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Transition Metals

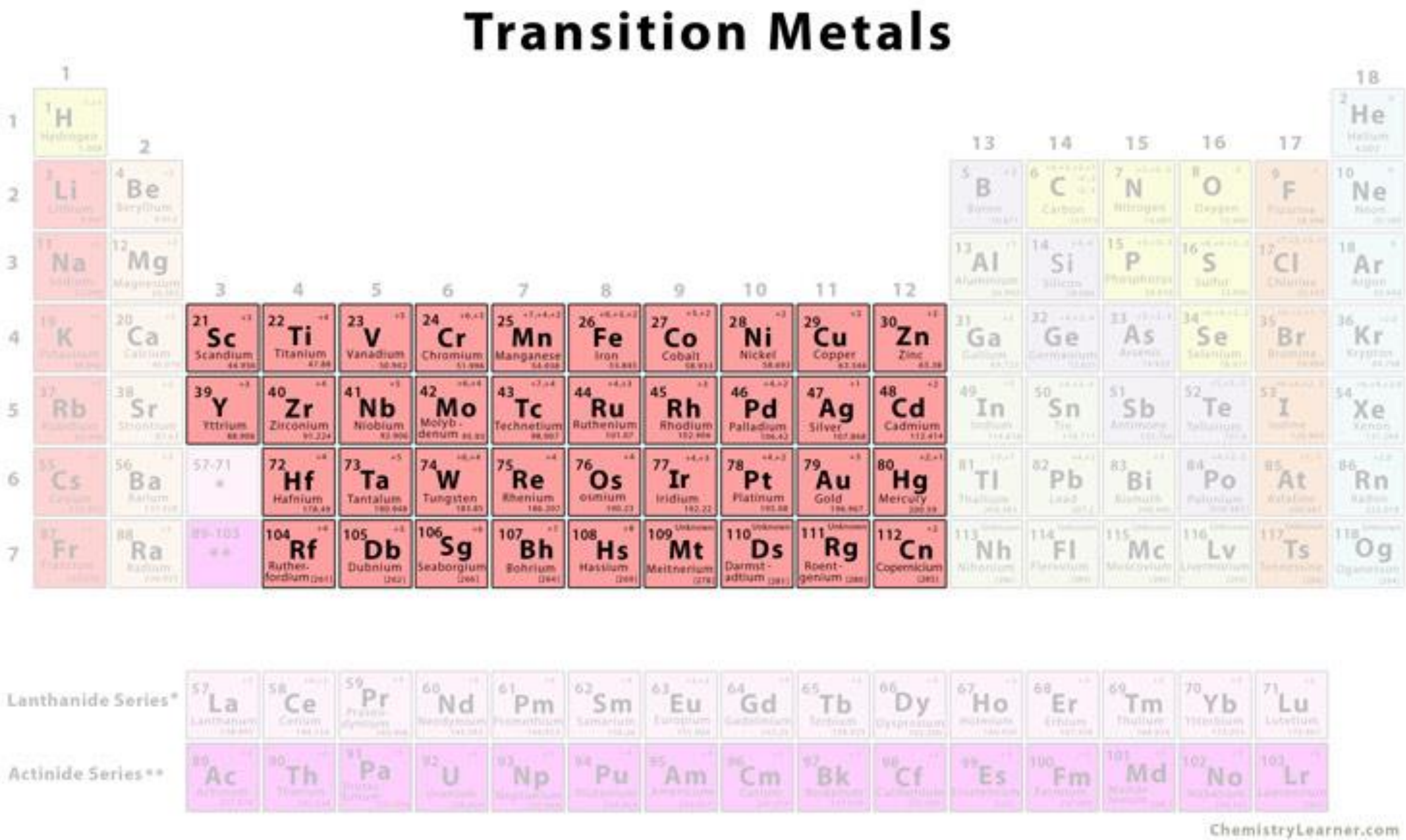
Unit – III: Transition Metals (15 L)

Groups 6 and 7: Chromium, manganese, K_2CrO_4, $K_2Cr_2O_7$, CrO_2Cl_2, $KMnO_4$, chrome alum.

Groups 8, 9 and 10: Iron, cobalt and nickel, principles of isolation of Ni (excluding details), composition and uses of alloys, steels, rusting of iron, galvanization and tin plating.

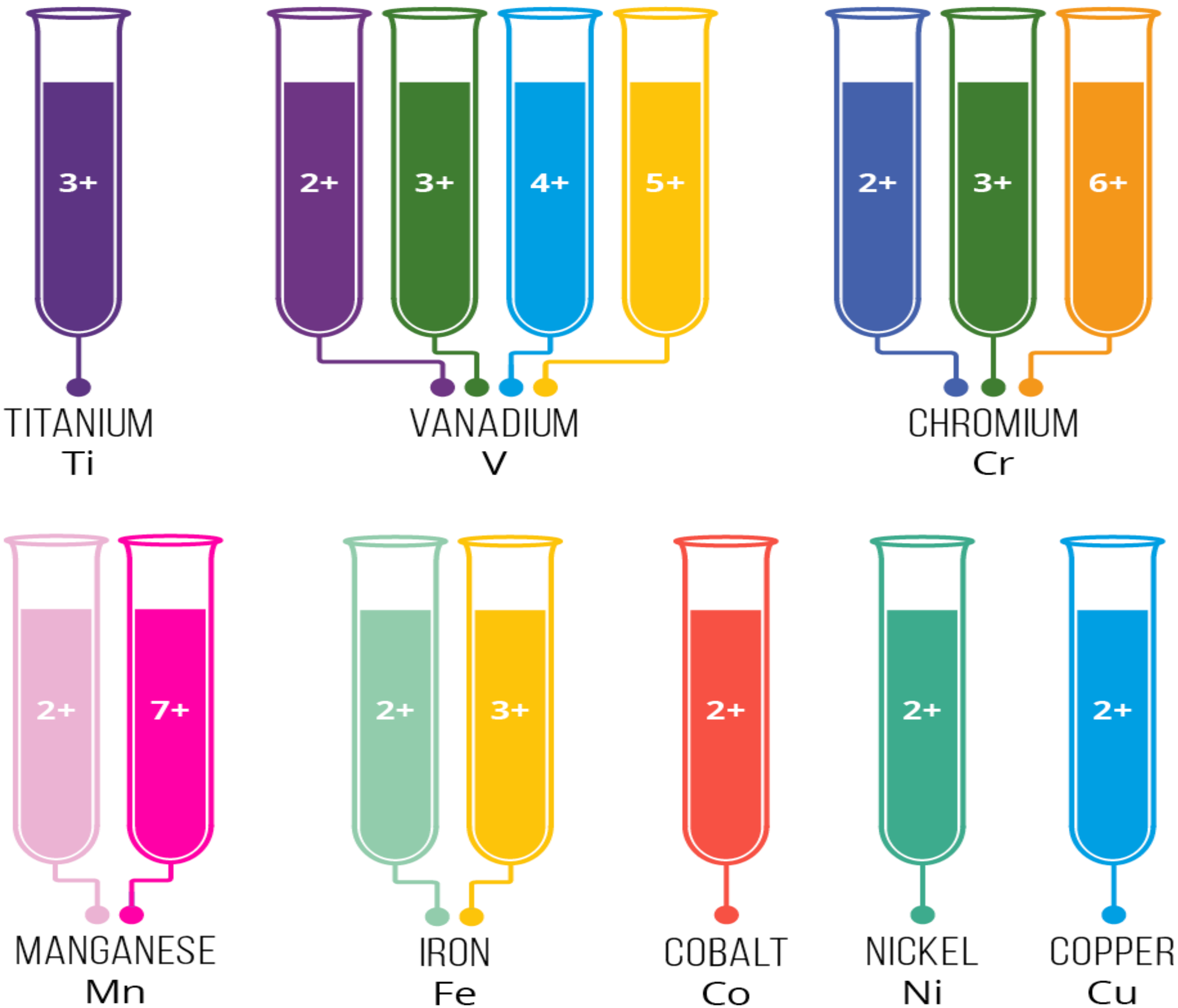
Group 11: Cu, Ag, Au, principles of Ag and Au isolation

Transition elements (also known as **transition metals**) are **elements** that have partially filled d orbitals. IUPAC defines **transition elements** as an **element** having a d subshell that is partially filled with electrons, or an **element** that has the ability to form stable cations with an incompletely filled d orbital.



