T.Y. B.Sc. (Sem. IV) (503) (CBCS)
Unit-2 Chpter-1 : ELECTROCHEMISTRY-1

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2.1 INTRODUCTION

- At different time, Definitions of oxidation and reduction is different, but complimentary

- Oxidation : Gaining Oxygen

  Losing Hydrogen

  Losing Electron(s)

  Increase in Positive Charge

  - Reduction : Losing Oxygen

    Gaining Hydrogen

    Gaining electron(s)

    Decrease in Positive Charge

- While the above first two definitions of oxidation and reduction are correct. The most useful definitions are 3rd- Involving loss or gain electrons and 4th - involving increases or decreases in charges in our rest of the discussion.
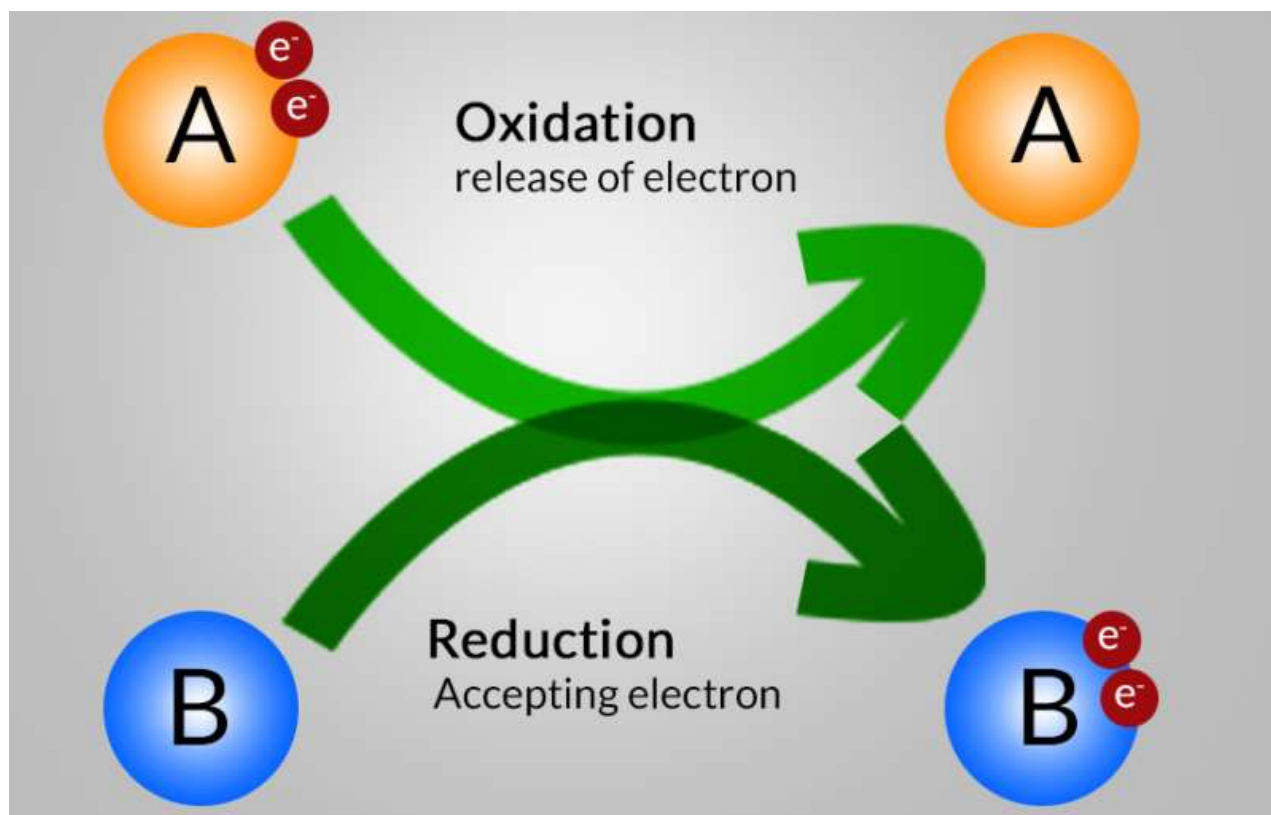
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- Now, Redox reactions are oxidation-reduction chemical reactions in which the reactants undergo a change in their oxidation states. The term 'redox' is a short. form of reduction-oxidation.

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- All the redox reactions can be broken down into two different processes - a reduction process and an oxidation process.

2.2 Electrolytes and their types:

- An electrolyte is a substance that dissociates in water into charged particles called ions. Positively charged ions are called cations. Negatively charged ions are called anions.

