Section–II (Electrochemical Cell)

3. Electrochemical Cell :

An electrochemical cell is a system consisting of electrodes that dip into an electrolyte and in which a chemical reaction either uses or generates an electric current.

A voltaic or galvanic cell is an electrochemical cell in which a spontaneous reaction generates an electric current.

A voltaic cell consists of two half-cells that are electrically connected. Each half cell is the portion of an electrochemical cell in which a half-reaction take place.

A simple half-cell can be made from a metal strip that dips into a solution of its metal ion. An example is the zinc-zinc ion half-cell (often called simply a zinc electrode), which consists of a zinc metal strip dipping into a solution of a zinc salt. Another simple half-cell consists of a copper metal strip dipping into a solution of a copper salt (copper electrode).

In a voltaic cell, two half-cells are connected in such a way that electrons flow from one metal electrode to another through an external circuit, and ions flow from one half-cell to another through an internal cell connection. Figure given below illustrates an atomic view of a voltaic cell consisting of a zinc electrode and a copper electrode. As long as there is an external circuit, electrons can flow through it from one electrode to another. Because zinc tends to lose electrons more readily than copper, zinc atoms in the zinc electrode lose electrons to produce zinc ions. These electrons flow through the external circuit to the copper electrode, where they react with the copper ions to produce copper metal, and an electric current flows through the external circuit.

The two half-cells must be connected internally to allow ions to flow between them. As zinc ions continue to be produced, the zinc ion solution begins to build up a positive charge. Similarly, as copper ions plate out as copper, the solution builds up a negative charge. The half cell reactions will stop unless positive ions can move from the zinc half-cell to the copper half cell, and negative ions from the copper half-cell can move to the zinc half-cell. It is necessary that these ion flow occur without mixing of the zinc ion and copper ion solutions. If copper ion come in contact with the zinc metal, for example, direct reaction would occur without an electric current being generated . The voltage would drop, and the battery would run down quickly.
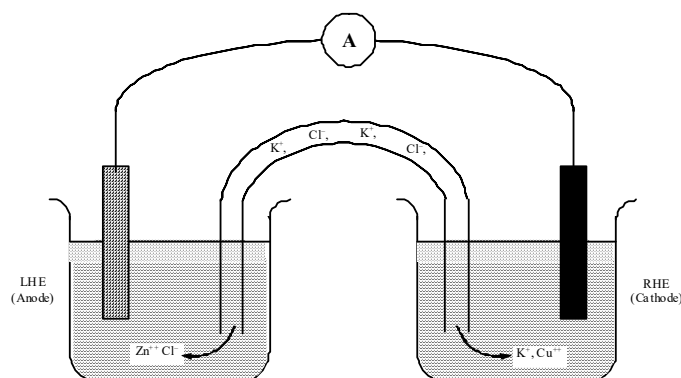

The two half-cells of a voltaic cell are connected by a salt bridge. A salt bridge is a tube of an electrolyte in a gel that is connected to the two half-cells of a voltaic cell; the salt bridge allows the flow of ions but prevents the mixing of the different solutions that would allow direct reaction of the cell reactants. The half-cells are connected externally so that an electric current flows.

The two half-cell reactions, as noted earlier, are

$$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^- \qquad \text{(oxidation half-reaction)}$$

$$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)} \qquad \text{(reduction half-reaction)}$$

The first half-reaction, in which a species loses electrons, is the oxidation half-reaction. The electrode at which oxidation occurs is called the anode. The second half-reaction which a species gains electrons, is the reduction half-reaction. The electrode at which reduction occurs is called the cathode. These definitions of anode and cathode hold for all electrochemical cells, including electrolytic cells.

Note that the sum of the two half-reaction

$$Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$$
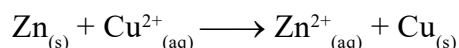
The net reaction that occurs in the voltaic cell, it is called the cell reaction.

Once you know which electrode is the anode and which is the cathode, you can determine the direction of electron flow in the external portion of the circuit. Electrons are given up by the anode (from the oxidation half-reaction) and thus flow from it, whereas electrons are used up by the cathode (by the reduction half-reaction) and so flow into this electrode. The anode in a voltaic cell has a negative sign, because electrons flow from it. The cathode in a voltaic cell has a positive sign.

Note :1.   The salt-bridge contains solution of strong ionic salts like $NaCl$, $NaNO_3$, KNO_3, KCl etc., which is soaked in a colloidal solution of agar-agar gel which permits the movement of ions of salts only.

2.   It maintains the electrical neutrality of the solutions in the two half-cells. In the absence of salt bridge, a reverse potential difference is set up in the two half-cells which results in breaking the continuous supply of voltage.
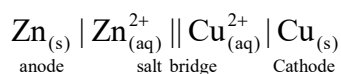
Cell Notation :

The efficiency of a cell depends on the tendency of LHE to lose electrons to RHE and the ability of RHE to receive electrons. Cell efficiency is measured in terms of emf (electromotive force), which is the difference in potentials of two electrodes due to which electrons flow from anode to cathode. EMF value of a cell is constant for given concentration of electrolyte, temperature and the pressure (in case of gases). Therefore, it depends on concentration, temperature and pressure.

EMF of a cell is measured in terms of the difference in electric potential (electrical pressure) between anode and cathode. Its unit is V(volt). The potential of half-cell is known as electrode potential, which is the tendency of an electrode to get oxidized or reduced. Thus, tendency to get oxidized is called oxidation potential and the tendency to get reduced is called reduction potential.

Cell Notation :   A cell can be represented as :
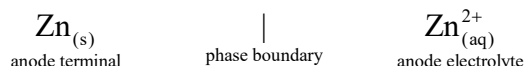LHE (Anode) $\|$ RHE (Cathode)

The anode or oxidation half-cell is always written on the left and the cathode or reduction half-cell is written on the right. The two electrodes are electrically connected by means of a salt bridge shown by two vertical bars.

$$\underset{\text{anode}}{Zn_{(s)}} \mid Zn^{2+}_{(aq)} \underset{\text{salt bridge}}{\|} Cu^{2+}_{(aq)} \mid \underset{\text{Cathode}}{Cu_{(s)}}$$

The half-cell which has higher reduction potential, acts as cathode and the electrode with lower reduction potential or higher oxidation potential acts as anode.

The cell terminals are at the extreme ends in this cell notation, and a single vertical bar indicates a phase boundary - say between a solid terminal and the electrode solution. For the anode of the same cell, you have

$$\underset{\text{anode terminal}}{Zn_{(s)}} \quad \underset{\text{phase boundary}}{|} \quad \underset{\text{anode electrolyte}}{Zn^{2+}_{(aq)}}$$

When the half-reaction involves a gas, an inert material such as platinum serves as a terminal and as an electrode surface on which the half-reaction occurs. The platinum catalyzes the half-reaction but otherwise is not involved in it. Hydrogen bubbles over a platinum plate that is immersed in an acidic solution. The cathode half-reaction is

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

The notation for the hydrogen electrode, written as a cathode, is

$$H^+_{(aq)} \,|\, H_{2(g)} \,|\, Pt \ \text{ or } H^+_{(aq)} \,|\, H_{2(g)}, \ Pt \qquad \text{or} \qquad H^+_{(aq)} \,|\, Pt \ H_2$$
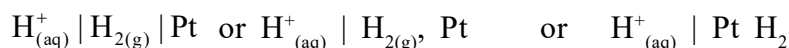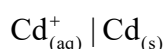
To write such an electrode as an anode, you simply reverse the notation:

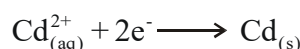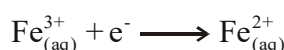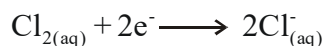$$Pt \,|\, H_{2(g)} \,|\, H^+_{(g)}$$
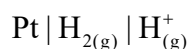
Here are several additional examples of this notation for electrodes (written as cathodes). A comma separates ions present in the same solution. We will write the cathode with oxidized species before reduced species, in the same order as in the half-reaction.