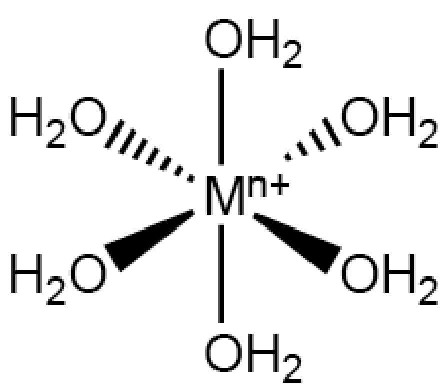
21 Sc Scandium 44.956	22 Ti Titanium 47.88	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.933	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.39
39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.95	43 Tc Technetium 98.907	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.906	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmium 112.411
	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.85	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.22	78 Pt Platinum 195.08	79 Au Gold 196.967	80 Hg Mercury 200.59
	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [268]	110 Ds Darmstadtium [269]	111 Rg Roentgenium [272]	112 Cn Copernicium [277]

Transition metal ions are usually colored



TRANSITION METAL ION COLOURS

Transition metals form coloured compounds and complexes. These colours can vary depending on the charge on the metal ion, and the number and type of groups of atoms (called ligands) attached to the metal ion. In aqueous solutions, the ions form complexes with the colours shown to the right.



HYDRATED TRANSITION METAL ION

Electrons are arranged around the nucleus of the metal atom in orbitals. Transition metals, unlike other metals, have partially filled d orbitals, which can hold up to 10 electrons. When ligands are present, some d orbitals become higher in energy than before, and some become lower. Electrons can then move between these higher and lower d orbitals by absorbing a photon of light. This absorption of light affects the percieved colour of the compound or complex. The wavelength of the light absorbed is affected by the size of the energy gap between the d orbitals, which is in turn affected by the type of ligand and the charge on the metal ion.

Group 6: Chromium

Cr is largely used in making stainless steel and other alloys.

Cr is also used in Cr plating which does not tarnish by Sulphur compounds in the atmosphere

Chromium Isolation

Cr is extracted from chromite via Cr_2O_3. The main steps are as follows:

(i) Aerial oxidation of chromite

$$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 = 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$$

(ii) Formation of sodium dichromate

$$2Na_2CrO_4 + H_2SO_4 = Na_2SO_4 + Na_2Cr_2O_7 + H_2O$$

(iii) Reduction of Cr(VI) to Cr(III)

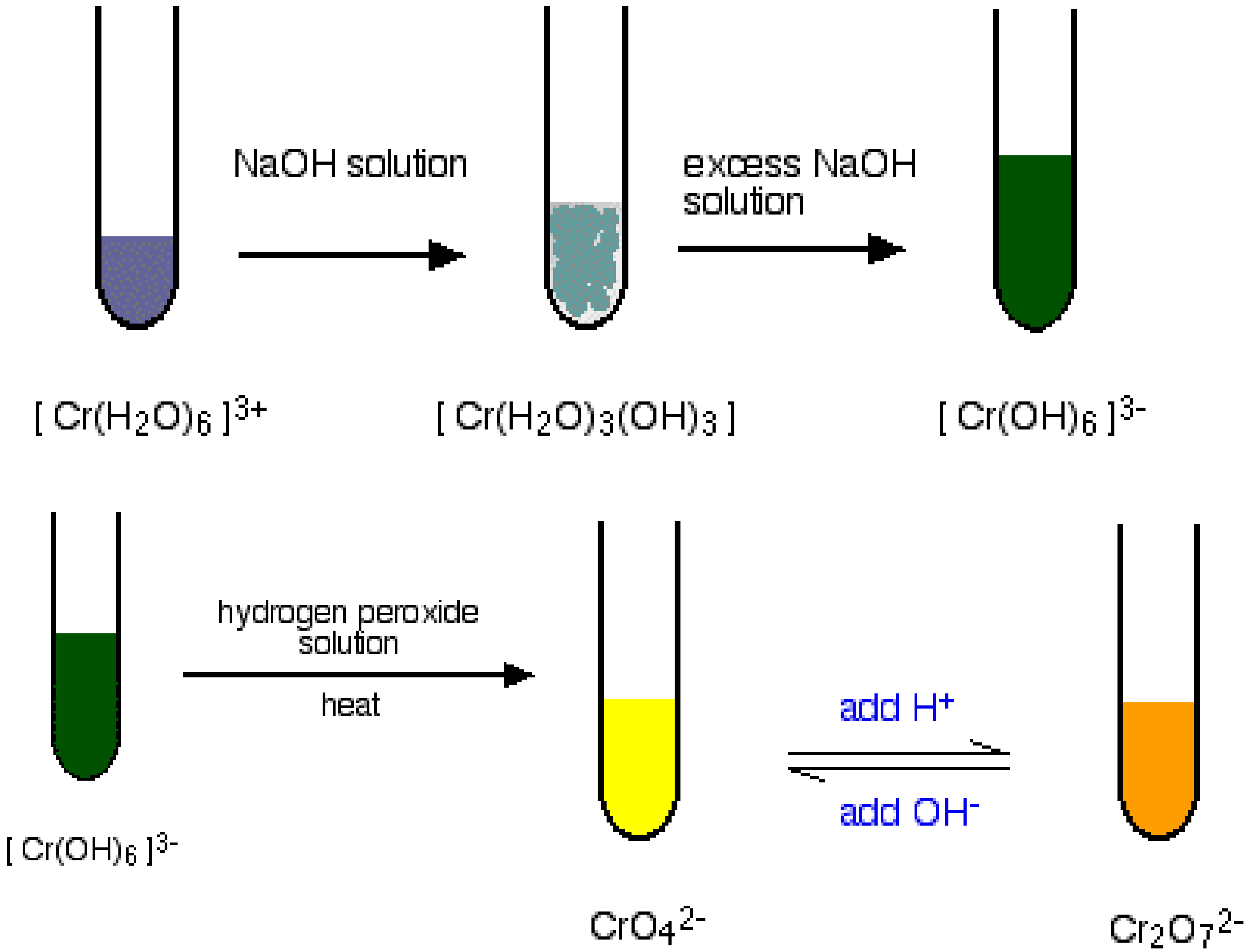
$$Na_2Cr_2O_7 + 2C = Cr_2O_3 + Na_2CO_3 + CO$$

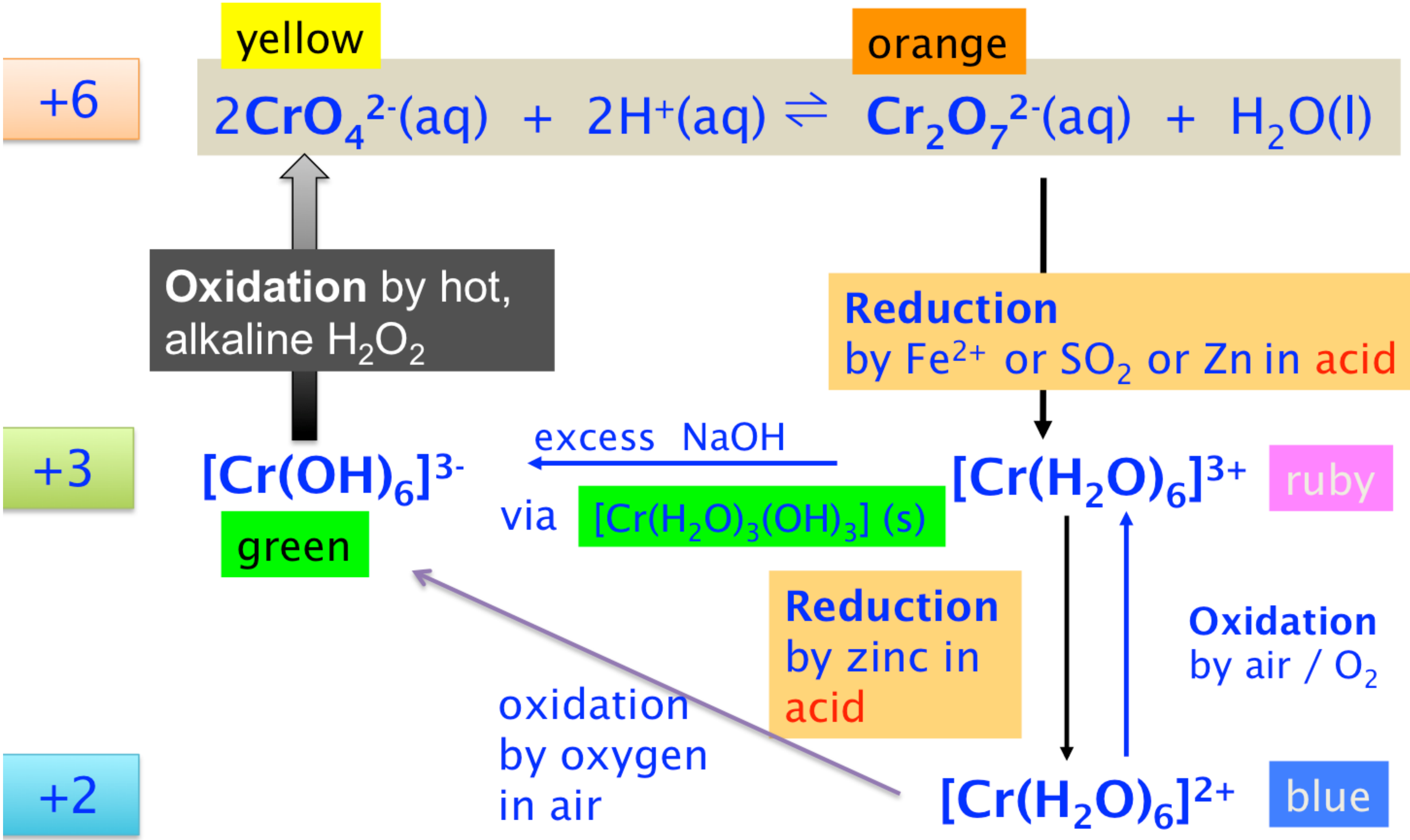
(iv) Reduction to metallic chromium by aluminothermy

