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29

Electromotive Force

CHAPTER

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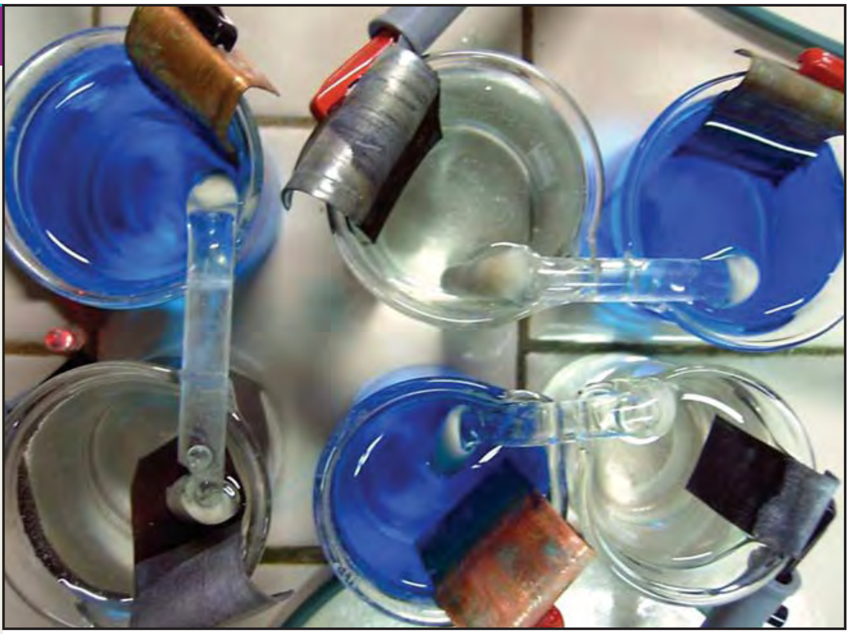


WHAT ARE HALF REACTIONS ?

Let us consider the reaction

$$2\,Na + Cl_2 \longrightarrow 2Na^+ + 2Cl^-$$

It occurs by the transfer of electrons from Na to Cl. Na loses an electron and is said to be oxidized to Na^+ ion. At the same time, Cl gains an electron and is reduced to Cl^- ion. Such a reaction which is brought about by loss of electrons (oxidation) and gain of electrons (reduction) simultaneously, is called an **Oxidation-Reduction reaction or Redox reaction** in brief. It may be noted that in the overall redox reaction no free electrons are generated.

The redox reaction can be considered as made up of two reactions. For example, the redox reaction

$$2Na + Cl_2 \longrightarrow Na^+ + 2Cl^-$$

is composed of two half-reactions :

$$2Na \longrightarrow 2Na^+ + 2e^- \qquad \textit{(oxidation)}$$

$$Cl_2 + 2e^- \longrightarrow 2Cl^- \qquad \textit{(reduction)}$$

Each of the two reactions shows just its oxidation or just the reduction portion of the overall redox reaction. Being half components of the redox reaction, these reactions are called

Half-reactions. The first half-reaction that proceeds by oxidation is often referred to as the **Oxidation half-reaction.** The second half-reaction that occurs by reduction, is referred to as the **Reduction half-reaction.** When the two half-reactions are added together, the sum is the net redox reaction.

We will see presently how redox reactions are a source of electric current in electrochemical cells.

ELECTROCHEMICAL CELLS

A device for producing an electrical current from a chemical reaction (redox reaction) is called an **electrochemical cell.**

How a Redox reaction can produce an electrical current ?

When a bar of zinc is dipped in a solution of copper sulphate, copper metal is deposited on the bar (Fig. 29.1). The net reaction is

$$\mathrm{Zn} + \mathrm{Cu}^{2+} \longrightarrow \mathrm{Zn}^{2+} + \mathrm{Cu}$$

This is a redox reaction and the two half-reactions are :

$$\mathrm{Zn} \longrightarrow \mathrm{Zn}^{2+} + 2e^-$$

$$\mathrm{Cu}^{2+} + 2e^- \longrightarrow \mathrm{Cu}$$

In this change, Zn is oxidized to give Zn^{2+} ions and Cu^{2+} ions are reduced to Cu atoms. The electrons released in the first half-reaction are used up by the second half-reaction. Both the half-reactions occur on the zinc bar itself and there is no net charge.

Now, let the two half-reactions occur in separate compartments which are connected by a wire (Fig. 29.2) The electrons produced in the left compartment flow through the wire to the other compartment. However the current will flow for an instant and then stop. The current stops flowing because of the charge build up in the two compartments. The electrons leave the left compartment and it would become positively charged. The right compartment receives electrons and becomes negatively charged. Both these factors oppose the flow of electrons (electrical current) which eventually stops.

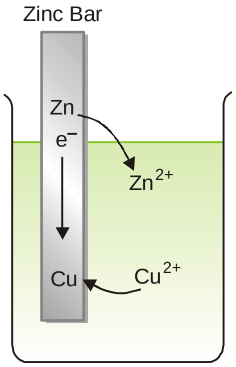


Figure 29.1
Redox reaction taking place on zinc bar itself.

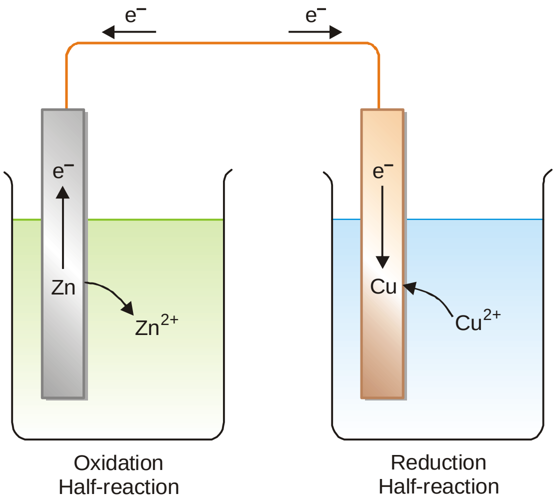


Figure 29.2
Separate half-reactions cause flow of electrons (current) in the wire connecting them.

This problem can be solved very simply. The solutions in the two compartments may be connected, say, by a **salt bridge.** The salt bridge is a U-tube filled with an electrolyte such as NaCl, KCl, or

K_2SO_4. It provides a passage to ions from one compartment to the other compartment without extensive mixing of the two solutions. With this ion flow, the circuit is complete and electrons pass freely through the wire to keep the net charge zero in the two compartments.

Voltaic Cells

A **Voltaic cell,** also known as a **galvanic cell** is one in which electrical current is generated by a spontaneous redox reaction. A simple voltaic cell is shown in Fig. 29.3. Here the spontaneous reaction of zinc metal with an aqueous solution of copper sulphate is used.

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

A bar of zinc metal (anode) is placed in zinc sulphate solution in the left container. A bar of copper (cathode) is immersed in copper sulphate solution in the right container. The zinc and copper electrodes are joined by a copper wire. A salt bridge containing potassium sulphate solution interconnects the solutions in the anode compartment and the cathode compartment.

The oxidation half-reaction occurs in the anode compartment.

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

The reduction half-reaction takes place in the cathode compartment.

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

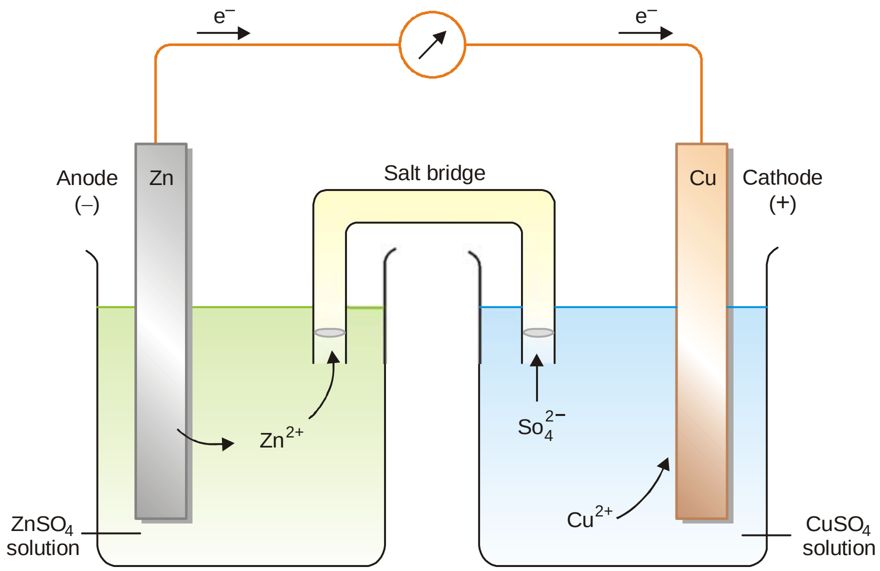


Figure 29.3
A simple voltaic (galvanic) cell.

When the cell is set up, electrons flow from zinc electrode through the wire to the copper cathode. As a result, zinc dissolves in the anode solution to form Zn^{2+} ions. The Cu^{2+} ions in the cathode half-cell pick up electrons and are converted to Cu atoms on the cathode. At the same time, SO_4^{2-} ions from the cathode half-cell migrate to the anode half-cell through the salt bridge. Likewise, Zn^{2+} ions from the anode half-cell move into the cathode half-cell. This flow of ions from one half-cell to the other completes the electrical circuit which ensure continuous supply of current. The cell will operate till either the zinc metal or copper ion is completely used up.

CELL TERMINOLOGY

Before taking up the study of the electrochemical cells, we should be familiar with a few common terms.

Current is the flow of electrons through a wire or any conductor.

Electrode is the material : a metallic rod/bar/strip which conducts electrons into and out of a solution.

Anode is the electrode at which oxidation occurs. It sends electrons into the outer circuit. It has negative charge and is shown as (–) in cell diagrams.

Cathode is the electrode at which electrons are received from the outer circuit. It has a positive charge and is shown as (+) in cell diagrams.

Electrolyte is the salt solutions in a cell.

Anode compartment is the compartment of the cell in which oxidation half-reaction occurs. It contains the anode.

Cathode compartment is the compartment of the cell in which reduction half-reaction occurs. It contains the cathode.

Half-cell. Each half of an electrochemical cell, where oxidation occurs and the half where reduction occurs, is called the half cell.

Daniel Cell

It is a typical voltaic cell. It was named after the British chemist John Daniel. It is a simple zinc-copper cell like the one described above.

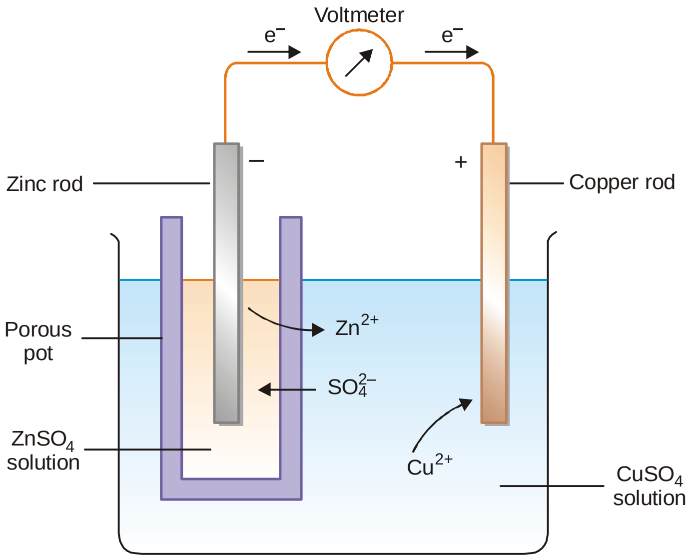
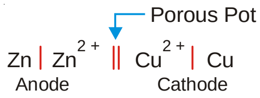


Figure 29.4
Daniel Cell.

In this cell the salt-bridge has been replaced by a porous pot. Daniel cell resembles the above voltaic cell in all details except that Zn^{2+} ions and SO_4^{2-} ions flow to the cathode and the anode respectively through the porous pot instead of through the salt-bridge. Inspite of this difference, the cell diagram remains the same.



Cell reaction

The flow of electrons from one electrode to the other in an electrochemical cell is caused by the half-reactions taking place in the anode and cathode compartments. The net chemical change obtained by adding the two half-reactions is called the **cell reaction.** Thus, for a simple voltaic cell described above, we have

(*a*) Half-reactions :

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

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

(*b*) Cell reaction by adding up the half-reactions :

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

Cell potential or emf

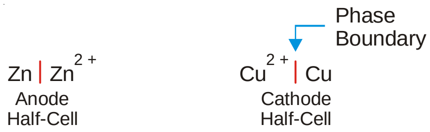
In a Zn-Cu voltaic cell, electrons are released at the anode and it becomes negatively charged. The negative electrode pushes electrons through the external circuit by electrical repulsions. The copper electrode gets positive charge due to the discharge of Cu^{2+} ions on it. Thus electrons from the outer circuit are attracted into this electrode. The flow of current through the circuit is determined by the 'push', of electrons at the anode and 'attraction' of electrons at the cathode. These two forces constitute the 'driving force' or 'electrical pressure' that sends electrons through the circuit. This driving force is called the **electromotive force** (abbreviated **emf**) or **cell potential.** The emf of cell potential is measured in units of volts (V) and is also referred to as **cell voltage.**

Cell diagram or Representation of a Cell

A cell diagram is an abbreviated symbolic depiction of an electrochemical cell. For this purpose, we will consider that a cell consists of two half-cells. Each half-cell is again made of a metal electrode contact with metal ions in solution.

IUPAC Conventions. In 1953 IUPAC recommended the following conventions for writing cell diagrams. We will illustrate these with reference to Zinc-Copper cell.

(1) a **single vertical line** (|) represents a phase boundary between metal electrode and ion solution (electrolyte). Thus the two half-cells in a voltaic cell are indicated as

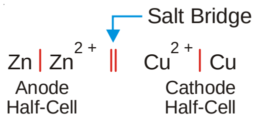


It may be noted that the metal electrode **in anode** half-cell is on the left, while **in cathode** half-cell it is on the right of the metal ion.

(2) A **double vertical line** (||) represents the salt bridge, porous partition or any other **means** of permitting ion flow while preventing the electrolyte from mixing.

(3) **Anode half-cell is written on the left** and **cathode half-cell on the right.**

(4) In the **complete cell diagram, the two half-cells are separated by a double vertical line (salt bridge) in between.** The zinc-copper cell can now be written as



(5) The symbol for an **inert electrode,** like the platinum electrode is often enclosed in a bracket. For example,

$$\mathrm{Mg} \mid \mathrm{Mg}^{2+} \parallel \mathrm{H}^{+} \overset{\text{Inert Electrode}}{\mid} \mathrm{H_2(Pt)}$$

(6) The value of emf of a cell is written on the right of the cell diagram. Thus a zinc-copper cell has emf 1.1V and is represented as

$$\mathrm{Zn} \mid \mathrm{ZnSO_4} \parallel \mathrm{CuSO_4} \mid \mathrm{Cu} \qquad E = +\,1.1\ \mathrm{V}$$

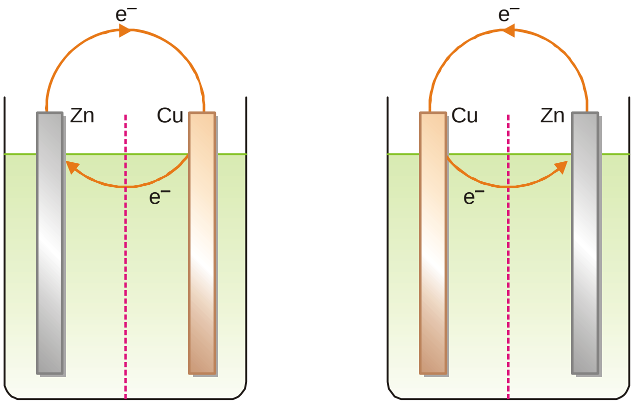
Convention regarding sign of emf value

The magnitude of the emf of a cell reflects the tendency of electrons to flow externally from one electrode to another. The electrons are transported through the cell solution by ions present and pass from the positive electrode (Cu in case of Daniel cell) to the negative electrode. This corresponds to a clockwise flow of electrons through the external circuit. Thus the emf of the cell is given the **+ve sign.** If the emf acts in the opposite direction through the cell circuit, it is quoted as –**ve value.** For example, Daniel cell has an emf of 1.1V and the copper electrode is positive. This can be expressed in two ways :

$$\mathrm{Zn} \mid \mathrm{ZnSO_4} \parallel \mathrm{CuSO_4} \mid \mathrm{Cu} \qquad E = +\,1.1\ \mathrm{V}$$

$$\mathrm{Cu} \mid \mathrm{CuSO_4} \parallel \mathrm{ZnSO_4} \mid \mathrm{Zn} \qquad E = -\,1.1\ \mathrm{V}$$

The negative sign indicates that the cell is not feasible in the given direction. The reaction will take place in the reverse direction.



E = + 1.1V

E = – 1.1V

Figure 29.5
Illustration of emf sign in Daniel cell.

