

Physical Chemistry

Electrochemistry II: Voltaic or Galvanic cells

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Introduction

An electrochemical cell consists of two electrodes. An electrode is a metallic conductor in contact with an ionic conductor called an electrolyte, usually a solution of an acid, base or salt or a pure liquid. The two electrodes in a cell may be in contact with the same electrolyte as is always the case in an electrolytic cell where electrolysis occurs, i.e., non-spontaneous chemical reaction is brought about by an externally applied electromotive force (e.m.f.). The e.m.f. of a cell can be defined as the difference in potential between

the two electrodes on an open circuit. In contrast, a galvanic or voltaic cell produces an electric current because of spontaneous reactions at the two electrodes which may be in contact with the same or different electrolytes. In the latter case, the two electrode compartments are connected by a salt bridge for electrical contact between the electrolytes. A salt bridge is a double bent glass tube containing a concentrated solution of an electrolyte (usually KCl, KNO₃ or NH₄NO₃) with comparable ionic mobilities of the cation and the anion. The solution is, in general, made up in a gel (e.g., agar) to minimise the mixing of the solutions of the two half cells.

An electrode, i.e., a metallic conductor in contact with an electrolyte, develops an electrical potential called the electrode potential. In a galvanic or voltaic cell, the e.m.f. of the cell is the algebraic sum of the electrode potentials of the two electrodes with universally agreed sign conventions. Each of the electrodes in contact with the electrolyte solution is also called a half cell.

As a galvanic cell functions, i.e., delivers current, at the two electrodes spontaneous chemical reactions take place, which when combined gives the overall chemical reaction called the cell reaction. It is the energy of this chemical reaction that generates the e.m.f. of the cell. In such cases, the cell is called a chemical cell. In some cells there is no overall chemical reaction but the e.m.f. is generated because of the difference in the concentrations of either the electrolytes or the electrodes. Various types of electrochemical cells are shown in Figure 1.

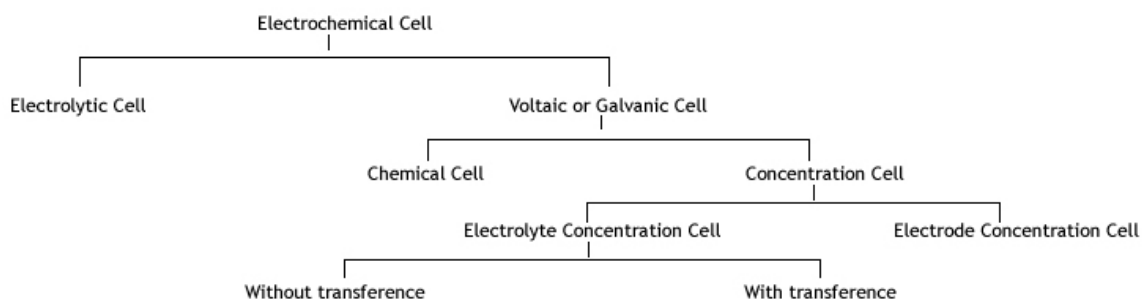


Fig. 1 : Various types of electrochemical cells

At this moment the electrolysis experiments on a laboratory scale or electroplating may be recalled. On a large scale, electrolysis finds application in the extraction of sodium, magnesium, aluminium, production of chlorine, etc.

In this chapter we would focus on Voltaic or Galvanic cells and discuss :

1. Reversible cells.
2. Types of reversible electrodes, their representation and electrode reactions.
3. Representation of various types of chemical cells combining suitable electrodes.

4. Expression for electrode potentials.
5. Expression for the e.m.f. of a cell and the standard e.m.f. of the cell.
6. Standard Hydrogen Electrode (SHE) and assignment of values to electrode potentials.
7. Electrochemical series.
8. Measurement of the reversible e.m.f. of a cell.
9. Standard cell : Weston Cadmium Cell.
10. Reference electrodes.
11. Calculation of the thermodynamic properties(ΔG , ΔS and ΔH) of a cell reaction.

Reversible Cells

When a galvanic cell operates, the electrical work done can be related to the free energy change (ΔG) associated with the chemical or other processes occurring in the cell only if the cell functions reversibly in the thermodynamic sense. This requires that the e.m.f. of the cell can be exactly balanced by an equal external source of e.m.f. applied in opposition. Under this condition, the chemical and other changes that occur in the cell should come to a stop and as a consequence the cell should deliver no current. Further, the cell processes should occur to a very very small extent in their spontaneous or non-spontaneous direction proportionally when the externally applied e.m.f. is suitably adjusted so as to be infinitesimally greater ($E+dE$) or infinitesimally smaller ($E-dE$) than the e.m.f. (E) of the cell. Thus in such conditions, when a very very small current passes through the cell, the cell can be considered to be in equilibrium for all practical purposes, i.e., the cell processes will be close to the ideal concept of the thermodynamic reversibility. This is required since otherwise the thermodynamic properties of the overall cell reaction cannot be determined as the relationship between these properties and the properties of a galvanic cell such as these e.m.f. are deduced on the assumption of reversible functioning of the cell in the thermodynamic sense.

Reversible Electrodes

Electrodes in a reversible cell are necessarily reversible electrodes. Seven types of such electrodes are frequently used.

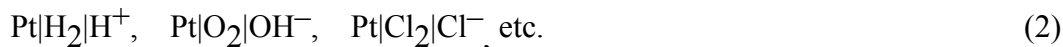
i) A metal in contact with a solution that contains its ions. Such electrodes are generally represented by M/M^{n+} and the equilibrium that is established is



Zn in zinc sulphate solution, Cu in copper sulphate solution, etc are the examples. The electrodes are reversible with respect to the respective ions (M^{n+}),

ii) A nonmetal in contact with a solution of its own ions constitutes an electrode similar to the one discussed above. Since nonmetals are not conductors of electricity, in such cases an inert metal (usually platinum) is used for electrical contact. Hydrogen, oxygen, chlorine, etc. are bubbled through the solution around the Pt electrodes dipped in

solution containing their respective ions (OH^- ions for oxygen). Electrodes of these types are represented by

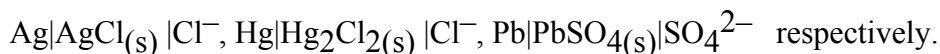


The equilibrium established at the respective electrodes are



The electrodes are reversible with respect to H^+ , Cl^- and OH^- ions respectively. Generally the platinum used is platinised platinum which facilitates adsorption of gases.

iii) The third type of electrodes is constituted of metals coated with porous layers of insoluble (sparingly soluble) salts of the respective metals in contact with a solution containing soluble salts with the same anion as the respective insoluble salts. These are exemplified by silver-silver chloride, calomel (Hg_2Cl_2), lead-lead sulphate, etc. electrodes. These are represented by

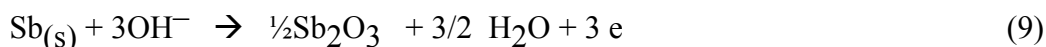


The equilibrium established at the respective electrodes are



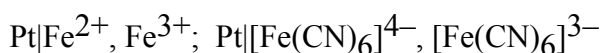
The electrodes are reversible with respect to Cl^- , Cl^- and SO_4^{2-} ions respectively.

iv) A metal coated with a porous layer of insoluble oxide of the metal in contact with OH^- ions constitutes a metal—insoluble oxide electrode, e.g., $\text{Sb}|\text{Sb}_2\text{O}_3|\text{OH}^-$. The electrode reaction will be



This electrode is reversible with respect to the OH^- ions

(v) When a platinum electrode is in contact with a solution containing the oxidised and the reduced forms of a redox system, one obtains a redox electrode. Examples are



The corresponding equilibria established at the electrodes, are



(vi) Amalgam electrode. Here the concentration of the metal in the electrode is variable, e.g., Na / Na^+ . Sodium in contact with water catches fire but when amalgamated (Na(Hg)) it does not and hence Na(Hg) can be used as an electrode.

(vii) Membrane electrode

The complete cells

An electrochemical cell is a combination of two electrodes or half cells immersed in the same or different electrolyte solutions. The first type is represented as follows



The complete cell is shown below

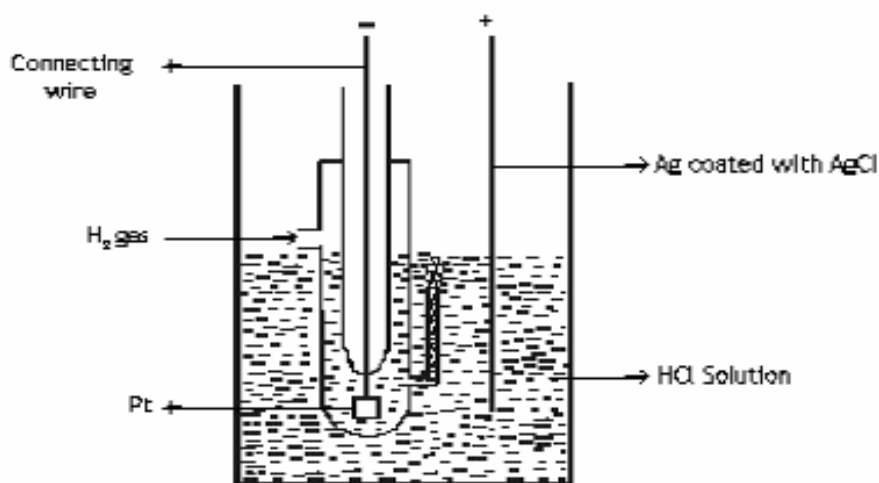
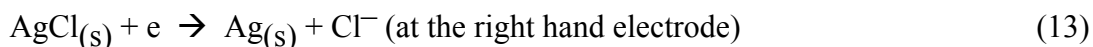
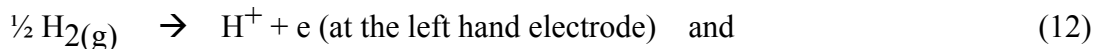


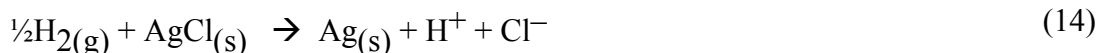
Fig. 2 : A cell with hydrogen electrode without liquid junction

Both the electrodes are dipped in the same HCl solution. The hydrogen electrode is reversible with respect to H^+ ions and the Ag-AgCl electrode with respect to Cl^- ions. In this type of cells there is no junction between two different electrolytes and the cell is without liquid junction (hence without any liquid junction potential)

The processes that spontaneously occur at the two electrodes are



The overall spontaneous reaction occurring in the cell is



This spontaneous redox reaction generates the cell e.m.f. and electrons flow from the left hand to the right hand electrode through the metallic wire connecting the two electrodes externally. This is how the cell delivers current during its operation. Current direction, by convention, is taken to be the direction of flow of positive charge which means that it is opposite to the direction of flow of electrons.

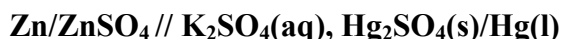
In the above representation of the cell (eqn. 11) by convention oxidation occurs at the left hand electrode (negative electrode) and reduction at the right hand one (positive electrode). The first one is called the anode and the second, the cathode.

Example 1 : Device a cell in which the overall reaction is

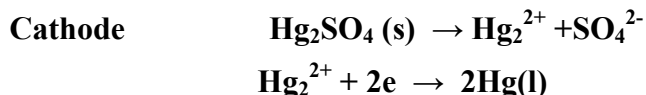
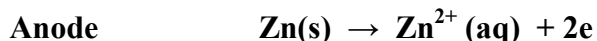


and write the separate electrode reactions.

