

UNIT-15

Analytical Chemistry

1. PRINCIPLES OF QUALITATIVE AND QUANTITATIVE ANALYSIS

Analytical Chemistry is concerned with answering the questions:

- **What** chemical species are present in a sample?
- **How much** of each chemical species is present?

Analytical Chemistry is vital in the following areas:

- Quality control in the process industries
 - of starting materials
 - of intermediates
 - of products
 - ◆ confirmation of **purity**
 - ◆ identification of impurities
- Environmental analysis
 - **Monitoring and control** of pollutants in streams that are to be released to the environment (in gas, liquid or solid form)
 - Measurement of pollutants in the environment (air/river/ground)
 - ◆ NO_x, SO_x, hydrocarbons in atmosphere
 - ◆ Organic chemicals (polychlorinated biphenyls, detergents)
 - ◆ Toxic heavy metals (lead, cadmium, mercury)
- Clinical and biological studies
 - Measurement of nutrients, including trace metals
 - Measurement of naturally produced chemicals (cholesterol, sugar, urea)
 - Measurement of drug levels in body
- Geological assays
 - Measurement of metal concentrations in ores and minerals
 - Measurement of oil/gas concentrations in rocks
- Fundamental and applied research
 - Chemical engineering: how much conversion (or separation) do we obtain under these conditions?
 - Organic molecule synthesis: what compound have we made?

Analytical Chemistry is thus vital in the process industries and in research laboratories.

- **Qualitative analysis** is the identification of elements, functional groups, or particular compounds in a sample.
- **Quantitative analysis** is the determination of the amount of a particular element, species or compound in a sample.

Analytical Chemists need to be good at careful accurate measurements, statistics and error analysis:

- samples of known concentration must often be prepared for calibration purposes

- samples must not become contaminated
- for environmental analysis, more than one measurement is often performed on more than one sample to draw conclusions.

On a process plant, analytical chemistry is normally performed “off-line”:

- a sample of product is removed and sent to the lab for testing – might take hours or days
- for plant control purposes, we may need to infer composition indirectly
 - e.g. from T and P measurements and a model of how conversion (or separation) varies with T and P
- numerous off-line analytical techniques.

However, an increasing number of analytical techniques can now be performed “on-line”

- sample the process stream “in situ”
- the plant can then be controlled using the direct composition measurement
- fewer techniques, and most will only work for certain reactions/products.

Classical (old-fashioned) analytical chemistry is based on techniques such as:

- **Titration:** volume of a standard reagent reacting with the sample is measured
 - Acid-base titrations: e.g. monitor the colour of a solution containing a pH-sensitive indicator as an acid (or base) is added.
 - Complexation titrations: e.g. monitor the pH of a solution whilst reagent EDTA, ethylene diaminetetraacetic acid ($\text{HOOCCH}_2)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{COOH})_2$, is added:
 - ♦ EDTA reacts in a 1:1 molar ratio with almost all metal cations (except alkali metals), enabling the metal cation concentration to be determined.
- **Gravimetry:** measurements based on mass. Simple examples are:
 - Mass lost on heating of a solid gives the amount of water of crystallisation.
 - Mass of precipitate formed during a reaction can be measured.
 - ♦ For instance, adding excess silver nitrate solution to determine the concentration of chloride ions present.
- **Electrochemical methods:**
 - pH measurement.
 - Ion-selective electrodes.

QUALITATIVE INORGANIC ANALYSIS

In qualitative analysis the given mixture is analysed for acidic and basic radicals i.e. for anions and cations that it contains.

Depending upon the quantity of sample made available it is classified as :

Macro Analysis 0.1 – 1g

Semi-micro Analysis 10-100 mg

Micro Analysis 1-10 mg

The common procedure for testing an unknown sample is to make its solution and then test this solution for different ions present. Steps involved in the systematic analysis of a given sample are

(a) Preliminary Tests :

- Colour and smell
- Flame Test
- Borax Bead Test

(b) Tests for Acid Radicals (Anions) :

- (i) Dil. Acid test (dil. H_2SO_4)
- (ii) Conc. Acid test (conc. H_2SO_4)
- (iii) We tests for acid radicals

(c) Wet Tests for Basic Radicals
(a) Preliminary Tests
(i) Colour and smell

Colour	Ion Indicated
Blue/Bluish Green	Cu^{2+} or Ni^{2+}
Greenish	Ni^{2+}
Light Green	Fe^{2+}
Dark Green	Cr^{3+}
Pink	Co^{2+}
Light Pink, Flesh colour or earthy colour	Mn^{2+}
Dark Brown	Fe^{3+}

Smell	Ion Indicated
Ammonical smell	NH_4^+
Vinegar like smell	CH_3COO^-
Smell of rotten eggs	S^{2-}

(ii) Flame Test

Colour of Flame	Ion Indicated
Brick Red	Ca^{++}
Crimson Red	Sr^{++}
Grassy Green	Ba^{++}
Bright-Bluish Green	Cu^{++}

(iii) Borex Bead Test

Colour of bead in oxidizing flame	Ion Indicated
Green in hot, light brown in cold	Copper (Cu^{++})
Pinkish violet in both hot and cold	Manganese (Mn)
Yellowish brown in hot and pale yellow in cold	Iron (Fe^{++})
Brown in hot and pale brown in cold	Nickel (Ni^{++})

(b) (i) Dilute Sulphuric Acid Test

Gas evolved	Ion Indicated
Colourless, odourless gas which turns water milky (CO_2)	CO_3^{2-}
Colourless, pungent smell, which turns acidified potassium dichromate paper green (SO_3)	SO_3^{2-}
Colourless, smell like that of rotten eggs, turns lead acetate paper black (H_2S)	S^{2-}
Raddish brown in colour, pungent smell, turns ferrous sulphate solution black (NO_2)	NO_2^-

(ii) Concentrated Sulphuric Acid Test

Gas Involved	Ion Indicated
Colourless gas with pungent smell, white flame with NH_4OH , white ppt. with AgNO_3 solution (HCl)	Cl^-
Reddish brown vapours with pungent smell, turns starch paper yellow but does not turn FeSO_4 solution black (Br_2)	Br^-
Deep violet vapours with pungent smell, turns starch paper blue	I^-
Reddish brown gas with pungent smell, turns FeSO_4 solution black (NO_3)	NO_3^-
Colourless vapours, vinegar smell, turns blue litmus red (CH_3COOH)	CH_3COO^-

(iii) Wet Tests for Acid Radicals :

 (a) Carbonate (CO_3^{2-}) :

Reaction with dilute HCl.



CO_2 gas when passed in lime water


 (b) Sulphite (S^{2-}) :

Lead Acetate Test :



Black ppt.

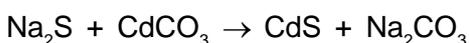
Sodium Nitroprusside Test :



Sodium Nitroprusside

Violet or Purple Colour

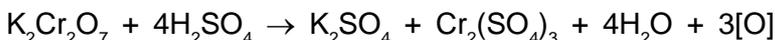
Cadmium Carbonate Test :



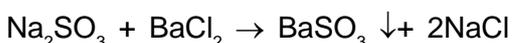
Yellow ppt.

 (c) Sulphite (SO_3^{2-}) :

Potassium Dichromate Test :



Barium Chloride Test :



White ppt.

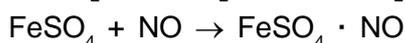
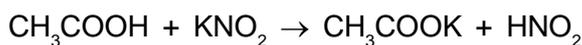


Potassium Permanganate Test :



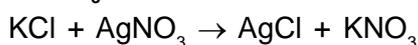
(d) Nitrite (NO₂²⁻) :
Potassium Iodide Test :


Liberated iodine turns starch paper blue.

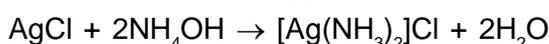
Ferrous Sulphate Test :


Dark Brown

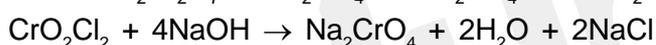
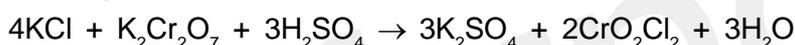
(e) Chloride (Cl⁻) :
MnO₂ Test :

AgNO₃ Test :


White ppt.



Soluble complex

Chromyl Chloride Test :


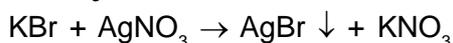
Chromyl Chloride Sod. Chromate



Lead chromate

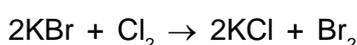
Yellow ppt.

(f) Bromide (Br⁻) :
MnO₂ Test :

AgNO₃ Test :


pale yellow ppt.

Pale yellow ppt. of silver bromide is sparingly soluble in NH₄OH.

Chlorine water Test :


Bromine being soluble in CCl₄ imparts an orange colour to the layer.

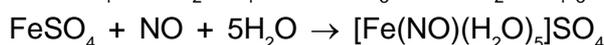
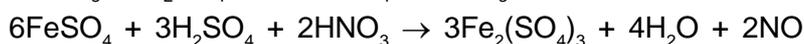
(g) Iodide (I⁻) :
MnO₂ Test :

AgNO₃ Test :

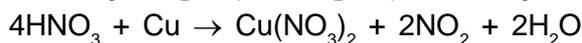
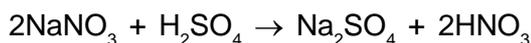

yellow ppt.

Chlorine Water Test :

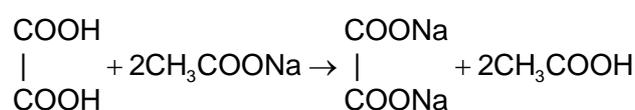
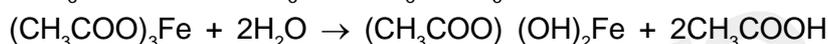
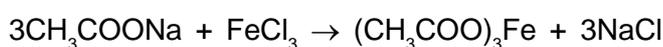

Iodine being soluble in CCl₄ imparts a violet colour to the CCl₄ layer.

(h) Nitrate (NO₃⁻) :
Ring Test :


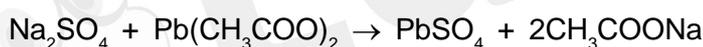
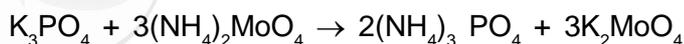
Brown ring

Copper Test :


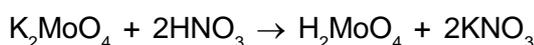
Reddish brown

(i) Acetate (CH₃COO⁻) :
Oxalic Acid Test :

Ferric Chloride Test :

(j) Sulphate (SO₄²⁻) :
Barium Chloride Test :

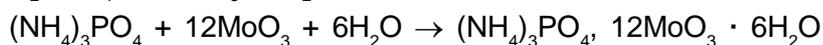

White ppt.

Lead Acetate Test :

(k) Phosphate (PO₄³⁻) :
Ammonium Molybdate Test :


Amm. Molybdate



Molybdate acid



Amm. Phospho molybdate

(yellow ppt.)

Magnesia Mixture Test :


Disodium Hydrogen

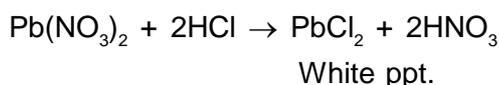
Mag. Amm. Phosphate

Phosphate

(white ppt.)

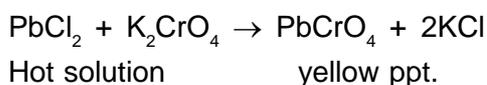
Classification of Basic Radicals (Cations) into Group

Group	Group Reagent	Cations	Form of ppt.
I (silver group)	Dilute HCl	Pb ²⁺	Chlorides
II (copper group)	H ₂ S in presence of dilute HCl	Pb ²⁺ , Hg ²⁺ , Cd ²⁺ , Cu ²⁺ etc.	Sulphides
III (Iron group)	NH ₄ OH in presence of NH ₄ Cl.	Fe ³⁺ , Al ³⁺	Hydroxides
IV (Zinc group)	H ₂ S in presence of NH ₄ OH	Ni ²⁺ , Zn ²⁺ , Mn ²⁺ , Co ²⁺	Sulphides
V (Calcium group)	(NH ₄) ₂ CO ₃ in presence of NH ₄ OH	Ca ²⁺ , Ba ²⁺ , Sr ²⁺	Carbonates
VI (Alkali group)		NH ₄ ⁺ , Mg ²⁺	

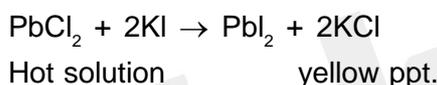
Reactions Involved in Group I Analysis :

Confirmatory Tests :

(i) On cooling, the precipitate settles down as PbCl₂ is less soluble in cold water.

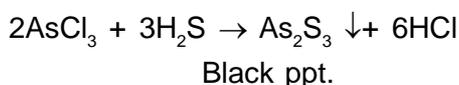
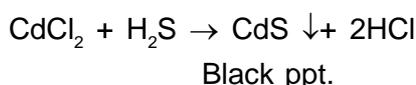
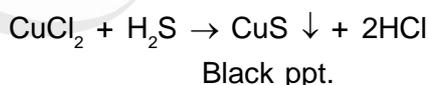
(ii) Potassium chromate test



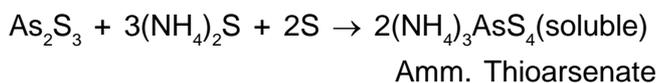
(iii) Potassium iodide test


Relation Involved in Group II Analysis :

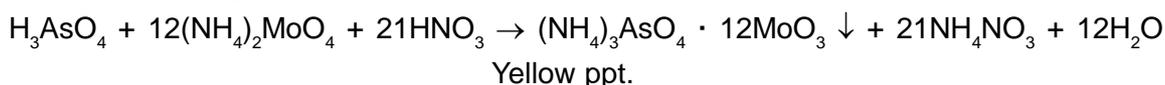
Passing of H₂S gas through the acidified original solution will provide the precipitate of radicals Hg²⁺, Pb²⁺, Cu²⁺, Cd²⁺ and As³⁺ as their sulphides.