Cathode	Cathode Reaction
$Cl_{2(g)} \,|\, Cl^-_{(aq)} \,|\, Pt$	$Cl_{2(aq)} + 2e^- \longrightarrow 2Cl^-_{(aq)}$
$Fe^{3+}_{(aq)}, \ Fe^{2+}_{(aq)} \,|\, Pt$	$Fe^{3+}_{(aq)} + e^- \longrightarrow Fe^{2+}_{(aq)}$
$Cd^+_{(aq)} \,|\, Cd_{(s)}$	$Cd^{2+}_{(aq)} + 2e^- \longrightarrow Cd_{(s)}$
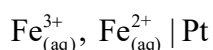
You can write the overall cell reaction from the cell notation by first writing the appropriate half-cell reactions, multiplying as necessary, and then summing so that the electrons cancel.
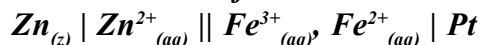
Illustration 8.

Writing the cell Reaction from the Cell Notation
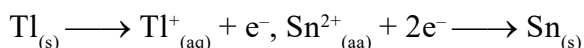
(a) *Write the cell reaction for the voltaic cell*

$$Tl_{(s)} \,|\, Tl^+_{(aq)} \,||\, Sn^2_{(aq)} \,|\, Sn_{(s)}$$

(b) *Write the cell reaction for the voltaic cell*

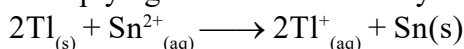$$Zn_{(z)} \,|\, Zn^{2+}_{(aq)} \,||\, Fe^{3+}_{(aq)}, \ Fe^{2+}_{(aq)} \,|\, Pt$$

Problem strategy: The cell notation gives the species involved in each half-reaction. Complete the balance each half-reaction, then multiply by factors so that when you add the half-reactions, the electrons cancel. The result is the cell reaction.
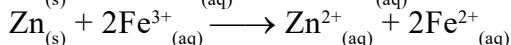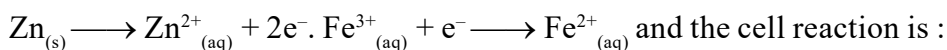
Solution :

(a) The half-cell reactions are

$$Tl_{(s)} \longrightarrow Tl^+_{(aq)} + e^-, \ Sn^{2+}_{(aa)} + 2e^- \longrightarrow Sn_{(s)}$$

Multiplying the anode reaction by 2 and then summing the half-cell reactions gives

$$2Tl_{(s)} + Sn^{2+}_{(aq)} \longrightarrow 2Tl^+_{(aq)} + Sn(s)$$

(b) The half cell reactions are

$$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-. \ Fe^{3+}_{(aq)} + e^- \longrightarrow Fe^{2+}_{(aq)} \text{ and the cell reaction is :}$$
$$Zn_{(s)} + 2Fe^{3+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + 2Fe^{2+}_{(aq)}$$

To fully specify the voltaic cell, it is necessary to give the concentrations of solutions or ions and the pressure of gases. In the cell notation, these are written within parentheses for each species.

For example : $Zn_{(s)} \mid Zn^{2+} (1.0 \text{ M}) \parallel H^+ (1.0 \text{ M}) \mid H_2 (1.0 \text{ atm}) \mid Pt$

Nature of Electrodes :

The various types of electrodes used and the chemical reactions which take place are:

Gas Electrodes : Here the inert electrode is present in contact with the gas at 1 atm pressure (unless specified) and its ions in the solution e.g. Hydrogen gas electrode, etc. It is denoted as :

$H^+ \mid H_2$ (1 atm) $\mid$ Pt and the chemical reaction is $H^+ + e^- \longrightarrow \frac{1}{2} H_{2(g)}$.
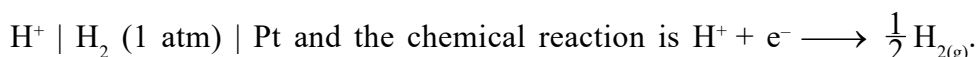
The nature of inert electrode should be such that, when the external voltage is changed even by small amount from the equilibrium value, the reaction will proceed one way or the other. Most suitable electrode is platinum with fine coat of platinum powder or platinum black.

Oxidation – Reduction Electrode : Here the inert electrode (generally platinum) is dipping in the solution which contains ions of species having two oxidation states, e.g. platinum electrode dipping in solution containing stannous and stannic. It is denoted as Sn^{4+}, $Sn^{2+} \mid Pt$ and chemical reaction is $Sn^{4+} + 2e^- \longrightarrow Sn^{2+}$. The solution can be a neutral species present in two oxidation stages e.g. H^+, Q, $QH_2 \mid Pt$.

Where QH_2 is the hydroquinone an Q is quinine. It is commonly it is commonly known as quinhydrone electrode. The chemical reaction is :
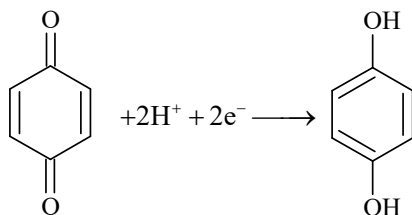
Meta-Metal Ion Electrode : Here the metal electrode dips in a solution containing its ions and the metal electrode takes part in chemical reaction. Reactivity of the metal should be intermediate otherwise the reactive metals will react with water and cannot act as electrodes. The example is the copper electrode dipping in copper sulphate solution. It is denoted as $M^{n+} \mid M$ in general and in particular Cu^{2+} (c) $\mid$ Cu and c is the concentration. The chemical reaction is $Cu^{2+} + 2e^- \longrightarrow Cu_{(s)}$.
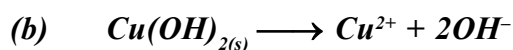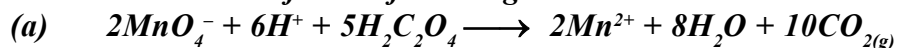
Metal-Insoluble Salt Anion Electrode : Here the metal electrode is in contact with its ions (generally the anion). The most common is the calomel electrode. This consists of mercury, mercurous chloride (Hg_2Cl_2) and saturated solution of KCl. But the concentration of Cl^- ions can be different. The chemical reaction taking place is :
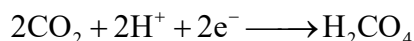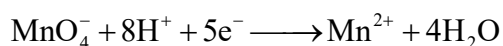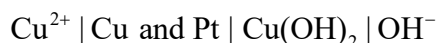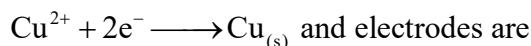
$$\frac{1}{2} Hg_2Cl_{2(s)} + e^- \longrightarrow Hg_{(s)} + Cl^- \quad \text{and} \quad Cl^- \mid HgCl_2 \mid Hg \mid Pt$$
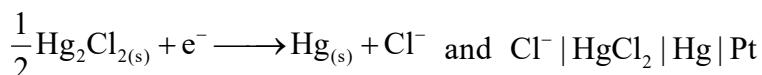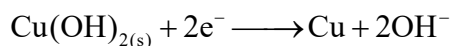
Similarly lead amalgam lead sulphate electrode is depicted as $SO_4^{2-} \mid PbSO_4 \mid Pb(Hg)$ and the chemical reaction is $PbSO_{4(s)} + 2e^- \longrightarrow Pb_{(s)} + SO_4^{2-}$

Illustration 9.