Ans.1 : The cell reaction shows that Zn is oxidized to Zn^{2+} and Hg^{1+} is reduced to $\text{Hg}(\text{l})$. Therefore Zn electrode will be written in the LHS and the Hg electrode is in RHS. Therefore the cell should be written as



From the above cell one can write



Now summing up the above three eqns. We get



which was the given cell reaction.

It is well known that when a zinc plate is dipped into a copper sulphate solution, it becomes coated with a layer of copper and the spontaneous reaction is represented by the chemical equation



This reaction is the basis of the widely used Daniell cell. In copper sulphate solution, a porous pot with zinc sulphate solution in it is placed to avoid the mixing of the two solutions. A copper electrode is dipped in the copper sulphate solution and a zinc electrode in Zinc sulphate solution. The cell is conventionally represented as



The electrode processes are





The cell e.m.f. is generated by the spontaneous over-all cell reaction

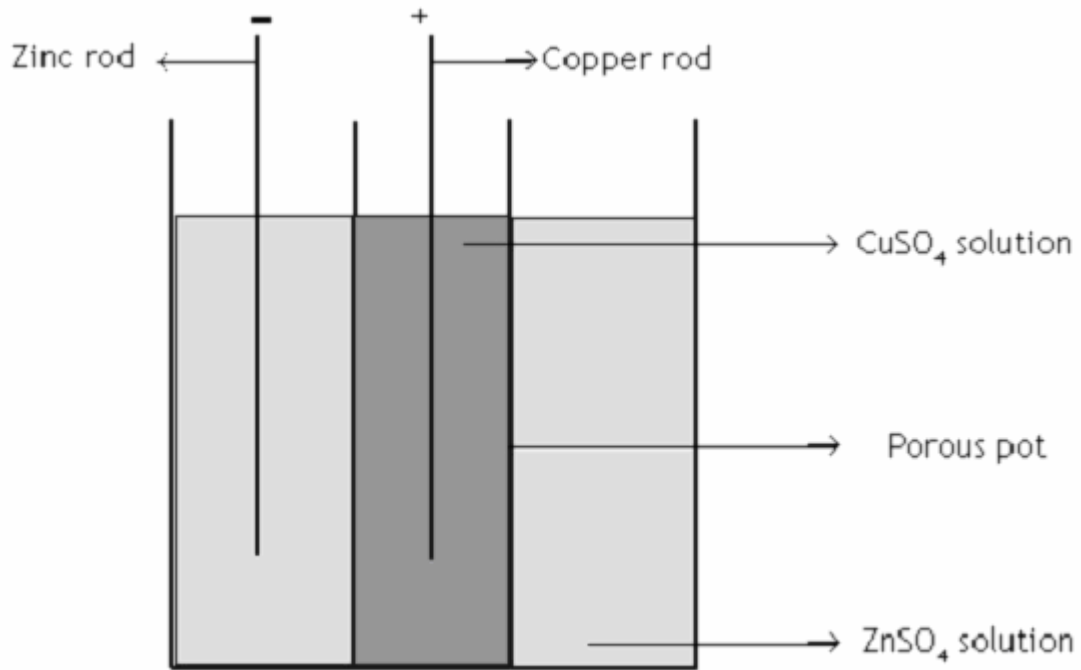
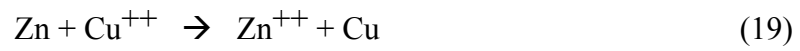


Figure 3 : The Daniell cell

It is possible to arrive at an expression for the electrode potential (E_e) of any reversible electrode.

The potential of the electrode, $\text{Cu}|\text{Cu}^{++}$ can be found by considering the electrode process as either reduction or oxidation (for reasons to be discussed later). Let us consider the reduction process



The reaction isotherm for the process is

$$\Delta G = \Delta G^\circ + RT \ln a_{\text{Cu}} / a_{\text{Cu}^{2+}} \quad (21)$$

The free energy change accompanying a complete chemical process is equal to the maximum work realized under reversible condition minus any pressure-volume (mechanical) work.

$$-\Delta G = W_{\text{rev}} - P\Delta V \quad (22)$$

Since the electrode process does not include any mechanical work

$$-\Delta G = W_{\text{rev}} = 2 F E_{\text{red}} \quad (23)$$

the only work being the electrical work where F is faraday, 2 is the number of electrons involved in the reaction and E_{red} is the reduction potential of the electrode. Substituting in the reaction isotherm we get

$$2 F E_{\text{red}} = -2 F E_{\text{red}}^0 + RT \ln 1/a_{\text{Cu}^{2+}} \quad (24)$$

$$E_{\text{red}}(\text{Cu}^{2+}, \text{Cu}) = E_{\text{red}}^0(\text{Cu}^{2+}, \text{Cu}) + RT/2F \ln a_{\text{Cu}^{2+}} \quad (25)$$

The activity of a solid being unity by convention. This is known as Nernst equation for electrode potential

Similarly, the electrode potential for the electrode, Zn/Zn^{++} considering the electrode process as reduction is given by

$$E_{\text{red}}(\text{Zn}^{2+}, \text{Zn}) = E_{\text{red}}^0(\text{Zn}^{2+}, \text{Zn}) + RT/2F \ln a_{\text{Zn}^{++}} \quad (26)$$

The above expressions are the reduction potentials of Cu/Cu^{++} and Zn/Zn^{++} electrodes. It is clear that the electrode potentials are dependent on the activity of the ion with respect to which the electrodes are reversible. As the state of unit activity is considered the standard state of the ions, $E_{\text{red}} = E_{\text{red}}^0$ when $a_{\text{Cu}^{++}} = 1$ and $a_{\text{Zn}^{++}} = 1$ for the copper and the zinc electrodes respectively. E_{red}^0 is the standard reduction potential of the electrode under consideration ..

Expression for the oxidation potential for an electrode, say Zn/Zn^{++} , can be arrived at in the same way as above considering the electrode process as oxidation $\text{Zn} \rightarrow \text{Zn}^{++} + 2e$. In this case,

$$E_{\text{ox}}(\text{Zn}^{2+}, \text{Zn}) = E_{\text{ox}}^0(\text{Zn}^{2+}, \text{Zn}) - RT/2F \ln a_{\text{Zn}^{++}} \quad (27)$$

The above expression for the oxidation potential is equal in magnitude but opposite in sign to the corresponding reduction potential.

The e.m.f. of the Daniell cell that comprises the two electrodes discussed above is given by

$E_{\text{cell}} = E_{\text{R}} - E_{\text{L}}$ where E_{R} and E_{L} are the electrode potentials (reduction potentials) of the right hand and the left hand electrodes in the Daniell cell represented by

$$\text{Zn}|\text{Zn}^{2+}||\text{Cu}^{2+}|\text{Cu} \quad (28)$$

$$E_{\text{cell}} = E_{\text{Cu}/\text{Cu}^{2+}}^0 + RT/2F \ln a_{\text{Cu}^{2+}} - (E_{\text{Zn}/\text{Zn}^{2+}}^0 + RT/2F \ln a_{\text{Zn}^{2+}}) \quad (29)$$

$$= (E_{\text{Cu}/\text{Cu}^{2+}}^0 - E_{\text{Zn}/\text{Zn}^{2+}}^0) - RT/2F (\ln a_{\text{Zn}^{++}} - \ln a_{\text{Cu}^{++}}) \quad (30)$$

(The double line, '||' between the two electrodes indicates that the electrolytes are joined by a salt bridge to minimise the liquid junction potential.)

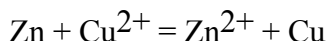
$$\text{or } E = E^\circ_{\text{Cell}} - \frac{RT}{2F} \ln \frac{a_{\text{Zn}^{2+}}}{a_{\text{Cu}^{2+}}} \quad (31)$$

This is the Nernst's equation for the e.m.f. of a cell.

Again, with reference to the Daniell cell

$\text{Zn}|\text{Zn}^{2+}(a_{\text{Zn}^{2+}})||\text{Cu}^{2+}(a_{\text{Cu}^{2+}})|\text{Cu}$, (ie. a cell where liquid junction is said to be negligible)

the overall cell reaction that occurs spontaneously as the cell delivers current is



We can directly arrive at an expression for the cell e.m.f. (Nernst equation) without considering the processes at the electrodes. The reaction isotherm for the reaction,

$$\Delta G = \Delta G^\circ + RT \ln (a_{\text{Cu}} \cdot a_{\text{Zn}^{2+}} / a_{\text{Zn}} \cdot a_{\text{Cu}^{2+}}) \quad (32)$$

$$\text{or, } \Delta G = \Delta G^\circ + RT \ln (a_{\text{Zn}^{2+}} / a_{\text{Cu}^{2+}}) \quad (33)$$

as the activity of a solid is equal to unity by convention,

$$\text{or, } -2F E = -2F E^\circ + RT \ln (a_{\text{Zn}^{2+}} / a_{\text{Cu}^{2+}}) \quad (34)$$

$$\text{or } E = E^\circ_{\text{cell}} - \frac{RT}{2F} \ln (a_{\text{Zn}^{2+}} / a_{\text{Cu}^{2+}}) \quad (35)$$

The expression for e.m.f. of any given cell can be arrived in a similar manner either by the use of expressions for the concerned individual electrode potentials or directly by considering the overall spontaneous cell reaction.

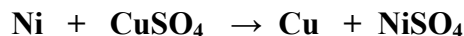
For an actual cell that delivers current as a result of an overall spontaneous cell reaction, the cell e.m.f. is necessarily positive irrespective of the sign convention for individual electrode potentials. Thus,

$$E_{\text{cell}} = E_{\text{R}} - E_{\text{L}} \quad (36)$$

where E_{R} and E_{L} represent reduction potentials of right and left hand electrodes respectively.

Example 2 : Can one store 1M copper sulphate solution in a nickel vessel ?
Given $E^0(\text{Ni}^{2+}, \text{Ni})$ and $E^0(\text{Cu}^{2+}, \text{Cu})$ are - 0.25 V and + 0.34 V respectively.

Ans 2 : To answer the question one needs to know whether there will be reaction of CuSO_4 solution with Ni metal. That is the possible reaction is



The cell corresponding to above reaction is $\text{Ni}|\text{Ni}^{2+}||\text{Cu}^{2+},\text{Cu}$

The E^0 of the above cell is $E^0 = E^0_R - E^0_L = 0.34 - (-0.25) = 0.59$ which means that the above given reaction is spontaneous and hence the given copper sulphate solution can not be stored in the nickel vessel

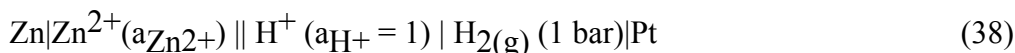
The Standard Hydrogen Electrode and assignment of values to electrode potentials

However real the existence of electrode potentials is, their direct measurement has not been possible; but the difference of potential between the two electrodes of a cell, i.e., the e.m.f. of the cell can be measured. To assign an electrode potential value to an electrode it is necessary to set up a cell coupling it with a standard hydrogen electrode (SHE) represented as



The pressure at which H_2 gas is bubbled and the activity determine the potential of this electrode, the standard potential of which is arbitrarily assigned as zero volt. The assigned value (zero volt) is independent of temperature as well as the solvent system.