$$Cr_2O_3 + 2Al \longrightarrow Al_2O_3 + 2Cr$$

$$2Cr_2O_3 + 3Si \longrightarrow 4Cr + 3SiO_2$$

Chromium ions: Color & Conversion between each other





+6
+3
+2
yellow
orange
$2CrO_4^{2-}(aq) + 2H^+(aq) \rightleftharpoons Cr_2O_7^{2-}(aq) + H_2O(l)$
Oxidation by hot, alkaline H_2O_2
Reduction by Fe^{2+} or SO_2 or Zn in acid
$[Cr(OH)_6]^{3-}$
green
excess NaOH
via $[Cr(H_2O)_3(OH)_3]$ (s)
$[Cr(H_2O)_6]^{3+}$
ruby
Reduction by zinc in acid
Oxidation by air / O_2
oxidation by oxygen in air
$[Cr(H_2O)_6]^{2+}$
blue

Preparation of $K_2Cr_2O_7$

Potassium dichromate $(K_2Cr_2O_7)$ is an orange coloured compound, very frequently used in laboratory as an oxidising agent as well as in a redox titration. It is generally prepared from chromit $(FeCr_2O_4)$ ore according to the following reactions:

(a) Fusion of chromite ore with sodium carbonate in excess of air.

$$FeCr_2O_4 + Na_2CO_3 + O_2 \rightarrow Na_2CrO_4 + Fe_2O_3 + CO_2$$

(b) Acidifying filetered sodium chromate solution with sulphuric acid.

$$Na_2CrO_4 + H_2SO_4 \rightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$

(c) Treating sodium dichromate with potassium chloride.

$$Na_2Cr_2O_7 + KCl \rightarrow K_2Cr_2O_7 + NaCl$$

Answer the following questions using above information.

If you are intially provided with 224 gm of pure chromite ore and 169.6gm of sodium carbonate, the minimum volume of air required at 1 atm and 273 K to consume at least one of the reactant completely, if aire contains 20% by volume of oxygen gas is :

Potassium dichromate

$$Cr_2O_7^{2-} + 14\,H^+ + 6e^- \rightleftharpoons 2\,Cr^{3+} + 7H_2O \qquad E^0 = 1.33\,V$$

- Dichromate titration : generally carried out in 1M-HCl
  or 1M-H_2SO_4 solution
  Formal potential for the half reaction : 1.0 to 1.1 V
  * Indefinitely stable : can be boiled without decomposition
    do not react with HCl
  * Primary standard reagent : available commercially
    modest cost
  * Disadvantage : Lower electrode potential
    Slow reaction rate
- Preparing Dichromate solutions
  - Reagent grade : Pure
    Drying at 150 - 200℃ before being weighted
  * Color of Dichromate : weak
    - Indicator : Diphenylamine sulfonic acid
      (oxidized form : violet, Reduced form : colorless)
- Applying potassium dichromate solutions

$$Cr_2O_7^{2-} + 6\,Fe^{2+} + 14\,H^+ \rightarrow 2Cr^{3+} + 6\,Fe^{3+} + 7\,H_2O$$

$K_2Cr_2O_7$: As Oxidising agent

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$ (1/2

Ionic equations

(i) Reaction of $K_2Cr_2O_7$ with I^-

$$Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O$$

(ii) Reaction of $K_2Cr_2O_7$ with $Fe^{2+}(aq)$ (1/2

$$Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \longrightarrow 2Cr^{3+} + 3Fe^{3+} + 7H_2O$$ (1/2

(iii) Reaction of $K_2Cr_2O_7$ with H_2S

$$Cr_2O_7^{2-} + 8H^+ + 3H_2S \longrightarrow 2Cr^{3+} + 3S + 7H_2O$$ (1/2

Chromyl Chloride, CrO_2Cl_2

It is most important oxohalides of chromium (VI). It is formed when an ionic chloride is heated with potassium dichromate and concentrated H_2SO_4:

Chromyl chloride test : When potassium dichromate is heated with conc. H_2SO_4 in the presence of a soluble chloride salt, the orange-red vapours of chromyl chloride (CrO_2Cl_2) are formed.

$$K_2Cr_2O_7 + 4NaCl + 6H_2SO_4 \xrightarrow{\text{heat}} 2KHSO_4 + 4NaHSO_4 + \underset{\substack{\text{chromyl chloride} \\ \text{(orange-red vapours)}}}{2CrO_2Cl_2}$$

Chromyl chloride vapours when passed through water give yellow-coloured solution containing chromic acid.

$$CrO_2Cl_2 + 2H_2O \rightarrow 2HCl + \underset{\text{Chromic acid. (yellow solution)}}{H_2CrO_4}$$

Chromyl chloride test can be used for the detection of chloride ion in any mixture.

Sodium Chromate, K_2CrO_4

Potassium chromate, K_2CrO_4 is obtained by adding K2CO3 (orKOH) to $K_2Cr_2O_7$.

$$K_2Cr_2O_7 + K_2CO_3 = 2K_2CrO_4 + CO_2$$

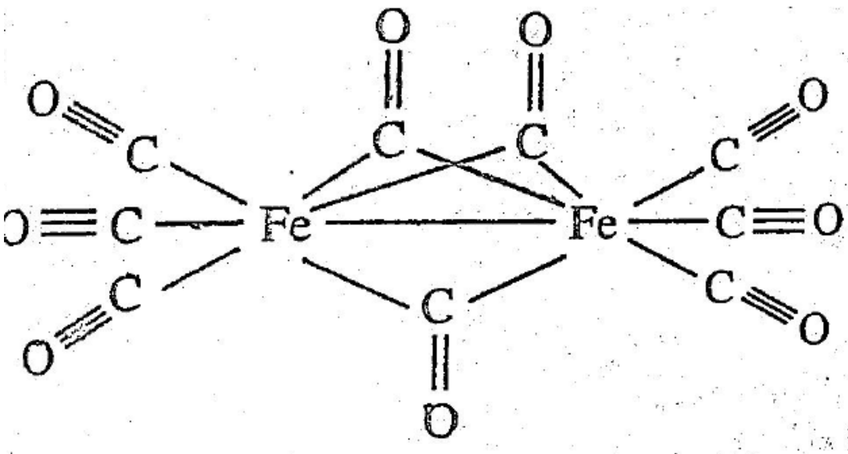
Use: It is used to make pigments for paints and inks, other chemicals, and as a wood preservative

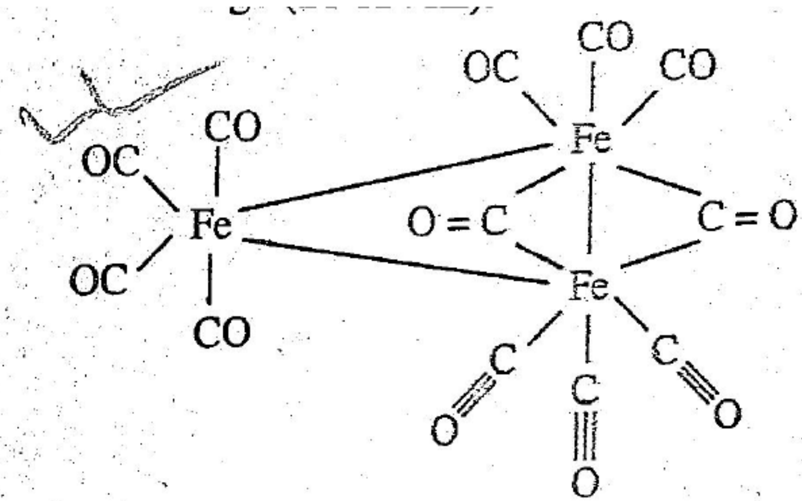
Chrome Alum

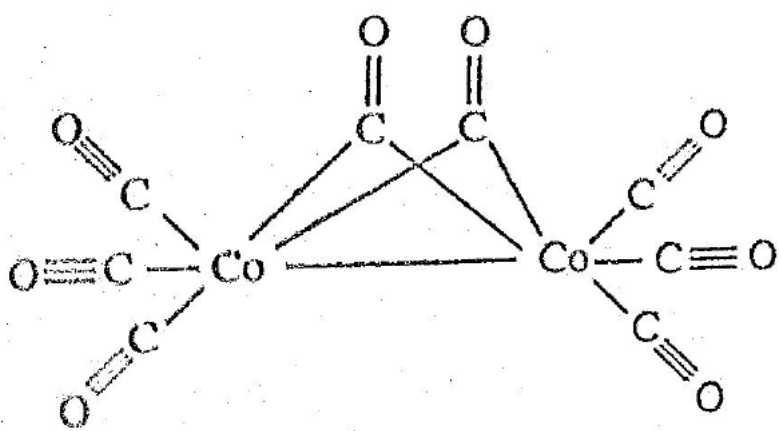
Chrome alum, $K_2SO_4.Cr_2(SO_4)_3.24H_2O$ may be obtained as deep purple octahedral crystal from mixed solution of the violet chromium (III) sulphate and potassium sulfate. It is generally prepared by reducing potassium dichromate in acidic solution with SO_2 (until the color changes to green)

