

ELECTRO CHEMISTRY

TOPIC-2

Electrolytic and redox reactions

VERY SHORT ANSWER QUESTIONS

1. What is electrochemical cell ?

Ans: It is a device in which a redox reaction takes place indirectly and the decrease in potential energy of the reaction appears as electrical energy.

2. What is cell notation?

Ans:

- Cell notation in chemistry is a shorthand way of expressing a certain reaction in an electrochemical cell.
- The cell anode and cathode (half-cells) are separated by two bars or slashes representing a salt bridge.
- The anode on the left and cathode on the right.
- Individual solid, liquid or aqueous phases within each half-cell are separated by a single bar.
- Concentrations of dissolved species, in each phase written in parentheses and the state of each phase (usually s (solid), l (liquid), g (gas) or aq. (aqueous solution)) is included in a subscript after the species name.

Example: For a Daniel cell

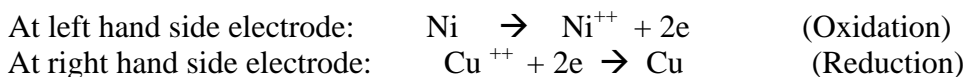


3. Write Cell reactions for

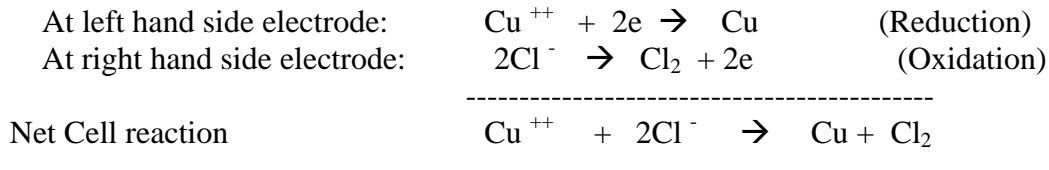
- a) $\text{Ni} / \text{Ni}^{++} // \text{Cu}^{++} / \text{Cu}$
 b) $\text{Cu}^{++} / \text{Cu} // \text{Cl}^- / \frac{1}{2} \text{Cl}_2 \text{.....?}$

Ans:

a) $\text{Ni} / \text{Ni}^{++} // \text{Cu}^{++} / \text{Cu}$:



b) $\text{Cu}^{++} / \text{Cu} // \text{Cl}^- / \frac{1}{2} \text{Cl}_2 :$



4. What is electrolytic cell?

Ans: Electrolytic cell: It is a device in which electrolysis (chemical reaction involving oxidation and reduction) is carried out by using electricity or in which conversion of electrical energy into chemical energy is done.

5. What is electrochemical cell?

Ans: Electrochemical cell is a system or arrangement in which two electrodes are fitted in the same electrolyte or in two different electrolytes which are joined by a salt bridge. Electrochemical cells are of two types:

- (a) Electrolytic cell
- (b) Galvanic or voltaic cell

6. What is Galvanic cell?

Ans: Galvanic or voltaic cell: It is a device in which a redox reaction is used to convert chemical energy into electrical energy, i.e., electricity can be obtained with the help of oxidation and reduction reaction. The chemical reaction responsible for production of electricity takes place in two separate compartments. Each compartment consists of a suitable electrolyte solution and a metallic conductor. The metallic conductor acts as an electrode. The compartments containing the electrode and the solution of the electrolyte are called half-cells. When the two compartments are connected by a salt bridge and electrodes are joined by a wire through galvanometer the electricity begins to flow. This is the simple form of voltaic cell.

7. What is salt Bridge?

Ans: Salt Bridge is usually an inverted U-tube filled with concentrated solution of inert electrolytes. An inert electrolyte is one whose ions are neither involved in any electrochemical change nor do they react chemically with the electrolytes in the two half-cells. Generally salts like KCl, KNO_3 , NH_4NO_3 , etc., are used. For the preparation of salt bridge, gelatin or agar-agar is dissolved in a hot concentrated aqueous solution of an inert electrolyte and the solution thus formed is filled in the U-tube. On cooling the solution sets in the form of a gel in the U-tube. The ends of the U-tube are plugged with cotton wool as to minimize diffusion effects. This is used as a salt bridge.