- Simply, an electrolyte is a substance that can conduct an electric current when melted or dissolved in water. Ex. HCl, NaOH, HI, H_2CO_3, NaCl, KCl, $NaNO_3$ etc....

- Glucose and urea do not dissociate in water because they have no electric charge. **Therefore, these substances are called non-electrolytes.**

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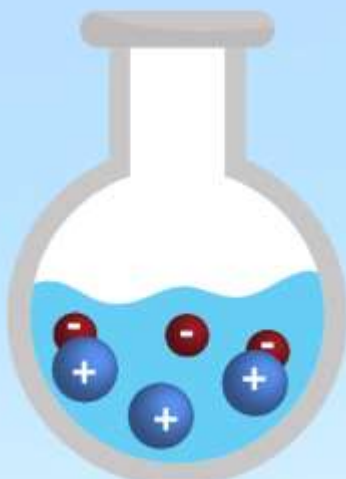**Rajkot-360001,**
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2.3 Oxidation number:

- Oxidation number in simple terms can be described as the number that is allocated to elements in a chemical combination. The oxidation number is basically the count of electrons that atoms in a molecule can share, lose or gain while forming chemical bonds with other atoms of a different element. Oxidation number is also referred to as oxidation state. Each atom that participates in an oxidation-reduction reaction is assigned an oxidation number that reflects its ability to acquire, donate, or share electrons.

- For example, The iron ion Fe^{3+} has an oxidation number of +3 because it can acquire three electrons to form a chemical bond, while the oxygen ion 02- has an oxidation number of -2 because it can donate two electrons. In an electronically neutral substance, the sum of the oxidation numbers is zero; for example, in hematite (Fe2O3) the oxidation number of the two iron atoms (+6 in total) balances the oxidation number of the three oxygen atoms (-6). Certain elements assume the same oxidation number in different compounds; fluorine, for example, has the oxidation number -1 in all its compounds. Others,

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notably the nonmetals and the transition elements, can assume a variety of oxidation numbers; for example, nitrogen can have any oxidation number between -3 (as in ammonia, NH3) and +5 (as in nitric acid, HNO3).

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2.4 Electrochemical Cell and electrolytic cell :

- **Electrochemistry is the study of production of electricity from energy released during spontaneous chemical reactions and the use of electrical energy to bring about non-spontaneous chemical transformations.**

- **Chemical Energy ⟷ Electrical Energy**

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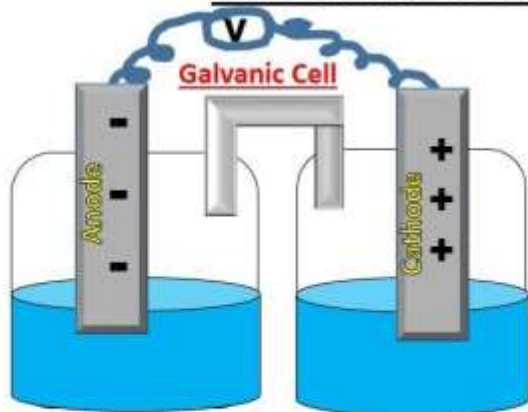**(AFFILIATED TO SAURASHTRA UNIVERSITY)**
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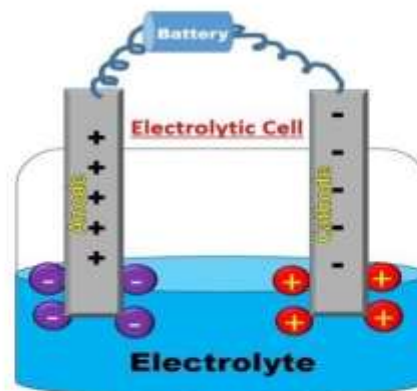**Rajkot-360001,**
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Galvanic Cell Vs Electrolytic Cell

Changes chemical energy into Electrical energy .
1. Anode is −ve
2. Cathode is +ve
3. Spontaneous reaction occurs.
4. Does not require external voltage source.

Changes electrical energy into Chemical reaction.
1. Anode is +ve
2. Cathode is −ve
3. Non–Spontaneous reaction occurs.
4. Require external voltage source.

- A spontaneous chemical process can take place on its own and in such a process the Gibb's energy of the system decreases. This energy gets converted to electrical energy. These interconversions are carried out in equipment called Electrochemical Cells.

- Thus, a device used to convert chemical energy produced in a redox reaction into electrical energy is called an electrochemical cell.