Sulphides of Group IIA (copper group) are insoluble in yellow ammonium sulphide while that of IIB (Arsenic groups) are soluble. By treating with yellow ammonium sulphide groups IIA and IIB are separated.


Confirmatory Test for Arsenic :

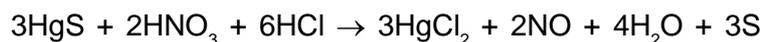
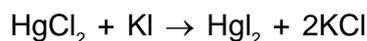

(i) **Ammonium Molybdate Test :**



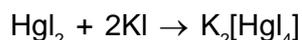
(ii) Magnesia Mixture Test :


White ppt.

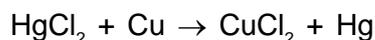
Mercury (Hg²⁺) : Black HgS is insoluble in 50% nitric acid. It dissolves in aqua-regia forming HgCl₂.


(i) Potassium Iodide Test :


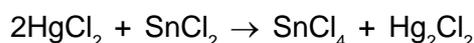
Red ppt.



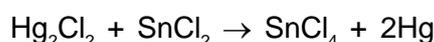
Soluble

(ii) Stannous Chloride Test :


white deposit

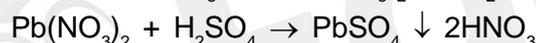
(iii) Stannous Chloride Test :


White



Grey

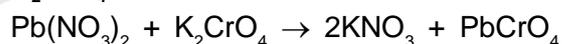
Lead (Pb²⁺) : Black ppt. of Pbs dissolves in 50% nitric acid. On adding H₂SO₄, lead sulphate is precipitated.



White

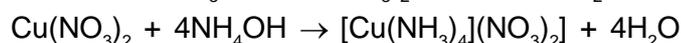
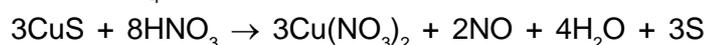
(i) KI Test :


Yellow

(ii) K₂CrO₄ Test :


Yellow

Copper (Cu²⁺) : Black ppt. of CuS dissolves in 50% nitric acid and blue solution is obtained on addition of excess of NH₄OH



Blue solution

(i) Potassium Ferrocyanide Test :


(Chocolate brown) colour

(ii) Potassium Iodide Test :


White ppt.

Cadmium (Cd²⁺) : The yellow ppt. is dissolved in 50% nitric acid

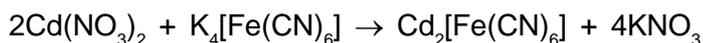


(i) **Sodium Hydroxide Test** :



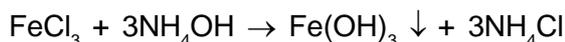
White ppt.

(ii) **Potassium Ferrocyanide Test** :

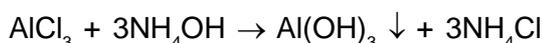


White ppt.

Reactions involved in Group III Analysis

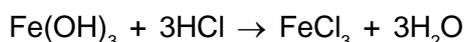


Reddish brown

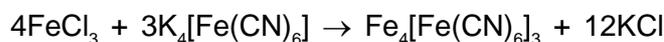


White

Iron (Fe³⁺) : The reddish brown ppt. of Fe(OH)₃ is dissolved in HCl.



(i) **Potassium Ferrocyanide Test** :



Ferric ferrocyanide

(Prussian Blue)

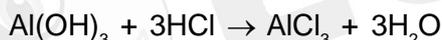
(ii) **Potassium Sulphocyanide Test** :



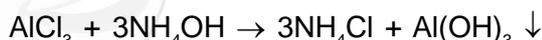
Ferric Sulphocyanide

(Blood Red)

Aluminium (Al³⁺) :



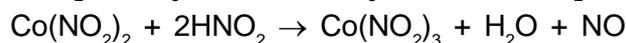
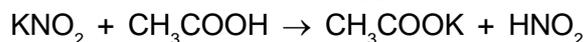
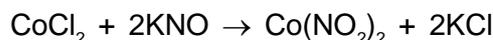
(dissolution)



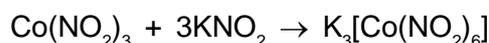
Reaction Involved in Group IV Analysis

Cobalt (Co²⁺) :

(i) **Potassium Nitrite Test** :



Cobaltic Nitrite



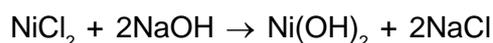
Yellow ppt.

(ii) **Ammonium Thiocyanate Ether Test** :

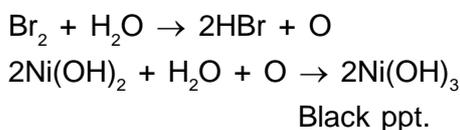


Nickel (Ni²⁺) :

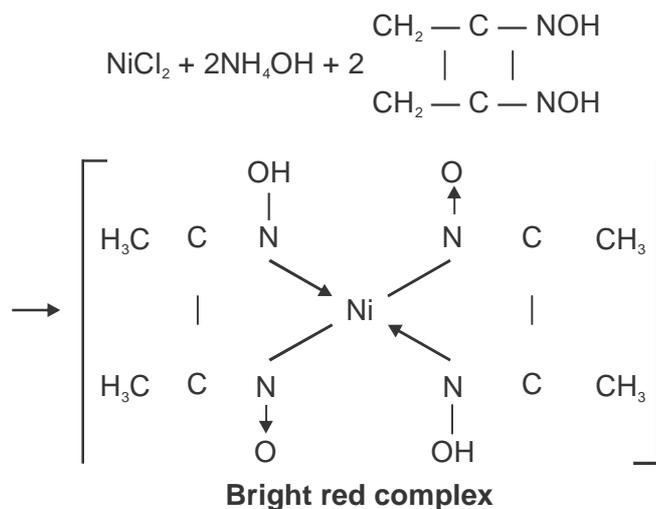
(i) **Sodium Hydroxide-Bromine Water Test** :



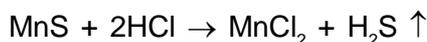
Green ppt.



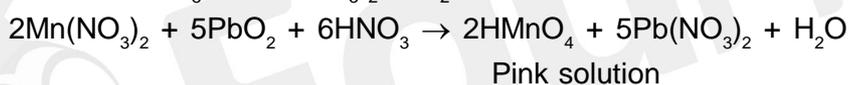
(ii) Dimethyl Glyoxime Test :



Manganese (Mn^{2+}) : Manganese sulphide dissolves in dilute HCl to form Manganese chloride and H_2S is boiled off.



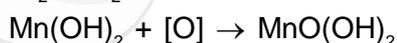
(i) PbO_2 Test :



(ii) NaOH and Br_2 Water Test :

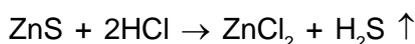


White ppt.

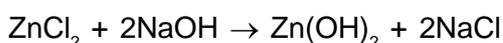


Brown ppt.

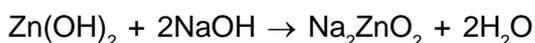
Zinc (Zn^{2+}) :



(i) NaOH Test :

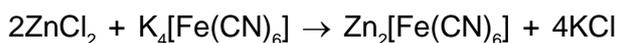


White ppt.



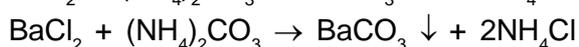
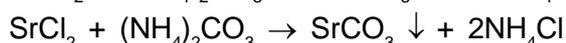
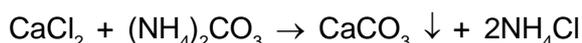
Soluble

(ii) Potassium Ferrocyanide Test :



White or Bluish white ppt.

Reactions Involved in Group V Analysis :

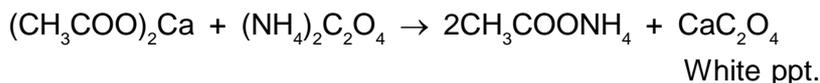


These insoluble carbonates dissolve in acetic acid and form soluble acetates.

Calcium (Ca²⁺) : White ppt. of CaCO₃ is dissolved in hot dilute acetic acid

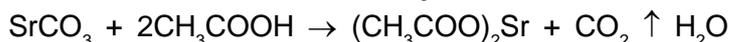


(i) **Ammonium Oxalate Test**

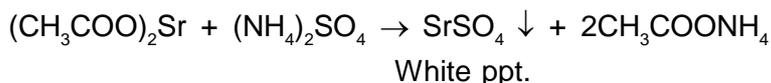


(ii) **Flame Test** : Calcium imparts brick red colour to the flame.

Strontium (Sr²⁺) : White precipitate of SrCO₃ is dissolved in hot dilute acetic acid.



(i) **Ammonium Sulphate Test** :

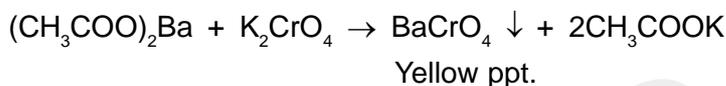


(ii) **Flame Test** : Strontium imparts crimson red colour to the flame.

Barium (Ba²⁺) : White precipitate of BaCO₃ is dissolved in hot dilute acetic acid.



(i) **Potassium Chromate Test** :



(ii) **Flame Test** : Barium produces grassy green colour to the flame.

Reactions Involved in Group VI Analysis :

Ammonium (NH₄⁺) :



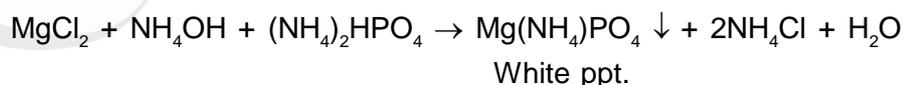
Nessler's Reagent Test :



Nessler's Reagent

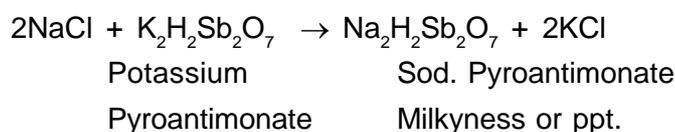
Magnesium (Mg²⁺) :

Ammonium Phosphate Test :



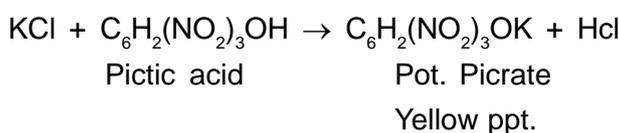
Sodium (Na⁺) :

Potassium Pyroantimonate Test :

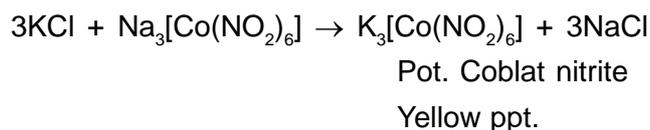


Potassium (K⁺) :

(i) **Picric Acid Test** :

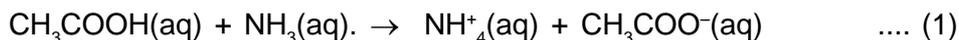


(ii) **Sodium Cobaltinitrite Test** :



Acid–Base Reactions

A useful definition of acids and bases is that independently introduced in 1923 by Johannes Brønsted and Thomas Lowry. In the Brønsted-Lowry definition, an acid is a proton donor and a base is a proton acceptor. Note the connection in these definitions—defining a base as a proton acceptor implies that there is an acid available to donate the proton. For example, acetic acid, CH_3COOH , donates a proton to ammonia, NH_3 , which serves as the base.



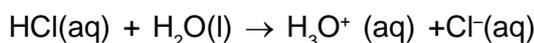
When an acid and a base react, the products are a new acid and a new base. For example, the acetate ion, CH_3COO^- , in reaction 1 is a base that can accept a proton from the acidic ammonium ion, NH_4^+ , forming acetic acid and ammonia. We call the acetate ion the conjugate base of acetic acid, and the ammonium ion is the conjugate acid of ammonia.

Strong and Weak Acids

The reaction of an acid with its solvent (typically water) is an acid dissociation reaction.

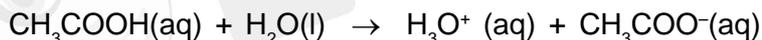
We divide acids into two categories—strong and weak—based on their ability to donate a proton to the solvent.

A **strong acid**, such as HCl, almost completely transfers its proton to the solvent, which acts as the base.



We use a single arrow (\rightarrow) in place of the equilibrium arrow (\rightleftharpoons) because we treat HCl as if it completely dissociates in aqueous solutions. In water, the common strong acids are hydrochloric acid (HCl), hydroiodic acid (HI), hydrobromic acid (HBr), nitric acid (HNO_3), perchloric acid (HClO_4), and the first proton of sulfuric acid (H_2SO_4).

A **weak acid**, of which aqueous acetic acid is one example, does not completely donate its acidic proton to the solvent. Instead, most of the acid remains undissociated, with only a small fraction present as the conjugate base.

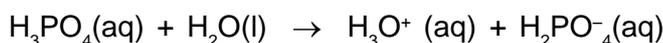


The equilibrium constant for this reaction is an acid dissociation constant, K_a , which we write as

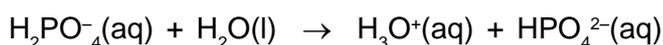
$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]} = 1.75 \times 10^{-5}$$

The magnitude of K_a provides information about a weak acid's relative strength, with a smaller K_a corresponding to a weaker acid. The ammonium ion, NH_4^+ , for example, with a K_a of 5.702×10^{-10} , is a weaker acid than acetic acid.

