10 ELECTROCHEMISTRY

Student Learning Outcomes [C-11-A-56 to C-11-B-78]

After studying this chapter, students will be able to:

- Define the terms redox, oxidation, reduction, and disproportionation (in terms of electron transfer and changes in oxidation number). **(Knowledge)**
- Apply the concept of oxidation numbers in identifying oxidation and reduction reactions. **(Application)**
- Identify the oxidizing and reducing agents in a redox reaction. **(Knowledge)**
- Describe the role of oxidizing and reducing agents in the redox reaction. **(Understanding)**
- Apply the concept of changes in oxidation numbers to balance chemical equations. **(Application)**
- Explain how electrolytic cells convert the electrical energy into chemical energy, with oxidation at the anode and reduction at the cathode. **(Understanding)**
- Predict the identities of substances liberated during electrolysis based on the state of the electrolyte, position in the redox series, and concentration. **(Knowledge)**
- Apply the relationship between the Faraday constant, Avogadro constant, and the charge on the electron to solve problems. **(Application)**
- Calculate the quantity of charge passed during electrolysis and the mass or volume of substance liberated during electrolysis. **(Application)**
- Deduce the Avogadro constant by an electrolytic method. **(Application)**
- Define the terms standard electrode potential and standard cell potential. **(Knowledge)**
- Describe the standard hydrogen electrode (SHE) and the methods used to measure the standard electrode potentials. **(Understanding)**
- Calculate the standard cell potentials by combining the potentials of two standard electrodes and then use these to predict the feasibility of a reaction and the direction of electron flow in a simple cell. **(Application)**
- Deduce the relative reactivity of elements compounds, and ions as oxidizing agents or reducing agents from their electrode potential values. **(Application)**
- Construct redox equations using relevant half- equations. **(Application)**
- Explain how voltaic (galvanic) cells convert energy from spontaneous, exothermic chemical processes to the electrical energy, with oxidation at the anode and reduction at the cathode. **(Understanding)**
- Explain how voltaic cells convert the chemical energy from redox reactions to the electrical energy using Cu-Zn galvanic cell as an example. **(Understanding)**
- Explain how electrode potentials vary with the concentrations of aqueous ions and use the Nernst equation to predict this quantitatively. **(Understanding)**

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- Explain the concept of the activity series of metals and how it relates to the ease of oxidation. **(Understanding)**
- Deduce the feasibility of redox reactions from activity series or reaction data. **(Understanding)**
- Explain the merits of photovoltaic cells as sustainable ways of meeting energy demands by making reference to the photovoltaic principle. **(Understanding)**
- Explain the use of the Winkler Method to measure biochemical oxygen demand (BOD) and its use as a measure of water pollution. **(Understanding)**

The branch of chemistry which deals with the interconversion of electrical and chemical energy is called electrochemistry.

10.1 OXIDATION, REDUCTION, AND REDOX REACTIONS

Oxidation is a process involving loss of electron or electrons.

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

$$Zn^{\circ} \rightarrow Zn^{+2} + e^{-}$$

Here Fe^{+2} and Zn^{0} have lost electrons, therefore they are oxidized.

Reduction is a process involving gain of electron or electrons.

$$Cl^{0} + e^{-} \rightarrow Cl^{-1}$$

$$Cu^{+2} + 2e^{-} \rightarrow Cu^{0}$$

In these examples, Cl^{0} and Cu^{2+} have gained electrons; therefore, they are reduced.

Oxidation and reduction always take place together. The reactions in which this happens are called **redox reactions**.

Interesting Information

Photosynthesis is a redox reaction which provides food for the entire planet, and another one is respiration that keeps us alive, both are redox reactions.

There are two ways of finding out whether a substance has been oxidized or reduced during a chemical reaction:

- Electron transfer
- Changes in oxidation number

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10.2 OXIDATION NUMBER AND ITS SIGNIFICANCE

The oxidation number are also called oxidation state. An oxidation number is a number given to each atom or ion in a compound that shows us its degree of oxidation. It is the apparent charge on an atom (per atom) of an element in a molecule or an ion. Oxidation number can be positive, negative or zero. The + or – sign must always be included. Higher positive oxidation number means that an atom or ion is more oxidized. Higher negative oxidation number means that an atom or ion is more reduced.

10.2.1 Oxidation Number Rules

The oxidation number of any atom or ion can be deduced by using oxidation number rules. It is important to note that an oxidation number refers to a single atom in a compound, molecule or ion.

i. The oxidation number of any uncombined element is zero. For example, the oxidation number of each atom in S_8, H_2, Cl_2, Na, Mg and Zn is zero.

ii. In either a compound or an ion, the more electronegative element is given the negative oxidation number. In HF, fluorine has -1 oxidation number.

iii. In compounds, many atoms or ions have fixed oxidation numbers, group 1 alkali metals are always +1, group 2 alkaline earth elements are always +2, group 3 elements +3, group 17 halogens in binary compounds are always –1, hydrogen is +1 (except in metal hydrides, such as NaH, where it is –1), oxygen is –2 (except in peroxides, where it is –1, and in F_2O, where it is +2).

iv. The oxidation number of an element in a mono-atomic ion is always the same as the charge on the ion, for example, Cl^- is –1, Al^{3+} is +3.

v. In compounds, the algebraic sum of the oxidation numbers of all the elements is zero. For example HCl and NaCl.

vi. In polyatomic ions, the algebraic sum of oxidation number equals the charge on the ion. For example, NH_4^+, CO_3^{-2} and SO_4^{-2}.

vii. For transition metals and many non-metals, Ox. No. cannot be fixed as they show variable Ox. states. Therefore, there Ox. Nos. are always determined by calculations.

While applying the oxidation number rules in the following examples, 'Ox. No.' as an abbreviation for oxidation number is used.

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Keep in Mind!

- Hydrogen shows -1 oxidation state with all metals.
- Hydrogen shows +1 oxidation state with all non-metals.
- Oxygen shows negative oxidation state with all metals.
- Oxygen shows negative oxidation state with all non-metals except fluorine
- Oxygen shows -2, -1 and -1/2 in H_2O, Na_2O_2, and KO_2 respectively.

10.2.2 Finding Oxidation Number of an Element in a Compound or a Radical

The oxidation number or state of any atom of an element present in a compound or a radical can be determined by making use of the above-mentioned rules.

Compounds of a metal with a non-metal

A metal always has the positive Ox. No. and nonmetals have the negative Ox. state

For example, in sodium sulfide, $Na_2\underline{S}$:

$$2(+1) + S = 0$$

$$S = -2$$

Compounds of a non-metal with a non-metal

In compounds containing two different non-metals, the sign of the Ox. No. depends on the electronegativity of each atom. The most electronegative element is given the negative sign.

Sample Problem 10.1

Find the oxidation No. of S in Sulfur dioxide, SO_2.

$$S + 2(-2) = 0$$

$$S = +4$$

$$\text{Ox. No. of S} = +4$$

Compound ions

Compound ions are ions with two or more different atoms. Examples are the sulfate ion, SO_4^{2-}, and the nitrate ion, NO_3^-.

Sample Problem 10.2

Calculate the oxidation number (Ox. No.) of sulphur in SO_4^{2-}.

Solution

$$[\text{Ox. No. of S}] + 4\,[\text{Ox. No. of O}] = -2$$

$$S + 4\,(-2) = -2$$

$$S = +6$$

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Thus, the oxidation number of sulphur in SO_4^{2-} is +6.

Quick Check 10.1

a) Define oxidation and reduction in terms of electron transfer with examples.

b) Define oxidation and reduction in terms of change in oxidation number with examples.

c) Determine Ox. No. of:

i) Oxygen (N) in Na_2O

ii) Iodine (I) in ICl_3

iii) Nitrogen (N) in NO_3^{1-}

iv) Chromium (Cr) in $K_2Cr_2O_7$

v) Manganese (Mn) in KMnO4.

10.3 DISPROPORTIONATION REACTION

A disproportionation reaction is a chemical reaction where a single substance acts as both the oxidizing and reducing agent, resulting in two different products with different oxidation states. This type of reaction involves the simultaneous oxidation and reduction of the same element.