Calculating the emf of a cell

The emf of a cell can be calculated from the half-cell potentials of the two cells (anode and cathode) by using the following formula

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cathode}} - E_{\text{anode}} \\ &= E_R - E_L \qquad \text{(IUPAC convention 3)} \end{aligned}$$

where E_R and E_L are the reduction potentials of the right-hand and left-hand electrodes respectively. It may be noted that absolute values of these reduction potentials cannot be determined. These are found by connecting the half-cell with a standard hydrogen electrode whose reduction potential has been arbitrarily fixed as zero.

MEASUREMENT OF EMF OF A CELL

The emf of an unknown cell can be measured with the help of a **potentiometer** (Fig. 29.6). It consists of a wire AB which is about one metre long. The two ends of this wire are connected to a working battery W. A standard cell C_1 (*i.e.*, a cell of known emf) is connected to the end A. At the other end, the cell C_1 is connected to a galvanometer through a key K_1. The galvanometer is then joined to a sliding contact that moves on the wire AB. The cell C_2 whose emf is to be measured is similarly connected to the key K_2, the galvanometer and then the sliding contact. By using the key K_1, the cell C_1 is put into the circuit and the contact is moved to and fro along AB. When no current flows through the galvanometer, the point of contact X_1 is recorded. Then by using the key K_2, the cell C_2 is put into the circuit and the procedure is repeated to find the corresponding point X_2. The emf of the cell C_2 is calculated by using the following equation :

$$\frac{\text{emf of } C_2}{\text{emf of } C_1} = \frac{\text{distance } AX_2}{\text{distance } AX_1}$$

Cell emf's can also be measured by electronic voltmeters of the analog or digital type.

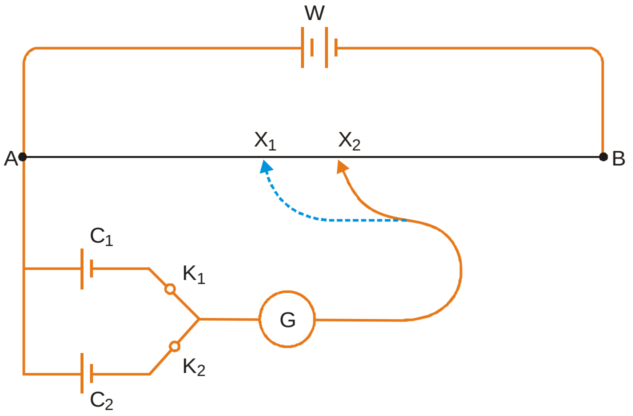


Figure 29.6
Measuring the emf of a cell with a potentiometer.

WESTON STANDARD CELL

A standard cell is one which provides a constant and accurately known emf. The Weston cadmium cell is most widely used as a standard cell. It is constructed in a H-shaped glass tube (Fig. 29.7). The positive electrode consists of mercury covered with a paste of solid mercurous sulphate (Hg_2SO_4) over which is placed a layer of cadmium sulphate crystals. The negative electrode is 12.5% cadmium amalgam, Cd(Hg), covered with cadmium sulphate crystals. The entire cell is filled with saturated cadmium sulphate solutions and sealed.

The cell reactions are :

at anode : $Cd + SO_4^{2-} \rightleftharpoons CdSO_4 + 2e^-$

at cathode : $Hg_2SO_4 + 2e^- \rightleftharpoons 2Hg + SO_4^{2-}$

Overall reaction : $Cd + Hg_2SO_4 \rightleftharpoons CdSO_4 + 2Hg$

The emf of a cadmium standard cell is 1.0183 (V) at 20°C. It varies only slightly (0.0000406 volt/degree) with change of temperature. The emf remains constant for many years.

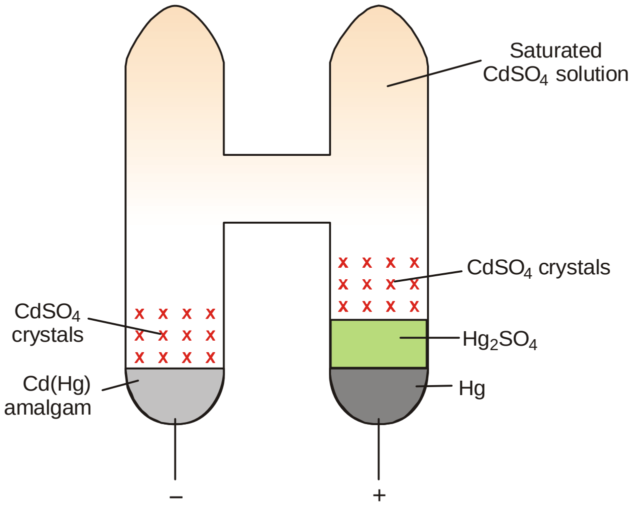


Figure 29.7
Weston cadmium standard cell.

REVERSIBLE CELLS

A familiar example of a reversible cell is the Daniel cell (Fig. 29.8a). We know that electrons flow from zinc electrode to copper electrode due to the net cell-reaction.

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

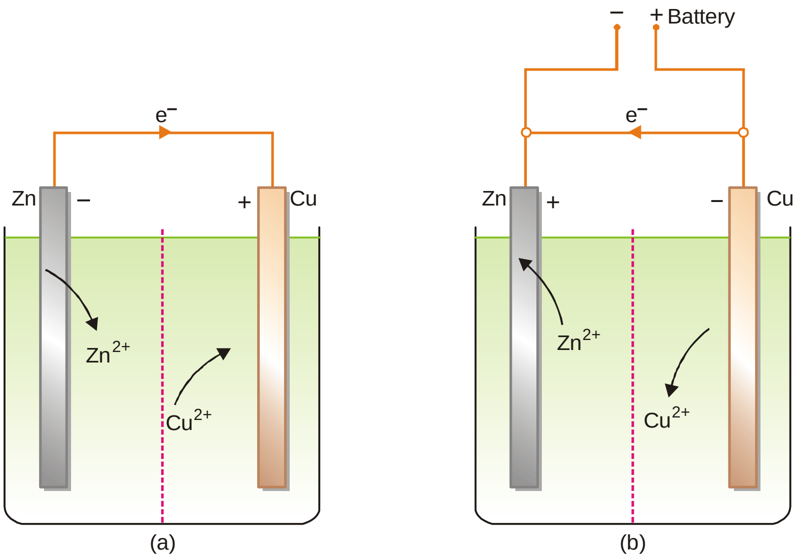


Figure 29.8
Reversible Daniel cell : (*a*) Zn-Cu cell in which current flows from left to right; (*b*) Cu-Zn cell in which current flows from right to left on application of external emf.

However, when the two electrodes are connected to an external battery that opposes the cell emf, the above reaction is reversed (Fig. 29.8 *b*). Cu from the copper electrode dissolves to form Cu^{2+} ion and Zn^{2+} ion is discharged on the zinc electrode to give Zn atom. The overall reaction taking place in the cell may be written as

$$\begin{array}{rcl} \text{Cu} & \longrightarrow & \text{Cu}^{2+} + 2e^- \\ \text{Zn}^{2+} + 2e^- & \longrightarrow & \text{Zn} \\ \hline \text{Cu} + \text{Zn}^{2+} & \longrightarrow & \text{Cu}^{2+} + \text{Zn} \end{array}$$

With the help of a potentiometer (Fig. 29.6), the cell emf is exactly balanced by the external emf. At the balance point, no current will flow through the circuit. Now let the external emf increase and then decrease by an infinitesimal amount. A minute current will flow first to the left and then to the right. This reversal of the cell current is accompanied by a corresponding change in the direction of the cell reaction. This type of reversible behaviour is a feature of the reversible cells. **A reversible cell** may be defined as : **a cell that operates by reversal of the cell current and direction of cell reaction by infinitesimal change of emf on either side of the balance point.**

All voltaic cells are reversible cells.

RELATION BETWEEN EMF AND FREE ENERGY

When a cell produces a current, the current can be used to do work–to run a motor, for instance. Thermodynamic principles can be employed to derive a relation between electrical energy and the maximum amount of work, W_{max}, obtainable from the cell. The maximum amount of work obtainable from the cell is the product of charge flowing per mole and maximum potential difference, E, through which the charge is transferred.

$$W_{max} = -nFE \qquad \text{...(1)}$$

where n is the number of moles of electrons transferred and is equal to the valence of the ion participating in the cell reaction. F stands for Faraday and is equal to 96,500 coulombs and E is the emf to the cell.

According to thermodynamics, the maximum work that can be derived from a chemical reaction is equal to the free energy (ΔG) for the reaction.

$$W_{max} = \Delta G \qquad \text{...(2)}$$

Therefore from (1) and (2), we can write

$$\Delta G = -nFE \qquad \text{...(3)}$$

According to Gibbs-Helmholtz equation, the decrease in free energy of a system at constant pressure is given by the expression

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

where – ΔH is the decrease in heat content of the system or heat of the reaction at constant pressure.

Substituting the value of ΔG from (3)

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

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

$$E = \frac{-\Delta H}{nF} + T\left(\frac{\partial E}{\partial T}\right)_p$$

The temperature coefficient of the emf of the cell (∂E/∂T), at constant pressure, therefore, determines whether the electrical energy would be equal to, more or less than the heat of reaction. Accordingly, three cases may arise:

Case 1. When the temperature coefficient is zero *i.e.*,

$$(\partial E/\partial T)_p = 0, \text{ then}$$

$$nFE = -\Delta H$$

Case 2. When the temperature coefficient is +ve *i.e.*,

$$(\partial E/\partial T)_p > 0, \text{ then}$$

$$nFE > -\Delta H$$

The additional energy will come either from the surroundings or the temperature of the cell would fall.

Case 3. When the temperature coefficient is negative *i.e.*,

$$(\partial E/\partial T)_p < 0, \text{ then}$$

$$nFE < -\Delta H$$

The excess energy will be given either to the surroundings or the temperature of the cell would rise.

If the heat of the reaction (or free energy change) and the temperature coefficient of a cell are known, we can calculate the emf, E, of the cell. For example, in case of a Daniel cell $(\partial E/\partial T)_p$ is nearly zero, $n = 2$ and $\Delta H = -50{,}100$ Cals.

Since 1 Cal = 4.185 Volt-Coulomb,

$$E = \frac{-\Delta H}{nF} = \frac{-4.185 \times (-50{,}100)}{2 \times 96{,}500}$$

$$= 1.09 \text{ V}$$

Thus the emf of Daniel cell is 1.09 volts. Conversely, if the emf of a reversible cell and its temperature coefficient $(\partial E/\partial T)_p$ are known, ΔH (or ΔG) can be calculated. The heats of reaction calculated from emf measurements are nearly the same as derived from thermal measurements.

Single electrode potential

An electrochemical cell consists of two half-cells. With an open-circuit, the metal electrode in each half-cell transfers its ions into solution. Thus an individual electrode develops a potential with respect to the solution. The potential of a single electrode in a half-cell is called the **Single electrode potential.** Thus in a Daniel cell in which the electrodes are not connected externally, the anode Zn/Zn^{2+} develops a negative charge and the cathode Cu/Cu^{2+}, a positive charge. The amount of the charge produced on individual electrode determines its single electrode potential.

The single electrode potential of a half-cell depends on : (*a*) concentration of ions in solution; (*b*) tendency to form ions; and (*c*) temperature

Standard emf of a cell

The emf generated by an electrochemical cell is given by the symbol E. It can be measured with the help of a potentiometer. The value of emf varies with the concentration of the reactants and products in the cell solutions and the temperature of the cell. When the emf of a cell is determined under standard conditions, it is called **the standard emf.** The standard conditions are (*a*) 1 M solutions of reactants and products; and (*b*) temperature of 25°C. Thus standard emf may be defined as : **the emf of a cell with 1 M solutions of reactants and products in solution measured at 25°C.**

Standard emf of a cell is represented by the symbol **E°.** With gases 1 atm pressure is a standard condition instead of concentration.

For a simple Zn-Cu voltaic cell, the standard emf, E°, is 1.10 V. This means that the emf of the cell operated with $[Cu^{2+}]$ and $[Zn^{2+}]$ both at 1 M and 25°C is 1.10 V. That is,

$$Zn \mid Zn^{2+}(aq, 1\underline{M}) \parallel Cu^{2+}(aq, 1\underline{M}) \mid Cu \qquad E^{o} = +1.1 \text{ V}$$

Determination of emf of a half-cell

By a single electrode potential, we also mean the emf of an isolated half-cell or its half-reaction. The emf of a cell that is made of two half-cells can be determined by connecting them to a voltmeter. However, there is no way of measuring the emf of a single half-cell directly. A convenient procedure to do so is to combine the given half-cell with another standard half-cell. The emf of the newly constructed cell, E, is determined with a voltmeter. The emf of the unknown half-cell, $E°_?$, can then be calculated from the expression

$$E_{measured} = E_R - E_L$$

If the standard half-cell acts as anode, the equation becomes.

$$E_R = E_{measured} \qquad (\because E_L = 0)$$

On the other hand, if standard half-cell is cathode, the equation takes the form

$$E_L = -E_{measured} \qquad (\because E_R = 0)$$

The standard hydrogen half-cell or **Standard Hydrogen Electrode (SHE),** is selected for coupling with the unknown half-cell. It consists of a platinum electrode immersed in a 1 M solution of H^+ ions maintained at 25°C. Hydrogen gas at one atmosphere enters the glass hood and bubbles over the platinum electrode. The hydrogen gas at the platinum electrode passes into solution, forming H^+ ions and electrons.

$$H_2 \longrightarrow 2H^+ + 2e^-$$

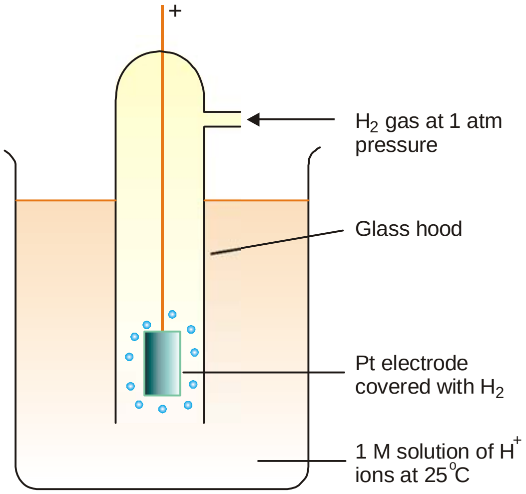


Figure 29.9
The standard hydrogen electrode.

The emf of the standard hydrogen electrode is arbitrarily assigned the value of zero volts. So, SHE can be used as a standard for other electrodes.

The half-cell whose potential is desired, is combined with the hydrogen electrode and the emf of the complete cell determined with a voltmeter. The emf of the cell is the emf of the half-cell.

$$\begin{aligned} E^\circ_{cell} &= E^\circ_R - E^\circ_L \\ &= 0 - 0.76 = -0.76 \text{ V} \end{aligned}$$

For example, it is desired to determine the emf of the zinc electrode, $Zn \mid Zn^{2+}$. It is connected with the SHE as shown in Fig. 29.10. The complete electrochemical cell may be represented as :

$$Zn \mid Zn^{2+} \parallel H^+ \mid H_2 \text{ (1 atm)}, Pt$$

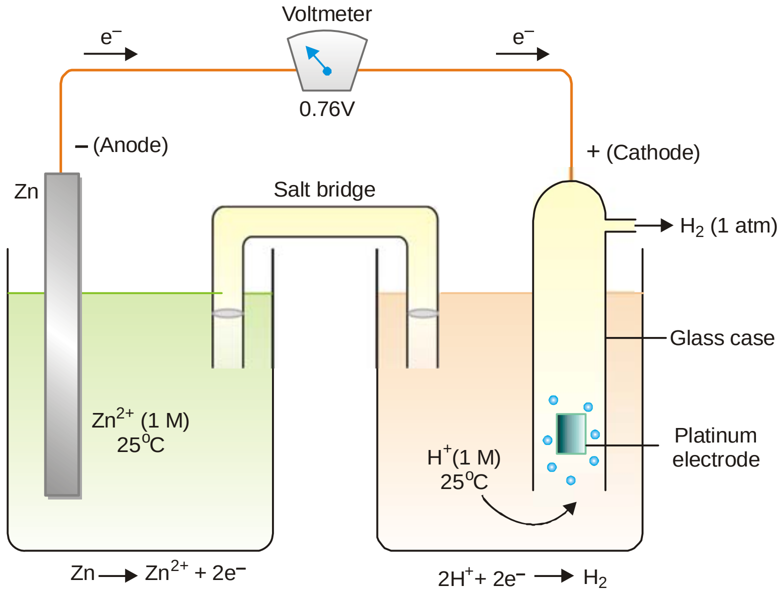


Figure 29.10
The zinc electrode (Zn, Zn^{2+}) coupled with hydrogen electrode.

The emf of the cell has been found to be – 0.76V which is the emf of the zinc half-cell. Similarly, the emf of the copper electrode, Cu^{2+} | Cu can be determined by pairing it with the SHE when the electrochemical cell can be represented as :

$$\text{Pt}, H_2\,(1\text{ atm}) \mid H^+ \parallel Cu^{2+} \mid Cu$$

The emf of this cell has been determined to be 0.34 V which is the emf of the copper half-cell.

$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{Cu/Cu^{2+}} - E^\circ_{\text{SHE}} \\ &= 0.34 - \text{Zero} \\ &= 0.34\text{ V} \end{aligned}$$

The two situations are shown in Fig. 29.11.