- For eg.

Daniel Cell, Voltaic Cell, Galvanic cell

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- These reactions occur in two different portions of the Daniel cell. The reduction half reaction occurs on the copper electrode while the oxidation half reaction occurs on the zinc electrode. These two portions of the cell are also called half-cells or redox couples.

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2.5 Cell description conventions:

In order to make it easier to describe a given electrochemical cell, a special symbolic notation has been adopted. In this notation the cell of Fig. 2 would be

Zn*(s)* | Zn²⁺*(aq)* || Cu²⁺*(aq)* | Cu*(s)*

In this notation, the vertical bars indicate *phase boundaries*; the double vertical bar in the middle denotes the phase boundary between the two solutions. As a matter of convention, the chemical species that undergo *reduction* when the cell reaction proceeds to the right according to the net equation are shown on the *right* side, and those that undergo *oxidation* are shown on the *left*. Note carefully that this is entirely independent of the physical location of the two electrodes in the actual cell in Fig. 2.

There are several other conventions relating to cell notation and nomencla- ture that you are expected to know:

- The *anode* is where *oxidation* occurs, and the *cathode* is the site of *reduc- tion*. In an actual cell, either electrode can have either

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identity, depending on the direction in which the net cell reaction is occurring.

- If electrons flow from the left electrode to the right electrode when the cell operates in its spontaneous direction, the potential of the right electrode will be higher than that of the left, and the cell potential will be *positive*.

- "Conventional current flow" is from positive to negative, which is opposite to the direction of the electron flow. This means that if the electrons are flowing from the left electrode to the right, a galvanometer placed in the external circuit would indicate a current flow from right to left

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2.6 Electrodes and electrode reactions:

The electron-transfer step that takes place at each electrode is known as the *electrode reaction*. The substance that loses or receives the electron is called the *electroactive species*.

In the example of the Zn/Cu cell we have been using, the electrode reaction involves a metal and its hydrated cation; we call such electrodes *metal-metal ion* electrodes. There are a number of other kinds of electrodes which are widely encountered in electrochemistry and analytical chemistry.

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metallic electrode

product ion leaves surface and re-acquires hydration shell

surface-adsorbed ions can exchange electrons with metal

excess of anions in this region to compensate charge of adsorbed cations

incoming cation with hydration shell of water molecules which must be pushed off before ion can attach to surface
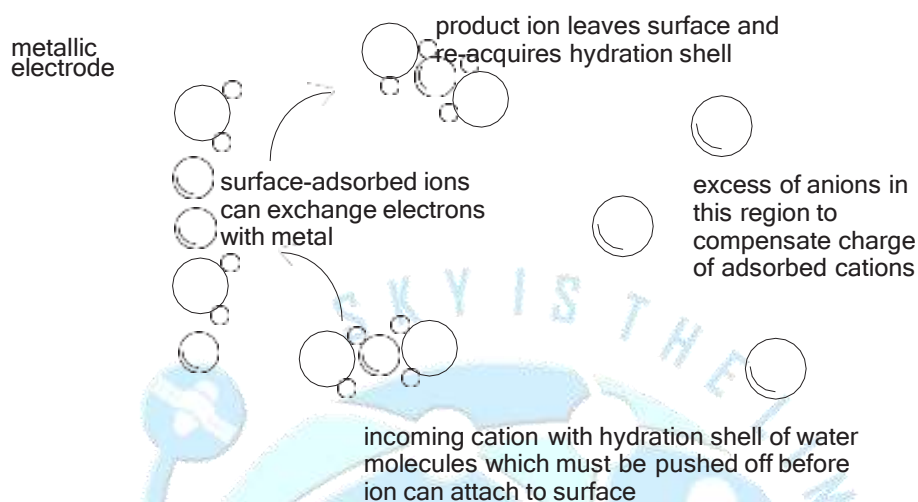
Figure 3: Electron-transfer at an electrode

Ion-ion electrodes Many electrode reactions involve only ionic species, such as Fe^{2+} and Fe^{3+}. If neither of the electroactive species is a metal, some other metal must serve as a conduit for the supply or removal of electrons from the system. In order to avoid complications that would arise from electrode re- actions involving this metal, a relatively inert substance such as platinum is commonly used. Such a half cell would be represented as
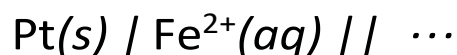
$$Pt(s) \mid Fe^{2+}(aq) \mid\mid \cdots$$