8. What is the Significance of Salt Bridge?

Ans: Significance of salt bridge: The following are the functions of the salt bridge:

- (i) It connects the solutions of two half-cells and completes the cell circuit.
- (ii) It prevents transference or diffusion of the solutions from one half-cell to the other.
- (iii) It keeps the solutions in two half-cells electrically neutral. In anodic half cell, positive ions pass into the solution and there shall be accumulation of extra positive charge in the solution around the anode which will prevent the flow of electrons from anode. This does not happen because negative ions are provided by salt bridge. Similarly, in cathodic half-cell negative ions will accumulate around cathode due to deposition of positive ions by reduction. To neutralize these negative ions, sufficient number of positive ions is provided by salt bridge. Thus, salt bridge maintains electrical neutrality.
- (iv) It prevents liquid-liquid junction-potential, i.e., the potential difference which arises between two solutions when in contact with each other.

A broken vertical line or two parallel vertical lines in a cell reaction indicates the salt bridge.



Salt bridge can be replaced by a porous partition which allows the migration of ions without allowing the solutions to intermix.

9. What is Standard Electrode potential?

Ans: **STANDARD ELECTRODE POTENTIAL:** In order to compare the electrode potentials of various electrodes, it is necessary to specify the concentration of the ions present in solution in which the electrode is dipped and the temperature of the half-cell. The potential difference developed between metal electrode and the solution of its ions of unit molarity (1M) at 25°C (298 K) is called standard electrode potential.

According to the IUPAC convention, the reduction potential alone be called as the electrode potential (E^0), i.e., the given value of electrode potential be regarded as reduction potential unless it is specifically mentioned that it is oxidation potential. Standard reduction potential of an electrode means that reduction reaction is taking place at the electrode. If the reaction is reversed and written as oxidation reaction, the numerical value of electrode potential will remain same but the sign of standard potential will have to be reversed. Thus

$$\text{Standard reduction potential} = - (\text{Standard oxidation potential})$$

or
$$\text{Standard oxidation potential} = - (\text{Standard reduction potential})$$

SHORT ANSWER QUESTIONS

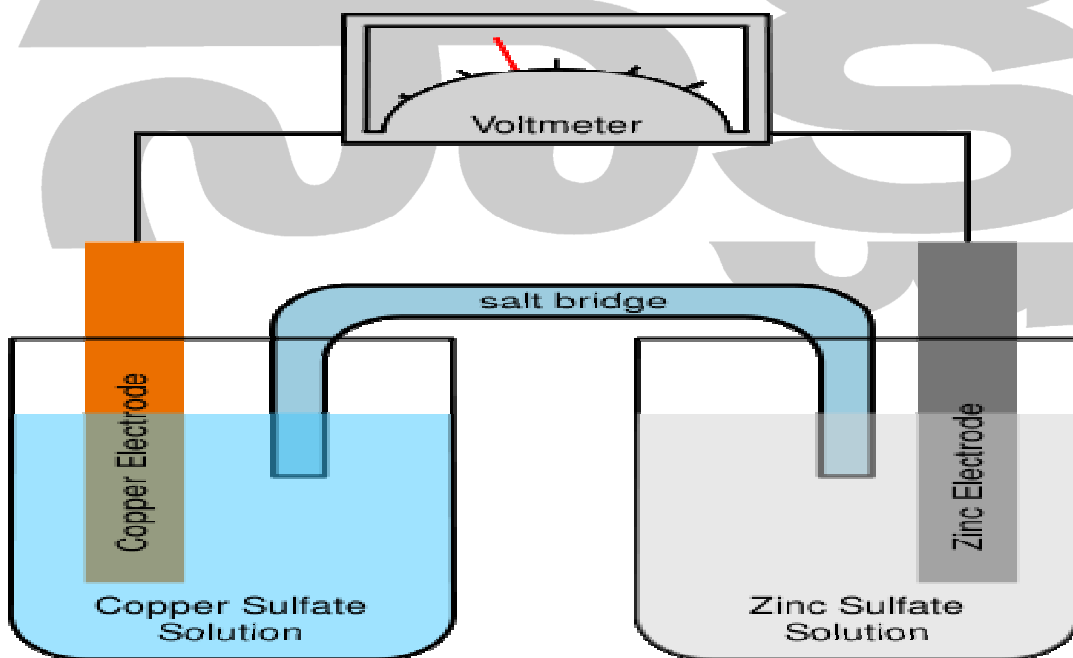
1. What are galvanic cells/ give two examples?

