Oxidation-Reduction Reactions

- oxidation-reduction reactions are also called **redox reactions**
- all redox reactions involve the transfer of electrons from one atom to another
- spontaneous redox reactions are generally exothermic, and we can use their released energy as a source of energy for other applications

Development of oxidation and reduction reaction concept

1. **Reaction of reduction oxidation based on releasing (lossing) and gaining of oxygen**

   a. **Oxidation reaction**

   Oxidation reaction is a reaction of gaining (capturing) of oxygen by a substance

   Example :

   $$CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{g)}$$

   $$P_{4(s)} + 5O_{2(g)} \longrightarrow 2P_2O_{5(s)}$$

   b. **Reduction reaction**

   Reduction reaction is a reaction of releasing (losing) of oxygen from a oxide compound

   Example:

   $$CuO_{(s)} + H_{2(g)} \longrightarrow Cu_{(s)} + H_2O_{(g)}$$

   $$Fe_2O_{3(s)} + 3CO_{(g)} \longrightarrow 2Fe_{(s)} + 3CO_{2(g)}$$

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   $$Fe_2O_{3(s)} + 3CO_{(g)} \longrightarrow 2Fe_{(s)} + 3CO_{2(g)}$$

What do you mean by oxidation and reduction ?

- Oxidation can be defined as addition of oxygen/electronegative element to a substance or removal of hydrogen/ electropositive element from a substance.
- Reduction can be defined as removal of oxygen/electronegative element from a substance or addition of hydrogen/ electropositive element to a substance.

Oxidation and ReductionAnother Def

- in order to convert a free element into an ion, the atoms must gain or lose electrons
  - of course, if one atom loses electrons, another must accept them
- reactions where electrons are transferred from one atom to another are redox reactions
- atoms that lose electrons are being oxidized, atoms that gain electrons are being reduced

$$2\ Na(s) + Cl_2(g) \rightarrow 2\ Na^+Cl^-(s)$$

$Na \rightarrow Na^+ + 1\ e^-$ oxidation

$Cl_2 + 2\ e^- \rightarrow 2\ Cl^-$ reduction

What is an oxidizing and reducing agent ?

- Oxidising agent: a reagent which increases the oxidation number of an element of a given substance. These reagents are called oxidants.
- Reducing agent: a reagent that lowers the oxidation number of a given element . These reagents are also called reductants.

Oxidation–Reduction

- oxidation and reduction must occur simultaneously
  - if an atom loses electrons another atom must take them
- the reactant that reduces an element in another reactant is called the **reducing agent**
  - the reducing agent contains the element that is oxidized
- the reactant that oxidizes an element in another reactant is called the **oxidizing agent**
  - the oxidizing agent contains the element that is reduced

$$2\ Na(s) + Cl_2(g) \rightarrow 2\ Na^+Cl^-(s)$$

Na is oxidized, Cl is reduced

Na is the reducing agent, Cl_2 is the oxidizing agent

Oxidation and Reduction

A Better Definition

- oxidation occurs when an atom's oxidation state increases during a reaction
- reduction occurs when an atom's oxidation state decreases during a reaction

$$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O$$

$$\begin{array}{cccccc} -4 & +1 & 0 & +4 & -2 & +1 \quad -2 \end{array}$$

oxidation

reduction

Will a Reaction Take Place?

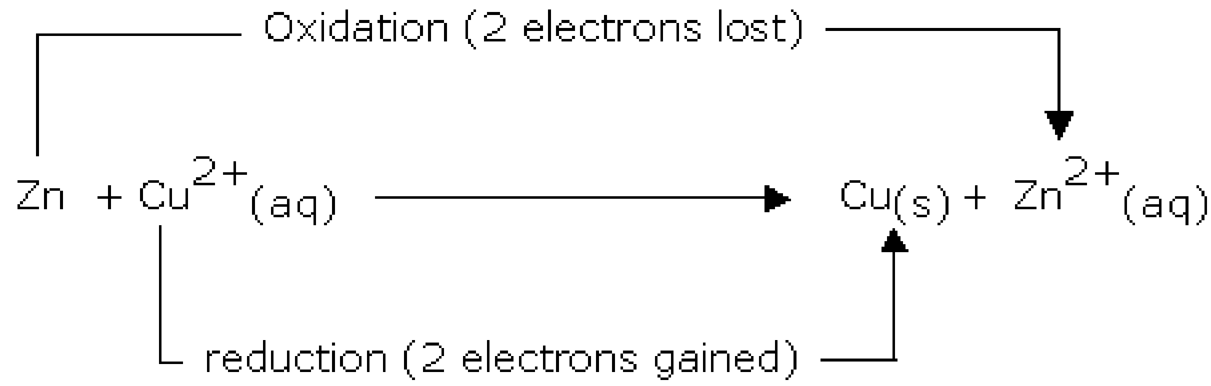
- reactions that are energetically favorable are said to be **spontaneous**
  - they can happen, but the activation energy may be so large that the rate is very slow
- the relative reactivity of metals can be used to determine if some redox reactions are spontaneous

Electron transfer reactions

- Place a strip of metallic zinc in an aqueous solution of copper nitrate , for about one hour. You may notice that the strip becomes coated with reddish metallic copper and the blue colour of the solution disappears. Formation of Zn2+ ions among the products can easily be judged when the blue colour of the solution due to Cu2+ has disappeared. If hydrogen sulphide gas is passed through the colourless solution containing Zn2+ ions, appearance of white zinc sulphide, ZnS can be seen on making the solution alkaline with ammonia.
- The reaction between metallic zinc and the aqueous solution of copper nitrate is :-

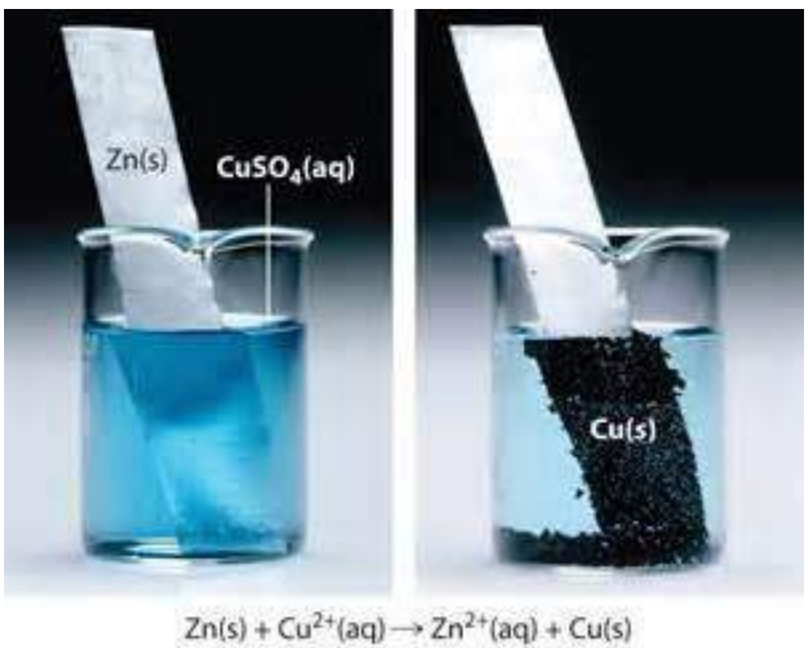
$$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$$