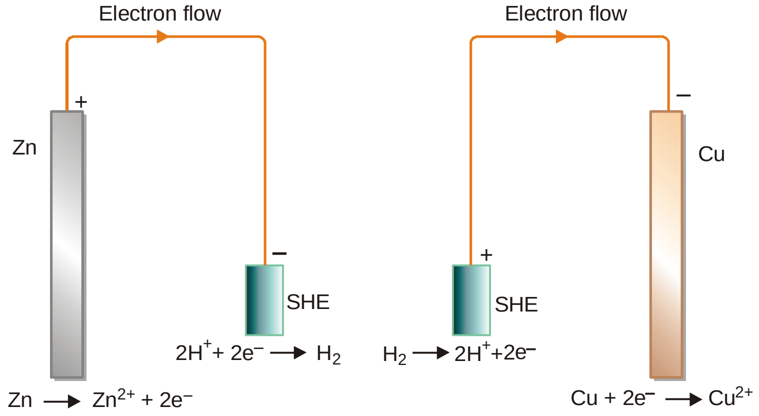


Figure 29.11
SHE can act both as cathode and anode when joined with another half-cell.

When it is placed on the right-hand side of the Zinc electrode, the hydrogen electrode reaction is

$$2H^+ + 2e^- \longrightarrow H_2$$

The electrons flow to the SHE and it acts as the cathode.

When the SHE is placed on the left hand side, the electrode reaction is

$$H_2 \longrightarrow 2H^+ + 2e^-$$

The electrons flow to the copper electrode and the hydrogen electrode as the anode. Evidently, **the SHE can act both as anode and cathode** and, therefore can be used to determine the emf of any other half-cell electrode (or single electrode).

IUPAC convention places the SHE on the left-hand side

In the procedure for determining the emf of a given half-cell, the standard hydrogen electrode can be placed on the left-hand or the right-hand. In the convention adopted by the IUPAC (International Union of Pure and Applied Chemistry), the SHE is always placed on the left-hand side of the half-cell under study. The electrons flow from left-to-right and the given half-cell electrode gains electrons (reduction). The observed emf of the combined electrochemical cell is then the emf of the half-cell on the right-hand. Such emf values of half-cells, or half reactions, are known as the **Standard reduction potentials or Standard potentials.** However, if the SHE be placed on the right-hand side of the given half-cell, the potential so obtained is called as the **Standard oxidation potential.** The latter potentials are the standard potentials with the sign reversed, the only difference being that cells have been turned around.

According to IUPAC convention, the standard reduction potentials alone are the standard potentials. The values of the standard potentials at 25°C (298 K) for some common Reduction Half-reactions are listed in Table **29.1.**

TABLE 29.1. STANDARD REDUCTION POTENTIALS AT 25°C (298 K)

Reduction Half-reaction	$E°$ (V)
$F_2 + 2e^- \longrightarrow 2F^-$	2.87
$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$	1.78
$PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \longrightarrow PbSO_4 + 2H_2O$	1.69
$Au^{3+} + 3e^- \longrightarrow Au$	1.50
$Cl_2 + 2e^- \longrightarrow 2Cl^-$	1.36
$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$	1.23
$MnO_2 + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2H_2O$	1.21
$Br_2 + 2e^- \longrightarrow 2Br^-$	1.09
$Fe^{3+} + e^- \longrightarrow Fe^{2+}$	0.77
$MnO_4^- + e^- \longrightarrow MnO_4^{2-}$	0.56
$Cu^{2+} + 2e^- \longrightarrow Cu$	0.34
$\mathbf{2H^+ + 2e^- \longrightarrow H_2}$	**0.00**
$Sn^{2+} + 2e^- \longrightarrow Sn$	−0.14
$Cd^{2+} + 2e^- \longrightarrow Cd$	−0.40
$Zn^{2+} + 2e^- \longrightarrow Zn$	−0.76
$H_2 + 2e^- \longrightarrow 2H^-$	−2.23
$Mg^{2+} + 2e^- \longrightarrow Mg$	−2.37
$Na^+ + e^- \longrightarrow Na$	−2.71
$Li^+ + e^- \longrightarrow Li$	−3.05

USING STANDARD POTENTIALS

In Table 29.1 the standard reduction potentials (E°) are arranged in the order of increasing potentials. The relative position of electrodes (M/M^+) in the table can be used to predict the reducing or oxidising ability of an electrode.

The electrodes that are relatively positive indicate that reduction reaction involving addition of electrons,

$$M^+ + e^- \longrightarrow M$$

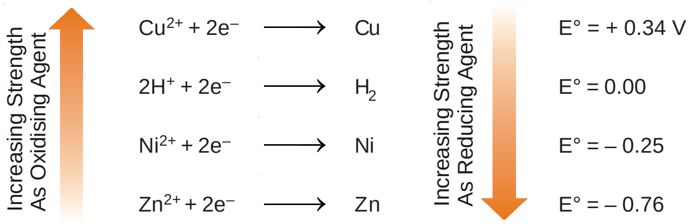
is possible. In case of relatively negative potential involving loss of electrons,

$$M \longrightarrow M^+ + e^-$$

is indicated. It also follows that the system with higher electrode potential will be reduced by the system with lower electrode potential.

Predicting the Oxidising or Reducing Ability

Let us consider a series of elements Cu, H_2,Ni, Zn and their ions. These four elements could act as reducing agents. On the other hand, their ions Cu^{2+}, H^+, Ni^{2+} and Zn^{2+} can act as electron acceptors or oxidising agents. If we list the respective half-reactions (or electrodes) in order of descending E° values, we will have placed the oxidising agents in descending order of their ability to attract electrons.



$Cu^{2+} + 2e^- \longrightarrow Cu$ E° = + 0.34 V

$2H^+ + 2e^- \longrightarrow H_2$ E° = 0.00

$Ni^{2+} + 2e^- \longrightarrow Ni$ E° = – 0.25

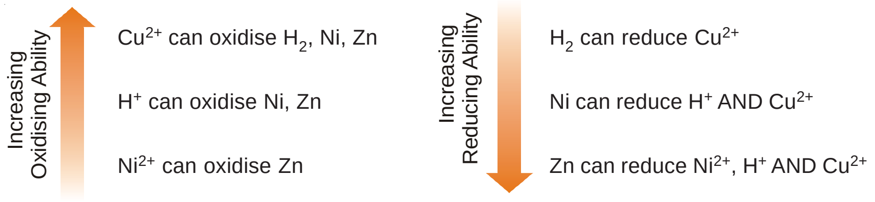
$Zn^{2+} + 2e^- \longrightarrow Zn$ E° = – 0.76

It is noteworthy that the value of E° becomes more negative down the series. This means that Cu^{2+} is the best oxidising agent (most electron-attracting ion) of those in the list. That is, Cu^{2+} shows the greatest tendency to be reduced. Conversely, Zn^{2+} is the worst oxidising agent, being the least electron-attracting ion. Of the elements Cu, H_2, Ni and Zn, Zn is the best reducing agent (best electron donor), since E° for the half-reaction

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

has the most positive value. By the reasoning, Cu is the worst reducing agent.

The table of half reaction potentials above tells us that at standard conditions the following reactions occur spontaneously.



Cu^{2+} can oxidise H_2, Ni, Zn

H^+ can oxidise Ni, Zn

Ni^{2+} can oxidise Zn

H_2 can reduce Cu^{2+}

Ni can reduce H^+ AND Cu^{2+}

Zn can reduce Ni^{2+}, H^+ AND Cu^{2+}

Some important points concerning the Table of Standard Reduction Potentials (Table 29.1) are:

(1) The more positive the value of E°, the better the oxidising ability (the greater the tendency to be reduced) of the ion or compound, on moving upward in the Table.

(2) The more negative the value of E° the better the reducing ability of the ions, elements or compounds on moving downward in the Table.

(3) Under standard conditions, any substance in this Table will spontaneously oxidise any other substance lower than it in the Table.

Predicting cell emf

The standard emf, E°, of a cell is the standard reduction potential of right-hand electrode (cathode) minus the standard reduction potential of the left-hand electrode (anode). That is,

$$\begin{aligned} E^\circ_{cell} &= E^\circ_{right} - E^\circ_{left} \\ &= \text{Cathode potential} - \text{Anode potential} \end{aligned}$$

Let us predict the emf of the cell

$$Zn(s) \,|\, Zn^{2+}(aq) \,||\, Ag^{+}(aq) \,|\, Ag$$

by using the E° values from the Table

$$\begin{aligned} E^\circ_{cell} &= E^\circ_{R} - E^\circ_{L} \\ &= 0.80 - (-0.763) \\ &= 0.80 + 0.763 \\ &= 1.563 \text{ V} \end{aligned}$$

The answer is so clear from Fig. 29.12.

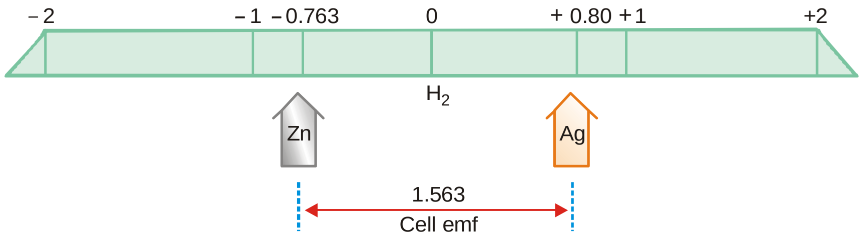


Figure 29.12
Diagrammatic representation of Cell emf.

Predicting Feasibility of Reaction

The feasibility of a redox reaction can be predicted with the help of the electrochemical series. The net emf of the reaction, E_{cell}, can be calculated from the expression

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

In general, if E°_{cell} = + ve, the reaction is feasible

E°_{cell} = – ve, the reaction is not feasible

SOLVED PROBLEM 1. Predict whether the reaction

$$2\,Ag(s) + Zn^{2+}(aq) \longrightarrow Ag^{+}(aq) + Zn(s)$$

is feasible or not. Consult the table for the E° values.

SOLUTION

The cell half reactions are

Anode : $2Ag(s) \longrightarrow 2Ag^{+}(aq) + 2e^{-}$ $E^\circ = 0.80$ V

Cathode : $Zn^{2+}(aq) + 2e^{-} \longrightarrow Zn(s)$ $E^\circ = -0.763$ V

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

$$\therefore \quad \begin{aligned} E^\circ_{cell} &= -0.763 \text{ V} - 0.80 \\ &= -1.563 \end{aligned}$$

Since E°_{cell} is negative, the given reaction is **not feasible**.

SOLVED PROBLEM 2. Determine the feasibility of the reaction

$$2Al(s) + 2Sn^{4+}(aq) \longrightarrow 2Al^{3+} + 3Sn^{2+}(aq)$$

Consult the table for the E° values.

SOLUTION

The given reaction consists of the following half reactions

Anode : $2Al(s) \longrightarrow 2Al^{3+} + 6e^-$ $E° = -1.66$ V

Cathode : $3Sn^{4+} + 6e^- \longrightarrow 3Sn^{2+}$ $E° = +0.15$

$$E°_{cell} = 0.15 - (-1.66)$$
$$= 1.81 \text{ V}$$

Since $E°_{cell}$ is positive, the reaction is **feasible**.

Predicting whether a metal will displace another metal from its salt solution or not

As already shown, the metals near the bottom of the electrochemical series are strong reducing agents and are themselves oxidised to metal ions. On the contrary, the metals lying higher up in the series are strong oxidising agents and their ions are readily reduced to the metal itself. For example, zinc lying down below the series is oxidised to Zn^{2+} ion, while copper which is higher up in the series is produced by reduction of Cu^{2+} ion.

$$Zn \longrightarrow Zn^{2+} + 2e^-$$
$$Cu^{2+} + 2e^- \longrightarrow Cu\downarrow$$

Thus when zinc is placed in $CuSO_4$ solution, Cu metal gets precipitated. In general we can say that **a metal lower down the electrochemical series can precipitate the one higher up in the series.**

Silver cannot precipitate Cu from $CuSO_4$, solution, since both metals have positions higher up in the series and are strong oxidising agents.

Predicting whether a metal will displace hydrogen from a dilute acid solution

Any metal above hydrogen in the electrochemical series is a weaker reducing agent than hydrogen itself and cannot reduce H^+ to H_2. Any metal lying below hydrogen is a stronger reducing agent than hydrogen and will convert H^+ to H_2. This explains why Zn lying below hydrogen reacts with dil H_2SO_4 to liberate H_2, while Cu lying above hydrogen does not react.

$$Zn + H^+ (\text{dil } H_2SO_4) \longrightarrow Zn^{2+} + H_2\uparrow$$
$$Cu + H^+ (\text{dil } H_2SO_4) \not\longrightarrow Cu^{2+} + H_2$$

THE NERNST EQUATION

We know experimentally that the potential of a single electrode or half-cell varies with the concentration of ions in the cell. In 1889 Walter Nernst derived a mathematical relationship which enable us to calculate the half-cell potential, E, from the standard electrode potential, E°, and the temperature of the cell. This relation known as the **Nernst equation** can be stated as

$$E = E° - \frac{2.303\,RT}{nF}\log K \qquad ...(1)$$

where
$E°$ = standard electrode potential
R = gas constant
T = Kelvin temperature
n = number of electrons transferred in the half-reaction
F = Faraday of electricity
K = equilibrium constant for the half-cell reaction as in equilibrium law

Calculation of Half-cell potential

For an oxidation half-cell reaction when the metal electrode M gives M^{n+} ion,

$$M \longrightarrow M^{n+} + ne^-$$

the Nernst equation takes the form

$$E = E° - \frac{2.303\,RT}{nF}\log\frac{[M^{n+}]}{[M]} \qquad \text{...(2)}$$

The concentration of solid metal [M] is equal to zero. Therefore, the Nernst equation can be written as

$$E = E° - \frac{2.303\,RT}{nF}\log[M^{n+}] \qquad \text{...(3)}$$

Substituting the values of R, F and T at 25°C, the quantity 2.303 RT/F comes to be 0.0591. Thus the Nernst equation (3) can be written in its simplified form as

$$E = E° - \frac{0.0591}{n}\log[M^{n+}]$$

This is the equation for a half-cell in which oxidation occurs. In case it is a reduction reaction, the sign of E will have to be reversed.

SOLVED PROBLEM. What is the potential of a half-cell consisting of zinc electrode in 0.01M $ZnSO_4$ solution at 25°C, E° =0.763 V.

SOLUTION

The half-cell reaction is

$$Zn \longrightarrow Zn^{2+} + 2e^- \qquad (oxidation)$$

The Nernst equation for the oxidation half-cell reaction is

$$E = E° - \frac{0.0591}{n}\log[Zn^{2+}]$$

The number of electrons transferred $n = 2$ and E° =0.763 V.

Substituting these values in the Nernst equation we have

$$E = 0.763 - \frac{0.0591}{2}\log(0.01)$$

$$= 0.763 - \frac{0.0591}{2}(-2)$$

$$= 0.763 + 0.0591 = \mathbf{0.8221\ V}$$

Calculation of Cell potential

The Nernst equation is applicable to cell potentials as well. Thus,

$$E_{cell} = E°_{cell} - \frac{0.0591}{n}\log K$$

K is the equilibrium constant of the redox cell reaction.

SOLVED PROBLEM. Calculate the emf of the cell.

$$Zn \mid Zn^{2+}(0.001M) \parallel Ag^{+}(0.1M) \mid Ag$$

The standard potential of Ag/Ag^+ half-cell is + 0.80 V and Zn/Zn^{2+} is – 0.76 V.

SOLUTION

Step 1. Write the half-cell reactions of the anode and the cathode. Then add the anode and cathode half reactions to obtain the cell reaction and the value of $E°_{cell}$.

$$\begin{array}{llll} \text{Cathode :} & 2Ag^+ + 2e^- \longrightarrow 2Ag & & E° = +0.80\ V \\ \text{Anode :} & Zn \longrightarrow Zn^{2+} + 2e^- & & E° = -0.76\ V \\ \hline \text{Cell :} & Zn + 2Ag^+ \rightleftharpoons Zn^{2+} + 2Ag & & E° = 1.56\ V \end{array}$$

Step 2. K for the cell reaction $= \dfrac{[Zn^{2+}]}{[Ag^+]^2}$

substitute the given values in the Nernst equation and solving for E_{cell}, we have

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{n} \log K$$

$$= 1.56 - \frac{0.0591}{2} \log \frac{[Zn^{2+}]}{[Ag^+]^2}$$

$$= 1.56 - \frac{0.0591}{2} \log \frac{[10^{-3}]}{[10^{-1}]^2}$$

$$= 1.56 - 0.02955 \ (\log 10^{-1})$$

$$= 1.56 + 0.02955$$

$$= \mathbf{1.58955\ V}$$

Calculation of Equilibrium constant for the cell reaction

The Nernst equation for a cell is

$$E_{cell} = E°_{cell} - \frac{0.0591}{n} \log K$$

At equilibrium, the cell reaction is balanced and the potential is zero. The Nernst equation may, now, be written as

$$0 = E°_{cell} - \frac{0.0591}{n} \log K$$

or $$\log K = \frac{nE°_{cell}}{0.0591}$$

SOLVED PROBLEM. Calculate the equilibrium constant for the reaction between silver nitrate and metallic zinc.

