**Note:** When dilute Hydrochloric or sulphuric acid is added to the chromate solution, the yellow colour turns orange due to the formation of dichromate.

 2CrO42- + 2H+ Cr2O72-(aq) + H2O

 Yellow orange

Chromate ion is also a very strong oxidizing agent and can be reduced to chromium III.

 CrO42-(aq) + 8H+(aq) + 3e Cr3+(aq) + 4H2O(l)

 Yellow green

**Qn.** Acidified potassium chromate was added to iron (II) solution state what was observed.

Half reaction: Fe2+(aq) Fe3+(aq) + e

Overall equation:

CrO42-(aq) + 8H+(aq) + 3Fe2+(aq) 3Fe3+(aq) + Cr3+(aq) + 4H2O(l)

 Yellowish pale green greenish brown solution

1. **Dichromate (Cr2O72-)**

Properties

* They are orange in colour.
* It consists of two chromate ions which are jointed together by one oxygen atom.

 O O

 Cr Cr

 O O O O O

* Dichromate is only stable in acidic medium

**Prepn**

Dichromate is prepared by acidifying chromate solution

 2CrO42-(aq) + 2H+(aq) Cr2O72-(aq) + H2O (l)

1. **Potassium dichromate**

It is prepared by mixing hot saturated sodium dichromate and potassium chloride.

2KCl (aq) +NaCr2O7 (aq) K2Cr2O7 (aq) + 2NaCl(s)

The precipitate sodium chloride is filtered off

1. **Sodium dichromate**

It is prepared by acidifying sodium chromate solution

2Na2CrO4 (aq) +H2S04 (aq) Na2Cr2O7 (aq) + H2O (l) + Na2SO4 (aq)

 **OXIDISING REACTION OF DICROMATES**

Dichromate’s acts as powerful oxidizing agents when acidified with dilute hydrochloric acid (they act as electron accepts)

Cr2O7-2(aq) + 14H+ (aq)+ 6e 2Cr3+ (aq) + 7H2O(l)

1. **Oxidation of sulphite ion to sulphate:**

When acidified dichromate is added to the solution of *sulphite* ion the orange colour of acidified dichromate turns green.

1st half eqn: Cr2O72-(aq) + 14H+(aq) + 6e 2Cr3+(aq) + 7H2O(l)

2nd half eqn: SO32-(aq) + H2O (l) SO42-(aq) + 2e + 2H+ (aq)

**Overall:** Cr2O72-(aq) + 3SO32-(aq) + 8H+(aq) 2Cr3+(aq) + 3SO42-(aq) + 4H2O(l)

**(ii) Oxidation of ethanol to ethanal.**

1st half eqn: 1 Cr2O72-(aq) + 14H+(aq) + 6e 2Cr3+(aq) + 7H2O(l)

2nd half eqn: 3 CH3CH2OH(l) CH3CHO(l) + 2H+(aq) + 2e

Overall eqn: Cr2O72-(aq) + 8H+(aq) + 3CH3CH2OH(l) 2Cr3+(aq) + 7H2O(l) + 3CH3CHO(l)

1. **Oxidation of ethanal to ethanoic acid**

1st half eqn: 1 Cr2O72-(aq) + 14H+(aq) + 6e 2Cr3+(aq) + 7H2O(l)

2nd half eqn: 3 CH3CHO(l) + H2O(l) CH3COOH + 2H+(aq) + 2e

Overall: Cr2O72-(aq) + 8H+(aq) + 3CH3CHO(l) 2Cr3+(aq) + 4H2O(l) +3CH3COOH

1. **Oxidation of nitrite ions in solution to Nitrate ions in solution.**

1st half eqn: 1 Cr2O72-(aq) + 14H+(aq) + 6e 2Cr3+(aq) + 7H2O(l)

