Chapter 16

Electrochemistry

Student Learning Outcomes

After studying this chapter, students will be able to:

- Define redox reactions as simultaneous oxidation and reduction in terms of oxygen, hydrogen, electrons and changes in oxidation state
- Use roman numerals to indicate oxidation number of an element in a compound
- Identify oxidizing and reducing agents in a redox reaction
- Recognize that the oxidation number of elements in their free state is zero
- Derive the formula of ionic compounds from ionic charges and oxidation numbers
- Identify that the oxidation number of a monatomic ion is the same as the charge on the ion
- Explain that the sum of the oxidation numbers in a neutral compound is zero
- Explain that the sum of the oxidation numbers in an ion is equal to the charge on the ion
- Identify redox reactions by the colour changes involved when using acidified aqueous potassium manganate (VII) to (II) or aqueous potassium iodide
- Define electrolysis as decomposition of ionic compound, in molten or aqueous solution, by passage of electric current
- Identify and label in simple electrolytic cells, the anode (+), cathode (-), electrolyte and direction of flow of electrons in external circuit,
- Describe the transfer of charge in external circuit, movement of ions in the electrolyte and transfer of electrons at electrodes
- Identify the products formed at electrodes and describe the observations made during the electrolysis of molten lead (II) chloride, concentrated dilute sulfuric acid using inert electrodes (platinum or carbon/graphite)
- State that hydrogen- oxygen fuel cell uses hydrogen and oxygen to produce electricity with water as the only chemical product
- Describe the advantages and disadvantages of using hydrogen-oxygen fuel cells in comparison with gasoline /petrol engines in vehicles.
- Define corrosion and discuss methods to prevent it. (some examples may include barrier method such as using paint, galvanizing, electroplating; sacrificial protection such as using magnesium blocks in ships)
- Identify the products formed at electrodes and describe the observations made during the electrolysis of dilute copper (II) sulphate using inert electrode or copper electrode
- Predict the identity of products of electrolysis of a halide compound in dilute or concentrated solution
- Construct ionic half- equations for reaction at either electrode.
- Describe electroplating and its applications.
- Sketch a schematic diagram for a voltaic cell e.g., Daniel cell
- Use the voltage data given for voltaic cells to determine order of reactivity of any two metals

16.1 Oxidation Number of Atoms in compounds and Ions

The assignment of oxidation number to atoms in compounds and ions helps us to identify whether the reaction involves oxidation and reduction or not. It also helps to identify oxidizing and reducing agents in a given oxidation-reduction reaction. Oxidation numbers are also used to write chemical formulas and names of the chemical compounds. This concept also helps to keep track of the new distribution of electrons during an oxidation-reduction reaction.

The oxidation number is an apparent charge on an atom in a compound or an ion. It may have a positive or a negative sign.

The oxidation number of atoms can be found out by applying the following rules.

1. Atom present in a free element has an oxidation number zero.
   Example: The oxidation number of sodium in sodium metal is zero. Similarly, oxidation number of oxygen in ozone(O_3) is also zero.
2. For monoatomic ions, the oxidation number is equal to the charge present on the ion.
   Example: The oxidation number of Ca^{2+} is +2 while that of Al^{3+} is +3.
3. The elements present in group 1 (except hydrogen) in the periodic table are assigned oxidation number +1, those of group 2, +2 and those of group 3, +3.
4. In binary compounds the more electronegative atom is always assigned a negative oxidation number. For example, fluorine, being the most electronegative atom, will always be given -1 oxidation number. Similarly, in NH_3 and H_2S, nitrogen and sulphur are assigned the oxidation number of -3 and -2 respectively.
5. The elements of group 17 are normally given oxidation number -1 when they are combined with less electronegative element.
   Example: Chlorine in all such compounds as HCl, PCl_3, $CHCl_3$ has been assigned an oxidation number -1.
6. Hydrogen is assigned an oxidation number +1 when it is in combination with more

Point to note

Oxidation numbers do not represent the real electrical charges present on atoms except in simple ions. However, the oxidation numbers are useful for keeping track of the redox reactions.

electronegative atoms while it is given oxidation number -1 when it is combined with less electronegative atoms.

Example: In HCl, the oxidation number of hydrogen is +1, while in sodium hydride (NaH) it bears an oxidation number -1.

Point to note

The term oxidation state is also used interchangeably of oxidation number. In water, hydrogen has an oxidation number of +1 and it is said to be in the +1 oxidation state.

7. The element oxygen is assigned an oxidation number -2 in most of its compounds.
8. The sum of oxidation numbers of all the atoms present in a neutral compound is always zero. In a polyatomic ion the sum of oxidation numbers is equal to the charge present on that ion.

16.1 Example

Assign oxidation number to sulphur in SO_4^{2-}

Solution:

$$S + 4O = -2$$
$$S + 4(-2) = -2$$
$$S - 8 = -2$$
$$S = 8 - 2$$
$$S = +6$$

The oxidation number of S in SO_4^{2-} is +6.

16.2 Example

Find out the oxidation number of manganese in $KMnO_4$.

Solution:

$$K + Mn + 4O = 0$$
$$(+1) + Mn + 4(-2) = 0$$
$$Mn - 7 = 0$$
$$Mn = +7$$

The oxidation number of Mn is $KMnO_4$ is +7.

16.3 Example

Find out the oxidation number of Fe in Fe_2O_3.

Solution:

$$2Fe + 3O = 0$$
$$2Fe + 3(-2) = 0$$
$$2Fe - 6 = 0$$
$$2Fe = +6$$
$$Fe = +3$$

Oxidation number of one atom of Fe is +3

16.1 Quick Check!

Assign oxidation number to the marked atom of the following compounds:

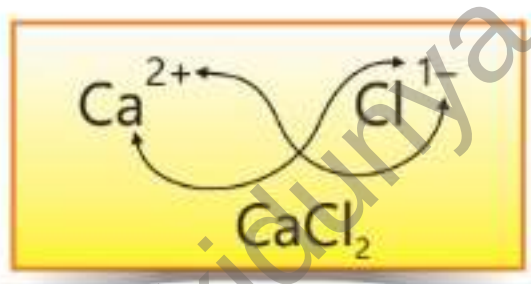
$K_2\underline{Cr_2}O_7$, $(NH_4)_2\underline{SO_4}$

16.2 Writing Chemical Formulas of Ionic Compounds by applying Oxidation Numbers

We can write the chemical formula of a compound if we know the oxidation numbers of its constituent elements. The periodic table and the electronic structure of the atoms can help us in predicting the principal oxidation number of the element. The formula of the compound may then be written using the oxidation number of the atoms present in that compound. For example, we shall write the formula of calcium chloride in the following way.

The element calcium is present in group II of the periodic table and its principal oxidation number is +2.

Chlorine is present in Group 17 and we know that when it is attached with less electronegative element in binary compounds its oxidation number is -1. The formula for calcium chloride will, therefore, be $CaCl_2$ because only with this formula the sum of the oxidation numbers of both the elements will add upto zero.

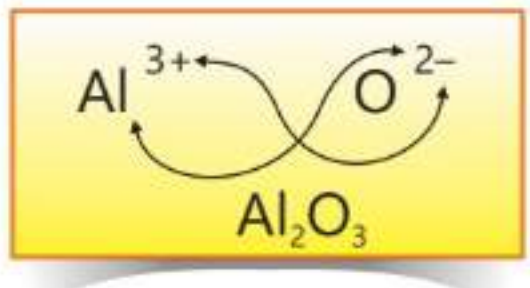


16.4 Example

Write the chemical formula of aluminum oxide with the help of oxidation numbers of the elements involved.