When an electrode such as Zn^{2+}/Zn is combined with SHE to set up the cell



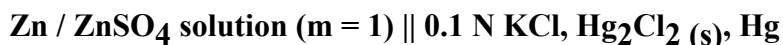
The e.m.f. for the cell is given by,

$$E_{\text{cell}} = E_R - E_L \quad (36)$$

where E_R and E_L are the reduction potentials of the right hand and the left hand electrodes. The standard potential of SHE is equal to zero by arbitrary choice. Thus, the measured potential of the above cell is the electrode potential of the $\text{Zn}|\text{Zn}^{2+}$ electrode.

Example 3. Write the cell produced by a combination of $\text{Zn} | \text{ZnSO}_4$ solution ($m = 1$) and a decinormal calomel electrode ($E_{\text{cl}} = +0.334 \text{ V}$) and show the electrode reaction and the overall reaction. Calculate the e.m.f. of the cell given that for ZnSO_4 at $m = 1$, $\gamma_{\pm} = 0.045$ and $E^0 (\text{Zn} | \text{ZnSO}_4) = -0.76 \text{ V}$ (standard reduction potential). Also find the free energy change of the overall cell reaction to show that the cell as written can spontaneously deliver current.

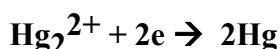
The cell may be written as



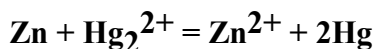
The reaction (oxidation) at the left hand electrode



and the reaction (reduction) at the right hand electrode



The overall reaction is



The e.m.f. (E_{cell}) is given by

$$E_{\text{cell}} = E_{\text{R}} - E_{\text{L}}$$

$$= 0.334 \text{ V} - (E^{\circ} + RT/2F \ln a_{\text{Zn}^{2+}})$$

$$= 0.334 \text{ V} + 0.76 \text{ V} - \{(2.303 \times 8.31 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}) / (2 \text{ mol} \times$$

$$96500 \text{ C mol}^{-1})\} \log m_{\pm} \gamma_{\pm}$$

$$= 1.094 \text{ V} - (0.0591 / 2) \log 0.045 \text{ V} \quad (m_{\pm} = 1)$$

$$= 1.094 \text{ V} + 0.0397 \text{ V}$$

$$= 1.1337 \text{ V}$$

$$\Delta G = -nF E$$

$$= -2 \times 96500 \text{ C mol}^{-1} \times 1.1337 \text{ V}$$

$$= -218804 \text{ J mol}^{-1}$$

The large negative value of ΔG shows that the overall reaction in the cell as written is spontaneous, i.e., the cell delivers current when the electrodes are externally connected. The positive e.m.f. of the cell also points to the same truth.

The sign convention of standard electrode potential

The standard reduction potential of an electrode is considered as the standard electrode potential. Since SHE is arbitrarily assigned the potential, $E^{\circ}_{\text{H}} = 0$, the electrodes in which the reduced state is a stronger reducing agent than hydrogen such as the electrode Zn^{2+}/Zn , the **standard potential (reduction potential)** is negative by convention. The electrodes in which the reduced state is a weaker reducing agent than hydrogen such as Cu^{2+}/Cu , the **standard potential (reduction potential)** is positive by convention.

Electrochemical series

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

ferrous/stannous in acid medium a strong reducing agent usually used in analytical practice.

Table 1: The standard electrode potential (reduction potential) of various redox systems

Redox system (In the order of decreasing reducing property of the reduced state)	Standard electrode potential	Half reaction
$\text{Li}^+ \text{Li}$	-3.05	$\text{Li}^+ + \text{e} = \text{Li}$
$\text{K}^+ \text{K}$	-2.93	$\text{K}^+ + \text{e} = \text{K}$
$\text{Ca}^{2+} \text{Ca}$	-2.87	$\text{Ca}^{2+} + 2\text{e} = \text{Ca}$
$\text{Na}^+ \text{Na}$	-2.71	$\text{Na}^+ + \text{e} = \text{Na}$
$\text{Mg}^{2+} \text{Mg}$	-2.36	$\text{Mg}^{2+} + 2\text{e} = \text{Mg}$
$\text{Al}^{3+} \text{Al}$	-1.66	$\text{Al}^{3+} + 3\text{e} = \text{Al}$
$\text{Zn}^{2+} \text{Zn}$	-0.76	$\text{Zn}^{2+} + 2\text{e} = \text{Zn}$
$\text{Pb}^{2+} \text{Pb}$	-0.13	$\text{Pb}^{2+} + 2\text{e} = \text{Pb}$
$\text{H}^+ \frac{1}{2}\text{H}_2$	0.00 (by arbitrary choice)	$\text{H}^+ + \text{e} = \frac{1}{2}\text{H}_2$
$\text{Sn}^{4+} \text{Sn}^{2+}$	+0.15	$\text{Sn}^{4+} + 2\text{e} = \text{Sn}^{2+}$
$\text{Cu}^{2+} \text{Cu}^+$	+0.16	$\text{Cu}^{2+} + \text{e} = \text{Cu}^+$
$\text{Bi}^{3+} \text{Bi}$	+0.20	$\text{Bi}^{3+} + 3\text{e} = \text{Bi}$
$\text{Cu}^{2+} \text{Cu}$	+0.34	$\text{Cu}^{2+} + 2\text{e} = \text{Cu}$
$\text{Fe}(\text{CN})_6^{3+} \text{Fe}(\text{CN})_6^{4+}$	+0.36	$[\text{Fe}(\text{CN})_6]^{3-} + \text{e} =$
$[\text{Fe}(\text{CN})_6]^{4-}$		
$\text{ClO}_4^- \text{ClO}_3^-$	+ 0.36	$\text{ClO}_4^- + \text{H}_2\text{O} + 2\text{e} = \text{ClO}_3^- + 2\text{OH}^-$
$\text{I}_2 \text{I}^-$	+ 0.53	$\text{I}_3^- + 2\text{e} = 3\text{I}^-$
$\text{MnO}_4^- \text{MnO}_4^{2-}$	+ 0.56	$\text{MnO}_4^- + \text{e} = \text{MnO}_4^{2-}$
$\text{Fe}^{3+} \text{Fe}^{2+}$	+ 0.77	$\text{Fe}^{3+} + \text{e} = \text{Fe}^{2+}$
$\text{NO}_3^- \text{NO}_2$	+ 0.80	$\text{NO}_3^- + 2\text{H}^+ + \text{e} = \text{NO}_2 + \text{H}_2\text{O}$

$\text{ClO}^- \text{Cl}^-$	+ 0.89	$\text{ClO}^- + \text{H}_2\text{O} + 2\text{e} = \text{Cl}^- + 2\text{OH}^-$
$\text{NO}_3^- \text{NO}$	+ 0.96	$\text{NO}_3^- + 4\text{H}^+ + 3\text{e} = \text{NO} + 2\text{H}_2\text{O}$
$\text{Br}_2 \text{Br}^-$	+ 1.09	$\text{Br}_2 + 2\text{e} = 2\text{Br}^-$
$\text{O}_2 \text{O}^{2-}$	+ 1.23	$\text{O}_2 + 4\text{H}^+ + 4\text{e} = 2\text{H}_2\text{O}$
$\text{O}_3 \text{O}_2$	+ 1.24	$\text{O}_3 + \text{H}_2\text{O} + 2\text{e} = \text{O}_2 + 2\text{OH}^-$
$\text{Cr}_2\text{O}_7^{2-} \text{Cr}^{3+}$	+ 1.33	$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e} = 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$
$\text{MnO}_4^- \text{Mn}^{2+}$	+ 1.51	$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e} = \text{Mn}^{2+} + \text{H}_2\text{O}$
$\text{Ce}^{4+} \text{Ce}^{3+}$	+ 1.61	$\text{Ce}^{4+} + \text{e} = \text{Ce}^{3+}$
$\text{H}_2\text{O}_2 \text{H}_2\text{O}$	+ 1.78	$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e} = 2\text{H}_2\text{O}$
$\text{Co}^{3+} \text{Co}^{2+}$	+ 1.81	$\text{Co}^{3+} + \text{e} = \text{Co}^{2+}$
$\text{S}_2\text{O}_8^{2-} \text{SO}_4^{2-}$	+ 2.05	$\text{S}_2\text{O}_8^{2-} + 2\text{e} = 2\text{SO}_4^{2-}$
$\text{O}_3 \text{O}_2$	+ 2.07	$\text{O}_3 + 2\text{H}^+ + 2\text{e} = \text{O}_2 + \text{H}_2\text{O}$
$\text{F}_2 \text{F}^-$	+ 2.87	$\text{F}_2 + 2\text{e} = 2\text{F}^-$

Measurement of the e.m.f. of a Voltaic Cell

Measurement of the e.m.f. of a reversible cell requires that during measurement only a very negligibly small current is drawn from the cell so that the electrode systems and the cell as a whole do not depart to any significant extent from their respective equilibrium states under the conditions of measurement. Obviously the reversible cell e.m.f (ideally, the open circuit e.m.f., i.e., when no current is drawn from the cell) cannot be measured by a voltmeter that will draw an appreciable current disturbing the equilibrium of the processes occurring in the cell. In order to avoid this, the measurement of the thermodynamic value (equilibrium value) of the e.m.f. of a galvanic cell is made using a potentiometer.

PQ is nothing but a long wire (Fig. 4) of considerably high resistance. The resistance per unit length of the wire is accurately known at the experimental temperature and does not vary to any significant extent due to slight changes in temperature. B represents a battery of cells (storage cells, usually) of a fixed e.m.f. joined across PQ. X is the cell, the e.m.f. of which is to be determined. S is a standard cell, the e.m.f. of which is not only accurately reproducible but remains constant over considerable period of time and has a low temperature coefficient. S' is a two way switch by which either the cell X or the cell S can be brought into the circuit. The e.m.f. of B is opposed by either X or S depending

on whether X or S is brought into the circuit, through the galvanometer G to a sliding contact C_X or C_S on PQ. The contact points, C_X or C_S , is adjusted to a null, i.e., no current flows through the galvanometer. This is very nearly as good as an open circuit. At the null point, the fall of potential (E_X) between P and C_X (when X is in the circuit) due to B is accurately compensated by the e.m.f. of the cell, X, under study. Likewise when S is brought into the circuit, the fall of potential (E_S) between P and C_S