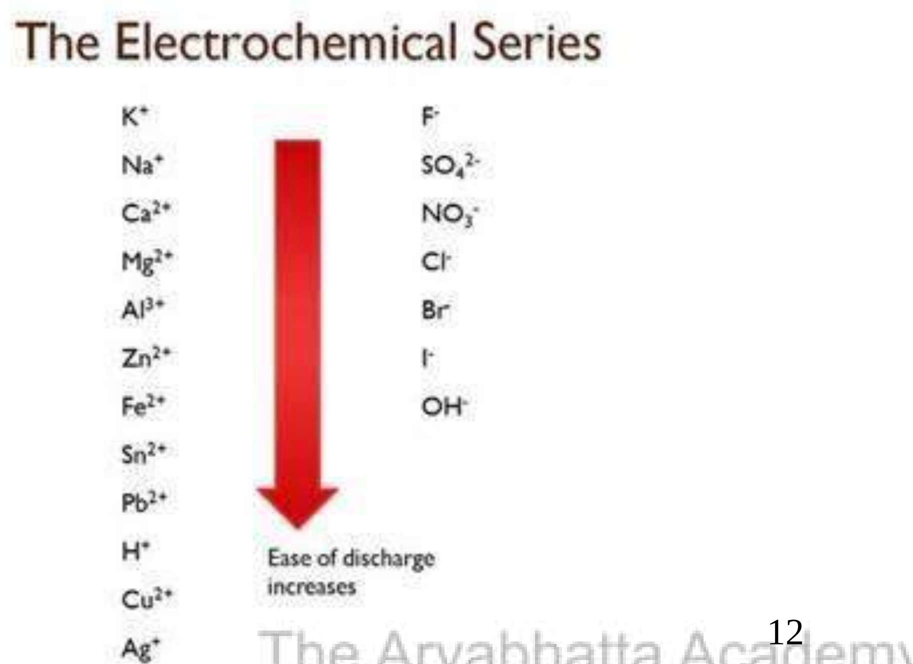
- In this reaction , zinc has lost electrons to form Zn2+and, therefore, zinc is oxidised. Evidently, now if zinc is oxidised, releasing electrons , copper ions is reduced by gaining electrons from zinc.



At this stage we may investigate the state of equilibrium for the reaction represented by equation . For this purpose, let us place a strip of metallic copper in a zinc sulphate solution. No visible reaction is noticed and attempt to detect the presence of Cu2+ ions by passing H2S gas through the solution to produce black colour cupric sulhpide. CuS, does not succeed. Cupric sulphide has such a low solubility that this is an extremely sensitive test. Cu2+ cannot be detected. Hence the equilibrium For the reaction favours the products over the reactants.

- This suggests that we might develop a table in which metals and their ions are listed on the basis of their tendency to release electrons just as we do in the case of acids to indicate the strength of the acids. As a matter of fact we have already made certain comparisons. By comparison we have come to know that zinc releases electrons to copper and copper releases electrons to silver and therefore electron releasing tendency is in the order Zn>Cu>Ag .





2. Reduction oxidation reaction based on electron transfer

a. Oxidation reaction

Oxidation reaction is a reaction of **electron releasing** **(lossing)** from a substance.

Example:

$$Na \longrightarrow Na^{+} + e^{-}$$

$$Mg \longrightarrow Mg^{2+} + 2\,e^{-}$$

$$Cu \longrightarrow Cu^{2+} + 2\,e^{-}$$

b. Reduction reaction

Reduction reaction is a reaction of **electron gaining** by a substance.

Example:

$$Cl_2 + 2e^{-} \longrightarrow 2Cl^{-}$$

$$S + 2\,e^{-} \longrightarrow S^{2-}$$

Stock notation

- Stock notation is the notation used where the oxidation state of the element is represented by roman numerals.

Chemical Formulae	Stock Notation
FeO	Fe(II)O
Fe_2O_3	Fe(III)O
CuO	Cu(II)O
Cu_2O	Cu(I)O

IUPAC Nomenclature

The compound that is formed by the elements have more than one type of oxidation number , its name diferentiated by the Roman number writing in the bracket in the back of that element name. The **Roman number** shows the **value of oxidation number** of that element.

The compound that is formed by the element only has one type of oxidation number, the Roman number does not need writen.

This **IUPAC nomenclature** applies in both **ionic and covalent compounds.**

Examples **IUPAC name** of **binary covalent compound**:

CO	: carbon(II) oxide	(oxidation number of C = +2)
CO_2	: carbon(IV) oxide	(oxidation number of C = +4)
P_2O_3	: phosphorus(III) oxide	(oxidation number of P = +3)
N_2O_5	: nitrogen(V) oxide	(oxidation number of N = +5)
Cl_2O_7	: chlorine(VII) oxide	(oxidation number of Cl = +7)

Oxidation state

- For reactions that are not metal + nonmetal, or do not involve O_2, we need a method for determining how the electrons are transferred
- chemists assign a number to each element in a reaction called an **oxidation state** that allows them to determine the electron flow in the reaction
- **Basically oxidation number denotes the oxidation state of the element in a compound according to a set of rules formulated on the basis that electron fair in a covalent bond belongs entirely to the more electrovalent bond.**

Common Oxidation States

Chemical species	Oxidation state and remarks
Any element eg Fe, O_2 , S_8	**zero**
Oxygen in any compound	**-2 except in peroxides example H_2O_2 or Na_2O_2 then oxygen atom has oxidation state of -1 or in F_2O , then oxygen atom has oxidation state of +2**
Fluorine in any compound	**-1 being most electronegative**
Hydrogen in any compound	**+1 except in metal hydrides example NaH then hydrogen atom has oxidation state of -1 as metals have a greater tendency to lose electrons**
Chlorine, bromine, iodine	**-ve oxidation state if bonded to less electronegative element eg NaCl; then Cl = -1.** **+ve oxidation state if bonded to more electronegative element eg ClO^- , then Cl = +1; ClO_3^- , then Cl = +5**

Oxidation Number

Oxdidation number is **a number** that states **electrical charge possessed by each one element atom** in **the molecular compound or the ion.**

In the **molecules of ionic compound**, electrical charge contained element atom **can be raised** by **transfering of electrons**.

In the formation of ionic bond:

-Metal atom losses electron to form the positive ion.

-Nonmetal atom gains electron to form the negative ion.

In the molecule of **MgF_2**, consist of **Mg^{2+} ion** with charge of **2+** dan **F^- ion** with charge of **1–**

Said that in the molecule of **MgF_2**, **oxidation number of Mg** is **+2**, and **oxidation number** of **F** is **-1**.

In the molecule of covalent compound, the raising of the electrical charge each element atom is caused by its existence the difference of electronegativity of element, so that occur polarization covalent bond.

In the polar covalent compound, the more electronegative atom become more negative charge and the other atom become more positive charge.

In the polar covalent compound of **H_2O, H** contain **1+** and **O** contain **2–**

Determining Oxidation Numbers of Elements

The oxidation number of an element in the molecule or in the ion, by use the rules of oxidation numbers can be determined.