Monoprotic weak acids, such as acetic acid, have only a single acidic proton and a single acid dissociation constant. Other acids, such as phosphoric acid, have more than one acidic proton, each characterized by an acid dissociation constant. We call such acids polyprotic weak acids. Phosphoric acid, for example, has three acid dissociation reactions and three acid dissociation constants.



$$K_{a1} = \frac{[\text{H}_2\text{PO}_4^-][\text{H}_3\text{O}^+]}{[\text{H}_3\text{PO}_4]} = 7.11 \times 10^{-3}$$



$$K_{a2} = \frac{[\text{HPO}_4^{2-}][\text{H}_3\text{O}^+]}{[\text{H}_2\text{PO}_4^-]} = 6.32 \times 10^{-8}$$

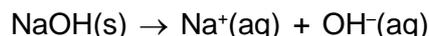


$$K_{a3} = \frac{[\text{PO}_4^{3-}][\text{H}_3\text{O}^+]}{[\text{HPO}_4^{2-}]} = 4.5 \times 10^{-13}$$

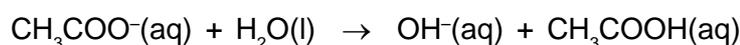
The decrease in the acid dissociation constants from K_{a1} to K_{a3} tells us that each successive proton is harder to remove. Consequently, H_3PO_4 is a stronger acid than H_2PO_4^- , and H_2PO_4^- is a stronger acid than HPO_4^{2-} .

Strong and Weak Bases

The most common example of a strong base is an alkali metal hydroxide, such as sodium hydroxide, NaOH, which completely dissociates to produce hydroxide ion.



A weak base, such as the acetate ion, CH_3COO^- , only partially accepts a proton from the solvent, and is characterized by a base dissociation constant, K_b . For example, the base dissociation reaction and the base dissociation constant for the acetate ion are

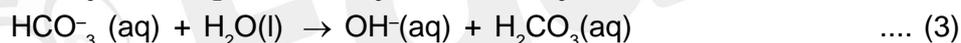
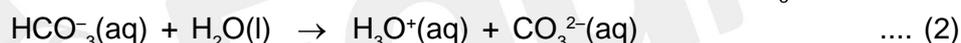


$$K_b = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} = 5.71 \times 10^{-10}$$

A polyprotic weak base, like a polyprotic acid, has more than one base dissociation reaction and more than one base dissociation constant.

Amphiprotic Species

Some species can behave as either a weak acid or as a weak base. For example, the following two reactions show the chemical reactivity of the bicarbonate ion, HCO_3^- , in water.



A species that is both a proton donor and a proton acceptor is called amphiprotic. Whether an amphiprotic species behaves as an acid or as a base depends on the equilibrium constants for the competing reactions. For bicarbonate, the acid dissociation constant for reaction (2)

$$K_{a2} = \frac{[\text{CO}_3^{2-}][\text{H}_3\text{O}^+]}{[\text{HCO}_3^-]} = 4.69 \times 10^{-11}$$

is smaller than the base dissociation constant for reaction (3)

$$K_{b2} = \frac{[\text{H}_2\text{CO}_3][\text{OH}^-]}{[\text{HCO}_3^-]} = 2.25 \times 10^{-8}$$

Because bicarbonate is a stronger base than it is an acid, we expect an aqueous solution of HCO_3^- to be basic.

Dissociation of Water

Water is an amphiprotic solvent because it can serve as an acid or as a base. An interesting feature of an amphiprotic solvent is that it is capable of reacting with itself in an acid–base reaction.



We identify the equilibrium constant for this reaction as water's dissociation constant, K_w ,

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.00 \times 10^{-14} \quad \dots (5)$$

which has a value of 1.0000×10^{-14} at a temperature of 24°C . The value of K_w varies substantially with temperature. For example, at 20°C K_w is 6.809×10^{-15} , while at 30°C K_w is 1.469×10^{-14} . At 25°C , K_w is 1.008×10^{-14} , which is sufficiently close to 1.00×10^{-14} that we can use the latter value with negligible error.

An important consequence of equation (5) is that the concentration of H_3O^+ and the concentration of OH^- are related. If we know $[\text{H}_3\text{O}^+]$ for a solution, then we can calculate $[\text{OH}^-]$ using equation (5)

Example-

What is the $[\text{OH}^-]$ if the $[\text{H}_3\text{O}^+]$ is $6.12 \times 10^{-5} \text{ M}$?

Solution

$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.00 \times 10^{-14}}{6.12 \times 10^{-5}} = 1.63 \times 10^{-10}$$

The pH Scale

Equation (5) allows us to develop a pH scale that indicates a solution's acidity. When the concentrations of H_3O^+ and OH^- are equal a solution is neither acidic nor basic; that is, the solution is neutral. Letting

$$[\text{H}_3\text{O}^+] = [\text{OH}^-]$$

substituting into equation (5)

$$K_w = [\text{H}_3\text{O}^+]^2 = 1.00 \times 10^{-14} \text{ and solving for } [\text{H}_3\text{O}^+] \text{ gives}$$

$$[\text{H}_3\text{O}^+] \sqrt{1} = \sqrt{1.00 \times 10^{-14}} = 1.00 \times 10^{-7}$$

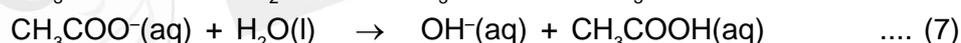
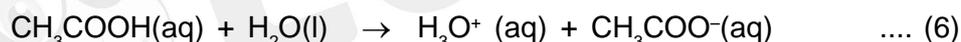
A neutral solution has a hydronium ion concentration of $1.00 \times 10^{-7} \text{ M}$ and a pH of 7.00. For a solution to be acidic the concentration of H_3O^+ must be greater than that for OH^- , which means that

$$[\text{H}_3\text{O}^+] > 1.00 \times 10^{-7} \text{ M}$$

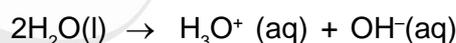
The pH of an acidic solution, therefore, must be less than 7.00. A basic solution, on the other hand, has a pH greater than 7.00.

Tabulating Values for K_a and K_b

A useful observation about acids and bases is that the strength of a base is inversely proportional to the strength of its conjugate acid. Consider, for example, the dissociation reactions of acetic acid and acetate.



Adding together these two reactions gives the reaction



for which the equilibrium constant is K_w . Because adding together two reactions is equivalent to multiplying their respective equilibrium constants, we may express K_w as the product of K_a for CH_3COOH and K_b for CH_3COO^- .

$$K_w = K_{a,\text{CH}_3\text{COOH}} \times K_{b,\text{CH}_3\text{COO}^-}$$

For any weak acid, HA, and its conjugate weak base, A^- , we can generalize this to the following equation.

$$K_w = K_{a,\text{HA}} \times K_{b,\text{A}^-} \quad \dots (8)$$

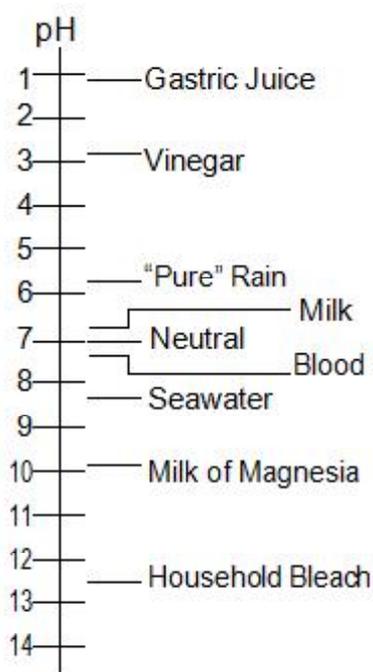


Figure : Scale showing the pH value for representative solutions.

Milk of Magnesia is a saturated solution of $\text{Mg}(\text{OH})_2$.

The relationship between K_a and K_b for a conjugate acid–base pair simplifies our tabulation of acid and base dissociation constants.



Eduncle

2. REDOX REACTIONS

Redox

Oxidation may be defined as electron loss and reduction as electron gain.

The following equations represent examples of redox reactions and the half equations clearly show the transfer of electrons.

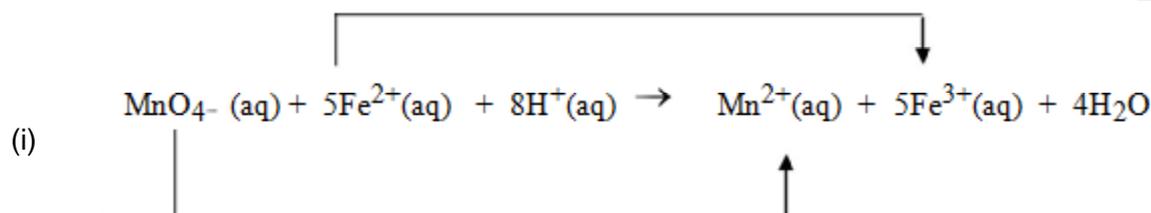
- $2\text{I}^-(\text{aq}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{Cl}^-(\text{aq}) + \text{I}_2(\text{aq})$
 - $2\text{I}^-(\text{aq}) - 2\text{e}^- \rightarrow \text{I}_2(\text{aq})$ oxidation
 - $\text{Cl}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{Cl}^-(\text{aq})$ reduction
- $\text{Zn}(\text{s}) + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu}(\text{s})$
 - $\text{Zn}(\text{s}) - 2\text{e}^- \rightarrow \text{Zn}^{2+}(\text{aq})$ oxidation
 - $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$ reduction

(a) Oxidation state or oxidation number

Oxidation is an increase in oxidation number and reduction is a decrease in oxidation number.

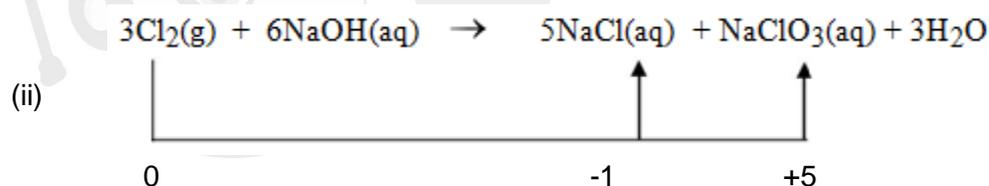
Examples

Consider the changes in oxidation state (number) in the following



the element manganese changes from +7 to +2 and so has been reduced.

Summary	Manganese	+7	→	+2	change -5
	Iron	5 × +2	→	5 × +3	change +5



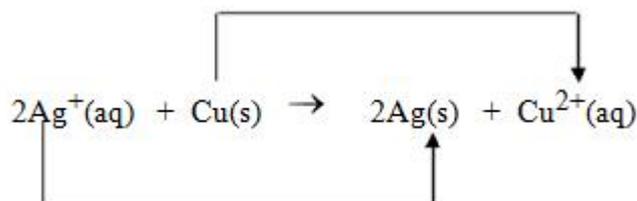
Oxidation state

Six chlorine atoms oxidation state zero change to five chloride ions oxidation state -1 and chlorine in one ClO_3^- ion with oxidation state +5

Chlorine is simultaneously oxidised and reduced. This is called **disproportionation**.

Summary	Chlorine	6 × 0 (5 × 1) + (1 × +5)	change zero
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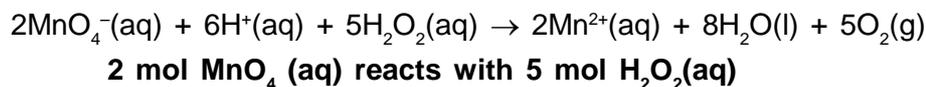
(iii) One copper atom changes from 0 to +2 so has been oxidised



two silver ions change from +1 to 0 so have been reduced

Summary	Silver	2 × +1	→	0	change -2
	Copper	0	→	+2	change +2

The overall equation is:



The use of potassium dichromate(VI) in volumetric analysis

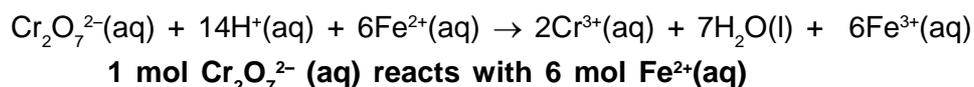
Here the orange aqueous potassium dichromate(VI) is placed in the burette but this time an indicator is required e.g. during the oxidation of aqueous iron(II) ions.



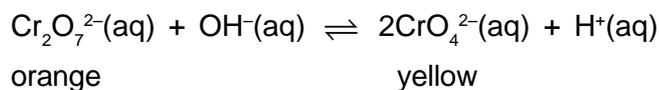
Since the ion-electron half equation for $\text{Cr}_2\text{O}_7^{2-}$ is:



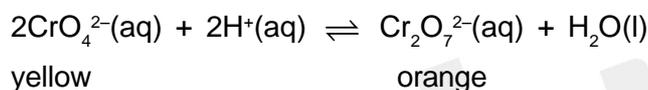
The overall equation is:



Note that the interconversion of dichromate(VI), $\text{Cr}_2\text{O}_7^{2-}(\text{aq})$, and chromate(VI), $\text{CrO}_4^{2-}(\text{aq})$, is **NOT** redox as the chromium does not change its oxidation number.



or



The oxidation number of the chromium is +6 in both of these ions.

This is an acid/base equilibrium and shows that dichromate(VI) ions are stable in acidic solution and chromate(VI) is stable in alkaline solution.

The use of sodium thiosulfate(VI) in volumetric analysis

Aqueous sodium thiosulfate(VI) is oxidised by aqueous iodine.