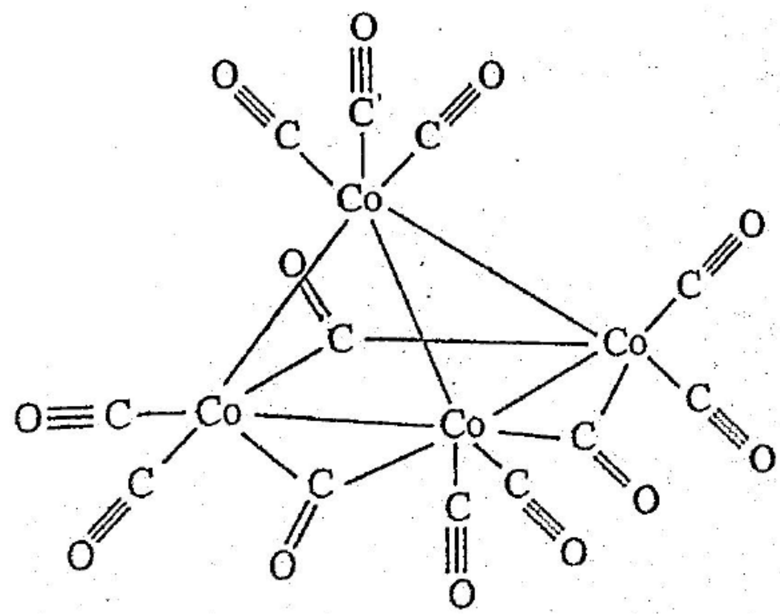
Uses: Chrome alum is used as a mordant in dyeing and in ‘tanning’ of leather.

Some carbonyl compound structure of Fe & Co









Sodium Nitroprusside: Use & Preparation

$$Na_2[Fe(CN)_5NO] + Na_2S = Na_4[Fe(CN)_5NOS]$$

Sodium nitroprusside also gives a rose-red coloration with sulphites, forming $Na_4[Fe(CN)_5(NO)SO_3]$. With alkali, a red nitro-complex is formed:

$$Na_2[Fe(CN)_5NO] + 2NaOH \longrightarrow Na_4[Fe(CN)_5NO_2] + H_2O$$

"Sodium nitroprusside", $Na_2[Fe(CN)_5NO]$, (sodium pentacyanonitrosylferrate(II)), may be prepared by heating $K_4Fe(CN)_6$ with 30% HNO_3. The brown solution obtained is cooled when KNO_3 separates first. The filtrate, on neutralization by Na_2CO_3, concentration and cooling, yields ruby-red rhombic crystals of $Na_2[Fe(CN)_5NO] \cdot 2H_2O$.

$$[Fe(CN)_6]^{4-} + 4H^+ + NO_3^- \longrightarrow [Fe(CN)_5NO]^{2-} + CO_2 + NH_4^+.$$

Prussian Blue formation& Test of presence of special element 'N' in organic Compound

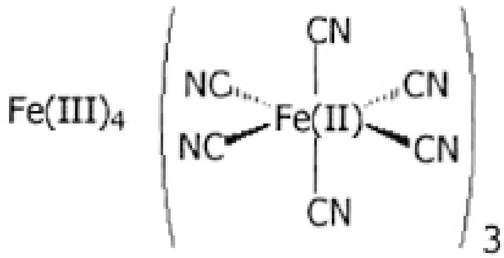
$$Na + C + N \xrightarrow{\text{Fuse}} NaCN$$

$$FeSO_4 + 6NaCN \longrightarrow \underset{(A)}{Na_4[Fe(CN)_6]} + Na_2SO_4$$

(*A*) changes to Prussian blue $Fe_4[Fe(CN)_6]_3$ on reaction with $FeCl_3$.

$$4FeCl_3 + 3Na_4[Fe(CN)_6] \longrightarrow Fe_4[Fe(CN)_6]_3$$

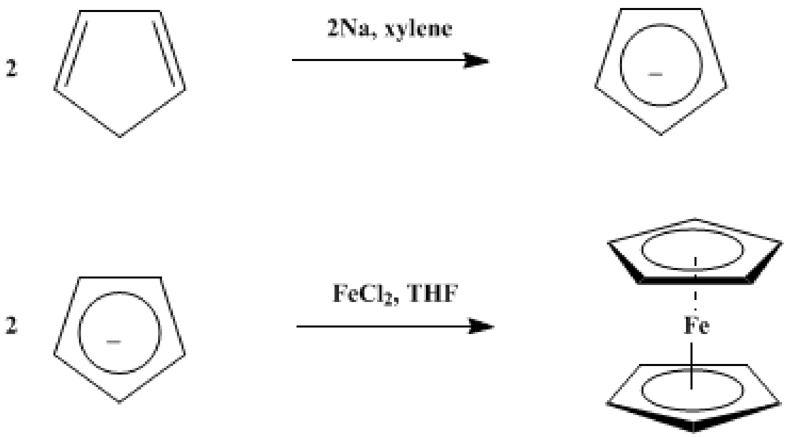
Prussian blue Insoluble



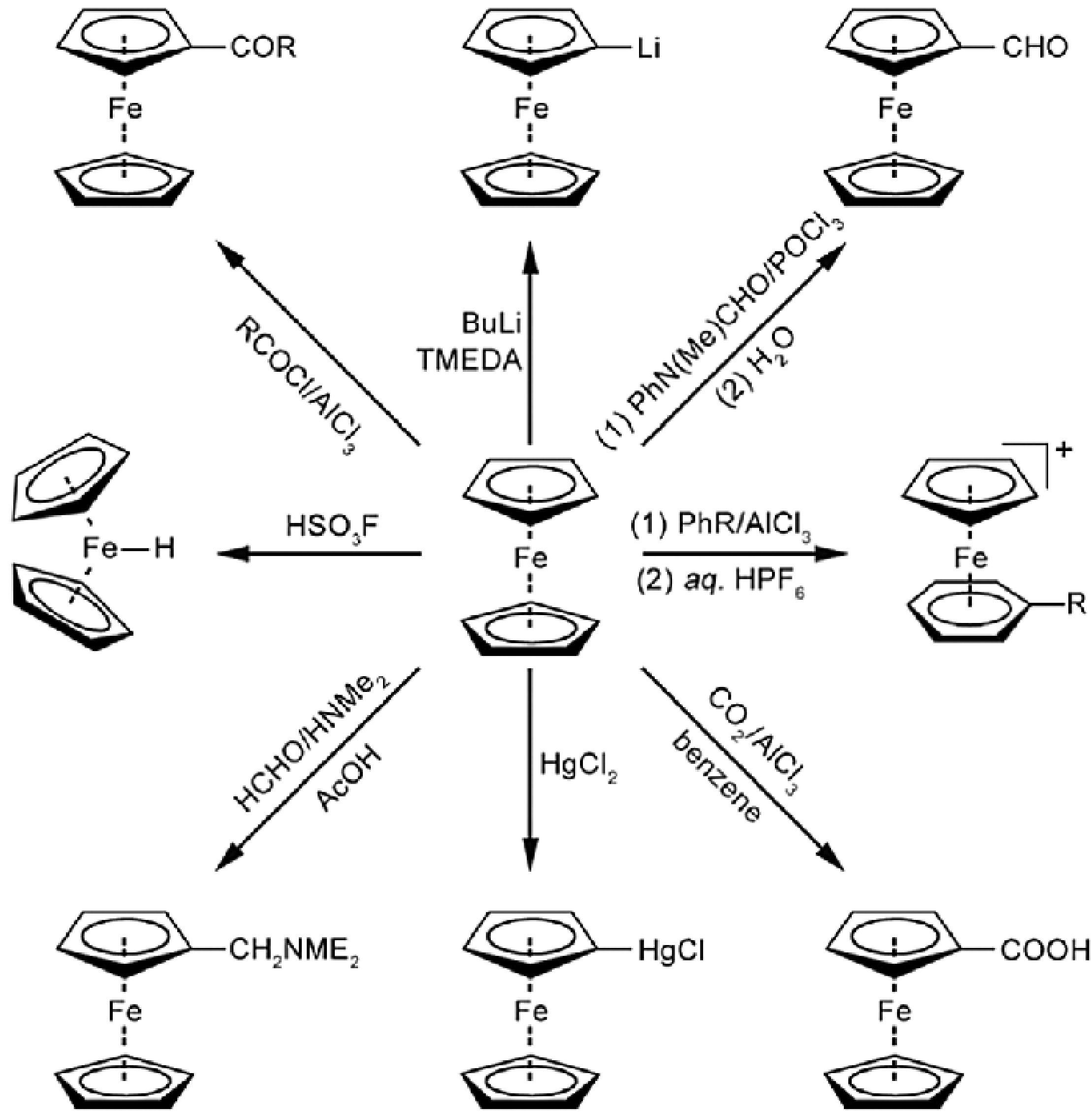
Ferrocene

Preparation:

$$\frac{2}{3}\,FeCl_3 + \frac{1}{3}\,Fe \longrightarrow FeCl_2$$



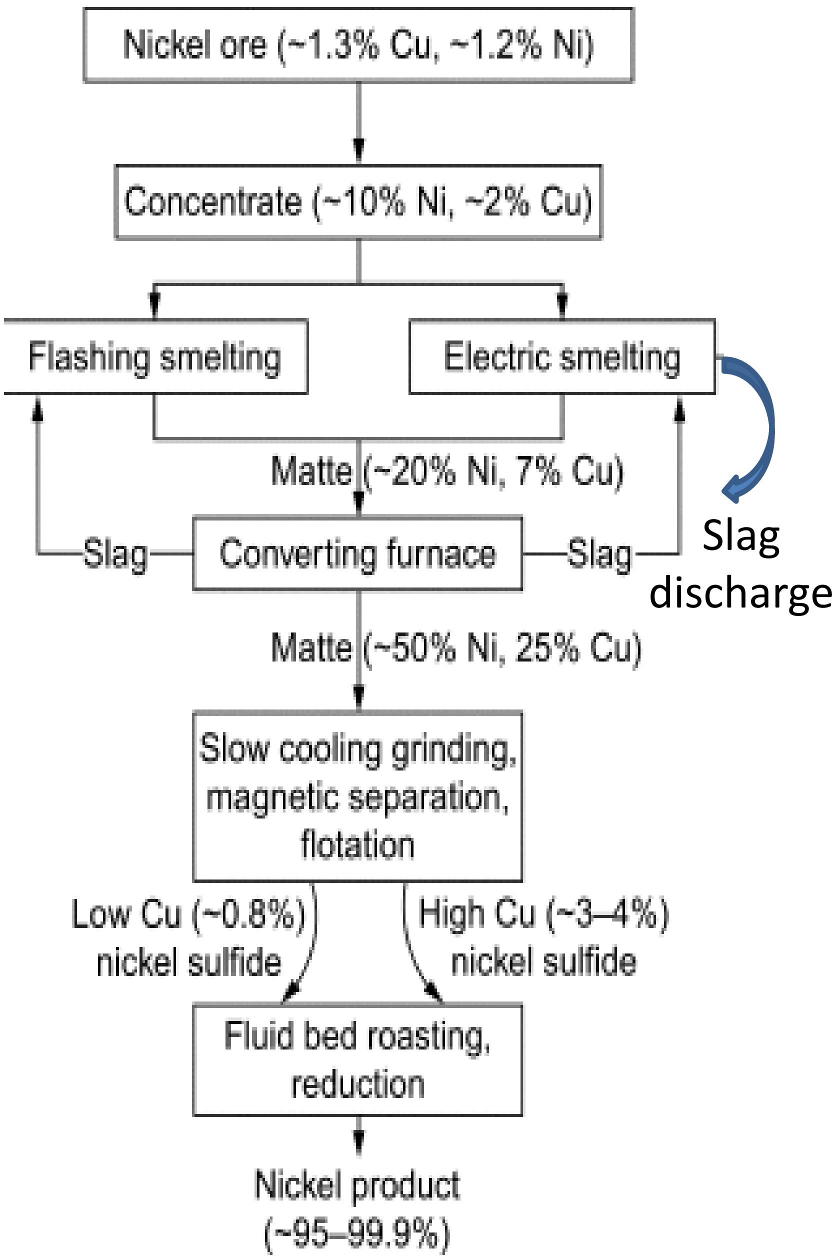
Reaction:

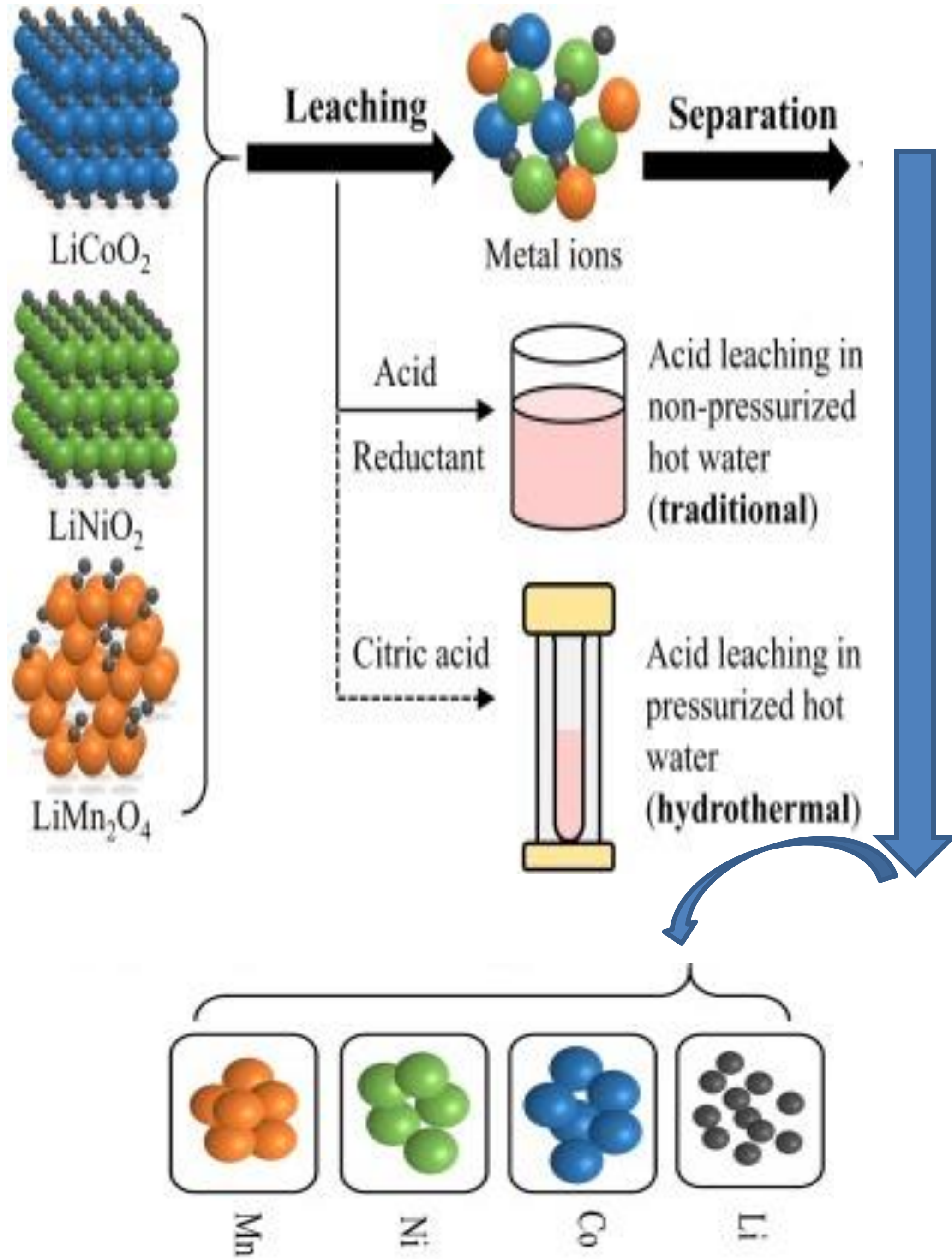


Use:

Ferrocene and its derivatives are antiknock agents used in the fuel for petrol engines. They are safer than previously used tetraethyllead

Principle of Isolation of Ni





REFINING:

1.MOND PROCESS

The purest metal is obtained from nickel oxide by the Mond process , which achieves a purity of greater than 99.99%.