•Write down the molecular or ionic formula which will be determined oxidation number its element and between one atom of element and the others, given enough space.

•Write each oxidation number of elements in below it and write x for element that will be determined its oxidation number.

•Use the rules of oxidation number, that is rule of number 7 or 8, for determine x value.

Example:

Determine the following element oxidation number

a. S in molecule of H_2SO_4

b. Cr in ion of $Cr_2O_7^{2-}$

Given : Molecule of H_2SO_4

Ion of $Cr_2O_7^{2-}$

Find : a. oxidation number of S in H_2SO_4

b. oxidation number of Cr in $Cr_2O_7^{2-}$

Solution :

Rules for determining oxidation number

- (1) In elements in the free or the uncombined state each atoms bears an oxidation number of zero.
- (2)For ions composed of only 1 atom the oxidation number is equal to the charge on the ion.
- (3)For oxygen in the case of superoxide's and peroxides oxidation state is assigned to oxygen as -1 or –(½).

- (4)The second exception with oxygen is with the fluorides and di-fluorides here the oxygen has an oxidation state of +2 and+1.
- (5)The number assigned to oxygen will depend upon the bonding state of oxygen but this will have a positive number.
- (6)the oxidation state of hydrogen is +1, except when it is bonded with elements with binary compounds. When it is bonded with lithium , beryllium it has the oxidation state of -1.

- (7)In all its compounds fluorine has an oxidation state of -1.other halogens like chlorine , bromine and iodine have also the oxidation state as -1.except oxoanions and oxoacids.
- (8)The algebraic sum of the oxidation number of all the atoms in a compound must be zero. In polyatomic ions the algebraic sum of all the oxidation numbers of atoms of the ion must be equal to the charge on the ion.

Oxidation Number basic Rules

1. **Oxidation number of free elements**

   Free elements (include molecular elements: H_2, O_2, O_3, N_2, F_2, Cl_2, Br_2, I_2, P_4, S_8) have oxidation number of 0 (zero).

2. **Oxidation number of fluorine**

   In its compounds, oxidation number of **F** always –**1**.

3. **Oxidation number of hydrogen**

   In its compounds, oxidation number of **H** always **+1.**
   Except, hydrogen in the **hydride** compounds (compound of H with metal), oxidation number of **H,** is –**1**
   Example:
   In the compound of H_2O, NH_3, H_2S, HCl, HNO_3, H_2SO_4, oxidation number of **H,** is **+1**
   In the **hydride compound,** like LiH, NaH, MgH_2, oxidation number of **H,** is –**1**

Rules for Assigning Oxidation States

5. in their compounds, nonmetals have oxidation states according to the table below
   - nonmetals higher on the table take priority

Nonmetal	Oxidation State	Example
F	-1	CF_4
H	+1	CH_4
O	-2	CO_2
Group 7A	-1	CCl_4
Group 6A	-2	CS_2
Group 5A	-3	NH_3

A. Reduction oxidation reaction based on oxidation number change

a. Oxidation reaction

Oxidation reaction is a chemical reaction which is accompanied by **increasing of oxidation number.**

Example:

$$Al_{(s)} \longrightarrow Al^{3+}_{(aq)}$$

$$S^{2-}_{(aq)} \longrightarrow S_{(s)}$$

b. Reduction reaction

Reduction reaction is a chemical reaction which is accompanied by **decreasing of oxidation number.**

Example:

$$Sn^{4+}_{(aq)} \longrightarrow Sn^{2+}_{(aq)}$$

$$Cl_{2(g)} \longrightarrow 2\,Cl^{-}_{(g)}$$

b. Generally, **metallic elements of group B** has oxidation number more than one type.

Example:

Table 8.1.

Oxidation numbers of several elements of group B

Elements of group B		*Oxidation numbers*
Name	*Symbol*	
Zink	*Zn*	*+2*
Silver	*Ag*	*+1*
Copper	*Cu*	*+1, +2*
Gold	*Au*	*+1, +3*
Iron	*Fe*	*+2, +3*
Lead	*Pb*	*+2, +4*

6. Oxidation number of monoatomic ion

Oxidation number of mono atomic ions is **equal to the charge on that ion**

Example:

Na^{+} ion has oxidation number of **+1**

Ba^{2+} ion has oxidation number of **+2**

Fe^{3+} ion has oxidation number of **+3**

Cl^{-} ion has oxidation number of –**1**

S^{2-} ion has oxidation number of –**2**

7. **The sum** of oxidation number of element atoms in **a compound molecule** is **equal to 0 (zero)**

$\sum$ o. n. of element in compound molecule = 0

Example: H_2O

$$\begin{aligned} (\text{o.n. of H x 2}) + (\text{o.n. of O x 1}) &= 0 \\ \{(+1)\ x2\} + \{(-2)\ x\ 1\} &= 0 \\ \{+2\} + \{-2\} &= 0 \end{aligned}$$

8. **The sum** of oxidation number of element atoms in **a polyatomic ion** is **equal to the charge** on that ion.

$\sum$ o. n. of element in ion = charge of ion

Example: OH^-

$$\begin{aligned} (\text{o.n. of O x 1}) + (\text{o.n. of H x 1}) &= -1 \\ \{(-2)\ x\ 1\} + \{(+1)\ x\ 1\} &= -1 \\ \{-2\} + \{+1\} &= -1 \end{aligned}$$

a. H_2SO_4

$o.\ n.\ H = +1, \quad o.\ n.\ O = -2, \quad o.\ n.\ S = x$

$$\begin{array}{ccc} H_2 & S & O_4 \\ +1 & x & -2 \end{array}$$

$\sum o.\ n.$ element in molecule = 0

(2 x o. n. H) + (1 x o.n. S) + (4 x o.n. O) = 0

{ 2 x (+1) } + { 1 x (x) } + { 4 x (–2) = 0

(+2) + (x) + (–8) = 0

$x = +8 - 2 \qquad x = +6$

The oxidation number of S in H_2SO_4 is **+6**

.$Cr_2O_7^{-2}$

$o.\ n.\ O = -2, \quad o.\ n.\ Cr = x$

$$\begin{array}{cc} (Cr_2 & O_7)^{2-} \\ x & -2 \end{array}$$

$\sum o.\ n.$ of element in ion = charge of ion

(2 x o. n. Cr) + (7 x o.n. O) = –2

{ 2 x (x) } + { 7 x (–2) } = –2

(2x) + (–14) = –2 $\qquad 2x = +14 - 2 \qquad x = \frac{+12}{2}$

$x = +6$

The oxidation number of Cr in $Cr_2O_7^{-2}$ is **+6**

Example 1

$$MnO_4^{-} + 5Fe^{2+} + 8H^{+} \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

+7 +2 +2 +3

Let the oxidation state of Mn be *x*.

Thus, in MnO_4^-, $x + 4(-2) = -1$

$x = +7$

- <u>Manganese is reduced from oxidation state of +7 in MnO_4^- to +2 in Mn^{2+}, while iron is oxidised from oxidation state of +2 in Fe^{2+} to +3 in Fe^{3+}.</u>

Limitations of oxidation number

- The main limitation of oxidation number is that oxidation number cannot be assigned a particular species.
- The secondary limitation is that in recent past it has been found out that the oxidation process is visualized as a decrease in electron density and reduction process as an increase in electron density around the atom(s) involved in the reaction.