Ans:

Galvanic or voltaic cell: It is a device in which a redox reaction is used to convert chemical energy into electrical energy, i.e., electricity can be obtained with the help of oxidation and reduction reaction. The chemical reaction responsible for production of electricity takes place in two separate compartments. Each compartment consists of a suitable electrolyte solution and a metallic conductor. The metallic conductor acts as an electrode. The compartments containing the electrode and the solution of the electrolyte are called half-cells. When the two compartments are connected by a salt bridge and electrodes are joined by a wire through galvanometer the electricity begins to flow. This is the simple form of voltaic cell.

Examples are 1) Daniel Cell 2) Voltaic Cell\

1) Daniel cell



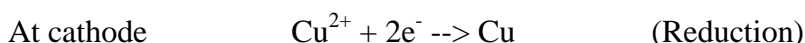
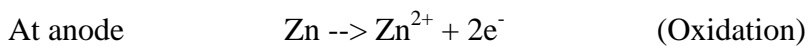
The Daniel cell consists of Zn rod dipped in $ZnSO_4$ solution and Cu rod dipped in $CuSO_4$ solutions of desired concentrations and the two electrodes are connected externally to a volt meter and a load. The containers are connected by a suitable salt bridge. Thus Daniel cell is formed It gives an emf of 1.1 V.

The galvanic cell, as the one shown in the figure, are conventionally described using the following notation:



(anode)-----(cathode)

The Half reaction of Daniel Cell is shown below. Reduction potential of Zn is less than copper, hence Zn acts as anode and copper as cathode.



2. What is Single electrode potential and write Nernst equation for single electrode potentials?

Ans: When a metal is placed in a solution of its ions, the metal acquires either a positive or negative charge with respect to the solution. On account of this, a definite potential difference is developed between the metal and the solution. This potential difference is called electrode potential or single electrode potential.

For example, when a plate of zinc is placed in a solution having Zn^{2+} ions, it becomes negatively charged with respect to solution and thus a potential difference is set up between zinc plate and the solution. This potential difference is termed the electrode potential of zinc. Similarly, when copper is placed in a solution having Cu^{2+} ions, it becomes positively charged with respect to solution. A potential difference is set up between the copper plate and the solution. The potential difference thus developed is termed as electrode potential of copper. The potential difference is established due to the formation of electrical double layer at the

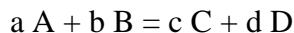


The potential difference developed between metal electrode and the solution of its ions of unit molarity (1M) at 25°C (298 K) is called standard electrode potential. According to the IUPAC convention, the reduction potential alone be called as the electrode potential (E°), i.e., the given value of electrode potential be regarded as reduction potential unless it is specifically mentioned that it is oxidation potential.

The General Nernst Equation

The general Nernst equation correlates the Gibb's Free Energy ΔG and the EMF of a chemical system known as the galvanic cell.

For the reaction,



Reaction Quotient 'Q; is given by,

$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

It has been shown and we know that,

$$\Delta G = \Delta G^\circ + R T \ln Q$$

and

$$\Delta G = - n F E. \text{ and } \Delta G^\circ = - n F E^\circ$$

Therefore,

$$- n F E = - n F E^\circ + R T \ln Q$$

where, R = gas constant (8.314 J mol⁻¹ K⁻¹),

T = temperature (in K),

Q = reaction quotient

and, F = Faraday constant (96,500 C)

$$E = E^\circ - \frac{R T}{n F} \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

This is known as the *Nernst* equation.

The equation allows us to calculate the cell potential of any galvanic cell for any concentrations. Some examples are given in the next section to illustrate its application.