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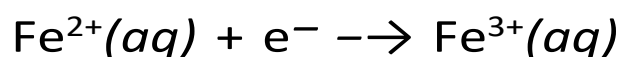**(AFFILIATED TO SAURASHTRA UNIVERSITY)**
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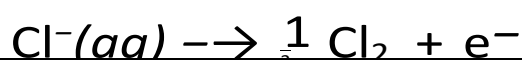**Nr. Lalpari lake, Behind old Marketing Yard, Amargadh, Bhichari,**
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and the half-cell reaction would be

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

The reaction occurs at the surface of the electrode (Fig. 3). The electroactive ion diffuses to the electrode surface and adsorbs (attaches) to it by van der Waals and coulombic forces. In doing so, the waters of hydration that are normally at- tached to any ionic species must be displaced. This process always costs energy; if a lot of work is required, then only a small fraction of the ions will attach to the surface long enough to undergo electron transfer, and the reaction will be slow. The actual electron-transfer occurs by quantum-mechanical tunnelling.

Gas electrodes Some electrode reactions involve a gaseous species such as H_2, O_2, or Cl_2. Such reactions must also be carried out on the surface of a metallic conductor such as platinum. A typical reaction of considerable commercial importance is

$$Cl^-(aq) \longrightarrow \tfrac{1}{2} Cl_2 + e^-$$

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2.7 Standard half-cell potentials

Although many applications of electrochemical cells involve a flow of current between the two electrodes, the most fundamental kind of measurement we can make is of the voltage, or EMF between the electrodes in the absence of any cell current. This voltage, which we usually refer to as the *cell potential*, is the potential difference between the electrodes, and is the difference between the *half-cell potentials* of the right and left sides:

$$E_{cell} = \Delta V = V_{right} - V_{left} \quad (2)$$

Each of the half-cell potentials is in turn a potential difference between the electrode and the solution, so for our example cell the above relation can be expanded to

$$E_{cell} = V_{Cu} - V_{soln} + V_{soln} - V_{Zn} \quad (3)$$

It is important to understand that individual half-cell potentials are not directly measurable; there is no way you can determine the potential difference between a piece of metal and a

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solution. Attaching one lead of a voltmeter to the metal and dipping the other in the solution would simply create a new half-cell involving the immersed metallic conductor.

The fact that individual half-cell potentials are not directly measurable does not prevent us from defining and working with them. If we cannot determine the absolute value of a half-cell potential, we can still measure its value in relation to the potentials of other half cells. In particular, if we adopt a reference half- cell whose potential is arbitrarily defined as zero, and measure the potentials of various other electrode systems against this reference cell, we are in effect

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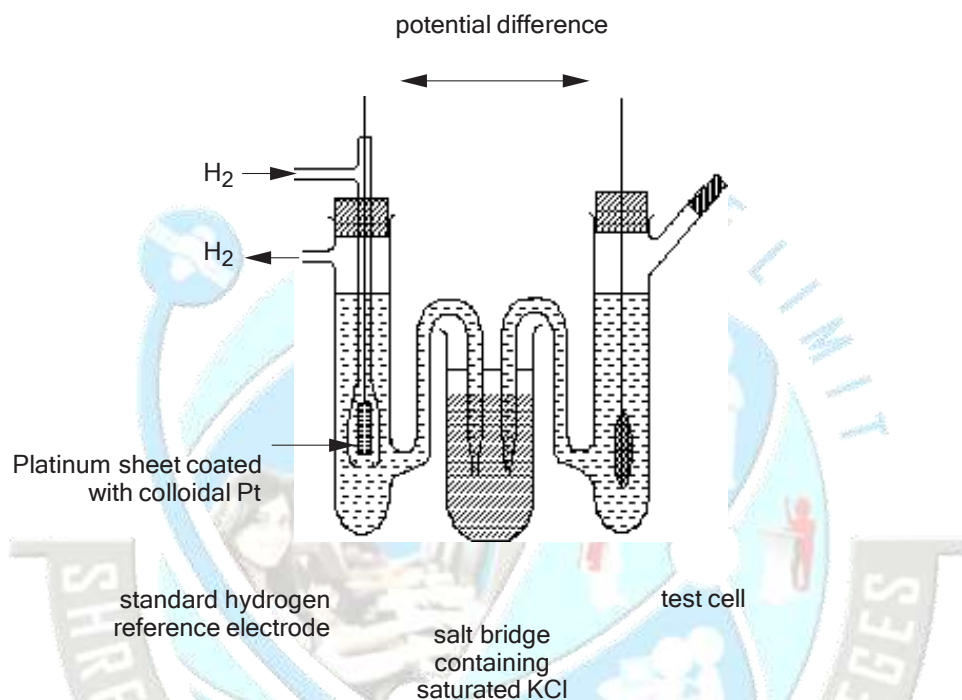**Rajkot-360001,**
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Figure 4: Cell for measurement of standard potentials

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measuring the half-cell potentials on a scale that is relative to the potential of the reference cell.