Write cell electrode for the following reactions :

(a) $2MnO_4^- + 6H^+ + 5H_2C_2O_4 \longrightarrow 2Mn^{2+} + 8H_2O + 10CO_{2(g)}$

(b) $Cu(OH)_{2(s)} \longrightarrow Cu^{2+} + 2OH^-$

Solution :

(a)   Half-cell reactions are

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

$$2CO_2 + 2H^+ + 2e^- \longrightarrow H_2CO_4$$

$$MnO_4^-, Mn^{2+}, H^+ \mid Pt \text{ and } Pt \mid CO_2 \mid H^+$$

(b)   Half-cell reactions are

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

$$Cu^{2+} + 2e^- \longrightarrow Cu_{(s)} \text{ and electrodes are}$$

$$Cu^{2+} \mid Cu \text{ and } Pt \mid Cu(OH)_2 \mid OH^-$$

4. Standard Cell EMF and Standard Electrode Potential :

A cell emf is a measure of the driving force of the cell reaction. This reaction occurs in the cell as separate half-reactions: an oxidation half-reaction and a reduction half-reaction. The general forms of these half-reactions are

Reduced species $\longrightarrow$ oxidized species + ne⁻   (oxidation/anode)

Oxidized species + ne⁻ $\longrightarrow$ reduced species   (reduction/cathode)
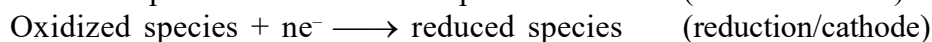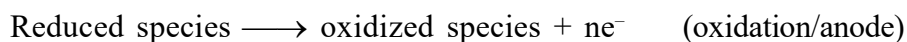
E_{cell} = oxidation potential + reduction potential

If you can construct a table of reduction potentials, you will have a list of strengths of oxidizing agents, in addition to having a way of calculating cell emf's.

You can look at an oxidation half-reaction as the reverse of a corresponding reduction half-reaction. The oxidation potential for an oxidation half-reaction equals to negative of the reduction potential for the reverse half-reaction(which is a reduction).

Oxidation potential for a half-reaction = reduction potential for the reverse half-reaction.

This means that in practice you need to tabulate only oxidation potential or reduction potentials. The choice, by convention, is to tabulate reduction potentials. We call these electrode potentials, and we denote them by the symbol E (without the subscript cell, as in E_{cell}).

$$Zn_{(s)} \mid Zn_{(aq)}^{2+} \parallel Cu_{(aq)}^{2+} \mid Cu_{(s)}$$
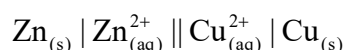
The half-reaction are : $Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$; $Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$

The first half-reaction is an oxidation. If you write E_{Zn} for the electrode potential corresponding to the reduction half-reaction $Zn^{2+}_{(aq)} \longrightarrow Zn_{(s)}$, then $-E_{Zn}$ is the potential for the oxidation half-reaction $Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$. The copper half-reaction is a reduction. Write E_{Cu} for the electrode potential.

The cell emf is the sum of the potentials for the reduction and oxidation half-reactions. For the cell we have been describing, the emf is the sum of the reduction potential (electrode potential) for the copper half-cell and the oxidation potential (negative of the electrode potential) for the zinc half-cell.

$$E_{cell} = E_{Cu} + (-E_{Zn}) = E_{Cu} - E_{Zn}$$

Note that the cell emf equals the difference between the two electrode potentials. You can think of the electrode potential as the electric potential on the electrode, and you obtain the cell emf as a potential difference in which you subtract the anode potential from the cathode potential.

$$E_{cell} = E_{cathode} - E_{anode}$$

The electrode potential is an intensive property. This means that its value is independent of the amount of species in the reaction. Thus, the electrode potential for the half-reaction.

$$2\ Cu^{2+}_{(aq)} + 4e^- \longrightarrow 2\ Cu_{(s)} \text{ is the same as for } Cu^{2+}_{(aq)} \longrightarrow Cu_{(s)}$$
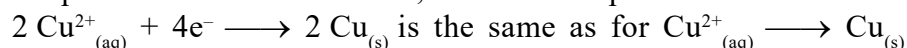
Note :1. If E_{cell} is positive, then the cell reaction is spontaneous

2. If in a cell reaction, more than one electron is involved, the standard electrode potential does not change but the standard free energy of the chemical reaction will be multiple of FE^0, i.e. then actual value of n should be used.

Tabulating Standard Electrode Potential : The emf of a voltaic cell depends on the concentrations of substances and the temperature of the cell. For purposes of tabulating electrochemical data, it is usual to choose thermodynamic standard-state conditions for voltaic cells. The standard emf, E^0_{cell}, is the emf of a voltaic cell operating under standard-state conditions (solute concentrations are each 1 M, gas pressures are each 1 atm, and the temperature has a specified value – usually 25°C). Note the superscript degree sign (0), which signifies standard-state conditions.

If you can derive a table of electrode potentials, you can calculate cell emf's from them. This provides a great advantage over tabulating cell emf's. From a small table of electrode potentials, you can obtain the emf's of all the cells that you could construct from pairs of electrodes. For instance, a table of 40 electrode potentials would give the emf's of nearly 800 voltaic cells.

However, it is not possible to measure the potential of a single electrode; only emf's of cells can be measured. What you can do is measure the emf's of cells constructed from various electrodes connected in turn to one particular electrode, which you choose as a reference. You arbitrarily assign this reference electrode a potential equal to zero and obtain the potentials for the other electrodes by measuring the emf's. By convention, the reference chosen for comparing electrode potentials is the standard hydrogen electrode.

The standard electrode potential, E^0, is the electrode potential when the concentrations of solutes are 1 M, the gas pressures are 1 atm, and the temperature has a specified value (usually 25°C). The superscript degree sign (0) signifies standard state conditions.

To understand how standard electrode potentials are obtained, look at how you would find the standard electrode potential. E^0, for the zinc electrode. You connect a standard zinc electrode to a standard hydrogen electrode. When you measure the emf of the cell with a voltmeter, you obtain 0.76V, with the zinc electrode acting as the anode.

Now write the cell emf in terms of the electrode potentials.