For example, the decomposition of hydrogen peroxide (H_2O_2) to form water (H_2O) and oxygen (O_2) is a disproportionation reaction:

$$2H_2O_{2(\ell)} \longrightarrow 2H_2O_{(\ell)} + O_{2(g)}$$

Oxidation number of oxygen in H_2O_2 = -1

Oxidation number of oxygen in H_2O = -2 (Oxygen is reduced from -1 to -2)

Oxidation number of oxygen in O_2 = 0 (Oxygen is oxidized from -1 to 0)

Similarly

$$6NaOH_{(aq)} + 3Cl_2^0(g) \rightarrow 5NaCl^{-1}_{(aq)} + NaCl^{+5}O_{3(aq)} + 3H_2O$$

Oxidation number of chlorine atoms in Cl_2 = 0

Oxidation number of chlorine in NaCl = –1 (Cl is reduced from 0 to -1)

Oxidation number of chlorine in $NaClO_3$ = +5 (Cl is oxidized from 0 to +5)

10.4 OXIDIZING AGENT (OXIDANT) AND REDUCING AGENT (REDUCTANT)

An **oxidizing agent** (atom, ion or molecule) is that substance which oxidizes some other substance, and is itself reduced to a lower oxidation state by gaining one or more electrons, while, a **reducing agent** (atom, ion or molecule) is that substance which reduces some other substance, and is itself oxidized to a higher oxidation state by losing one or more electrons.

If an element X gains one or more electrons and is converted into X^- anion, the element X is said to be acting as an oxidizing agent, since it withdraws an electron from the other atom, in this process oxidation number of X has decreased that is:

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For oxidizing agent $X + e^- \longrightarrow X^-$

[Ox. No.= 0] [Ox. No. = -1]

(Higher Oxidation State) (Lower Oxidation State)

For example, $Cl + e^- \longrightarrow Cl^-$

On other hand, if an element M loses one electron and is converted to M^+ cation, the element M is said to be acting as a reducing agent, since it is providing electrons, it gets higher oxidation state. Thus,

For reducing agent $M \longrightarrow M^+ + e^-$

[Ox. No. = 0] [Ox. No. = +1]

(Lower Ox. No.) (Higher Ox. No.)

For example, $Na \longrightarrow Na^+ + e^-$

Quick Check 10.2

a) Identify the oxidized species and reduced species in the following equations. Also identify the oxidizing and reducing agents on the reactant side.

i. $Fe_2O_{3(s)} + CO_{(g)} \rightarrow Fe_{(s)} + CO_{2(g)}$ ii. $CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(\ell)}$

b) Identify the species in the following reaction which undergoes both oxidation and reduction.

i. $2Na_2O_{2(s)} + 2H_2O_{(\ell)} \rightarrow 4NaOH_{(aq)} + O_{2(g)}$

ii. $P_{4(s)} + 3OH^-_{(aq)} + 3H_2O_{(\ell)} \rightarrow PH_{3(g)} + 3H_2PO_2^-{}_{(aq)}$

10.5 BALANCING OF REDOX EQUATIONS BY OXIDATION NUMBER METHOD

Carry out the following steps for balancing of redox equations by oxidation number method:

i. Write down the skeleton equation of the redox reaction under consideration.

ii. Identify the elements, which undergo a change in their oxidation number during the reaction.

iii. Record the oxidation number above the symbols of the element, which have undergone a change in the oxidation number.

iv. Indicate the change in oxidation number by arrows joining the atoms on both sides of the equation. It shows number of electrons gained or lost.

v. Equate the increase or decrease in the oxidation number, i.e., electrons gained or lost by multiplying with a suitable digit.

vi. Balance the rest of the equation by inspection (hit and trial) method.

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Keep in Mind!

a) If an element in a species undergoes only increase in oxidation number or decrease in oxidation number in a reaction. The specie containing such element is written once on the RHS of the equation.

$$Zn_{(s)} + HCl_{(aq)} \longrightarrow ZnCl_{2(aq)} + H_{2(g)}$$

b) If an element in a species undergoes both increase in oxidation number or decrease in oxidation number simultaneously in a reaction (as in case of self-redox or disproportionation reaction). The specie containing such element is written twice on the RHS of the equation. First for increase in oxidation number while second is written for decrease in oxidation number.

$$Cl_2 + NaOH + Cl_2 \longrightarrow NaCl + H_2O + NaOCl$$

c) If an element in a species undergoes increase or decrease in oxidation number as well as no change in oxidation number in a reaction. The specie containing such element is also written twice. First, for change in oxidation number while second is for no change in oxidation number.

$$HNO_3 + Cu + HNO_3 \longrightarrow Cu(NO_3)_2 + H_2O + NO_2$$

$$HCl + K_2Cr_2O_7 + HCl \longrightarrow Cl_2 + KCl + CrCl_3 + H_2O$$

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Sample Problem 10.4

Balance the following equation by oxidation number method.

$$K_2Cr_2O_7 + HCl \rightarrow KCl + CrCl_3 + Cl_2 + H_2O$$

Solution:

1. Write down the oxidation number of each element.

$$K^{1+}{}_2Cr^{6+}{}_2O^{2-}{}_7 + H^{1+}Cl^{1-} \rightarrow Cl^0{}_2 + K^{1+}Cl^{1-} + Cr^{3+}Cl^{1-}{}_3 + H^{1+}{}_2O^{2-}$$

2. Identify the elements that show change in oxidation number on both sides.

$$K_2^{1+}\ Cr_2^{6+}\ O_7^{2-} + H^{1+}Cl^{1-} \rightarrow Cl_2^0 + K^{1+}Cl^{1-} + Cr^{3+}Cl_3^{1-} + H_2^{1+}O^{2-} \text{ ..... (i)}$$

$6e^-$

$2e^-$

Here, Cr undergoes a change in oxidation state from +6 to +3 and it is reduced (acts as an oxidizing agent) while $CrCl_3$ undergoes a change in oxidation state from -1 to 0 and it is oxidized (acts as a reducing agent).

3. Multiply Cl_2 with 3 and Cr with 2 to balance the loss and gain of electrons.

$$K_2Cr_2O_7 + HCl \rightarrow 3Cl_2 + KCl + 2CrCl_3 + H_2O$$

4. Balance the remaining equation by inspection method.

   i) Balance K on both sides by multiplying KCl by 2.

$$K_2Cr_2O_7 + HCl \rightarrow 3Cl_2 + 2KCl + 2CrCl_3 + H_2O$$

ii) To balance Cl atoms, multiply HCl with 14.

$$K_2Cr_2O_7 + 14HCl \rightarrow 3Cl_2 + 2KCl + 2CrCl_3 + H_2O$$

iii) To balance oxygen, multiply H_2O by 7.

$$K_2Cr_2O_7 + 14HCl \rightarrow 3Cl_2 + 2KCl + 2CrCl_3 + H_2O$$

Did you know?

Sequence of the balancing the chemical equation using inspection (hit and trial) method. Firstly, balance atoms of all elements except nitrogen, oxygen and hydrogen. Secondly, balance atoms of nitrogen (if in the equation).

Thirdly, balance atoms of oxygen (if in the equation).

Lastly, balance atoms of hydrogen (if in the equation).

Quick Check 10.3

Balance the given equations by oxidation number method.

i. $Fe_2O_{3(s)} + CO_{(g)} \rightarrow Fe_{(s)} + CO_{2(g)}$

ii. $MnO_{2(s)} + HCl_{(aq)} \rightarrow MnCl_{2(aq)} + H_2O_{(l)} + Cl_{2(g)}$

iii. $Fe^{2+}_{(aq)} + MnO^{4-}_{(aq)} \rightarrow Fe^{3+}_{(aq)} + Mn^{2+}_{(aq)}$

iv. $K_2Cr_2O_{7\,(aq)} + FeSO_{4\,(aq)} + H_2SO_{4\,(aq)} \rightarrow Cr_2(SO_4)_{3\,(aq)} + Fe_2(SO_4)_{3(aq)} + K_2SO_{4(aq)} + H_2O_{(l)}$

10.6 ELECTROLYTIC CELL

An electrolytic cell is a device that converts electrical energy into chemical energy through a process called **electrolysis**. It consists of two electrodes, typically made of metal or another conductive material, which are immersed in an electrolyte.

When a direct electric current is applied, one electrode becomes negatively charged (the cathode) and the other positively charged (the anode).