The concentration of oxidising agents can be determined by reaction with excess aqueous iodide ions, and then titrating the iodine released with aqueous sodium thiosulfate. The aqueous sodium thiosulfate is placed in the burette; the oxidising agent is pipetted into the conical flask which contains excess aqueous potassium iodide. The sodium thiosulfate solution is run into the flask until the colour due to iodine fades to a pale straw colour. At this point starch solution is added as indicator, turning the mixture dark blue. The end point is reached when the blue colour is completely discharged.

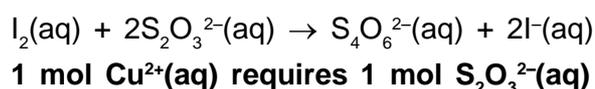
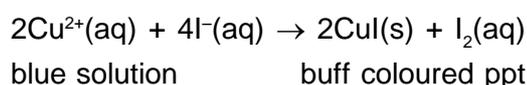
The ion-electron half equation is:



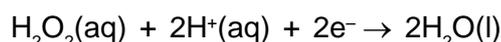
Here are some oxidising agents which can be determined by sodium thiosulfate titrations.

(i) Aqueous copper(II) salts

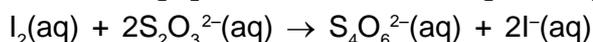
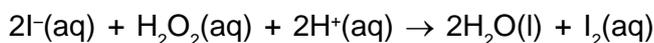
Aqueous copper(II) ions oxidise aqueous iodide ions



(ii) Aqueous hydrogen peroxide



The potassium iodide must be acidified with dilute sulfuric acid.

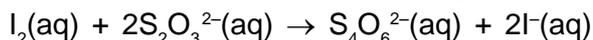
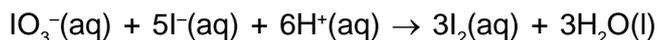


1 mol $\text{H}_2\text{O}_2(\text{aq})$ requires 2 mol of $\text{S}_2\text{O}_3^{2-}(\text{aq})$

(iii) Aqueous potassium iodate(V)

As potassium iodate(V) can be obtained in a very pure state, it can be used to standardise aqueous sodium thiosulfate.

In the presence of excess acid, potassium iodate(V) will oxidise aqueous iodide ions.



1 mol $\text{IO}_3^-(\text{aq})$ requires 6 mol $\text{S}_2\text{O}_3^{2-}(\text{aq})$

The specification requires, "use titration and other data to carry out appropriate calculations".

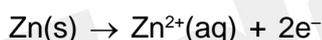
(b) Electrode processes

Electrode processes involve oxidations and reductions e.g. during electrolysis, oxidation takes place at the anode and reduction takes place at the cathode.

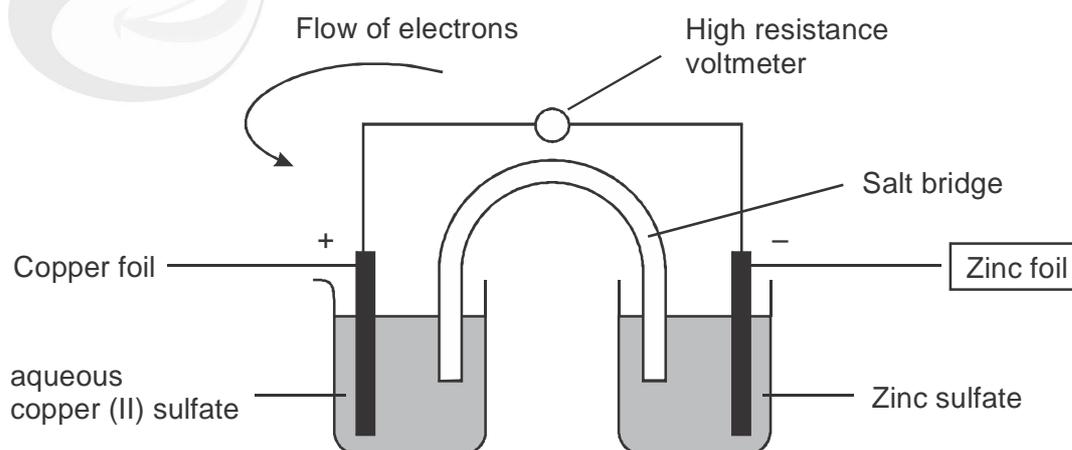
Many industrial processes involve electrolysis e.g. reactive metals such as sodium and aluminium are extracted electrolytically, the metal ions gaining electrons at the cathodes of the electrolytic cells.

Consider the changes that occur when small pieces of zinc metal are dropped into aqueous copper(II) sulfate. If the mixture is stirred, gradually the blue colour of the solution begins to fade and a reddish deposit is seen on the pieces of zinc and at the bottom of the beaker.

A redox reaction has taken place.



The aqueous zinc ion is colourless and the blue colour of the aqueous copper(II) ion disappears as the ions are reduced to the metal. If the two halves of the reaction are kept separate, chemical energy is changed into electrical energy producing a voltage.



The salt bridge is needed to allow ions to flow from one solution to the other while the two solutions themselves are kept separate.

Electrons are released at the zinc electrode and will flow through the external wire to the copper electrode where copper ions accept electrons.

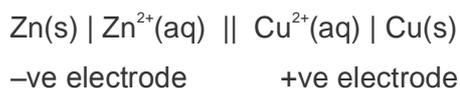
The emf of this cell is of the order of 1.1 volts.

By convention the cell is represented by a cell diagram but note that a cell diagram is not the same as a diagram of a cell which is the diagram above.

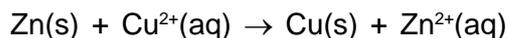
This cell diagram representing the above system is

Substance being
oxidised

Substance being
reduced



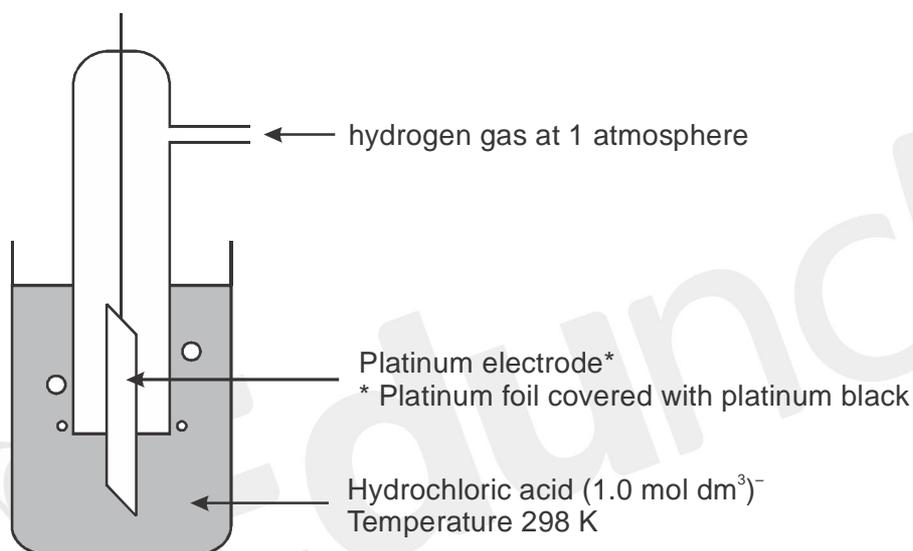
This cell diagram represents



The standard hydrogen electrode

As can be seen above a combination of two electrodes produces an emf.

By convention all such emfs are measured with respect to the standard hydrogen electrode.



By convention the electrode process at the platinum electrode $2\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{H}_2(\text{g})$ is taken as the standard and other potentials are measured with respect to it.

Electrode potential

By definition, the electrode potential of a half cell, say $\text{Zn} \mid \text{Zn}^{2+}(\text{aq})$, is the emf of a cell represented by the cell diagram



When conditions are standard i.e. 298K and unit concentrations (1.0 mol dm^{-3}) the emf is called the **Standard Electrode Potential (E)**.

The sign of the electrode potential is the sign of the right hand electrode in the cell diagram.

The emf of a cell is measured using a high resistance voltmeter which takes no current itself. The emf is the potential difference across the cell when it takes no current. The emf is a measure of the maximum amount of energy which can be given by the cell.

Some Standard Electrode Potentials

Reaction	E° / V
$\text{Li}^+(\text{aq}) + e^- \rightleftharpoons \text{Li}(\text{s})$	- 3.04
$\text{K}^+(\text{aq}) + e^- \rightleftharpoons \text{K}(\text{s})$	- 2.92
$\text{Ca}^{2+}(\text{aq}) + 2e^- \rightleftharpoons \text{Ca}(\text{s})$	- 2.76
$\text{Na}^+(\text{aq}) + e^- \rightleftharpoons \text{Na}(\text{s})$	- 2.71
$\text{Mg}^{2+}(\text{aq}) + 2e^- \rightleftharpoons \text{Mg}(\text{s})$	- 2.38
$\text{Al}^{3+}(\text{aq}) + 3e^- \rightleftharpoons \text{Al}(\text{s})$	- 1.66
$2\text{H}_2\text{O}(\text{l}) + 2e^- \rightleftharpoons \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$	- 0.83
$\text{Zn}^{2+}(\text{aq}) + 2e^- \rightleftharpoons \text{Zn}(\text{s})$	- 0.76
$\text{Cr}^{3+}(\text{aq}) + 3e^- \rightleftharpoons \text{Cr}(\text{s})$	- 0.74
$\text{Fe}^{2+}(\text{aq}) + 2e^- \rightleftharpoons \text{Fe}(\text{s})$	- 0.41
$\text{Ni}^{2+}(\text{aq}) + 2e^- \rightleftharpoons \text{Ni}(\text{s})$	- 0.23
$\text{Sn}^{2+}(\text{aq}) + 2e^- \rightleftharpoons \text{Sn}(\text{s})$	- 0.14
$\text{Pb}^{2+}(\text{aq}) + 2e^- \rightleftharpoons \text{Pb}(\text{s})$	- 0.13
$\text{Fe}^{3+}(\text{aq}) + 3e^- \rightleftharpoons \text{Fe}(\text{s})$	- 0.04
$2\text{H}^+(\text{aq}) + 2e^- \rightleftharpoons \text{H}_2(\text{g})$	0.00
$\text{Sn}^{4+}(\text{aq}) + 2e^- \rightleftharpoons \text{Sn}^{2+}(\text{aq})$	+0.15
$\text{Cu}^{2+}(\text{aq}) + e^- \rightleftharpoons \text{Cu}^+(\text{aq})$	+0.16
$\text{Cu}^{2+}(\text{aq}) + 2e^- \rightleftharpoons \text{Cu}(\text{s})$	+0.34
$\text{Cu}^+(\text{aq}) + e^- \rightleftharpoons \text{Cu}(\text{s})$	+0.52
$\text{I}_2(\text{s}) + 2e^- \rightleftharpoons 2\text{I}^-(\text{aq})$	+0.54
$\text{Fe}^{3+}(\text{aq}) + e^- \rightleftharpoons \text{Fe}^{2+}(\text{aq})$	+0.77
$\text{Hg}_2^{2+}(\text{aq}) + 2e^- \rightleftharpoons 2\text{Hg}(\text{l})$	+0.80
$\text{Ag}^+(\text{aq}) + e^- \rightleftharpoons \text{Ag}(\text{s})$	+0.80
$\text{Hg}^{2+}(\text{aq}) + 2e^- \rightleftharpoons \text{Hg}(\text{l})$	+0.85
$2\text{Hg}^{2+}(\text{aq}) + 2e^- \rightleftharpoons \text{Hg}_2^{2+}(\text{aq})$	+0.90
$\text{NO}_3^-(\text{aq}) + 4\text{H}^+(\text{aq}) + 3e^- \rightleftharpoons \text{NO}(\text{g}) + 2\text{H}_2\text{O}(\text{l})$	+0.96
$\text{Br}_2(\text{l}) + 2e^- \rightleftharpoons 2\text{Br}^-(\text{aq})$	+1.07
$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4e^- \rightleftharpoons 2\text{H}_2\text{O}(\text{l})$	+1.23
$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6e^- \rightleftharpoons 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$	+1.33
$\text{Cl}_2(\text{g}) + 2e^- \rightleftharpoons 2\text{Cl}^-(\text{aq})$	+1.36
$\text{Ce}^{4+}(\text{aq}) + e^- \rightleftharpoons \text{Ce}^{3+}(\text{aq})$	+1.44
$\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5e^- \rightleftharpoons \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$	+1.51
$\text{H}_2\text{O}_2(\text{aq}) + 2\text{H}^+(\text{aq}) + 2e^- \rightleftharpoons 2\text{H}_2\text{O}(\text{l})$	+1.78
$\text{Co}^{3+}(\text{aq}) + e^- \rightleftharpoons \text{Co}^{2+}(\text{aq})$	+1.82
$\text{F}_2(\text{g}) + 2e^- \rightleftharpoons 2\text{F}^-(\text{aq})$	+2.87

Note that some standard electrode potentials above are given for cells containing ions in different oxidation states e.g. $\text{Fe}^{3+}(\text{aq}) + \text{e} \rightleftharpoons \text{Fe}^{2+}(\text{aq})$.

Physically these cells use an inert platinum electrode to allow the passage of electrons. The cell diagram for determining the standard electrode potential is written

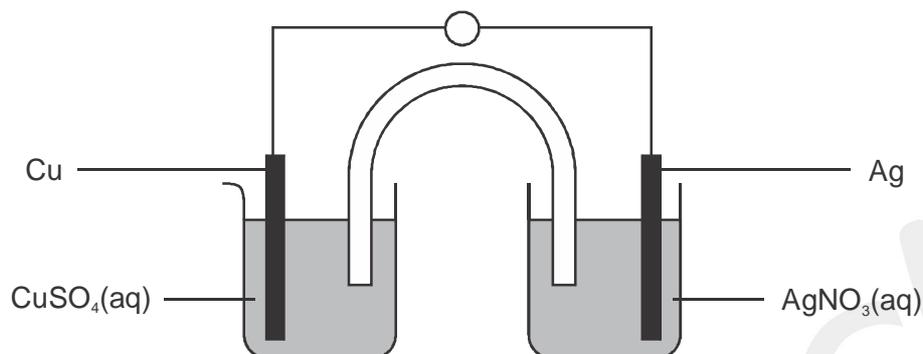


and standard conditions apply.