The cell is $Zn_{(s)} | Zn^{2+}_{(aq)} \| H^+_{(aq)} | H_{2(g)} |$ Pt and the half-reactions with corresponding half-cell potentials (oxidation or reduction potentials) are : $Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$; $-E^0_{Zn}$

The cell emf is the sum of the half-cell potentials. $E_{cell} = E^0_{H_2} + (-E^0_{Zn})$

Substitute 0.76V for the cell emf and 0.00V for the standard hydrogen electrode potential. This gives $E^0_{Zn} = -0.76V$.

Proceeding in this way, you can obtain the electrode potential for a series of half-cell reactions. Table given below lists standard electrode potentials for selected half-cells at 25°C.

| Cathode (Reduction) Half Reaction	Standard Potential E(V)
$Li^+_{(aq)} + e^- \longrightarrow Li_{(s)}$	-3.04
$Na^+_{(aq)} + e^- \longrightarrow Na_{(s)}$	-2.71
$Mg^{2+}_{(aq)} + 2e^- \longrightarrow Mg_{(s)}$	-2.38
$Al^{3+}_{(aq)} + 3e^- \longrightarrow Al_{(s)}$	-1.66
$2H_2O_{(l)} + 2e^- \longrightarrow H_{2(g)} + 2OH^-_{(aq)}$	-0.83
$Zn^{2+}_{(aq)} + 2e^- \longrightarrow Zn_{(s)}$	-0.76
$Cr^{3+}_{(aq)} + 3e^- \longrightarrow Cr_{(s)}$	-0.74
$Fe^{2+}_{(aq)} + 2e^- \longrightarrow Fe_{(s)}$	-0.41
$Cd^{2+}_{(aq)} + 2e^- \longrightarrow Cd_{(s)}$	-0.40
$Ni^{2+}_{(aq)} + 2e^- \longrightarrow Ni_{(s)}$	-0.23
$Sn^{2+}_{(aq)} + 2e^- \longrightarrow Sn_{(s)}$	-0.14
$Pb^{2+}_{(aq)} + 2e^- \longrightarrow Pb_{(s)}$	-0.13
$Fe^{2+}_{(aq)} + 2e^- \longrightarrow Fe_{(s)}$	-0.04
$2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)}$	0.00
$Sn^{4+}_{(aq)} + 2e^- \longrightarrow Sn^{2+}_{(aq)}$	0.15
$Cu^{2+}_{(aq)} + e^- \longrightarrow Cu^+_{(aq)}$	0.16
$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$	0.34
$IO^-_{(aq)} + H_2O_{(l)} + 2e^- \longrightarrow I^-_{(aq)} + 2OH^-_{(aq)}$	0.49
$Cu^+_{(aq)} + e^- \longrightarrow Cu_{(s)}$	0.52
$I_{2(s)} + 2e^- \longrightarrow 2I^-_{(aq)}$	0.54
$Fe^{3+}_{(aq)} + e^- \longrightarrow Fe^{2+}_{(aq)}$	0.77
$Hg^{2+}_{2(aq)} + 2e^- \longrightarrow Hg_{(aq)}$	0.80
$Ag^{2+}_{(aq)} + 2e^- \longrightarrow 2Ag_{(l)}$	0.80
$Ag^+_{(aq)} + e^- \longrightarrow Ag_{(l)}$	0.85
$ClO^-_{(aq)} + H_2O_{(l)} + 2e^- \longrightarrow Cl^-_{(aq)} + 2OH^-_{(aq)}$	0.90
$Hg^{2+}_{(aq)} + 2e^- \longrightarrow Hg_{(aq)}$	0.90
$NO^{3-}_{(aq)} + 4H^+_{(aq)} + 3e^- \longrightarrow NO_{(g)} + 2H_2O_{(l)}$	0.96
$Br_{2(l)} + 2e^- \longrightarrow 2Br^-_{(aq)}$	1.07
$O_{2(g)} + 4H^+_{(aq)} + 4e^- \longrightarrow 2H_2O_{(aq)}$	1.23
$Cr_2O^2_{7(aq)} + 8H^+_{(aq)} + 6e^- \longrightarrow 2Cr^{3+}_{(aq)} + 7H_2O_{(l)}$	1.33
$Cl_{2(g)} + 2e^- \longrightarrow 2Cl^-_{(aq)}$	1.36
$MnO^-_{4(aq)} + 8H^+_{(aq)} + 6e^- \longrightarrow Mn^{2+}_{(aq)} + 4H_2O_{(l)}$	1.49
$H_2O_{2(aq)} + 2H^+_{(aq)} + 2e^- \longrightarrow 2H_2O_{(l)}$	1.78
$S_2O^{2-}_{6(aq)} + 2e^- \longrightarrow 2SO^{2-}_{4(aq)}$	2.01
$F_{2(g)} + 2e^- \longrightarrow 2F^-_{(aq)}$	2.87

Strength of Oxidising and Reducing Agents :

Standard electrode potentials are useful in determining the strengths of oxidizing and reducing agents under standard-state conditions. Because electrode potentials are reduction potentials those reduction half-reactions in the table with the larger (that is more positive) electrode potentials have the greater tendency to go left to right as written. A reduction half-reaction has the general form.

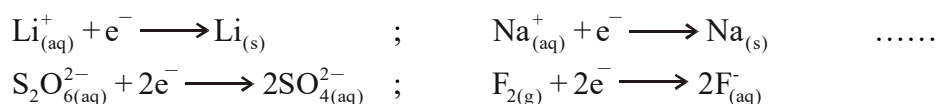Oxidised species + ne⁻ $\longrightarrow$ reduced species.
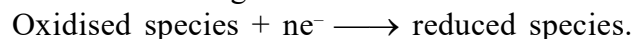
The oxidized species acts as an oxidizing agent. Consequently, the strongest oxidizing agents in a table of standard electrode potentials are the oxidized species corresponding to half-reactions with the largest (most positive) E^0 values.

Those reduction half-reactions with lower (that is, more negative) electrode potentials have a greater tendency to go right to left. That is,

Reduced species $\longrightarrow$ oxidized species + ne⁻
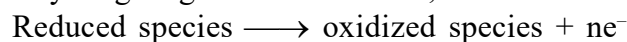
The reduced species acts as a reducing agent. Consequently, the strongest reducing agents in a table of standard electrode potentials are the reduced species corresponding to half-reactions with the smallest (most negative) E^0 values.

The first two and last two entries in the table are as follows :

$$Li^+_{(aq)} + e^- \longrightarrow Li_{(s)} \qquad ; \qquad Na^+_{(aq)} + e^- \longrightarrow Na_{(s)} \qquad \ldots\ldots$$

$$S_2O^{2-}_{6(aq)} + 2e^- \longrightarrow 2SO^{2-}_{4(aq)} \quad ; \qquad F_{2(g)} + 2e^- \longrightarrow 2F^-_{(aq)}$$

The strongest oxidizing agents are the species on the left side in the last two entries in the table. The strongest reducing agents are the species on the right side in the first two entries in the table.

Standard EMF of a cell (E^0)

E^0 = difference in potentials of two half-cells

E^0 = {standard oxidation potential of anode – standard oxidation potential of cathode}

$$E^0_{cell} = (E^0_{oxidation})_{anode} - (E^0_{oxidation})_{cathode}$$

OR

E^0 = {standard reduction potential of a cathode – standard reduction potential of anode}

$$E^0_{cell} = (E^0_{reduction})_{cathode} - (E^0_{reduction})_{anode}$$
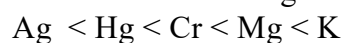
Example 10.

