Electromotive force of Galvanic cells

Galvanic cell is a device in which the free energy of a physical or chemical process is converted into electrical energy. Such cell usually consists of two electrodes immersed in one or more electrolytes. When electrodes are connected externally, a chemical reaction occurs in the cell involving oxidation at one electrode and reduction at other electrode. According to the latest conventions the electrode at which oxidation occurs is called anode while the electrode at which reduction occurs is called cathode.

We distinguish two types of electrochemical cells based on the general thermodynamic nature of the reaction:

1. A voltaic cell (or galvanic cell) uses a spontaneous reaction ($\Delta G < 0$) to generate electrical energy. In the cell reaction, the difference in chemical potential energy between higher energy reactants and lower energy products is converted into electrical energy. This energy is used to operate the load—flashlight bulb, CD player, car starter motor, or other electrical device. In other words, the system does work on the surroundings. All batteries contain voltaic cells.

2. An electrolytic cell uses electrical energy to drive a nonspontaneous reaction (($\Delta G > 0$). In the cell reaction, electrical energy from an external power supply converts lower energy reactants into higher energy products. Thus, the surroundings do work on the system. Electroplating and recovering metals from ores involve electrolytic cells.
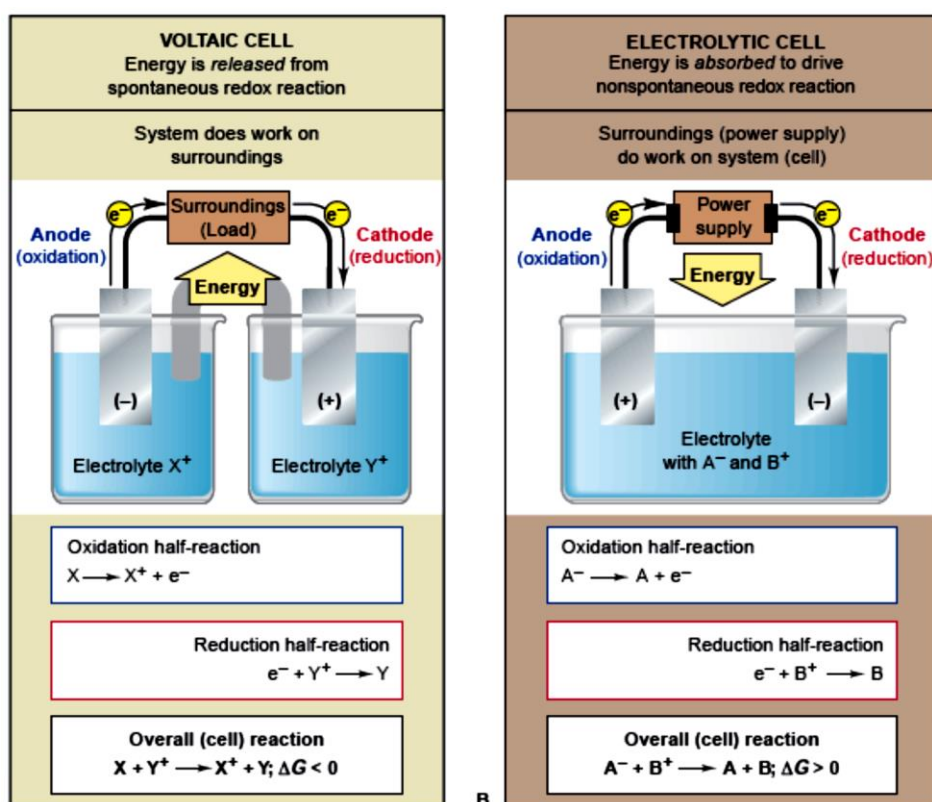

Figure 1. Voltaic cell and electrolytic cell

The two types of cell have certain design features in common (Figure 1). Two electrodes, which conduct the electricity between cell and surroundings, are dipped into an electrolyte, a mixture of ions (usually in aqueous solution) that are involved in the reaction or that carry the charge. An electrode is identified as either anode or cathode depending on the half-reaction that takes place there:

• The oxidation half-reaction occurs at the anode. Electrons are lost by the substance being oxidized (reducing agent) and leave the cell at the anode.

• The reduction half-reaction occurs at the cathode. Electrons are gained by the substance being reduced (oxidizing agent) and enter the cell at the cathode.

Consider for instance a copper rode dipping in a solution of copper sulphate and a zinc rod dipping in a solution of zinc sulphate as in the **Daniell cell**. The two metal rods are connected through an ammeter and the two solutions are connected through salt bridge ie an inverted U shaped glass tube filled with a solution of potassium chloride. As soon as the circuit is closed current starts flowing which is indicated by deflection in the voltmeter. The flow of current is accompanied by the following process.

1. **The oxidation half-cell**. In this case, the anode compartment consists of a zinc bar (the anode) immersed in a Zn^{2+} electrolyte (such as a solution of zinc sulfate, $ZnSO_4$). The zinc bar is the reactant in the oxidation half-reaction. It passes into the solution as Zn^{2+} ions liberating two electrons and it conducts the released electrons out of its half-cell.

2. **The reduction half-cell**. In this case, the cathode compartment consists of a copper bar (the cathode) immersed in a Cu^{2+} electrolyte [such as a solution of copper(II) sulfate, $CuSO_4$]. Copper metal is the product in the reduction half reaction. The Cu^{2+} ions extract two electrons each from the copper rod and are discharged as copper metal on the copper electrode. The process involves reduction

3. **Relative charges on the electrodes**. The electrode charges are determined by the source of electrons and the direction of electron flow through the circuit. In this cell, zinc atoms are oxidized at the anode to Zn^{2+} ions and electrons. The Zn^{2+}ions enter the solution, while the electrons enter the bar and then the wire. The electrons flow left to right through the wire to the cathode, where Cu^{2+} ions in the solution accept them and are reduced to Cu atoms. As the cell operates, electrons are continuously generated at the anode and consumed at the cathode. Therefore, the anode has an excess of electrons and a negative charge relative to the cathode. In any voltaic cell, the anode is negative and the cathode is positive.

4. **The purpose of the salt bridge**. The cell cannot operate unless the circuit is complete. The oxidation half-cell originally contains a neutral solution of Zn^{2+} and SO_4^{2-} ions, but as Zn atoms in the bar lose electrons, the solution would develop a net positive charge from the Zn^{2+} ions entering. Similarly, in the reduction half-cell, the neutral solution of Cu^{2+} and SO_4^{2-} ions would develop a net negative charge as Cu^{2+} ions leave the solution to form Cu atoms. If the half-cells do not remain neutral, the resulting charge imbalance would stop cell operation. To avoid this situation and enable the cell to operate, the two halfcells are joined by a salt bridge, which acts as a "liquid wire," allowing ions to flow through both compartments and complete the circuit. The salt bridge shown in

Figure 2 is an inverted U tube containing a solution of the nonreacting ions Na^+ and SO_4^{2-} in a gel. The solution cannot pour out, but ions can diffuse through it into or out of the half-cells. To maintain neutrality in the reduction half-cell (right; cathode compartment) as Cu^{2+} ions change to Cu atoms, Na^+ ions move from the salt bridge into the solution (and some SO_4^{2-} ions move from the solution into the salt bridge). Similarly, to maintain neutrality in the oxidation half-cell (left; anode compartment) as Zn atoms change to Zn^{2+} ions, SO_4^{2-} ions move from the salt bridge into that solution (and some Zn^{2+} ions move from the solution into the salt bridge). Thus, as Figure 2 shows, the circuit is completed as electrons move left to right through the wire, while anions move right to left and cations move left to right through the salt bridge.
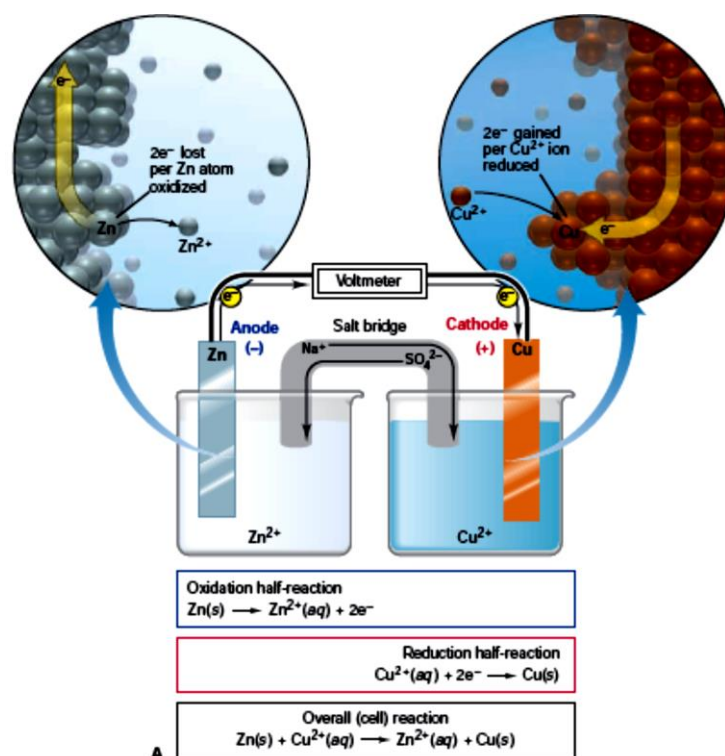

Figure 2. Daniel cell

Cell Potential: Out put of a voltaic cell

The purpose of a voltaic cell is to convert the free energy change of a spontaneous reaction into the kinetic energy of electrons moving through an external circuit (electrical energy). This electrical energy is proportional to the difference in electrical potential between the two electrodes, which is called the **cell potential** (E_{cell}); it is also called the voltage of the cell or the **electromotive force** (emf). Electrons flow spontaneously from the negative to the positive electrode, that is, toward the electrode with the more positive electrical potential. Thus, when the cell operates spontaneously, there is a positive cell potential:

$$E_{cell} > 0 \text{ for a spontaneous process}$$

The more positive E_{cell} is, the more work the cell can do, and the farther the reaction proceeds to the right as written. A negative cell potential, on the other hand, is associated with a nonspontaneous cell reaction. If $E_{cell} = 0$, the reaction has reached equilibrium and the cell can do no more work.

The SI unit of electrical potential is the volt (V), and the SI unit of electrical charge is the coulomb (C). By definition, for two electrodes that differ by 1 volt of electrical potential, 1 joule of energy is released (that is, 1 joule of work can be done) for each coulomb of charge that moves between the electrodes. Thus,

$$1 \text{ V} = 1 \text{ J/C}$$

Notation for a Voltaic Cell

A useful shorthand notation describes the components of a voltaic cell. For example, the notation for the Zn/Cu^{2+} cell is

$$Zn(s) \mid Zn^{2+}(aq) \parallel Cu^{2+}(aq) \mid Cu(s)$$
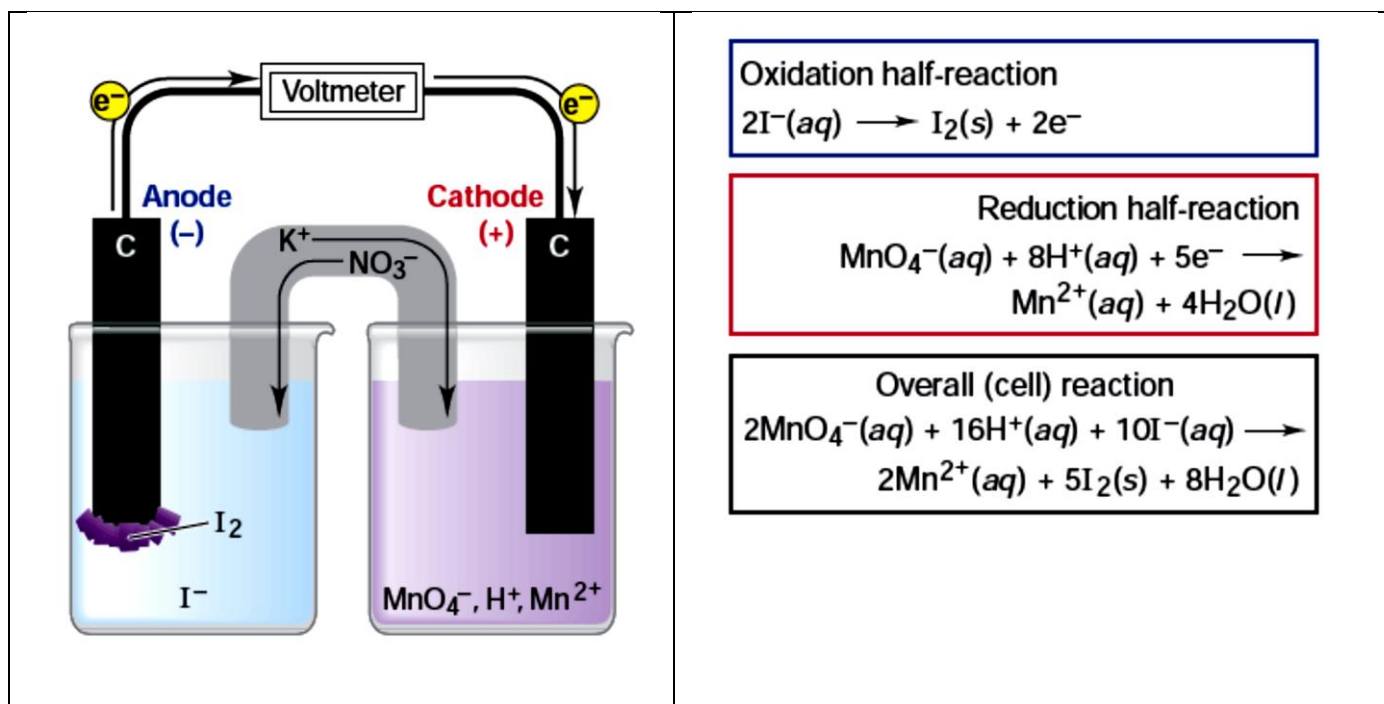
Key parts of the notation are