Solution:

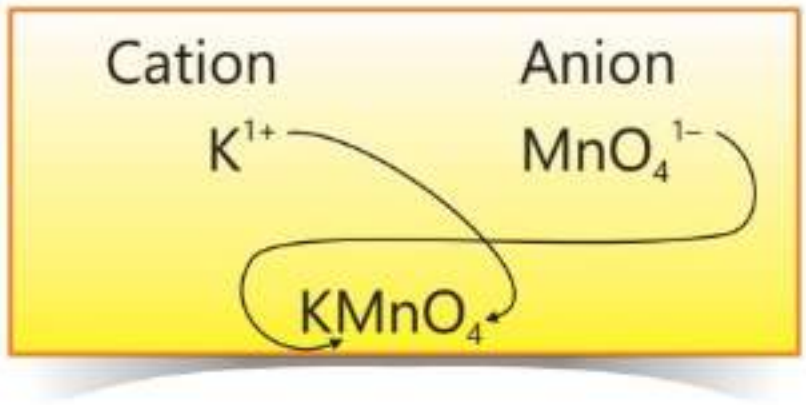
Aluminum is present in Group 13 so its principal oxidation number shall be +3. Oxygen being more electronegative atom normally shows –2 oxidation state in normal oxides. The formula of aluminum oxide will then be Al_2O_3 because the some of oxidation numbers of both elements will be equal to zero with this formula.



16.3 Writing Chemical Formulas of Ionic Compounds using Ionic Charges

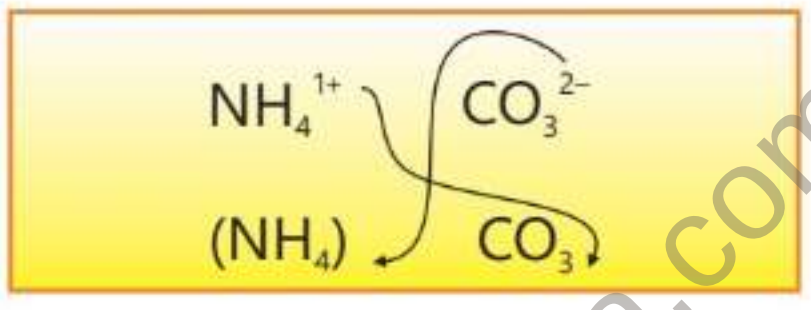
In order to write the formula of potassium permanganate, write first the

formulae of permanganate ion, MnO_4^{1-} and potassium ion K^{1+}. Then combine the two ions together to form an electrically neutral compound.



The formula for potassium permanganate will, therefore, be $KMnO_4$.

When writing the formulae of ionic compounds containing more than one polyatomic ions, we take the formula of the ion in brackets and indicate the number of such ions with a subscript. The formula for ammonium carbonate will be written as follows.

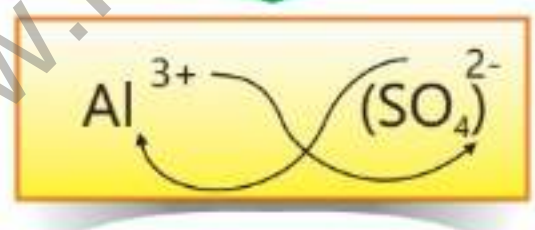


The formula for ammonium carbonate will, therefore, be $(NH_4)_2CO_3$.

16.5 Example

Write down the formula for aluminum sulphate.

Solution:



The formula for aluminum sulphate is $Al_2(SO_4)_3$.

Examples of several polyatomic ions are given in Table 16.1

Table 16.1 – Common Polyatomic ions

CH_3COO^-	acetate	$Cr_2O_7^{2-}$	dichromate	NO_2^{1-}	nitrite
NH_4^{1+}	ammonium	HCO_3^{1-}	bicarbonate	$C_2O_4^{2-}$	oxalate
CO_3^{2-}	carbonate	HSO_4^{1-}	bisulfate	ClO_4^{1-}	perchlorate
ClO_3^{1-}	chlorate	HSO_3^{1-}	bisulfite	MnO_4^{1-}	permanganate
ClO_2^{1-}	chlorite	OH^{1-}	hydroxide	PO_4^{3-}	phosphate
CrO_4^{2-}	chromate	ClO^{1-}	hypochlorite	SO_4^{2-}	sulfate
CN^{1-}	cyanide	NO_3^{1-}	nitrate	SO_3^{2-}	sulfite

16.2 Quick Check!

1. Write the formulae of the following ionic compounds with the help of oxidation numbers of their constituent atoms.
   Aluminum nitride, Sodium sulfite and Sodium hydrogen carbonate.
2. Write the formulae of following ionic compounds with the help of charges present on their ions.
   Ammonium acetate, Calcium phosphate and Potassium chromate.

16.4 Oxidation and Reduction

Oxidation and reduction are simultaneous but opposite processes. They always occur together. Oxidation and reduction changes are described in three principal ways.

(A) Oxidation

1. Oxidation is defined as a process in which oxygen is either added or hydrogen is removed.

For example;

(i) Oxygen combines with other elements in the formation of their oxides. Elements in these processes are said to be oxidized and oxygen is reduced.

Rusting of iron or burning of magnesium in air are oxidation processes.

$$4Fe_{(s)} + 3O_{2(g)} \longrightarrow 2Fe_2O_{3(s)}$$

$$2Mg_{(s)} + O_{2(g)} \longrightarrow 2MgO_{(s)}$$

In the above reactions Fe and Mg are being oxidized while oxygen is being reduced. Oxygen is an oxidising agent while iron and magnesium are reducing agents.

(ii) Hydrogen is removed from a compound by oxygen in the following examples; hydrogen is removed from CH_4 and HCl by oxygen or a compound containing oxygen.

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

$$4HCl_{(aq)} + MnO_{2(s)} \longrightarrow MnCl_{2(aq)} + Cl_{2(g)} + 2H_2O_{(l)}$$

CH_4 and HCl in these reactions are being oxidized while O_2 and MnO_2 are being reduced. CH_4 and HCl are called reducing agents while O_2 and MnO_2 are called oxidising agents.

2. Oxidation is a process in which electron or electrons are lost.

For example; Copper may lose one or two electrons to give Cu^{1+} or Cu^{2+} ions respectively. In both these processes, we say, copper is being oxidised. Hence, copper is called an reducing agent.

$$Cu \longrightarrow Cu^{1+} + e^-$$

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

3. Oxidation is process in which oxidation number or oxidation state of an element increases.

In the above two processes, the oxidation number of copper has increased from zero to +1 [Cu (I)] and +2 [Cu (II)] respectively.

(B) Reduction

1. Reduction is defined as either addition of hydrogen or removal of oxygen.

For example,

(i) hydrogen is added in chlorine to give hydrogen chloride gas.

$$H_{2(g)} + Cl_{2(g)} \longrightarrow 2HCl_{(g)}$$

(ii) In the following reaction, hydrogen is heated with metal oxide when oxygen comes out of the compound and combines with hydrogen to give a molecule of water.

$$CuO_{(s)} + H_{2(g)} \xrightarrow{\text{Heat}} Cu_{(s)} + H_2O_{(l)}$$

In the above examples, Cl_2 and CuO are being reduced and hydrogen (in both cases) is being oxidized. Cl_2 and CuO are called oxidizing agents while hydrogen in both the reactions will be reducing agent.

2. Reduction is a process in which electron or electrons are gained. For example,

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

$$Mn^{7+} + 5e^- \longrightarrow Mn^{2+}$$

In both the above examples, ions of iron and manganese are being reduced. Hence, they are called oxidising agents.

3. Reduction is a process in which oxidation number of an element decreases. In the above examples oxidation number of iron is reduced

from +3 [Fe(III)] to +2[Fe(II)] while oxidation number of manganese is reduced from +7[Mn(VII)] to +2 [Mn(II)].

16.5 Oxidation-Reduction Reactions

A chemical reaction which involves simultaneous oxidation and reduction is called an oxidation-reduction or redox reaction. The reaction may involve the complete transference of electron or electrons to form ionic bonds or a partial transfer or shift of electron or electrons to form covalent bonds.

Potassium permanganate acts as a very powerful oxidising agent in acidic medium. It oxidizes oxalic acid into carbon dioxide. During the reaction the dark purple solution of potassium permanganate changes to colourless as shown in Figure 16.1. In the presence of dilute sulphuric acid the reaction proceeds as follows.