SOLUTION

Step 1. Write the equation for the reaction

$$2Ag^+ + Zn \rightleftharpoons Zn^{2+} + 2Ag \qquad E°cell = 1.56\ V$$

Step 2. Substitute values in the Nernst equation at equilibrium

$$\log K = \frac{nE°_{cell}}{0.0591}$$

$$0 = 1.56 - 0.03 \log K$$

$$-1.56 = -0.03 \log K$$

$$\log K = \frac{-1.56}{-0.03} = 52$$

$$K = \mathbf{1 \times 10^{52}}$$

OTHER REFERENCE ELECTRODES

The standard hydrogen electrode (SHE) is not the most convenient standard electrode to use in the laboratory. The gas has to be carefully controlled and hydrogen gas can form explosive mixtures with air. Any other electrode system whose potential has been determined relative to the SHE can also be used as **Secondary standard electrode.**

(1) The Standard Silver-Silver Electrode

In this electrode system, silver wire (or strip) is covered with silver chloride (a highly insoluble substance). It is dipped in potassium chloride solution in which the concentration of Cl^- ion is 1 M This electrode can be represented as

$$\text{Ag, AgCl} \mid \text{Cl}^- \text{(1 M)}$$

The half-cell reaction of the Ag-AgCl electrode is

$$\text{AgCl} + e^- \longrightarrow \text{Ag} + \text{Cl}^-$$

We can set up a cell involving this electrode and the hydrogen electrode

$$\text{Pt , H}_2 \mid \text{H}^+ \text{(1 M)} \parallel \text{Cl}^- \text{(1 M)} \mid \text{AgCl, Ag}$$

with a KCl salt bridge connecting the two solutions. The emf of the combined cell is found to be 0.2224 V. Thus the standard electrode potential for the silver-silver chloride electrode is 0.2224 V.

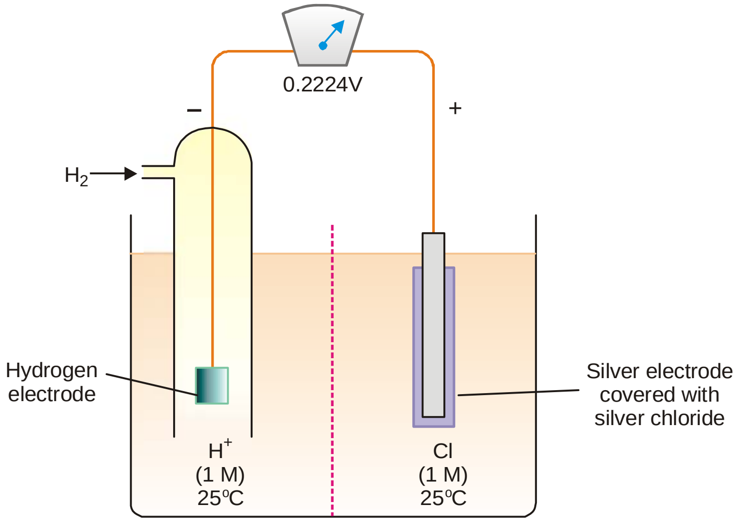


Figure 29.13
Schematic diagram of Ag-AgCl electrode coupled with SHE (salt bridge replaced by porous partition).

(2) The Calomel Electrode

It is the most commonly used secondary standard reference electrode. The standard calomel electrode, **SCE,** consists of a wide glass-tube with a narrow side-tube. It is set up as illustrated in Fig. 29.14. A platinum wire is dipping into liquid mercury covered with solid mercurous chloride (Hg_2Cl_2, calomel). The tube is filled with a 1 M solution of KCl (or saturated KCl solution). The side-tube containing KCl solution provides the salt bridge which connects the electrode to any other electrode.

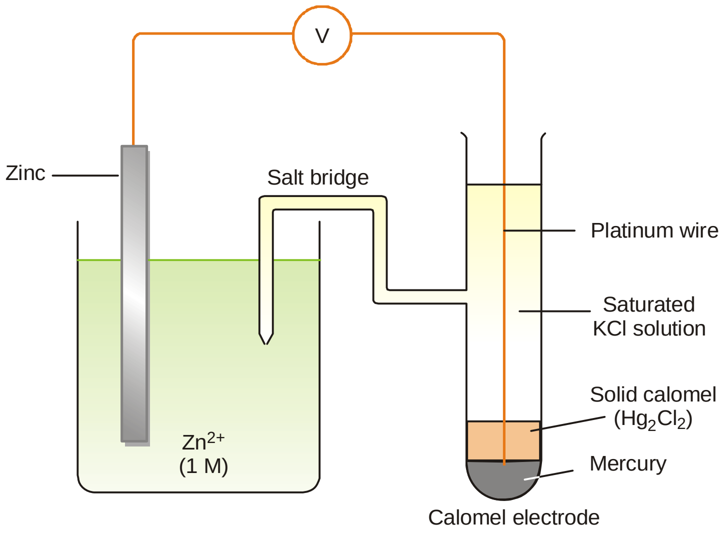


Figure 29.14
The calomel electrode coupled with zinc electrode to determine its emf.

The calomel electrode is represented as

$$Cl^{-}\,(1M)\,|\,Hg_2Cl_2,\,Hg$$

and the half-cell reaction is

$$Hg_2Cl_2 + 2e^{-} \longrightarrow 2Hg + 2Cl^{-}$$

The emf of the cell

$$Pt,\,H_2\,|\,H^{+}\,\|\,KCl\,(1\,M)\,|\,Hg_2Cl_2,\,Hg$$

at 25°C is + 0.280 V. That is, the calomel electrode emf with respect to the standard hydrogen electrode is + 0.280 V. This means that **0.280 must be added to any electrode potential measured against a calomel electrode.** This would give the standard potential on the standard hydrogen scale.

Note. The potential of the calomel electrode depends on the concentration of KCl solution taken in the half-cell. Thus for 0.1M KCl solution emf is 0.3338 Volt; for 1M solution emf is 0.2800 Volt; and for saturated KCl solution emf is 0.2415 Volt.

Determination of emf of the standard zinc half-cell using calomel electrode

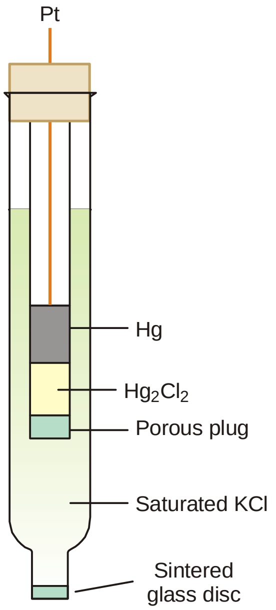
The zinc half-cell is connected with the standard calomel electrode as shown in Fig. 29.14. The emf of the complete cell is then measured with the help of a voltmeter. It is found to be 1.040 V. Since zinc forms the negative electrode of the cell, its emf with respect to calomel electrode will be – 1.040 V. The addition of 0.280 gives the standard electrode potential of zinc.

$$(-1.040 + 0.280) = -0.76\text{ V}$$

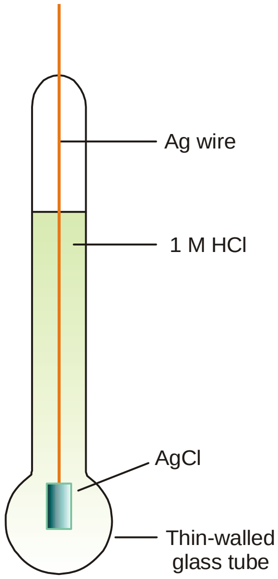
The dipping calomel electrode

For many purpose, a calomel electrode is manufactured as a self-contained unit. It is used by simply dipping the tip of the electrode in the solution of another electrode whose emf is to be determined. This type of electrode is often referred as the dipping calomel electrode (Fig. 29.15).

The mercury and calomel (Hg_2Cl_2) are held in a narrow central tube by a porous cotton wool plug. A platinum wire dips into the mercury. The KCl saturated solution contained in the electrode makes contact with the other electrode solution through a sintered glass disc. This disc functions as a 'salt bridge' between the two electrode solutions. Thus a galvanic cell is set up and its emf is measured with the help of a voltmeter.



■ **Figure 29.15**
A dipping calomel electrode.



■ **Figure 29.16**
Glass electrode

The Glass Electrode

A commonly used secondary standard electrode is the so-called glass electrode. Its emf is determined by coupling with a standard calomel electrode (SCE). The glass electrode provides one of the easiest methods for measuring the pH of a given solution.

A simple type of glass electrode (Fig. 29.16) consists of a glass tube having a thin-walled bulb at the lower end. The bulb contains a 1M HCl solution. Sealed into the glass-tube is a silver wire coated with silver chloride at its lower end. The lower end of this silver wire dips into the hydrochloric acid, forming silver-silver chloride electrode. The glass electrode may be represented as

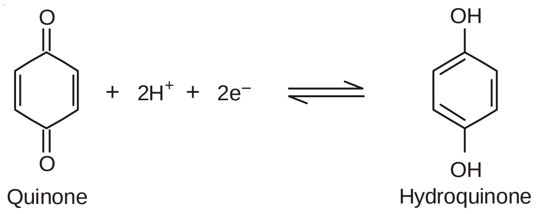
$$\text{Ag, AgCl} \mid \text{1 M HCl} \,\vdots\, H^+ \text{ (Test Solution)}$$

When placed in a solution, the potential of the glass electrode depends on the H^+ ion concentration of the solution. The potential develops across the glass membrane as a result of a concentration difference of H^+ ions on the two sides of the membrane. This happens much in the same way as the emf of a concentration cell develops.

The potential of a glass electrode can be determined against a standard calomel electrode (SCE).

Quinhydrone Electrode

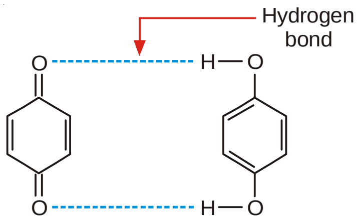
It is a widely used secondary standard electrode. It involves the redox reaction between quinone (Q) and hydroquinone (QH_2),



or, simply

$$Q + 2H^+ + 2e^- \rightleftharpoons QH_2$$

The hydroquinone half-cell consists of a platinum strip immersed in a saturated solution of quinhydrone at a definite H^+ ion concentration (buffered solution). Quinhydrone is a molecular compound which gives equimolar amounts of quinone and hydroquinone in solution. The electrode system may be represented as



$$\text{Pt} \mid QH_2, Q, H^+$$

The potential developed is measured against a hydrogen electrode or calomel electrode. The emf with respect to a standard hydrogen electrode is 0.2875 V at 25°C.

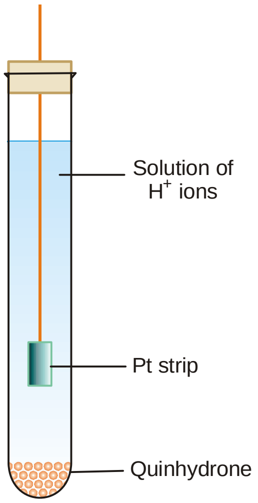


Figure 29.17
The Quinhydrone Electrode.

DETERMINATION OF pH OF A SOLUTION

A half-cell is set up with the test solution as electrolyte. The emf of the cell depends on the concentration of H^+ ions or pH of the solution. The emf of the half-cell is determined by coupling it with another standard half-cell and measuring the emf of the complete cell. The commonly used standard electrodes are :

(*a*) The hydrogen electrode

(*b*) The quinhydrone electrode

(*c*) The glass electrode

Using Hydrogen electrode

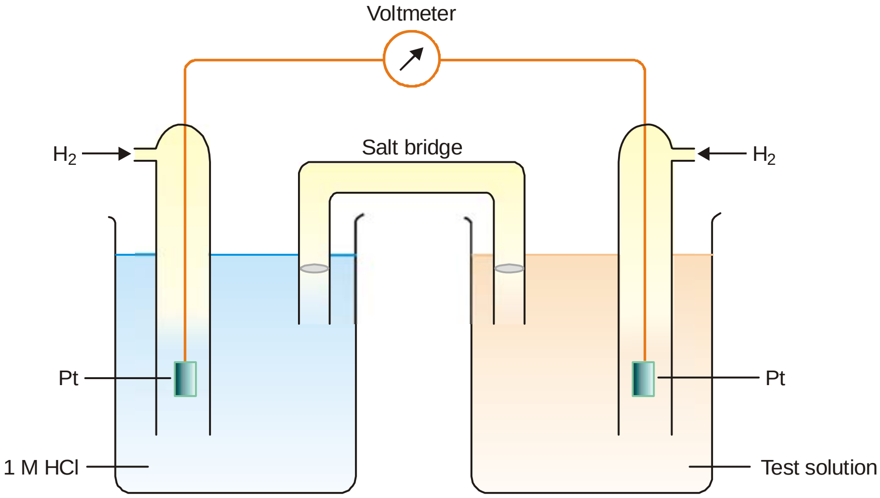


Figure 29.18
Determination of pH with Hydrogen electrode.

A standard hydrogen electrode is coupled with another hydrogen electrode which contains the solution of unknown pH (Fig. 29.18). In both half-cells hydrogen gas is used at 1 atm pressure and 25°C. The emf of the complete cell

$$\text{Pt} \mid H_2\,(1\text{ atm}) \mid H^+\,(1\text{M}) \parallel H^+\,(\text{Unknown}) \mid H_2\,(1\text{ atm}) \mid \text{Pt}$$

is recorded experimentally.

Calculations. The second electrode reaction is

$$H^+ + e^- \rightleftharpoons \tfrac{1}{2}H_2$$

The electrode potential of the second half-cell is given by the Nernst equation

$$E = E° + \frac{2.303\,RT}{nF}\log\frac{[H^+]}{H_2^{1/2}}$$

Since $H_2^{1/2} = 1$ and $E° = 0$, we have

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

Substituting the values of R, T and n (charge number of H^+) and F (Faraday constant), the expression becomes

$$E = 0.0591\log[H^+]$$

or $$E = -0.0591\text{ pH} \qquad \text{...(A)}$$

The emf of the E_{cell}, is given as

$$E_{cell} = E_{right} - E_{left}$$

The left-hand electrode is the standard hydrogen electrode and its emf will be zero.

∴ $$E_{cell} = E_{right} = -(-0.0591)\text{ pH}$$

Using A, $$E_{cell} = -(-0.0591 \times \text{pH}) = 0.0591 \times \text{pH}$$

or $$\text{pH} = \frac{E_{cell}}{0.059}$$

Knowing the observed value of emf of the cell, we can calculate pH of the test-solution.

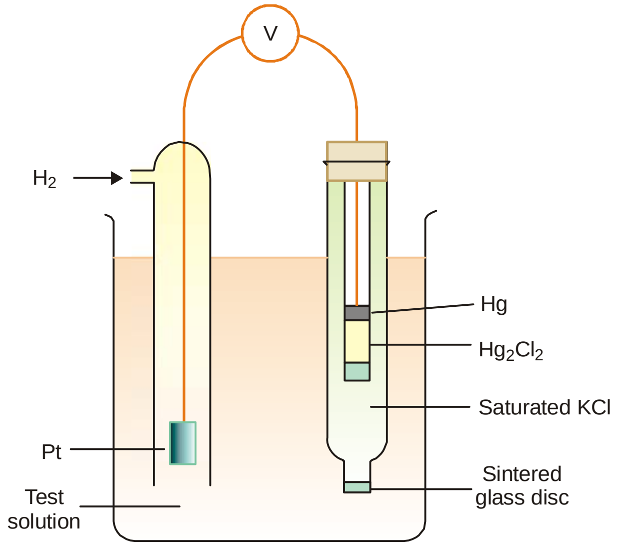


Figure 29.19
A calomel electrode coupled with unknown hydrogen electrode.

Using SCE instead of SHE

A hydrogen electrode containing solution of unknown pH is paired with a standard calomel electrode (Fig. 29.19). The complete cell may be represented as

$$\text{Pt, } H_2 \text{(1 atm)} \mid H^+ \text{(Unknown)} \parallel \text{KCl (Sat Solution)} \mid Hg_2Cl_2 \mid Hg$$

By noting the emf of the cell with the help of a voltmeter, the pH of the unknown solution can be calculated as follows :

The emf of the cell will be given by the expression

$$\begin{aligned} E_{cell} &= E_{right} - E_{left} \\ &= 0.2415 - (-0.0591 \times \text{pH}) \qquad \text{...(from eq A)} \\ E_{cell} &= 0.2415 + 0.0591 \times \text{pH} \end{aligned}$$

or

$$\text{pH} = \frac{E_{cell} - 0.2415}{0.0591}$$

Merits and demerits. The hydrogen electrode give absolute values of pH while other electrodes yield relative values. However, it is not convenient for routine measurement of pH because :

(1) It requires hydrogen gas and is difficult to set up and transport.
(2) It requires considerable volume of test solution.
(3) The test solution might 'poison' the surface of the platinum electrode.
(4) The potential of the electrode is already by changes in barometric pressure.