- The components of the anode compartment (oxidation half-cell) are written *to the left* of the components of the cathode compartment (reduction half-cell).
- A single vertical line represents a phase boundary. For example, $Zn(s) \mid Zn^{2+}(aq)$ indicates that the *solid* Zn is a *different* phase from the *aqueous* Zn^{2+}. A comma separates the half-cell components that are in the *same* phase. For example, the notation for the voltaic cell housing the reaction between I^- and MnO_4^- shown in Figure 21.6 is

$$\text{graphite} \mid I^-(aq) \mid I_2(s) \parallel H^+(aq), MnO_4^-(aq), Mn^{2+}(aq) \mid \text{graphite}$$
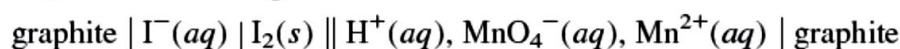
  That is, in the cathode compartment, H^+, MnO_4^-, and Mn^{2+} ions are all in aqueous solution with solid graphite immersed in it. Often, we specify the concentrations of dissolved components; for example, if the concentrations of Zn^{2+} and Cu^{2+} are 1 *M*, we write

$$Zn(s) \mid Zn^{2+}(1 M) \parallel Cu^{2+}(1 M) \mid Cu(s)$$
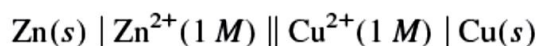
- Half-cell components usually appear in the same order as in the half-reaction, and electrodes appear at the far left and far right of the notation.
- A double vertical line indicates the separated half-cells and represents the phase boundary on either side of the salt bridge (the ions in the salt bridge are omitted because they are not part of the reaction).
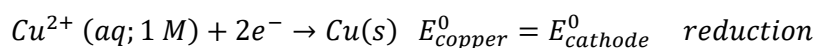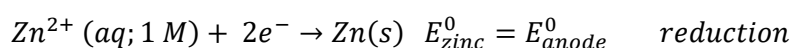
Oxidation half-reaction

$$2I^-(aq) \longrightarrow I_2(s) + 2e^-$$

Reduction half-reaction

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

Overall (cell) reaction

$$2MnO_4^-(aq) + 16H^+(aq) + 10I^-(aq) \longrightarrow 2Mn^{2+}(aq) + 5I_2(s) + 8H_2O(l)$$

The standard cell potential

The measured potential of a voltaic cell is affected by changes in concentration as the reaction proceeds and by energy losses due to heating of the cell and the external circuit. Therefore, in order to compare the output of different cells, we obtain a standard cell potential (E^0_{cell}), the potential measured at a specified temperature (usually 298 K) with no current flowing and all components in their standard states: 1 atm for gases, 1 M for solutions, the pure solid for electrodes. Under the standard condition ie $[Zn^{2+}]$ = $[Cu^{2+}]$ = 1 M, the cell produces 1.10 V at 298 K.

$$Zn(s) + Cu^{2+}(aq; 1\,M) \rightarrow Zn^{2+}(aq; 1\,M) + Cu(s) \quad E^0_{cell} = 1.1\,V$$
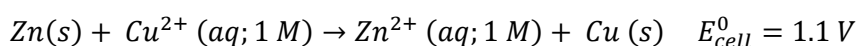
Standard electrode potential

Just as each half-reaction makes up part of the overall reaction, the potential of each half-cell makes up a part of the overall cell potential. The standard electrode potential ($E^0_{half-cell}$) is the potential associated with a given half-reaction (electrode compartment) when all the components are in their standard states. By convention, a standard electrode potential always refers to the half reaction written as a reduction. For the zinc-copper reaction, for example, the standard electrode potentials for the zinc half-reaction (E^0_{zinc}, anode compartment) and for the copper half-reaction (E^0_{copper}, cathode compartment) refer to the processes written as reductions:

$$Zn^{2+}(aq; 1\,M) + 2e^- \rightarrow Zn(s) \quad E^0_{zinc} = E^0_{anode} \quad reduction$$

$$Cu^{2+}(aq; 1\,M) + 2e^- \rightarrow Cu(s) \quad E^0_{copper} = E^0_{cathode} \quad reduction$$

The overall cell reaction involves oxidation of zinc at anode, not the reduction of zinc and so we reverse the zinc half reaction.

$$Zn(s) \ \rightarrow \ Zn^{2+} \ (aq; 1\,M) + \ 2e^- \quad oxidation$$

$$Cu^{2+} \ (aq; 1\,M) + \ 2e^- \rightarrow Cu(s) \quad reduction$$
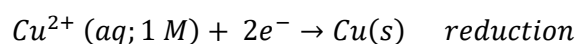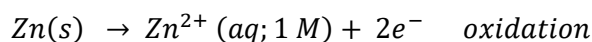
The overall reaction is the sum of these half reactions.

$$Zn(s) \ + Cu^{2+}(aq; 1\,M) \rightarrow Zn^{2+} \ (aq; 1\,M) + \ Cu(s)$$
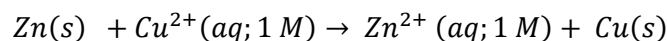
Because electrons flow spontaneously toward the copper electrode (cathode), it must have a more positive $E^0_{half-cell}$ than the zinc electrode (anode). Therefore, to obtain a positive E^0_{cell}, we subtract E^0_{zinc} from E^0_{copper}

$$E^0_{cell} = E^0_{copper} - E^0_{zinc}$$

The standard cell potential is the difference between the standard electrode potential of the cathode (reduction) half-cell and the standard electrode potential of the anode (oxidation) half-cell:

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

The measurement of cell potential

The simplest method of measuring the potential of an electrochemical cell is to balance it against an equal and opposite potential difference in the slidewire of a potentiometer. Figure 3 shows a potentiometer circuit with the cell connected in it. The battery B sends a current i through the slidewire R. The contact S is adjusted until no deflection is observed on the galvanometer G. At the null point, the potential of the cell is balanced by the potential difference between the points S and P of the slidewire. The slidewire is calibrated so that the potential drop ir between the points S and P can be read directly. If the resistance of the cell is very large, the potentiometer setting may be moved over a wide range without producing a sensible deflection on the galvanometer. In this case a high impedance electronic voltmeter must be used.
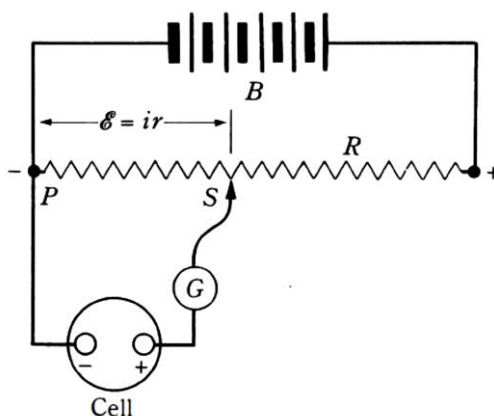

Figure 3. Potentiometer circuit

Reversibility

In the foregoing treatment of electrodes and cells we assumed implicitly that the electrode or cell was in equilibrium with respect to certain chemical and electrical transformations. By definition such an electrode or cell is reversible. To correlate measured values of cell potentials with the ones calculated by the Nernst equation, the measured values must be equilibrium or reversible values; the potentiometric measurement in which no current is drawn from the cell is ideally suited for the measurement of reversible potentials.

A cell is said to be reversible if it fulfills the following conditions:

(a)   Suppose the EMF of the cell is E_{cell}. If an external EMF of the same magnitude is applied to balance the EMF of the cell no current should flow to and from the cell.

(b)   If the external EMF is decreased by an infinitesimal amount dE_{cell}, a small current should flow from the cell and a chemical reaction, proportional to the quantity of electricity passing, should take place in the cell.

(c)   If the external EMF is increased by an infinitesimal amount dE_{cell}, the current should flow in the opposite direction, proportional to the quantity of electricity passing and the cell reaction should be reversed. If the cell does not satisfy these conditions, it is said to be irreversible.

Some common type of reversible electrodes

1. **Metal-Metal ion electrode** An electrode of this type consist of a metal rod dipping in a solution containing its own ions, as for example, zinc rod dipping in zinc sulphate solution or a copper rode dipping in copper sulphate solution. If the metal is univalent the electrode reaction may be represented as

$$M^+(aq) + e^- \leftrightharpoons M\ (s)$$
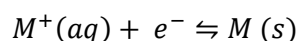
If the metal rode behaves as positive electrode the equilibrium will shift towards right. The concentration of M+ ions in solution will therefore decrease. If on other hand metal rod behaves as negative electrode the above equilibrium will shift towards left. The concentration of the M+ ions in solution will therefore increase. The electrode is reversible with respect to M^+ ions.

The electrodes in general can be represented as

$$M(s)|\ M^{n+}(aq)$$
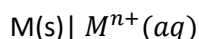
2. **Gas electrodes**

(a) **Hydrogen electrode** Hydrogen gas bubbling in a solution of an acid (say HCl) forms an electrode of this type. The equilibrium in this case is represented as

$$H^+(aq) + e^- \leftrightharpoons \frac{1}{2}H_2(g)$$
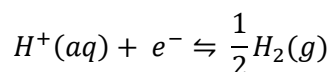
The electrode is reversible with respect to hydrogen ion.

Since hydrogen gas is non conducting platinum or some other metal which is not attacked by the acid and easily comes into equilibrium with hydrogen is used for making electrical contact with the circuit. Such electrodes are called inactive electrodes. Commonly used inactive electrodes are graphite and platinum. The electrode is represented as

$$Pt \text{ (s)} \mid H_2 \text{ (g)} \mid H^+ \text{ (aq)}$$
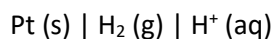
Hydrogen electrode has been used as standard reference half-cell with standard electrode potential defined as zero. The standard reference half-cell is a **standard hydrogen electrode (SHE)**, which consists of a specially prepared platinum electrode immersed in a 1 M aqueous solution of a strong acid, H^+(aq) [or H_3O^+ (aq)], through which H_2 gas at 1 atm is bubbled. Thus, the reference half-reaction is

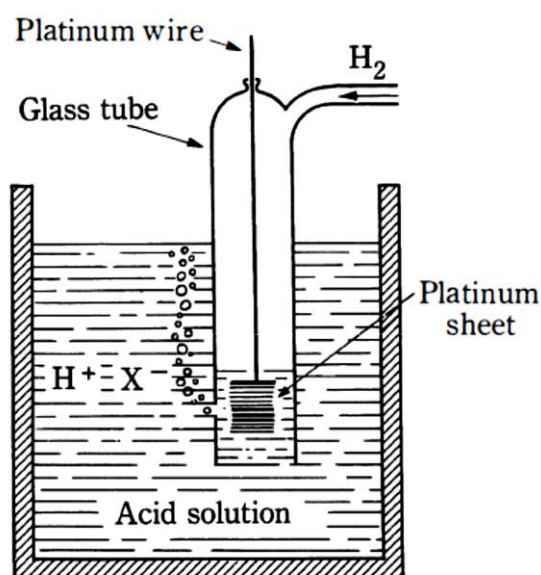$$2H^+(aq, 1\,M) + 2e^- \leftrightharpoons H_2(g; 1\,atm) \quad E^0_{reference} = 0.00V$$
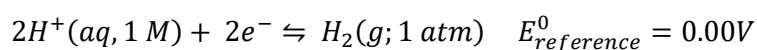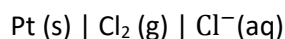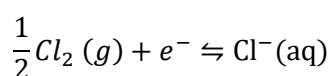