Electrode potential of the metals in their respective solution are provided. Arrange the metals in their increasing order of reducing power.
$K^+/K = -2.93V$, $Ag^+/Ag = +0.80V$, $Hg^+/Hg = +0.79V$, $Mg^{2+}/Mg = -2.37V$
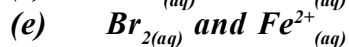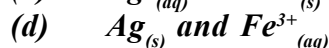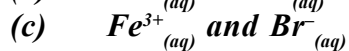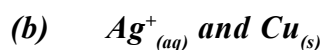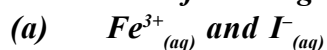*$Cr^{3+}/Cr = -0.74V$*

Solution :

We know that the reducing power of a metal depends upon its tendency to lose electrons. Thus lower the reduction potential, more the tendency to get oxidized and thus more will be the reducing power. Hence increasing order of reducing power is:

Ag < Hg < Cr < Mg < K

Example 11.

Using the standard electrode potentials predict the reaction, if any, that occurs between the following :

(a) $Fe^{3+}_{(aq)}$ and $I^-_{(aq)}$ (b) $Ag^+_{(aq)}$ and $Cu_{(s)}$

(c) $Fe^{3+}_{(aq)}$ and $Br^-_{(aq)}$ (d) $Ag_{(s)}$ and $Fe^{3+}_{(aq)}$
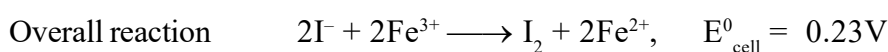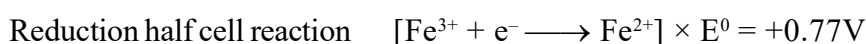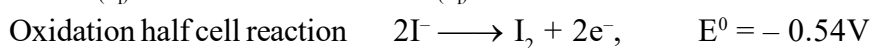
(e) $Br_{2(aq)}$ and $Fe^{2+}_{(aq)}$

Given : $E^0_{Fe^{3+}/Fe^{2+}} = +0.77V$, $E_{I_2/I^-} = +0.54V$ $E^0_{Ag^+/Ag} = +0.80V$, $E^0_{Cu^{2+}/Cu} = +0.34V$
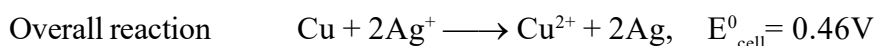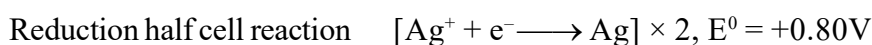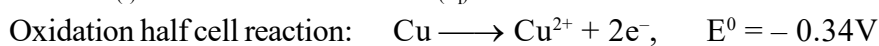
$E^0_{Br_2/Br^-} = +1.08V$

Solution :

(a) Here $I^-_{(aq)}$ loses electrons and $Fe^{3+}_{(aq)}$ gains electrons. Thus

Oxidation half cell reaction $2I^- \longrightarrow I_2 + 2e^-$, $E^0 = -0.54V$

Reduction half cell reaction $[Fe^{3+} + e^- \longrightarrow Fe^{2+}] \times E^0 = +0.77V$

_____

Overall reaction $2I^- + 2Fe^{3+} \longrightarrow I_2 + 2Fe^{2+}$, $E^0_{cell} = 0.23V$
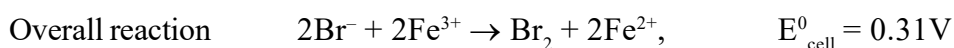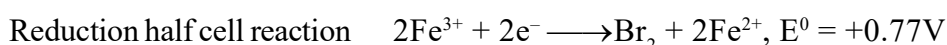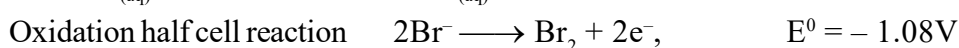
Since E^0_{cell} is +ve, the reaction is spontaneous i.e., the reaction does take place.

(b) Here $Cu_{(s)}$ loses electrons and $Ag^+_{(aq)}$ gains electrons. Thus
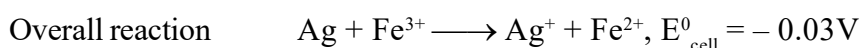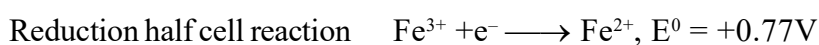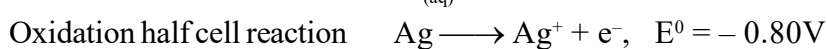
Oxidation half cell reaction: $Cu \longrightarrow Cu^{2+} + 2e^-$, $E^0 = -0.34V$

Reduction half cell reaction $[Ag^+ + e^- \longrightarrow Ag] \times 2$, $E^0 = +0.80V$

_____

Overall reaction $Cu + 2Ag^+ \longrightarrow Cu^{2+} + 2Ag$, $E^0_{cell} = 0.46V$

Since E^0_{cell} is +ve, the reaction is spontaneous

(c) Here $Br^-_{(aq)}$ loses electrons and $Fe^{3+}_{(aq)}$ gains electrons. Thus

Oxidation half cell reaction $2Br^- \longrightarrow Br_2 + 2e^-$, $E^0 = -1.08V$

Reduction half cell reaction $2Fe^{3+} + 2e^- \longrightarrow Br_2 + 2Fe^{2+}$, $E^0 = +0.77V$

_____

Overall reaction $2Br^- + 2Fe^{3+} \rightarrow Br_2 + 2Fe^{2+}$, $E^0_{cell} = 0.31V$

Since E^0_{cell} is –ve, the reaction is non-spontaneous, i.e., reaction does not take place.

(d) Here Ag loses electrons and $Fe^{3+}_{(aq)}$ gains electrons. Thus

Oxidation half cell reaction $Ag \longrightarrow Ag^+ + e^-$, $E^0 = -0.80V$

Reduction half cell reaction $Fe^{3+} + e^- \longrightarrow Fe^{2+}$, $E^0 = +0.77V$

_____

Overall reaction $Ag + Fe^{3+} \longrightarrow Ag^+ + Fe^{2+}$, $E^0_{cell} = -0.03V$

Since E^0_{cell} is –ve, the reaction is non-spontaneous, i.e., reaction does not take place.

(e) Here $Fe^{2+}_{(aq)}$ loses electrons and $Br_{2(aq)}$ gains electrons. Thus

Oxidation half cell reaction $2Fe^{2+} \longrightarrow 2Fe^{3+} + 2e^-$, $E^0 = -0.77$

Reduction half cell reaction $Br_2 + 2e^- \longrightarrow 2Br^-$, $E^0 = +1.08V$

_____

Overall reaction $2Fe^{2+} + Br_2 \rightarrow 2Fe^{3+} + 2Br^-$, $E^0_{cell} = +0.31V$
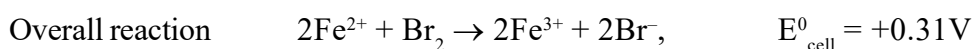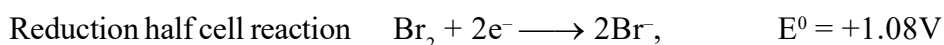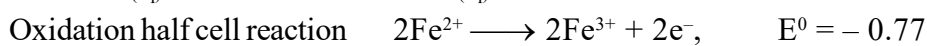
Since E^0_{cell} is +ve, the reaction is spontaneous, i.e., the reaction does not take place.