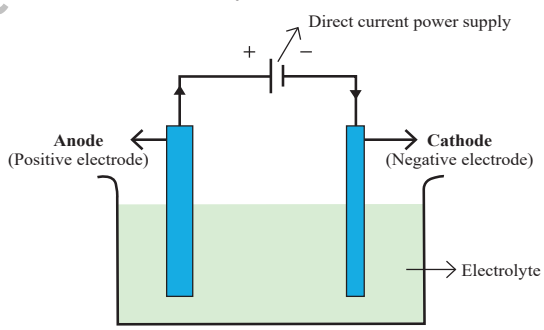

Figure 10.1 Main parts of an electrolytic cell

In an electrolytic cell, positive ions in the electrolyte migrate towards the cathode, where they gain electrons (a reduction process), while negative ions move towards the anode, where they lose electrons (an oxidation process). This movement of ions and transfer of electrons results in chemical changes at the electrodes, effectively converting electrical energy into chemical energy.

Electrolytic cells are used in the electrolysis of sodium chloride to produce sodium metal and chlorine gas, the refining and plating of metals, and the production of chemicals like caustic soda. Electrolysis is generally carried out in an electrolysis cell as shown in **Figure 10.1**.

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- In the electrolysis cell, the electrolyte is the compound that is ionized; it is either a molten ionic compound or a concentrated aqueous solution of ions.
- The electrodes are, made from either carbon (graphite) or metal, which conduct electricity to and from the electrolyte, the anode is the positive electrode, the cathode is the negative electrode.
- The power supply must be direct current.
- The actual structure of the cell will vary according to the element extracted.

10.7 REDOX REACTIONS IN ELECTROLYSIS

During electrolysis, the positive ions (cations) move to the cathode. When they reach the cathode, they gain electrons from the cathode.

For example,

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

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

Gain of electrons is reduction and it always occurs at the cathode. If metal atoms are formed, they may be deposited as a layer of metal on the cathode. Alternatively, they may form a molten layer in the cell. If hydrogen gas is formed, it bubbles off.

The negative ions (anions) move to the anode. When they reach the anode, they lose electrons to the anode. Loss of electrons is oxidation. Oxidation always occurs at the anode.

For example:

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

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

Electrolysis is a redox reaction. For example, when molten zinc chloride ($ZnCl_2$) is electrolyzed, the electrode reactions are:

Cathode: $Zn^{2+}_{(\ell)} + 2e^- \longrightarrow Zn_{(s)}$ (Reduction)

Anode: $2Cl^-_{(\ell)} \longrightarrow Cl_{2(s)} + 2e^-$ (Oxidation)

The electron loss at the anode balances the electron gain at the cathode. The overall reaction is $ZnCl_{2(\ell)} \longrightarrow Zn_{(s)} + Cl_{2(g)}$

Quick Check 10.4

Molten copper (II) bromide ($CuBr_2$) is electrolyzed using inert electrodes.

i. Which ions are present in this solution?
ii. Name the electrode on which the formation of copper metal occurs?
iii. Give the half-equation that represents the formation of copper metal.
iv. Write the half-equation for the formation of bromine on the other electrode.

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10.8 MASS OF A SUBSTANCE DEPOSITED DURING ELECTROLYSIS

The mass of a substance produced at an electrode during electrolysis is proportional to the time over which a constant electric current passes and the strength of the electric current.

Combining current and time, we get the relationship:

$$Q = I \times t$$

Where Q = Charge (in coulombs, C)

I = Current (in amperes, A)

t = Time (in seconds, s)

The mass of a substance produced at (or removed from) an electrode during electrolysis is proportional to the quantity of electricity (in coulombs) which passes through the electrolyte.

The quantity of electricity is often expressed in terms of a unit called the **Faraday** (symbol F). 1 Faraday is the quantity of electric charge carried by 1 mole of electrons or 1 mole of singly charged ions. Its value is 96500 C mol^{-1}.

During the electrolysis of silver nitrate solution, silver is deposited at the cathode.

$$\underset{1\ mol}{Ag^{+}_{(aq)}} + \underset{1\ mol}{e^{-}} \longrightarrow \underset{1\ mol}{Ag_{(s)}}$$

1 Faraday of electricity (96500 C) is required to deposit 1 mole of silver (107.9g). During the electrolysis of copper(II) sulfate solution, copper is deposited at the cathode.

$$\underset{1\ mol}{Cu^{2+}_{(aq)}} + \underset{2\ mol}{2e^{-}} \longrightarrow \underset{1\ mol}{Cu_{(s)}}$$

The equation shows that 2 moles of electrons are needed to produce 1 mole of copper from Cu^{2+} ions. So, it requires 2 Faradays of electricity (2 × 96500 C) to deposit 1 mole of copper (63.5g).

No. of Faraday = No. of moles of electrons gained or lost

10.9 AMOUNT OF SUBSTANCE PRODUCED DURING ELECTROLYSIS

The value of F can be used to calculate the mass of substance deposited at an electrode and the volume of gas produced at an electrode.

Sample Problems 10.5

Calculate the mass of lead (Pb) deposited at the cathode during electrolysis when a current of 1.50 A flows through molten lead(II) bromide ($PbBr_2$) for 20.0 min. (relative atomic mass, *A*r value: [Pb] = 207; F = 96500 C mol^{-1})

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Solution:

Step 1 Write the half-equation for the reaction.

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

Step 2 Find the number of coulombs required to deposit 1 mole of product at the electrode.

2 moles of electrons are required per mole of Pb formed $= 2F$

$= 2 \times 96500$

$= 193000 \text{ C mol}^{-1}$

Step 3 Calculate the charge transferred during the electrolysis.

$Q = I \times t$

$= 1.50 \times 20 \times 60$

$= 1800 \text{ C}$

Step 4 Calculate the mass by simple proportion using the relative atomic mass.

193000 C deposits 1 mole Pb, which is 207 g Pb

so, 1800 C deposits = $1.93 \text{ g Pb} \left(\frac{207}{193000} \times 1800\right)$

10.10 AVOGADRO'S CONSTANT BY THE ELECTROLYTIC METHOD

The Avogadro constant, N_A, is the number of specified particles (atoms, molecules, or ions) in 1 mole. An electrolytic method can be used to find a value for the Avogadro constant by calculating the charge associated with 1 mole of electrons.

$$N_A = \frac{\textbf{Charge on 1 mole of electrons}}{\textbf{Charge on 1 electron}}$$

The charge on the electron can be calculated by experiment. The results show us that the charge on the electron is approximately 1.60×10^{-19} C.

10.10.1 Finding the Charge on 1 Mole of Electrons

The charge on 1 mole of electrons can be found from a simple electrolytic experiment. The apparatus for this is shown in **Figure 10.2**.

The procedure is to weigh the pure copper anode and pure copper cathode separately arrange the apparatus during the electrolysis of aqueous copper(II) sulfate as shown in **Figure 10.2.**

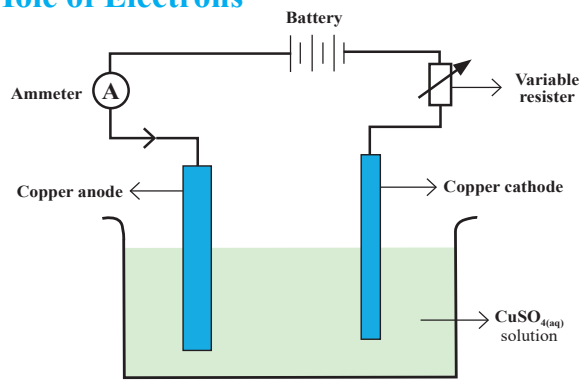

Figure 10.2 Apparatus for calculating the mass of copper deposited

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The variable resistor is used to keep the passing current constant about 0.2 amperes. Pass a constant electric current for a measured time interval, e.g., 40 min. Remove the cathode and anode and wash and dry them with distilled water and then with propanone. Reweigh the cathode and anode.

The cathode increases in mass because copper is deposited. The anode decreases in mass because the copper goes into solution as copper ions. The decrease in the mass of the anode is measured. This is preferred because the copper does not always stick to the cathode very well.