Figure 4. Standard hydrogen electrode

(b) **Chlorine electrode**

In this electrode, chlorine gas at a given pressure is bubbled into a solution of hydrochloric acid. The electrode is represented as
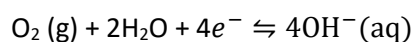
$$Pt \text{ (s)} \mid Cl_2 \text{ (g)} \mid Cl^- \text{(aq)}$$

And the electrode reaction is written as

$$\frac{1}{2}Cl_2 \text{ (g)} + e^- \leftrightharpoons Cl^- \text{(aq)}$$

(c) **Oxygen electrode**

In this electrode oxygen gas at a given pressure is bubbled through a solution containing hydroxyl OH^- ions. The electrode reaction is written as

$$O_2 \text{ (g)} + 2H_2O + 4e^- \leftrightharpoons 4OH^-\text{(aq)}$$

But since equilibrium between oxygen gas and hydroxyl ions in solution cannot be established quickly, oxygen electrode does not behave truly as reversible electrode
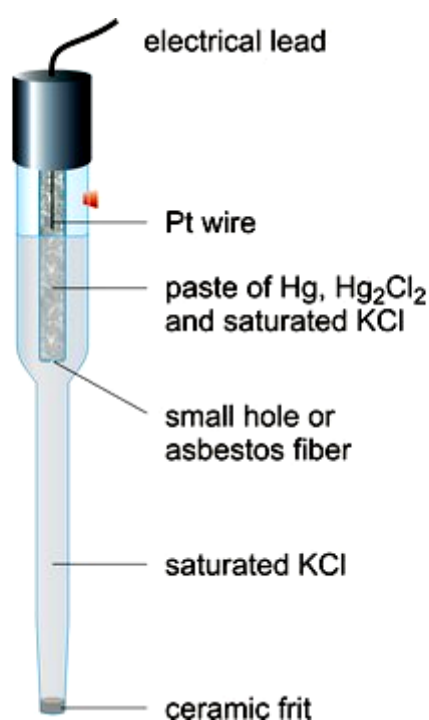
(3) **Metal insoluble Metal salt Electrode**

These electrodes consist of metal and sparingly soluble salt of the same metal dipping in a solution of a soluble salt having the same anion. An important electrode of this type is calomel electrode.
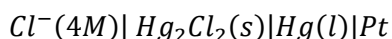
Calomel Electrode

The use of hydrogen electrode is cumbersome for two reasons : (i) a stream of pure gas at a given pressure has to be bubbled around the platinum for electrical contact and (ii) the platinum is prone to poisoning because of possible impurities in the gas. Except for very accurate work, several reference electrodes have come into wide use because of the reproducibility of the electrode potentials and their easy method of construction.
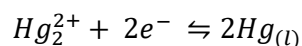
The most widely used reference electrode is calomel electrode (CE). The calomel electrode (CE) is a reference electrode based on the reaction between elemental mercury and mercury(I) chloride. It has been widely replaced by the silver chloride electrode, however the calomel electrode has a reputation of being more robust. The aqueous phase in contact with the mercury and the mercury(I) chloride (Hg_2Cl_2, "calomel") is a solution of potassium chloride in water. If saturated solution of KCl is used then the electrode is called Saturated calomel electrode (SCE).

The cell notation of the electrode is written as

$$Cl^-(4M)|\ Hg_2Cl_2(s)|Hg(l)|Pt$$

The electrode is based on the redox reaction

$$Hg_2^{2+} +\ 2e^- \leftrightharpoons 2Hg_{(l)}$$

The electrode potential is

$$E =\ E^0 - \frac{RT}{2F} ln \frac{1}{a_{Hg_2^{2+}}}$$

The electrode is reversible with respect to Cl⁻ ions. For common use three different concentrations of potassium chloride (0.1 N, 0.01N and saturated) are used to obtain decinormal, normal and saturated calomel electrodes. The potentials of these have been measured against SHE and are known accurately at different temperatures. At 25 °C, these are respectively +0.334 V (decinormal KCl), +0.280 V (0.01 normal KCl) and +0.2444 (saturated KCl). The SCE is used in pH measurement, cyclic voltametry and general aqueous electrochemistry.

4. **Oxidation reduction electrode**

The term oxidation reduction electrode is used for those electrodes in which the potential is developed from the presence of ions of the same substance in two different valence states. Such a electrode is set up by inserting an inactive electrode (usually platinum) in an appropriate solution. Thus when a platinum wire is inserted in a solution containing Fe^{2+} and Fe^{3+} ions, it is found that wire acquires a potential. The same thing will happen when ions of Ce^{3+} and Ce^{4+} ions. The potential of the electrode arises from the tendency of the ions in one oxidation state to change into other more stable oxidation state.

The electrode reactions may be represented as follows

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

$$Ce^{4+}(aq)\ + e^- \leftrightharpoons Ce^{3+}(aq)$$
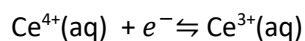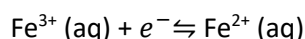
Another important slightly different oxidation reduction electrode is the so called **quinhydrone electrode** which consists of platinum wire placed in a solution containing hydroquinone (QH_2) and quinone in equimolar amounts. The electrode reaction is represented as follows
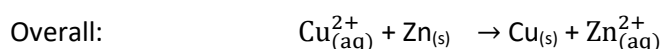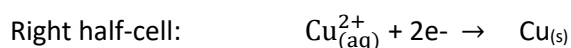
Quinhydrone electrode: Quinone-Hydroquinone Electrode
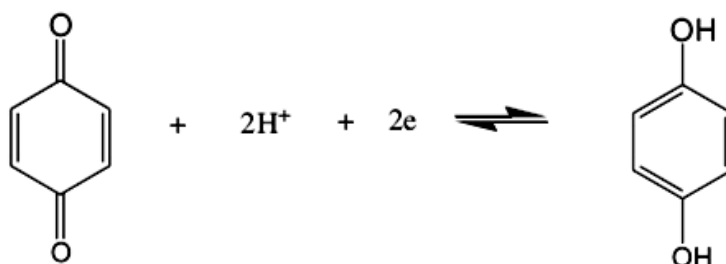
The electrode may by represented as Pt| Q, QH$_2$| HCl

Chemical reactions in electrochemical cells and Nernst equation

If the half-cells are connected through the external circuit, Zn atoms leave the Zn electrode to form Zn^{2+}in solution, and Cu^{2+} ions are deposited as Cu atoms on the Cu electrode. In the external circuit, it is observed that electrons flow through the wires and the resistor in the direction from the Zn electrode to the Cu electrode. These observations are consistent with the following electrochemical reactions:

Right half-cell: $Cu^{2+}_{(aq)} + 2e- \rightarrow Cu_{(s)}$

Left half-cell: $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e-$

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

In the left half-cell, Zn is being oxidized to Zn^{2+}, and in the right half-cell, Cu^{2+} is being reduced to Cu. By convention, the electrode at which oxidation occurs is called the anode, and the electrode at which reduction occurs is called the cathode.

How are the cell voltage and ΔG_R for the overall reaction related? This important relationship can be determined from the electrochemical potentials of the species involved in the overall reaction of the Daniell cell:

$$\Delta G_R = (\tilde{\mu}_{Zn^{2+}} + \tilde{\mu}_{Cu}) - (\tilde{\mu}_{Cu^{2+}} + \tilde{\mu}_{Zn})$$

where $\tilde{\mu}$ is called electrochemical potential

$$\Delta G_R = \mu^0_{Zn^{2+}} - \mu^0_{Cu^{2+}} + RT \ln \frac{a_{Zn^{2+}}}{a_{Cu^{2+}}}$$

$$\Delta G_R = \Delta G_R^0 + RT \ln \frac{a_{Zn^{2+}}}{a_{Cu^{2+}}} \qquad (1)$$

If this reaction is carried out reversibly, the electrical work done is equal to the product of the charge and the potential difference through which the charge is moved. However, the reversible work at constant pressure is also equal to ΔG. Therefore, we can write the following equation

$$\Delta G_R = -nFE \quad (2)$$

E is the measured potential difference generated by spontaneous chemical reaction which is known as electromotive force and n is the number of electrons involved in the redox reaction. The measured cell voltage is directly proportional to ΔG.

$$-2FE = \Delta G^0 + RT \ln \frac{a_{Zn^{2+}}}{a_{Cu^{2+}}}$$

For standard state conditions $a_{Zn^{2+}} = a_{Cu^{2+}} = 1$, so above equation will become $\Delta G^0 = -2FE^0$

$$E = E^0 - \frac{RT}{2F} \ln \frac{a_{Zn^{2+}}}{a_{Cu^{2+}}}$$

For a general overall electrochemical reaction involving transfer of n moles of electrons,

$$E = E^0 - \frac{RT}{nF} \ln \frac{a_{Zn^{2+}}}{a_{Cu^{2+}}} \quad (3)$$

$$E = E^0 - \frac{RT}{nF} \ln Q \quad (4)$$

Where Q is the familiar reaction quotient. The preceding equation is known as **Nernst equation**. At 298.15 K, the Nernst equation can be written as

$$E = E^0 - \frac{0.05916\,V}{n} \log Q \quad (5)$$

Effect of electrolyte concentration on electrode potential

Consider an electrode consisting of a metal in contact with a solution of its own cations. As an example we may consider zinc rode in contact with a solution of zinc sulphate furnishing Zn^{2+} ions. The following equilibrium will be established considering that the reaction from left to right involves reduction

$$Zn^{2+}_{(aq)} + 2e^- \rightarrow Zn_{(s)}$$
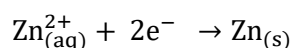
The decrease in free energy accompanying the electrode reaction in accordance with

$$2FE = 2FE^0 - RT \ln \frac{a_{Zn}}{a_{Zn^{2+}}}$$

$$E = E^0 - \frac{RT}{2F} \ln \frac{a_{Zn}}{a_{Zn^{2+}}}$$

$$E = E^0 + \frac{RT}{2F} \ln \frac{a_{Zn^{2+}}}{a_{Zn}}$$

$$E = E^0 + \frac{RT}{2F} \ln a_{Zn^{2+}} \quad \text{(for all solids a=1)}$$

$$E = E^0 + \frac{RT}{2F} \ln [Zn^{2+}] \quad (7) \quad \text{as an approximation}$$

Where E is the electrode potential of zinc electrode under the operating conditions and E^0 is the standard electrode potential of zinc electrode i.e the potential developed on the zinc rod when it is in contact with solution of Zn^{2+} ions of unit activity. Hence, the general expression for the electrode potential of a metal M in contact with M^{n+} ions, involving the electrode reaction may be written as

$$M^{n+}_{(aq)} + ne^- \leftrightharpoons M_{(s)}$$

$$E = E^0 + \frac{RT}{nF} \ln [M^{n+}]$$

$$E = E^0 + \frac{0.05916\,V}{n} \log[M^{n+}] \quad (8)$$

The above equation gives the effect of the concentrations of M^{n+} ion on the potential of M^{n+}, M electrode is known as the Nernst equation.

Application of standard potentials

Cell potentials are a convenient source of data on equilibrium constants and the Gibbs energies, enthalpies, and entropies of reactions. In practice the standard values of these quantities are the ones normally determined.

(a) Electrochemical series

In terms of standard electrode potentials it has been possible to draw an electrochemical series indicating the oxidising /reducing power of the oxidised /reduced state of a redox system. The reduced state of a system higher up in the series will reduce the oxidised state of a system lower down in the series and itself will get oxidised. In other words, the oxidised state of a system lower down in the series will oxidise the reduced state of a system higher up in the series. That is a stronger oxidising agent (the oxidised state of a redox system) occurs lower down in the series and a stronger reducing agent (the reduced state of a redox system) occurs higher up in the series.

Dr. Biju A R

Most Strongly Reducing (The metal is least easily oxidized.)

Gold
(most positive reduction potential)

Platinum

Palladium

Silver

Rhodium

Copper

Mercury
(Hydrogen; zero reduction potential by convention)

Lead

Tin

Nickel

Iron

Zinc

Chromium

Vanadium

Manganese

Magnesium

Sodium

Calcium

Potassium

Rubidium

Cesium

Lithium
(most negative reduction potential)

Least Strongly Reducing (The metal is most easily oxidized.)