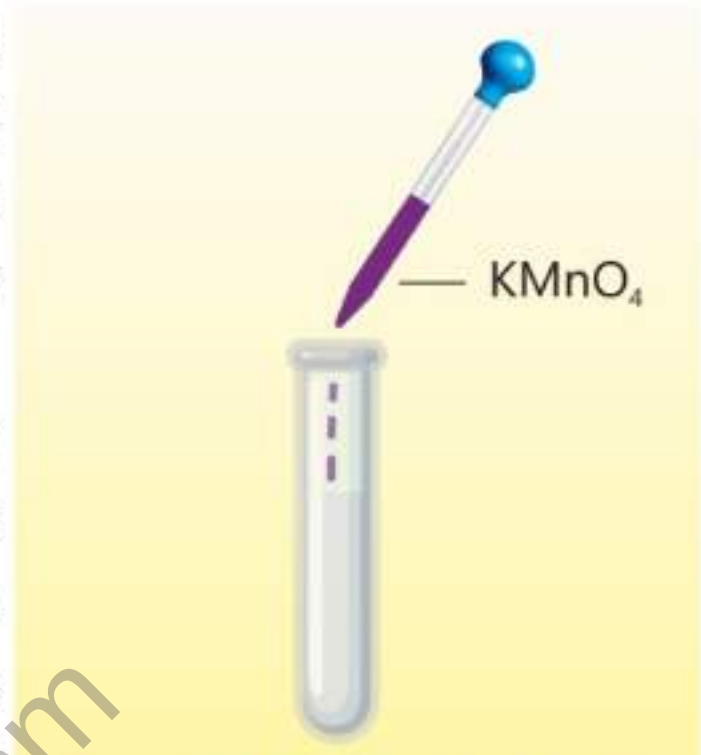


Figure 16.1: Decolourization

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$

$$\left[[O] + H_2C_2O_4 \longrightarrow 2CO_2 + H_2O\right] 5$$

$$2KMnO_{4(aq)} + 3H_2SO_{4(aq)} + 5H_2C_2O_{4(aq)} \longrightarrow K_2SO_{4(aq)} + 2MnSO_{4(aq)} + 10CO_{2(g)} + 8H_2O_{(l)}$$

Let us assign oxidation number to each element in these compounds to find out the oxidising and reducing agents.

$$\overset{+1\ +7\ 4(-2)}{2KMnO_4} + 3\overset{2(+1)+6\ 4(-2)}{H_2SO_4} + 5\overset{2(+1)\ 2(+3)\ 4(-2)}{H_2C_2O_4} \longrightarrow \overset{2(+1)+6\ 4(-2)}{K_2SO_4} + 2\overset{+2\ +6\ 4(-2)}{MnSO_4} + 10\overset{+4\ 2(-2)}{CO_2} + 8\overset{2(+1)\ -2}{H_2O}$$

$$Mn^{+7} \xrightarrow{+5e^-} Mn^{+2} \qquad \text{(Reduction)}$$

$$C^{+3} \xrightarrow{-e^-} C^{+4} \qquad \text{(Oxidation)}$$

Oxidation number of manganese has decreased from +7 to +2 and that of carbon has increased from +3 to +4.

So, each manganese atom accepts five electrons to get reduced and each carbon atom loses one electron to get oxidized. $KMnO_4$ is therefore an oxidizing

agent while oxalic acid in this reaction acts as a reducing agent.

Aqueous potassium iodide is also oxidized to iodine in acidified potassium permanganate. The formation of iodine in this reaction results in a colour change, typically from colourless to yellow-brown.

$$\overset{+1\ +7\ 4(-2)}{2\,KMnO_{4(aq)}} + \overset{2(+1)+6\ 4(-2)}{8\,H_2SO_{4(aq)}} + \overset{+1\ -1}{10\,KI_{(aq)}} \longrightarrow \overset{+2\ +6\ 4(-2)}{6\,K_2SO_{4(aq)}} + \overset{+2\ +6\ 4(-2)}{2\,MnSO_{4(aq)}} + \overset{0}{5I_{2(aq)}} + \overset{2(+1)\ -2}{8\,H_2O_{(l)}}$$

$$Mn^{+7} \xrightarrow{+5e^-} Mn^{+2} \quad \text{(Reduction)}$$

$$2I^{-1} \xrightarrow{-2e^-} I_2^0 \quad \text{(Oxidation)}$$

In this reaction, the permanganate ion (Mno_4^{4-}) is reduced to manganese (II) ion (Mn^{2+}) and the iodide ion (I^{1-}) is oxidized to iodine (I_2). Potassium permanganate, therefore, acts as an oxidizing agent while potassium iodide acts as a reducing agents.

16.3 Quick Check!

Identify the oxidising agent and the reducing agent in the following reactions.

(i) $2CuSO_4 + 4KI \longrightarrow 2CuI + I_2 + 2K_2SO_4$

(ii) $H_2S + Cl_2 \longrightarrow S + 2HCl$

16.6 Electrolysis

When electricity is passed through fused ionic compounds or their aqueous solutions, they are decomposed into their constituents. Such compounds are called Electrolytes and the process is called Electrolysis. During electrolysis, a non-spontaneous chemical reaction takes place with the help of electrical energy.

The process of electrolysis can be carried out in an electrolytic bath called an electrolytic cell with the help of two electrodes through which electric current enters and leaves the cell, These electrodes may be made of graphite or any other metal.

Anode: It is a positive electrode through which electrons enter the external circuit.

Cathode: It is a negative electrode through which electrons leave the external circuit.

Electrolyte present in the cell is in the form of freely moving ions. During electrolysis, the electrolyte is decomposed into its components by applying an external voltage. Thus external voltage source (battery) forces the non-spontaneous reaction to occur by pumping electrons towards one of the electrodes, thereby, giving it a negative charge. The positive ions of

the electrolyte are attracted towards the negative electrode and get reduced by accepting electrons from it, making it the cathode. The battery simultaneously withdraws electrons from the other electrode, giving it a positive charge. The negative ions of the electrolyte are attracted towards this and get oxidized by losing their electrons, making it the anode. Electrons flow in the external circuit while ions move towards their respective electrodes inside the cell. If the oxidation and reduction at the electrodes cease, the flow of electricity in the external circuit also stops.

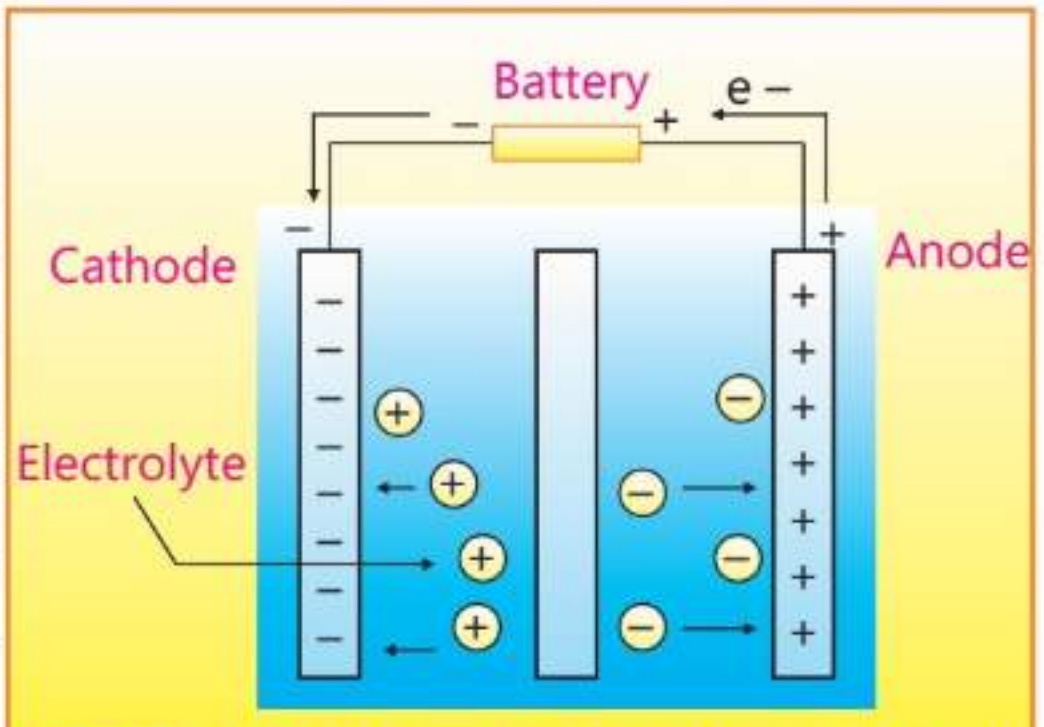


Figure 16.2: Electrolysis in a electrolytic cell

THINGS TO KNOW

	Electrode	Function	Charge
Battery	Anode	Oxidiation	Negative
	Cathode	Reduction	Positive
Electrolytic Cell	Anode	Oxidation	Positive
	Cathode	Reducation	Negative

The terms anode and cathode always refer to the electrodes at which oxidiation and reduction occur respectively. However, the charges carried by electrodes in a battery and electrolytic cell are different.