SOLVED PROBLEM. The emf of the following cell at 25°C is 0.445V.

$$\text{Pt, } H_2 \text{ (1 atm)} \mid H^+ \text{ (test solution)} \parallel \text{KCl (sat solution)} \mid Hg_2Cl_2 \mid Hg$$

Calculate the pH of the unknown solution, $E_{cell} = 0.2415$.

SOLUTION

$$\begin{aligned} E_{cell} &= 0.445 \text{ V (given)} \\ E^\circ_{cell} &= E^\circ_{Right} - E^\circ_{left} = 0.2415 - 0 = 0.2415 \text{ V} \end{aligned}$$

Using the relation

$$E_{cell} = E_{right} - E_{left}$$
$$0.445 = 0.2415 - (-0.0591 \times pH)$$
$$0.445 = 0.2415 + 0.0591 \times pH$$
$$\therefore \quad pH = \frac{0.445 - 0.2415}{0.0591} = \frac{0.2035}{0.0591}$$
$$= \mathbf{3.44}$$

Using Glass electrode

A glass electrode is immersed in the solution of unknown pH. It is coupled with a standard calomel electrode (SCE) as shown in Fig. 29.20. The emf of the complete cell

Ag , AgCl | 1M HCl | Glass || Solution of Unknown pH || SCE

can be determined experimentally.

Calculations

The potential of the glass electrode, E_G, at 25°C is given by equation

$$E_G = E°_G + \frac{2.303\,RT}{F} pH$$
$$= E°_G + 0.0591\ pH \qquad ...(A)$$

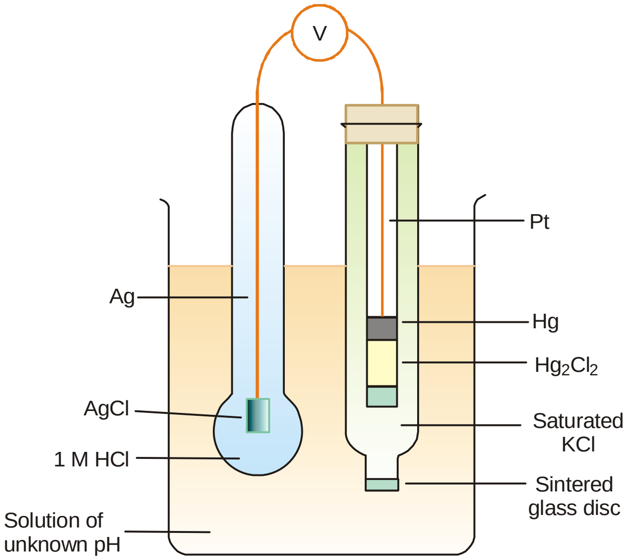


Figure 29.20
A glass electrode coupled with standard calomel electrode.

We know that

$$E_{cell} = E_R - E_L$$
i.e.,
$$E_{cell} = E_{SCE} - E_G$$
Substituting the value of E_G from (A)
$$E_{cell} = E_{SCE} - E°_G - 0.0591 \times pH$$
or
$$pH = \frac{E_{SCE} - E°_G - E_{cell}}{0.0591} \qquad ...(B)$$

The value of the potential of calomel electrode is known while E_{cell} can be found experimentally. Therefore, we can find pH of a given solution if $E°_G$ is known. It can be determined by using a solution of known pH in the cell and measuring $E_{cell.}$ This value of $E°_G$ is constant for a particular glass electrode and can be used for any subsequent determinations of pH of unknown solutions with the help of equation (B).

The potential of the cell, E_{cell}, cannot be measured using ordinary potentiometer or voltmeter as the resistance of the glass membrane is very high and the current small. Therefore, an electronic voltmeter is required which reads pH directly.

Merits and demerits of Glass electrode

A glass electrode is universally used because

(1) It is simple to operate.

(2) It is not easily poisoned.

(3) Its activity is not affected by strong oxidising and reducing agents.

(4) Since E°_G depends on a particular glass electrode used, it is not a universal constant and also changes with time. Hence a glass electrode only compares pH values while the hydrogen electrode measures pH absolutely.

Using Quinhydrone electrode

A platinum electrode is suspended in a solution whose pH is to be determined. The solution is saturated with quinhydrone compound. This half-cell is then combined with a standard calomel electrode (SCE). The complete cell can be represented as

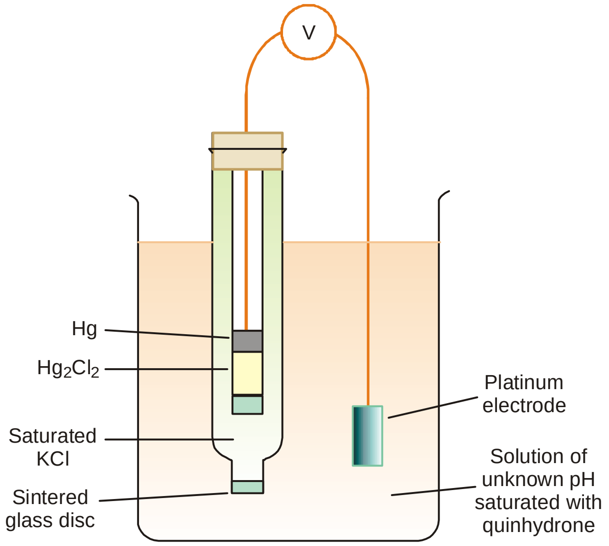


Figure 29.21
Quinhydrone electrode coupled with standard calomel electrode.

SCE || Solution of Unknown pH Saturated with Quinhydrone || Pt

The emf of the complete cell (E_{cell}) is determined with the help of a voltmeter.

Calculations. The reduction half-cell reaction of quinhydrone electrode is

$$Q + 2H^+ + 2e^- \rightleftharpoons QH_2$$

The potential, E_Q, of the quinhydrone electrode depends on the concentration of H^+ ions in solution. As worked out from Nernst equation, it is given by the relation

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

$$\text{or} \qquad E_Q = E_Q^\circ + \frac{2.303\,RT}{F}\text{pH} \qquad ...(1)$$

The standard reduction potential, E_Q°, of the quinhydrone electrode is 0.6996. Thus from (1) we have

$$E_Q = 0.6996 + 0.0591 \times \text{pH} \qquad ...(2)$$

We know that

$$E_{cell} = E_{right} - E_{left}$$

$$\textit{i.e.,} \qquad E_{cell} = E_Q - E_{SCE}$$

Substituting the value of emf of standard calomel electrode, E_{SCE}, which is 0.2415, and the value of E_Q from (2), we have

$$E_{cell} = 0.6996 + 0.0591 \times \text{pH} - 0.2415$$

$$\text{Hence} \qquad 0.0591\ \text{pH} = 0.4581 - E_{cell}$$

$$\text{pH} = \frac{0.4581 - E_{cell}}{0.0591}$$

Merits and demerits. (1) Quinhydrone electrode is easily set up by simply immersing a platinum strip in the test solution.

(2) The pH values are very accurate even in the presence of oxidising ions which interfere with the working of a hydrogen electrode.

(3) It does not give satisfactory results for solutions whose pH is more than 8.5 due to the ionisation or oxidation of hydroquinone.

SOLVED PROBLEM. Find the pH of a solution placed in a hydroquinone half-cell which was coupled with standard calomel electrode. The emf of the combined cell was determined to be 0.123 V at 25°C.

$$E_{calomel} = 0.2415\ \text{V}\ ;\ E_Q^\circ = 0.6996\ \text{V}$$

SOLUTION

$$E_{cell} = E_Q - E_{SCA} \qquad ...(1)$$

But we know that

$$E_Q = E_Q^\circ - \frac{2.303\,RT}{F}\text{pH}$$

$$= 0.6996 - 0.0591\ \text{pH}$$

Substituting the values of E_Q and E_{SCA} in equation (1), we have

$$0.123 = (0.6996 - 0.0591\ \text{pH}) - 0.2415 = 0.4581 - 0.0591\ \text{pH}$$

$$\text{pH} = \frac{0.4581 - 0.123}{0.0591}$$

$$\text{pH} = \frac{0.3351}{0.0591} = \mathbf{5.67}$$

POTENTIOMETRIC TITRATIONS

In a potentiometric titration, a suitable electrode immersed in the solution to be titrated acts as the 'indicator'. The **indicator electrode** is paired with a reference electrode and the two electrodes are connected to an electronic voltmeter. The emf of the indicator electrode changes gradually with the change of concentration of ions caused by the addition of titrant from the burette. The equivalence point is indicated by a sharp change in electrode potential.

Since the reference electrode potential has a constant value, any change in the indicator electrode potential is reflected by a similar change in the cell potential. Therefore, the equivalence point can be found by plotting a graph between the cell emf and the volume of titrant added from the burette. A sharp rise of the curve shows the equivalence point and the corresponding volume on the graph is the volume of the solution used for the titration.

The potentiometric titrations may be of three types :

(*a*) Acid-base titrations
(*b*) Oxidation-reduction titrations
(*c*) Precipitation titrations

Acid-base Titrations

The apparatus used for potentiometric acid-base titrations is shown in Fig. 29.22.

A hydrogen electrode or a glass electrode is immersed in solution of the acid whose strength is to be determined. The glass electrode is coupled with a standard calomel electrode. The cell thus formed is connected to the potentiometer or electronic voltmeter. When alkali is added, pH of the solution changes. The emf of the cell also changes with pH of the solution in accordance with the relation.

$$E = E^\circ + 0.0591 \text{ pH}$$

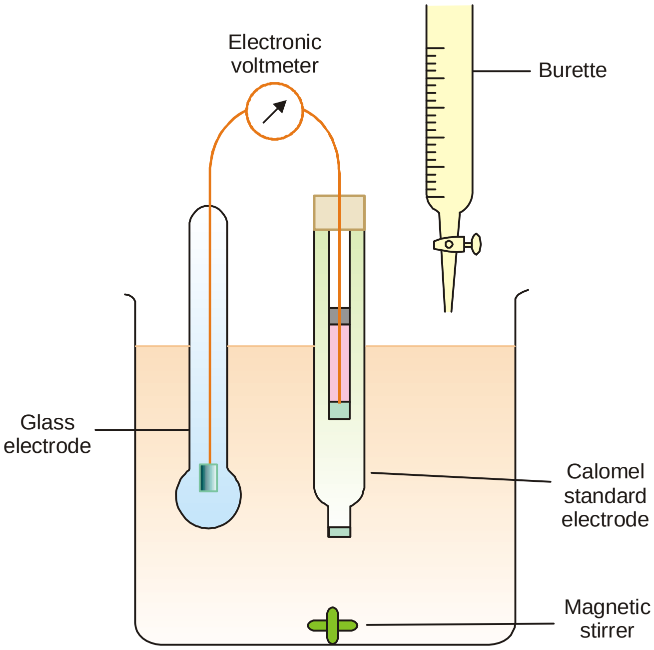


Figure 29.22
Apparatus for potentiometric acid-base titrations.

The standard alkali solution is then added from the burette in small volumes. After each addition, the emf of the cell is recorded. The emf is then plotted against the volume of alkali added. The shape of the curve for the titration of a strong acid against strong alkali (HCl versus NaOH) is shown in Fig.

29.23 (*a*). The steepest portion of the curve indicates the equivalence point. However, when the solutions are very dilute, or weak acids or bases, are involved, the steepness of the curve is less marked and it is difficult to judge the end-point. In such a case, we plot the slope of the curve, $\Delta E/\Delta V$ against the volume of alkali used. The maximum of the curve indicates the end-point.

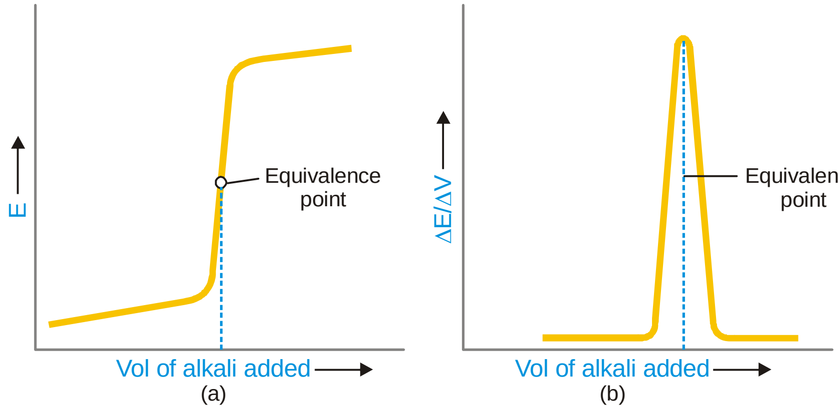


Figure 29.23
Potentiometric titration curve of an acid and a base.

Oxidation-reduction Titrations

The titration of ferrous ions (Fe^{2+}) with ceric ions (Ce^{4+}) is an example of oxidation-reduction (or redox) titration. Fe^{2+} ion is oxidised to Fe^{3+} ion, while Ce^{4+} is reduced to Ce^{3+} ion.

$$Fe^{2+} + Ce^{4+} \longrightarrow Fe^{3+} + Ce^{3+}$$

This titration can be carried in the apparatus shown in Fig. 29.24. The indicator electrode is a shiny platinum strip dipping in the solution of Fe^{2+} ions, and it is connected to a standard calomel electrode. The Ce^{4+} solution is added from the burette and the cell potential, E, recorded after each addition.

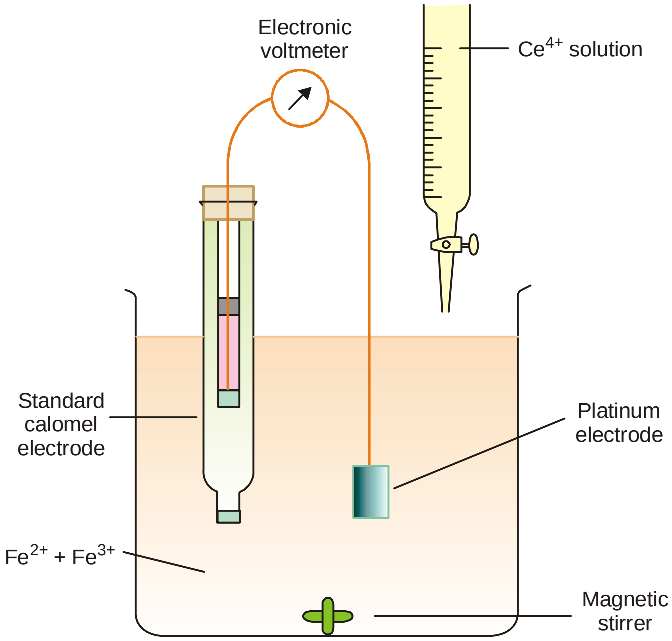


Figure 29.24
Apparatus for potentiometric titration of Fe^{2+} with Ce^{4+}.

The potential of the platinum electrode depends on the ratio [Fe^{3+}]/[Fe^{2+}]. The potential of the cell, E, also changes with the change of the ratio [Fe^{3+}]/[Fe^{2+}]. Therefore, the cell potential changes with the addition of Ce^{4+} ions from the burette. Fig. 29.25 shows how the potential of the cell changes during the titration. At the equivalence point there is a sharp rise of potential which indicates the end-point.

Potentiometric titrations of this type are particularly useful for coloured solutions in which an indicator cannot be employed.

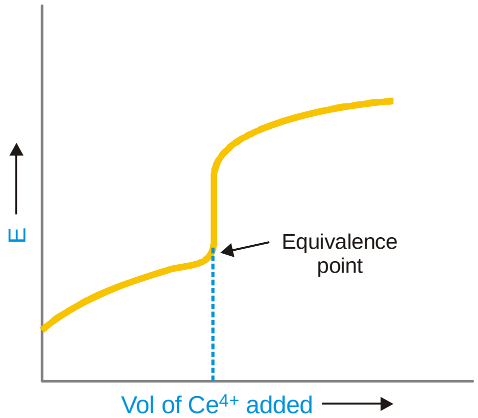


Figure 29.25
Potentiometric titration curve of Fe^{2+} ions and Ce^{4+} ions.

Precipitation Titration

A typical precipitation titration is that of sodium chloride solution against silver nitrate solution. The apparatus set up for the purpose is shown in Fig. 29.26. A silver electrode dipping in the unknown sodium chloride solution is coupled with a calomel electrode through a salt bridge. However, if the calomel electrode were in direct contact with a solution containing excess silver ions, chloride would seep through the sintered base and react to form an insoluble layer of silver chloride.