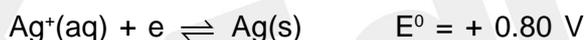
The uses of standard electrode potentials

To calculate the emf of a cell made by combining different electrodes.

Consider the following practical setup.

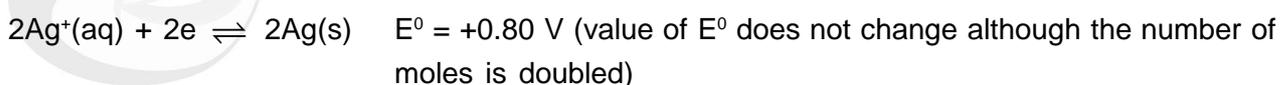


From the table above



Careful observation shows that silver is deposited on the silver electrode and the copper electrode starts to dissolve. The reaction with the more positive E° will proceed in the forward direction because reduction is more favourable.

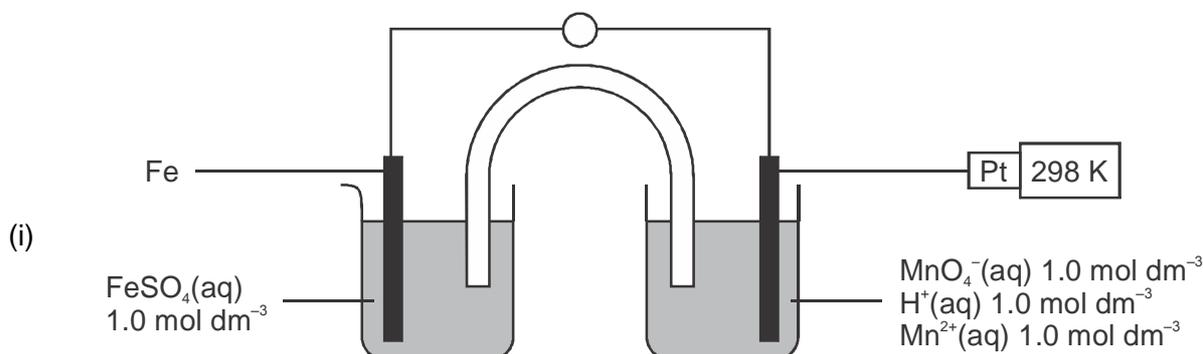
The overall reactions are



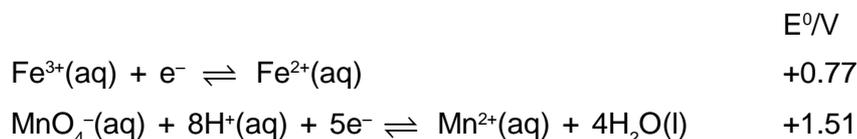
Overall we can add the two equations to obtain the overall redox equation and also add the E° values $\text{Cu}(\text{s}) + 2\text{Ag}^+(\text{aq}) \rightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{Ag}(\text{s}) \quad E^{\circ} = +0.46 \text{ V}$

This value agrees with the experimentally determined value under standard conditions and a positive value for E° means that the reaction is feasible.

Other examples of redox cell chemistry

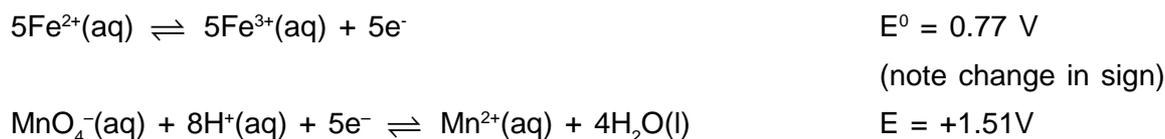


From the table above



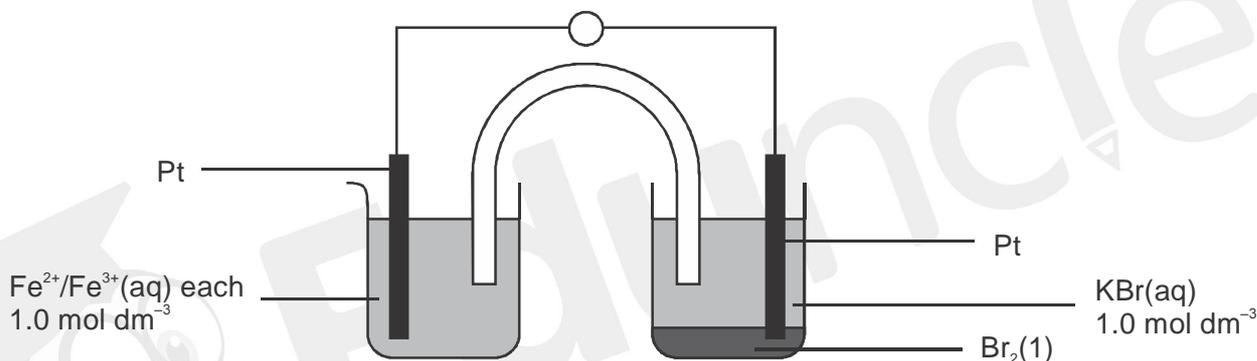
MnO_4^- has the more positive E^0 value so this reaction proceeds in the forward direction and acidified potassium manganate(VII) oxidises iron(II).

Rearranging

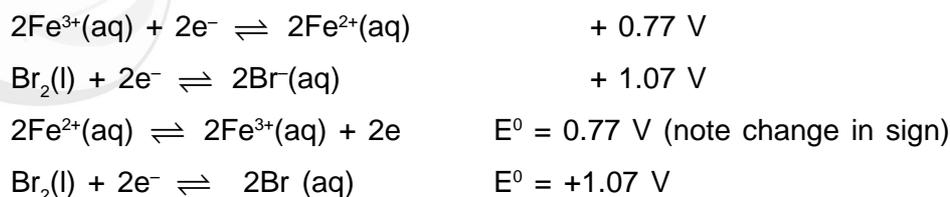


The Fe electrode is negatively charged and the Pt electrode is positively charged meaning that electrons would flow from the iron to the platinum if the cell were short circuited.

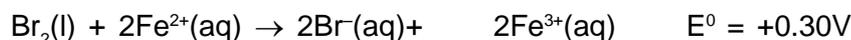
(ii) State what the spontaneous reaction would be in the following set up.



From the table of standard redox potentials



The spontaneous reaction is



Applications

Redox processes occur widely in chemistry..

Very few metals occur uncombined or as "native" metals (gold and silver, and to some extent copper, occur as the metal).

Mercury can be obtained by heating its oxide. Most metals are obtained from their ores by reduction. Metals such as iron and copper are obtained by chemical reduction whereas very reactive metals such as sodium, potassium and aluminium are extracted by electrolytic reduction.

Electrolysis is important in other industrial processes, e.g. in the extraction of the halogens fluorine, chlorine and bromine in which the halide ions are oxidised to the halogen by electrolysis.

Oxidation-Reduction Reactions

Academic Resource Center

Introduction :

- Oxidation-reduction reactions are also known as redox reactions
- Def : Redox reactions describe all chemical reactions in which there is a net change in atomic charge
- It is a class of reactions that include :
 - formation of a compound from its elements
 - all combustion reactions
 - reactions that generate electricity
 - reactions that produce cellular energy

Terminology

- The key idea is the net movement of electrons from one reactant to the other
- Oxidation is the loss of electrons
- Reduction is the gain of electrons
- Oxidizing agent is the species doing the oxidizing
- Reducing agent is the species doing the reducing

Redox Illustration

- $H_2 + F_2 \rightarrow 2HF$
- Oxidation (electron loss by H_2)
 - $H_2 \rightarrow 2H^+ + 2e^-$
- Reduction (electron gain by F_2)
 - $F_2 + 2e^- \rightarrow 2F^-$



Oxidation Number

- Oxidation number (O.N.) is also known as oxidation state
- It is defined as the charge the atom would have if electrons were not shared but were transferred completely
- For a binary ionic compound, the O.N. is equivalent to the ionic charge
- For covalent compounds or polyatomic ions, the O.N. is less obvious and can be determined by a given set of rules

Rules for Assigning an Oxidation Number

General Rules

1. For an atom in its elemental form (Na, O₂): O.N. = 0
2. For a monatomic ion: O.N. = ion charge
3. The sum of O.N. values for the atoms in a molecule or formula unit of a compound equals to zero.
(equals to the ion's charge if it is a polyatomic ion)

Rules for Specific Atoms or Periodic Table Groups

- For Group 1A(1) : O.N. = +1 in all compounds
- For Group 2A(2) : O.N. = +2 in all compounds
- For hydrogen : O.N. = +1 in combination with nonmetals
O.N. = -1 in combination with metals and boron
- For fluorine : O.N. = -1 in all compounds
- For oxygen : O.N. = -1 in peroxides
O.N. = -2 in all other compounds (except with F)
- For Group 7A(17) : O.N. = -1 in combination with metals, nonmetals (except O), and other halogens lower in the group

Ex.1 Determine the oxidation number (O.N.) of each element in these compounds :

- | | |
|-----------------------------|---------------------------|
| (A) CaO (s) | (B) KNO ₃ (s) |
| (C) NaHSO ₄ (aq) | (D) CaCO ₃ (s) |
| (E) N ₂ (g) | (F) H ₂ O (l) |

Sol.1 Simply apply the rules for assigning an oxidation number as described earlier

- | | |
|---|--|
| (A) $\begin{array}{c} +2 \quad -2 \\ \quad \\ \text{CaO (s)} \end{array}$ | (B) $\begin{array}{c} +1 \quad +5 \quad -1 \\ \quad \quad \\ \text{K N O}_3 \text{ (s)} \\ \text{N} = 0 - (+1) - 3(-2) = +5 \end{array}$ |
| (C) $\begin{array}{c} +1 \quad +1 \quad +6 \quad -2 \\ \quad \quad \quad \\ \text{NaHSO}_4 \text{ (aq)} \\ \text{S} = 0 - (+1) - (+1) - 4(-2) = +5 \end{array}$ | (D) $\begin{array}{c} +2 \quad +4 \quad -2 \\ \quad \quad \\ \text{CaCO}_3 \text{ (s)} \\ \text{C} = 0 - (+2) - 3(-2) = +4 \end{array}$ |
| (E) $\begin{array}{c} 0 \\ \\ \text{N}_2 \text{ (g)} \end{array}$ | (F) $\begin{array}{c} +1 \quad -2 \\ \quad \\ \text{H}_2\text{O (l)} \end{array}$ |

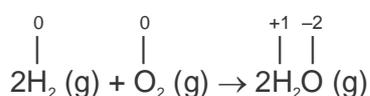
Ex.2 Identify the oxidizing agent and reducing agent in each of the following :

- $2\text{H}_2 \text{ (g)} + \text{O}_2 \text{ (g)} \rightarrow 2\text{H}_2\text{O (g)}$
- $\text{Cu (s)} + 4\text{HNO}_3 \text{ (aq)} \rightarrow \text{Cu(NO}_3)_2 \text{ (aq)} + 2\text{NO}_2 \text{ (g)} + 2\text{H}_2\text{O (l)}$

Sol.2 Assign oxidation numbers and compare.

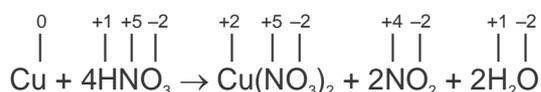
Oxidation is represented by an increase in oxidation number

Reduction is represented by a decrease in oxidation number



- O₂ was reduced (O.N. of O: 0 → -2); O₂ is the oxidizing agent

- H₂ was oxidized (O.N. of H: 0 → +1); H₂ is the reducing agent



- Cu was oxidized (O.N. of Cu: 0 → +2); Cu is the reducing agent

- HNO₃ was reduced (O.N. of N: +5 → +4); HNO₃ is the oxidizing agent

Balancing Redox Equations

- When balancing redox reactions, make sure that the number of electrons lost by the reducing agent equals the number of electrons gained by the oxidizing agent

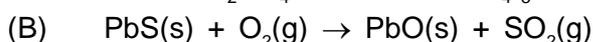
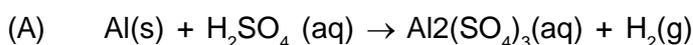
- Two methods can be used :
 1. Oxidation number method
 2. Half-reaction method

Balancing Redox Equations

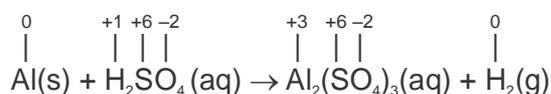
Method 1 : Oxidation number method

1. Assign oxidation numbers to all elements in the reaction
2. From the changes in O.N., identify the oxidized and reduced species
3. Compute the number of electrons lost in the oxidation and gained in the reduction from the O.N. changes
4. Multiply one or both of these numbers by appropriate factors to make the electrons lost equal the electrons gained, and use the factors as balancing coefficients
5. Complete the balancing by inspection, adding states of matter

Ex.3 Use the oxidation number method to balance the following equations:



Sol.3 (A) Step 1. Assign oxidation numbers to all elements



Step 2. Identify oxidized and reduced species

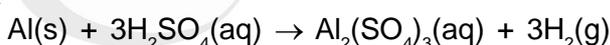
- Al was oxidized (O.N. of Al: 0 → +3)
- H_2SO_4 was reduced (O.N. of H: +1 → 0)

Step 3. Compute e^- lost and e^- gained

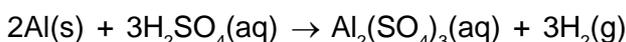
- In the oxidation: $3e^-$ were lost from Al
- In the reduction: $1e^-$ was gained by H

Step 4. Multiply by factors to make e^- lost equal to e^- gained, and use the factors as coefficients

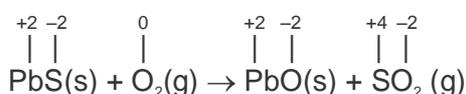
- Al lost $3e^-$, so the $1e^-$ gained by H should be multiplied by 3. Put the coefficient 3 before H_2SO_4 and H_2 .