Example 12.

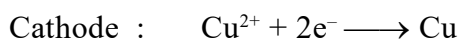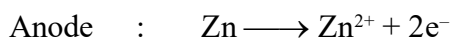   *Calculate the values for cell*

$$Zn \left| \begin{matrix} Zn^{2+}_{aq} \\ 1\,M \end{matrix} \right| \left| \begin{matrix} Cu^{2+}_{aq} \\ 1\,M \end{matrix} \right| Cu$$ *(i)*   *cell reaction and*   *(ii)*   *e.m.f. of cell*

    Given : $E^0_{Cu^{2+}/Cu} = +0.35V;\ E^0_{Zn^{2+}/Zn} = -0.76V$
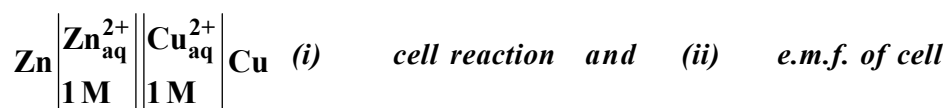
Solution :

(i) E^0_{OP} for $Cu/Cu^{2+} = -0.35V$

        E^0_{OP} for $Zn/Zn^{2+} = +0.76V$

        More is E^0_{OP}, more is tendency to show oxidation and thus Zn will oxidize and Cu^{2+} will reduce.

        Anode   : $Zn \longrightarrow Zn^{2+} + 2e^-$

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

        ———————————————

        Cell reaction $Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$

(ii)   Also , $E^0_{cell} = E^0_{OP_{Zn/Zn^{2+}}} + E^0_{RP_{Cu^{2+}/Cu}} = 0.76 + 0.35 = 1.11V$

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5. Dependence of emf of a Cell on Concentration :

The emf of a cell depends on the concentration of ions and on gas pressures. For that reason, cell emf's provide a way to measure ion concentration. The pH meter, for example, depends on the variation of cell emf with hydrogen ion concentration. You can relate cell emf's for various concentrations of ions and various gas pressures to standard electrode potentials by means of an equation first derived by the German Walther Nernst (1864 – 1941).

Nernst Equation

Recall that the free-energy change ,

    $\Delta G = \Delta G^o + RT\,l\,nQ$

Here Q is the thermodynamic reaction quotient. The reaction quotient has the form of the equilibrium constant, except that the concentrations and gas pressures are those that exist in a reaction mixture at a given instant. You can apply this equal to a voltaic cell. In that case, the concentrations and gas pressures are those that exist in the cell at a particular instant. If you substitute , $\Delta G = -nFE_{cell}$ and $\Delta G^0 = -nFE^0_{cell}$ into this equation, you obtain.

$$-nFEE_{cell} = -nFEE^0_{cell} + RT\ lnQ$$

The result rearranges to give the Nernst equation, an equation relating the cell emf to its standard emf and the reaction quotient.

$$E_{cell} = E^0_{cell} - \frac{RT}{nF}\ln Q \text{ or } E_{cell} = E^0_{cell} - \frac{2.303RT}{nF}\log Q$$

If you substitute 298K (25°C) for the temperature in the Nernst equation and put in values for R and F, you get (using common logarithms).

$$E_{cell} = E^0_{cell} - \frac{0.0592}{n}\log Q \text{ (values in volts at 25°C)}$$

You can show from the Nernst equation that the cell emf, E_{cell}, decreases as the cell reaction proceeds. As the reaction occurs in the voltaic cell, the concentrations of products increase and the concentrations of reactants decrease. Therefore, Q and log Q increase. The second term in the Nernst equation, (0.0592/n) log Q, increases, so that the difference E^0_{cell} – (0.0592/n) log Q decreases. Thus, the cell emf, E_{cell}, becomes smaller. Eventually the cell emf goes to zero, and the cell reaction comes to equilibrium.

For Galvanic Cell : $Zn_{(s)} \mid Zn^{2+} (x_1) \parallel Cu^{2+} (x_2) \mid Cu_{(s)}$

Let us assume Zn to be anode and Cu to be cathode, though this can be correct only when the emf of the cell is positive.

Thus, $E_{cell} = E_C - E_A$

For cathode $\qquad Cu^{2+} + 2e^- \longrightarrow Cu_{(s)}$

For anode $\qquad Zn^{2+} + 2e^- \longrightarrow Zn_{(s)}$

Therefore $\qquad E_{Cu^{2+}/Cu} = E^0_{Cu^{2+}/Cu} = \dfrac{0.059}{2} \log \dfrac{1}{[Cu^{2+}]}$

$$E_{Zn^{2+}/Zn} = E^0_{Zn^{2+}/Zn} - \dfrac{0.059}{2} \log \dfrac{1}{[Zn^{2+}]}$$

Putting these values in (1), we get

$$E_{cell} = E^0_{cell} - \dfrac{0.059}{2} \log \dfrac{[Zn^{2+}]}{[Cu^{2+}]}$$

Electromotive Force

Potential difference is the difference in electric potential (electrical pressure) between two points. You measure this quantity in volts. The volt, V, is the SI unit of potential difference. The electrical work expended in moving a charge though a conductor is

Electrical work = charge × potential difference

Corresponding SI units for the terms in this equation are

Joules = coulombs × volts

The Faraday constant, F is the magnitude of charge on one mole of electrons; it equals 9.65×10^4 C (96.500 coulombs). The faraday is a unit of charge equal to 9.65×10^4C. In moving this quantity of charge (one faraday of charge) from one electrode to another, the numerical value of the work done by a voltaic cell is the product of the faraday constant F times the potential difference between the electrodes. The work w is the negative of this, because the voltaic cell loses energy as it does work on the surroundings.

w = – F × potential difference.

In the normal operation of a voltaic cell, the potential difference (voltage) across the electrodes is less than the maximum possible voltage of the cell. One reason for this is that it takes energy or work to drive a current through the cell itself. The decrease in cell voltage as current is drawn reflects this energy expenditure within the cell; and the greater the current, the lower the voltage. Thus, the cell voltage has its maximum value only when no current flows. The situation is analogous to measuring the difference between the pressure of water in a faucet and that of the outside atmosphere. The maximum potential difference between the electrodes of a voltaic cell is referred to as the electromotive force (emf) of the cell, or E^0_{cell}.

We can now write an expression for the maximum work obtainable from a voltaic cell. Let n be the number of electrons transferred in the overall cell equation. The maximum electrical work of a voltaic cell for molar amounts of reactants (according to the cell

equation as written) is :
$$W_{max} = nFE^0_{cell}$$
Here E^0_{cell} is the cell emf, and F is the Faraday constant, $9.65 \times 10^4 C$

Example 13.