As a reference cell we use the half cell whose reaction is

$$\frac{1}{2} H_2(g) \longrightarrow H^+ + e^- \quad (4)$$

This is the *hydrogen electrode*, an example of a gas electrode as was discussed above. When this electrode is set up under standardized conditions, it becomes the *standard hydrogen electrode*, sometimes abbreviated *SHE*.

In order to measure the relative potential of some other electrode M^{2+}/M, we can set up a cell

$$Pt \mid H_2(g) \mid H^+(aq) \mid\mid M^{2+}(aq) \mid M(s) \quad (5)$$
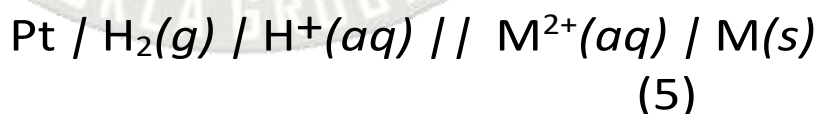
whose net reaction is

$$H_2(g) + M^{2+} \longrightarrow 2H^+ + M(s)$$
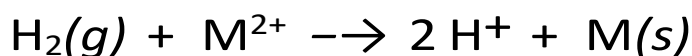
In analogy with Eq 3, the potential difference between the platinum and M electrodes will be

$$E_{cell} = V_M - V_{soln} + V_{soln} - V_{Pt}$$

$$Na^+ + e^- \rightarrow \quad Na(s) \qquad -2.71$$

$Zn^{2+} + e^- \rightarrow$	$Zn(s)$	−.76
$Fe^{2+} + e^- \rightarrow$	$Fe(s)$	−.44
$Cd^{2+} + e^- \rightarrow$	$Cd(s)$	−.40
$Pb^{2+} + 2e^- \rightarrow$	$Pb(s)$	−.126
$2H^+ + 2e^- \rightarrow$	**$H_2(g)$**	**0.000**
$AgCl(s)+ e^- \rightarrow$	$Ag(s)+ Cl^-(g)$	+.222
$Hg_2Cl_2(s)+ 2e^- \rightarrow$	$2Cl^-(g)+ Hg(l)$	+.2676
$Cu^{2+} + 2e^- \rightarrow$	$Cu(s)$	+.337
$I_2(s)+ 2e^- \rightarrow$	$2I^-(s)$	+.535
$Fe^{3+} + e^- \rightarrow$	$Fe^{2+}(aq)$	+.771
$Ag^+ + e^- \rightarrow$	$Ag(s)$	
	$+.799\,O_2(g)+ 4H^+ \,+$	
$4e^- \rightarrow \quad 2\,H_2O(l)$	$+1.23\,Cl_2(g)+ 2e^- \rightarrow$	
	$2Cl^-(g)$	
	$+1.36$	

but since the difference V_{soln} V_{Pt} is by definition zero for the hydrogen half-cell, the cell potential we measure corresponds to

$E_{cell} = V_M - V_{soln}$

which is just the potential of the half-cell

$M^{2+} + 2e^- \longrightarrow M(s)$
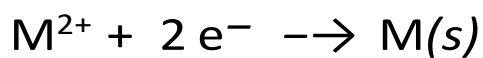
By carrying out a series of measurements in which various other systems are substituted for the M^{2+}/M couple, we can construct a table in which the various half-cell reactions are arranged in order of their potentials. The conventional way of doing this, as shown in Table 3, is to write the half-cell reactions as re- ductions, and to place them in the order of increasing (more positive) potentials. The resulting values are known as the *standard half-cell potentials*, denoted by $E°$.

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2.9 Question Bank

Answer the following in detail (2,3,5 marks Combined)

1) Write a short note on electrochemical cell with diagram.

2) Differentiate electrochemical and electrolytic cell.

3) Define EMF and note down application of the following.

4) Write a short note on primary reference electrode along with diagram.

5) Draw a diagram of standard calomel electrode and give redox reaction for SCE.

6) Construct the cell by using following potential value and find standard cell potential.

$E°_{Sn+2/Sn}$ = -0.136 V

$E°_{Cu+2/Cu}$ = 0.34 V

Have a happy Learning!