16.7 Electrolysis of a Concentrated Aqueous Solution of Sodium Chloride (Brine) using inert electrodes (Graphite /Pt)

The electrolysis of a concentrated solution of sodium chloride, also called brine, produces hydrogen gas at the cathode, chlorine gas at the anode, and sodium hydroxide solution as a by-product.

The electrolytic cell used in this electrolysis is shown in Figure 16.3 . The cathode used in this cell is made of platinum while the anode must be made of graphite to avoid the reaction with chlorine gas.

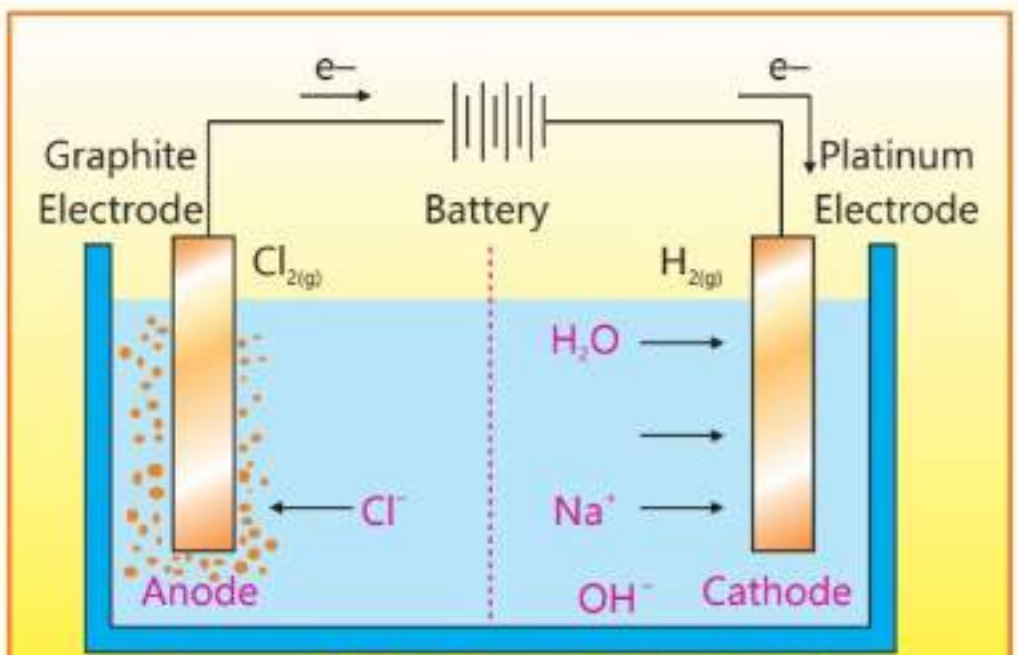


Figure 16.3: Electrolysis of brine

The following ions are present in the solution

$Na^+_{(aq)}, Cl^-_{(aq)}$ from sodium chloride

$H^+_{(aq)}, OH^-_{(aq)}$ from water

Na^+ and H_2O, both migrate towards the cathode. Since water molecules and hydrogen ions have a greater tendency to get reduced as compared to sodium ions (Na^+), so they pick up electrons from the cathode to form hydrogen gas.

At the Cathode

$$2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)}$$

or

$$2H_2O + 2\,e^- \longrightarrow H_{2(g)} + 2OH^-$$

The ionic equilibrium of water is, thus, disturbed due to the discharge of H^+ and more water molecules are ionized to restore it.

Did You Know?

Spontaneous reactions occur naturally without any energy input, while non-spontaneous reactions require a continuous input of energy.

The solution around the cathode becomes alkaline due to the formation of hydroxide ions (OH^-).

At the Anode

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

The solution gradually gets alkaline due to the presence of OH^-. The volumes of hydrogen and chlorine gases obtained are equal.

The overall equation for this electrolysis is:

$$2\,NaCl_{(aq)} + 2H_2O_{(l)} \longrightarrow H_{2(g)} + Cl_{2(g)} + 2NaOH_{(aq)}$$

16.8 Electrolysis of Dilute and Concentrated Aqueous solutions of Metal Halides

When the aqueous solutions of metal halides are subjected to electrolysis, the situation becomes more complicated due to the presence of water. Water is a very weak electrolyte and upon ionization it gives very small amount of hydrogen and hydroxide ions.

$$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$$

This will mean that the electrolyte will consist of more than one type of ions which will approach both cathode and anode. Hence there can be a choice over which ions will get discharged.

For example, if an aqueous solution of sodium chloride is electrolyzed, both sodium and hydrogen cations are attracted towards the cathode and both chlorides and hydroxide ions are attracted towards the anode. Which of these ions will preferentially be discharged depends upon the tendency of the elements to lose or gain electrons. The elements present at the top of electrochemical series shown in Table (16.2) possess more tendency to lose electrons as compared to the elements present at the bottom.

If a metal is below hydrogen in the electrochemical series, then the metal ion is discharged. Metals like this include copper and silver. If dilute copper chloride is electrolyzed, copper metal is obtained at the cathode.

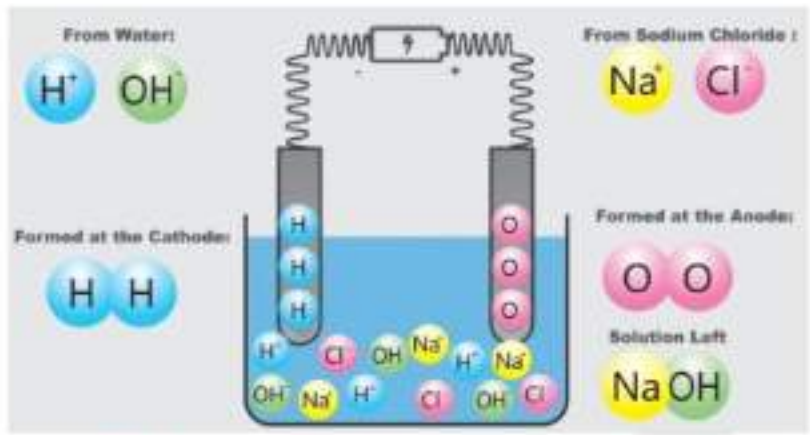


Figure 16.4: Electrolysis of dilute solutions of halides

If a metal is placed higher in the electrochemical series then hydrogen ion is discharged. Metals like this include lithium, sodium and magnesium. If dilute solution of sodium chloride is electrolyzed, hydrogen gas is obtained at the cathode.

Metals like lead and nickel present a more complicated picture. If aqueous solutions of halides of these metals are electrolyzed, then the products obtained at the cathode depends on the concentrations of the halide solutions. If the solution is concentrated then metal is deposited at the cathode. If the solution is very dilute, hydrogen is evolved. At in-between concentrations both metal and hydrogen are obtained.

At anode, the electrolysis of dilute solutions of halides will deposit oxygen because hydroxide ions are preferentially discharged due to their higher concentrations.

Reaction at the Cathode

$$2M^{+}_{(aq)} + 2e^{-} \longrightarrow 2M_{(s)}$$

$$2H^{+}_{(g)} + 2e^{-} \longrightarrow H_{2(g)}$$

or $$2H_2O_{(l)} + 2e^{-} \longrightarrow H_{2(g)} + 2OH^{-}_{(aq)}$$

Reaction at the Anode

$$2X^{-}_{(g)} \longrightarrow X_{2(g)} + 2e^{-}$$

$$4\,OH^{-}_{(aq)} \longrightarrow O_{2\,(g)} + 2H_2O_{(l)} + 4e^{-}$$

Interesting Information!