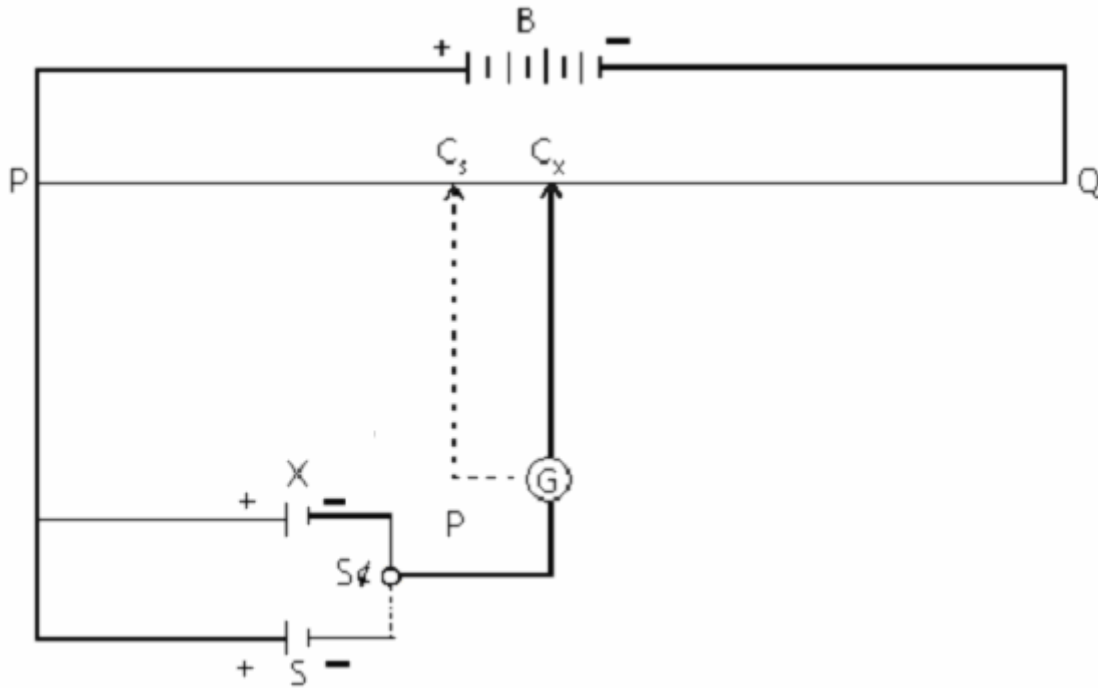


Fig. 4 The Potentiometer circuit

due to B is accurately compensated by the e.m.f. of the standard cell, S. So one obtains

$$E_X / E_S = (\text{Resistance of the part of PQ between P and } C_X / \text{Resistance of the part of PQ between P and } C_S) = (\text{The length } PC_X / \text{The length } PC_S) \quad (39)$$

Since the e.m.f., E_S , of the standard cell and the resistance per unit length of the potentiometer wire (PQ) are accurately known, E_X can be calculated. The method as described above is known as Poggendorf's compensation method.

The modern compact and direct reading potentiometers operate on the same principle. The wire, PQ is replaced by a number of resistance coils provided with a movable contact along with a slide wire for accurate adjustment. When calibrated with a standard cell, the e.m.f. of a cell under study can be directly read up to 0.01mV.

The standard cell widely used for e.m.f. measurement is the normal Weston Cadmium Cell represented below.



The e.m.f. of the cell is 1.014636 V at 298 K and has a temperature coefficient of $-5 \times 10^{-5} \text{ V K}^{-1}$.

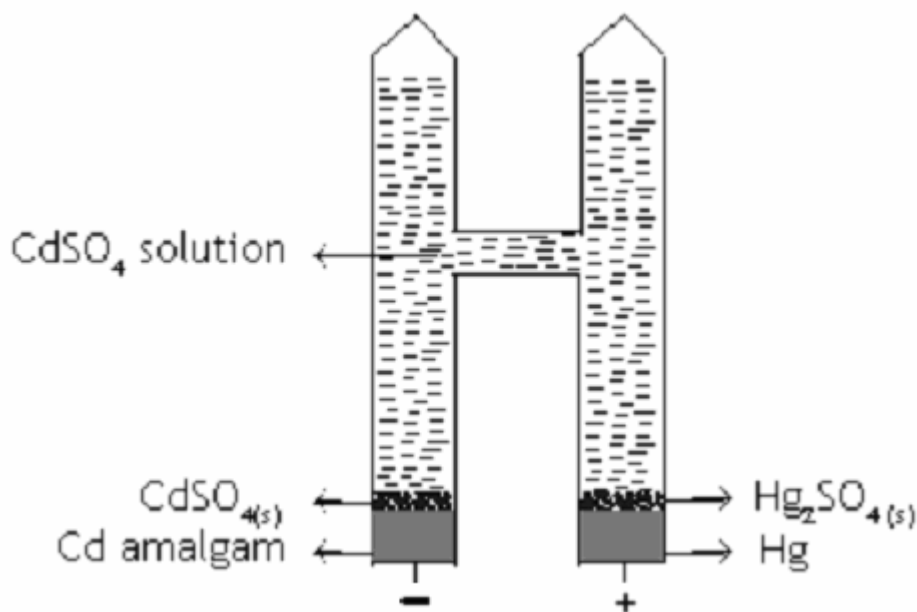


Fig. 5. Weston Cadmium Cell

Reference Electrodes

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

The most widely used reference electrode is the calomel (Hg_2Cl_2) electrode which is made up of mercury in contact with a solution of potassium chloride saturated with mercurous chloride.



The electrode reaction is



and the electrode potential

$$E = E^{\circ} - (RT/2F) \ln a_{Cl^-} \quad (42)$$

The electrode is reversible with respect to Cl^- ions. For common use three different concentrations of potassium chloride (0.1 N, 0.01N and saturated) are used to obtain decinormal, normal and saturated calomel electrodes. The potentials of these have been measured against SHE and are known accurately at different temperatures. At 25°C, these are respectively +0.334V (decinormal KCl), +0.280 (normal KCl) and +0.242 (saturated KCl).

Liquid Junction Potential and the Salt Bridge

As discussed earlier, the different solutions have to be in contact in some cells as in the Daniell cell. The $ZnSO_4$ in this case, is placed in a porous pot which prevents direct mixing of it with the $CuSO_4$ solution, but allows the passage of ions. But due to the unequal mobilities of the ions an additional potential arises at the junction of the two electrolytes, called the liquid junction potential. It is possible to calculate it for some simple cases and allowance may be made to obtain the e.m.f. of the cell with reasonable accuracy. In most cases, however, the calculation of the liquid junction potential poses a difficulty and because of the approximations, the results may not be of significance.

Use of a salt bridge keeps the liquid junction potential reasonably low, if not altogether eliminated..

A strong solution of either KCl or NH_4NO_3 in agar solution is prepared. It is poured hot into a double bent U-tube kept in an inverted condition and allowed to cool when the agar sets into a gel. Two end of this tube are put into the two solutions avoiding mixing but bridging them to maintain electrical contact. Because of the comparable ionic mobilities of K^+ and Cl^- (NH_4^+ and NO_3^-) liquid junction potential is kept at a low value. When KCl cannot be used as with a Ag-electrode, NH_4NO_3 is used in the salt bridge.

Thermodynamic quantities of cell reactions

The Gibbs free energy change at a given temperature for the overall cell reaction for an electrochemical cell can be obtained from the reversible e.m.f. (E) of the cell determined by Poggendorf's compensation method.

$$\Delta G = -nF E \quad (43)$$

where n is the number of faradays of electricity delivered by the cell. E is positive by convention and being an intensive quantity, does not depend on how the stoichiometric equation for the spontaneous overall cell reaction is written. But ΔG being an extensive quantity does depend on how the overall cell reaction is written. The same is true about the corresponding enthalpy and the entropy changes (ΔH and ΔS). These thermodynamic quantities are usually expressed in $kJ\ mol^{-1}$ (ΔS in $J\ K^{-1}\ mol^{-1}$) when these become intensive quantities.

From thermo dynamics we have,

$$\Delta = - \left[\partial \Delta G / \partial T \right]_p \quad (44)$$

$$\text{or } \Delta S = nF[\partial E/\partial T]_p \quad (45)$$

$$\text{since } -\Delta G = nF E$$

The temperature coefficient of the cell e.m.f., $(\partial E/\partial T)_p$ can be obtained by determining the e.m.f at various temperatures.

Again from thermodynamics we have,

$$\Delta G = \Delta H - T\Delta S \quad (46)$$

$$\text{or } -n F E = \Delta H - T\Delta S \quad (47)$$

$$\text{or } \Delta H = -n F E + T\Delta S \quad (48)$$

$$\text{or } \Delta H = -n F E + T n F [\partial E/\partial T]_p \quad (49)$$

Thus the enthalpy change associated with the overall cell reaction for a reversible cell can be determined from the reversible e.m.f. (E) and the temperature coefficient of the reversible e.m.f. of the cell, $(\partial E/\partial T)_p$. The equilibrium constant is related to standard Gibbs free energy, ΔG^0 (or $-n F E^0$). Hence we obtain

$$\text{Since } \Delta G^0 = -RT \ln K \quad (50)$$

$$\text{or } -n F E^0 = -RT \ln K \quad (51)$$

$$\ln K = -[n F E^0/RT] \quad (52)$$

The above equation enables one to calculate the equilibrium constant of an overall cell reaction at a given temperature from the experimentally determined value of the standard e.m.f. of the cell at the same temperature.

We have seen earlier that the Weston Cadmium Cell has an e.m.f. (E) of 1.01463 V at 298 K and a temperature coefficient of $-5.00 \times 10^{-5} \text{ V K}^{-1}$. These two data help us to calculate the thermodynamic quantities of the overall cell reaction.

$$\Delta G = -n F E$$

$$= -2 \times 96500 \text{ C mol}^{-1} \times 1.01463 \text{ V}$$

$$= -195824 \text{ J mol}^{-1}$$

$$\Delta S = nF[\partial E/\partial T]_p$$

$$= 2 (96500 \text{ C mol}^{-1}) \times (-5.00 \times 10^{-5}) \text{ V K}^{-1}$$

$$= -9.65 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta H = \Delta G + T \Delta S$$

$$= -195824 \text{ J mol}^{-1} + 298 \text{ K} (-9.65 \text{ J mol}^{-1} \text{ K}^{-1})$$

$$= -198700 \text{ J mol}^{-1}$$

Acids and Bases

According to Brönsted and Lowry definition, an acid is a proton donor and a base is a proton acceptor. Water is an amphiprotic solvent, i.e., it can act both as an acid and as a base. In the presence of an acid that has greater proton donating ability than water, water acts as a base and in the presence of a base that has greater proton accepting ability than water, water acts as an acid. Thus in the presence of a strong acid (fully ionised in aqueous medium) such as HCl, water acts as a base and the process is represented as



acid base conjugate acid conjugate base

In the presence of a weak acid such as CH_3COOH (feebly ionised in aqueous medium) the process is represented by the equilibrium established at a given temperature,



Acid base conjugate acid conjugate base

In the presence of a strong base (fully ionised in aqueous medium) such as NaOH



base acid conjugate base of the acid

In the presence of a weak base (feebly ionised in aqueous medium) such as NH_3 , the process is represented by the equilibrium established at a given temperature,



base acid conjugate acid

Thus we see that the anion of an acid is a base. The stronger the acid, the weaker is the anion (conjugate base of the acid) as a base. This makes the chloride ion so weak as a base that the process,



base acid

does not occur to any significant extent since HCl is a strong acid. On the other hand, the weaker the acid, the stronger is the anion (conjugate base of the acid) as a base. Thus the acetate ion is a strong base because of the reaction,



base acid

which represents an equilibrium set up in the aqueous medium at a given temperature, largely shifted towards the right.

Likewise the cation of a base is an acid. The stronger the base, the weaker is the cation (conjugate acid of the base) as an acid. Thus Na^+ is so weak as an acid that the process



acid base

does not occur to any significant extent since NaOH is a strong base. On the other hand, the weaker the base, the stronger is the cation as an acid. Thus NH_4^+ is a strong acid because of the reaction,



acid base

which is an equilibrium set up in aqueous medium, largely shifted towards the right.