Calculate the standard e.m.f. of the reaction $Fe^{3+} + 3e^- \rightarrow Fe_{(s)}$ $E^0_3 = ?$

Given $Fe^{3+} + e^- \rightarrow Fe^{2+}$ $E^0_1 = 0.771V$ *$Fe^{2+} + 2e^- \rightarrow Fe_{(s)}$ $E^0_2 = -0.44V$*

Solution :

With the help of calculation of free energy
$$\Delta G^0_1 = -nFE^0 = -(1)(F)(0.771V) = -0.771V$$
$$\Delta G^0_2 = -(2)(F)(0.44) = 0.88FV$$
$$\Delta G^0_3 = -(3)(F)(E^0) = -3FE^0V$$
The free energy change for the unknown process can be obtained as
$$\Delta G^0_3 = \Delta G^0_1 + \Delta G^0_2$$
$$-3FE^0 = -0.771F + 0.88F = 0.109F$$
or $$E^0 = -\frac{0.109}{3} = -0.036V$$

Example 14.

The standard electrode potentials of the electrode $Cu^{2+}|Cu$ and $Ag^+|Ag$ are 0.34V and 0.7991V respectively. What would be the concentration of Ag^+ in a solution containing 0.06M of Cu^{2+} ion such that both the metals can be deposited together. Assume that activity coefficients are unity and both silver and copper do not dissolve among themselves.

Solution :

The individual reactions are :
$$Cu^{2+} + 2e^- \longrightarrow Cu_{(s)} \qquad ; \qquad Ag^+ + e^- \longrightarrow Ag_{(s)}$$
The electrode potentials given by Nernst equation

$$E(Cu^{2+} | Cu) = E^0 = \frac{0.0591}{2} \log \frac{1}{[Cu^{2+}]} = 0.037 - \frac{(0.0591)}{2} \log \frac{1}{0.06} = 0.037 - 0.036 = 0.301$$

$$E(Ag^+ | Ag) = 0.7991 - \frac{0.0591}{1} \log \frac{1}{[Ag^+]}$$

Two metals will be deposited together when the electrode potentials are equal i.e.

$$0.301 = 0.7991 - 0.0591 \log \frac{1}{[Ag^+]} \qquad\qquad i.e. \log \frac{1}{[Ag^+]} = \frac{0.7991 - 0.301}{0.0591} = 8.428$$

$$\frac{1}{[Ag^+]} = 10^{8.428}$$

or $[Ag^+] = 10^{-8.428} = 0.37 \times 10^{-8} \text{ mol dm}^{-3}$

EXERCISE I

ELECTROLYTIC CELL :

Q.1 Calculate the no. of electrons lost or gained during electrolysis of
(a) 3.55 gm of Cl^- ions (b) 1 gm Cu^{2+} ions (c) 2.7 gm of Al^{3+} ions

Q.2 How many faradays of electricity are involved in each of the case
(a) 0.25 mole Al^{3+} is converted to Al.

(b) 27.6 gm of SO_3 is convered to SO_3^{2-}

(c) The Cu^{2+} in 1100 ml of 0.5 M Cu^{2+} is converted to Cu.

Q.3 0.5 mole of electron is passed through two electrolytic cells in series. One contains silver ions, and the other zinc ions. Assume that only cathode reaction in each cell is the reduction of the ion to the metal. How many gm of each metals will be deposited.

Q.4 The electrosynthesis of MnO_2 is carried out from a solution of $MnSO_4$ in H_2SO_4 (aq). If a current of 25.5 ampere is used with a current efficiency of 85%, how long would it take to produce 1 kg of MnO_2?

Q.5 A constant current of 30 A is passed through an aqueous solution of NaCl for a time of 1.0 hr. How many grams of NaOH are produced? What is volume of Cl_2 gas at S.T.P. produced?

Q.6 If 0.224 litre of H_2 gas is formed at the cathode, how much O_2 gas is formed at the anode under identical conditions?

Q.7 If 0.224 litre of H_2 gas is formed at the cathode of one cell at S.T.P., how much of Mg is formed at the cathode of the other electrolytic cell.

Q.8 Assume 96500 C as one unit of electricity. If cost of electricity of producing x gm Al is Rs x, what is the cost of electricity of producing x gm Mg?

Q.9 Chromium metal can be plated out from an acidic solution containing CrO_3 according to following equation:
$CrO_3(aq) + 6H^+ (aq) + 6e^- \rightarrow Cr(s) + 3H_2O$
Calculate :
(i) How many grams of chromium will be plated out by 24000 coulombs and
(ii) How long will it take to plate out 1.5 gm of chromium by using 12.5 ampere current

Q.10 Calculate the quantity of electricity that would be required to reduce 12.3 g of nitrobenzene to aniline, if the current efficiency for the process is 50 percent. If the potential drop across the cell is 3.0 volts, how much energy will be consumed?

Q.11 How long a current of 2A has to be passed through a solution of $AgNO_3$ to coat a metal surface of $80cm^2$ with 5μm thick layer? Density of silver = $10.8 g/cm^3$.

Q.12 3A current was passed through an aqueous solution of an unknown salt of Pd for 1Hr. 2.977g of Pd^{+n} was deposited at cathode. Find n.

Q.13 50mL of 0.1M $CuSO_4$ solution is electrolyzed with a current of 0.965 A for a period of 200 sec. The reactions at electrodes are:
Cathode : $Cu^{2+} + 2e^- \rightarrow Cu(s)$ Anode : $2H_2O \rightarrow O_2 + 4H^+ + 4e.$
Assuming no change in volume during electrolysis, calculate the molar concentration of Cu^{2+}, H^+ and SO_4^{2-} at the end of electrolysis.

Q.14 A metal is known to form fluoride MF_2. When 10A of electricity is passed through a molten salt for 330 sec., 1.95g of metal is deposited. Find the atomic weight of M. What will be the quantity of electricity required to deposit the same mass of Cu from $CuSO_4$?

Q.15   10g fairly concentrated solution of $CuSO_4$ is electrolyzed using 0.01F of electricity. Calculate:
(a)The weight of resulting solution   (b)Equivalents of acid or alkali in the solution.

Q.16   An electric current is passed through electrolytic cells in series one containing $Ag(NO_3)$(aq.) and other H_2SO_4(aq). What volume of O_2 measured at 25°C and 750mm Hg pressure would be liberated from H_2SO_4 if
(a) one mole of Ag^+ is deposited from $AgNO_3$ solution
(b) 8×10^{22} ions of Ag^+ are deposited from $AgNO_3$ solution.

Q.17   Cadmium amalgam is prepared by electrolysis of a solution of $CdCl_2$ using a mercury cathode. How long should a current of 5A be passed in order to prepare 12% Cd–Hg amalgam on a cathode of 2gm Hg (Cd=112.4)

Q.18   After electrolysis of NaCl solution with inert electrodes for a certain period of time. 600 mL of the solution was left. Which was found to be 1N in NaOH. During the same time, 31.75 g of Cu was deposited in the copper voltameter in series with the electrolytic cell. Calculate the percentage yield of NaOH obtained.