This process has three steps:

1. Nickel oxide reacts with Syngas at 200 °C to give nickel, together with impurities including iron and cobalt.

$$NiO(s) + H_2(g) \rightarrow Ni(s) + H_2O(g)$$

2. The impure nickel reacts with carbon monoxide at 50–60 °C to form the gas nickel carbonyl, leaving the impurities as solids.

$$Ni(s) + 4\,CO(g) \rightarrow Ni(CO)_4(g)$$

3. The mixture of nickel carbonyl and Syngas is heated to 220–250 °C, resulting in decomposition back to nickel and carbon monoxide:

$$Ni(CO)_4(g) \rightarrow Ni(s) + 4\,CO(g)$$

Composition and Uses of Alloys

Name	Composition	Use
Brass	Cu (60 to 80%), Zn (40 to 20%)	For making household utensils
Bronze	Cu (75 to 90%), Sn (25 to 10%)	For making coins, idols, utencils
German Silver	Cu (60%), Zn (25%), Ni (15%)	For making utensils
Magnelium	Mg (5%), Al (95%)	For making aircraft frame
Rolled Gold	Cu (90%), Ni (10%)	For making cheap ornaments
Monel metal	Cu (70%), Ni (30%) containers	For making alkali resistant
Bell metals	Cu (80%), Sn (20%)	For making bells
Gun metal	Cu (85%), Zn (10%), Sn (5%)	Used for engineering purposes
Solder	Sn (50-75%), Pb (50-25%)	Soldering of metals
Duralium	AI (95%), Cu (4%), Mg (0 5%), Mn (0 5%)	In aircraft manufacturing
Steel	Fe (98%), C (2%)	For making nails, screws, bridges
Stainless Steel	Fe (82%) Cr, Ni (18%)	For making cooking utensils, knives

- *An alloy is a mixture* of two *or more metals.*

Steels

Steels is essentially a refined alloy with respect to the elements which accompany the crude iron From blast furnace, especially C, S and P. It is often alloyed with other metals to impact desired Properties. Steel making thus consists essential refining a cast iron followed by the addition of alloying element.

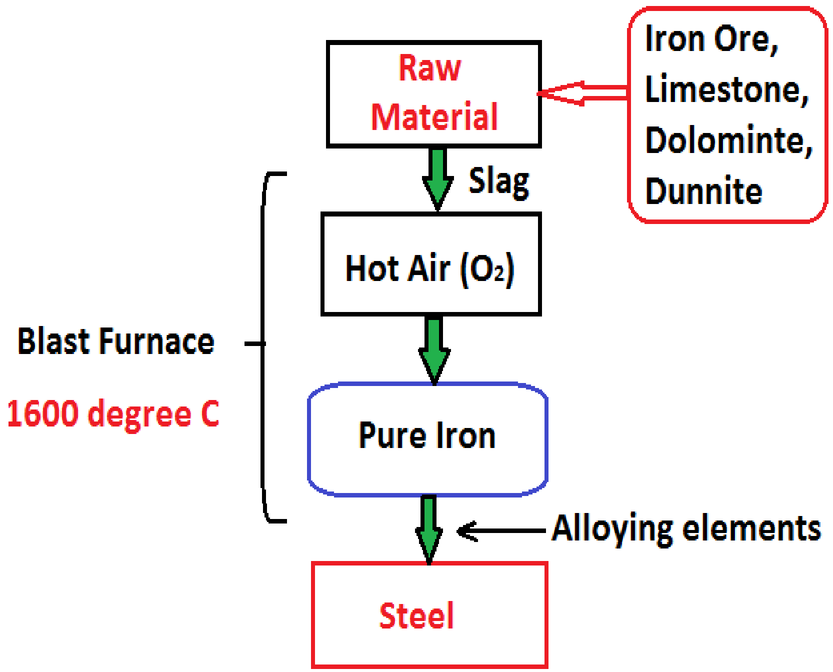
Steel is an alloy of iron having varying carbon percentage. When the carbon percentage in iron is less than 2% it is termed as steel and more than 2% but less than 6% it is called cast iron.

Steel is an alloy of iron and carbon with other elements or interstitial solid solution of carbon in iron. Theoretically, steel has a maximum of 2.11% carbon but in practice, the amount of carbon rarely exceeds 0.8%

All steel production processes consists of the same general principle.

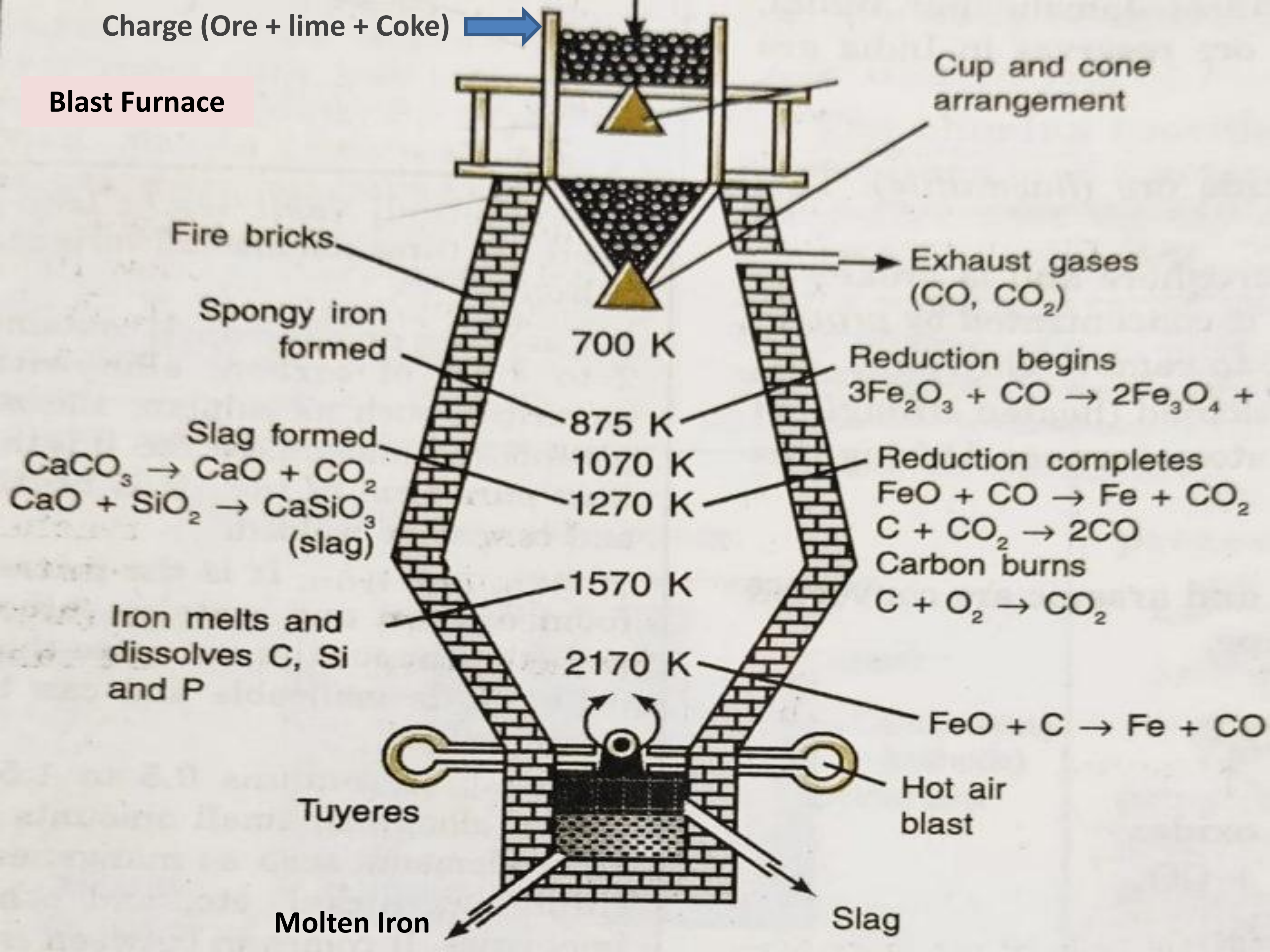
(i) Removal of C, S and P from pig-iron by oxidation. Mn and Si also form oxides which combine With lime added to form slag.

(ii) Separation of slag followed by addition of requisite quantities of deoxidiser and Other alloying elements.



Use: Iron is principally used as a structural. Mild steel is most widely used. Machine parts, tools, And materials are made of various kinds of alloy steels.

Blast Furnace



Types of steel

Steel which an alloy of iron can be classified based on carbon percentage and other alloying elements to improve the strength of steel.

Carbon steel: Carbon steel is a type of steel based on carbon percentage(%) it contains.

Low carbon steel (carbon % below 0.25): Has good formability, weld ability, low strength and low cost. Applications in deep drawing, chain, pipe, wire and making nails.

Medium carbon steel (carbon % in between 0.25 and 0.55): Has good toughness, ductility, relatively good strength and may be hardened by quenching. Applications in rolls, axles, screws, cylinders and crankshafts etc.