It must be borne in mind that because of the strong field around H^+ , it always exists as H_3O^+ (hydrated hydrogen ion called the hydronium ion) in aqueous medium. We often write H^+ bearing in mind that it is actually H_3O^+ .

Strengths of acids and bases

The relative strengths of weak electrolytes such as weak acids and weak bases in aqueous medium are expressed in terms of the values of their respective equilibrium constant of the very nominal dissociation reaction, called the ionisation constant or the dissociation constant of the weak acids or the weak bases.

The dissociation of a weak acid (HA) may be represented as



where the equilibrium established at a given temperature is well shifted towards the left. The dissociation constant (K'_a) is given by the law of mass action,

$$K'_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}][\text{H}_2\text{O}]} \quad (62)$$

The terms in the square bracket represent the respective molar concentrations of the species involved in the equilibrium. $[\text{H}_2\text{O}]$ is the molar concentration of water in water, i.e., number of moles of water per 1000 ml (1000 g of water for dilute solutions). Thus,

$$[\text{H}_2\text{O}] = 1000 \text{ g} / 18 \text{ g mol}^{-1} = 55.5 \text{ mol}, \text{ a constant} \quad (63)$$

$$\text{So we have, } K_a = \{ [\text{H}^+][\text{A}^-] \} / [\text{HA}] \text{ taking } \{ K' [\text{H}_2\text{O}] \} = K_a \quad (64)$$

writing H^+ for H_3O^+ for the sake of simplicity.

The higher the value of $[\text{H}^+]$ for a given concentration at equilibrium at a given temperature, i.e., the higher the value of the dissociation constant, K_a , the greater is the

strength of the acid. Thus, the dissociation constant of a weak electrolyte is a measure of the strength of the electrolyte.

Let us consider the equilibrium at a given temperature



where α is the degree of dissociation, i.e., the number of moles of the acid dissociated per mole of the acid and c is the molar concentration of the acid. Now,

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{\alpha^2 c}{1-\alpha} \quad (66)$$

For a weak electrolyte at a given molar concentration (c), α is given by the molar conductivity ratio

$$\alpha = \Lambda_m / \Lambda_m^\circ \quad (67)$$

where Λ_m is the molar conductivity at the concentration $c \text{ mol L}^{-1}$ and Λ_m° is the same at infinite dilution.

Knowing α at a given temperature and concentration, K_a may be determined.

Recalling the equation

$$K_a = \frac{\alpha^2 c}{1-\alpha} \quad (68)$$

$$\text{we have, } K_a = \alpha^2 c \quad (\alpha \ll 1 \text{ for weak electrolytes}) \quad (69)$$

$$\text{or } K_a = \alpha^2 / v \quad (70)$$

where $v = \frac{1}{c}$, i.e., the volume of the solution per mole of the solute expressed in litre per mole.

$$\text{Now, } \alpha = \sqrt{K_a v} \quad (71)$$

The degree of dissociation of a weak electrolyte varies directly as the square root of dilution, i.e., a weak electrolyte is more and more ionised with decreasing concentration (increasing dilution) which is known as Ostwald dilution law.

The expression for the dissociation constant (K_b) of a weak base (B) can be obtained by considering the equilibrium established at a given temperature in aqueous medium



base conjugate acid

Since the base is weak, the above equilibrium is well shifted to the left. According to the law of mass action

$$K_b = \{[BH^+][OH^-]\} / [B] \quad (73)$$

since $[H_2O]$ is a constant, it is incorporated into K_b ,

Acids with more than one dissociable hydrogen ion are called polyprotic acids. These are dissociated in stages and the dissociation constants for the first, second, etc stages of dissociation are called the respectively first, second, etc dissociation constants. For a weak polyprotic acid the acidity is largely due to the first stage of dissociation as is evident from the values of the dissociation constant for the different stages.

The pH scale

For the ready reference to the state of acidity and alkalinity of dilute aqueous solutions, the pH scale has been devised to avoid cumbersome use of negative exponents. It is defined as $pH = -\log [H^+]$. The equilibrium $H_2O \rightleftharpoons H^+ + OH^-$ exists in water because of its feeble ionization.. The corresponding equilibrium constant is given by

$$K_w' = [H^+][OH^-]/[H_2O]$$

The denominator, $[H_2O]$ is the molar concentration of water in water, i.e., moles of water per 1000 mL (1000g for dilute aqueous solution) of water, is a constant at a constant temperature. Thus

$$K_w' [H_2O] = [H^+][OH^-].$$

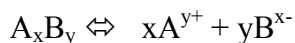
The new constant on the left hand side is called the ionic product of water and is denoted by K_w . So $K_w = [H^+][OH^-]$.

$$\text{Or } -\log K_w = -\log [H^+] - \log [OH^-].$$

$$pK_w = pH + pOH$$

For neutral aqueous solutions, $[H^+] = [OH^-]$, i.e., $pH = pOH$. Experimental value of K_w is 1.0×10^{-14} at 25°C which makes $pK_w = 14$. Thus $pH + pOH = 14$. Hence for neutral aqueous solution at 25°C , $2pH = 14$ and $pH = pOH = 7$.

For not too dilute aqueous solutions of strong electrolytes A_xB_y , the $[A^+]$ is replaced by the mean ionic activity ($a_{\pm}$) of the electrolyte producing the A^+ ion to account for the departure from ideal behaviour due to interionic interactions. The mean ionic activity ($a_{\pm}$) of the strong electrolyte producing cations and anions as



in solution is given by $a_{\pm} = a^{1/(x+y)}$

where $a = m_+^x m_-^y \gamma_+^x \gamma_-^y$ and m_+ , m_- are the molal concentration of cations and anions respectively. γ_+ and γ_- are their corresponding activity coefficients. The mean ionic activity coefficients $\gamma_{\pm} = (\gamma_+^x \gamma_-^y)^{1/(x+y)}$. If m is the molal concentration of the strong electrolyte A_xB_y then $m_+ = m \gamma_+$ and $m_- = m \gamma_-$.

Example 4 : Calculate the percent ionization and the pH of a 0.1M aqueous acetic acid solution ($K_a = 1.8 \times 10^{-5}$).

Ans 4 : Since acetic acid is a very weak electrolyte, using eqn 68 and 69, we can write

$$\alpha = (K_a/c)^{1/2} = (1.8 \times 10^{-5}/10^{-1})^{1/2} = 1.34 \times 10^{-2}.$$

Therefore the percent ionization is only 1.34.

This means that in a 0.1M aqueous acetic acid solution only 134 molecules out of 10,000 molecules will be ionized.

Further using eqn. 65 we know $[H^+] = c \cdot \alpha = 1.34 \times 10^{-2} \times 10^{-1} = 1.34 \times 10^{-3}$.

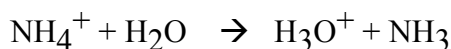
Therefore $pH = -\log [H^+] = -\log (1.34 \times 10^{-3}) = 2.88$

Hydrolysis of salts

Hydrolysis means decomposition by water, i.e. a reaction of ester with water results in a carboxylic acid and an alcohol. Salts are fully ionised in aqueous solution. So the hydrolysis of a salt is either the hydrolysis of the cation or the anion or of both and because of that there is a change in the pH of the solution.

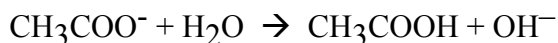
The aqueous solutions of salts of strong acids and strong bases maintain the neutral pH of aqueous solution i.e. around pH 7. This means that on the overall basis there is no hydrolysis of salts of this type.

When we consider the solution of a salt of strong acid and weak base such as NH_4Cl , the very weak Cl^- is not hydrolysed but the NH_4^+ ion which is a much stronger acid than water, being the conjugate acid of the weak base NH_3 , is hydrolysed. The hydrolytic equilibrium is



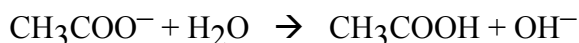
This makes an aqueous solution of NH_4Cl , in fact, aqueous solution of salts of strong acids, and weak bases, acidic.

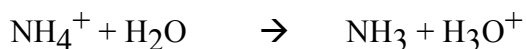
In the case of solutions of a salt of weak acid and a strong base such as CH_3COONa , the weak Na^+ is not hydrolysed but the CH_3COO^- being the conjugate base of the weak acid CH_3COOH acts as a stronger base than water and establishes the hydrolytic equilibrium



This makes the aqueous solutions of all salts of weak acids and strong bases alkaline.

When we come to the case of aqueous solution of salt of a weak acid and a weak base such as CH_3COONH_4 , both the cation and the anion are hydrolysed and the hydrolytic equilibria





are established.

One of the above reactions tends to make the solution alkaline and the other acidic. Whether the pH of the aqueous solution of any salt of a weak acid and a weak base, will be acidic or alkaline, is determined by the relative strength (indicated by the respective K_a and K_b values). Since NH_3 as a base in aqueous solution has nearly the same strength as acetic acid as an acid, i.e., K_b (ammonia) $\approx K_a$ (acetic acid). The aqueous solution of $\text{CH}_3\text{COONH}_4$ has a pH close to 7, at 25°C .

Expressions for the of hydrolysis constant (K_h) and the pH of aqueous solutions of salts of different types

Salt of a strong acid (HA) and a weak base (B), BA.

The salt BA will be fully ionised in aqueous solution



A^- , the conjugate base of the strong acid, HA, will not hydrolyse.

B^+ , the conjugate acid of the weak base, B, will hydrolyse.



$$K'_h = \{[\text{BOH}][\text{H}^+]\} / \{[\text{B}^+][\text{H}_2\text{O}]\} \quad (76)$$

The terms in the square bracket indicate the equilibrium molar concentrations of the respective species.

The hydrolysis constant, K_h can be written as

$$K'_h [\text{H}_2\text{O}] = K_h = \{[\text{BOH}][\text{H}^+]\} / [\text{B}^+] \quad (77)$$

$[\text{H}_2\text{O}]$ can be taken as a constant in dilute aqueous solution.

Because of self ionisation of water and feeble dissociation of the weak base, BOH, we have two other expressions true for the aqueous solution of the salt, BA

$$K_w = [\text{H}^+][\text{OH}^-] ; K_b = [\text{B}][\text{OH}]/[\text{BOH}] \quad (78)$$

$$\text{Thus we see that } K_h = K_w / K_b \quad (79)$$

If x is the degree of hydrolysis at equilibrium and c is the molar concentration of the salt, we have



$$\text{Thus, } K_h = \frac{x^2 c}{(1-x)} \quad (81)$$

$$\text{Therefore, } cx = (c \cdot K_h)^{1/2} \text{ when } x \text{ is negligibly small} \quad (82)$$

$$\text{Now } cx = [H^+] = (cK_w/K_b)^{1/2} \text{ (using eqn. 80 and 79)} \quad (83)$$

$$\text{or, } \log [H^+] = \frac{1}{2} \log c + \frac{1}{2} \log K_w - \frac{1}{2} \log K_b \quad (84)$$

$$\text{or, } pH = \frac{1}{2} pK_w - \frac{1}{2} pK_b - \frac{1}{2} \log c \quad (85)$$

Following an identical procedure one may arrive at the following useful relationships :

For hydrolysis of a salt of a strong base and a weak acid (Solution is alkaline)

$$K_w / K_a = K_h = \frac{x^2 c}{(1-x)} \quad (86)$$

$$pH = \frac{1}{2} pK_w + \frac{1}{2} pK_a + \frac{1}{2} \log c \quad (87)$$

For hydrolysis of a salt of a weak acid and a weak base

$$K_w / K_a K_b = K_h = \frac{x^2}{(1-x)^2} \quad (88)$$

$$pH = \frac{1}{2} pK_w + \frac{1}{2} pK_a - \frac{1}{2} pK_b \quad (89)$$

In this case, the pH of the solution will be acidic or alkaline depending on the relative strengths of the weak acid and the base. If they are of nearly equal strength e.g., ammonium acetate ($K_b(\text{ammonia}) \approx K_a(\text{acetic acid})$), the solution will be nearly neutral.