Electrolysis played a crucial role in the discovery and industrial production of elements like fluorine and aluminum.

Table 16.2 – Electrochemical Series

Stronger reducing agent ↑ / Weaker oxidizing agent ↓

Electrode	Half Reaction	Standard Potential (V)
Lithium	$Li^+ (aq) + e^- \rightleftharpoons Li (s)$	-3.04
Potassium	$K^+ (aq) + e^- \rightleftharpoons K (s)$	-2.93
Calcium	$Ca^{2+} (aq) + 2e^- \rightleftharpoons Ca (s)$	-2.86
Sodium	$Na^+ (aq) + e^- \rightleftharpoons Na (s)$	-2.71
Magnesium	$Mg^{2+} (aq) + 2e^- \rightleftharpoons Mg (s)$	-2.37
Aluminum	$Al^{3+} (aq) + 3e^- \rightleftharpoons Al(s)$	-1.66
Water	$2H_2O (l) + 2 e^- \rightleftharpoons H_2 (g) + 2 OH^- (aq)$	-0.82
Zinc	$Zn^{2+} (aq) + 2e^- \rightleftharpoons Zn (s)$	-0.76
Iron (II)	$Fe^{2+} (aq) + 2e^- \rightleftharpoons Fe (s)$	-0.44
Cadmium	$Cd^{2+} (aq) + 2e^- \rightleftharpoons Cd (s)$	-0.40
Nickel	$Ni^{2+} (aq) + 2e^- \rightleftharpoons Ni (s)$	-0.25
Lead	$Pb^{2+} (aq) + 2e^- \rightleftharpoons Pb (s)$	-0.12
Hydrogen	$2 H^+ (aq) + 2e^- \rightleftharpoons H_2 (g)$	0
Sulfur	$S (aq) + 2H^+ (aq) + 2e^- \rightleftharpoons H_2 S (aq)$	0.14
Tin	$Sn^{4+} (aq) + 2e^- \rightleftharpoons Sn^{2+} (aq)$	0.15
Copper	$Cu^{2+} (aq) + 2e^- \rightleftharpoons Cu (s)$	0.34
Iodine	$I_2 (g) + 2e^- \rightleftharpoons 2I^- (aq)$	0.53
Iron (III)	$Fe^{3+} (aq) + e^- \rightleftharpoons Fe^{2+} (aq)$	0.77
Silver	$Ag^+ (aq) + e^- \rightleftharpoons Ag (s)$	0.79
Bromine	$Br_2 (g) + 2e^- \rightleftharpoons 2Br^- (aq)$	1.06
Chlorine	$Cl_2 (g) + 2 e^- \rightleftharpoons 2Cl^- (aq))$	1.35
Gold	$Au^+ (aq) + e^- \rightleftharpoons Au (s)$	1.69
Hydrogen peroxide	$H_2O_2 (aq) + 2H^+ (aq) + 2 e^- \rightleftharpoons 2H_2 O(l)$	1.77
Fluorine	$F_2 (g) + 2e^- \rightleftharpoons 2F^- (aq)$	2.87

Weaker reducing agent ↓ / Stronger oxidizing agent ↓

16.9 Electrolysis of Concentrated Aqueous Solutions of Metal Halides

If the concentrated aqueous solutions of metal halides are electrolyzed the hydrogen ions are discharged at the cathode if the metal is present higher than hydrogen in electrochemical series. For example, electrolysis of concentrated aqueous solution of sodium chloride will produce hydrogen gas at the cathode. However, for less reactive metals like

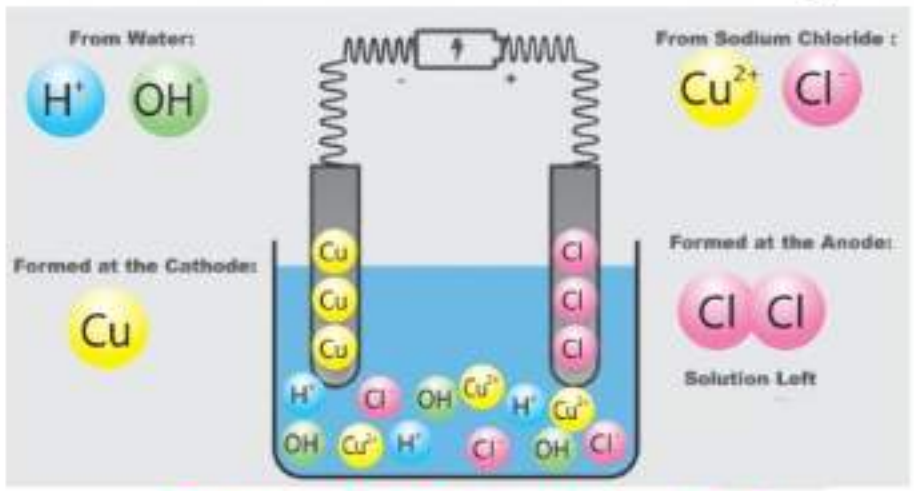


Figure 16.5: Electrolysis of concentrated solution of copper chloride

copper and silver the metal ions are discharged at the cathode.

At the anode, the halide ions are preferentially discharged due to their higher concentration.

Reaction at the Cathode

$$2M^{+}_{(aq)} + 2e^{-} \longrightarrow 2M_{(s)}$$
$$2H^{+} + 2e^{-} \longrightarrow H_2$$

Reaction at the Anode

$$2X^{-} \longrightarrow X_{2\,(g)} + 2e^{-}$$

16.10 Electrolysis of Molten Lead (II) Chloride

Lead (II) chloride is solid at room temperature. To make it an electrolyte it must be heated upto 501 °C to get molten lead chloride. Heat will render ions free to move and conduct electricity. The molten lead is then taken in a heated crucible where its temperature is maintained above 500 °C.

Two inert electrodes (graphite or platinum) are then immersed in it. Upon electrolysis the lead (II) ions will move towards the cathode where thy are discharged forming lead in the liquid state. The chloride ions migrate towards the anode where they lose electrons to give chlorine gas. The electrolysis must be carried out at the temperature above the melting point of lead chloride.

Reaction at the Cathode

$$Pb^{2+}_{(l)} + 2e^{-} \longrightarrow Pb_{(l)} \quad \text{(Reduction)}$$

Reaction at the Anode

$$2Cl^{-}_{(l)} \longrightarrow Cl_{2(g)} + 2e^{-} \quad \text{(Oxidation)}$$

Overall Reaction

$$PbCl_{2(l)} \longrightarrow Pb_{(l)} + Cl_{2(g)}$$

16.11 Electrolysis of Dilute solution of Sulphuric Acid using inert electrodes (Carbon or Pt)

Electrolysis of dilute aqueous solution of sulphuric acid produces hydrogen and oxygen gases. In other words this electrolysis involves the decomposition of water. Inert electrodes like platinum or graphite are used for this electrolysis because they did not react with the electrolyte.

In an aqueous solution of dilute sulphuric acid H^{+} and SO_4^{2-} are given by sulphuric acid while the ionization of water forms H^{+} and OH^{-}.

At the cathode, hydrogen ions gain electrons to give hydrogen gas. At the anode both SO_4^{2-} and OH^{-} are attracted but OH^{-} lose electrons to give oxygen

gas. Sulphate ions are not discharged at the anode because they are difficult to be oxidized compared to hydroxide ions. As the electrolysis moves ahead, the concentration of sulphuric acid increases because the water present is being decomposed.

Reaction at the Cathode

$$2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)} \quad \text{(Reduction)}$$

Reaction at the Anode

$$4\,OH^-_{(aq)} \longrightarrow O_{2(g)} + 2H_2O_{(l)} + 4e^- \quad \text{(Oxidation)}$$

16.12 Electrolysis of Dilute Aqueous solution of Copper Sulphate using Inert electrodes or Copper electrodes

The electrolysis of aqueous solution of copper(II) sulphate with inert electrodes result in the decomposition of water and the copper(II) sulphate. Copper metal is deposited at the cathode (inert) and oxygen gas is produced at the anode (inert).