Paradox of fractional oxidation number

- Sometimes we come across compounds having fractional oxidation number.
- Examples C_3O_2 where carbon has the oxidation state of 4/3.

Br_3O_8 where bromine has a oxidation state of 16/3.

$Na_2S_4O_6$ where sodium has an oxidation state of 2.5 .

- Fractional oxidation states are often used to represent the average oxidation states of several atoms of the same element in a structure.
- Br3O8 has a oxidation state of 16/3 whereas it actually possess a oxidation state of +4 and +6.
- Similarly thiosulphate ion exhibits oxidation state of +5 and 0 and hence the average or fractional oxidation state becomes 2.5.(in reality it possess +5 and +5 oxidation state)!
- Similarly carbon suboxide experiences a fractional oxidation state of 4/3 whereas each carbon has a oxidation state of +2 and +2.

Redox Reaction

In the chemical reaction, oxidation reaction and reduction reaction always occur together, it is called **oxidation reduction reaction** abreviated **as redox reaction.**

In the redox reaction occurs transfering of electrons from the substance that undergo oxidation to the substance that undergo reduction. Therefore, **redox reaction** is also called ***reaction of transfering electrons***

Special charateristic redox reaxtion is **the oxidation number change**.

- **Oxidation** : lossing electron, increasing oxidation number.
- **Reduction** : gaining electron, decreasing oxidation number.

The chemical reaction that does not espoused oxidation number change (increasing or decreasing in oxidation number) called **non-redox reaction.**

Example:

1. Redox reaction

Reaction of copper(II) oxide with hydrogen gas to form copper and water vapor

$$\begin{array}{ccccccc} \underline{\mathbf{Cu}}O_{(s)} & + & \underline{\mathbf{H}}_{2(g)} & \longrightarrow & \underline{\mathbf{Cu}}_{(s)} & + & \underline{\mathbf{H}}_2O_{(g)} \quad \text{(redox)} \\ +2 & & 0 & & 0 & & +1 \end{array}$$

(red)

o. n. of Cu decreases from +2 to 0

Changing** in o.n.of Cu is – **2

(o x.)

o. n. of H increases from 0 to +1

Total changing** in o.n. of H is **+2

 In the redox reaction:

total number of increasing in oxidation number in oxidation reaction = total number of decreasing in oxidation number in reduction reaction.

Example problem :

Given a redox reaction:

$$3S_{(s)} + 2KClO_{3(s)} \longrightarrow 3SO_{2(g)} + 2KCl_{(s)}$$

a.Identify and under line, element atoms of reactants undergo change in oxidation number.

b.Determine the reactants that undergo reduction - oxidation include their product, and calculate its oxidation number change

c. Determine the reactant behaves as oxidant and reductant.

Answer:

a. In the redox reaction:

$$3\,\underline{\mathbf{S}}_{(s)} + 2\,K\underline{\mathbf{Cl}}O_{3(s)} \longrightarrow 3\,\underline{\mathbf{S}}O_{2(g)} + 2\,K\underline{\mathbf{Cl}}_{(s)}$$

0 (+5) (+4) (-1)

Element atoms undergo change in oxidation number is:

- S : oxidation number of S **increases** from 0 to +4
- Cl : oxidation number of Cl element atom in $KClO_3$ **decreases** from +5 to -1

b. In the redox reaction:

$$3\,\underline{S}_{(s)} + 2\,K\underline{Cl}O_{3(s)} \longrightarrow 3\,\underline{S}O_{2(g)} + 2\,K\underline{Cl}_{(s)}$$

0 (+5) (+4) (-1)

(0) (Ox) S is oxidized into SO_2 (+12)

The total increasing o.n. of S (three atoms) is +12

(+10) $KClO_3$ is reduced into KCl (Red) (-2)

The total decreasing o.n. of Cl (two atoms) is -12

c. In the redox reaction:

$$3\,\underline{S}_{(s)} + 2\,K\underline{Cl}O_{3(s)} \longrightarrow 3\,\underline{S}O_{2(g)} + 2\,K\underline{Cl}_{(s)}$$

0 (+5) (+4) (-1)

S undergoes **oxidation**

The element of **S** is **reducing agent**

$KClO_3$ undergoes **reduction**

The compound of $\mathbf{KClO_3}$ is **oxidizing agent**

Types of redox reactions

- There are 5 types of redox reactions :-

Combination reactions

Decomposition reaction

Displacement reactions

Double displacement reactions

Disproportion reactions

Non-redox reactions

- The oxidation states of the elements remained unchanged in the following reactions:
- Neutralisation reactions:

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

$$CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O$$

Non-redox reactions

- The oxidation states of the elements remained unchanged in the following reactions:
- Precipitation reactions:

$$CuSO_{4(aq)} + 2NaOH_{(aq)} \longrightarrow Cu(OH)_{2(s)} + Na_2SO_{4(aq)}$$

$$2KI_{(aq)} + Pb(NO_3)_{2(aq)} \longrightarrow PbI_{2(s)} + 2KNO_{3(aq)}$$

Non-redox reactions

- The oxidation states of the elements remained unchanged in the following reactions:
- Complex formation:

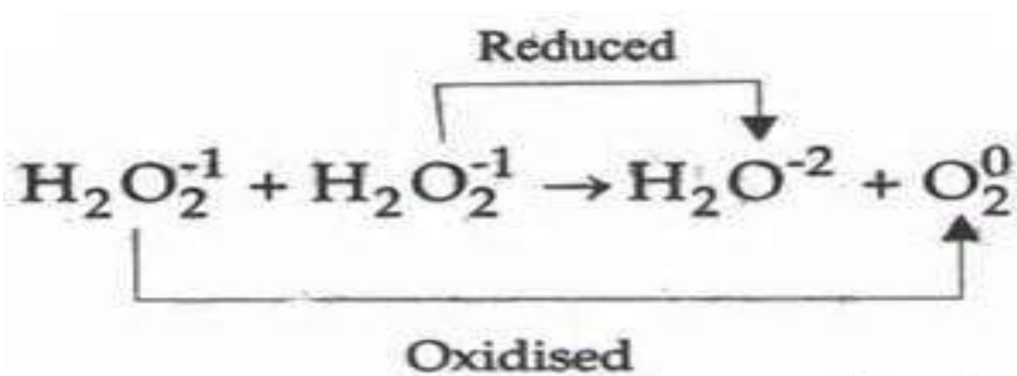
$$Cu^{2+}{}_{(aq)} + 4NH_{3(aq)} \longrightarrow \left[Cu\left(NH_3\right)_4\right]^{2+}_{(aq)}$$

ligand

Tetraammine copper(II) complex (deep blue solution)

Disproportionation reactions

- These are a special type of reactions where an element in one oxidation state is simultaneously oxidised and reduced.
- One of the reacting substances in a disproportion reaction always contains an element that can exist in at least 3 oxidation states.
- The element in the form of reacting substance is in the intermediate oxidation state.



- Hypochlorite ion formed in a disproportion reaction oxidises the colour bearing stains of the substances to colourless compounds.
- Fluorine is the most electronegative element and hence it cannot exhibit any positive oxidation state.
- Fluorine does not show a disproportion tendency.