High carbon steel (carbon % higher than 0.55): Has high strength and hardness, wear-resistance and moderate ductility. Application in rolling mills, rope wire, screwdrivers, hammers, wrenches, bands saws etc.

Alloy steels: Alloy steel contains different alloying elements like manganese, cobalt, titanium, silicon, nickel, copper, aluminium, chromium etc. Alloy steels are widely used in the auto industry, power industry, transformers and piping industry.

Stainless steel: One of the most used steels in household items is stainless steel. Steel having 10% to 20% chromium makes steel stain free. There are three types of stainless steels namely austenitic, martensitic and Ferritic. Major applications of stainless steel are kitchen utensils, surgical items, dental equipment etc.

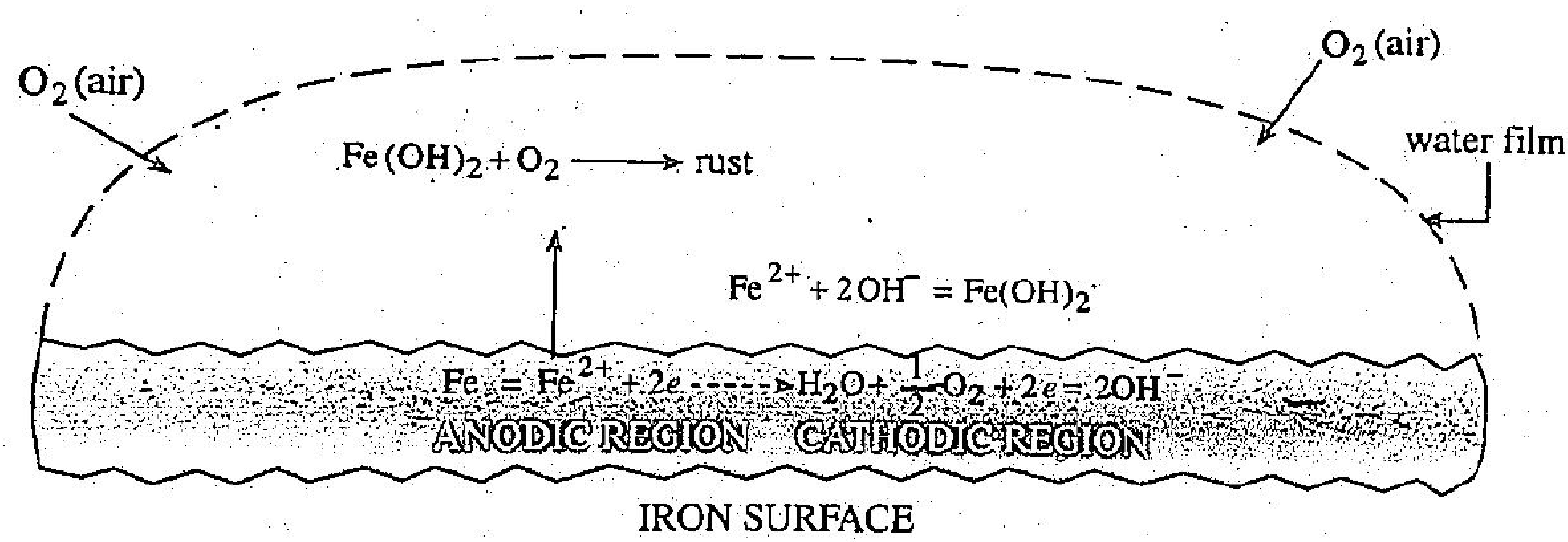
Tool steel: Tool steel contains tungsten, cobalt, molybdenum, vanadium as alloying elements. Tool steel applications include bars, sheets, strips, valve fittings, flanges, packaging items etc.

Alloy Steel and Composition

Sl No.	Alloy Steel	Composition
1	Stainless Steel	Chromium (10-20%)
2	Nickel Steel	Nickel (~3.5%)
3	Invar Steel	Nickel (30-40%)
4	Vanadium Steel	Vanadium (0.1-2%)
5	Tungsten Steel	Tungsten (14-20%)
6	Manganese Steel	Manganese (12-15%)
7	Molybdenum Steel	Molybdenum (0.2-0.3%)

Rusting of Iron

Rusting of iron is the most important types of atmospheric corrosion. It is well known that a freshly cleaned surface of iron soon get covered with a brown layer of hydrated iron (III) oxide, Commonly known as rust. Both oxygen and water are necessary for rust formation, but other factors influence the rate of rusting considerably. These include impurities or stress on the iron Surface, availability of dissolved oxygen and electrolytes in contact with the iron surface.



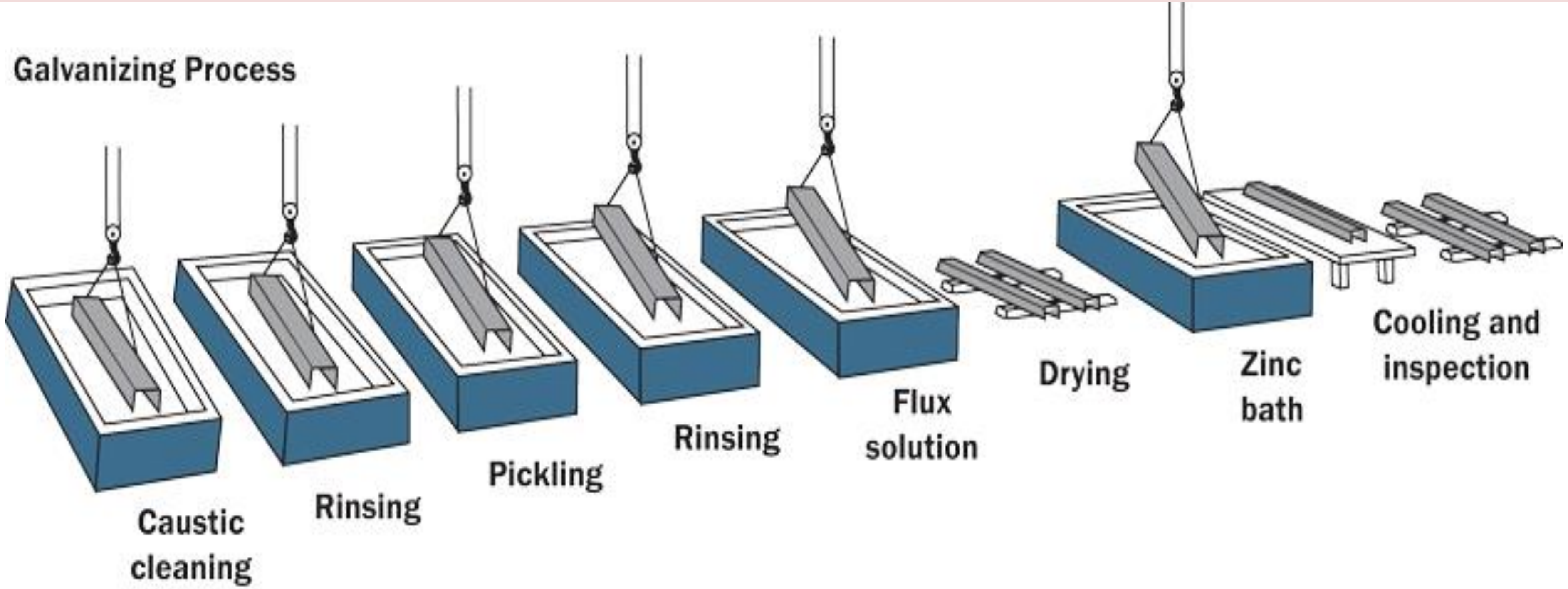
As the humidity exceeds about 80 percent, the rate of corrosion becomes rapid with the formation of common red rust.

Galvanization

Galvanization is a process used for the protection of steel or iron from rusting. In this process, a protective zinc coating is applied on the iron surface. The most common method of galvanizing is to hot dip the metal in a bath of molten zinc.