Reaction at the Cathode

$$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)} \quad \text{(Reduction)}$$

Reaction at the Anode

$$4\,OH^-_{(aq)} \longrightarrow O_{2(g)} + 2H_2O_{(l)} + 4e^- \quad \text{(Oxidation)}$$

16.4 Quick Check!

Why carbon electrodes are used in the electrolysis of concentrated solution of NaCl?

Since the concentration of copper ions decreases slowly so the blue colour of the solution fades away with the passage of time.

If copper electrodes are used instead of inert electrodes, the copper metal atoms from the copper anode start going into the solution in the form of copper ions and the electrode mass starts decreasing.

Reaction at the Cathode

$$Cu^{2+}_{(aq)} + 2e \longrightarrow Cu_{(s)} \quad \text{(Reduction)}$$

Reaction at the Anode

$$Cu_{(s)} \longrightarrow Cu^{2+}_{(aq)} + 2e \quad \text{(Oxidation)}$$

16.13 Fuel cells

Fuel cells provide a method in which chemical energy is converted to electrical energy. These cells use gaseous fuels like hydrogen and oxygen to produce electricity. A fuel cell is composed of two hollow tubes which act as

electrodes. They are made of porous compressed carbon saturated with platinum which acts as a catalyst. The electrolyte used in this cell is aqueous potassium hydroxide. At the anode, hydrogen is oxidized to water and at the cathode oxygen is reduced to hydroxide ions.

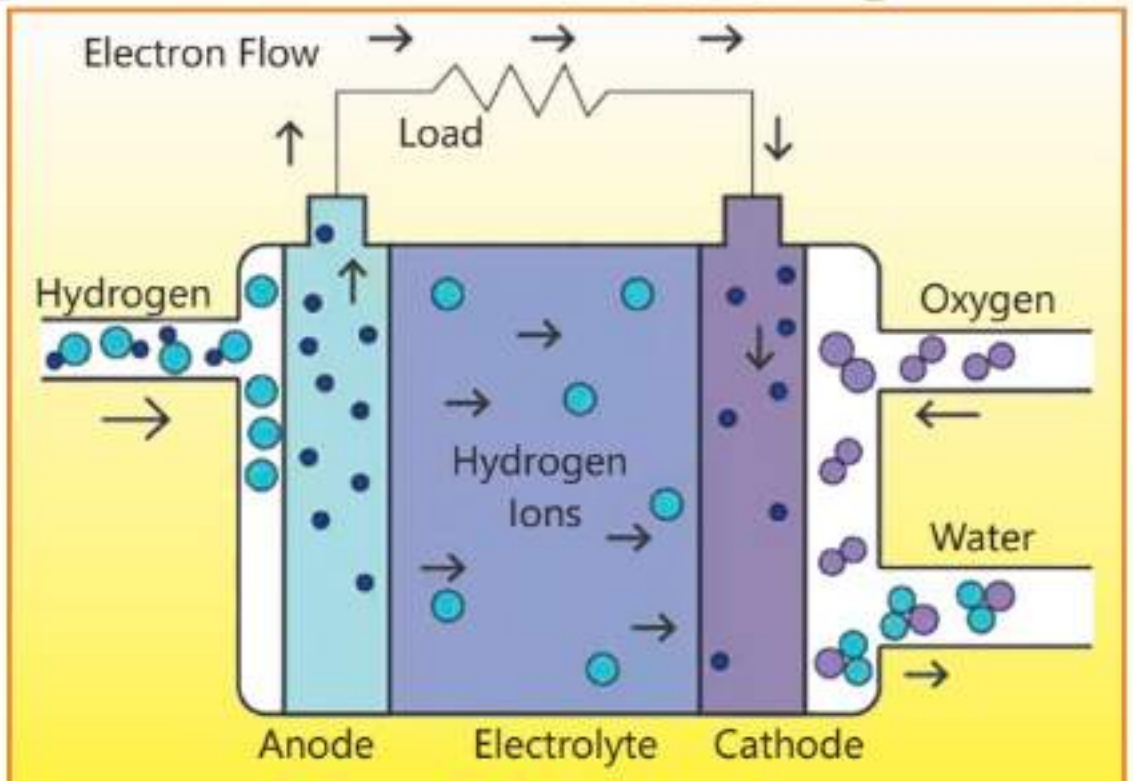


Figure 16.6: Fuel cell

At Anode

$$[H_{2(g)} + 2OH^-_{(aq)} \longrightarrow 2H_2O_{(l)} + 2e^-]2$$

At Cathode

$$O_{2(g)} + 2H_2O_{(l)} + 4e^- \longrightarrow 4OH^-$$

Overall Reaction

$$2H_{2(g)} + O_{2\,(g)} \longrightarrow 2H_2O_{(l)}$$

The fuel cell produces electricity and water continuously provided the reactants are continuously supplied. They are very efficient because they convert 75% of the bond energy of fuels to electricity.

Advantages

1. The hydrogen-oxygen fuel cells have a clear advantage over the traditional fossil fuels, petrol and diesel, used to drive the vehicles. They produce zero emission of carbon dioxide because water is the only product. Fossil fuels, on the other hand, produce carbon dioxide, nitrogen oxides and sulphur oxides which are very harmful to the environment.
2. Fuel cells can convert a large proportion of chemical energy present in fuels into electrical energy as compared to the energy conversion of the fossil fuels. In other words, they are more efficient.
3. Fuel cells produce less noise pollution.
4. Hydrogen used in fuel cells can be obtained from renewable sources like solar or wind power. This fact renders fuel cells more sustainable.

Disadvantages

1. Fuel cells at present, are very expensive because the production of hydrogen by electrolysis of water incurs high cost.
2. Hydrogen being highly inflammable requires very special storage and transportation facilities which further increases the cost of fuel cells.
3. Fuel cells and electric motors are less durable than petrol and diesel engines so they are not so long lasting.

16.5 Quick Check!

Which other electrolyte can be used in hydrogen-oxygen fuel cell?

16.14 Corrosion

Corrosion is a natural process due to which a metal suffers gradual decay when it interacts chemically with its environment. During this interaction the surface of metal is coated with compounds such as oxides, sulphides and carbonates.

A common example is rusting of iron, where iron reacts with oxygen and water present in the atmosphere to form hydrated iron (III) oxide. Once iron begins to rust, the process will continue as rust is porous and allows both air and moisture to come into contact with fresh metal underneath. Hence, all the metal will corrode given enough time.

The process of corrosion of iron appears to require two important chemicals, oxygen and water, which are involved in the following electrochemical reactions. Iron loses electrons to form Fe (II) ions.

$$2Fe_{(s)} \longrightarrow 2Fe^{2+}_{(aq)} + 4e^-$$

Oxygen gains these electrons in the presence of water to form hydroxide ions.

$$O_{2(g)} + 2H_2O_{(aq)} + 4e^- \longrightarrow 4OH^-_{(aq)}$$

Fe^{2+} then react with more oxygen and water to form iron (III) hydroxide which is rust.

$$Fe^{2+}_{(aq)} + 2OH^-_{(aq)} \longrightarrow Fe(OH)_{2(s)}$$

$$4Fe(OH)_{2(s)} + O_{2(g)} + 2H_2O_{(l)} \longrightarrow 4Fe(OH)_{3(s)}$$

Prevention of Corrosion

Coating of the metal surface

Corrosion can be avoided by coating the metal surface with some barriers that prevent the contact of metal surface with the atmosphere. For this purpose, the metal surfaces are protected by either greasing with oil or painting. Other methods of protection are galvanizing, electroplating and sacrificial protection.

Galvanization

Galvanization is a common method to protect iron or steel from rusting. It involves the dipping of an iron sheet in a bath of molten zinc. A layer of zinc metal gets deposited on the iron sheet and prevents rusting. Tin cans are actually steel cans which have been coated with a thin layer of tin.

Sacrificial Protection

In sacrificial protection a more reactive metal like zinc or magnesium is used which will corrode in place of the less reactive metal like iron. Magnesium is often employed to protect steel in buried fuel tanks and pipe lines and ship hulls submerged in sea water.