Auto Redox Reaction (Disproportionation)

Auto redox reaction is a reaction of reduction and oxidation that occur in the same substance (reactant).

Example of auto redox reaction:

Reaction of chlorine gas with sodium hydroxide solution

$$\underline{\mathbf{Cl}}_{2(g)} + 2\,NaOH_{(aq)} \longrightarrow Na\,\underline{\mathbf{Cl}}_{(aq)} + Na\,\underline{\mathbf{Cl}}\,O_{(aq)} + H_2O_{(l)}$$

$0 \qquad\qquad\qquad\qquad -1 \qquad\qquad +1$

(reduction)

o. n. of Cl ***decreases*** *from 0 into –1*

(oxidation)

o. n. of Cl ***increases*** *from 0 into + 1*

Disproportionation Reaction

- Example:
  Is this a disproportionation reaction?

$$NH_4NO_3 \longrightarrow N_2O + 2H_2O$$

-3 **+5** **+1**

This is NOT a disproportionation reaction

- Disproportionation requires that the <u>same</u> atom is both oxidised and reduced simultaneously.
- In this case, <u>different</u> atoms (of nitrogen) are oxidised and reduced.

A Special Redox reaction: Disproportionation

- Example
- Is it possible
- Chlorine is simultaneously reduced from oxidation state of 0 in Cl_2 to -1 in Cl^-, and oxidised from oxidation state of 0 in Cl_2 to +1 in ClO^-.

$$\underset{0}{Cl_2} + 2OH^- \longrightarrow \underset{+1}{ClO^-} + \underset{-1}{Cl^-} + H_2O$$

Balancing Redox Reactions thorugh half reaction method

There are several basic steps

1. Assign oxidation numbers to the species in the reaction
2. Find the substance oxidized and the substance reduced
3. Write half reactions for the oxidation and reduction
4. Balance the atoms that change in the half reaction
5. Determine the electrons transferred and balance the electrons between the half reactions
6. Combine the half reactions and balance the remaining atoms
7. Check your work. Make sure that both the atoms and charges balance

Identify the Oxidizing and Reducing Agents in Each of the Following

$$3\ H_2S + 2\ NO_3^- + 2\ H^+ \rightarrow 3\ S + 2\ NO + 4\ H_2O$$

$$MnO_2 + 4\ HBr \rightarrow MnBr_2 + Br_2 + 2\ H_2O$$

Identify the Oxidizing and Reducing Agents in Each of the Following

red ag ox ag

$$3\ H_2S + 2\ NO_3^- + 2\ H^+ \rightarrow 3\ S + 2\ NO + 4\ H_2O$$

+1 -2 +5 -2 +1 0 +2 -2 +1 -2

oxidation

reduction

ox ag red ag

$$MnO_2 + 4\ HBr \rightarrow MnBr_2 + Br_2 + 2\ H_2O$$

+4 -2 +1 -1 +2 -1 0 +1 -2

oxidation

reduction

Balancing Redox Reactions

1) assign oxidation states and determine element oxidized and element reduced

$$Fe^{2+} + MnO_4^- \longrightarrow Fe^{3+} + Mn^{2+}$$

+2 +7 -2 +3 +2

oxid

red

2) separate into oxidation & reduction half-reactions

$$Fe^{2+} \longrightarrow Fe^{3+}$$

$$MnO_4^- \longrightarrow Mn^{2+}$$

3) balance half-reactions by mass
   a) first balance atoms other than O and H
   b) then balance O by adding H_2O to side that lacks O
   c) finally balance H by adding H^+ to side that lacks H

$$Fe^{2+} \longrightarrow Fe^{3+}$$

$$MnO_4^- \longrightarrow Mn^{2+}$$

$$MnO_4^- \longrightarrow Mn^{2+} + 4H_2O$$

$$MnO_4^- + 8H^+ \longrightarrow Mn^{2+} + 4H_2O$$

BALANCING REDOX REACTIONS

Example #1

Write a balanced equation to describe the reaction between zinc metal with aqueous lead (II) nitrate.

$$\overset{0}{Zn}_{(s)} + \overset{+2}{Pb}(\overset{+5}{N}\overset{-2}{O}_3)_{2(aq)} \rightarrow \overset{0}{Pb}_{(s)} + \overset{+2}{Zn}(\overset{+5}{N}\overset{-2}{O}_3)_{2(aq)}$$

$$Zn_{(s)} \rightarrow Zn^{2+}{}_{(aq)} + 2e^-$$

$$Pb^{2+}{}_{(aq)} + 2e^- \rightarrow Pb_{(s)}$$

Redox reaction: $Pb^{2+}{}_{(aq)} + Zn_{(s)} \rightarrow Pb_{(s)} + Zn^{2+}{}_{(aq)}$

Example #2

Write the balanced redox equation for the reaction of MnO_4^- in an acidic solution with H_2SO_3 resulting with the products of Mn^{2+} and SO_4^{2-}.

You can use half-reactions from the Half Reactions Table

Reduction: $2MnO_{4\,(aq)}^{-} + 16H^{+}_{(aq)} + \cancel{10e^-} \rightarrow 2Mn^{2+}_{(aq)} + 8H_2O_{(l)}$ $\boxed{x\ 2}$

Oxidation: $5H_2SO_{3(aq)} + 5H_2O_{(l)} \rightarrow 5SO_{4\,(aq)}^{2-} + 20H^{+}_{(aq)} + \cancel{10e^-}$

$$2MnO_{4\,(aq)}^{-} + 5H_2SO_{3(aq)} \rightarrow 2Mn^{2+}_{(aq)} + 3H_2O_{(l)} + 5SO_{4\,(aq)}^{2-} + 4H^{+}_{(aq)}$$

Example #5

Balance the following redox reaction which occurs in an acidic solution:

$$Cr_2O_7^{2-} + Fe^{2+} \rightarrow Cr^{3+} + Fe^{3+}$$

Which half-reaction is reduction? Which is oxidation?

$$Cr_2O_7^{2-} \rightarrow Cr^{3+}$$

$$Fe^{2+} \rightarrow Fe^{3+}$$

Reduction: $Cr_2O_7^{2-} + 14H^+ + \cancel{6e^-} \rightarrow 2Cr^{3+} + 7H_2O$

Oxidation: $6Fe^{2+} \rightarrow 6Fe^{3+} + \cancel{6e^-}$ $\boxed{\times 6}$

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

BALANCING REDOX REACTIONS

Example #6

Balance the following redox reaction which occurs in a basic solution:

$$SO_3^{2-} + MnO_4^- \rightarrow SO_4^{2-} + MnO_2$$

Which half-reaction is reduction? Which is oxidation?