Any change in the cell potential is due to changes in concentration of Ag^+ ions around the silver electrode.

$$Ag^+ + e \longrightarrow Ag$$

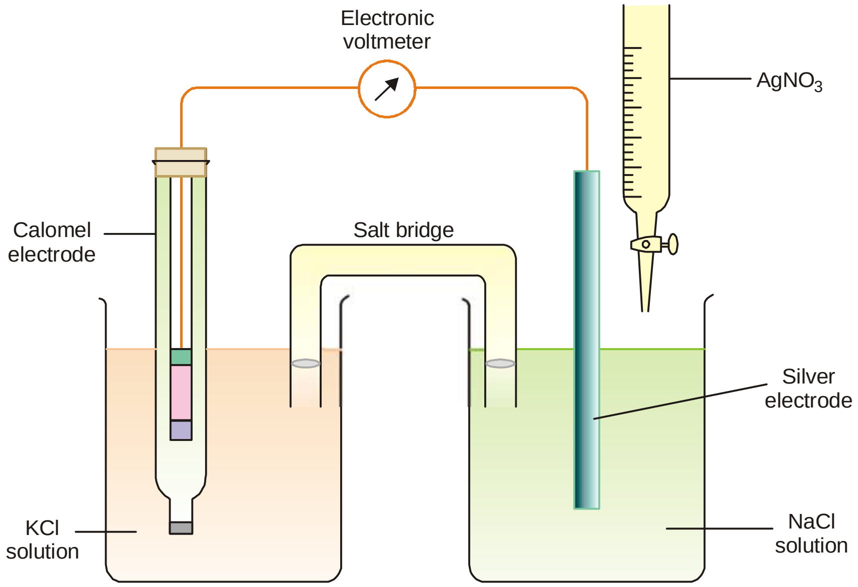
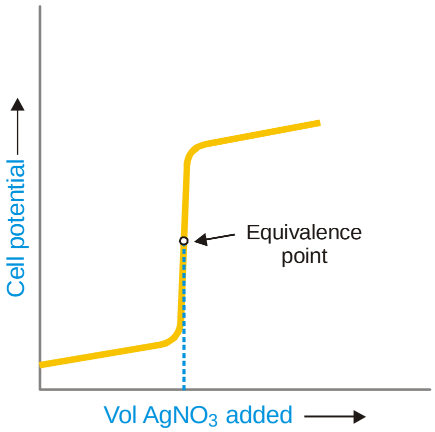


Figure 29.26
Potentiometric titration of sodium chloride against silver nitrate solution.

Initially the concentration of Ag^+ ions will be zero. But as silver nitrate is added from the burette, silver chloride is precipitated. Now the solution will contain a small concentration of Ag^+ ions formed by the slight dissociation of silver chloride. This concentration will increase slightly as Cl^- ions are removed in order to maintain the solubility product $K_{SP} = [Ag^+][Cl^-]$. After the equivalence point, the concentration of Ag^+ ions and, therefore the silver electrode potential will rise very sharply owing to the presence of excess of Ag^+ ions. The volume of $AgNO_3$ solution used to reach the equivalence point as shown in Fig. 29.27.



■ **Figure 29.27**
Potentiometric titration curve.

OVERVOLTAGE OR OVERPOTENTIAL

In an electrolysis cell the discharge of an ion on the cathode would occur at the standard half-reaction potential indicated in Table 29.1. Thus the H^+ ions will discharge at the cathode at E° = 0.00 V. It has been experimentally found to be nearly true using platinum black (*i.e.*, finely divided platinum) as the cathode. However with other metal electrodes, for example, mercury and zinc, the voltage needed for the discharge of H^+ ions (evolutions of H_2) is considerable higher than 0.00 V. The difference between the observed voltage (E) and the standard half-reaction voltage (E°) is called-the **hydrogen overpotential.** The values for hydrogen overpotentials on some metals are listed in Table 29.2.

TABLE 29.2. HYDROGEN OVERPOTENTIALS ON SOME METAL CATHODES IN DILUTE H_2SO_4

Cathode	Overpotentials
Mercury	0.78 V
Zinc	0.70 V
Copper	0.23 V
Silver	0.15 V
Platinum black	0.00 V

The hydrogen potentials are particularly well known. But an overpotential exists for any gas at any electrode and is defined as : **the additional potential, over and above the standard electrode potential, which is needed to secure the evolution of the gas.**

$$\text{Overpotential} = E - E°$$

How Overvoltage Occurs ?

The overpotentials arise on account of the energy required for the adsorption of gas to occur on metal surface. The mechanism of, for example, of liberation of hydrogen gas by the discharge of H^+ ions is

Step 1. Discharge of H^+ ions to form H atoms :

$$H^+ + e^- \longrightarrow H$$

Step 2. Adsorption of H atoms on the cathode surface.

Step 3. Combination of adsorbed atoms to give hydrogen molecules :

$$2H \longrightarrow H_2$$

The step 2 may present obstacle. Although the adsorption of gas occurs readily on platinum black, it is very difficult on the metals like mercury and zinc. Therefore the evolution of hydrogen on these metals upon electrolysis of dilute H_2SO_4 occurs at potentials higher than E°.

Concentration Cells

Cell potentials depend on concentration of the electrolyte. Thus a cell can be constructed by pairing two half-cells in which identical electrodes are dipping in solution of different concentrations of the same electrolyte. Such a cell called **concentration cell.** It may be described as : **a cell in which emf arises as a result of different concentrations of the same electrolyte in the component half-cells.**

A typical concentration cell is shown in Fig. 29.28. It consists of two silver electrodes, one immersed in 0.1 M silver nitrate solution and the other in 1 M solution of the same electrolyte. The two solutions are in contact through a membrane (or a salt bridge). When the electrodes are connected by a wire, it is found experimentally that electrons flow from the electrode in more dilute (0.1M) solution to that in the more concentrated (1 M) solution.

Explanation. The concentration of Ag^+ ions in the left compartment is lower (0.1M) and in the right compartment it is higher (1M). There is a natural tendency to equalise the concentration of Ag^+ ions in the two compartments. This can be done if the electrons are transferred from the left compartment to the right compartment. This electron transfer will produce Ag^+ ions in the right compartment by the half-cell reactions :

$$Ag - e^- \longrightarrow Ag+ \qquad (\textit{left compartment})$$

$$Ag^+ + e^- \longrightarrow Ag \qquad (\textit{right compartment})$$

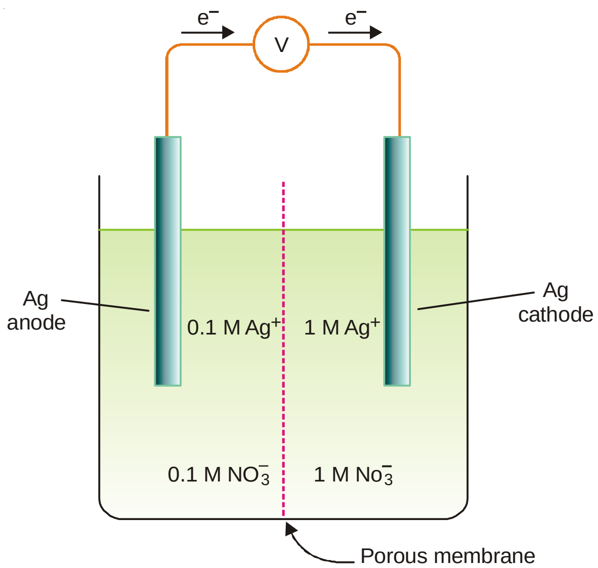


Figure 29.28
A typical concentration cell.

Thus in a bid to equalise concentration of Ag^+ ions in the two compartments the cell will develop emf (Le Chatelier's Principle) to cause the transfer of electrons. Eventually, the solutions in two compartments will have equal Ag^+ ion concentration and there will be no emf recorded.

Emf of Concentration Cell

Suppose the concentrations in the two half-cells are C_1 and C_2 at 25°C, C_2 being greater than C_1. Then emf, E, of the concentration cell will be given by the difference between the two electrode potentials. In terms of Nernst equation

$$E = \left(E_M + \frac{0.0591}{n}\log C_2\right) - \left(E_M + \frac{0.0591}{n}\log C_1\right)$$

$$= \frac{0.0591}{n}\log\left[\frac{C_2}{C_1}\right]$$

where E_M is the standard electrode potential of the metal M and n is the valence of the ions in contact with it. For example, the emf, E, of the concentration cell

$$Ag \mid Ag^+ (1\ M) \parallel (0.1M)\ Ag^+ \mid Ag$$

can be found by substituting the values in the above equation.

$$E = \frac{0.0591}{1}\log\frac{1M}{0.1M}$$

$$= 0.0591$$

Determination of Solubility of Sparingly soluble salts

The ionic concentration of a solution can be calculated from the emf of a concentration cell. In case of a sparingly soluble salt, the salt can be supposed to be completely ionised even in saturated solutions. Hence the ionic concentration is proportional to the solubility of the salt.

Suppose we want to find the solubility of silver chloride. This can be done by measuring the emf, E, of the cell.

$$Ag \mid N/100\ AgNO_3 \mid Glass \parallel Saturated\ AgCl \mid Ag$$

The emf of the cell at 25°C is given by the relation

$$E = \frac{0.0591}{n}\log\frac{C_2}{C_1}$$

Here, n, the valence of Ag+ ion is 1 and the concentration of Ag^+ in N/100 $AgNO_3$ solution is 0.01 gram ion per liter.

Hence,
$$E = \frac{0.0591}{1}\log\frac{0.01}{C_1}$$

From the above expression, the concentration of AgCl in gram ions of silver per litre can be calculated. Multiplying this by 143.5, the molecular weight of silver chloride, we get the solubility of AgCl in grams per liter.

SOLVED PROBLEM. The emf of the cell

$$Ag \mid AgI\ in\ 0.045\ M\ KI \parallel 0.045\ M\ AgNO_3 \mid Ag$$

is 0.788 at 25°C. Calculate (*i*) the solubility product of AgI and (*ii*) the solubility of AgI in water at 25°C.

SOLUTION

Calculation of K_{SP}

At 25°C the concentration of Ag^+ in the cathodic half-cell is 0.045M and the concentration of I^- ion in anodic half-cell is 0.045 M KI.

Let the concentration of Ag^+ ion in the anodic half-cell due to solubility of AgI be C_1.

$$\therefore \qquad E = \frac{0.0591}{1}\log\frac{0.045}{C_1}$$

$$\text{or} \qquad 0.788 = \frac{0.0591}{1}\log\frac{0.045}{C_1}$$

$$\text{or} \qquad \log\frac{0.045}{C_1} = \frac{0.788}{0.0591} = 13.33$$

$$\text{or} \qquad \frac{0.045}{C_1} = 2.138 \times 10^{13}$$

$$C_1 = \frac{0.045}{2.138 \times 10^{13}} = \mathbf{2.105 \times 10^{-15}}$$

Calculation of Solubility

$$\text{Solubility of AgI} = \sqrt{K_{SP}}$$

$$= \sqrt{0.9472 \times 10^{-18}}$$

$$= 0.9732 \times 10^{-9} \text{ g mol litre}^{-1}$$

$$= 0.9732 \times 10^{-9} \times 143.5 \text{ g litre}^{-1}$$

$$= \mathbf{1.396 \times 10^{-6} \text{ g litre}^{-1}}$$

Determination of Valence

The expression for the emf, *E*, of a concentration cell is

$$E = \frac{0.059}{n}\log_{10}\frac{C_2}{C_1} \qquad \text{...(A)}$$

where *n* is the valence of the metallic ion in solution, while C_1 and C_2 are the concentrations of the ions in the two half-cells. Knowing the experimental values of E, C_1 and C_2, *n* can be calculated.

For example, the valence of mercury in mercurous nitrate, $Hg_2(NO_2)_2$, can be determined by the **Concentration cell method.** The following cell is constructed

$$Hg \,|\, 0.05N\ Hg_2(NO_3)_2 \,||\, 0.5N\ Hg_2(NO_3)_2 \,|\, Hg$$

and its emf found experimentally is 0.029 Volts.

Let C_1 be the concentration of mercurous ion in 0.05 N $Hg_2(NO_3)_2$ solution in the left half-cell and C_2 be the concentration of mercurous ion in 0.5N $Hg_2(NO_3)_2$ solution in the right half-cell.

Substituting the values in the expression (A), we have

$$0.029 = \frac{0.0591}{n}\log\frac{0.5}{0.05}$$

$$= \frac{0.0591}{n}\log 10 = \frac{0.0591}{n}$$

$$\text{Therefore,} \qquad n = \frac{0.0591}{0.029} = 2$$

EXAMINATION QUESTIONS

1. Define or explain the following terms :
(*a*) Redox reaction (*b*) Electrochemical cells
(*c*) EMF (*d*) Free energy
(*e*) Nernst equation (*f*) Concentration cells

2. What are concentration cells? Describe and discuss a concentration cell without transference. (*Nehu BSc, 2000*)

3. What is meant by Hydrogen Electrode? How would you make use to this electrode for determination of H^+ ion concentration in a solution? What are the advantages and disadvantages of this electrode? (*Agra BSc, 2000*)

4. Describe the construction and working of calomel electrode. (*Delhi BSc, 2000*)

5. (*a*) What is a reference electrode? Name two and discuss the working of any one reference electrode.
(*b*) Write the cell reactions for the following electrochemical cells :

$$Cd \mid Cd^{2+} \parallel KCl \parallel Hg_2Cl_2(s) \mid Hg$$

$$Pt \mid H_2 \text{ (1 bar)}, HCl \parallel AgCl(s) \mid Ag$$

(*Madras BSc, 2000*)

6. (*a*) Explain why emf of an electrochemical cell cannot be measured with the help of a voltmeter.
(*b*) Describe the applications of emf measurement in the determination of equilibrium constant of a cell reaction. (*Nagpur BSc, 2000*)

7. Write short notes on :
(*a*) Calomel electrode (*b*) Standard hydrogen electrode
(*c*) Standard Cadmium cell (*d*) Amalgam electrode (*Jiwaji BSc, 2000*)

8. Give an account of electrochemical series and its applications. (*Jiwaji BSc, 2000*)

9. What do you understand by the liquid junction potential? How does it arise? How is the liquid junction potential eliminated? (*Madurai BSc, 2000*)

10. (*a*) What is meant by standard electrode potential? Name and write the half reaction of a Calomel reference electrode.
(*b*) Explain why metallic sodium reacts with H^+ to liberate H_2, whereas platinum metal is unreactive to H^+. (*Mizoram BSc, 2002*)

11. (*a*) What do you mean by electrode potential?
(*b*) Describe the important applications of emf measurements. (*MD Rohtak BSc, 2002*)

12. (*a*) Describe how hydrogen electrode is used for the measurement of pH of aqueous solutions.
(*b*) Give one example each of electrolytic concentration cells with and without transference. Also write the cell reactions and expressions for the emf of these cells. (*Guru Nanak Dev BSc, 2002*)

13. Discuss in brief the determination of the following from emf measurements:
(*a*) pH of a solution (*b*) Dissociation constants of acids
(*c*) Solubility of sparingly soluble salt (*Allahabad BSc, 2002*)

14. (*a*) Discuss the principle of determination of pH of a solution with the help of a glass electrode.
(*b*) From the cell reaction in a cell

$$Hg_2Cl_2(s) + H_2(1\text{ atm}) \rightarrow 2Hg + 2H^+(a = 1)$$

the $E°$ of the cell at 25°C is 0.2676 volt and $\left(\frac{\partial E^o}{\partial T}\right)_P = -31.9 \times 10^{-4}$ volt deg^{-1}. Calculate $\Delta H°$ and $\Delta S°$.

Answer. 33.299 kJ; –6.1567 J K^{-1} (*Vidyasagar BSc, 2002*)

15. (*a*) Find out EMF of a concentration cell without transference.
(*b*) Calculate the free energy change of the following cell at 25°C.

$$\text{Sn} \mid \text{Sn}^{2+}\ (0.5\ \text{N}) \parallel \text{Pb}^{2+}\ (0.3\ \text{N}) \mid \text{Pb}$$

The standard EMF of the cell is 0.14 V.

Answer. –25.7539 kJ (*Allahabad BSc, 2002*)

16. Derive an expression for ΔG, ΔH and ΔS in terms of emf of a cell and temperature coefficient of emf. (*Jamia Millia BSc, 2002*)

17. (*a*) How is equilibrium constant of the cell reaction calculated?

(*b*) Calculate the EMF of the cell :

$$\text{Zn} \mid \text{Zn}^{2+}\ (0.001\ \text{M}) \parallel \text{Ag}^{+}\ (0.1\ \text{M}) \mid \text{Ag}$$

The standard potential of Ag | Ag^+ half cell is 0.080 V and Zn | Zn^{2+} is –0.76 volt.

Answer. 1.492 V (*Arunachal BSc, 2002*)

18. (*a*) Write the type of the following reversible electrodes :

(*i*) Quinhydrone (*ii*) Saturated Calomel

(*iii*) Normal hydrogen electrode (*iv*) Silver-Silver electrode

(*b*) Write cell reaction and calculate E° for the cell :

$$\text{Zn} \mid \text{Zn}^{2+}\ (1\ \text{M}) \parallel \text{Fe}^{2+}\ (1\ \text{M}),\ \text{Fe}^{3+}\ (1\ \text{M});\ \text{Pt}$$

Given $E°\ (\text{Fe}^{3+}, \text{Fe}^{2+}) = 0.77$ V, $E°\ (\text{Zn}^{2+}, \text{Zn}) = 0.76$ V

Answer. 0.1534 V (*HS Gaur BSc, 2002*)

19. Calculate EMF of the following cell at 298 K.

$$\text{Cd (Hg)}\ (a = 0.1) \mid \text{Cd SO}_4\ (\text{Soln}) \mid \text{Cd (Hg)}\ (a = 0.01)$$

Answer. 0.0295 V (*Nagpur BSc, 2002*)

20. Calculate the standard emf and standard free energy change for the reaction :

$$\tfrac{1}{2}\text{Cu(s)} + \tfrac{1}{2}\text{Cl}_2\text{(g)} \rightleftharpoons \tfrac{1}{2}\text{Cu}^{2+} + \text{Cl}^- \quad \text{at } 25°\text{C}$$

Given $E°_{Cl_2, Cl^-} = 1.36$ V; $E°_{Cu^{+2}, Cu} = 0.34$V; F = 96500

Answer. 196.86 kJ (*Mizoram BSc (H), 2002*)

21. The equilibrium constant for the reaction :

$$\text{Zn(s)} + \text{Sn}^{2+} \rightleftharpoons \text{Zn}^{2+} + \text{Sn(s)}$$

is 1.122×10^{21} at 298 K. Calculate the standard potential of Zn | Zn^{2+} if $E°_{Zn^2/Zn} = 0.140$ V

Answer. –0.4820 V (*Mumbai BSc, 2002*)

22. Zn gives H_2 gas when it reacts with H_2SO_4 but Ag does not. Explain.($E°_{zn^2/zn} = -0.76$ V and $E°_{\text{Ag+/Ag}} = 0.80$ V) (*Delhi BSc, 2003*)

23. (*a*) Consider a cell in which the overall reaction is $2\ \text{Cu}^{2+} \rightarrow \text{Cu}^{2+} + \text{Cu}$.