Step 5. Complete the balancing by inspection



Part B : Step 1. Assign oxidation numbers to all elements



Step 2. Identify oxidized and reduced species

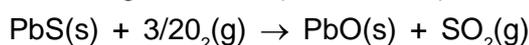
- PbS was oxidized (O.N. of S: -2 → +4)
- O_2 was reduced (O.N. of O: 0 → -2)

Step 3. Compute e^- lost and e^- gained

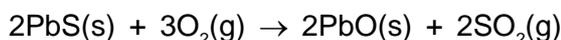
- In the oxidation : $6e^-$ were lost from S
- In the reduction : $2e^-$ were gained by each O

Step 4. Multiply by factors to make e^- lost equal to e^- gained, and use the factors as coefficients

- S lost $6e^-$, O gained $4e^-$ ($2e^-$ each O). Thus, put the coefficient $3/2$ before O_2 .



Step 5. Complete the balancing by inspection

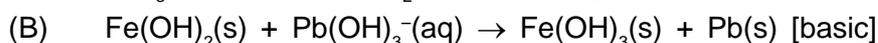
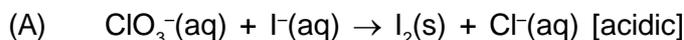


Balancing Redox Equations

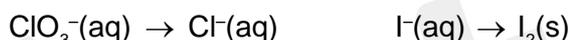
Method 2: Half-reaction method

1. Divide the skeleton reaction into two half-reactions, each of which contains the oxidized and reduced forms of one of the species
2. Balance the atoms and charges in each half-reaction
 - Atoms are balanced in order: atoms other than O and H, then O, then H
 - Charge is balanced by adding electrons
 - To the left in reduction half-reactions
 - To the right in oxidation half-reactions
3. If necessary, multiply one or both half-reactions by an integer to make the number of e⁻ gained equal to the number of e⁻ lost
4. Add the balanced half-reactions, and include states of matter
5. Check that the atoms and charges are balanced

Ex.4 Use the half-reaction method to balance the following equations:



Sol.4 Step 1. Divide the reaction into half-reactions

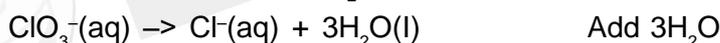


Step 2. Balance atoms and charges in each half-reaction

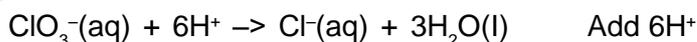
- Atoms other than O and H



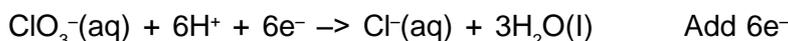
- Balance O atoms by adding H₂O molecules



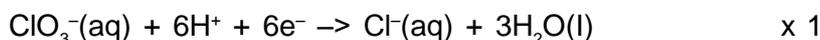
- Balance H atoms by adding H⁺ ions



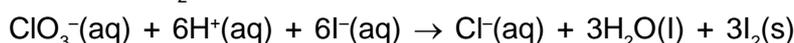
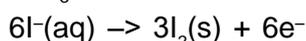
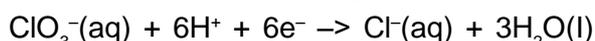
- Balance charge by adding electrons



Step 3. Multiply each half-reaction by an integer to equalize number of electrons



Step 4. Add the half-reactions together



Step 5. Check that atoms and charges balance

- Reactants (Cl, 3O, 6H, 6I, -1) → products (Cl, 3O, 6H, 6I, -1)

- ClO_3^- is the oxidizing agent

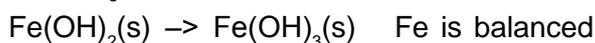
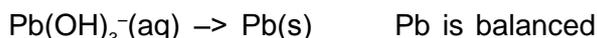
- I⁻ is the reducing agent
- The only difference in balancing a redox equation that takes place in basic solution is in Step 4.
- At this point, we add one OH⁻ ion to both sides of the equation for every H⁺ ion present
- The H⁺ ions on one side are combined with the added OH⁻ ions to form H₂O, and OH⁻ ions appear on the other side of the equation

Step 1. Divide the reaction into half-reactions

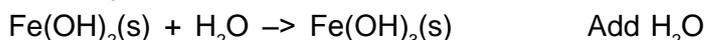
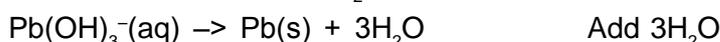


Step 2. Balance atoms and charges in each half-reaction

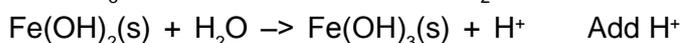
– Atoms other than O and H



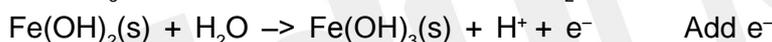
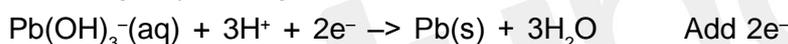
– Balance O atoms by adding H₂O molecules



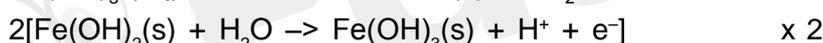
– Balance H atoms by adding H⁺ ions



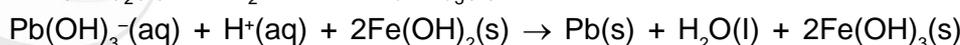
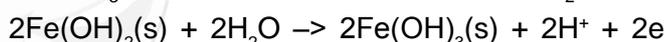
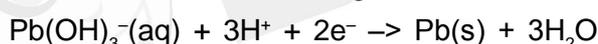
– Balance charge by adding electrons



Step 3. Multiply each half-reaction by an integer to equalize number of electrons



Step 4. Add the half-reactions together



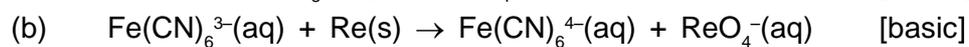
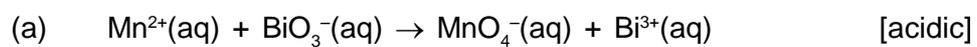
Step 5. Check

– Reactants (Pb, 7O, 7H, 2Fe, -1) → products (Pb, 7O, 7H, 2Fe, -1)

- Pb(OH)₃⁻ is the oxidizing agent
- Fe(OH)₂ is the reducing agent

Practice Problem

- Identify the oxidizing and reducing agents in the following :
 - $8\text{H}^+(\text{aq}) + 6\text{Cl}^-(\text{aq}) + \text{Sn(s)} + 4\text{NO}_3^-(\text{aq}) \rightarrow \text{SnCl}_6^{2-}(\text{aq}) + 4\text{NO}_2(\text{g}) + 4\text{H}_2\text{O(l)}$
 - $2\text{MnO}_4^-(\text{aq}) + 10\text{Cl}^-(\text{aq}) + 16\text{H}^+(\text{aq}) \rightarrow 5\text{Cl}_2(\text{g}) + 2\text{Mn}^{2+}(\text{aq}) + 8\text{H}_2\text{O(l)}$
- Use the oxidation number method to balance the following equations and then identify the oxidizing and reducing agents :
 - $\text{HNO}_3(\text{aq}) + \text{C}_2\text{H}_6\text{O(l)} + \text{K}_2\text{Cr}_2\text{O}_7(\text{aq}) \rightarrow \text{KNO}_3(\text{aq}) + \text{C}_2\text{H}_4\text{O(l)} + \text{H}_2\text{O(l)} + \text{Cr(NO}_3)_3(\text{aq})$
 - $\text{KClO}_3(\text{aq}) + \text{HBr(aq)} \rightarrow \text{Br}_2(\text{l)} + \text{H}_2\text{O(l)} + \text{KCl(aq)}$
- Use the half-reaction method to balance the following equations and then identify the oxidizing and reducing agents :



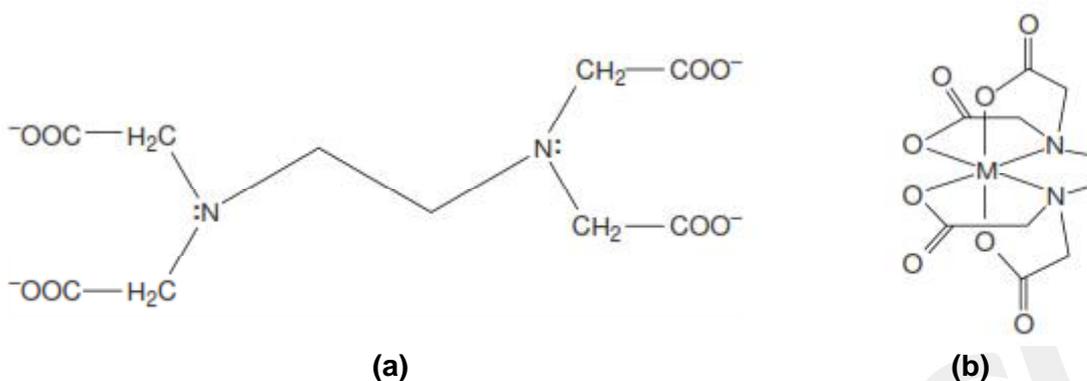
References

- Silberberg, Martin. Chemistry The Molecular Nature of Matter and Change. New York : McGraw-Hill Science/Engineering/Math, 2008.



3. CHEMISTRY AND PROPERTIES OF EDTA

Ethylenediaminetetraacetic acid, or EDTA, is an aminocarboxylic acid. The structure of EDTA is shown in Figure (a & b) EDTA, which is a Lewis acid, has six binding sites (the four carboxylate groups and the two amino groups), providing six pairs of electrons. The resulting metal–ligand complex, in which EDTA forms a cage-like structure around the metal ion (Figure a & b), is very stable. The actual number of coordination sites depends on the size of the metal ion; however, all metal–EDTA complexes have a 1:1 stoichiometry.



Complexing Metals

The unusual property of EDTA is its ability to chelate or complex metal ions in 1:1 metal-to-EDTA complexes. The fully deprotonated form (all acidic hydrogens removed) of EDTA binds to the metal ion. The equilibrium or formation constants for most metals, especially the transition metals, are very large, hence the reactions are shifted to the complex. Many of the reactions are pH dependent, especially the weaker forming complexes with Ca^{+2} or Mg^{+2} .



Metal analysis can be done by titration with EDTA and the use of a metal ion indicator. The pioneering work with EDTA was done by Gerold Schwarzenbach in the 1940's. The common reagent for making EDTA solutions is $\text{Na}_2\text{H}_2\text{Y} \cdot 2\text{H}_2\text{O}$. The values of K_f increase with the charge on the metal ion and as ionic radius decreases with constant charge. Water hardness, mostly from dissolved Ca^{+2} and Mg^{+2} , is determined by EDTA titration at $\text{pH} = 10$.

This is EDTA acting as a hexadentate ligand or all six sites on the EDTA bind to the metal ion. A number of metal-EDTA complexes have been reported to have the EDTA acting as a pentadentate ligand (only five sites on EDTA bind, one carboxylic group does NOT). A water molecule or another ligand is in the sixth site, so the complexes are still octahedral in geometry.

Uses of EDTA

Because of its strong complexing ability for most metal ions, it is used in the food industry as a sequestering agent.

The complexing of the metal ion may prevent further reactions, such as binding metals that are cofactors for enzymes, or just remove a metallic taste, such as metal contamination added during processing.

This same property allows EDTA use for incidents of lead poisoning by the medical profession.

EDTA is added to stored blood in blood banks as an anticoagulant to bind Ca^{+2} ion.

Another major use of EDTA has been in detergents to act as a builder (chelates metals) especially as a replacement for phosphates, a major nutrient in wastewater.

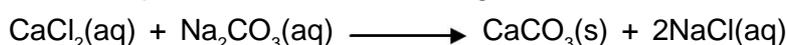
4. PRECIPITATION REACTIONS

Precipitation reactions involve mixing two solutions of Water soluble salts, Aqueous Solutions (denoted "aq"), to form a solid salt. An example is the reaction between soluble Lead Nitrate, $\text{Pb}(\text{NO}_3)_2(\text{aq})$, and Potassium Iodide, $\text{KI}(\text{aq})$, to form the insoluble salt Lead Iodide, $\text{PbI}_2(\text{s})$; which precipitates out as a bright yellow solid. At the same time, the Water soluble salt Potassium Nitrate, $\text{KNO}_3(\text{aq})$, is also formed.



These reactions are Double Displacement reactions, otherwise known as Metathesis Reactions, because the cations effectively change places. Here, the Pb^{2+} cation displaces the K^+ cation and combines with the Iodide (I^-) to form PbI_2 . Likewise, the K^+ cation displaces the Pb^{2+} cation to combine with the Nitrate (NO_3^-) to form KNO_3 .