Q.19   Three electrolytic cells A, B, C containing solution of $ZnSO_4$, $AgNO_3$ and $CuSO_4$, respectively are connected in series. A steady current of 2 ampere was passed through them until 1.08 g of silver deposited at the cathode of cell B. How long did the current flow? What mass of copper and of zinc were deposited?

Q.20   Copper sulphate solution (250 mL) was electrolysed using a platinum anode and a copper cathode. A constant current of 2 mA was passed for 16 minutes. It was found that after electrolysis the concentration of the solution was reduced to 50% of its original value. Calculate the concentration of copper sulphate in the original solution.

Q.21   A solution of $Ni(NO_3)_2$ is electrolysed between platinum electrodes using a current of 5 ampere for 20 mintue. What mass of Ni is deposited at the cathode?

Q.22   A current of 3.7A is passed for 6hrs. between Ni electrodes in 0.5L of 2M solution of $Ni(NO_3)_2$. What will be the molarity of solution at the end of electrolysis?

GALVANIC CELL :
Representation of Cell diagrams, complete and half cell reactions :

Q.23   Make complete cell diagrams of the following cell reactions :
(a) Cd^{2+} (aq) + Zn (s) $\longrightarrow$ Zn^{2+} (aq) + Cd (s)
(b) $2Ag^+$ (aq) + H_2 (g) $\longrightarrow$ $2H^+$ (aq) + 2Ag (s)
(c) Hg_2Cl_2 (s) + Cu (s) $\longrightarrow$ Cu^{2+} (aq) + $2Cl^-$ (aq) + 2Hg (l)

(d) $Cr_2O_7^{2-}$ (aq.) + $14H^+$ (aq) + $6Fe^{2+}$ (aq) $\longrightarrow$ $6Fe^{3+}$ (aq) + $2Cr^{3+}$ (aq) + $7H_2O$ (l)

Q.24   Write cell reaction of the following cells :
(a) $Ag \mid Ag^+$ (aq) $\mid\mid Cu^{2+}$ (aq) $\mid Cu$

(b) $Pt \mid Fe^{2+}, Fe^{3+} \mid\mid MnO_4^-, Mn^{2+}, H^+ \mid Pt$

(c) $Pt, Cl_2 \mid Cl^-$ (aq) $\mid\mid Ag^+$ (aq) $\mid Ag$
(d) $Pt, H_2 \mid H^+$ (aq) $\mid\mid Cd^{2+}$ (aq) $\mid Cd$

Q.25   Write half cells of each cell with following cell reactions :

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

(b) $2Fe^{3+}\,(aq) + Sn^{2+}\,(aq) \longrightarrow 2Fe^{2+}\,(aq) + Sn^{4+}\,(aq)$

(c) $MnO_4^-\,(aq) + 8H^+\,(aq) + 5Fe^{2+}\,(aq) \longrightarrow 2Fe^{3+}\,(aq) + Mn^{2+}\,(aq) + 4H_2O\,(l)$

(d) $Pb\,(s) + Br_2\,(l) \longrightarrow Pb^{2+}\,(aq) + 2Br^-\,(aq)$

Electrode potential and standard electrode potential :

Q.26   For the cell reaction $2Ce^{4+} + Co \longrightarrow 2Ce^{3+} + Co^{2+}$

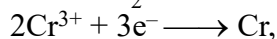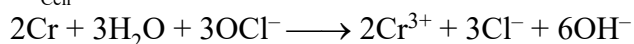E^o_{cell} is 1.89 V. If $E^o_{Co^{2+}|Co}$ is -0.28 V, what is the value of $E^o_{Ce^{4+}|Ce^{3+}}$?

Q.27   Determine the standard reduction potential for the half reaction :

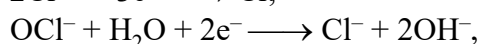$Cl_2 + 2e^- \longrightarrow 2Cl^-$
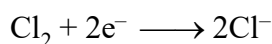
Given $Pt^{2+} + 2Cl^- \longrightarrow Pt + Cl_2$, $E^o_{Cell} = -0.15$ V

$Pt^{2+} + 2e^- \longrightarrow Pt$ $E^\circ = 1.20$ V

Q.28   What is E^o_{Cell} if

$2Cr + 3H_2O + 3OCl^- \longrightarrow 2Cr^{3+} + 3Cl^- + 6OH^-$

$2Cr^{3+} + 3e^- \longrightarrow Cr$, $E^\circ = -0.74$ V

$OCl^- + H_2O + 2e^- \longrightarrow Cl^- + 2OH^-$, $E^\circ = 0.94$ V

ANSWER KEY
EXERCISE I

Q.1   (a) 6.02×10^{22} electrons lost, (b) 1.89×10^{22} electrons gained, (c) (b) 1.80×10^{23} electrons gained

Q.2   (a) 0.75 F, (b) 0.69 F, (c)1.1 F   Q.3   (i) 54 gm, (ii) 16.35 gm

Q.4 1.023×10^5 sec   Q.5   1.12 mol, 12.535 litre

Q.6   0.112 litre   Q.7   0.24 gms

Q.8   Rs. 0.75x   Q.9   (i) 2.1554 gm ; (ii) 1336. 15 sec

Q.10   115800C, 347.4 kJ   Q.11   t = 193 sec

Q.12   n = 4   Q.13 $Cu^{2+} = 0.08M$, $H^+ = 0.04M$, $SO_4^{2-} = 0.1M$

Q.14   A = 114, Q = 5926.8C   Q.15   Final weight = 9.6g,0.01Eq of acid

Q.16   (a) $V(O_2)$=6.2L, (b)$V(O_2) = 0.824L$ Q.17   t = 93.65 sec.

Q.18   60 %   Q.19   (i) 482.5 sec (ii) 0.3175 gm (iii) 0.327 gm

Q.20 $7.958 \times 10^{-5}M$ Q.21   1.825 g   Q.22   2M

Q.23   (a) $Zn\,|\,Zn^{2+}\,||\,Cd^{2+}\,|\,Cd$, (b) $Pt,\,H_2\,|\,H^+\,||\,Ag^+\,|\,Ag$, (c) $Cu\,|\,Cu^{2+}\,||\,Cl^-\,|\,Hg_2Cl_2\,|\,Hg$

(d) $Pt\,|\,Fe^{2+},\,Fe^{3+}\,||\,Cr_2O_7^{2-},\,Cr^{3+}\,|\,Pt$

Q.24   (a) $2Ag + Cu^{2+} \longrightarrow 2Ag^+ + Cu$, (b) $MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$

(c) $2Cl^- + 2Ag^+ \longrightarrow 2Ag + Cl_2$, (d) $H_2 + Cd^{2+} \longrightarrow Cd + 2H^+$

Q.25   Anode   Cathode

(a) $Zn\,|\,Zn^{2+}$ $H^+,\,H_2\,|\,Pt$

(b) $Pt\,|\,Sn^{2+},\,Sn^{4+}$ $Fe^{3+},\,Fe^{2+}\,|\,Pt$

(c) $Pt\,|\,Fe^{2+},\,Fe^{3+}$ $MnO_4^-,\,Mn^{2+}\,|\,Pt$

(d) $Pb\,|\,Pb^{2+}$ $Br_2,\,Br^-\,|\,Pt$]

Q.26   1.61 V   Q.27   1.35 V   Q.28   1.68 V