The electrochemical series lists the metallic elements in the order of their reducing power as measured by their standard potentials in aqueous solution: low reduces high

We have seen that for two redox couples, Ox_1/Red_1 and Ox_2/Red_2, and the cell

$$Red_1, Ox_1 \ || \ Red_2, Ox_2 \quad E^0_{cell} = E^0_2 - E^0_1$$
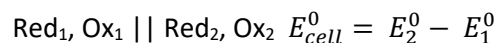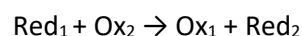
that the cell reaction
$$Red_1 + Ox_2 \rightarrow Ox_1 + Red_2$$
Has K > 1 as written if $E^0_{cell} > 0$ and therefore if $E^0_2 > E^0_1$ ie the reduction potential for reaction 2 is more positive than the reaction 1. Therefore, the relative strength of a species as an oxidizing agent follows the order of the numerical value of its reduction potential in the table on the left side

The electrochemical series shown in Table is obtained if the oxidation of neutral metals to their most common oxidation state is considered. For example, the entry for gold in Table refers to the reduction reaction

$$Au^{3+}_{(aq)} + 3e^- \rightarrow Au_{(s)} \quad E^0 = 1.498 \ V$$
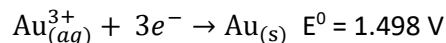
In a redox couple formed from two entries in the list shown in Table, the species lying higher in the list will be reduced, and the species lying lower in the list will be oxidized in the spontaneous reaction. For example, the table predicts that the spontaneous reaction in the copper–zinc couple is

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

and not the reverse reaction

(b) The determination of the E^0 of a half cell

Since the values of equilibrium constants are obtained from the standard half-cell potentials, the method of obtaining the E^0 of a half-cell has great importance. Suppose we wish to determine the go of the E^0 silver-silver ion electrode. Then we set up a cell that includes this electrode and another electrode the potential of which is known; for simplicity we choose the SHE as the other electrode. Then the cell is
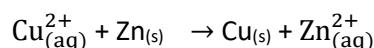
SHE || Ag⁺/Ag

The cell reaction is Ag⁺ + 1e- ⇋ Ag, and the cell potential is

$$E = E_{Ag^+/Ag} = E^0_{Ag^+/Ag} - \frac{RT}{F} \ln \frac{Ag}{a_{Ag^+}}$$

$$E = E^0_{Ag^+/Ag} - \frac{RT}{F} \ln \frac{1}{a_{Ag^+}} \qquad (9)$$

$$E = E^0_{Ag^+/Ag} + \frac{RT}{F} \ln(a_{Ag^+}) \qquad (10)$$

$$E = E^0_{Ag^+/Ag} + 0.05916\,V \log\,(a_{Ag^+}) \qquad (11)$$

If the solution were an ideal dilute solution, we could replace a Ag^+ by m^+ = m, the molality of the silver salt. Equation would become

$$E = E^0_{Ag^+/Ag} + 0.05916\,V \log\,(m) \qquad (12)$$

By measuring E at several values of m and plotting E versus log m, a straight line of slope 0.05916 V would be obtained, as in Fig. 5. The intercept on the vertical axis, m = 1 , would be the value of E^0. However life is not so simple. We cannot replace a_{Ag^+} by m and hope for any real accuracy in our equation. In an ionic solution, the activity of an ion can be replaced by the mean ionic activity $a_\pm = \gamma_\pm m_\pm$. If the solution contains only silver nitrate, then $m_\pm$ = m ; and Eq. (11) becomes

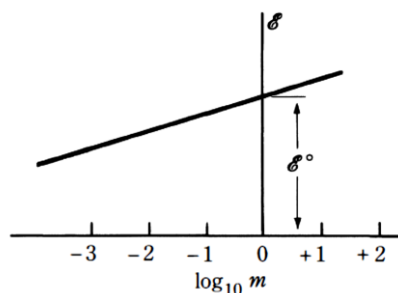$$E = E^0_{Ag^+/Ag} + 0.05916\,V \log\,(m) + 0.05916 \log(\gamma_\pm) \qquad (13)$$

Figure 5. Ideal dependence of E on m

If the measurements are carried to solutions dilute enough so that the Debye-Huckel limiting law, is valid, then $\log(\gamma_\pm) = -\left(0.5092\,V\frac{kg^{1/2}}{mol^{1/2}}\right) m^{1/2}$ and we can reduce the equation to

$$E - 0.05916\,V \log\,(m) = E^0_{Ag^+/Ag} - \left(0.03012\,V\frac{kg^{1/2}}{mol^{1/2}}\right) m^{1/2} \qquad (14)$$

From the measured values of E and m, the left-hand side of this equation can be calculated. The left-hand side is plotted against $m^{1/2}$; extrapolation of the curve to $m^{1/2}$ = 0 yields an intercept equal to $E^0_{Ag^+/Ag}$ .The plot is shown schematically in **Figure 6**. It is by this method that accurate values of E^0 are obtained from the measured values of the E of any half-cell.
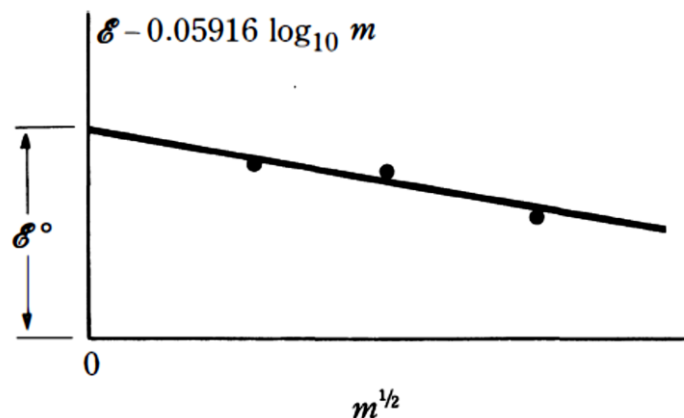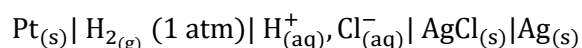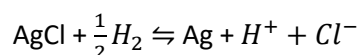
Figure 6. Plot to obtain E⁰ by extrapolation

(c) Determination of activity and activity coefficients from cell potentials

Once an accurate value of E⁰ has been obtained for a cell, then the potential measurements yield values of the activity coefficients directly. Consider the cell

$$Pt_{(s)}|\ H_{2_{(g)}}\ (1\ atm)|\ H^+_{(aq)}, Cl^-_{(aq)}|\ AgCl_{(s)}|Ag_{(s)}$$

The cell reaction is

$$AgCl + \frac{1}{2}H_2 \leftrightharpoons Ag + H^+ + Cl^-$$

The cell potential is

$$E = E^0 - \frac{RT}{F}\ln(a_{H^+}a_{Cl^-}) \qquad (15)$$

According to Eq. (15), the potential of the cell does not depend on the individual ion activities but on the product $a_{H^+}a_{Cl^-}$. As it turns out there is no measurable quantity that depends on an individual ion activity. Consequently, we replace the product $a_{H^+}a_{Cl^-}$ by $a^2_{\pm}$. Since in HCl $m_{\pm} = m$, we have $a^2_{\pm} = (\gamma_{\pm}m)^2$ this reduces equation 15 to

$$E = E^0 - \frac{2RT}{F}\ln(\gamma_{\pm}) - \frac{2RT}{F}ln(m) \quad (16)$$

At 25 °C

$$E = E^0 - 0.1183\ V\ \ln(\gamma_{\pm}) - 0.1183\ V\ ln(m) \quad (17)$$

Having determined E⁰ we see that values of E determine the values of $\gamma_{\pm}$ at every values of m. Conversely if the values $\gamma_{\pm}$ is known at all values of m, the cell potential E can be calculated from equation 16 and equation 17 a function of m. The measurement of cell potentials is the most powerful method of obtaining values of activities of electrolytes. Experimentally it is, in many cases at least, much easier to handle than measurements of colligative properties.
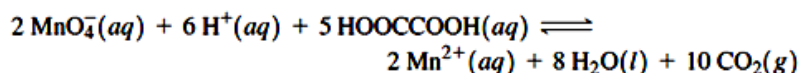
(d) The relationship between cell emf and equilibrium constant

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If the electrode reaction is allowed to proceed until equilibrium is reached $\Delta G = 0$, so that E = 0. For equilibrium state reaction quotient Q = K, therefore
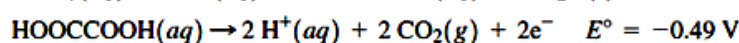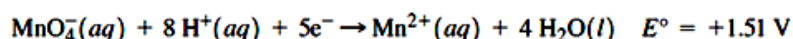
$$E^0 = \frac{RT}{nF} \ln K \quad (18)$$

The equation shows that a measurement of standard state cell potential for which a_i = 1 for all species in redox reaction allows K for overall reaction to be determined.

Problem 1

$$2\,MnO_4^-(aq) + 6\,H^+(aq) + 5\,HOOCCOOH(aq) \rightleftharpoons$$
$$2\,Mn^{2+}(aq) + 8\,H_2O(l) + 10\,CO_2(g)$$

The reduction and oxidation half-reactions are

$$MnO_4^-(aq) + 8\,H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4\,H_2O(l) \quad E° = +1.51\ V$$

$$HOOCCOOH(aq) \rightarrow 2\,H^+(aq) + 2\,CO_2(g) + 2e^- \quad E° = -0.49\ V$$

To eliminate the electrons in the overall equation, the first equation must be multiplied by 2, and the second equation must be multiplied by 5; $E°$ is unchanged by doing so. However, n is affected by the multipliers. In this case n = 10. Therefore,

$$\Delta G° = -nFE° = -10 \times 96485\ C\ mol^{-1} \times (1.51\ V + 0.49\ V)$$
$$= -1.93 \times 10^2\ kJ\ mol^{-1}$$

$$\ln K = -\frac{\Delta G°}{RT} = \frac{1.93 \times 10^2\ kJ\ mol^{-1}}{8.314\ J\ K^{-1}\ mol^{-1} \times 298.15\ K} = 778$$

We know that

$$\Delta G_R = \Delta G_R^0 + RT \ln Q$$

$$-nFE = -nFE^0 + RT \ln Q$$

$$E = E^0 - \frac{RT}{nF} \ln Q$$

$$E = \frac{RT}{nF} \ln K - \frac{RT}{nF} \ln Q$$

$$E = \frac{0.05916}{n} \log K - \frac{0.05916}{n} \log Q \quad (19)$$

Knowing the EMF of the cell and concentrations of reactants and products of the cell reaction, we can calculate equilibrium constant of the cell reaction.

Problem 2

Calculate equilibrium constant of the cell reaction $2Ag^+ + Zn \rightleftharpoons 2\,Ag + Zn^{2+}$ occurring in the zinc-silver cell at 25°C when $[Zn^{2+}]$ = 0.10 M and $[Ag^+]$ = 10 M. The EMF of the cell is found to be 1.62 volt.

$$E = \frac{0.05916}{n} \ln K - \frac{0.05916}{n} \log \frac{[Ag]^2[Zn^{2+}]}{[Ag^+]^2[Zn]}$$

$$1.62 = \frac{0.05916}{2} \ln K - \frac{0.05916}{2} \log \frac{[Zn^{2+}]}{[Ag^+]^2}$$

$$1.62 = \frac{0.05916}{2} \log K - \frac{0.05916}{2} \log \frac{0.10}{10}$$

(e) Determination of thermodynamic quantities

Obtaining reaction Gibbs energies and reaction entropies from cell potentials

$$\Delta G_R^0 = -nFE^0$$

$$dG = Vdp - SdT$$

$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$

$$\Delta S_R^0 = -\left(\frac{\partial \Delta G_R^0}{\partial T}\right)_p = nF\left(\frac{\partial E^0}{\partial T}\right)_p \quad (20)$$

Therefore the measure of temperature dependence of E^0 can be used to determine ΔS_R^0

Relationship between electrical energy and enthalpy for a cell reaction

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

$$-\Delta G^0 = -\Delta H^0 + T\Delta S^0$$

$$-\Delta G^0 = -\Delta H^0 - T\left(\frac{\partial \Delta G_R^0}{\partial T}\right)_p \quad (12) \text{ Gibbs Helmholtz equation}$$

$$-\Delta G^0 = -\Delta H^0 - T\left(\frac{\partial(-nFE^0)}{\partial T}\right)_p$$

$$nFE^0 = -\Delta H^0 + TnF\left(\frac{\partial E^0}{\partial T}\right)_p \quad (21)$$

Evidently whether the electrical energy nFE is equal to or greater or less than the enthalpy of the cell reaction (ΔH), depend up on the sign of $\left(\frac{\partial E}{\partial T}\right)_p$ i.e up on the sign of the temperature coefficient of EMF of the cell. It is zero the electrical energy will be equal to the enthalpy of the cell reaction. If it is positive the EMF of the cell increases with rise in temperature, the electrical energy will be greater than the enthalpy of cell reaction. The additional energy will be supplied to the cell by the surroundings and if that is not possible, the temperature of the cell will fall during working. If $\left(\frac{\partial E}{\partial T}\right)_p$ is negative, the electrical energy will be smaller than the enthalpy of the reaction. The difference between the two values will be given out as heat to the surroundings and if that is not possible the

temperature of the cell increases during it operation. In the case of Daniel cell $\left(\frac{\partial E}{\partial T}\right)_p$ is very small therefore electrical energy is very close to the enthalpy of the cell reaction. To find ΔH we can use equation 21.

$$\Delta H = -nFE + TnF \left(\frac{\partial E}{\partial T}\right)_p \quad (22)$$

Thus by measuring the standard EMF of a cell at a series of temperature, we can calculate the thermodynamic quantities $\Delta G^0, \Delta S^0$ and ΔH^0 for the cell reaction. As a matter of fact since the EMF measurements can be carried out with good accuracy, the determination of thermodynamic quantities by this method is more accurate than their determination from calorimetry or from equilibrium constant determination.