Example 5 : Calculate the hydrolysis constant, the degree of hydrolysis, the pH and the pOH (separately) of a 0.05M aqueous sodium benzoate solution at 25°C ($K_a = 6.4 \times 10^{-5}$)

Ans . 5 : From eqn. 87 we know $K_h = K_w / K_a = 1.0 \times 10^{-14} / 6.4 \times 10^{-5} = 1.56 \times 10^{-10}$.

Further the hydrolytic equilibrium can be written as



Therefore $K_h = \frac{cx \cdot cx}{c(1-x)} = \frac{cx^2}{(1-x)}$ where K_h , c and x are hydrolysis constant, concentration and degree of hydrolysis respectively. As x is very small $K_h = cx^2$. Therefore the degree of hydrolysis $x = (K_h/c)^{1/2} = (1.56 \times 10^{-10} / 0.05)^{1/2} = 5.586 \times 10^{-5}$. This means that about 56 benzoate molecules will

hydrolyse in a million molecule.

$$\text{Further } \text{pOH} = -\log [\text{OH}^-] = -\log (cx) = -\log (0.05 \times 5.586 \times 10^{-5}) = 5.55$$

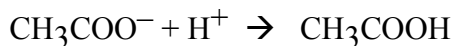
$$\text{Hence } \text{pH} = 14 - \text{pOH} = 14 - 5.55 = 8.45$$

$$\begin{aligned} \text{Alternatively using eqn. 88 one can write } \text{pH} &= \frac{1}{2} \text{pK}_w + \frac{1}{2} \text{pK}_a + \frac{1}{2} \log c \\ &= 7 + 2.1 - 0.65 = 8.45 . \end{aligned}$$

Buffer Solution

A buffer solution is a solution of known pH that is resistant to changes in pH on addition of small amount of acid or alkali or on dilution. Thus it is a solution of a constant given pH that has a reserve capacity of neutralising a little acid or alkali and thereby maintaining a steady pH.

A buffer solution is made by combination of a weak acid or base and its salt in solution. Thus a solution containing acetic acid and sodium acetate acts as a buffer solution. On addition of a little acid, the CH_3COO^- (a strong base being the conjugate base of the weak acid, CH_3COOH) react with the added hydrogen ion as



where the equilibrium is almost completely shifted to the right because of large excess of CH_3COO^- . When a little alkali is added, CH_3COOH (very little ionised) reacts with the added OH^- ions as

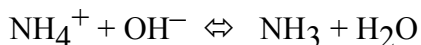


where the equilibrium is almost completely shifted to the right.

A solution containing NH_3 and NH_4Cl also acts as a buffer solution. Added small amount of acid is consumed by the reaction



The equilibrium is very largely shifted to the right. On the other hand when small amount of alkali is added it is consumed by the reaction



The equilibrium is almost completely shifted to the right because of the large excess of NH_4^+ .

To arrive at an expression for the pH of a buffer solution containing weak acid (HA) and its salt (A^-), we recall the ionisation equilibrium of the weak acid,



$$\text{K}_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \quad (90)$$

$$\text{or } [H^+] = \{K_a [HA]\} / [A^-] = \{K_a [\text{acid}]\} / [\text{salt}] \quad (91)$$

In this equilibrium the concentration of A^- ion will be because of the dissociation of salt as well as the acid. However the acid being a weak acid and the salt being completely dissociated, the A^- ion concentration due to ionisation of the acid can be neglected as the acid dissociation is suppressed by the A^- ions from the salt (common ion effect). Now taking logarithm of both sides one can write

$$-\log_{10} [H^+] = -\log_{10} K_a + \log \{[\text{salt}] / [\text{acid}]\} \quad (92)$$

$$\text{i.e. } \text{pH} = \text{p}K_a + \log \{[\text{salt}] / [\text{acid}]\} \quad (93)$$

which is known as Henderson equation.

Following an identical procedure, it can be shown that for a buffer solution of a weak base and its salt,

$$\text{pOH} = \text{p}K_b + \log \{[\text{salt}] / [\text{base}]\} \quad (94)$$

(Recalling $K_w = [H^+] [OH^-]$ we have, $-\log K_w = -\log [H^+] - \log [OH^-]$)

$$\text{or } \text{p}K_w = \text{pH} + \text{pOH} \quad (95)$$

since at 25°C $K_w = 10^{-14}$, $\text{pH} + \text{pOH} = 14$ at 25°C)

$$\text{or } \text{pH} = 14 - \text{pOH} = 14 - (\text{p}K_b + \log [\text{salt}] / [\text{base}]) \quad (96)$$

Hence for a neutral solution at 25°C , $\text{pH} = \text{pOH}$, i.e., both are equal to 7. However K_w changes with change in temperature and hence neutral water pH is not 7 at every temperature. The above Henderson eqn (eqns. 93,94) indicates that the buffer capacity i.e. the resistance to change in pH is maximum when $[\text{salt}] = [\text{acid}]$ or $[\text{salt}] = [\text{base}]$. That is buffer capacity is maximum when $\text{pH} = \text{p}K_a$ or when $\text{pH} = \text{p}K_b$. The buffer capacity is reduced when the $[\text{salt}] / [\text{acid}]$ or $[\text{salt}] / [\text{base}]$ departs from unity. The buffer capacity (β) is equal to $(db/d\text{pH})$ where db is the amount of base added and $d\text{pH}$ is the corresponding change in pH. Usually reasonable buffer capacity is obtained when the above ratio lies between 10 to 0.1. That is the pH of the buffer solution lies in the range of $\text{p}K_a \pm 1$. For pOH it will be in the range of $\text{p}K_b \pm 1$.

Here below are presented some of the useful buffer solutions with their pH range.

Buffer solutions	pH range
1. Acetic acid – Na-acetate	3.7-5.6
2. Boric acid and borax	6.8-9.2
3. Phthalic acid and Pot.acid phthalate	2.2-3.8
4. Na_2HPO_4 and NaH_2PO_4	5.9-8.0

Buffer solutions are very important for both industrial and biological systems. In industrial systems they are useful in electroplating, in manufacture of photographic materials, in synthesis of dyes, in various estimation processes, as culture media for bacterial growth and so on. Animal blood is also a buffer solution. Human blood has pH of about 7.4. We can eat various types of food because of the buffer property of the blood.

Example 6 : Calculate the pH of a mixture of 0.01M acetic acid and 0.05M sodium acetate solutions ($pK_a = 4.8$).

Ans.: It is a mixture of weak acid and its salt and hence it will behave as a buffer solution and Henderson-Hasselbalch eqn can be used. Therefore

$$pH = pK_a + \log [\text{salt}]/[\text{acid}] = 4.8 + \log (0.05/0.01) = 5.5$$

Determination of Solubility Product from Electrode Potentials

Solubility product of a sparingly soluble salt from standard electrode potential can be determined accurately even if it is too low for direct analytical determination. For this purpose, a cell is to be designed for which the overall cell reaction correspond to the solubility equilibrium of the salt. For silver chloride, the cell should be a combination of an Ag/AgCl electrode and an Ag/Ag⁺, i.e., silver electrode. As usual, the cell should be so written that oxidation takes place at the left hand electrode and reduction at the right hand one. The standard electrode potentials (reduction potentials) are as follows

Electrodes	Electrode reactions	Standard electrode potentials at 298 K
AgCl(s) Ag	$\text{AgCl} + e \longrightarrow \text{Ag} + \text{Cl}^-$	$E^\circ = +0.22$
Ag Ag ⁺	$\text{Ag}^+ + e \longrightarrow \text{Ag}$	$E^\circ = +0.80$
Subtracting we get $\text{AgCl(s)} \rightarrow \text{Ag}^+ + \text{Cl}^-$		(97)

which is the solubility equilibrium of AgCl at a given temperature and the overall reaction of the cell Ag/Ag⁺, Cl⁻ / AgCl(s)/ Ag .

(For the E° of cell, the cell should be set up as



i.e., an Ag|Ag⁺ and an AgCl|Ag electrode are dipped into a saturated solution of silver chloride in water at 298 K.) . The equilibrium constant K of the above reaction is

$K = \{a_{\text{Ag}^+} a_{\text{Cl}^-}\}/a_{\text{AgCl}}$. Since activity of solid is taken as unity,

$K = \{a_{\text{Ag}^+} a_{\text{Cl}^-}\}$, the activity product. (98)

For dilute solution where activity coefficients are close to unity, one can write

$$\{[\text{Ag}^+][\text{Cl}^-]\} = K_{sp}, \text{ the solubility product.} \quad (99)$$

If c is the solubility of AgCl in solution then $[\text{Ag}^+] = [\text{Cl}^-] = c$.

$$\text{Therefore } K_{sp} = c^2. \quad (100)$$

The E^0_{cell} of the above cell is $E^0_R - E^0_L = 0.22 - 0.80 = -0.58 \text{ V}$. (101)

The negative value of E^0_{cell} points to the fact that the overall cell reaction is nonspontaneous. The reverse reaction $\text{Ag}^+ + \text{Cl}^- \rightarrow \text{AgCl(s)}$ is the precipitation reaction and is a spontaneous one. The cell as designed above will deliver no current. However one can use thermodynamic equations to calculate the solubility product. By using the following relations

$$-\Delta G^0 = nFE^0 = RT \ln K_{\text{sp}} \quad (102)$$

(K_{sp} is the equilibrium constant of the cell reaction)

Therefore $\log K_{\text{sp}} = nFE^0 / 2.303 RT$ (103)

$$\log K_{\text{sp}} = \{1 \times 96500 \text{ C mol}^{-1} \times (-0.58 \text{ V})\} / \{2.303 \times 8.314 \text{ JK}^{-1}\text{mol}^{-1} \times 298\text{K}\}$$

$$= -9.81 \quad (104)$$

Therefore $K_{\text{sp}} = 1.55 \times 10^{-10}$ (105)

Hence c , the solubility of AgCl is $(1.55 \times 10^{-10})^{1/2} = 1.25 \times 10^{-5} \text{ moles L}^{-1}$. (106)

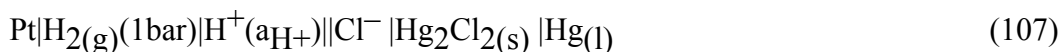
However it should be noted that it is possible to obtain a spontaneous reaction and corresponding positive E^0 by changing the polarity of the electrodes in the above given cell. One can hence get the equilibrium constant of the $\text{Ag}^+ + \text{Cl}^- \rightarrow \text{AgCl(s)}$ and the inverse of that will be K_{sp} .

Measurement of pH by e.m.f. methods

The pH or the hydrogen ion concentration of a solution can be determined by measuring the e.m.f. of a cell in which one of the electrodes is reversible with respect to hydrogen ions. We shall discuss the principles of three such methods using electrodes reversible with respect to hydrogen ions.