Oxidation: $6OH^- + 3SO_3^{2-} + 3H_2O \rightarrow 3SO_4^{2-} + 6H_2O + \cancel{6e^-}$ $\boxed{x\ 3}$

Reduction: $8H_2O + 2MnO_4^- + \cancel{6e^-} \rightarrow 2MnO_2 + 4H_2O + 8OH^-$ $\boxed{x\ 2}$

$$3SO_3^{2-} + H_2O + 2MnO_4^- \rightarrow 3SO_4^{2-} + 2MnO_2 + 2OH^-$$

Redox reactions as the basis for titrations

- In one situation, the reagent itself is intensely coloured. Here in this case the permanganate ion it acts as a self indicatorhere the end point is reached after the vlast of the reductant is oxidised and the first lasting tinge of pink colour appears at low concentration.
- This ensures minimal overshoot in colour beyond the equivalence point , the point where the reductant and the oxidant are equal in terms of their mole stoichiometry.
- if there is no dramatic auto-colour change there are indicators which are oxidised immediately after the last bit of the reactant is consumed, producing a dramatic colour change. The best example is afforded by
- Dichromate salt , which is not a self indicator, but oxidises the indicator substance diphenylamine just after the equivalence point to produce an intense blue colour, thus signaling the end point.
- There is yet another method which is interesting and quite common. Its use is restricted to those reagents which are able to

- For example,

This method relies on the facts iodine gives an intense blue colour starch and has very specific reaction with thiosuphate ion which is too a redox reaction.

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

Iodide remains a solution containing KI or KI3

On addition of starch after the liberation of iodide from the reaction of Cu 2+ ions on iodide ions , an intense blue colour appears , this colour disappears as soon as iodine is consumed by thiosuphate ions . Thus the end point can be tracked easily by stoichiometric calculations

Activity Series of Metals

- listing of metals by reactivity
- free metal higher on the list displaces metal cation lower on the list
- metals above H will dissolve in acid

$Zn + Fe^{2+} \rightarrow Fe + Zn^{2+}$

$Cu + Fe^{2+} \rightarrow$ no reaction

$Zn + 2\,H^{+} \rightarrow H_2 + Zn^{2+}$

Fe is below Zn, so Zn metal will displace Fe^{2+}

$Zn(s) + 2\,H^{+}(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$

react with O_2 in the air to make oxides

react with O_2 in the air to make oxides

displace H_2

K
Ba
Sr
Ca
Na
Mg
Al
Mn
Zn
Cr
Fe
Cd
Co
Ni
Sn
Pb
H
Sb
As
Bi
Cu
Hg
Ag
Pd
Pt
Au

from cold H_2O (K – Na)

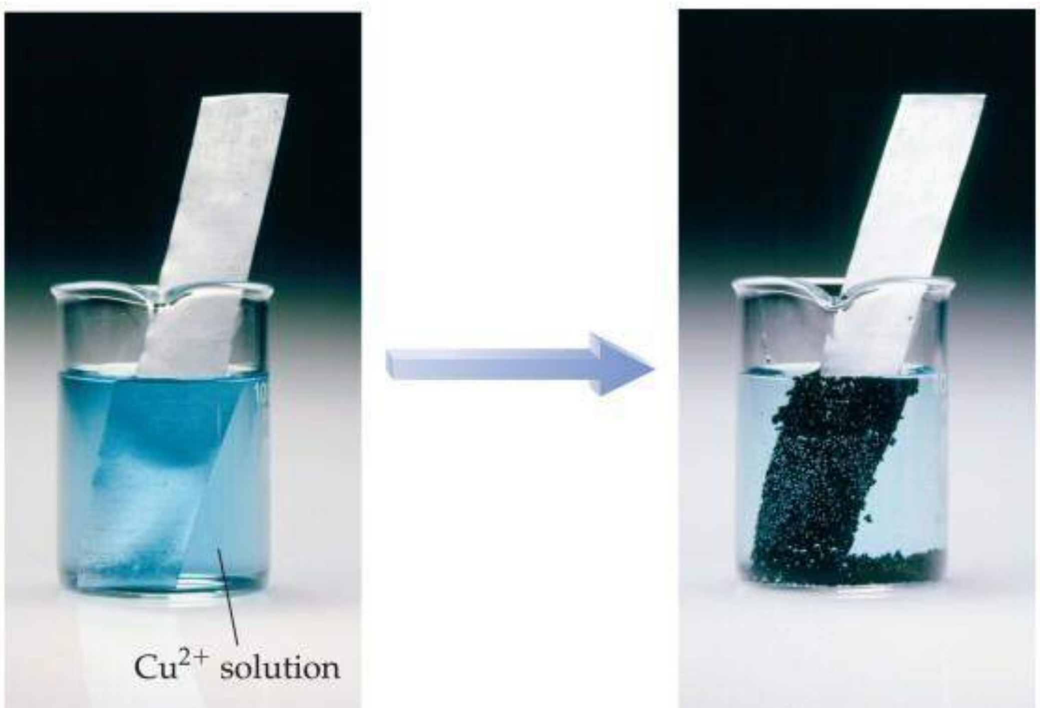
from steam (Mg – Cd)

from acids (Co – Pb)

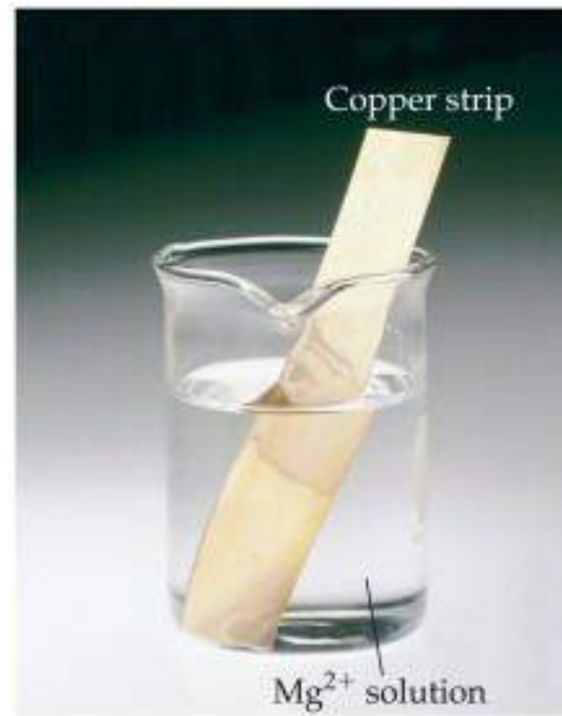
Mg will react with Cu^{2+} to form Mg^{2+} and Cu metal