As another example, consider the following metathesis reaction in aqueous solution:



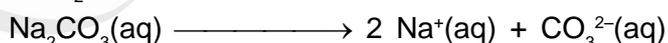
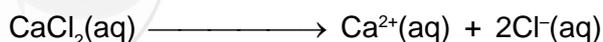
This is a type of reaction, in which two compounds exchange parts, takes the general form:



For our Calcium Chloride example, the exchange takes the following form:



The reaction goes in a particular direction because one of the products is effectively removed from the reaction mixture. Here, one of the products, CaCO_3 , is a solid that comes out of solution. Such reactions depend on the lack of solubility of one product. We can understand what is going on by considering what happens when we dissolve a salt in water. Each soluble salt will dissociate into its constituent ions.



When we mix together two solutions of soluble ionic compounds, we initially get a solution of four different ions, consisting of a cation and anion from each compound.

However, one of the pairs of the cations and anions produce a compound which is insoluble in water, and it precipitates.

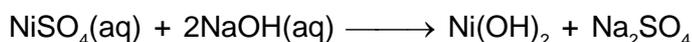


In the case of our example, NaCl remains in solution as $\text{Na}^+(\text{aq})$ and $\text{Cl}^-(\text{aq})$ ions because this ionic compound is soluble in water.

When predicting the products of a precipitation reaction, we first write the double displacement products, and then check the solubility of each to see if a precipitate forms. As an example, consider mixing solutions of Nickel Sulfate and Sodium Hydroxide:



Here the Nickel Ion (Ni^{2+}) and Sodium Ion (Na^+) will exchange places. Because the Nickel carries a +2 charge, and the Hydroxide Ion has a -1 charge (OH^-), combining them will result in a compound of chemical formula $\text{Ni}(\text{OH})_2$. Likewise, combining the Sodium Ion (Na^+) with the Sulfate Ion (SO_4^{2-}) will result in the compound Na_2SO_4 . Writing this in the chemical equation gives:

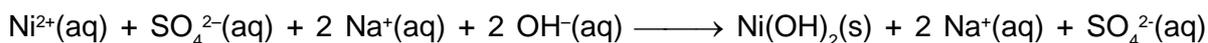


Note I have had to balance this equation with a stoichiometric coefficient of “2” for NaOH. Finally, we check our Solubility Rules to see that $\text{Ni}(\text{OH})_2$, as a Hydroxide, will be insoluble and that Na_2SO_4 will be soluble. Hence, we can include these designations in the chemical equation:

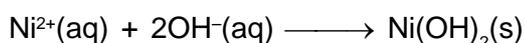


Hence, a precipitate, $\text{Ni}(\text{OH})_2$, does form.

We should also notice that the Na^+ and SO_4^{2-} don't undergo any chemical change. We can see this by writing this chemical equation in Total Ionic form; where each aqueous ionic species is written as the separate ions formed in solution:



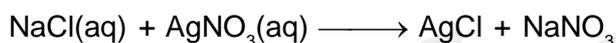
In this form, we see the Sodium (Na^+) and Sulfate (SO_4^{2-}) ions do not change. They are thus referred to as Spectators. Only the Nickel (Ni^{2+}) and Hydroxide (OH^-) ions react to form the precipitate. Thus, the Net Ionic Equation can be written so as to involve only those species undergoing a chemical change:



As a final example, consider what happens when an aqueous solution of Sodium Chloride is mixed with an aqueous solution of Silver Nitrate.



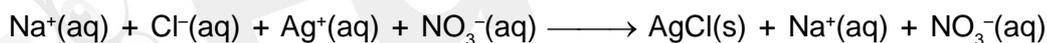
Our double-displacement products will be AgCl and NaNO_3 :



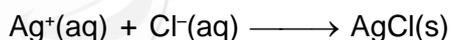
Checking our Solubility Rules tells us AgCl will be insoluble in Water, but NaNO_3 will dissolve. So, we have:



We can now write this reaction in its Total Ionic form:



Note, the Na^+ and NO_3^- ions do not participate in the chemistry, and are therefore Spectator Ions. Hence, the Net Ionic Equation for this reaction is:



5. ORGANIC ANALYTICAL REAGENTS FOR THE DETERMINATION OF INORGANIC SUBSTANCES

Determination	Reagents
Aluminium	Alizarin Red S
	Aluminon
	Aluminon + Cetyltrimethylammonium bromide
	Chrome Azurol S
	Chrome Azurol S + Cetyltrimethylammonium bromide
	Chromazol KS + Cetylpyridinium bromide
	Eriochrome Cyanine R
	Eriochrome Cyanine R + Cetyltrimethylammonium bromide
	8-Hydroxyquinoline
	Ammonia
Antimony	Brilliant Green
	Bromopyrogallol Red
	Rhodamine B
	Silver diethyldithiocarbamate
	Silver diethyldithiocarbamate
Arsenic	Silver diethyldithiocarbamate
Barium	Sulfonazo III
Beryllium	Beryllon II
	Chrome Azurol S
	Chrome Azurol S + Cetyltrimethylammonium bromide
	Eriochrome Cyanine R
	Eriochrome Cyanine R + Cetyltrimethylammonium bromide
	Dithizone
	Pyrocatechol Violet
Bismuth	Pyrocatechol Violet + Cetyltrimethylammonium bromide
	Thiourea
	Xylenol Orange
	Azomethine H
	Carminic acid
	Curcumin
	Methylene Blue
Boron	Fluorescein
	Phenol Red
Bromide	Fluorescein
	Phenol Red
Cadmium	2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol
	Cadion
	Dithizone
	4-(2-Pyridylazo)resorcinol
Calcium	Chlorophosphonazo III
	Glyoxal-bis(2-hydroxyanil)

	Murexide
	Phthalein Purple
Cerium	N-benzoyl-N-phenylhydroxylamine
	8-Hydroxyquinoline
Chlorine	N,N-Diethyl-1,4-phenylenediamine
Chromium	1,5-Diphenylcarbazine
	4-(2-Pyridylazo)resorcinol
	4-(2-Pyridylazo)resorcinol + Tetradecyldimethylbenzylammonium chloride
	4-(2-Pyridylazo)resorcinol + Hydrogen peroxide
Cobalt	Nitroso-R salt
	1-Nitroso-2-naphthol
	2-Nitroso-1-naphthol
	4-(2-Pyridylazo)resorcinol
	4-(2-Pyridylazo)resorcinol + Diphenylguanidine
Copper	Bathocuproine
	Bathocuproine disulfonic acid
	Dithizone
	Neocuproine
	Cuprizone
	4-(2-pyridylazo)resorcinol + Tetradecyldimethylbenzylammonium chloride
Cyanide	Barbituric Acid + Pyridine
	Barbituric Acid + Pyridine-4-carboxylic acid
Fluoride	Alizarin Fluorine blue + Lanthanum(III) ion
	Eriochrome Cyanine R + Zirconium(IV) ion
Gallium	Pyrocatechol violet + Diphenylguanidine
	8-Hydroxyquinoline
	1-(2-Pyridylazo)-2-naphthol
	4-(2-Pyridylazo)resorcinol
	Rhodamine B
	Xylenol Orange
	Xylenol Orange + 8-Hydroxyquinoline
Germanium	Brilliant Green + Molybdate
	Phenylfluorone
Gold	5-(4-Diethylaminobenzylidene) rhodanine
	Rhodamine B
Hafnium	Arsenazo III
Indium	Bromopyrogallol Red
	Chrome Azurol S
	Chrome Azurol S + Cetyltrimethylammonium bromide
	Dithizone

	8-Hydroxyquinoline
	1-(2-Pyridylazo)-2-naphthol
	4-(2-Pyridylazo)resorcinol
Iodide	Neocuproine + Copper(II)
Iodine	Starch
Iridium	Rhodamine 6G + Tin(II)
	N,N-Dimethyl-4-nitrosoaniline
Iron	Bathophenanthroline
	Bathophenanthroline disulfonic acid
	2,2'-Bipyridyl
	Chrome Azurol S + Cetyltrimethylammonium bromide
	1,10-Phenanthroline
	1,10-Phenanthroline + Bromothymol Blue
	Ferrozine
Lanthanum	Arsenazo III
Lead	Dithizone
	Sodium diethyldithiocarbamate
	4-(2-Pyridylazo)resorcinol
Lithium	Thoron
Magnesium	Eriochrome Black T
	8-Hydroxyquinoline
	8-Hydroxyquinoline + Butylamine
	Titan Yellow
	Xylidyl Blue
Manganese	Formaloxime
Mercury	Dithizone
	Michler's thioketone
	Xylenol Orange
Molybdenum	Bromopyrogallol Red + Cetylpyridium chloride
	Phenylfluorone
	Toluene-3,4-dithiol
Nickel	2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol
	Dimethylglyoxime
	Dimethylglyoxime + Oxidant
	2,2'-Furildioxime
	2-(2-Pyridylazo)-2-naphthol
	4-(2-Pyridylazo)resorcinol
Niobium	N-Benzoyl-N-phenylhydroxylamine
	Pyrocatechol + EDTA or 2,2'-Bipyridyl or 1-(2-thenoyl)-
	3,3,3,-trifluoroacetone
	Bromopyrogallol red
	Bromopyrogallol red + Cetylpyridinium chloride

	4-(2-Pyridylazo) resorcinol
	Sulfochlorophenol S
	Xylenol Orange
Nitrate	Brucine
	Chromotropic acid
	Sulfanilamide + N-(1-Naphthyl)ethylenediamine dihydrochloride
Nitrite	Sulfanilamide + N-(1-Naphthyl)ethylenediamine dihydrochlorine
	Sulfanilic acid + 1-Naphthylamine
Osmium	1,5-Diphenylcarbazine
Palladium	2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol
	Dithizone
	2-Nitroso-1-naphthol
	4-(2-Pyridylazo)resorcinol
Phosphate	Rhodamine B + Molybdate
	Malachite Green + Molybdate
Platinum	Sulfochlorophenolazorhodamine
	Dithizone
	2-Mercaptobenzothiazole
Rare Earths	Arsenazo I
	Arsenazo III
	Xylenol Orange
Rhenium	2,2'-Furildioxime
Rhodium	1-(2-Pyridylazo)-2-naphthol
Ruthenium	1,10-Phenanthroline
	Thiourea
	1,4-Diphenylthiosemicarbazide
Scandium	Alizarin red S
	Arsenazo III
	Chrome Azurol S
	Xylenol Orange
Selenium	3,3'-Diaminobenzidine
	2,3-Diaminonaphthaline
Silver	Dithizone
	Eosin + 1,10-Phenanthroline
Sulfate	Methylthymol blue + Barium (II)
Sulfide	N,N,-Dimethyl-1,4-phenylenediamine
Sulfite	Pararosaniline + Formaldehyde
Tantalum	Methyl Violet
	4-(2-Pyridylazo)resorcinol
	Phenylfluorone
Tellurium	Diethyldithiocarbamate
	Bismuthiol II

Thallium	Brilliant green Dithizone Rhodamine B
Thorium	Arsenazo III Thoron Xylenol Orange Xylenol Orange + Cetyltrimethylammonium bromide
Tin	Pyrocatechol violet (and + Cetyltrimethylammonium bromide) Gallein Phenylfluorone Toluene-3,4-dithiol + Dispersant
Titanium	Chromotropic acid Diantipyrinylmethane Tiron
Tungsten	Pyrocatechol Violet Tetraphenylarsonium chloride + Thiocyanate Toluene-3,5-dithiol
Uranium	Arsenazo III 2-(5-Bromo-2-pyridylazo)diethylaminophenol Chlorophosphonazo III 1-(2-Pyridylazo)-2-naphthol
Vanadium	N-Benzoyl-N-phenylhydroxylamine 8-Hydroxyquinoline 4-(2-pyridylazo)resorcinol
Yttrium	Alizarin Red S Arsenazo III Xylenol Orange
Zinc	Dithizone 1-(2-Pyridylazo)-2-naphthol Xylenol Orange Zircon
Zirconium	Alizarin Red S Arsenazo III Pyrocatechol Violet Morin Xylenol Orange

6. NUCLEAR CHEMISTRY

THE NATURE OF NUCLEAR REACTIONS

radioactivity - the spontaneous decay of an unstable nucleus with accompanying emission of radiation.

nuclide - atom with a specific number of protons and neutrons in its nucleus.

⇒ There are 271 stable nuclides in nature, others are radioactive

radionuclide - unstable isotope that undergoes nuclear decay

⇒ All isotopes of elements with ≥ 84 protons are radioactive; specific isotopes of lighter elements are also radioactive. (E.g. ${}_1^3\text{H}$)

nucleons = protons + neutrons

Nuclear reactions differ from ordinary chemical reactions

- Atomic numbers of nuclei may change (elements are converted to other elements or an element can be converted to an isotope of that element).
- Protons, neutrons, electrons and other elementary particles may be involved in a nuclear reaction.
- Reactions occur between particles in the nucleus.
- Matter is converted to energy & huge amounts of energy are released.
- Nuclear reactions involve a specific isotope of an element; different isotopes of an element may undergo different nuclear reactions.

Types of Radioactive Decay:

1) alpha, α , emission

α particles - high energy and low speed + charged particles; ${}_2^4\text{He}$ (helium-4)

E.g. emission of an α particle: ${}_{92}^{238}\text{U} \rightarrow {}_{90}^{234}\text{Th} + {}_2^4\text{He}^4$

2) beta, β , emission

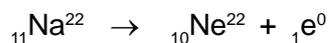
β particles – high energy and high speed – charged electrons: ${}_{-1}^0\text{e}^0$

E.g. emission of a β particle: ${}_{90}^{234}\text{Th} \rightarrow {}_{91}^{234}\text{Pa} + {}_{-1}^0\text{e}^0$

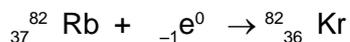
During β decay, a neutron is converted into a proton: ${}_0^1\text{n}^1 \rightarrow {}_1^1\text{p}^1 + {}_{-1}^0\text{e}^0$

3) gamma, γ , emission; gamma emission accompanies other types of decay γ particles-high energy photons, very penetrating: ${}_0^0\gamma^0$

4) positron, ${}_1^0\text{e}^0$, emission - same mass, but opposite charge of electron



5) Electron capture - β particle is captured instead of emitted



NUCLEAR STABILITY

Nuclear Stability

- Nuclei containing 2, 8, 20, 50, 82, or 126 protons or neutrons are generally more stable than nuclei that do not possess these “magic” numbers.
- As the atomic number increases, more neutrons are needed to help bind the nucleus together, so there is a high neutron:proton ratio.
- Nuclei of elements with > 83 protons are unstable due to the large number of nucleons present in the tiny nucleus; by undergoing radioactive decay unstable nuclei can form more stable nuclei.