Calculate $\Delta G°$ for the reaction, if $E° = +\ 0.184$ V at 298 K.

(*b*) Employing Nernst equation for the dependence of H^+ ion concentration on the potential of hydrogen electrode, show that

$$E_{\text{H}^+, \text{H}_2} = 0.0591 \text{ pH at } 25°\text{C}$$

Answer. –35.512 kJ (*Guru Nanak Dev BSc, 2003*)

24. Calculate the free energy change of the following cell at 25°C :

$$\text{Sn} \mid \text{Sn}^{2+}\ (0.5\ \text{N}) \parallel \text{Pb}^{2+}\ (0.3\ \text{N}) \mid \text{Pb}$$

The standard EMF of the cell is 0.14 volt.

Answer. – 27.020 kJ (*Allahabad BSc, 2003*)

25. Write the cell reaction for the cell

$$\text{Zn} \mid \text{ZnSO}_4\text{(aq)} \parallel \text{CuSO}_4\text{(aq)} \mid \text{Cu}$$

and calculate the equilibrium constant. Given $E°_{Zn\,|\,Zn^{2+}} = 0.76$V; $E°_{Cu|Cu^{2+}} = -0.37$ V at 25°C.

Answer. 5.7×10^{-39} (*Goa BSc, 2003*)

26. For the cell :

$$\mathrm{Zn} \mid \mathrm{Zn^{2+}}\ (c = 1.0\ \mathrm{M}) \parallel \mathrm{Cu^{2+}}\ (c = 1.0\ \mathrm{M}) \mid \mathrm{Cu}$$

the standard emf is 1.10 volts at 25°C. Write down the cell reaction and calculate standard Gibbs free energy change (ΔG).

Answer. –212.3 kJ (*Avadh BSc, 2003*)

27. (*a*) What are primary and secondary reference electrodes? Give one example of each.

(*b*) Describe saturated calomel electrode. Write the electrode reaction when the electrode acts as cathode. (*Arunachal BSc, 2003*)

28. (*a*) Discuss the effect of temperature on the EMF of an electrochemical cell.

(*b*) Discuss the use of EMF measurements to determine the hydrolysis constant of a salt.

(*Nagpur BSc, 2003*)

29. (*a*) Derive Nernst equation showing effect of electrolyte concentration on the potential of an oxidation-reduction electrode.

(*b*) "A salt bridge can minimise the liquid junction potential" – Explain. For the potentiometric titration of $AgNO_3$ against KCl what type of salt bridge should be used and why? (*Kalyani BSc, 2003*)

30. (*a*) What is a reversible cell? Derive expression for the thermodynamic parameters from the EMF of such a cell.

(*b*) Write down the electrode and overall cell reaction for the cell :

$$\mathrm{Pt} \mid \mathrm{H_2}(1\ \mathrm{atm}),\ \mathrm{H^+}(a = 1) \parallel \mathrm{KCl}(a = 1),\ \mathrm{AgCl(s)} \mid \mathrm{Ag}$$ (*Sambalpur BSc, 2003*)

31. What is a salt bridge? Explain its function in an electrochemical cell. (*Punjabi BSc, 2003*)

32. What are oxidation and reduction potentials? What is their use for predicting the feasibility of a reaction?

(*Purvanchal BSc, 2003*)

33. (*a*) How are the emf of a cell and entropy of the reaction related?

(*b*) Explain the phenomenon of liquid junction potential. (*Guru Nanak Dev BSc, 2003*)

34. Calculate the free energy change of the following cell at 25°C :

$$\mathrm{Sn} \mid \mathrm{Sn^{2+}}(a = 0.6) \parallel \mathrm{Pb^{2+}}(a = 0.3) \mid \mathrm{Pb}$$

the standard emf of the cell is 0.014 volt.

Answer. 986.23 J (*Delhi BSc, 2003*)

35. (*a*) Distinguish between cell potential and electromotive force.

(*b*) Summarise the differences between galvanic and electrolytic cell

(*c*) Describe the use of emf measurements to determine the pH of aqueous solutions. Include in your answer a reference of both hydrogen electrode and glass electrode.

(*Guru Nanak Dev BSc, 2004*)

36. (*a*) Calomel electrode is used as a reference electrode, give reasons. Describe its construction and working.

(*b*) What is meant by temperature coefficient of EMF? How is it related to ΔS?

(*c*) With the help of EMF measurements how is solubility and solubility product of a sparingly soluble salt determined? (*Dibrugarh BSc, 2004*)

37. (*a*) What is the basic difference between the voltage and emf of the cell? Explain.

(*b*) Define electrode potential. How is it different from liquid junction potential? How and why the later is eliminated?

(*c*) What will be the reaction in the cell which is made by combining standard Cd half cell with standard Cu half cell? Also calculate the emf of the cell. The standard oxidation potential of half cells are 0.403 and –0.337 volt.

Answer. (*c*) – 0.790V (*Madurai BSc, 2004*)

38. (*a*) What are concentration cells? How do they differ from chemical cells? Derive an expression of the emf of a concentration cell with transference reversible to cations.

(*b*) Describe with the help of diagram the working of a glass electrode and show how it can be used to determine the pH of a solution. (*Banaras BSc, 2004*)

39. Calculate the emf of a cell containing two hydrogen electrodes, the negative one is in contact with 10^{-6} M OH^- ions and the positive one is in contact with 0.05 M H^+.

Answer. 0.395 V (*Avadh BSc, 2005*)

40. Determine the equilibrium constant of the following reaction at 298 K

$$2Fe^{3+} + Sn \rightleftharpoons 2Fe^{2+} + Sn^{4+}$$

From the obtained value of equilibrium constant predict whether Sn^{2+} ion can reduce Fe^{3+} to Fe^{2+} quantitatively or not.

Answer. 1.4215×10^{31} (*Delhi BSc, 2005*)

41. Calculate the standard electrode potential of Ni^{2+}/Ni electrode, if the cell potential of the cell

$$Ni \mid Ni^{2+} \ (0.01 \text{ M}) \parallel Cu^{2+} \ (0.1 \text{ M}) \mid Cu$$

is 0.59 V.

Answer. – 0.2205 V (*Madras BSc, 2005*)

42. For a cell

$$Ag(s) \mid AgNO_3 \ (0.01 \text{ M}) \parallel AgNO_3 \ (1.0 \text{ M}) \mid Ag(s)$$

(a) Calculate the emf at 25 °C

(b) Will the cell generate emf when two concentrations become equal.

Answer. 0.1184 V , No (*Baroda BSc, 2006*)

43. A cell contains two hydrogen electrodes. The negative electrode is in contact with solution of 10^{-6} M hydrogen ions. The emf of the cell is 0.118 volt at 25 °C. Calculate the concentration of H^+ ion at positive electrode ?

Answer. 1×10^{-4} M (*Mumbai BSc, 2006*)

44. Calculate the emf of the cell

$$Cr \mid Cr^{3+} \ (0.1 \text{ M}) \parallel Fe^{2+} \ (0.01 \text{ M}) \mid Fe$$

Given $E^o_{Cr^{3+}/Cr} = 0.75$ V $\qquad E^o_{Fe^{2+}/Fe} = -0.45$ V

Answer. 0.2607 V (*Madras BSc, 2006*)

MULTIPLE CHOICE QUESTIONS

1. In the reaction

$$Zn(s) + 2HCl \rightarrow ZnCl_2(aq) + H_2(g)$$

(*a*) zinc is oxidized

(*b*) the oxidation number of chlorine remains unchanged

(*c*) the oxidation number of hydrogen changes from +1 to 0.

(*d*) all are correct

Answer. (*d*)

2. Electrolytic cells are electrochemical cells in which ______ reactions are forced to occur by the input of electrical energy.

(*a*) spontaneous (*b*) non-spontaneous

(*c*) exothermic (*d*) endothermic

Answer. (*b*)

3. In any electrochemical cell, the cathode is always ______.

(*a*) a nonmetal

(*b*) attached to a battery

(*c*) the electrode at which some species gain electrons

(*d*) the electrode at which some species lose electrons

Answer. (*c*)

4. In an electrolytic cell, the charge on the electrode that gives electrons to the species in solution is _____; the chemical change that occurs at this electrode is called _______.

(*a*) positive; oxidation (*b*) positive, reduction

(*c*) negative, oxidation (*d*) negative, reduction

Answer. (*d*)

5. In a galvanic cell the following reaction takes place:

$$2H_2O \leftrightarrow O_2(g) + 4H^+ + 4e^-$$

It occurs at the

(*a*) cathode (*b*) anode

(*c*) cathode and anode (*d*) none of these

Answer. (*b*)

6. The site of oxidation in an electrochemical cell is

(*a*) the anode (*b*) the cathode

(*c*) the electrode (*d*) the salt bridge

Answer. (*a*)

7. Which statement below is not true for the reaction?

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

(*a*) Fe^{3+} is being reduced

(*b*) the oxidation state of Fe has changed

(*c*) Fe^{3+} could be referred to as an oxidizing agent in this reaction

(*d*) both Fe^{3+} and Fe^{2+} are called anions

Answer. (*d*)

8. $Zn \rightarrow Zn^{2+} + 2e^-$, $\varepsilon° = +0.76$ V, $Cr^{3+} + 3e^- \rightarrow Cr$, $\varepsilon° = -0.74$ V

The anode in this cell is

(*a*) Zn (*b*) Cr

(*c*) Zn^{2+} (*d*) Cr^{3+}

Answer. (*a*)

9. Which of the following statements is correct concerning the reaction:

$$Fe^{2+} + 2H^+ + NO_3^- \rightarrow Fe^{3+} + NO_2 + H_2O$$

(*a*) Fe^{3+} is oxidized and H^+ is reduced

(*b*) Fe^{2+} is oxidized and nitrogen is reduced

(*c*) Fe^{2+} and H^+ are oxidized

(*d*) Oxygen is oxidized

Answer. (*b*)

10. Which of the following is a half-reaction?

(*a*) $Zn + Cu_2^+ \rightarrow Zn_2^+ + Cu$ (*b*) $H^+ + OH^- \rightarrow H_2O$

(*c*) $Ag^+ + e^- \rightarrow Ag$ (*d*) $Ag^+ + Cl^- \rightarrow AgCl$

Answer. (*c*)

11. Which of the following statements associated with electrochemical cells is incorrect?

(*a*) the function of a salt bridge in an electrochemical cell is to complete the circuit

(*b*) cell potential is the potential difference in a voltaic cell

(*c*) a Bronsted-Lowry acid-base reaction can be the basis of the net reaction in a chemical cell

(*d*) a half-reaction corresponds to one electrode in a voltaic cell

Answer. (*c*)

12. Write the cell diagram for the reaction below

$$Cl_2(g) + 2Ag(s) \rightarrow 2Ag^+(aq) + 2Cl^-(aq)$$

(*a*) $Ag \,|\, Ag^+(aq) \,|\, Cl_2(g), Cl^-(aq) \,|\, Pt$

(*b*) $Ag \,|\, Ag^+(aq), Cl^-(aq) \,|\, Cl_2(g) \,|\, Pt$

(*c*) $Pt, Cl_2(g) \,|\, Cl^-(aq) \,||\, Ag^+(aq) \,|\, Ag$

(*d*) $Ag \,|\, Ag^+(aq) \,||\, Cl_2(g), Cl^-(aq) \,|\, Pt$

Answer. (*d*)

13. Write the balanced equation for the voltaic cell made from Ag^+/Ag and Cu^{2+}/Cu and calculate $E°_{cell}$.

(*a*) $2\,Ag^+(aq) + Cu(s) \rightarrow 2\,Ag(s) + Cu_2^+,\ E°_{cell} = 1.260$ V

(*b*) $2\,Ag^+(aq) + Cu(s) \rightarrow Ag(s) + 2\,Cu_2^+,\ E°_{cell} = 1.140$ V

(*c*) $2\,Ag^+(aq) + Cu(s) \rightarrow 2\,Ag(s) + Cu^{2+},\ E°_{cell} = 0.460$ V

(*d*) $2\,Ag^+(aq) + Cu(s) \rightarrow 2\,Ag(s) + Cu_2^+,\ E°_{cell} = 1.140$ V

Answer. (*c*)

14. Which of the following statements associated with batteries is incorrect?

(*a*) in a dry cell, the reaction $Zn \rightarrow Zn^{2+}$ continues to occur even when the battery is not being used

(*b*) secondary batteries are rechargeable

(*c*) the cell reaction in a primary battery is not reversible

(*d*) electrodes with greater surface area give a greater potential

Answer. (*d*)

15. When this redox reaction

$$PbO + [Co(NH_3)_6]^{3+} \rightarrow PbO_2 + [Co(NH_3)_6]^{2+}$$

is balanced in BASIC solution, there are

(*a*) reactants include $2OH^-$. Products include $2H_2O$

(*b*) reactants include $2OH^-$. Products include $2Co(NH_3)_6^{\ 2+}$

(*c*) reactants include $2H_2O$. Products include $2OH^-$

(*d*) products include $2OH^-$ and $1Co(NH_3)_6^{\ 2+}$

Answer. (*b*)

16. Given the nickel-cadmium battery reaction :

$$2NiOOH + Cd + 2H_2O \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} 2Ni(OH)_2 + Cd(OH)_2$$

What occurs during discharge in the nickel-cadmium battery?

(*a*) Ni^{3+} is reduced to Ni^{2+}

(*b*) Ni^{2+} is reduced to Ni^{3+}

(*c*) Ni^{3+} is oxidized to Ni^{2+}

(*d*) Ni^{2+} is oxidized to Ni^{3+}

Answer. (*a*)

17. What is indicated when a chemical cell's voltage ($E°$) has dropped to zero?

(*a*) the concentration of the reactants has increased

(*b*) the concentration of the products has decreased

(*c*) the cell reaction has reached equilibrium

(*d*) the cell reaction has completely stopped

Answer. (*c*)

18. Given the redox reaction :

$$2Cr(s) + 3Cu^{2+}(aq) \rightarrow 3Cr^{3+}(aq) + 3Cu(s)$$

Which reaction occurs at the cathode in an electrochemical cell?

(*a*) reduction of $Cu^{2+}(aq)$	(*b*) reduction of Cu(s)
(*c*) oxidation of $Cr^{3+}(aq)$	(*d*) oxidation of Cr(s)

Answer. (*a*)

19. Which metal is used as a coating on steel to limit corrosion?

(*a*) Na	(*b*) Ca
(*c*) K	(*d*) Zn

Answer. (*d*)

20. Given the cell reaction:

$$2H_2O(l) \longrightarrow 2H_2(g) + O_2(g)$$

The cell is best described as

(*a*) an electrolytic cell in which an exothermic reaction occurs

(*b*) an electrolytic cell in which an endothermic reaction occurs

(*c*) a galvanic cell in which an exothermic reaction occurs

(*d*) a galvanic cell in which an endothermic reaction occurs

Answer. (*b*)

21. Given the reaction:

$$Pb(s) + Cu^{2+}(aq) \rightarrow Pb^{2+}(aq) + Cu(s)$$

What is the reducing agent?