(f) **Determination of solubility product of sparingly soluble salt**

Refer page number 27

(g) **Determination of pH**

(i) By using hydrogen electrode Refer page number 28

(ii) By using quinhydrone electrode Refer page number 29

(h) **Determination of transport numbers**

Refer page number 23 equation 28a

Activity and Mean Activity of an electrolyte

Consider a uni-univalent electrolyte, like HCl in aqueous solution. Let a_+ and a_- be the hypothetical activities of H$^+$ and Cl^- ions, respectively in a solution of a given concentration. The activity a of the electrolyte is defined by the expression.
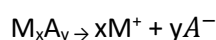
$$a = a_+ a_-$$

while the mean ionic activity $a_\pm$ of the electrolyte is defined by the expression

$$a_\pm = \sqrt{a_+ a_-}$$

Thus while the activity of an electrolyte is given by the product of activities of component ions, the mean ionic activity of the electrolyte is given by the geometric mean of activities of component ions.

$$(a_\pm)^2 = a_+ a_- = a$$

Consider an electrolyte M$_x$A$_y$ ionizing as

$$M_xA_y \rightarrow xM^+ + yA^-$$

For the sake of simplicity the charge on each cation is represented by single plus and that on each anion is by a single minus sign. Accordingly, the activity of the electrolyte is the case is given by

$$a = (a_+)^x (a_-)^y$$

$$= (a_\pm)^{x+y}$$

If m is the concentration of the electrolyte in terms of molality ie number of moles per kg of the solvent , then the molality of the cation, m_+= xm and the molality of anions $m_- = ym$

The activity and molality are known to be related by the expression

$$a = \gamma m$$

Where γ is the activity coefficient

The activity of the electrolyte M_xA_y is therefore given by

$$a = (\gamma_+ m_+)^x (\gamma_- m_-)^y$$

$$= (\gamma_+ xm)^x (\gamma_- ym)^y$$

$$= x^x y^y (\gamma_\pm m)^{x+y}$$

where $\gamma_\pm$ is the mean ionic activity coefficient related with γ_+ and γ_- by the expression

$$(\gamma_\pm)^{x+y} = (\gamma_+)^x (\gamma_-)^y$$

For a univalent electrolyte like HCl or NaCl x = 1 and y = 1

$$a = (a_\pm)^2$$

$$a = (\gamma_\pm m)^2$$

The quantity measured by experiment is either a or mean ionic activity of the electrolyte $a_\pm$ at a given molality m. Hence mean activity coefficient $\gamma_\pm$ of the electrolyte at a given concentration(molality) can be easily calculated.

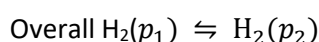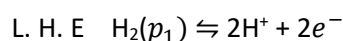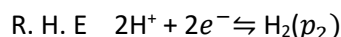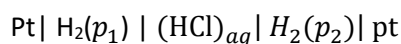For a uni-bivalent electrolyte like Na_2SO_4 x =2 and y =1

$$a = (a_\pm)^3$$

$$a = 2^2 \times 1 (\gamma_\pm m)^3$$

$$= 4\, \gamma_\pm^3 m^3$$

Concentration Cells

Dr. Biju A R

Concentration cells are of two types (1) Electrode concentration cell and (2) Electrolyte concentration cell

(1) **Electrode concentration cell**

In these cells two like electrodes at different concentrations are dipping in the same solution. Two hydrogen electrodes at unequal gas pressures immersed in the same solution of hydrogen ions constitute the electrode concentration cell. This may be represented as

$$\text{Pt}| \, H_2(p_1) \, | \, (HCl)_{aq} | \, H_2(p_2)| \, \text{pt}$$

$$\text{R. H. E} \quad 2H^+ + 2e^- \leftrightharpoons H_2(p_2)$$

$$\text{L. H. E} \quad H_2(p_1) \leftrightharpoons 2H^+ + 2e^-$$

$$\text{Overall } H_2(p_1) \leftrightharpoons H_2(p_2)$$

This reaction is evidently independent of the concentration of the electrolyte. At moderate pressure, H_2 can be considered as ideal gas and so the ration of the activities can be considered to be equal to the ratio of the gas pressures. Hence the Nernst equation may be written as

$$E = E^0 - \frac{0.05916}{2} log\left(\frac{p_2}{p_1}\right)$$

By definition $E^0 = 0$ so

$$E = -0.02958 \, log\left(\frac{p_2}{p_1}\right)$$

$$E = 0.02958 \, log\left(\frac{p_1}{p_2}\right)$$

When $p_2 < p_1$ the emf is positive so that whole process is spontaneous being equivalent to the expansion of the H_2 gas.

(2) **Electrolyte concentration cell**

In these cells, the two electrodes of the same metal are dipping in solutions of metal ions of different concentrations hence of different activities one such a cell is represented below.

$$\text{Zn} \, | \, Zn^{2+} \, (a_+)_1 \, || \, Zn^{2+} \, (a_+)_2 \, | \, \text{Zn}$$

In this case both the electrodes are of the same metal Zn and these are in contact with solutions of the same ions (Zn^{2+}). The concentrations and hence activities of the ions are however different. Let $(a_+)_1$ and $(a_+)_2$ be the activities of zinc ions in the two electrolytes surrounding the electrodes. The two electrolytes which are generally $ZnSO_4$ solutions are separated each other by salt bridge.

The reactions occurring are

R. H. E $Zn^{2+} \, (a_+)_2 + 2e^- \leftrightharpoons Zn_{(s)}$

L.H.E $Zn^{2+} \, (a_+)_1 + 2e^- \leftrightharpoons Zn_{(s)}$

Overall $$\qquad\qquad Zn^{2+}(a_+)_2 \leftrightharpoons Zn^{2+}(a_+)_1$$

The net process thus involves the transfer of 1 moles of Zn^{2+} ions from the solutions in which activity is $(a_+)_2$ to the solution in which the activity is $(a_+)_1$

According to the Nernst equations
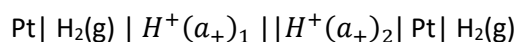
$$E_R = E_{ele}^0 - \frac{RT}{nF} ln \frac{1}{(a_+)_2}$$

$$E_R = E_{ele}^0 + \frac{RT}{nF} ln(a_+)_2$$

$$E_L = E_{ele}^0 + \frac{RT}{nF} ln(a_+)_1$$
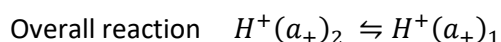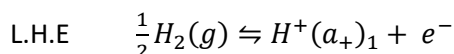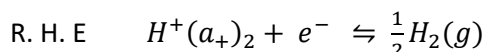
$$E_{Cell} = \frac{RT}{nF} ln \frac{(a_+)_2}{(a_+)_1}$$

For the process to be spontaneous, emf should be positive and hence $(a_+)_2 > (a_+)_1$

Consider another concentration cell represented by

$$Pt|\ H_2(g)\ |\ H^+(a_+)_1\ ||H^+(a_+)_2|\ Pt|\ H_2(g)$$

In this case both the electrodes are hydrogen gas electrodes which are in contact with hydrogen ions of different activities. The two solutions which are generally solutions of hydrochloric acid are separated by salt bridge.

The following process takes place at the two electrodes

R. H. E $\qquad H^+(a_+)_2 + e^- \leftrightharpoons \frac{1}{2}H_2(g)$

L.H.E $\qquad \frac{1}{2}H_2(g) \leftrightharpoons H^+(a_+)_1 + e^-$

Overall reaction $\quad H^+(a_+)_2 \leftrightharpoons H^+(a_+)_1$

The emf of the cell will be given as before

$$E_{Cell} = \frac{RT}{nF} ln \frac{(a_+)_2}{(a_+)_1}$$

Types of electrolyte concentration cells

Electrolyte concentration cells in which solutions of the same electrolyte of different concentrations are used are of two types. In one of the types, two solutions are in direct contact with each other. The transference of ions from one solution to other take place directly such cell are called **concentration cell with transference**. In the second type the two electrolyte solutions are not in direct contact with each other and transference of ions from one solution to the other does not take place directly. These are called **concentration cell without transference**. The two solutions are separated from each other by means of salt bridge or by some other means.

If the two electrode systems that compose a cell involve electrolytic solutions of different composition, there will be a potential difference across the boundary between the two solutions. This potential difference is called the liquid junction potential, or the diffusion potential. To illustrate how such a potential difference arises, consider two silver-silver chloride electrodes, one in contact with a concentrated HCl solution, activity = a_1 the other in contact with a dilute HCl solution, activity = a_2 ; Fig. 3(a). If the boundary between the two solutions is open, the H^+ and Cl^- ions in the more concentrated solution diffuse into the more dilute solution. The H^+ ion diffuses much more rapidly than does the Cl^- ion (Fig. 7b). As the H^+ ion begins to outdistance the Cl^- ion, an electrical double layer develops at the interface between the two solutions (Fig. 3c). The potential difference across the double layer produces an electrical field that slows the faster moving ion and speeds the slower moving ion. A steady state is established in which the two ions migrate at the same speed ; the ion that moved faster initially leads the march.
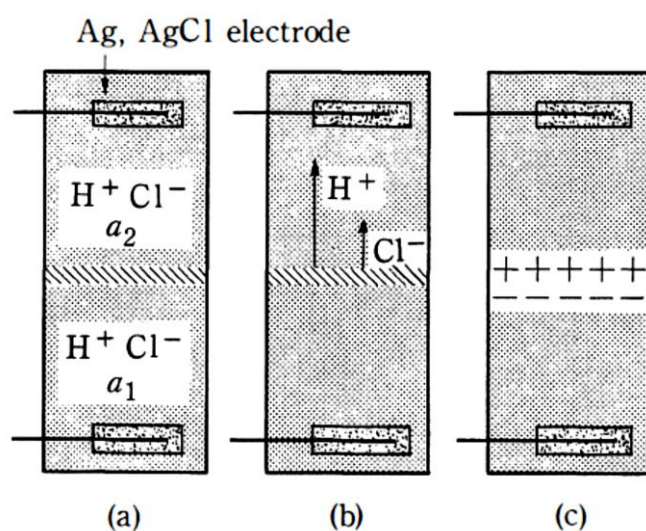
Ag, AgCl electrode

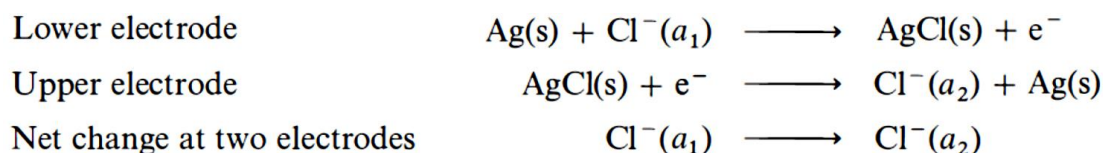**Figure 7**.Development of a junction potential

The diffusion from the concentrated to the dilute solution is an irreversible change; however, if it is very slow-slow enough that the interface does not move appreciably in the time we require to make the measurements-then we may consider the system at "equilibrium" and ignore the motion of the boundary. However, the additional potential difference in the liquid junction will show up in the measurements of the cell potential. Choosing the lower electrode as the left-hand electrode, the symbol for this cell is