10.10.2 Calculating charge on an electron

A sample calculation is shown below, using a current of 0.20 A for 34 min.

mass of anode at start of the experiment = 56.530 g

mass of anode at end of experiment = 56.394 g

mass of copper removed from anode = 0.136 g

quantity of charge passed Q = I × t

= 0.20 × 34 × 60

= 408 C

As the amount of copper removed is 0.13 g

So, 0.13 g of copper requires = 408 C

1 g of copper requires $= \frac{408}{0.136}$

63.5 g of copper requires $= \frac{408}{0.136} \times 63.5$

= 190500 C

But the equation for the electrolysis shows that 2 moles of electrons are needed to produce 1 mole of copper:

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

The charge on 1 mole of electrons $= \frac{190500}{2} = 95{,}250$ C

If the charge on one electron is 1.60×10^{-19} C,

Charge on an electron $= \frac{95250}{6.2 \times 10^{23}} = 1.58 \times 10^{-19}$ C

This is in good agreement with the accurate value of 6.02×10^{23} mol^{-1}.

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Quick Check 10.5

a) An aqueous solution of silver nitrate is electrolysed. Calculate the mass of silver deposited at the cathode when the electrolysis is carried out for exactly 35 min using a current of 0.18 A. (Ar [Ag] = 108; F = 96 500 C mol^{-1})

b) An electric current of 1.04 A was passed through a solution of dilute sulfuric acid for 6.00 min. The volume of hydrogen produced at STP was 41.5 cm^3.

i. How many coulombs of charge were passed during the experiment?

ii. How many coulombs of charge are required to liberate 1 mole of hydrogen gas? (F = 96 500 C mol^{-1})

10.11 ELECTRODE POTENTIALS

(Ease of oxidation and reduction)

During the redox processes, a redox equilibrium exists between two chemically related species that are in different oxidation states. When a metal is put into a solution of its ions, an electric potential (voltage) is established between the metal and the metal ions in solution. This is called electrode potential and it indicates the ease of oxidation or reduction of a substance. For example, when a copper rod is placed in an aqueous solution of its ions, the following equilibrium exists:

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

There are two opposing reactions in this equilibrium.

a) Metal atoms from the electrode entering the solution as metal ions. This leaves electrons on the electrode.

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

b) Ions in solution accepting electrons from the metal electrode and get deposited as metal atoms on the surface of the electrode.

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

The redox equilibrium is established when the rate of electron gain equals the rate of electron loss.

For unreactive metals such as copper, if this equilibrium is compared with the equilibrium set up by other metals, the equilibrium.

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

$Cu^{2+}_{(aq)}$ ions are therefore relatively easy to reduce. They gain electrons readily to form copper metal.

For reactive metals such as vanadium, the equilibrium lies further over to the left.

$$V^{2+}_{(aq)} + 2e^- \longleftarrow V_{(s)}$$

$V^{2+}_{(aq)}$ ions are therefore relatively difficult to reduce. They gain electrons much less readily by comparison. The position of equilibrium differs for different combinations of metals placed in solutions of their ions.

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10.11.1 Electrical Double Layer

It is thought that the absolute electrode potentials cannot be measured due to the formation of an electrical double layer, when an element is placed in a solution of its ions. For example, when zinc is placed in a solution containing zinc ions, a few number of zinc atoms on the surface of the metal is converted to zinc ions, which go into solution. This leaves an excess of electrons on the surface of the zinc electrode.

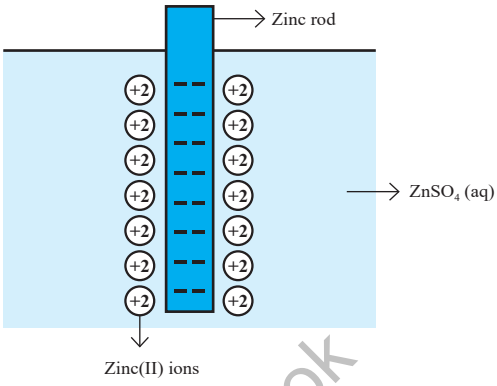

Figure 10.3 Formation of electrical double layer

The solution around the metal now has excess Zn^{2+} ions. Some of these cations near the surface of the zinc are attracted to its surface. So, an electrical double layer is formed. This buildup of charge causes an electric potential (voltage) between the metal and the metal ions in solution as shown in **Figure 10.3**.

Due to the formation an electrical double layer, the potential cannot directly be measured. But the difference in potential between the metal/metal ion system and another system can be measured. We call this value the **electrode potential**, E. Electrode potential is measured in volts. The system we use for comparison is the **standard hydrogen electrode (SHE)**.

10.12 STANDARD HYDROGEN ELECTRODE (SHE)

The standard hydrogen electrode is one of several types of half-cell that can be used as reference electrode. **Figure 10.4** shows a standard hydrogen electrode.

This electrode consists of:

- Hydrogen gas at 101 kPa pressure, in equilibrium with H^+ ions of concentration 1.00 mol dm^{-3}
- A platinum electrode covered with platinum black in contact with the hydrogen gas and the H^+ ions.

The platinum black is finely divided platinum, which allows close contact of hydrogen gas and H^+ ions in solution so that equilibrium between H_2 gas and H^+ ions is established quickly. The platinum electrode is inert. Standard electrode potential E^o values for all half-cells are measured relative to this electrode.

When connected to another half-cell, the value read on the voltmeter gives the standard electrode potential for that

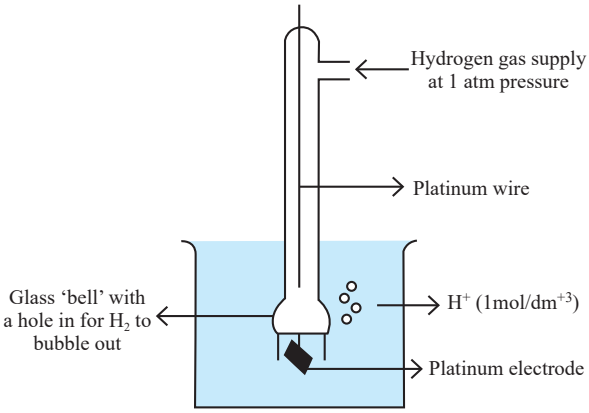

Figure 10.4 Standard hydrogen electrode (SHE)

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half-cell. The half-equation for the hydrogen electrode can be written:

$$2H^+_{(aq)} + 2e^- \rightleftharpoons H_{2(g)} \qquad E^\circ = 0.00\ V$$

It means that hydrogen gas and hydrogen ions have equal tendency to lose and gain electron.

10.13 STANDARD ELECTRODE POTENTIAL (E°)

The voltage of an electrochemical cell will also depend on concentration, temperature, and pressure of the gas. Therefore, we should use standard conditions when comparing electrode potentials.

These are:

- concentration of ions at 1.00 mol dm^{-3}
- a temperature of 25 °C (298 K)
- any gases should be at a pressure of 1 atmosphere (101 kPa)
- the value of the electrode potential of the half-cell is measured relative to the standard hydrogen electrode.

Under these conditions, the electrode potential we measure is called the **standard electrode potential**. This has the symbol, E^O. It is spoken of as '**E standard**'.

"The standard electrode potential for a half-cell is the voltage measured under standard conditions with a standard hydrogen electrode (SHE) as the other half-cell".

10.14 MEASURING STANDARD ELECTRODE POTENTIALS

There are three main types of half-cell whose E^O value can be obtained when connected to a standard hydrogen electrode (SHE):

- metal/metal ion half-cell (Cu^{2+}/Cu^0)
- non-metal/non-metal ion half-cell (Cl^{1-}/Cl_2) (Pt or C electrode is used)
- ion/ion half-cell. (Fe^{2+}/Fe^{3+}) (Pt or C electrode is used)

Figure 10.5 shows how to measure the E^O value for a Cu^{2+}/Cu half-cell. The Cu^{2+}/Cu half-cell is connected to the SHE and the voltage measured. The voltage is +0.34 V. The two half-equations are:

$$Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)} \qquad E^O = +0.34\ V$$

$$H^+_{(aq)} + e^- \rightleftharpoons 1/2\ H_{2(g)} \qquad E^O = 0.00\ V$$

The E^O values show us that Cu^{2+} ions are easier to reduce than H^+ ions (they have a more positive E^O value). Cu^{2+} ions are more likely to gain electrons than H^+ ions. So Cu^{2+} ions will accept electrons from the H^+/H_2 half-cell and H_2 will lose electrons to the Cu^{2+}/Cu half-cell.