2nd half eqn: 3 NO2-(l) + H2O(l) NO3- (l) + 2H+(aq) + 2e

Overall: Cr2O72-(aq) + 8H+(aq) + 3NO2-(l) 2Cr3+(aq) + 4H2O(l) +3NO3-

1. **Oxidation of Sn2+**

1st half eqn: Cr2O72-(aq) + 14H+(aq) + 6e 2Cr3+(aq) + 7H2O(l)

2nd half eqn: Sn2+ Sn4+(aq) + 2e

Overall eqn: Cr2O72-(aq) + 14H+ + 3Sn2+(aq) 3Sn2+(aq) + 2Cr3+(aq) + 7H2O(l)

1. **Oxidation Fe2+**

1st half eqn: Fe2+(aq) Fe3+(aq) + e

Overall eqn: Cr2O72-(aq) + 14H+(aq) + 6Fe2+(aq) 2Cr3+(aq) + 7H2O(l) + 6Fe3+(aq)

**ACTION OF HEAT ON DICHROMATES**

The dichromate’s of K and Na decompose when strongly heated to produce chromium (III) oxide, chromate and oxygen gas.

4K2Cr2O7 heat 2Cr2O3(s) + 4K2CrO4(s) + 3O2 (g)

**Chromium dichloride dioxide (CrO2Cl2)/[Chromyl chloride]**

It is a dark red liquid prepared by reacting chromium (vi)oxide with conc HCl.

CrO3(s) + 2HCl(aq) CrO2Cl2(l) + H2O(l)

Chromyl chloride hydrolyze in water to form chromic (vi) acid and aqueous hydrogen chloride.

CrO3Cl2 (s) +2H2O (l) H2CrO4 (aq) + 2HCl(aq)

OR

2CrO2CL2(l) +3H2O(l) H2Cr2O7 (aq)+4HCl(aq)

Chromium dichloride is also a powerful oxidizing agent

 CH3  CrO2Cl2 CHO

 CHO H+/Cr2O72- COOH

**Test for chromium (iii) ion**

1. *Reagents: dilute sodium hydroxide solution*

 A green ppt soluble in excess to form a green solution

Cr3+(aq) + 3OH(aq) Cr(OH)3(s)

 Green ppt

In excess:

Cr (OH)3+ 3OH(aq) Cr(OH)63-(aq)

1. **Reagents:** *Dilute ammonia solution:*

A gray green ppt slightly soluble in excess turns pink on standing. When chromium (iii) ion solution is boiled with NaOH and Hydrogen peroxide ayellow solution is formed.

2Cr3(OH)3(s) + 4OH(aq) 3H2O2(i) 2CrO42-(aq) +8H2O(i)

Qns:

1. a) List the ores of chromium
2. Discuss how chromium can be extracted from the named ore

**Solution**

1. Ores of chromium

Chromite or chrome iron ore (FeCr2O4 or FeOCr2O3)

*Extraction*

1. *Carbon reduction process*

Chromite is heated with carbon in the electric furnace to obtain liquid chromium

FeCr2O4(S) +4C(S) Fe(l) +2Cr(l) +4CO(g)

The liquid chromium is separated from liquid iron by distillation

The chromium obtained can be cooled to solidify

**Other methods**

*(a)The electrolytic process*

The process is used chiefly in electroplating of steel parts to improve appearance and prevent rusting. The steel is first plated with Cu or Ni since Cr does not deposit well directly on the steel. The object to be plated is then made the cathode in a plating bath which usually contains chromium in +6 & +3 states CrO3 and Cr2(SO4)3 with H2SO4 present. The temperature (usually 310K) and current have to be controlled. Chromium is then deposited with a bright bluish – white appearance

At cathode Cr3+(aq) +3e Cr(s) .

1. *The thermite process with aluminium*

Chromium (iii) oxide is mixed with pounded aluminium. The mixture as fired by a piece of burning magnesium ribbon inserted into sodium peroxide. This starts the reaction at one point. It is exothermic enough to spread through the material in a violent process.

Cr2O3(aq) +2Al(s) Al2O3(S) +2Cr(l)

As used in industries, the reaction is known as Goldschimst process and yields 99% pure chromium.