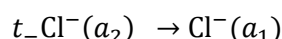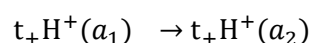$$Ag|\ AgCl|Cl^-(a_1)\ \vdots\ Cl^-(a_2)|AgCl|Ag$$
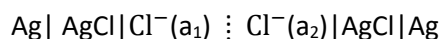
where dashed vertical bar represents the junction between two aqueous phases. We can calculate the potential of the cell if we assume that on the passage of one mole of electrical charge through the cell all of the changes take place reversibly. Then the potential of the cell is given by

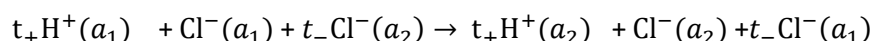$$-FE = \sum_i \Delta G_i \quad (23)$$

$\Delta G_i$is the sum of all the Gibbs energy changes in the cell that accompany the passage of one mole of positive charge upward through the cell. These Gibbs energy changes are

23

Lower electrode	$Ag(s) + Cl^-(a_1) \longrightarrow AgCl(s) + e^-$
Upper electrode	$AgCl(s) + e^- \longrightarrow Cl^-(a_2) + Ag(s)$
Net change at two electrodes	$Cl^-(a_1) \longrightarrow Cl^-(a_2)$

In addition, at the boundary of the two solutions a fraction t_+ of the charge is carried by H^+ and a fraction t_- is carried by Cl^-. The fractions t_+ and t_- are the transference numbers, or transport numbers, of the ions. One mole of positive charge passing through the boundary requires that t_+ moles of H^+ ion are moved upward from the solution a_1 to the solution a_2, and t_- moles of Cl^- are moved downward from a_2 to a_1.

$$t_+H^+(a_1) \rightarrow t_+H^+(a_2)$$

$$t_-Cl^-(a_2) \rightarrow Cl^-(a_1)$$

Thus at the boundary

$$t_+H^+(a_1) + Cl^-(a_1) + t_-Cl^-(a_2) \rightarrow t_+H^+(a_2) + Cl^-(a_2) + t_-Cl^-(a_1)$$

The sum of the fractions must be unity so that $t_- = 1 - t_+$ using this value of t_- in the equation and rearranges to

$$t_+H^+(a_1) + t_+Cl^-(a_1) \rightarrow t_+H^+(a_2) + t_+Cl^-(a_2) \quad (24)$$

The cell reaction is the transfer of t_+ moles of HCl from the solution of a_1 to the solution of a_2. The total Gibbs energy change is

$$\Delta G = t_+\left[\mu^0_{H^+} + RT\ln(a_{H^+})_2 + \mu^0_{Cl^-} + RT\ln(a_{Cl^-})_2 - \mu^0_{H^+} - RT\ln(a_{H^+})_1 - \mu^0_{Cl^-} - RT\ln(a_{Cl^-})_1\right]$$
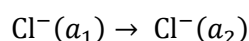
$$\Delta G = t_+RT\ln\left(\frac{(a_{H^+})_2(a_{Cl^-})_2}{(a_{H^+})_1(a_{Cl^-})_1}\right)$$

$$\Delta G = 2t_+RT\ln\frac{(a_\pm)_2}{(a_\pm)_1}$$

Since $a_{H^+}a_{Cl^-} = a_\pm^2$ Using equation 23 we have for the potential of the cell with transference

$$E_{wt} = -\frac{2t_+RT}{F}\ln\frac{(a_\pm)_2}{(a_\pm)_1} \quad (25)$$

If the boundary between the two solutions did not contribute to the cell potential, then the only change would be that contributed by the electrodes, which is

$$Cl^-(a_1) \rightarrow Cl^-(a_2)$$

$$\Delta G = \mu^0_{Cl^-} + RT\ln(a_{Cl^-})_2 - \mu^0_{Cl^-} - RT\ln(a_{Cl^-})_1$$

$$\Delta G = RT\ln\frac{(a_{Cl^-})_2}{(a_{Cl^-})_1}$$

Where a_{Cl^-} has been replaced by mean ionic activity $a_\pm$. The cell without transference has the potential

$$E_{wot} = -\frac{\Delta G}{F} = -\frac{RT}{F} ln\frac{(a_\pm)_2}{(a_\pm)_1} \quad (26)$$

The total potential of the cell with transference is that of cell without transference plus a junction potential, E_j. Thus

$$E_{wt} = E_{wot} + E_j \quad (27)$$

$$E_j = E_{wt} - E_{wot}$$

Using equations 25, 26 and 27 we will get

$$E_j = (1 - 2t_+)\frac{RT}{F} ln\frac{(a_\pm)_2}{(a_\pm)_1} \quad (28)$$

From the equation 28 it is apparent that if t_+ is near 0.5 the liquid junction potential will be small. By measuring the potential of the cell with and without transference it is possible to evaluate E_j and t_+

$$E_{wt} = 2t_+ E_{wot} \quad (28a)$$

Consider equation 28

$$E_j = (1 - t_+ - t_+)\frac{RT}{F} ln\frac{(a_\pm)_2}{(a_\pm)_1}$$

$$E_j = \left(1 - t_+ - (1 - t_-)\right)\frac{RT}{F} ln\frac{(a_\pm)_2}{(a_\pm)_1}$$

$$E_j = (t_- - t_+)\frac{RT}{F} ln\frac{(a_\pm)_2}{(a_\pm)_1} \quad (29)$$

It is evident from the equation 29 that the sign as well as the magnitude of L.J.P depend on the transference numbers of anions and cations. If the transference number of the anions and cations of the electrolyte are same ie $t_- = t_+$ then L.J.P is zero or negligibly small. If the transference number of cations is greater than that of anions the L.J.P is negative and if reverse is the case $t_- > t_+$ L.J.P is positive and will add the emf of the cell. Potassium chloride and ammonium nitrate are amongst the electrolyte in which transference numbers of the cations and anions are nearly same. The solutions of the electrolyte are therefore frequently used as salt bridge because liquid junction potential is then reduced to a minimum.

Salt bridge

A salt bridge consists of a U shaped glass tube and it consists of a saturated solution of a salt such as KCl/KNO₃/NH₄NO₃, whose ions have almost same migration velocities. The positive and negative ions of the salt in the salt bridge migrate with equal speed into cathode and anode compartments respectively, thereby avoiding liquid junction potential.

The functions of salt bridge are as follows: It provides a low resistance electrical connections between the two half cells. It keeps the solutions in the two half cells electrically neutral and also keeps the two solution separated without mixing.
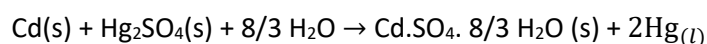
Elimination of liquid junction potential

The liquid junction potential interferes with the exact measurement of the electromotive force of a chemical cell, so its effect should be minimized as much as possible for accurate measurement. The most common method of eliminating the liquid junction potential is to place a salt bridge consisting of a saturated solution of potassium chloride (KCl) and ammonium nitrate (NH_4NO_3) with lithium acetate(CH_3COOLi) between the two solutions constituting the junction. When such a bridge is used, the ions in the bridge are present in large excess at the junction and they carry almost the whole of the current across the boundary. The efficiency of KCl/NH_4NO_3 is connected with the fact that in these salts, the transport numbers of anions and cations are the same.
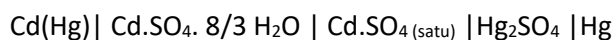
Weston Cadmium Cell

Weston cell is a standard cell. The EMF of a Weston cell remains constant for a long period of time provided that no appreciable current is drawn from the cell. Weston Cells are very rarely used as a source of energy; if any at all! Instead Weston cell is used as a voltage reference of standard EMF for electrical analysis and measurements. Weston cell is also called Cadmium cell because of it's use of cadmium. The standard voltage of a Cadmium cell was measured to be 1.0184 International Voltage which was latter refined and measured to be 1.0183 Volts.
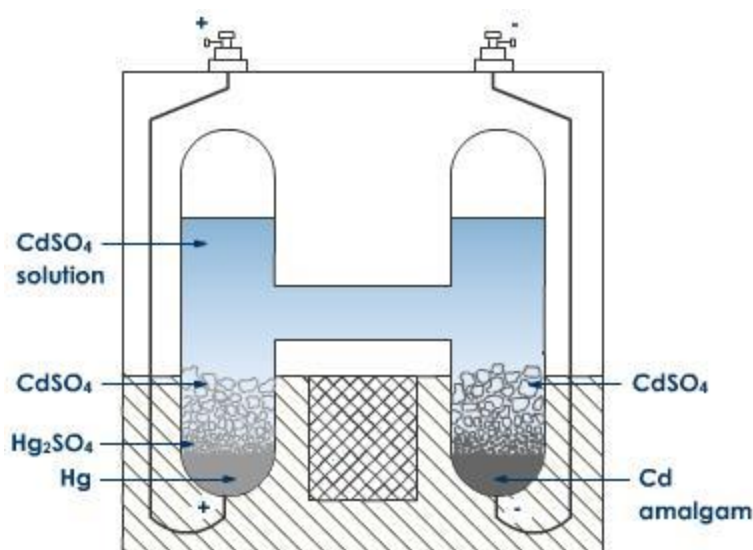
As shown on the figure above a Weston cell contains a H-Shaped glass vessel where, each leg is 25 mm in diameter which contains Conc. cadmium sulfate solution in the upper part and the paste of The right hand compartment consist of an amalgam of cadmium with mercury a an electrode and the left hand electrode is pure mercury. A paste of $CdSO_4 . \frac{8}{3} H_2O$ and Hg_2SO_4 act as a de-polarizers.

$$Cd(s) + Hg_2SO_4(s) + 8/3\ H_2O \rightarrow Cd.SO_4. 8/3\ H_2O\ (s) + 2Hg_{(l)}$$

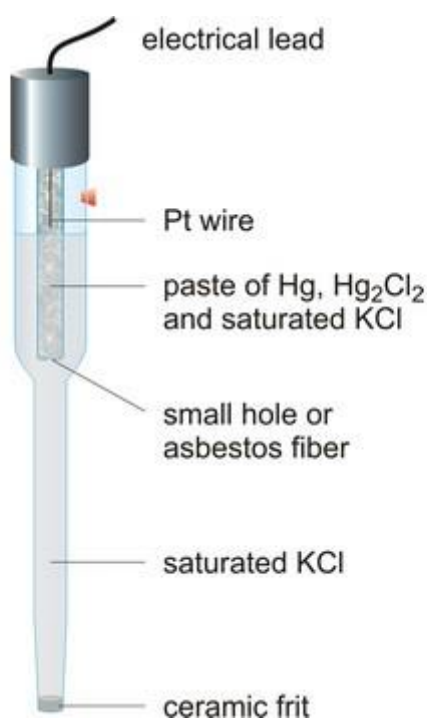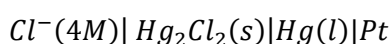$$Cd(Hg)|\ Cd.SO_4.\ 8/3\ H_2O\ |\ Cd.SO_{4\ (satu)}\ |Hg_2SO_4\ |Hg$$

Calomel Electrode

The use of hydrogen electrode is cumbersome for two reasons : (i) a stream of pure gas at a given pressure has to be bubbled around the platinum for electrical contact and (ii) the platinum is prone to poisoning because of possible impurities in the gas. Except for very accurate work, several reference electrodes, have come into wide use because of the reproducibility of the electrode potentials and their easy method of construction.

The most widely used reference electrode is calomel electrode (CE) The calomel electrode (CE) is a reference electrode based on the reaction between elemental mercury and mercury(I) chloride. It has been widely replaced by the silver chloride electrode, however the calomel electrode has a reputation of being more robust. The aqueous phase in contact with the mercury and the mercury(I) chloride (Hg_2Cl_2, "calomel") is a solution of potassium chloride in water. If saturated solution of KCl is used then the electrode is called Saturated calomel electrode (SCE).

The cell notation of the electrode is written as

$$Cl^-(4M)|\ Hg_2Cl_2(s)|Hg(l)|Pt$$

The electrode is based on the redox reaction

$$Hg_2^{2+} + 2e^- \leftrightharpoons 2Hg_{(l)}$$

The electrode potential is

$$E = E^0 - \frac{RT}{2F} \ln \frac{1}{a_{Hg_2^{2+}}}$$

The electrode is reversible with respect to Cl⁻ ions. For common use three different concentrations of potassium chloride (0.1 N, 0.01N and saturated) are used to obtain decinormal, normal and saturated calomel electrodes. The potentials of these have been measured against SHE and are known accurately at different temperatures. At 25 °C, these are respectively +0.334 V (decinormal KCl), +0.280 (normal KCl) and +0.2444 (saturated KCl). The SCE is used in pH measurement, cyclic voltametry and general aqueous electrochemistry.