Substituting all the values in the equation (R , T and F) the equation for metallic electrode becomes

$$E = E^\circ - \frac{0.059}{n} \log c$$

Where,

C= concentration of electrolyte solution

For non metallic electrode is given by

$$E = E^\circ - \frac{0.059}{n} \log \frac{\text{(Oxidised form)}}{\text{(Reduced form)}}$$

This equation is useful in calculation of electrode potentials of metal and non-metal electrodes.

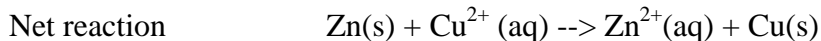
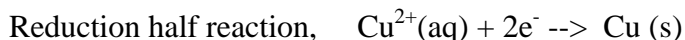
LONG ANSWER QUESTIONS

1. **What are galvanic cells? How are these represented? What is cell reaction and how is it written? Illustrate your answer?**

Ans: **Galvanic or voltaic cell:** It is a device in which a redox reaction is used to convert chemical energy into electrical energy, i.e., electricity can be obtained with the help of oxidation and reduction reaction. The chemical reaction responsible for production of electricity takes place in two separate compartments. Each compartment consists of a suitable electrolyte solution and a metallic conductor. The metallic conductor acts as an electrode. The compartments containing the electrode and the solution of the electrolyte are called half-cells. When the two compartments are connected by a salt bridge and electrodes are joined by a wire through galvanometer the electricity begins to flow. This is the simple form of voltaic cell.

Daniell Cell: Chemical energy is converted into electrical energy.

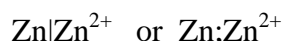
The net reaction is the sum of two half-cell reactions. The reaction in Daniel cell can be represented as



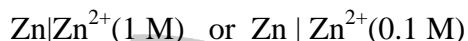
REPRESENTATION OF AN ELECTROCHEMICAL CELL (GALVANIC CELL)

The following universally accepted conventions are followed in representing an electrochemical cell:

- (i) The anode (negative electrode) is written on the left hand side and cathode (positive electrode) on the right hand side.
- (ii) A vertical line or semicolon (;) indicates a contact between two phases. The anode of the cell is represented by writing metal first and then the metal ion present in the electrolytic solution. Both are separated by a vertical line or a semicolon. For example,



The molar concentration or activity of the solution is written in brackets after the formula of the ion. For example:



- (iii) The cathode of the cell is represented by writing the cation of the electrolyte first and then metal. Both are separated by a vertical line or semicolon. For example,



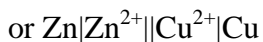
- (iv) The salt bridge which separates the two half-cells is indicated by two parallel vertical lines.
- (v) Sometimes negative and positive signs are also put on the electrodes.

The Daniell cell can be represented as:



Anode Salt bridge Cathode

Oxidation half-cell Reduction half-cell



2. What is Nernst equation? Calculate the EMF of the galvanic cell?

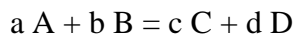


$$E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.766\text{V}$$

$$E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} = + 0.327 \text{ V}$$

Ans: The general Nernst equation correlates the Gibb's Free Energy ΔG and the EMF of a chemical system known as the galvanic cell.

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It has been shown and we know that,

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This is known as the *Nernst* equation.

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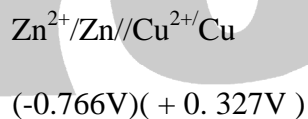
For non metallic electrode is given by

$$E = E^\circ - \frac{0.059}{n} \log \frac{\text{(Oxidised form)}}{\text{(Reduced form)}}$$

This equation is useful in calculation of electrode potentials of metal and non-metal electrodes.

$$E^\circ_{\text{zn}^{2+}/\text{zn}} = E^\circ + \frac{0.059}{2} \log (1.0) = 0.766 + 0 = -0.766\text{V}$$

$$E^\circ_{\text{cu}^{2+}/\text{cu}} = E^\circ + \frac{0.059}{2} \log (1.0) = +0.327 + 0 = +0.327\text{V}$$



$$\text{EMF of galvanic cell} = E_{\text{cell}} = E_{\text{cu}^{2+}/\text{cu}} - E_{\text{zn}^{2+}/\text{zn}} = 0.327 - (-0.766)$$

$$\therefore E_{\text{cell}} = 1.093 \text{ V}$$