16.6 Quick Check!

1. What conditions are required for rusting of iron.
2. If a sample of iron and a sample of zinc come into contact, which will corrode? Explain your answer.

The difference in the activity of the two metals (Mg and Fe) causes a current to flow between them, producing corrosion on the more active metal protecting the less active metal iron.

16.15 Electroplating

It is a process in which a metal is deposited on another metal electrolytically.

There are three main objectives of electroplating.

1. Decoration

To deposit the noble metals like gold and silver on the inexpensive metals to enhance their beauty.

2. Protection

To protect the metals from rusting as well as from the reaction of organic acids.

3. Repair

To weld the broken parts of the machinery by electrodeposition of metals. Generally copper, silver, chromium, nickel and gold are electroplated.

Procedure of Electroplating

The article to be electroplated is first cleaned with sand and then washed with caustic soda solution and finally with plenty of water. This article is then, made a cathode, while the metal to be deposited is made anode. The electrolyte is a salt of the metal being deposited and the electroplating is carried out in a tank made of cement, glass or wood. It is called an electrolytic tank.

This process of electroplating is shown in Figure16.7.

The electrolyte chosen should have the following properties:

1. very soluble in water
2. good conductor
3. not easily oxidized or reduced or hydrolyzed
4. inexpensive

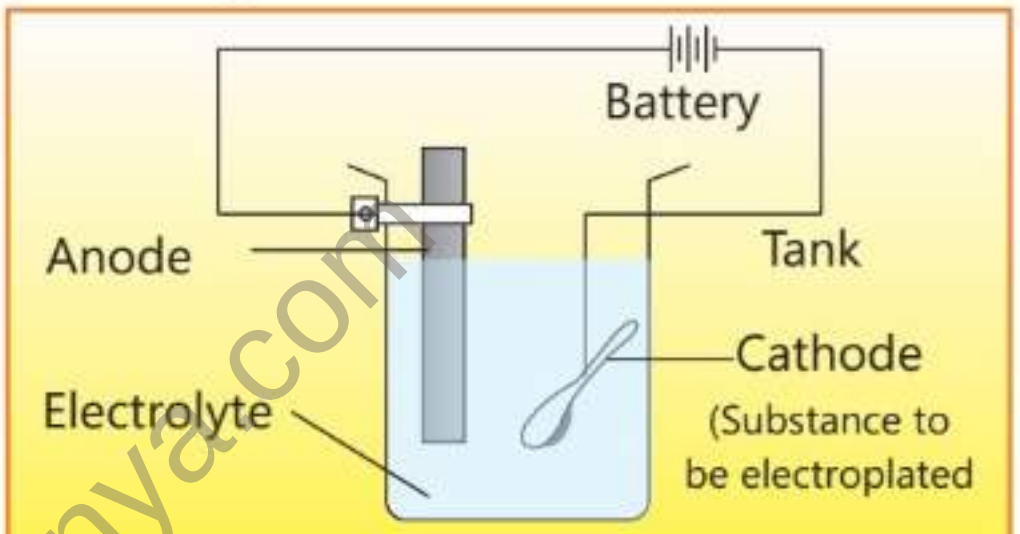


Figure 16.7 : Electroplating

Electrodes are dipped in the electrolytic tank containing the electrolyte and electric current is passed. A thin layer of the noble metal is deposited on the article to be electroplated. The following conditions should be fulfilled to get good deposits.

i. High current density
ii. Low temperature
iii. Higher concentration of the metal in its electrolyte

THINGS TO KNOW

A group of chemically unreactive and valuable metals are called noble metals. They include gold, silver and platinum.

Silver Plating

The procedure for silver plating is the same as described in the previous topic except that the electrolyte used is the solution of potassium argento cyanide, $K[Ag(CN)_2]$, and anode is of pure silver. The following ions are formed in the electrolytic solution.

$$K[Ag(CN)_2]_{(aq)} \rightleftharpoons K^+_{(aq)} + [Ag(CN)_2]^-_{(aq)}$$

$$[Ag(CN)_2]^-_{(aq)} \rightleftharpoons Ag^+_{(aq)} + 2CN^-_{(aq)}$$

When the electric current is passed, Ag^+ ions migrate towards the cathode and deposit after picking up electrons. Cyanide ions move towards the anode, where they react with silver to form AgCN, which combines with KCN to reproduce the electrolyte, $K[Ag(CN)_2]$.

Copper Plating

In copper plating, the anode is made of copper metal and the electrolyte is $CuSO_4$ to which a few drops of sulphuric acid are added to prevent its hydrolysis. The article to be electroplated is made the cathode. The following electrolytic reactions take place, at the electrodes.

At Anode:

$$Cu_{(s)} \longrightarrow Cu^{2+}_{(aq)} + 2e^-$$

At cathode:

$$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$$

Interesting Information!

Chromium plating is usually done on iron or on steel. As chromium metal does not directly adhere to the iron properly, therefore, iron is first copper or nickel plated.

16.7 Quick Check!

1. What is the principle behind electroplating?
2. How electroplating is used to repair worn-out areas of metal objects?

16.16 Galvanic Cells

As described earlier, the oxidation-reduction reactions take place at the electrodes when fused ionic compounds or the aqueous solutions of ionic compounds are electrolyzed. The reverse process may also occur. In other words, oxidation-reduction reactions can be used to produce electricity. This can be understood with a very simple process. Take a plate of zinc metal and dip it in an aqueous solution of copper sulphate. After some time, a pink layer of copper metal will appear on the zinc plate and the blue colour of the solution will become lighter. If the quantity of zinc is enough and sufficient time is allowed, the solution will become colourless. In this process, electrons are transferred from zinc to copper ions. Every copper ion gets two electrons from zinc atom to get deposited as a metallic copper atom. A zinc atom goes into the aqueous solution as Zn^{2+}. The reaction can be shown as follows.

$$Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$$

In other words, zinc is oxidized to $Zn^{2+}_{(aq)}$ while $Cu^{2+}_{(aq)}$ is reduced to copper

metal. This reaction can be made a basis for producing electric current in a galvanic cell which is named as Daniel cell.

Daniel cell uses oxidation-reduction reactions to produce electric current. In the above mentioned process, the oxidation-reduction reactions are taking place directly on the zinc electrode, so electricity can not be generated. However, if oxidation-reduction reactions are carried out in separate compartments, electricity can be generated. Such an arrangement is shown in Figure 16.8.

In this type of galvanic cell, a zinc plate is dipped in zinc sulphate solution while a copper plate is dipped in copper sulphate solution. The two solutions are kept separate by a porous partition through which ions can pass but the solutions cannot. The two electrodes are connected by a wire through a galvanometer which measures the electric current.