(*a*) $Pb^{2+}(aq)$	(*b*) $Cu^{2+}(aq)$
(*c*) Pb(s)	(*d*) Cu(s)

Answer. (*c*)

22. Given the reaction:

$$4HCl(aq) + MnO_2(s) \rightarrow MnCl_2(aq) + 2H_2O(l) + Cl_2(g)$$

The manganese is

(*a*) reduced and its oxidation number changes from +4 to +2

(*b*) reduced and its oxidation number changes from +2 to +4

(*c*) oxidized and its oxidation number changes from +4 to +2

(*d*) oxidized and its oxidation number changes from +2 to +4

Answer. (*a*)

23. What occurs when an atom is oxidized in a chemical reaction?

(*a*) a loss of electrons and a decrease in oxidation number

(*b*) a loss of electrons and an increase in oxidation number

(*c*) a gain of electrons and a decrease in oxidation number

(*d*) a gain of electrons and an increase in oxidation number

Answer. (*b*)

24. Standard cell potential is

(*a*) measured at a temperature of 25°C

(*b*) measured when ion concentrations of aqueous reactants are 1.00 M

(*c*) measured under the conditions of 1.00 atm for gaseous reactants

(*d*) all of the above

Answer. (*d*)

25. The standard reduction potentials in volts for Pb^{2+} and Ag^+ are –0.13 and +0.80, respectively. Calculate $E°$ in volts for a cell in which the overall reaction is

$$Pb + 2Ag^+ \rightarrow Pb^{2+} + 2Ag$$

(*a*) 1.73
(*b*) 0.67
(*c*) 0.93
(*d*) 1.47

Answer. (*c*)

26. Given the following information,

$$Fe^{3+}(aq) + H_2(g) \rightarrow 2H^+ + Fe^{2+},\ E°_{cell} = 0.77$$

Determine $E°$ for the reaction :

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

(*a*) 1.54
(*b*) 0.77
(*c*) 0.39
(*d*) – 0.77

Answer. (*b*)

27. Breathalyzers determine alcohol content via the redox reaction:

$$Cr_2O_7^{2-} + C_2H_5OH \rightarrow Cr^{3+} + C_2H_4O_2$$

Which substance is a reductant (reducing agent) and which is an oxidant (oxidizing agent)?

(*a*) C_2H_5OH, reductant; no oxidant
(*b*) C_2H_5OH, reductant; $Cr_2O_7^{2-}$, oxidant
(*c*) C_2H_5OH, oxidant; Cr^{3+}, reductant
(*d*) C_2H_5OH, reductant; Cr^{3+}, oxidant

Answer. (*b*)

28. Predict the products in the electrolysis of aqueous potassium bromide.

(*a*) hydrogen and bromine
(*b*) potassium metal and oxygen
(*c*) oxygen and bromine
(*d*) potassium metal and bromine

Answer. (*a*)

29. Which of the following statements associated with corrosion is incorrect?

(*a*) iron corrodes more readily than aluminium because iron is more active than aluminium
(*b*) cathodic protection prevents corrosion by using a sacrificial anode
(*c*) a corroding metal has both anodic and cathodic areas
(*d*) corrosion involves both oxidation and reduction

Answer. (*a*)

30. Which of the following shows a metal being oxidized?

(*a*) $2Na + 2H_2O \rightarrow 2NaOH + H_2$
(*b*) $Cu \rightarrow Cu^{2+} + 2e^-$
(*c*) $Cu^{2+} + 2e^+ \rightarrow Cu$
(*d*) Both (*a*) and (*b*)

Answer. (*d*)

31. It is possible to generate an electrical potential by inserting two strips of different metals into an acidic citrus fruit such as a lemon. Among other functions, the lemon serves as a salt bridge. Which shorthand notation would best describe a lemon into which has been inserted a strip of zinc and a strip of copper, with the two metal strips connected by a wire?

(*a*) $Zn(s) \mid Zn^{2+}(aq) \parallel O_2(g) \mid H_2O(I) \mid Cu(s)$
(*b*) $Zn(s) \mid Zn^{2+}(aq) \parallel H^+(aq) \mid H^2(g) \mid Cu(s)$
(*c*) $Cu(s) \mid Cu^{2+}(aq) \parallel O_2(g) \mid H_2O(I) \mid Zn(s)$
(*d*) $Zn(s) \mid Zn^{2+}(aq) \parallel Cu^{2+}(aq) \mid Cu(s)$

Answer. (*a*)

32. Write the net equation for the redox reaction that occurs in the voltaic cell with a $Cu(s) – Cu^{2+}(aq)$ electrode and a $Ag(s) – Ag^+(aq)$ electrode.

(*a*) $Cu^{2+}(aq) + 2Ag(s) \rightarrow Cu(s) + 2Ag^+(aq)$
(*b*) $Cu(s) + Cu^{2+}(aq) \rightarrow 2Ag^+(aq) + Ag(s)$
(*c*) $Cu(s) + 2Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$
(*d*) $2Ag^+(aq) + Ag(s) \rightarrow Cu(s) + Cu^{2+}(aq)$

Answer. (*c*)

33. Which of these statements about a galvanic cell are not true?

i. the cathode carries a positive sign

ii. the anions migrate toward the cathode

iii. the electrons are released through the anode

iv. reduction occurs at the anode

(*a*) i and iii (*b*) i and ii

(*c*) ii and iii (*d*) ii and iv

Answer. (*d*)

34. The half–reaction that occurs at the cathode during the electrolysis of molten sodium iodide is

(*a*) $2I^- \rightarrow I_2 + 2e^-$ (*b*) $I_2 + 2e^- \rightarrow 2I^-$

(*c*) $Na^+ + e^- \rightarrow Na$ (*d*) $Na \rightarrow Na^+ + e^-$

Answer. (*c*)

35. For a voltaic cell using Ag+ (1 M)/Ag and Cu^{2+}(1M)/Cu half cells, which of the following statements is false?

(*a*) electrons will flow through the external circuit from the copper electrode to the silver electrode

(*b*) reduction occurs at the silver electrode as the cell operates

(*c*) the mass of the copper electrode will decrease as the cell operates

(*d*) the concentration of Ag^+ will increase as the cell operates

Answer. (*d*)

36. In the lead storage battery

(*a*) a reversible reaction can occur to recharge the battery

(*b*) lead is oxidized to create a flow of electrons

(*c*) lead forms the cathode when it is being reduced

(*d*) all of the above

Answer. (*d*)

37. The advantages of fuel cells include

(*a*) they can be recharged by the addition of more material to be oxidized and/or reduced

(*b*) they can be made to produce little or no harmful pollutants

(*c*) they can be made to run very quietly

(*d*) all of the above

Answer. (*d*)

38. For the reaction

$$2In(s) + 6H^+(aq) \rightarrow 2In^{3+}(aq) + 3H_2(g), \quad E° = +0.34 \text{ V}$$

Determine the value of $E°_{red}$ for the half-reaction

$$In^{3+}(aq) + 3e^- \rightarrow In(s)$$

(*a*) – 0.17 (*b*) – 0.34

(*c*) 0.17 (*d*) 0.34

Answer. (*b*)

39. From a consideration of the following two half-reactions

Half Reaction	*E° (Volts)*
$Mn^{2+} + 2e^- \rightarrow Mn$	–1.18
$AuCl_4^- + 3e^- \rightarrow Au + 4Cl^-$	1.00

What is the standard cell potential for the reaction

$$3Mn + 2AuCl_4^- \rightarrow 3Mn^{2+} + 2Au + 8Cl^-$$

(*a*) –2.18 V (*b*) –0.18 V

(*c*) 0.18 V (*d*) 2.18 V

Answer. (*d*)

40. Determine the values of E°_{cell} and ΔG° for the reaction below.

$$O_2(g) + 4I^-(aq) + 4H^+(aq) \rightarrow 2H_2O(\ell) + 2I_2(s)$$

(*a*) $E^\circ_{\text{cell}} = 0.159$ V and $\Delta G^\circ = -2.68 \times 10^5$ J
(*b*) $E^\circ_{\text{cell}} = 0.694$ V and $\Delta G^\circ = -2.68 \times 10^5$ J
(*c*) $E^\circ_{\text{cell}} = 0.694$ V and $\Delta G^\circ = +2.68 \times 10^5$ J
(*d*) $E^\circ_{\text{cell}} = 1.764$ V and $\Delta G^\circ = -6.81 \times 10^5$ J

Answer. (*b*)

41. The standard reduction potentials of Cu^{2+} and Ag^+ in V are +0.34 and +0.80, respectively. Determine the value of E in volts for the following cell at 25°C

$$Cu \mid Cu^{2+}\ (1.00\ M) \parallel Ag^+\ (0.0010\ M) \mid Ag$$

(*a*) 0.37 V
(*b*) 0.55 V
(*c*) – 0.28 V
(*d*) 0.28 V

Answer. (*d*)

42. What is the potential of a half cell consisting of a platinum wire dipped into a solution 0.01M in Sn^{2+} and 0.001M in Sn^{4+} at 25°C?

(*a*) $E^\circ_{\text{oxid.}} + 0.059$
(*b*) $E^o_{\text{red.}} - \dfrac{0.059}{2}$
(*c*) $E^o_{\text{red.}} + \dfrac{0.059}{2}$
(*d*) $E^\circ_{\text{oxid.}} = -0.059$

Answer. (*b*)

43. A galvanic cell can be represented as

$Pt(s) \mid Sn^{2+}\ (aq,\ 1\ M),\ Sn^{4+}\ (aq,\ 1\ M) \parallel Fe^{2+}\ (aq,\ 1\ M)\ Fe^{3+}\ (aq,\ 1\ M) \mid Pt(s)$

What reaction is occurring at the anode?

(*a*) $Pt \rightarrow Pt^{2+} + 2e^-$
(*b*) $Sn^{2+} \rightarrow Sn^{4+} + 2e^-$
(*c*) $Pt \rightarrow Sn^{2+} + 2e^-$
(*d*) $Fe^{2+} \rightarrow Fe^{3+} + 1e^-$

Answer. (*d*)

44. What is the cell voltage of $Zn \mid Zn^{2+}\ (0.1\ M) \parallel Ag^+\ (0.1\ M) \mid Ag$?

The standard reduction potential for $Zn^{2+} + 2e^- \rightarrow Zn$ is –0.76 V and for $Ag^+ + e^- \rightarrow Ag$ is +0.80 V.

(*a*) –0.76 V
(*b*) +0.80 V
(*c*) +1.53 V
(*d*) +1.59 V

Answer. (*c*)

45. Calculate the voltage (*E*) of a cell with $E^\circ = 1.1$ volts, if the copper half-cell is at standard conditions but the zinc ion concentration is only .001 molar. Temperature is 25°C. The overall reaction is

$$Zn + Cu^{+2} \rightarrow Cu + Zn^{+2}$$

(*a*) 0.39 volt
(*b*) 1.43 volt
(*c*) 6.19 volt
(*d*) 1.19 volt

Answer. (*d*)

46. Suppose that an alkaline dry cell was manufactured using cadmium metal rather than zinc. What effect would this have on the cell emf ?

(*a*) no change
(*b*) the voltage would increase by 0.360 V
(*c*) the voltage would decrease by 0.360 V
(*d*) it would not work

Answer. (*c*)

47. Given $Zn \rightarrow Zn^{+2} + 2e^-$ with $E^\circ = +0.763$, calculate *E* for a Zn electrode in which $Zn^{+2} = 0.025$ M.

(*a*) 1.00 V
(*b*) 0.621 V
(*c*) 0.810 V
(*d*) 0.124 V

Answer. (*c*)

48. A strip of zinc is dipped in a solution of copper sulfate. Select the correct occurring half–reaction.

(*a*) $Co^{++} + 2e^- \rightarrow Co$, reduction
(*b*) $Cu + 2e^- \rightarrow Cu^{++}$, reduction
(*c*) $Cu \rightarrow Cu^{++} + 2e^-$, reduction
(*d*) $Zn \rightarrow Zn^{++} + 2e^-$, oxidation

Answer. (*d*)

49. A concentration cell is constructed by placing identical Zn electrodes in two Zn^{2+} solutions. If the concentrations of the two Zn^{2+} solutions are 0.10 M and 0.00010 M, respectively, what is the potential of the cell?

(*a*) + 0.763 V (*b*) + 0.089 V
(*c*) + 0.053 V (*d*) + 0.24 V

Answer. (*b*)

50. Calculate the potential (in volts) for the following voltaic cell at 25°C:

$$Cr/Cr^{3+}\ (0.10\ M)\ ||\ Cu^{2+}\ (0.0010\ M)\ /Cu$$

(*a*) 1.25 V (*b*) 1.33 V
(*c*) 1.41 V (*d*) 1.57 V

Answer. (*b*)

51. Calculate the cell potential for the voltaic cell that results when the following two half-cells are connected at 25°C:

(1) a platinum electrode inserted into a solution of 0.10 M Co^{3+} and 0.0010 M Co^{2+}
(2) a copper electrode inserted into a solution of 0.010 M Cu^{2+} ions

(*a*) 1.56 V (*b*) 1.30 V
(*c*) 1.48 V (*d*) 1.66 V

Answer. (*d*)

52. Calculate the potential (in volts) for the following voltaic cell at 25° C:

$$Ag/Ag^{+}\ (0.01\ M)\ ||\ MnO_4^{-}\ (0.1\ M);\ H^{+}\ (1\ M);\ Mn^{2+}\ (0.001\ M)/Pt$$

(*a*) +0.57 V (*b*) 0.71 V
(*c*) +0.85 V (*d*) +0.91 V

Answer. (*c*)

53. What is the equilibrium constant for the following at 25°C?

$$3Mn^{2+} + 2Cr \rightarrow 3Mn + 2Cr^{3+}$$

(*a*) 5.1×10^{44} (*b*) 1.3×10^{21}
(*c*) 2.5×10^{-45} (*d*) 8.0×10^{-23}

Answer. (*c*)

54. A voltaic cell has an $E°$ value of –1.00 V. The reaction _____.

(*a*) is spontaneous (*b*) has a positive $\Delta G°$
(*c*) has a negative $\Delta G°$ (*d*) has $K = 1$

Answer. (*b*)

55. Which of the following is FALSE regarding the salt bridge used in voltaic cells? The salt bridge _____.

(*a*) allows for the two half-cells to be kept separated
(*b*) maintains the electrical neutrality in each half cell
(*c*) allows mixing of the two electrode solutions
(*d*) is made of a medium through which ions can slowly pass

Answer. (*c*)

56. Which of the following can we use to measure pH?

(*a*) a glass electrode (*b*) a concentration cell
(*c*) a hydrogen electrode (*d*) all of these

Answer. (*d*)

57. Based on the following information, which will be the most effective oxidizing agent?

$Na^{+} + e^{-} \rightarrow Na$ $E° = -2.71$

$O^2 + 4e^- + 2H_2O \rightarrow 4OH^-$ $E° = +0.40$

$Cl_2 + 2e^- \rightarrow 2Cl^-$ $E° = +1.36$

(*a*) Na (*b*) Na^+

(*c*) O_2 (*d*) Cl_2

Answer. (*d*)

58. What is $\Delta G°$ at 298 K for the reaction

$$Hg(\ell) + 2Fe^{3+}(aq) \rightarrow Hg^{2+}(aq) + 2Fe^{2+}(aq)?$$

(*a*) +314 kJ (*b*) –16 kJ

(*c*) –314 kJ (*d*) 16 kJ

Answer. (*d*)

59. The salt bridge in the electrochemical cell serves to

(*a*) increase the rate at which equilibrium is attained

(*b*) increase the voltage of the cell

(*c*) maintain electrical neutrality

(*d*) increase the oxidation/reduction rate

Answer. (*c*)

60. Complete and balance the following equation. (All stoichiometric coefficients must be integers)

$$MnO_4^-(aq) + Cl^-(aq) \rightarrow Mn^{2+}(aq) + Cl_2(g) \text{ (acidic solution)}$$

How many hydrogen ions are needed and on which side of the equation must they appear?

(*a*) 16, on the left (*b*) 8, on the left

(*c*) 16, on the right (*d*) 4, on the left

Answer. (*a*)

61. Complete and balance the following equation. (All stoichiometric coefficients must be integers)

$$HClO(aq) + Br_2(g) \rightarrow BrO_3^-(aq) + Cl_2(g) \text{ (acidic solution)}$$

How many hydrogen ions are needed and on what side of the equation must they appear?

(*a*) 0 hydrogen ions are needed (*b*) 10, on the right

(*c*) 12, on the right (*d*) 2, on the left

Answer. (*a*)

62. What is $\Delta G°$ at 298 K for the reaction:

$$2VO_2^+(aq) + 4H^+(aq) + Cd(s) \rightarrow 2VO^{2+}(aq) + 2H_2O(\ell) + Cd^{2+}(aq)?$$

(*a*) –271 kJ (*b*) 1.403 J

(*c*) –135 kJ (*d*) –115 kJ

Answer. (*a*)

63. From a consideration of the following two half-reactions at 298 K,

Half Reaction	*E°* (*Volts*)
$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$	– 0.126
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$	– 0.447

What is the equilibrium constant for the following equation?

$Pb^{2+}(aq) + Fe(s) \rightarrow Pb(s) + Fe^{2+}(aq)$ $K_{eq} = e^{-\Delta G/RT}$

Faraday constant: 1 F = 96,485 C/mol. $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

(*a*) 3.7×10^{-6} (*b*) 2.7×10^5

(*c*) 7.2×10^{10} (*d*) 2.4×10^{19}

Answer. (*c*)

64. From a consideration of the following two half-reactions

Half Reaction	*E*°(*Volts*)
$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$	1.36
$Br_2(\ell) + 2e^- \rightarrow 2Br^-(aq)$	1.07

what is the standard free energy change at 25°C for the following reaction?

$$Cl_2(g) + 2Br^-(aq) \rightarrow Br_2(\ell) + 2Cl^-(aq)$$

Faraday constant: 1 F = 96,485 C/mol. $R = 8.314$ J mol^{-1} K^{-1}

(*a*) –112 kJ/mol (*b*) –56 kJ/mol

(*c*) –28 kJ/mol (*d*) 470 kJ/mol

Answer. (*b*)

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