Mg is above Cu on the Activity Series

but Cu will not react with Mg^{2+}



$$Mg(s) + Cu^{2+}(aq) \longrightarrow Mg^{2+}(aq) + Cu(s)$$



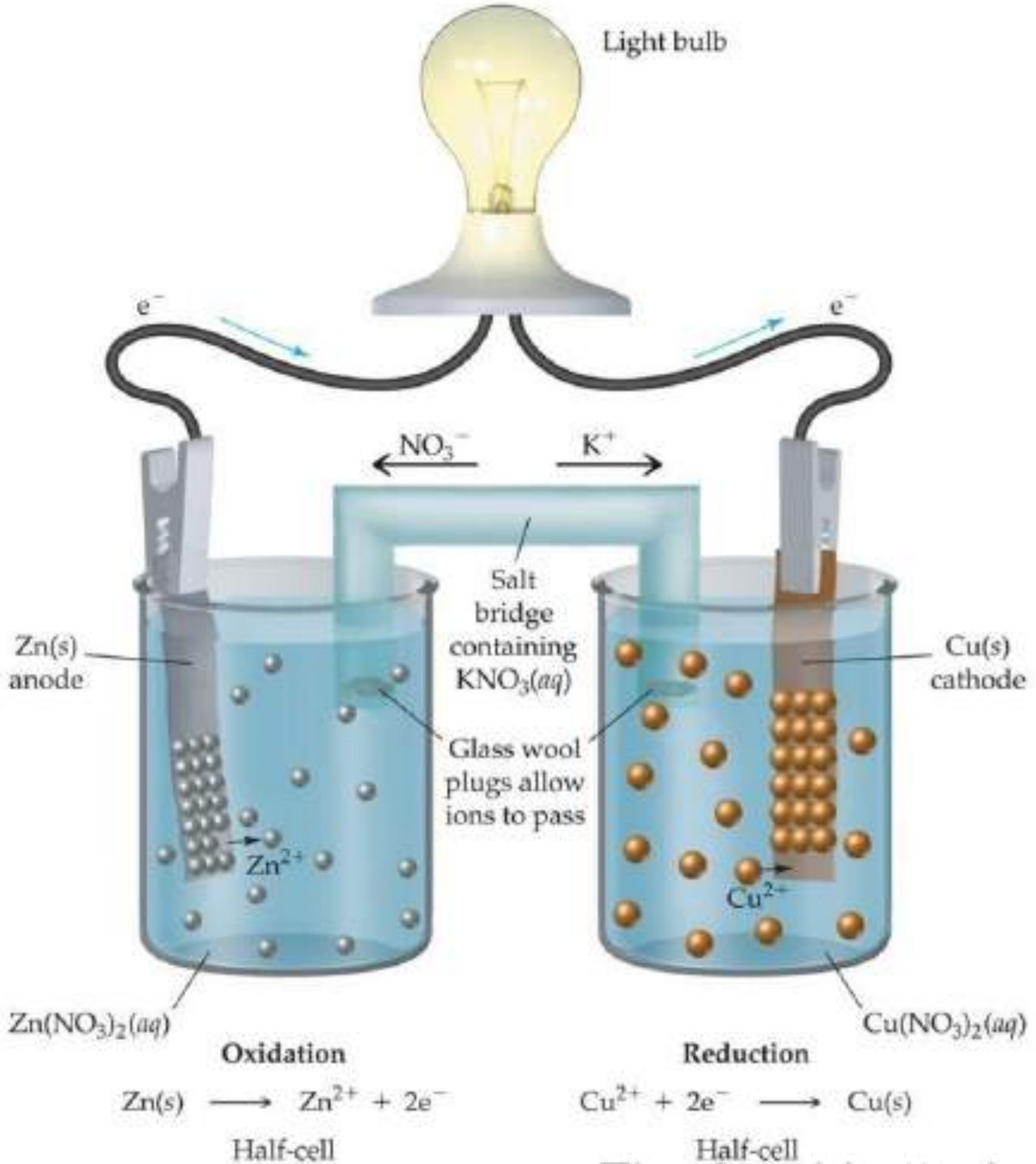
Electrochemical Cells

- **electrochemistry** is the study of redox reactions that produce or require an electric current
- the conversion between chemical energy and electrical energy is carried out in an **electrochemical cell**
- spontaneous redox reactions take place in a **voltaic cell**
  - also known as galvanic cells
  - batteries are voltaic cells
- nonspontaneous redox reactions can be made to occur in an **electrolytic cell** by the addition of electrical energy

Electrodes

- **Anode**
  - electrode where oxidation occurs
  - anions attracted to it
  - connected to positive end of battery in electrolytic cell
  - loses weight in electrolytic cell
- **Cathode**
  - electrode where reduction occurs
  - cations attracted to it
  - connected to negative end of battery in electrolytic cell
  - gains weight in electrolytic cell
    - electrode where plating takes place in electroplating

Voltaic Ce


Light bulb
e⁻
e⁻
NO_3^-
K^+
Salt bridge containing $KNO_3(aq)$
Zn(s) anode
Cu(s) cathode
Glass wool plugs allow ions to pass
Zn^{2+}
Cu^{2+}
$Zn(NO_3)_2(aq)$
$Cu(NO_3)_2(aq)$
Oxidation
$Zn(s) \longrightarrow Zn^{2+} + 2e^-$
Half-cell
Reduction
$Cu^{2+} + 2e^- \longrightarrow Cu(s)$
Half-cell

Redox reactions and electrode process

- <u>Redox couple:-</u>

It is defined as having together the oxidised and reduced forms of a substance taking part in an oxidation or reduction half reaction

This is represented by separating the oxidised form from the reduced form by a vertical line showing for e.g. solid/solution interface.

- Example:- Zn^{2+}/Zn ,Cu^{2+}/Cu.

In both cases oxidised form is put before the reduced form.

Experiment-daniell's cell

Now we put the beaker containing copper sulphate solution and the beaker containing zinc sulphate solution side by side . We connect solutions in two beakers by a salt bridge (a U-tube containing a solution of potassium chloride or ammonium nitrate usually solidified by boiling with agar agar and later cooling to a jelly like substance.)

This provides an electric contact between the two solutions without allowing them to mix with each other. The zinc and copper rods are connected by a metallic wire with a provision for an ammeter and a switch. The set-up is known as Daniell cell. When the switch is in the o position, no reaction takes place in either of the beakers and no current flows through the metallic wire.

- **As soon as the switch is on we get the following observations**:-

1. The transfer of electrons now does not take place directly from Zn to Cu^{2+} but through the metallic wire connecting the two rods as is apparent from the arrow which indicates the flow of current.
2. The electricity from solution in one beaker to solution in the other beaker flows by the migration of ions through the salt bridge. We know that the flow of current is possible only if there is a potential difference between the copper and zinc rods known as electrodes here.

Standard electrode potential

- The potential associated with each electrode is known as **electrode potential.**
- If the concentration of each species taking part in the electrode reaction is unity(which means that any gas at 1 atmospheric pressure) and further the reaction is carried out at 298K then the potential of each electrode is called **standard electrode potential. It is denoted by $E^{\underline{O}}$**
- **A negative E means that the Redox couple is stronger reducing agent than the H+**/H_2couple.

A positive **E means that the redox couple is weaker reducing agent than the H+**/H_2couple.

Types of Electrochemical Cells

Voltaic (or galvanic) cell: uses a spontaneous reaction ($\Delta G < 0$) to generate electrical energy.

Electrolytic cell: uses electrical energy to drive a non-spontaneous reaction ($\Delta G > 0$).

Contain two electrodes (anode and cathode) dipped into an aqueous electrolyte solution.

The oxidation half-reaction occurs at the **anode**; the reduction half-reaction occurs at the **cathode**.