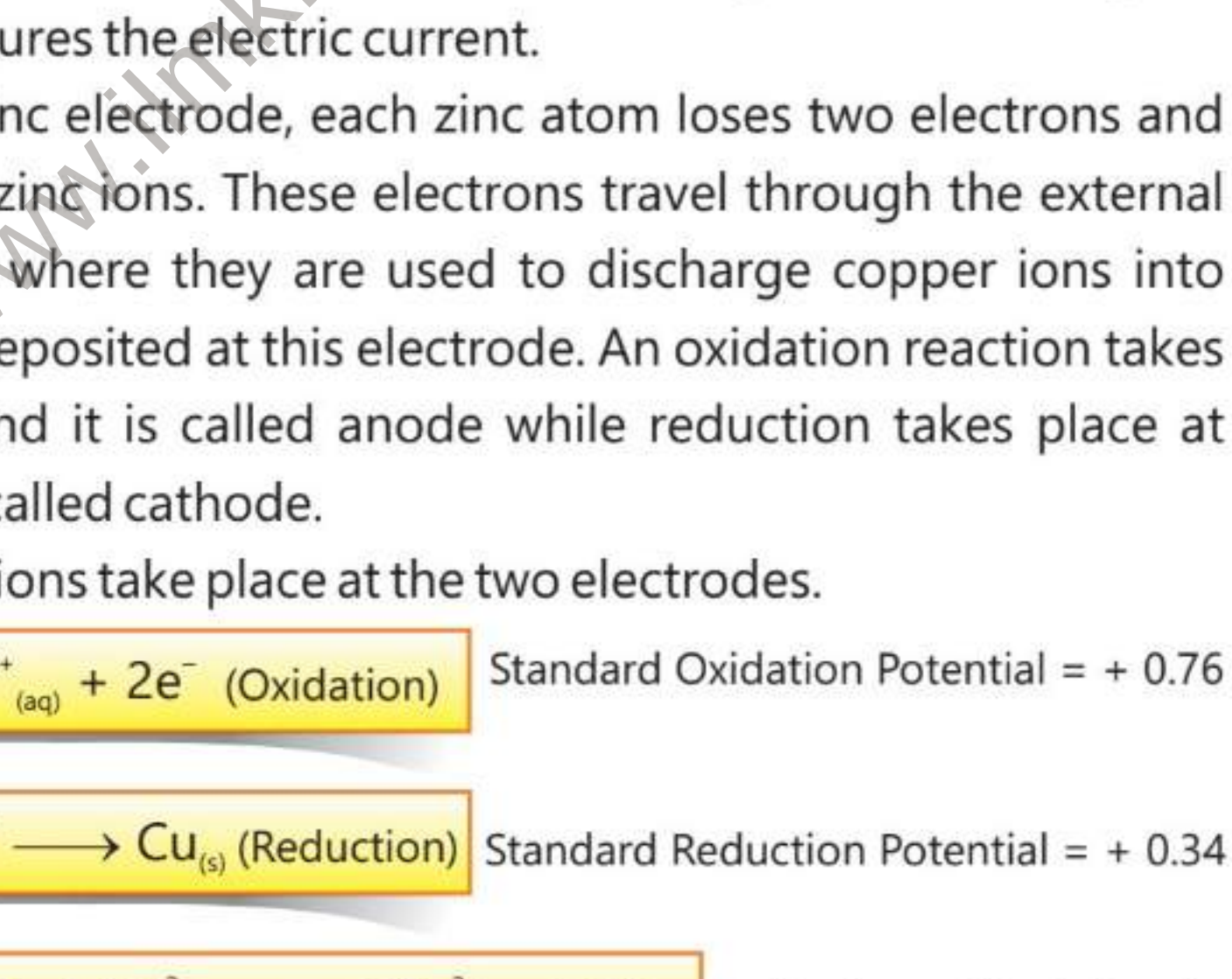


Figure 16.8: Daniel cell

At the surface of zinc electrode, each zinc atom loses two electrons and goes into the solution as zinc ions. These electrons travel through the external wire to copper electrode where they are used to discharge copper ions into copper atoms which are deposited at this electrode. An oxidation reaction takes place at zinc electrode and it is called anode while reduction takes place at copper electrode and it is called cathode.

The following reactions take place at the two electrodes.

At anode: $Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$ (Oxidation) Standard Oxidation Potential = + 0.76

At cathode: $Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$ (Reduction) Standard Reduction Potential = + 0.34

Overall cell reaction: $Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$ Cell voltage E^o = 1.10 volts

Both parts of the cell are called half cells. No reaction can take place in any

isolated half cell. Both the reactions take place simultaneously at both half cells. In this cell, electrons travel in the external circuit while ions travel through the porous partition in the internal circuit. Daniel cell produces a voltage of around 1.10 volts under standard conditions.

16.8 Quick Check!

1. Compare an electrolytic and a galvanic cell.
2. Write down the reactions which occur in a Zn-Mg galvanic cell.

16.17 Order of Reactivity of Metals using Voltage Data

The reactivity of metals can be found out by using voltage data obtained from galvanic cells. According to the available data the reactivity of metals depends upon how readily it is oxidized or lose electrons to form positive ions. If a galvanic cell is established between two metals, the more reactive metal will lose electrons and from positive ions. The voltage generated by this cell measures the comparative tendencies of the metals to lose electrons. A higher voltage indicates that the difference in the tendency of one metal (more reactive metal) to lose electron is far more than the other.

If a cell is established between magnesium and copper it produces a higher voltage than a cell established between iron and copper. This will mean that magnesium is more reactive than iron because it has a tendency to lose electrons more easily.

By measuring the voltage produced when different metal pairs are used in a voltaic cell, it is possible to determine the reactivity series of metals which is called electrochemical series. Metals placed higher in this series are considered more reactive and easily lose electrons than the metals placed lower in the series.

EXERCISE

A Multiple Choice Questions

Choose and tick the correct answer from the given choices.

1. The oxidation number of Mn in K_2MnO_4:

   (a) +7 (b) +5 (c) +6 (d) -6

2. Which element in the following reaction is being reduced?

   $$4HBr_{(aq)} + MnO_{2\ (s)} \longrightarrow MnBr_{2\ (aq)} + Br_{2\ (g)} + 2H_2O_{(l)}$$

   (a) Br (b) Mn (c) H (d) Both Mn and H

3. During electrolysis of dilute solution of H_2SO_4, using Pt electrodes, which process takes place at the cathode?
   (a) Reduction
   (b) Neither oxidation nor reduction
   (b) Oxidation
   (d) First oxidation and then reduction
4. Which product you will get at the anode when an aqueous solution of $CuSO_4$ is electrolysed using copper electrodes?
   (a) Cu
   (b) O_2
   (c) H_2
   (d) No product, instead copper metal will go into the solution as Cu^{2+}.
5. Which of the following statements is NOT correct about Zn-Cu electrochemical cell?
   (a) Anode is negatively charged
   (b) Reduction occurs at anode
   (c) Cathode is positively charged
   (d) Reduction occurs at cathode
6. Which product will be obtained at the anode when a concentrated solution of NaCl will be electrolysed?
   (a) Cl_2 (b) O_2
   (c) More O_2 and less Cl_2 (d) More Cl_2 and less O_2
7. When a dilute aqueous solution of $ZnCl_2$ is electrolysed which product you will get at the cathode?
   (a) H_2 (b) Zn (c) O_2 (d) Zn and O_2
8. What is produced at the cathode in hydrogen-oxygen fuel cell?
   (a) H^+ (b) O^{2-} (c) H_2O (d) OH^{1-}
9. Which of the following metals is highest in the electrochemical series?
   (a) Tin (b) Iron (c) Magnesium (d) Zinc

B Short Answer Questions

16.1 What happens when electricity is passed through an aqueous solution of NaCl?

16.2 What are the main objectives of electroplating?

16.3 Mention one difference between an electrolytic cell and a galvanic cell.

16.4 Through which electrode, electrons leave the electrolytic cell?

16.5 How does an electrolyte conduct electricity?

16.6 What will happen if a strip of Cu metal is dipped in $FeSO_4$ solution?

16.7 Why fuel cells are regarded as environment friendly?

C Constructed Response Questions

16.1 Calculate the oxidation number of chlorine atom in $Ca(ClO_3)_2$.

16.2 How can H_2O_2 behave as an oxidizing agent?

16.3 Why different products are formed at the electrodes when a dilute and concentrated aqueous solutions of NaCl are electrolysed?

16.4 Why corrosion becomes fast during rainy season?

16.5 If a galvanic cell is established between Cu and Ag, what reactions do you expect at the electrodes?

16.6 What is the function of a porous partition in a galvanic cell?

16.7 How do fuel cells produce electricity?

16.8 How can the chemical reactivity of metals be compared by using electrochemical series?

D Descriptive Questions

16.1 Explain with examples how the formula of ionic compound can be written using oxidation numbers.

16.2 Find the oxidation numbers of the indicated elements in the following compounds.

$Al(\overline{N}O_3)_3$, $H_2\overline{S}_2O_7$, $Na_2\overline{S}_2O_3$

16.3 Write down the formulae of the following compounds using ionic charges.

Sodium hypochlorite, calcium oxalate, ammonium phosphate and calcium nitrite

16.4 Describe the working of a fuel cell.

16.5 Discuss the electrolysis of concentrated solutions of metal halides.

16.6 Explain electroplating giving examples.

16.7 What is corrosion? Explain the reactions involved in corrosion of iron.