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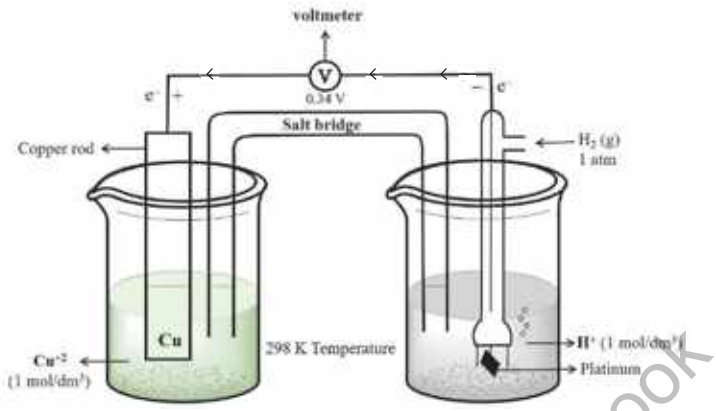

Figure 10.5 Measuring the standard electrode potential of a Cu^{2+}/Cu half-cell

Figure 10.6 shows how to measure the E^O value for a Zn^{2+}/Zn half-cell. The voltage of the Zn^{2+}/Zn half-cell is –0.76 V.

The two half-equations are:

$$2H^+_{(aq)} + 2e^- \rightleftharpoons H_{2(g)} \qquad E^O = 0.00\ V$$

$$Zn^{2+}_{(aq)} + 2e^- \rightleftharpoons Zn_{(s)} \qquad E^O = -0.76\ V$$

The E^O values show us that Zn^{2+} ions are more difficult to reduce than H^+ ions (they have a more negative E^O value). Zn^{2+} ions are less likely to gain electrons than H^+ ions. So, Zn will lose electrons to the H^+/H_2 half-cell and H^+ ions will gain electrons from the Zn^{2+}/Zn half-cell.

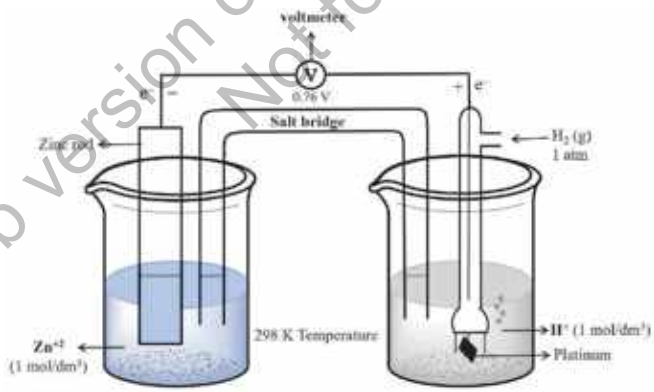

Figure 10.6 Measuring the standard electrode potential of a Zn^{2+}/Zn half-cell

From these two examples, we can see that:

- Reduction takes place at the positive terminal of the cell. For example, in the Zn^{2+}/Zn; H^+/H_2 cell:

$$2H^+_{(aq)} + 2e^{-1} \longrightarrow H_{2(g)}$$

- Oxidation takes place at the negative terminal of the cell. For example, in the Zn^{2+}/Zn; H^+/H_2 cell:

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

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10.15 ELECTROCHEMICAL CELL (GALVANIC CELL)

A cell in which the conversion of chemical energy into electrical energy takes place spontaneously in exothermic redox process with oxidation at anode and reduction at cathode. A galvanic cell is designed to take advantage of spontaneous transfer of electrons.

For example:

$$Cu^{2+} / Cu \;//\; Zn^{2+} / Zn \text{ cell } E^o = 1.10 \text{ V}$$

If we connect two half-cells together, we have made an electrochemical cell. We can measure the voltage of this cell. **Figure 10.7** shows a Cu^{2+}/Cu half-cell connected to a Zn^{2+}/Zn half-cell to make a complete electrochemical cell.

Half-cells are connected together using:

- wires connecting the metal rods in each half-cell to a high-resistance voltmeter; the electrons flow round this external circuit from the metal with the more negative (or less positive) electrode potential to the metal with the less negative (or more positive) electrode potential
- a salt bridge to complete the electrical circuit allowing the movement of ions between the two half-cells so that ionic balance is maintained; a salt bridge does not allow the movement of electrons.

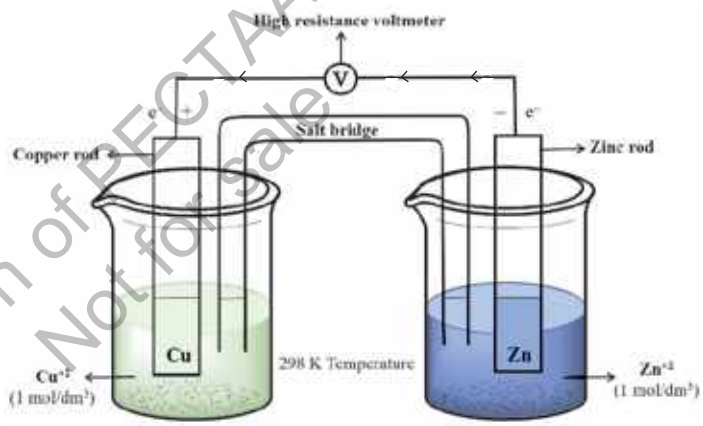

Figure 10.7 An electrochemical cell, made by connecting a Cu^{2+}/Cu half-cell to a Zn^{2+}/Zn half-cell.

A salt bridge can be made from a strip of filter paper (or other inert porous material) soaked in a saturated solution of potassium nitrate. The voltages for the half-cells in **Figure 10.7** can be represented by the following half-equations:

$$Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)} \qquad E^o = +0.34 \text{ V}$$

$$Zn^{2+}_{(aq)} + 2e^- \rightleftharpoons Zn_{(s)} \qquad E^o = -0.76 \text{ V}$$

An electrochemical cell is made by connecting a Cu^{2+}/Cu half-cell to a Zn^{2+}/Zn half-cell. The relative values of these voltages tell us that Zn^{2+} ions are more difficult to reduce than Cu^{2+} ions.

At the anode, zinc undergoes oxidation, losing electrons to form zinc ions:

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

These electrons travel through an external circuit to the cathode, where copper ions gain electrons and are reduced to form copper metal:

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

The overall cell reaction can be represented as:

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

This process effectively converts the chemical energy of the redox reaction into electrical energy, which can be connected to perform work.

The voltage generated by this cell is +1.10 V.

$$E^{o}_{cell} = E^{o}_{red} + E^{o}_{oxi} = +0.34 - (-0.76) = +1.10$$

In a Cu-Zn galvanic cell, zinc (Zn) serves as the anode, and copper ions (Cu^{2+}) in solution serve as the cathode.

Quick Check 10.6

a) What is the function of salt bridge in the voltaic cell?

b) Calculate the voltage of a cell having iron and copper electrodes.

$Fe_{(s)} \rightleftharpoons Fe^{2+}_{(aq)} + 2e^-$ $E^o = -0.44$ V

$Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)}$ $E^o = -0.44$ V

The E^O value for the Ag^+/Ag half-cell is more positive than for the Zn^{2+}/Zn half-cell. So, the Ag+/Ag half-cell is the positive pole and the Zn^{2+}/Zn half-cell is the negative pole of the cell.

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10.16 APPLICATIONS OF E^o VALUES

10.16.1 Direction of Electron Flow

We can deduce the direction of electron flow in the wires in the external circuit by comparing the E^O values for the two half-cells which make up the electrochemical cell. For example, in **Figure 10.9** these voltages are:

$Ag^+_{(aq)} + e^- \rightleftharpoons Ag_{(s)}$ $E^O = +0.80$ V

$Zn^{2+}_{(aq)} + 2e^- \rightleftharpoons Zn_{(s)}$ $E^O = -0.76$ V

The relative values of these voltages tell us that Zn^{2+} ions are more difficult to reduce than Ag^+ ions. So, Zn metal will lose electrons to the Ag^+/Ag half-cell and Ag^+ ions will accept electrons from the Zn^{2+}/Zn half-cell. The electrons move through the wires in the external circuit. They do not travel through the electrolyte solution. So, the electron flow is from the Zn^{2+}/Zn half-cell to the Ag^+/Ag half-cell. In other words, the flow is from the negative pole to the positive pole. Remember that the more positive pole attracts the negative electrons.