Glass electrode

A glass electrode is perhaps the most successful and ubiquitous electrochemical sensor. It provides information about the activity of hydronium ions, H_3O^+, in water. Because water, which mildly dissociates to H_3O^+ and OH^- ions, is the most common solvent medium, and chemical reactions in water largely depend on H_3O^+ activity, the ability to measure it is essential.
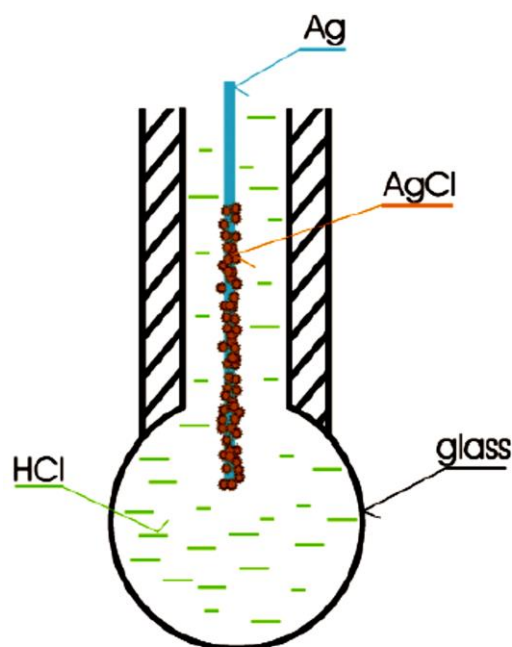
Figure 8 : Schematic diagram of glass electrode

Glass electrode consists of a glass bulb membrane, which gives it its name and an electrically insulating tubular body, which separates an internal solution and a silver/silver chloride electrode from the studied solution. The Ag/AgCl electrode is connected to a lead cable terminated with some connector that can hook up to a special voltmeter, the pH meter. The pH meter measures the potential difference and its changes across the glass membrane. A second point is obtained by connecting to a reference electrode, immersed in the studied solution. Often, this reference electrode is built in the glass electrode (a combination electrode), in a concentric double barrel body of the device.
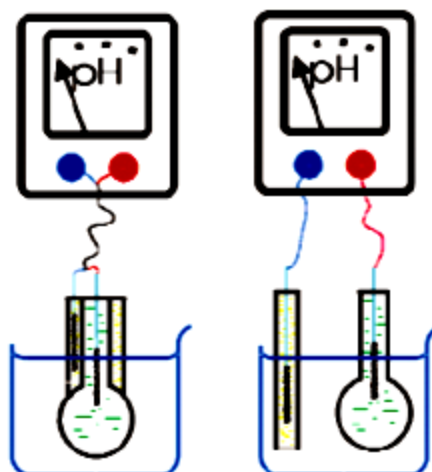
Fɪɢ. 9 . *Measurement with (left) a glass electrode, combination style; and (right) a separate glass electrode and a reference electrode.*

Figure 9: *shows a diagram of such a device. Figure 9a, the combination electrode and Fig. 9b, a glass electrode and separate reference electrode, are functionally identical.*

The glass membrane has two wall/solution interfaces and there is a potential build up on each of them with opposite polarity. But the pH inside the bulb is constant, because the internal solution is sealed. Therefore the inner surface potential is constant adding merely to an offset to the overall potential of the device. Additional contribution to the offset comes from potentials of the inner solution electrode and the reference electrode, which are also constant. The changes in the device potential are therefore due entirely to the pH changes of the outside solution and the potential of glass electrode/reference electrode setup is

$$E_{electrode} = E' + \frac{2.303RT}{F} \log a_{(H_2O^+)}$$

$$pH = -\log a_{(H_2O^+)}$$

$$E_{electrode} = E' - \frac{2.303RT}{F} pH$$

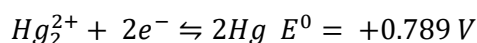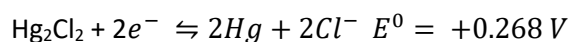**Determination of Solubility product of sparingly soluble salt**

The solubility product K_{sp} of the salt $AB_n \rightarrow A^{n+} + nB^-$; is defined as $K_{sp} = [A^{n+}][B^-]^n$ is an equilibrium constant and its value can be predicted from the knowledge of the standard electrode potentials. The electrodes are chosen such way that overall cell reaction is the solubility product equilibrium. A suitable galvanic cell is thus set up and its emf is determined experimentally. Even if measurements cannot be made, it is possible to arrive at the approximate values of K_{sp} from appropriate half cell reaction potentials as shown below

We will now illustrate the calculation of solubility product for Hg_2Cl_2 at 298K from electrode potentials
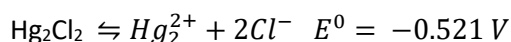
$$Hg_2Cl_2 \leftrightharpoons Hg_2^{2+} + 2Cl^-$$

$$K_{sp} = [Hg_2^{2+}][Cl^-]^2$$

We need to look for a reaction in which Hg₂Cl₂ take part and another reaction in which Hg_2^{2+} and Cl^- take part. The cell should be the combinations of Hg| Hg₂Cl₂ and Hg|Hg_2^{2+}. The reactions are

$$Hg_2Cl_2 + 2e^- \leftrightharpoons 2Hg + 2Cl^- \quad E^0 = +0.268\,V$$

$$Hg_2^{2+} + 2e^- \leftrightharpoons 2Hg \quad E^0 = +0.789\,V$$

Reaction 1 – reaction 2 gives

$$Hg_2Cl_2 \leftrightharpoons Hg_2^{2+} + 2Cl^- \quad E^0 = -0.521\,V$$

$$\Delta G^0 = -RT \ln K_{eq} = -nFE^0$$

$$K_{sp} = [Hg_2^{2+}][Cl^-]^2$$

$$K_{eq}[Hg_2Cl_2] = K_{sp}$$

Since the activity of solid is taken to be 1. Since the concentrations of most of the ions of these sparingly soluble salts are less than 10⁻⁴ M, activities have been replaced by concentrations.

$$RT \ln K_{sp} = nFE^0$$

$$\ln K_{sp} = \frac{nFE^0}{RT}$$

$$K_{sp} = e^{\frac{nFE^0}{RT}} \ or \ 10^{\left[\frac{nFE^0}{2.303RT}\right]}$$

Determination of pH by using hydrogen electrode

The potential of a hydrogen electrode in contact with a solution of H⁺ ions involving the reaction

$$H^+ + 1e^- \leftrightharpoons {}^1\!/_2\,H_2 \ (1\ atm)$$
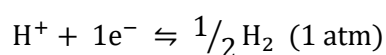
Is given by Nernst equation

$$E = E^0 + \frac{2.303RT}{F} \log\,[H^+]$$

By convention E^0 is taken as zero

$$E = \frac{2.303RT}{F} \log\,[H^+]$$

$$= 0.05916 \log\,[H^+] = -0.05916\,pH$$

Thus the potential of a hydrogen electrode depends upon the pH of the solution with which in contact. This can be determined by combining the hydrogen electrode with a reference electrode, say, calomel electrode, the complete cell is represented as

Pt | H₂ (1 atm)| H⁺(c = unknown) || KCl (sat, soln) | Hg₂Cl₂ (s) |Hg
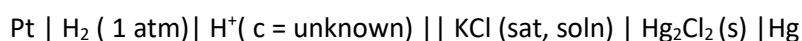
emf of the cell is determined by potentiometrically thus is given by

$$E = E_R - E_L = 0.2444 - (-0.05916 \, pH)$$

$$pH = \frac{E - 0.2444}{0.05916}$$

Using quinhydrone electrode

Quinhydrone, as it is called, is an equimolar mixture of quinone(Q) and hydroquinone(H_2Q). A small amount of quinhydrone (a sparingly soluble solid material) is added to the solution, the pH of which is to be determined and a Pt electrode is dipped into it.

Then it is combined with a saturated calomel electrode by means of a salt bridge to set up the cell,

$$Pt|Hg(l)\,|Hg_2Cl_2(s)|\,HCl\,|\,H_2Q, Q\,|\,Pt$$
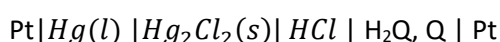
Emf of the cell is given by

$$E_{cell} = E_R - E_L = E_Q - E_{calomel}$$

$$E_{cell} = \left(E_Q^0 - \frac{2.303RT}{2F}\log\frac{a_{H_2Q}}{aQ\,(a_{H^+})^2}\right) - 0.2444$$

$$E_{cell} = 0.6994 - 0.05916\log\frac{1}{(a_{H^+})} - 0.2444$$

$$E_{cell} = 0.6994 + 0.05916\log a_{H^+} - 0.2444$$

$$E_{cell} = 0.6994 - 0.05916\,pH - 0.2444$$
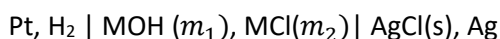
$$0.05916\,pH = 0.6994 - 0.2444 - E_{cell}$$

$$pH = \frac{0.6994 - 0.2444 - E_{cell}}{0.05916}$$

Determination of ionic product of water

Consider a cell without a liquid junction

$$Pt, H_2\,|\,MOH\,(m_1),\,MCl(m_2)|\,AgCl(s),\,Ag$$

For which

$$E = E^0 - \frac{RT}{F}\ln m_{H^+}m_{Cl^-}\gamma_{H^+}\gamma_{Cl^-}$$

$$k_w = \frac{a_{OH^-}a_{H^+}}{a_{H_2O}}$$

$$k_w = \frac{m_{H^+}m_{OH^-}\gamma_{H^+}\gamma_{OH^-}}{a_{H_2O}}$$

$$E = E^0 - \frac{RT}{F}\ln\frac{m_{Cl^-}\gamma_{Cl^-}k_w}{m_{OH^-}\gamma_{OH^-}}$$

$$E = E^0 - \frac{RT}{F}\ln k_w - \frac{RT}{F}\ln\frac{m_{Cl^-}}{m_{OH^-}} - \frac{RT}{F}\ln\frac{\gamma_{Cl^-}}{\gamma_{OH^-}}$$

$$E - E^0 + \frac{RT}{F}\ln\frac{m_2}{m_1} = -\frac{RT}{F}\ln k_w - \frac{RT}{F}\ln\frac{\gamma_{Cl^-}}{\gamma_{OH^-}}$$

The left hand side of equation is plotted as a function of ionic strength and we can determine $-\ln k_w$ when the intercept at C = 0, when $\frac{\gamma_{Cl^-}}{\gamma_{OH^-}} = 1$

Potentiometric titrations

In potentiometric titration the change in ionic concentration which can be measuring the potential of the suitable electrode. The potentiometric titrations are thus those titration in which involves the measurement of electrode potentials with addition of a titrant.

Potentiometric titrations are generally fall into three classes

(1) Acid base titrations

(2) Redox titrations

(3) Precipitation titrations

There are number of advantages of potentiometric titrations over the ordinary titrations involving the use of indicators. Potentiometric titration can be carried out in colored solutions while indicators cannot be used in such cases. Also in ordinary titrations one must have prior information about the relative strength of acids and bases before a proper indicator is selected. However no such information is required in the case of potentiometric titrations.

Acid-Base titrations

In an acid-base titration, the important information to obtain is the equivalence point. If there are a given number of moles of acid in the titration flask, the equivalence point is reached when that same number of moles of base have been added from the buret. The molarity of the base can then be calculated since the number of moles of base added is the same as the number of moles of acid in the flask, and the volume of the base added is also known. Often the pH of the solution will change dramatically at the equivalence point. An acid-base indicator works by changing color over a given pH range. If an indicator which changes color near the equivalence point is chosen, there is also a dramatic change in the color of the indicator at the equivalence point because the pH changes so rapidly. In a potentiometric acid-base titration, an indicator is not necessary. A pH meter is used to measure the pH as base is added in small increments (called aliquots) to an acid solution. A graph is then made with pH along the vertical axis and volume of base added along the horizontal axis. From this graph the equivalence point can be determined and the molarity of the base calculated.