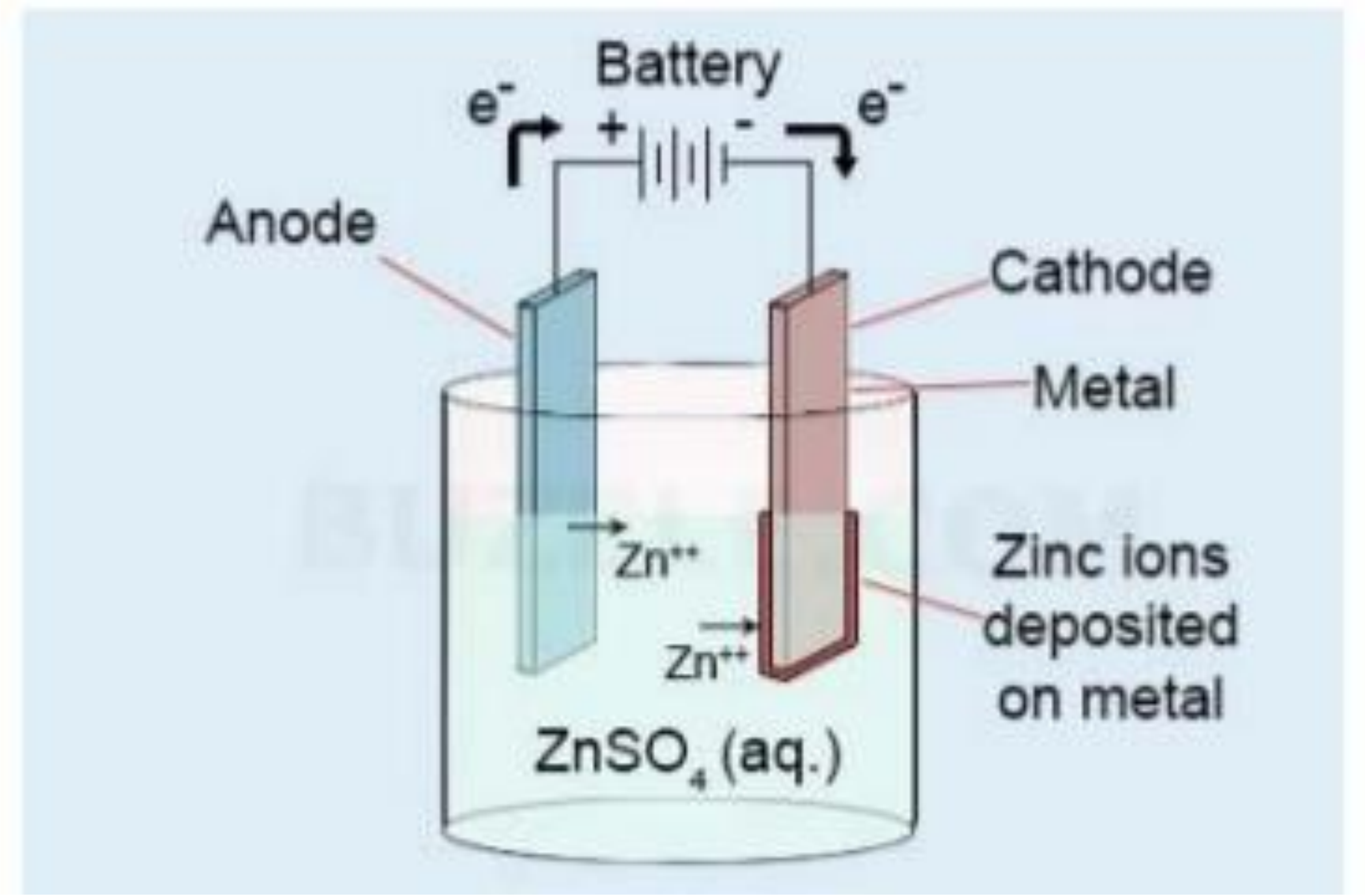
Zinc is more reactive metal than iron, hence it reacts with oxygen to form a protective oxide layer, which prevents inner iron from getting in contact with oxygen.

Having a metal galvanized provides it with anti-corrosion properties. Without using protective zinc coating, metal would be remain exposed to the different elements and oxidize as well as corrode quickly. As a matter of fact, galvanized steel can prove to be cost effective solution when compared to using materials like aluminum or austenitic stainless steel for preventing corrosion.



Zinc Plating

Principle



Zinc Plating

Surface preparation before coating mainly is:

- Chemical Cleaning
- Acid pickling
- Rinse
- Anodic electrocleaning
- Rinse
- Acid activation (not used for acid zinc plating)

Zinc Plating has the following types of electrolyte

- Acid zinc plating
- Alkaline Zinc Plating
- Alkaline Cyanide

Post-Treatment

- Rinse
- Baking (for high tensile bolts> 10.9
- Passivation (optional)
- Rinse
- Top-coats, lubrication (optional)

Important Ores of Some Common Metals

Metal	Ore
Sodium (Na)	NaCl (rock salt), $NaNO_3$(chile saltpetre), Na_3AlF_6 (cryolite)
Calcium (Ca)	$CaSO_4$. $2H_2O$ (gypsum), CaF_2 (fluorspar) $CaCO_3$ (limestone)
Magnesium (Mg)	$MgCO_3 \cdot CaCO_3$(dolomite),KCl.$MgCl_2$.$6H_2O$ (carnallite)
Aluminium (Al)	Al_2O_3.$2H_2O$ (bauxite), Na_3AlF_6 (cryolite), Al_2O_3 (Corundum) , Al_2O_3.H_2O (Diaspore)
Zinc (Zn)	ZnS (zinc blende), $ZnCO_3$ (calamine)
Iron (Fe)	Fe_2O_3 (haematite), Fe_3O_4 (magnetite), FeS_2 (iron pyrites)
Lead (Pb)	PbS (galena) , **$PbSO_4$** (anglesite)
Copper (Cu)	$CuFeS_2$ (copper pyrites), $CuCO_3$. Cu $(OH)_2$ (malachite)
Mercury (Hg)	HgS (cinnabar)
Silver (Ag)	Ag_2S (Argentite or silver glance), AgCl (horn silver)
Gold (Au)	Native (as free metal)

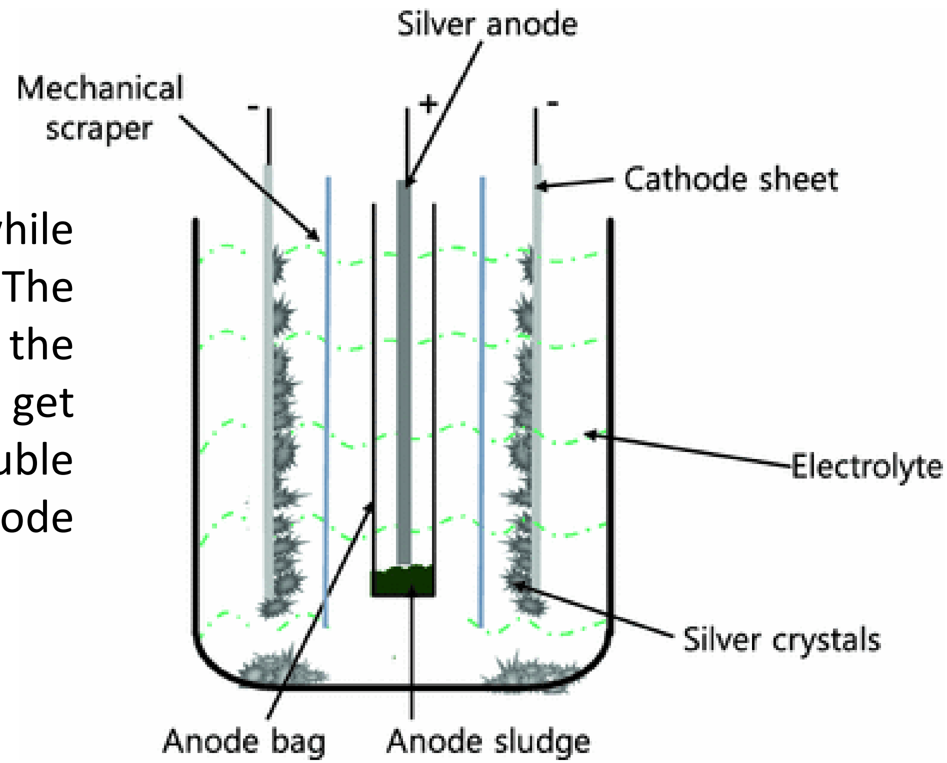
Principles of Isolation of Ag and Au

Extraction of Au and Ag involves leaching with metal CN-. This is also an oxidation reaction ($Ag \rightarrow Ag^+$ or $Au \rightarrow Au^+$). The metal later recovered by displacement method.

$4Au(s) + 8CN^-(aq) + 2H_2O + O_2(g) \rightarrow 4\,[Au(CN)_2]^-(aq) + 4OH^-(aq)$
$4\,[Au(CN)_2]^-(aq) + Zn(s) \rightarrow 2Au(s) + [Zn(CN)_4]^{2-}(aq)$

In this reaction Zn acts as a reducing agent.
Next refining of crude metal is done to get pure metal by electro refining method.

In this method, impure metal acts as anode while the cathode is a rod or sheet of pure metal. The electrolyte solution consists of soluble salt of the metal. On passing electricity pure metal get deposited on the cathod while the insoluble impurities are settle down below anode as anode mud or anode sludge



Ref.

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❖https://www.google.com/search?q=transition+metal&rlz=1C1ASUC_enIN712IN712&sxsrf=ALeKk01auMU9vZV3oU3kC2eKaWyoUmJNBw:1621957694468&source=lnms&tbm=isch&sa=X&ved=2ahUKEwjoleChlXwAhUk8HMBHSiECZQQ_AUoAXoECAEQAw&biw=1366&bih=657#imgrc=o07ZM0o4WABpRM

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