10.16.2 Feasibility of a Reaction Using E^o Values

Standard electrode potential values, E^O, give us a measure of how easy or difficult it is to oxidize or reduce a species. The E^O values are listed in order of increasingly negative values. For each half-equation, the more oxidized form is on the left and the more reduced form is on the right.

- The more positive the value of E^O, the greater the tendency for the half-equation to proceed in the forward direction, and the easier it is to reduce the species on the left of the half-equation.
- The less positive the value of E^O, the greater the tendency for the half-equation to proceed in the reverse direction, and the easier it is to oxidize the species on the right of the half-equation.

To check the feasibility of reaction between Mg^{2+} and Ag

$$Mg^{2+} + Ag \longrightarrow ?$$

We need half cell equations and E° values

$$Mg^{2+} + 2e^- \rightleftharpoons Mg \qquad E° = -2.32\ V$$

$$Ag^+ + 1e^- \rightleftharpoons Ag \qquad E° = +0.80\ V$$

Mg^{2+} are supposed to be reduced here and Ag is supposed to get oxidized, So calculating E° cell gives us

$$E°_{cell} = E°_{red} - E°_{ox}$$
$$= (-2.32) - (+0.80)$$
$$= -1.52V$$

Negative value of $E°_{cell}$ indicates the reaction is not feasible. On the other hand reaction between Ag^+ and Mg is feasible as for this reaction $E°_{cell}$ will be positive as given below.

$$E°_{cell} = E°_{red} - E°_{ox}$$
$$= (-0.80) - (-2.32)$$
$$= +1.52V$$

Therefore, the feasible reaction is

$$2Ag^+ + Mg_{(s)} \longrightarrow Mg^{2+}_{(aq)} + Ag_{(s)}$$

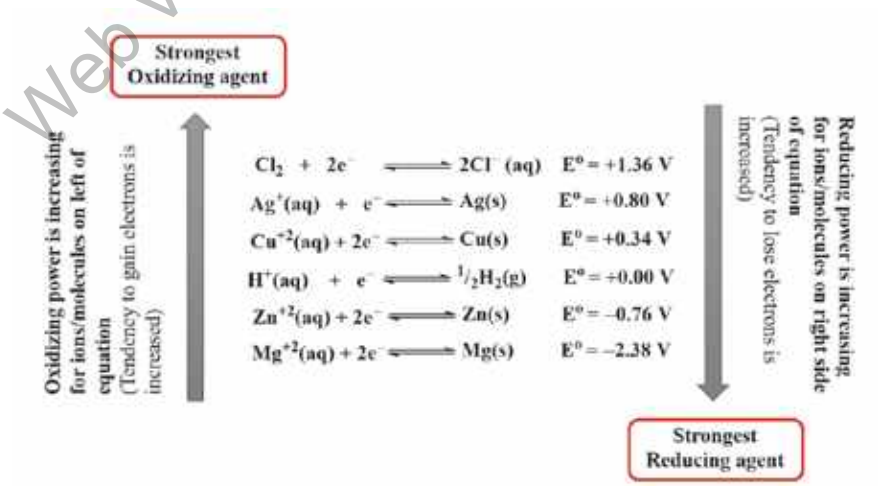

Figure 10.8 Standard electrode potentials for some oxidizing and reducing agents

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Quick Check 10.7

a) Explain the following keeping in view the standard electrode potential values (E^o Cl2/2Cl- = +1.36 V E^o ($Br_2/2Br^-$) = +1.07 V, E^o ($I_2/2I^-$) = +0.54 V)

i. The aqueous solution of iodine can be oxidized with bromide or iodide ions.

ii. Why bromine does not react with chloride ions?

10.16.3 Oxidising and Reducing Agents Using E^o Values

In the reaction between Cu and Zn^{2+}, Cu will not reduce Zn^{2+} ions to Zn. So how can we reduce Zn^{2+} ions? The answer is to react the Zn^{2+} ions with a stronger reducing agent, which should have an E^O value more negative than the E^O value for Zn^{2+}/Zn. In **Figure 10.13** we see that the half-equation Mg^{2+}/Mg has a more negative E^O value. So, Mg is a suitable reducing agent.

$$Zn^{2+}_{(aq)} + e^- \longrightarrow Zn_{(s)} \qquad E^O = -0.76\ V$$

$$Mg^{2+}_{(aq)} + 2e^- \longrightarrow Mg_{(s)} \qquad E^O = -2.38\ V$$

Zn^{2+} is the better oxidizing agent. It is more likely to accept electrons than Mg^{2+} ions. Mg is the better reducing agent. It is more likely to release electrons than Zn.

Compounds can also act as oxidizing and reducing agents. For example $KMnO_4$ (+0.54V) $K_2Cr_2O_7$ (+1.33V) are oxidizing agent because of there higher E° values. Whereas, KI and $FeSO_4$ are reducing gents due to their lower E° values.

10.17 VARIATION OF E^O WITH ION CONCENTRATION

The position of an equilibrium reaction is affected by changes in concentration, temperature and pressure. If we change the concentration or temperature of half-cell X, the electrode potential also changes. Under these non-standard conditions we use the symbol E for the electrode potential. Let us take an example of a metal/metal ion equilibrium:

Table 10.1 Variation of Potential with Ion Concentration

$[Fe^{3+}]$ (mol dm $^{-3}$)	$[Fe^{2+}]$ (mol dm $^{-3}$)	E^O (V)	Effect
> 1.00	1.00	+ 0.85	More positive
< 1.00	1.00	+ 0.70	Less positive
1.00	> 1.00	+0.70	Less positive
1.00	< 1.00	+0.85	More positive

Le-Chatelier's principle can be applied to redox equilibria. If we increase the concentration of the species on the left of the equation, the position of equilibrium will shift to the right. So, the value of E becomes more positive / less negative change in contraction of ions and

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its effect on E° is shown in **Table 10.1**. If two different ions are present in the half-cell, we have to consider both ions. Let us take the equilibrium between Fe^{3+} ions and Fe^{2+} ions as an example.

$$Fe^{3+} + e^- \rightleftharpoons Fe^{2+} \qquad E^O = +0.77\ V$$

1.00 mol dm^{-3} 1.00 mol dm^{-3}

10.18 NERNST EQUATION

If we consider a cell made up from a silver/silver ion electrode and a copper/copper (II) ion electrode, the reaction taking place is:

$$Cu_{(s)} + 2Ag^+_{(aq)} \longrightarrow Cu^{2+}_{(aq)} + 2Ag_{(s)} \qquad E^O = +0.46\ V$$

When E^o_{cell} is plotted against concentration we obtain a graph as shown in **Figure 10.9.**

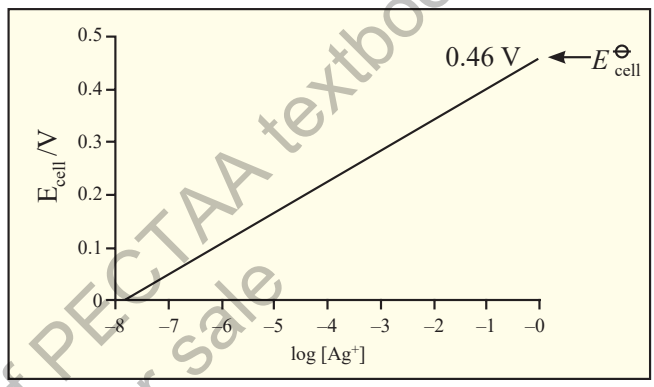

Figure 10.9 Increasing the concentration of silver ions in the cell reaction

Note that we have plotted the value of E_{cell} (non-standard conditions for the cell as a whole) against the logarithm of the silver ion concentration. The above redox cell reaction makes the value of E_{cell} more positive.

The effect of concentration and temperature on the value of E_{cell} can be deduced using the Nernst equation. For a given electrode, e.g., a $Cu_{(s)}/Cu^{2+}_{(aq)}$ electrode, the relationship is:

$$E = E^o + \frac{RT}{zF}\ \ell n\ \frac{[\text{oxidized form}]}{[\text{reduced form}]}$$

where,

E is the electrode potential under non-standard conditions

E^O is the standard electrode potential

R is the gas constant, 8.314 J K^{-1} mol^{-1}

T is the kelvin temperature

z is the number of electrons transferred in the reaction

F is the value of the Faraday constant in C mol^{-1}

ℓn is the natural logarithm

[oxidized] refers to the concentration of the oxidized form in the half-equation

[reduced] refers to the concentration of the reduced form in the half-equation.