The hydrogen electrode

A cell may be constructed as follows,



which is a combination of a hydrogen electrode dipped in the solution whose pH is to be determined and a calomel electrode connected by a KCl salt bridge to keep the liquid junction potential at a low value. The e.m.f. of the cell is given by

$$E_{\text{cell}} = E_R - E_L = E_{\text{calomel}} - E_H \quad (108)$$

where the electrode potentials are reduction potentials of calomel and hydrogen electrodes.

Since the potential of normal calomel electrode at 25°C is $+0.2802\text{V}$,

$$E_{\text{cell}} = 0.2802 - E_H = 0.2802 - (E^0_{\text{H}} + RT/F \ln a_{\text{H}^+}) \quad (109)$$

$$= 0.2802 - RT/F \ln a_{\text{H}^+} \quad (110)$$

Since $E^0_{\text{H}} = 0$ and $a_{\text{H}_2} = 1$ since the gas is at 1 bar

$$E_{\text{cell}} = 0.2802 - 0.0591 \log a_{\text{H}^+} \quad (111)$$

$$= 0.2802 + 0.0591 \text{ pH} \quad (112)$$

as $\text{pH} = -\log a_{\text{H}^+}$. For ordinary purposes activity is replaced by concentration and

$$\text{pH} = -\log C_{\text{H}^+}$$

$$\text{pH} = (E_{\text{cell}} - 0.2802) / 0.0591 \quad (113)$$

Thus from the experimentally determined value of E_{cell} , the pH of the solution can be obtained.

Example7: If the e.m.f. of the cell $\text{Pt}/\text{H}_2(\text{g}, 1\text{atm})/\text{H}^+(\text{xmolar})//\text{KCl}(0.1\text{M})/\text{Hg}_2\text{Cl}_2/\text{Hg}$ is 0.45V at 25°C, calculate the pH of the acid solution. (Electrode potential of the calomel electrode is 0.281V at 25°C).

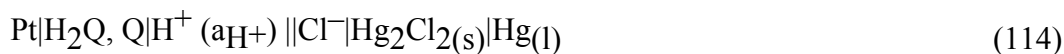
Ans. 7 : $E_{\text{cell}} = E_{\text{calomel}} - E_{\text{hydrogen}}$

$$E_{\text{hydrogen}} = E_{\text{calomel}} - E_{\text{cell}} = -0.0591 \text{ pH (from Nernst's eqn)}$$

$$\text{pH} = (E_{\text{cell}} - E_{\text{calomel}}) / 0.0591 = (0.45 - 0.281) / 0.0591 = 2.86$$

The quinhydrone electrode

Quinhydrone, as it is called, is an equimolar mixture of quinone(Q) and hydroquinone(H_2Q). A small amount of quinhydrone (a sparingly soluble solid material) is added to the solution, the pH of which is to be determined and a Pt electrode is dipped into it. Then it is combined with a decinormal calomel electrode by means of a salt bridge to set up the cell,



The e.m.f. of the cell is given by

$$E_{\text{cell}} = E_{\text{R}} - E_{\text{L}} = E_{\text{calomel}} - E_{\text{Q}} \quad (115)$$

$$\text{or } E_{\text{cell}} = 0.3358 - (E^\circ_{\text{Q}} + RT/2F \ln a_{\text{H}_2\text{Q}} / a_{\text{Q}} \cdot a_{\text{H}^+}^2) \quad (116)$$

Since the electrode reaction of the quinhydrone electrode is



Again $a_{\text{H}_2\text{Q}} / a_{\text{Q}} = 1$, we can write

$$E_{\text{cell}} = 0.3358 - E^\circ_{\text{Q}} + (RT / F) \ln a_{\text{H}^+} \quad (118)$$

$$= 0.3358 - 0.6994 - 0.0591 \text{ pH} \quad (E^\circ_{\text{Q}} = 0.6994\text{V})$$

$$\text{pH} = (-E_{\text{cell}} + 0.3358 - 0.6994) / 0.0591 \quad (119)$$

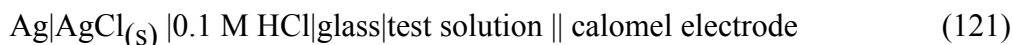
Thus by determining the cell e.m.f., it is possible to calculate the pH of the test solution. It should be noted that the quinhydrone electrode can not be used for systems where the pH of the solution is more than 8.

The Glass Electrode

A glass electrode is made up of a very thin (~0.05 mm) bulb of a special quality of glass of low melting point and comparatively low electrical resistance. The glass has a three dimensional network of Si-O and some cations, e.g., Li^+ , Na^+ , K^+ , Ca^{2+} , etc. with an overall negative charge. The movement of these cations inside the Si-O network imparts, though low, some electrical conductance to the glass bulb. The bulb contains a solution of a constant pH, say 0.1 M HCl, in which a silver-silver chloride electrode is dipped that has a definite potential. The bulb is put into the solution, the pH of which is to be determined. A potential difference is developed at the interface between the glass bulb and the test solution, which is dependent upon the hydrogen ion concentration, i.e., the pH of the test solution. It is to be noted that only H^+ ions are transported through the glass, i.e., $t_+ = 1$ and $t_- = 0$. The glass bulb which acts as a partition between the solution of constant pH inside and the test solution outside, is an example of an ion selective membrane electrode. Experiment shows that the potential of the glass electrode (E_G) varies with the activity of the hydrogen ions (a_{H^+}) in the test solution in the same way as that of the hydrogen electrode and we may write

$$E_G = E^\circ_G + RT/F \ln a_{\text{H}^+} \quad (120)$$

The glass electrode is usually combined with a calomel electrode by means of a salt bridge to set up the cell



The e.m.f. of the cell is given by

$$\begin{aligned} E &= E_R - E_L = E_{\text{calomel}} - (E_{\text{Ag-AgCl}} + E_G) \\ &= E_{\text{calomel}} - E_{\text{Ag-AgCl}} - E^\circ_G - RT/F \ln a_{\text{H}^+} \end{aligned} \quad (122)$$

$$= E_{\text{calomel}} - E_{\text{Ag-AgCl}} - E^\circ_G + 0.0591 \text{ pH} \quad (123)$$

The first three quantities on the right hand side are definite and can be had from standard tables. Thus the e.m.f. of the cell (glass-calomel combination) varies directly as the pH of the test solution. The e.m.f. of the cell cannot be determined by an ordinary potentiometer since the glass membrane has a high resistance compared to electrolytes. An electronic voltmeter is used.

Improved electronic devices have been developed so that it is possible to read directly the pH of the test solution to ± 0.01 pH unit in compact portable instruments. In this case, the unit as a whole is called a pH meter. The instrument is calibrated using buffer solutions of known pH before the pH of an unknown solution is measured.

Apart from ready and reasonably accurate determination of pH, the pH meter has special advantages, e.g., it is not affected by oxidising / reducing agents and is not easily poisoned. This makes a pH meter very useful in biochemical work.

The measurement of the standard potential (reduction potential) of an electrode

Let us consider the cell



The e.m.f. of the cell is given by

$$E = E_R - E_L$$

$$E = E_0 + RT/F \ln (a_{\text{AgCl}} / a_{\text{Ag}} \times a_{\text{Cl}^-}) - E_{\text{H}}^0 - RT/F \ln (a_{\text{H}^+} / a_{\text{H}_2}^{1/2}) \quad (125)$$

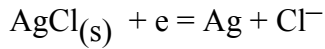
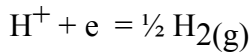
$$= E_0 - RT/F \ln a_{\text{Cl}^-} - RT/F \ln a_{\text{H}^+} \quad (126)$$

$$= E_0 - RT/F \ln a_{\text{H}^+} a_{\text{Cl}^-} \quad (127)$$

Since the overall cell reaction is



corresponding to the half reactions,



For an 1-1 electrolyte such as HCl

$$a_{\text{HCl}} = a_{\text{H}^+} a_{\text{Cl}^-} = a_{\pm}^2 \quad (129)$$

where $a_{\pm}$ is the mean activity of the ions.

$$\text{Thus, } E = E^0 - RT/F \ln a_{\pm}^2 \quad (130)$$

Single ion activities a_+ or a_- cannot be determined. We are obliged to speak in terms of the mean activity of the ions, $a_{\pm}$ and the mean molal ionic activity coefficients $\gamma_{\pm}$.

So we arrive at the expression

$$E = E^0 - RT/F \ln (\gamma_{\pm} m_{\pm})^2 = E^0 - 2RT/F \ln \gamma_{\pm} m_{\pm} \quad (131)$$

$$\text{or } E + 2RT/F \ln m_{\pm} = E^0 - 2RT/F \ln \gamma_{\pm} \quad (132)$$

From Debye - Hückel limiting law, it is known that for a 1-1 electrolyte

$$\ln \gamma_{\pm} = -A m^{1/2} \text{ where } A \text{ is a constant.}$$

After substitution we have,

$$E + 2RT/F \ln m_{\pm} = E^0 - (2RT/F) A m^{1/2} \quad (133)$$

The quantity on the right hand side is plotted against $m^{1/2}$ where m values correspond to dilute solutions so that the Debye Hückel limiting law holds good. The intercept at $m = 0$ gives E^0 , the standard electrode potential (reduction potential) of Ag-AgCl electrode.

When E° is known and E is measured accurately at low molalities, the mean ionic activity coefficients $\gamma_{\pm}$ of the electrolyte (HCl in this case) at different molalities can be estimated from the equation

$$E + 2RT/F \ln m_{\pm} = E^\circ - 2RT/F \ln \gamma_{\pm} \quad (134)$$

Example 8 : Calculate the mean ionic activity coefficient of 0.1 m HCl given that the e.m.f. of the cell $\text{PtH}_2(\text{g}) (1 \text{ bar}) | 0.1 \text{ m HCl} | \text{AgCl}(\text{s}), \text{Ag}$ is 0.3324 V at 25°C ($E^\circ = 0.2224 \text{ V}$)

Ans : We recall the expression for the e.m.f. of the cell at 25°C (Eqn. 133),

$$E = E^\circ - 0.1183 \log m_{\pm} - 0.1183 \log \gamma_{\pm}$$

so that we obtain $0.3324 = 0.2224 - 0.1183 \log 0.1 - 0.1183 \log \gamma_{\pm}$

$$\text{or } \log \gamma_{\pm} = (-0.3324 + 0.2224 + 0.1183) / 0.1183 = 0.0989$$

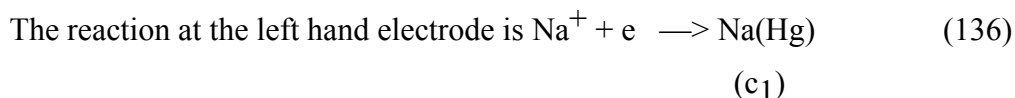
$$\text{or } \gamma_{\pm} = 0.796$$

Concentration Cells

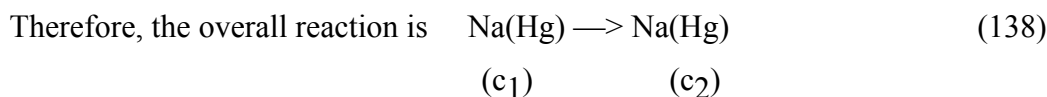
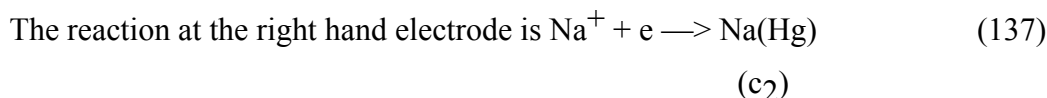
The concentration cells can be divided in two groups these are (1) Electrode concentration cell, e.g., $\text{Na(Hg)} (c_1) | \text{NaCl} | \text{Na(Hg)} (c_2)$ and (2) Electrolyte concentration cell, e.g., $\text{Ag} | \text{AgNO}_3 (c_1) | \text{AgNO}_3 (c_2) | \text{Ag}$. The electrolyte concentration cell can further be subdivided into a) cell with liquid junction and b) cell without liquid junction. Liquid junction means that the two electrolyte solutions in two half cells are in direct contact with each other.