Daniel's cell setup

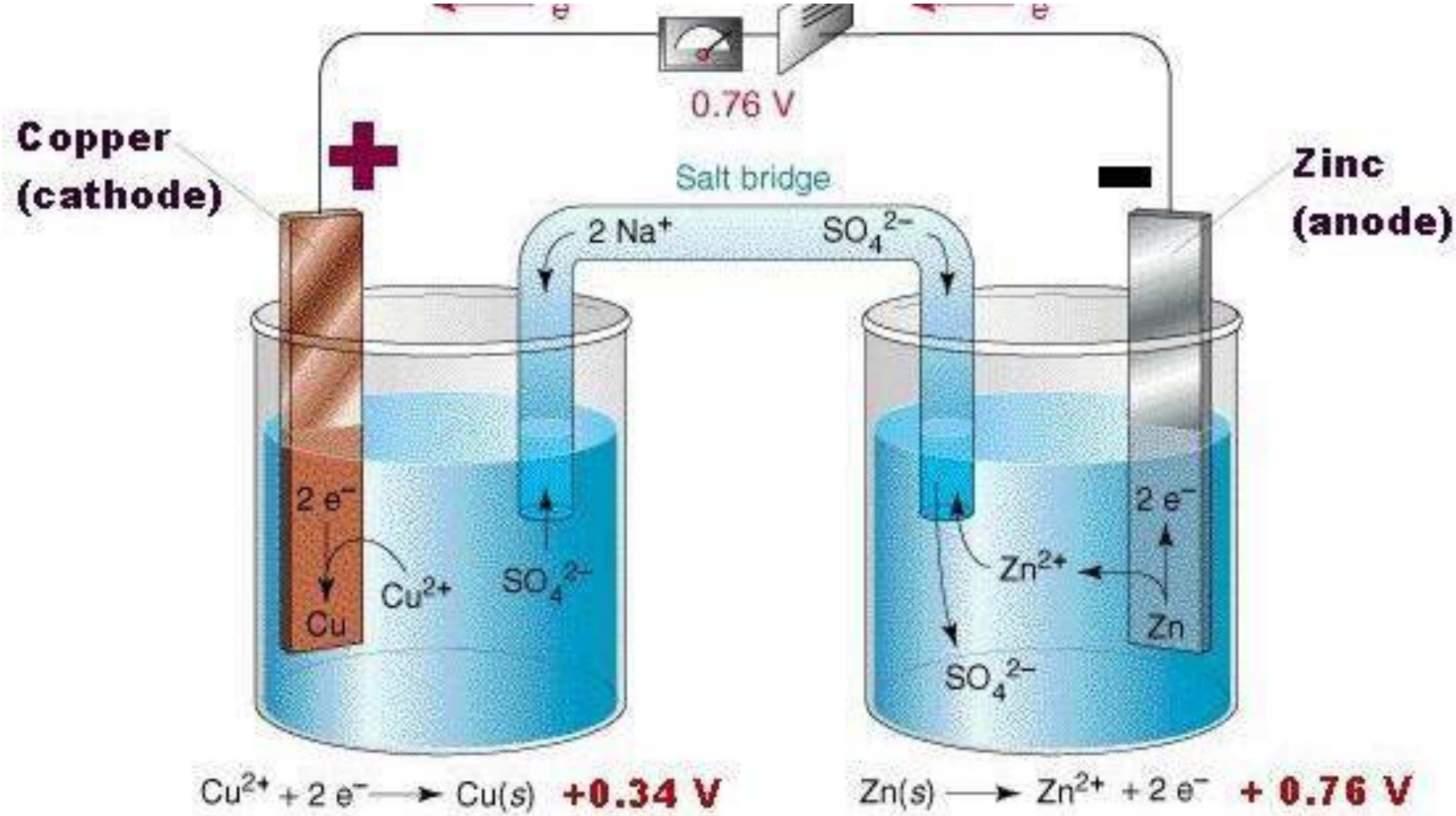


Table 8.1 The Standard Electrode Potentials at 298 K

Ions are present as aqueous species and H_2O as liquid; gases and solids are shown by g and s respectively.

Reaction (Oxidised form + ne^-	→ Reduced form)	$E^\ominus$ / V
$F_2(g) + 2e^-$	$\rightarrow 2F^-$	2.87
$Co^{3+} + e^-$	$\rightarrow Co^{2+}$	1.81
$H_2O_2 + 2H^+ + 2e^-$	$\rightarrow 2H_2O$	1.78
$MnO_4^- + 8H^+ + 5e^-$	$\rightarrow Mn^{2+} + 4H_2O$	1.51
$Au^{3+} + 3e^-$	$\rightarrow Au(s)$	1.40
$Cl_2(g) + 2e^-$	$\rightarrow 2Cl^-$	1.36
$Cr_2O_7^{2-} + 14H^+ + 6e^-$	$\rightarrow 2Cr^{3+} + 7H_2O$	1.33
$O_2(g) + 4H^+ + 4e^-$	$\rightarrow 2H_2O$	1.23
$MnO_2(s) + 4H^+ + 2e^-$	$\rightarrow Mn^{2+} + 2H_2O$	1.23
$Br_2 + 2e^-$	$\rightarrow 2Br^-$	1.09
$NO_3^- + 4H^+ + 3e^-$	$\rightarrow NO(g) + 2H_2O$	0.97
$2Hg^{2+} + 2e^-$	$\rightarrow Hg_2^{2+}$	0.92
$Ag^+ + e^-$	$\rightarrow Ag(s)$	0.80
$Fe^{3+} + e^-$	$\rightarrow Fe^{2+}$	0.77
$O_2(g) + 2H^+ + 2e^-$	$\rightarrow H_2O_2$	0.68
$I_2(s) + 2e^-$	$\rightarrow 2I^-$	0.54
$Cu^+ + e^-$	$\rightarrow Cu(s)$	0.52
$Cu^{2+} + 2e^-$	$\rightarrow Cu(s)$	0.34
$AgCl(s) + e^-$	$\rightarrow Ag(s) + Cl^-$	0.22
$AgBr(s) + e^-$	$\rightarrow Ag(s) + Br^-$	0.10
$2H^+ + 2e^-$	**$\rightarrow H_2(g)$**	**0.00**
$Pb^{2+} + 2e^-$	$\rightarrow Pb(s)$	–0.13
$Sn^{2+} + 2e^-$	$\rightarrow Sn(s)$	–0.14
$Ni^{2+} + 2e^-$	$\rightarrow Ni(s)$	–0.25
$Fe^{2+} + 2e^-$	$\rightarrow Fe(s)$	–0.44
$Cr^{3+} + 3e^-$	$\rightarrow Cr(s)$	–0.74
$Zn^{2+} + 2e^-$	$\rightarrow Zn(s)$	–0.76
$2H_2O + 2e^-$	$\rightarrow H_2(g) + 2OH^-$	–0.83
$Al^{3+} + 3e^-$	$\rightarrow Al(s)$	–1.66
$Mg^{2+} + 2e^-$	$\rightarrow Mg(s)$	–2.36
$Na^+ + e^-$	$\rightarrow Na(s)$	–2.71
$Ca^{2+} + 2e^-$	$\rightarrow Ca(s)$	–2.87
$K^+ + e^-$	$\rightarrow K(s)$	–2.93
$Li^+ + e^-$	$\rightarrow Li(s)$	–3.05

Increasing strength of oxidising agent

Increasing strength of reducing agent

1. A negative $E^\ominus$ means that the redox couple is a stronger reducing agent than the H^+/H_2 couple.
2. A positive $E^\ominus$ means that the redox couple is a weaker reducing agent than the H^+/H_2 couple.

THANK YOU