Suppose we want to titrate a solution of HCl against NaOH. Any electrode whose potential depends upon H^+ ion concentration (eg. Hydrogen electrode, glass electrode, quinhydrone electrode) is placed in the HCl solution. It is connected to a reference electrode for example calomel electrode. One of such galvanic cell is given as

$$Pt|\ H_2\ (1\ atm)|\ H+\ (c = unknown)\ ||\ KCl\ (satu)\ |\ Hg_2Cl_2\ (s)\ |Hg$$

The EMF of the cell is measure potentiometrically. It is given by

$$E = E_R - E_L = E_{calomel} - E_{hydrogen}$$

$$E_{calomel} = E^0 - \frac{RT}{2F} ln \frac{1}{a_{Hg_2^{2+}}}$$

$$E_{hydrogen} = E^0 - \frac{RT}{F} ln \frac{1}{a_{H+}}$$

$$E_{cell} = E^0 - \frac{RT}{2F} ln \frac{1}{a_{Hg_2^{2+}}} - E^0 + \frac{RT}{F} ln \frac{1}{a_{H+}}$$

$$E_{cell} = 0.2444 + \frac{RT}{F} ln \frac{1}{a_{H+}}$$

$$E_{cell} = 0.2444 - \frac{2.303RT}{F} log\ (a_{H+})$$

$$E_{cell} = 0.2444 + 0.05916\ pH$$

As titration proceeds the H^+ ion concentration goes on decreasing ie pH of the solution goes on increasing. It is evident that the EMF of the cell would increase by 0.0591 V for every ten fold decrease in the concentration of H^+ ion or unit increase in the pH of the solution. After the end point further addition of NaOH produce very little change in the H^+ ion concentration and hence there is very little change in the EMF of the cell. The plot of E against the volume of NaOH added is shown in Fig. As can be seen the EMF of the cell initially rises gradually and thereafter more rapidly near the equivalent point. Beyond the equivalent point the emf of the cell again increases slightly on adding the more of NaOH.

Redox titrations

Like acid-base titrations the redox titrations are also carried out potentiometrically. In this case the electrode reversible with respect to H^+ ion is replaced by an inert metal such as platinum wire, immersed in a solution containing both oxidized and reduced form of the same species. The electrode act as an oxidation reduction electrode.

Let us consider a redox reaction

$$Fe^{2+}(aq) + Ce^{4+}(aq) \leftrightharpoons Fe^{3+}(aq) + Ce^{3+}(aq)$$
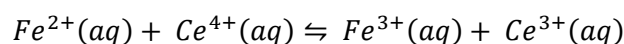
involving the oxidation of Fe^{2+} ions by Ce^{4+} ions being carried out potentiometrically. Prior to the addition of Ce^{4+} ions the solution contains only the Fe^{2+} ions and so we cannot calculate the potential. On addition of small amount titrant, a known amount of Fe^{2+} is converted to Fe^{3+} and we can calculate the potential from the Fe^{2+}/Fe^{3+} ratio by applying Nernst equation.

$$E_{elc} = E^0 - \frac{RT}{F} ln \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

$$E_{elc} = E^0 - 0.05916 \, log \frac{[Fe^{2+}]}{[Fe^{3+}]} \quad at \ 25\,°C$$

At equivalent point of our titration we have a following condition.

$$\underset{x}{Fe^{2+}} + \underset{x}{Ce^{4+}} \rightarrow \underset{C-x}{Fe^{3+}} + \underset{C-x}{Ce^{3+}}$$
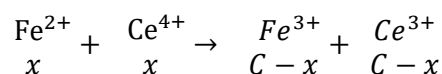
Where C is the concentration of Fe^{3+} ion, which we know since all of the Fe^{2+} is converted to Fe^{3+} ion (x is negligible compared to C) Now, we have an unknown quantity in both half-reactions, and so we must solve for x by equating the two Nernst equations. Then, we can calculate the potential from either half-reaction.

$$E_{eq} = E_1^0 - 0.05916 \, log \frac{[Fe^{2+}]}{[Fe^{3+}]} = E_2^0 - 0.05916 \, log \frac{[Ce^{3+}]}{[Ce^{4+}]}$$

Adding and simplifying keeping in mind that at the equivalence point

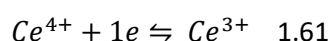$$[Fe^{2+}] = [Ce^{4+}] \ and \ [Fe^{3+}] = [Ce^{4+}] \ we \ get$$
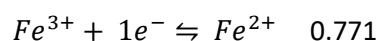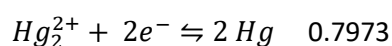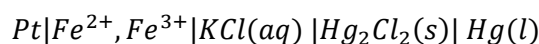
$$E_{eq} = \frac{E_1^0 + E_2^0}{2}$$

The numerical values of E_1^0 and E_2^0 are 0.77 V and 1.61 V respectively according to the equations

$$Fe^{3+}(aq) \leftrightharpoons Fe^{2+}(aq) \quad E_1^0 = 0.77 \, V$$

$$Ce^{4+}(aq) \leftrightharpoons Ce^{3+}(aq) \quad E_2^0 = 1.61 \, V$$
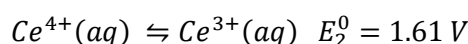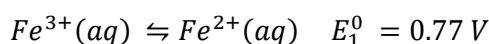
, Beyond the equivalence point $[Fe^{3+}] = 0$ as a result of which the electrode potential thereafter is controlled by only the $[Ce^{3+}]/[Ce^{4+}]$ ratio.

For potentiometric measurements the oxidation-reduction electrode (pt, $\frac{[Fe^{2+}]}{[Fe^{3+}]}$) is combined with the reference electrode e.g. Saturated calomel electrode, to form a galvanic cell which is represented as

$$Pt|Fe^{2+}, Fe^{3+}|KCl(aq)\,|Hg_2Cl_2(s)|\,Hg(l)$$

$$Hg_2^{2+} + 2e^- \leftrightharpoons 2\,Hg \quad 0.7973$$

$$Fe^{3+} + 1e^- \leftrightharpoons Fe^{2+} \quad 0.771$$

$$Ce^{4+} + 1e \leftrightharpoons Ce^{3+} \quad 1.61$$

Before the equivalent point the emf of the cell would be given by

$$E = E_R - E_L = 0.2444 - E_1^0 + 0.05916 \, log \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

$$= 0.2444 - 0.77 + 0.05916 \, log \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

After the equivalent point

$$Hg(l)| \, Hg_2Cl_2(s)|KCl(aq)|Ce^{4+}, Ce^{3+}|Pt$$
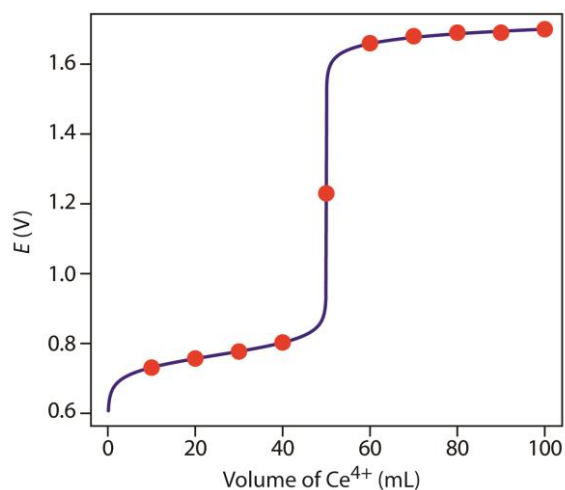
$$E = E_2^0 - 0.05916 \, log \frac{[Ce^{3+}]}{[Ce^{4+}]} - 0.2444$$

$$E = 1.61 - 0.05916 \, log \frac{[Ce^{3+}]}{[Ce^{4+}]} - 0.2444$$

At the equivalent point

$$E_{eq} = \frac{0.77 + 1.61}{2} - 0.2444$$

The emf of the cell is measured potentiometrically at each stage of titration and the emf data thus obtained is plotted against titrant volume to get the titration curve as shown below

Determination of transport numbers

The EMF of a concentration cell with transference is represented by W_{wt} is given by

$$E_{wt} = - \frac{2t_+ RT}{F} \ln \frac{(a_\pm)_2}{(a_\pm)_1}$$

The E.M.F of the same cell with the same solution but without transference is given by

$$E_{wot} = - \frac{RT}{F} \ln \frac{(a_\pm)_2}{(a_\pm)_1}$$

$$\frac{E_{wt}}{E_{wot}} = 2t_+$$

$$t_+ = \frac{E_{wt}}{2E_{wot}}$$

From the value of t_+ we calculate the value of t_-, as $t_- = 1 - t_+$

Fuel cell

Fuel cells are galvanic cells in which chemical energy of fuel is directly converted into the electrical energy. The conventional conversion of chemical energy of fuels into electrical energy is carried out by burning the fuel, using the heat energy to raise steam which is then used for spinning the turbines connected with electric generators. The efficiency of this process, which cannot exceed than that of reversible Carnot engine, varies from 20 to 40 percent. Fuel cells on other hand, convert about 75 % of the available chemical energy into electrical energy.

Hydrogen Oxygen Fuel cell

A common type of fuel cell is based on the combustion of hydrogen to form water
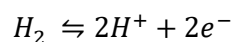
$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$$
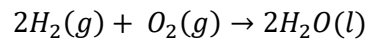
This is known as hydrogen-oxygen fuel cell
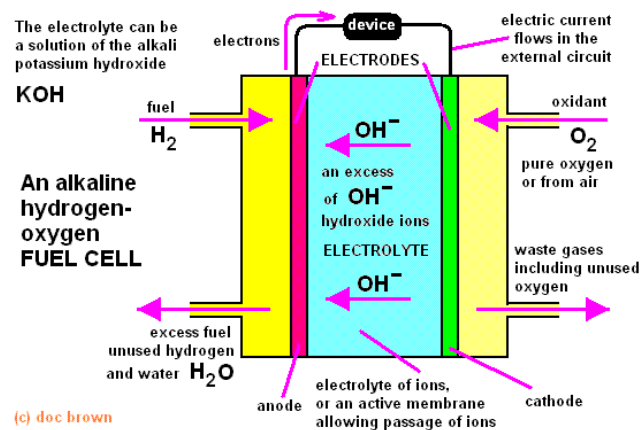
It consist of two electrodes made of porous graphite impregnated with a catalyst (platinum, silver or metal oxide). The electrodes are placed in an aqueous solution of KOH or NaOH. Oxygen and hydrogen are continuously fed into the cell under a pressure of about 50 atm. The gases diffuse into the electrode pores and so does the electrolyte solution.

The half cell reactions which occur at the electrodes are as follows

Oxidation half cell reaction. The hydrogen is oxidized to H⁺ ions which are neutralized by ⁻OH ions of the electrolyte:
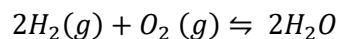
$$H_2 \leftrightharpoons 2H^+ + 2e^-$$

$$2H^+ + 2OH^- \leftrightharpoons 2H_2O$$

The net oxidation half-cell reaction is

$$H_2 + 2OH^- \leftrightharpoons 2H_2O + 2e^-$$
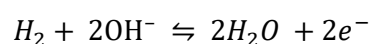
Reduction Half-Cell reaction. Reduction half cell reaction involves the reduction of oxygen to OH^- ions.

$$O_2\ (g) +\ 2H_2O\ + 4e^-\ \leftrightharpoons\ 4OH^-$$
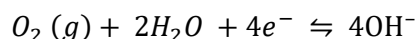
The overall fuel cell reaction is thus given by
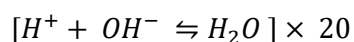
$$2H_2(g) + O_2\ (g) \leftrightharpoons\ 2H_2O$$

He EMF of the cell is found to be 1 volt.

The water produced vaporizes off since the cell is operated at temperature above 100°C. This can be condensed and used. In place of KOH or NaOH, phosphoric acid can also be used as an electrolyte. The cell is operated at about 200°C. At this temperature, phosphoric acid polymerises to pyrphosphoric acid which has considerably higher ionic conductivity than the parent acid.
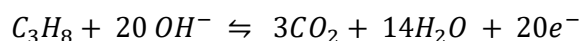
Hydrocarbon-Oxygen Fuel Cell.

Fuel cells based on the combustion of hydrocarbon such as CH_4, C_2H_6, C_3H_8 etc in the presence of catalysts, have also been operated. The half cell reaction with propane as the fuel are as follows.
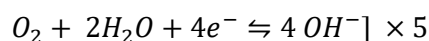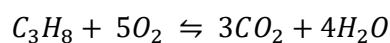
Oxidation Half-cell Reaction

$$C_3H_8 +\ 6H_2O \leftrightharpoons 3CO_2 +\ 20H^+ +\ 20e^-$$

$$[H^+ +\ OH^-\ \leftrightharpoons H_2O\ ] \times\ 20$$

The net oxidation half cell reaction is

$$C_3H_8 +\ 20\ OH^-\ \leftrightharpoons\ 3CO_2 +\ 14H_2O\ +\ 20e^-$$

Reduction Half-cell reaction

$$O_2 +\ 2H_2O + 4e^- \leftrightharpoons 4\ OH^-]\ \times 5$$

Overall fuel cell reaction

$$C_3H_8 +\ 5O_2\ \leftrightharpoons\ 3CO_2 + 4H_2O$$

The catalyst in this case is essentially platinum. This makes the fuel cell operation highly expensive.