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The natural logarithm, ℓn, is related to log to the base 10 by the relationship

$$\ell n\ x = 2.303 \log_{10} x$$

At standard temperature the values of R, T and F are constant

The equation then becomes

$$E = E^o + \frac{0.059}{z} \ell og \frac{[\text{oxidized form}]}{[\text{reduced form}]}$$

Sample problem 10.5

What is the electrode potential of a Zn electrode dept in a solution containing Zn^{2+} ions (0.1M), The e° value of Zn^{2+}/Zn is -0.76V

Using Half equation and E°,

$$Zn^{2+} + 2e^- \longrightarrow Zn \qquad E° = -0.76V$$

$$E = (-0.76) + \frac{8.31 \times 298}{2 \times 96500} \ell n\ (0.1)$$

$$E = -0.76 + (-0.029) = -0.78\ V$$

Since, concentration of Zn^{2+} is decreased to shift equilibrium backward and electrode potential decreases to -0.78 V

10.19 ACTIVITY SERIES OF METALS

The activity series of metals is a ranking of metals based on their reactivity, particularly their tendency to lose electrons and undergo oxidation. Metals higher in the activity series have more negative standard reduction potentials, meaning they are more likely to lose electrons and undergo oxidation. Hence such metals act as reducing agents. Metals at the top of the series are the most reactive with water, oxygen and acid. For example, alkali metals like cesium and sodium are highly reactive and oxidize readily, reacting vigorously with substances like water to form ions and release hydrogen gas.

In contrast, metals lower in the activity series, such as noble metals like gold and silver, do not oxidize easily. Metals at the bottom of the series are the least reactive with water, oxygen and acid. Thus, the position of a metal in the activity series directly correlates with its ease of oxidation and overall reactivity. Activity series of metals is actually reactivity series.

Thus, the activity series can be understood in terms of standard reduction potentials: metals with more negative potentials are more reactive and oxidize more readily, while those with more positive potentials are less reactive and oxidize less readily as given in **Table 10.2**.

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Table 10.2 Activity Series of Metals

Metals	Ions	E^0 (V)	Reaction Occurring	Trend
Li	Li^{1+}	-3.05	React with cold water, replacing hydrogen $2M_{(s)} + 2H_2O_{(l)} \longrightarrow 2MOH_{(aq)} + H_{2(g)}$	decreasing ease of oxidation, reactivity and acting as reducing agent
K	K^{1+}	-2.93		
Ba	Ba^{2+}	-2.90		
Sr	Sr^{2+}	-2.89		
Ca	Ca^{2+}	-2.87		
Na	Na^{1+}	-2.71		
Mg	Mg^{2+}	-2.37	React with steam, but not cold water, replacing hydrogen. $M_{(s)} + H_2O_{(l)} \longrightarrow MO_{(aq)} + H_{2(g)}$	
Al	Al^{3+}	-.1.66		
Zn	Zn^{2+}	-0.76		
Cr	Cr^{3+}	-0.74		
Fe	Fe^{2+}	-0.44		
Cd	Cd^{2+}	-O.40		
Co	Co^{2+}	-0.28	Do not react with water. React with acids, replacing hydrogen. $M_{(s)} + HCl_{(aq)} \longrightarrow MCl_{(aq)} + H_{2(g)}$	
Ni	Ni^{2+}	-0.25		
Sn	Sn^{2+}	-0.14		
Pb	Pb^{2+}	-0.13		
H_2	H^+	0.00	Included as reference	
Cu	Cu^{2+}	+0.34	Unreactive with water or acids.	
Hg	Hg^{2+}	+0.92		
Ag	Ag^{1+}	+0.80		
Pt	Pt^{2+}	+1.18		
Au	Au^{3+}	+1.50		

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10.20 FEASIBILITY OF REDOX REACTIONS FROM ACTIVITY SERIES OR REACTION DATA

The **activity series** is actually a reactivity series of metals, in order of reactivity from highest to lowest. It is used to determine the products of single displacement reactions; whereby metal M_1 will replace another metal M_2 in a solution if M_1 is **higher** in the series.

From the activity series of metals, we can determine whether the reaction is feasible or not. We sum up the potentials of half reactions, if potential of the cell is positive, the reaction is possible if negative, the reaction is not feasible. Let us see the reactions:

$$Fe^{2+}_{(aq)} + 2e^- \rightleftharpoons Fe_{(s)} \qquad E^o_{(ox)} = -0.44\ V$$

$$Ag^+_{(aq)} + 1e^- \rightleftharpoons Ag_{(s)} \qquad E^o_{(ox)} = +0.080\ V$$

The ovelall reaction is

$$Fe_{(s)} + 2Ag^+_{(aq)} \longrightarrow Fe^{2+}_{(aq)} + 2Ag_{(s)} \qquad E^o_{(cell)} = 0.080 - (-0.44) = +1.24\ V$$

The cell potential is **positive**; hence the reaction is **feasible**.

Consider another example:

From the activity series of metals, we have

$$Al^{3+}_{(aq)} + 3e^- \rightleftharpoons Al_{(s)} \qquad E^o_{(red)} = -1.66\ V$$

$$Ag^+_{(aq)} + 1e^- \rightleftharpoons Ag_{(s)} \qquad E^o_{(ox)} = +0.080\ V$$

$$Al^{3+}_{(aq)} + Ag_{(s)} \longrightarrow Al_{(s)} + Ag^+_{(aq)} \qquad E^o_{(red)} = -1.66 + 0.080 = -0.86\ V$$

The sum of E^O values of the two half-cell reactions is **negative**. Hence the reaction is **not feasible**.

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Quick Check 10.8

a) State the Nernst equation, why is it significant in electrochemistry.

b) What is the effect of variation in ion concentration on the standard electrode potential of a half reaction?

c) Give answers using E^o values ($E^o_{Ag+/Ag} = +0.80$ V, $E^o_{Cr2+/Cr} = -0.91$ V, $E^o_{Fe2+/Fe} = -0.44$ V

i. Which of Ag^+, Cr^{2+} and Fe^{2+}, is the strongest oxidizing agent? Which is the least oxidizing? Explain with reason.

ii. Arrange Ag, Cr and Fe in increasing order of their reducing powers.

d) What is the electrode potential of a Cu electrode dipped in a solution containing Cu^{2+} ions (0.01 M), The E^o value of Cu^{2+}/Cu^0 is +0.34 V.

e) What is the electrode potential of Cl^-/Cl_2 half cell at 25 ºC, if concentration of Cl^- is 0.05 mol dm^{-3}.

$$Cl_2 + 2e^- \rightleftharpoons 2Cl^- \qquad E^o = 1.36V$$

10.21 PHOTOVOLTAIC CELLS

The word 'photovoltaic' is composed of photo (light) and volt (electrical potential). The cell which converts light energy into electrical energy is called **photovoltaic cell**.

10.21.1 Principle of Photovoltaic Cells

The central principle behind the operation of PV cells is the photovoltaic effect, which involves the generation of voltage and electric current in a material upon exposure to light. The photovoltaic effect involves the excitation of electrons from the valence band to the conduction band in semiconductors, facilitated by the energy from photons. This process is improved by the presence of a PN junction, which separates the electrons and holes, creating a voltage that drives an electric current.

10.22.2 Merits of Photovoltaic Cell as Sustainable Source of Energy

i. The photovoltaic effect continues as long as light is present, making it a sustainable method for generating electricity.

ii. A photovoltaic system is a renewable energy source that converts sunlight into electrical energy.

iii. The photovoltaic systems use the sun's energy, making them a sustainable energy source that is independent of fossil fuels.

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10.22 WINKLER METHOD, BOD AND DO

Biochemical oxygen demand (BOD) is the capacity of organic matter in natural water to consume oxygen within a period of five days. The value of BOD is the amount of oxygen consumed as a result of biological oxidation of dissolved organic matter in the sample. The oxidation reaction is catalyzed by microorganisms which are already present in the natural water. It is measured experimentally through **Winkler method** by calculating the concentration of oxygen at the beginning and at the end of five days period, in which a sealed water sample is maintained in the dark at constant temperature at 25°C.