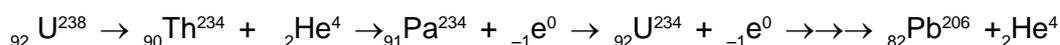
- Nuclei with both even numbers of both protons & neutrons are generally more stable than those with odd numbers:

# protons	# neutrons	# stable nuclei
even	even	164
even	odd	53
odd	even	50
odd	odd	4

NATURAL RADIOACTIVITY

Radioactive Decay Series

Many heavy elements undergo several sequential emissions before forming a more stable nuclei:



Kinetics of Radioactive Decay

- Different isotopes decay at different rates; rates vary from ms to days to years.
- Radioactive decay is a first order rate process; all radioactive substances have a characteristic half-life:

$$kt_{1/2} = 0.693 \quad t_{1/2} = \text{half-life}; k = \text{rate constant}$$

$$\ln \frac{A_t}{A_0} = -kt \quad A_0 = \text{initial activity or amount}; A_t = \text{activity after a certain time}$$

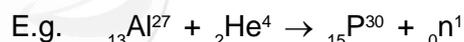
$$\frac{A_t}{A_0} = \text{fraction of material remaining after time } t$$

NUCLEAR TRANSMUTATION

Transmutation - Change of one element to another as a result of bombardment by high-energy particles (e.g. neutrons, electrons, and other nuclei).

- Rutherford prepared 1st synthetic nuclide, ${}^{17}\text{O}$, in 1919; Irene Curie prepared 1st radioactive nuclide, ${}^{30}\text{P}$, in 1934.
- All trans-Uranium elements ($Z > 92$) are both synthetic (man-made) and radioactive.

Nuclear transmutations can show α -, β -, and γ -emissions as well as production of protons, neutrons, and other isotopes:

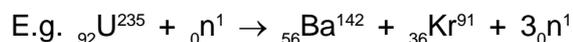


NUCLEAR FISSION

Fission - A nuclear reaction that releases energy as a result of splitting of large nuclei into smaller ones.

Nuclear Power plants use fission to split U-235 to produce energy:

1. U-235 is bombarded with slow neutrons - this produces smaller nuclei as well as more neutrons and energy.
2. A chain reaction results because each neutron produced can cause fission of another U-235 nucleus.



Critical mass - minimum mass required to sustain a chain reaction.

Control rods are made of B or Cd; these rods absorb neutrons so the process doesn't accelerate too rapidly. Rods are raised/lowered to control the speed of the process.

Fuel rods are made of U-235. ${}^{238}\text{U}$ is the most abundant U isotope but is not fissionable so uranium must be enriched to increase the amount of ${}^{235}\text{U}$.

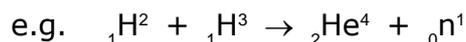
Moderator - slows down the neutrons. Water or other liquid coolant surround rods. The water serves to 1) slow down neutrons so they can collide with U-235; 2) transfer heat to steam generator.

Primary problems with nuclear power plants:

- 1) safety (Chernobyl and Three Mile Island had cooling system failures that led to reactor meltdowns. Chernobyl also did not have containment building around reactor.)
- 2) nuclear waste - some products will remain radioactive for thousands of years.

NUCLEAR FUSION

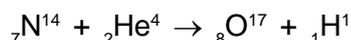
Fusion - A nuclear reaction that releases energy as a result of the union of smaller nuclei to form larger ones.



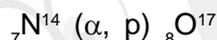
- Fusion generates even more energy than fission and creates little radioactive waste, so it would provide a wonderful source of energy.
- but, fusion requires very high temps (tens of millions of degrees Celsius) in order for nuclei to overcome strong repulsive forces – magnetic fusion reactors are being designed and tested.

NUCLEAR REACTIONS

The reactions in which nuclei of atoms interact with other nuclei or elementary particles such as α -particle, proton, neutron, deuteron, etc, resulting in the formation of new nuclei with or without liberation of one or more elementary particles, are called nuclear reactions. The particles resulting nuclear reactions are also called projectiles. In all the nuclear reactions, the total number of protons and neutrons are conserved. Nuclear reactions may be expressed as similar as chemical reactions, like



Here, the nucleus of nitrogen atom is converted into the nucleus of oxygen atom by α -particle and proton is also produced as a by-product. These reactions may be expressed by short hand notation, in which the projectile and the liberating particle are expressed by their symbols, in a small bracket in between the parent and the product nucleus. For example, the above reaction may also be expressed as :

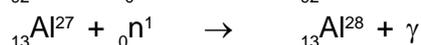


Some Differences Between Nuclear and Chemical Reactions

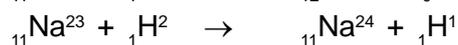
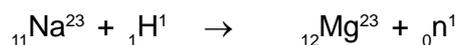
No.	Chemical reaction	Nuclear reaction
1	No new element is formed	New element is formed
2	Valence electrons of atoms participate	Only the nucleus of atoms participate
3	Balanced by the conservation of atoms	Balanced by the conservation of nuclear charge and mass number (total number of neutrons and protons)
4	Mass conservation is obeyed	Disobey mass conservation
5	May be exothermic or endothermic, liberating or absorbing relatively small amount of energy	May be exothermic or endothermic, liberating or absorbing relatively very high amount of energy
6	May be reversible	Irreversible
7	May obey kinetics of any order	Obeys only first order kinetics
8	Rate depends on external factors like temperature and the catalytic conditions	Rate is independent from any external condition

TYPES OF NUCLEAR REACTIONS :

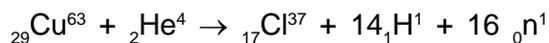
1. Projectile Capture Reactions :



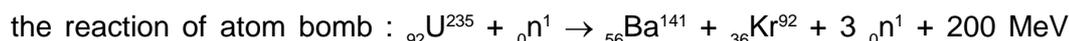
2. Particle - particle reactions :



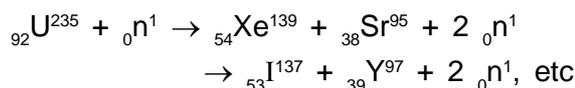
3. **Spallation reactions** : High speed projectiles with 400MeV bombarded on high nucleus giving smaller nucleus.



4. **Fission reactions** : It is the nuclear reaction in which a heavy nucleus is broken down by a slow or thermal neutron (energy about 0.04 eV) into two relatively smaller nuclei with the emission of two or more neutrons and large amount of energy. For example,



It is also found that products of nuclear fission reactions are not unique. Some more products are formed. The most probable mass numbers of the two nuclides formed are around 95 and 140 and an average of 2.5 neutrons is emitted out per fission.



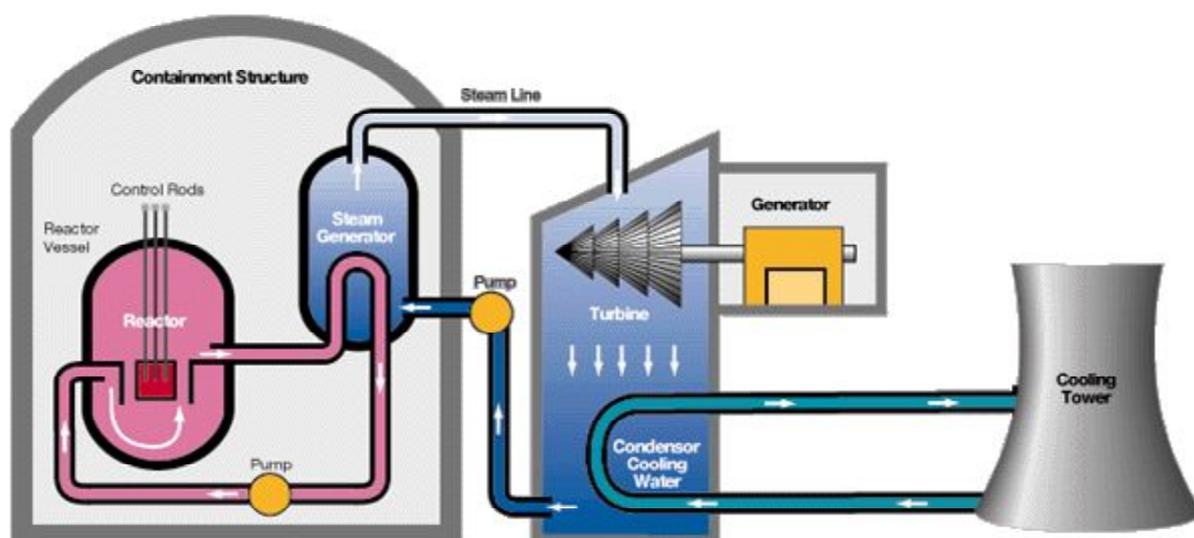
The destructive action of atom bomb is due to the following reasons :

- As some neutrons are produced in each fission, they may collide efficiently with the other U^{235} nuclei to produce more neutrons and thus the reaction occurs in chain like fashion. It results the emission of a large amount of energy in very small time.
 - Each product of fission is radioactive and hence increases the intensity of radiation in that region, resulting the problems due to radiations.
5. **Fusion reactions** : It is the nuclear reaction in which two or more light nuclei fused together to form heavier nuclei, with the evolution of tremendous amount of energy. In such reactions, relatively more stable nucleus having higher binding energy per nucleon is formed. Such reaction is difficult to occur because when the nuclei of different atoms come closer, they repel each other strongly. This is why, very high temperature of the order 10^6K is needed for the occurrence of such reactions. However, the overall reactions is highly exothermic due to large mass defect. Some examples of nuclear fusion reactions are :

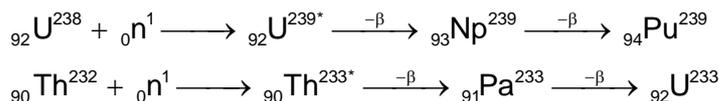


NUCLEAR REACTOR

A nuclear reactor is the furnace, place where nuclear fission reaction is performed to get energy. The essentials of nuclear reactor are :



1. **Fuel** : Nuclear fuels are of two types :
 - (i) **Fissile materials** : These are the nuclides which directly results chain reaction on bombardment with slow neutrons. Such nuclides are U^{235} , Pu^{239} , U^{233} , etc.
 - (ii) **Fertile material** : These are the nuclides which are non-fissile, but they may be converted in to a fissile material by the action of neutrons. Such nuclides are U^{238} and Th^{232} .

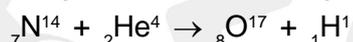


Such conversions are performed in a special type of nuclear reactor called Breeder Reactor.

2. **Moderator** : It is used to slow down the fast neutrons without absorbing them. Example: water, graphite, helium, D_2O etc.
3. **Control rods** : These are the rods of material which can absorb neutrons and hence control the fission reaction. Example : Cadmium, boron, etc.
4. **Coolant** : These are the material which transforms the energy produced in the fission reaction in to heat energy. Example : Liquid alloy of sodium and potassium, heavy water, polyphenyls, tcc.

ARTIFICIAL TRANSMUTATION

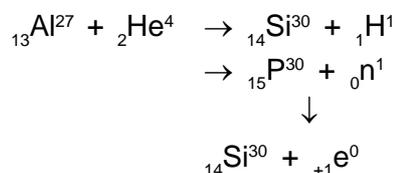
It is the method of conversion of atom of one element in to the atom of other element with the help of some particles like alpha particle, proton, deuteron, neutron, etc (called projectiles). The first such transmutation was performed by Rutherford. When N^{14} atoms were bombarded by very fast moving α -particles, the nitrogen atom has changed in to oxygen atom and proton is produced simultaneously



Later on, Rutherford and Chadwick shown that most of the nuclei may be transmuted by the suitable projectile. After the discovery of cyclotron, a particle accelerating machine, such transmutations become more easier.

ARTIFICIAL RADIOACTIVITY

When Irene Curie and F. Joliot bombarded the atoms of Al^{27} , B^{10} or Mg^{24} by fast moving α -particles, protons, neutrons and positrons were produced. They observed that the emission of protons and neutrons stop on stopping the bombardment but the emission of positron continues. They also observed that the rate of emission of positron decreases exponentially in the manner similar to natural radioactivity. They named the isotope emitting positron as **artificial radioisotope** and the phenomenon as **artificial radioactivity**.



NUCLEAR TRANSMUTATION

An experiment performed by Rutherford in 1919, however, suggested the possibility of producing radioactivity artificially. When he bombarded a sample of nitrogen with α particles, the following reaction took place :



An oxygen-17 isotope was produced with the emission of a proton. This reaction demonstrated for the first time the feasibility of converting one element into another, by the process of nuclear transmutation. Nuclear transmutation differs from radioactive decay in that the former is brought about by the collision of two particles.

7. APPLICATIONS OF RADIOACTIVE ISOTOPES

- Nuclear power plants
- Medical diagnosis and treatment e.g. PET scan monitors glucose metabolism in brain using C-11 isotope; I-131 measures activity of thyroid
- Carbon dating (measure amount of C-14 remaining in a sample)
- Synthesis of new elements
- Irradiation of food - preserves food & destroys parasites
- Nuclear Weapons (Atomic bombs and H bombs)