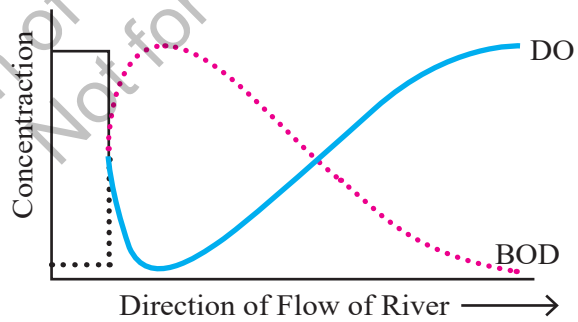

Figure 10.10 Inverse relationship between BOD and DO

Dissolved oxygen (DO) is defined as the amount of oxygen dissolved in water. It is dissolved either from the atmosphere or released by plants during photosynthesis in water. Its concentration is between 5 to 8 mg/dm^3. The minimum level of DO should be 5 mg/dm^3. Below 5 mg/dm^3, the water supposed to be polluted.

Dissolved Oxygen (DO) and Biochemical Oxygen Demand (BOD) have an inverse relationship as shown in **Figure 10.10**. As bacteria consume oxygen in the water while decomposing organic matter, BOD increases, leading to lower dissolved oxygen (DO) level.

Winkler method

Winkler method is a technique used to measure the amount of dissolved oxygen (DO) in water samples. It is based on the idea that dissolved oxygen (DO) in the sample solution, has oxidizing properties and reacts with KI. The amount of iodine formed is measured by titrating with sodium thiosulfate using starch as an indicator which turns the solution dark blue, indicating the endpoint. The amount of iodine formed is proportional to the amount of dissolved oxygen in the solution.

EXERCISE

MULTIPLE CHOICE QUESTIONS

Q.1 Four choices are given for each question. Select the correct choice.

I. The activity series of metals arranges metals in order of their:

a) Atomic mass
b) Density
c) Ease of oxidation
d) Ease of reduction

II. According to the activity series, which of the following metals would most readily displace hydrogen gas from dilute acids?

a) Copper (Cu)
b) Silver (Ag)
c) Magnesium (Mg)
d) Platinum (Pt)

III. The salt bridge allows transfer of ---------- in Zn-Cu voltaic cell.

a) Zn^{2+} ions
b) SO_4^{2-} ions
c) Both
d) None of these

IV. If Zn-Cu galvanic cell works ideally after complete discharge, both compartments will have:

a) $CuSO_4$ solution
b) $ZnSO_4$ solution
c) Cu^{+2} ions
d) Zn solid

V. Which of the following half-reactions represents a reduction process?

a) $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$
b) $Fe^{2+}_{(aq)} \rightarrow Fe^{3+}_{(aq)} + e^-$
c) $Cl_{2(g)} + 2e^- \rightarrow 2Cl^-_{(aq)}$
d) $2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)}$

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VI. Which of the following half-reactions represents the oxidation process occurring in the disproportionation of Cu+?

a) $Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$
b) $Cu^{+}_{(aq)} + e^- \rightarrow Cu_{(s)}$
c) $Cu^{+}_{(aq)} \rightarrow Cu^{2+}_{(aq)} + e^-$
d) $2Cu^{+}_{(aq)} \rightarrow Cu^{2+}_{(aq)} + Cu_{(s)}$

VII. If salt bridge is not used between two half cells in a Galvanic cell, then the voltage

a) Decrease slowly
b) Decrease rapidly
c) Does not change
d) Drop to zero

VIII. In an electrolysis experiment, if a charge of 96,500 Coulombs is passed through a solution, the amount of substance liberated or deposited at the electrode is directly related to:

a) Mass number of the ion
b) One mole of electrons being transferred
c) Avogadro's number of ions being discharged
d) Standard electrode potential of the metal ion

IX. The experimental determination of Avogadro's number through electrolysis typically involves measuring:

a) The current and voltage applied.
b) The mass of the substance deposited or liberated by a known charge.
c) The conductivity of the electrolytic solution.
d) The temperature changes during electrolysis.

X. The principle of measuring DO by Wrinkler's Method is based on

a) Iodimetry
b) Iodometry
c) Acid-Base titration
d) Complexometry

XI. A positive value for the standard electrode potential (E°) of a metal ion/metal half-cell (e.g., Cu^{2+}/Cu) indicates that:

a) The metal is a strong reducing agent.
b) The metal ion is readily oxidized.
c) The metal ion is readily reduced.
d) The metal will readily displace hydrogen from dilute acids.

XII. Which of the following changes would typically lead to an increase in the rate of electrolysis?

a) Decreasing the concentration of the electrolyte
b) Increasing the distance between the electrodes
c) Decreasing the surface area of the electrodes
d) Increasing the current passed through the electrolytic cell

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SHORT ANSWER QUESTIONS

Q.2 Attempt the following short-answer questions:

a. How and why electrical double layer is formed?

b. Why electrode potential of Cu is called reduction potential?

c. What are the advantages of salt bridge in a galvanic cell?

d. How can we predict the feasibility of a chemical reaction using the cell voltage?

e. During electrolysis of aqueous NaCl, why Na is not liberated at the cathode?

f. Calculate the Ox. No. of chromium (Cr) in the following compounds:

(i) $CrCl_3$ (ii) $Cr_2(SO_4)_3$ (iii) $Cr_2O_7^{2-}$

g. The order of decreasing reactivity of metals based on their position is K > Mg > Zn > Fe > Cu. Write balanced chemical equations for the reactions that would occur (if any) when:

i) Copper is added to a solution of magnesium sulfate.

ii) Iron is added to a dilute solution of hydrochloric acid.

h. Explain why some metals higher in the activity series can displace hydrogen from acids, while others lower in the series cannot.

i. Calculate the number of Faradays required to deposit 108 g of Ag^{1+}, 63.5 g of Cu^{2+} and 27 g of Al^{3+}.

j. In an electrolysis experiment, a current of 0.500 A was passed through a solution of $AgNO_3$ for 30.0 minutes. The mass of silver deposited on the cathode was found to be 0.503 g. Given that the molar mass of silver is 107.87 g mol^{-1} and the charge on a silver ion is +1. Calculate the value of Avogadro's number (N_A) from this data.

k. A cell is set up with a standard nickel electrode ($Ni^{2+}_{(aq)} + 2e^- \rightleftharpoons Ni_{(s)}$ $E^0 = -0.25$ V) and a standard cobalt electrode ($Co^{2+}_{(aq)} + 2e^- \rightleftharpoons Co_{(s)}$, $E^0 = -0.28$ V).

i) Identify which metal will be the anode and which will be the cathode. Justify your answer.

ii) Write the balanced overall cell reaction.

iii) Calculate the standard cell potential ($E°_{cell}$).

DESCRIPTIVE QUESTIONS

Q.3. How electrode potential varies with concentration of an aqueous solution? Use the NERST equation to explain this variation.

Q.4. How Avogadro's number can be derived using an electrolytic cell?

Q.5. Describe the construction and working principle of the Zn-Cu Galvanic cell.

Q.6. What is meant by Standard Hydrogen Electrode (SHE)? How it is used to measure the electrode potential of another electrode?

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NUMERICAL PROBLEMS

Q.7 Calculate the electrode potential for a zinc electrode immersed in a 0.010 mol dm^{-3} solution of zinc sulfate ($ZnSO_4$) at 298 K. The standard electrode potential (E°) for $Zn^{2+}_{(aq)} + 2e^- \rightleftharpoons Zn_{(s)}$ is -0.76 V. (Gas constant, R = 8.31 J K^{-1} mol^{-1}, Faraday constant, F = 96500 C mol^{-1})

Q.8. A constant current of 2.00 A is passed through a solution of copper(II) sulfate ($CuSO_4$) for 30.0 minutes. Calculate the mass of copper deposited at the cathode. (Molar mass of Cu = 63.5 g mol^{-1}, Faraday constant, F = 96500 C mol^{-1})

Q.9. A galvanic cell consists of a standard hydrogen electrode (SHE) and a $Ni^{2+}_{(aq)}/Ni_{(s)}$ half-cell. The measured cell potential at 298 K is 0.25 V, and the nickel electrode is the negative terminal.

a) Write the balanced overall cell reaction.

b) Determine the standard electrode potential (E°) of the $Ni^{2+}_{(aq)}/Ni_{(s)}$ half-cell.

c) Identify which electrode is the anode and which is the cathode.

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