Electrode concentration cell

An example of electrode concentration cell is



(oxidation occurs at the left hand electrode but conventionally the reaction is written as reduction.)



$$\text{and } E = - \frac{RT}{F} \ln c_2/c_1 \quad (139)$$

The amalgam concentration cells are electrode concentration cells and are very important in the study of alloys.

Similarly another example is $\text{Pt, H}_2(\text{g})(\text{P}_1)|\text{HCl Solution}|\text{H}_2(\text{g})(\text{P}_2), \text{Pt}$ (140)

The reaction at the left hand electrode is $\text{H}^+ + \text{e} \longrightarrow \frac{1}{2} \text{H}_2(\text{P}_1)$

(oxidation occurs at the left hand electrode but conventionally the reaction is written as reduction.)

The reaction at the right hand electrode is $\text{H}^+ + \text{e} \longrightarrow \frac{1}{2} \text{H}_2(\text{P}_2)$

The overall reaction is $\frac{1}{2} \text{H}_2(\text{P}_1) \longrightarrow \frac{1}{2} \text{H}_2(\text{P}_2)$ (141)

Therefore $\text{H}_2(\text{P}_1) \rightarrow \text{H}_2(\text{P}_2)$ for hydrogen molecule as the hydrogen is in the molecular state and not in the atomic state.

$$E = -(\text{RT}/\text{F}) \ln \text{P}_2/\text{P}_1 \quad (142)$$

Electrolyte concentration cell

As discussed earlier, the electrolyte concentration cell can be both with and without liquid junction. A cell without liquid junction can be written as follows

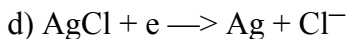
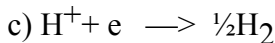
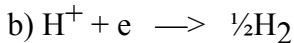
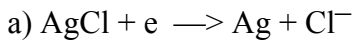
$\text{Ag, AgCl}|\text{HCl}|\text{H}_2|\text{HCl}|\text{AgCl, Ag} \dots\dots\dots (\text{A})$

In this case, it is obvious that we have actually two cells combined together. These two cells are

$\text{Ag, AgCl}|\text{HCl}(\text{c}_1)|\text{H}_2, \text{Pt} \dots\dots\dots (\text{B})$

$\text{Pt, H}_2|\text{HCl}(\text{c}_2)|\text{AgCl, Ag} \dots\dots\dots (\text{C})$

In the cell B, the oxidation occurs, in the Ag, AgCl electrode and reduction occurs in the hydrogen electrode whereas in cell C oxidation occurs in the hydrogen electrode and reduction in Ag, AgCl electrode. In cell A the following reactions occur



Total cell reaction is $\text{Cl}^-(\text{c}_1) \longrightarrow \text{Cl}^-(\text{c}_2)$ (143)

(The reactions a and c are really oxidation though conventionally they are written as reduction)

There is no direct contact and transfer of HCl from left hand side to right hand side or vice versa. There is of course change in the amount of HCl in the left hand side

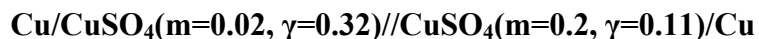


whereas HCl is formed in the right hand side by opposite reactions. The e.m.f. of the cell is given by

$$E = -(RT/F) \ln c_2/c_1 \quad (145)$$

These are also termed as chemical cell without transference.

Example 9 : Calculate the e.m.f. of the following concentration cell at 25°C



Ans 9 : On the left hand electrode $\text{Cu}^{2+}(m=0.02) + 2e \longrightarrow \text{Cu}$

On the right hand electrode $\text{Cu}^{2+}(m=0.2) + 2e \longrightarrow \text{Cu}$

Therefore the cell reaction is $\text{Cu}^{2+}(m=0.2) \longrightarrow \text{Cu}^{2+}(m=0.02)$

$$\begin{aligned} \text{Therefore } E_{\text{cell}} &= (RT/2F) \ln (0.2 \times 0.11 / 0.02 \times 0.32) \\ &= 0.0158\text{V} \end{aligned}$$

Cell with liquid junction

In this type of cell two electrolytes of the half cells are in contact with each other. Here there is no clear phase boundary between the two electrolyte solutions. Nernst's equation as discussed earlier takes in consideration all phase boundaries that are present in a cell. However, it does not consider the potential that arises because of the presence of the liquid junction. It is obvious though that the two liquids when in contact with each other will slowly but definitely mix with each other. There will be no stability of the measured e.m.f. However, there can be some way by which the diffusion can be slowed down to a very considerable extent though because of the different rates of diffusion of ions, there will be a potential difference across the liquid junction which will be in excess of the Nernst's potential (E_N). If E is the potential of the electrolyte solution of each of the half cells due to diffusion of ions, then the liquid junction potential, $E_j = E_R - E_L$ and the cell e.m.f.

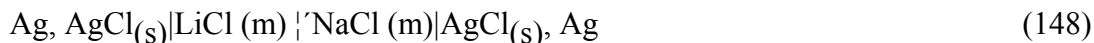
$$E_{\text{cell}} = E_j + E_N \quad (146)$$

$$\text{where } E_N = E_{\text{cell}}^{\circ} - (RT/nF) \ln [\text{Product}] / [\text{Reactant}] \quad (147).$$

For a Daniell cell, $\text{Zn}, \text{ZnSO}_4 | \text{CuSO}_4, \text{Cu}$, the cell e.m.f., $E_{\text{cell}} = E_j + E_N$

whereas for the cell $\text{Zn}, \text{ZnSO}_4 || \text{CuSO}_4, \text{Cu}$, the $E_{\text{Cell}} = E_N$. It should be clearly noted that Nernst's equation is applicable only in the case of a reversible cell and not in the case of an irreversible one. Cells with liquid junction are irreversible systems. Remember, $||$ indicates that the two solutions are separated by a salt bridge minimising E_j to a negligible value.

To measure the liquid junction potential one has to make a proper choice of the cell. For example, let us consider the following cell



In this case due to different mobilities of Li^+ and Na^+ , a liquid junction potential arises. The cell reaction of the above cell is



$$\text{Therefore, } E_{\text{cell}} = E_j - (RT/F) \ln \{ [\text{Cl}^-]_{\text{NaCl}} / [\text{Cl}^-]_{\text{LiCl}} \}. \quad (150)$$

However, the above relation is not exactly true if the concentration is reasonably high. For concentrated solutions, we should write,

$$E_{\text{cell}} = E_j - RT/F \ln \{ a_{\text{Cl}^-}(\text{NaCl}) / a_{\text{Cl}^-}(\text{LiCl}) \} \quad (151)$$

$$= E_j - RT/F \ln \{ c_{\text{Cl}^-}(\text{NaCl}) \cdot \gamma_{\text{Cl}^-}(\text{NaCl}) / c_{\text{Cl}^-}(\text{LiCl}) \cdot \gamma_{\text{Cl}^-}(\text{LiCl}) \} \quad (152)$$

where γ is the activity coefficient.

If LiCl and NaCl concentrations are exactly the same, then

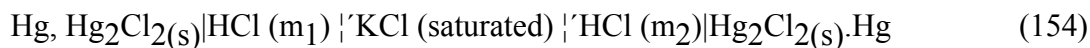
$$E_{\text{cell}} = E_j - (RT/F) \ln \{ \gamma_{\text{Cl}^-}(\text{NaCl}) / \gamma_{\text{Cl}^-}(\text{LiCl}) \} \quad (153)$$

For very dilute solutions activity coefficient terms can be taken to be unity (or for that matter may be taken to be equal in LiCl and NaCl). Then the measured e.m.f. of the cell, E_{cell} will be equal to the liquid junction potential, E_j .

Table 2: The liquid junction potential (E_j) of a few electrolyte combinations where $m = 0.01 \text{ mol / kg}$

Combination	$-E_j / \text{mV}$
LiCl – NaCl	2.6
LiCl – CsCl	7.8
HCl – NH_4Cl	– 27.1
HCl – LiCl	– 33.7

We have already mentioned earlier that a salt bridge is used to minimise the liquid junction potential (E_j). If a saturated KCl salt bridge is used then the liquid junction potential decreases to a very small value of about 1–2 mV which is negligible but it is almost not possible to get E_j equal to zero. If a cell of the following type is used



then E_j of the cell can be made almost zero as E_j of the left hand side will be almost equal but opposite in sign to E_j of the right hand side.

Concentration cell with transference

Let us consider the following cell



For left hand side $\text{H}^+(a_1) + e \longrightarrow \frac{1}{2} \text{H}_2$

and for the right hand electrode $\text{H}^+(a_2) + e \longrightarrow \frac{1}{2} \text{H}_2$.

Therefore, the total cell reaction is



Now if t_+ and t_- are the transference numbers of H^+ and Cl^- respectively, then one can say that t_+ moles of H^+ moves from right hand side to left hand side (i.e., $a_2 \rightarrow a_1$) whereas t_- moles of Cl^- moves from $a_1 \rightarrow a_2$ (due to electroneutrality requirement). This states that at the liquid junction the following transfer occurs



The free energy change for the above reaction is

$$\Delta G = RT \ln (a_{\pm 1} / a_{\pm 2})^{2t_-} = -nF E \quad (158)$$

$$\text{or, } E = 2t_-(RT/F) \ln(a_{\pm 1}/a_{\pm 2}) \text{ (for one electron change)} \quad (159)$$

In a cell without liquid junction the e.m.f. of the cell is given by

$$E_{\text{cell}} = 2(RT/F) \ln (a_{\pm 1}/a_{\pm 2}) \quad (160)$$

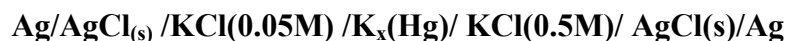
Comparison of the expressions for the e.m.f.s of cells with transference (E) and without liquid junction (E_{cell}) gives a method for the determination of the transport number.

$$t_- = E/E_{\text{cell}} \quad \text{and} \quad t_+ = 1 - E/E_{\text{cell}} \quad (161)$$

The above relations are true where the electrodes are cation reversible. However where the electrodes are anion reversible then

$$t_+ = E/E_{\text{cell}} \quad \text{and} \quad t_- = 1 - t_+. \quad (162)$$

Example 10 : The e.m.f. of the concentration cell



is 0.107 V. For the corresponding cell with transference the emf is 0.053 V.

What is the transport number of Cl^- ion ?

Ans. 10 : The electrodes of the above cell is chloride ion reversible. Therefore according to eqn 162

$$t_+ = E/E_{\text{cell}} = 0.053/0.107 = 0.495 \quad \text{and} \quad t_- = 1 - t_+ = 1 - 0.495 = 0.505.$$

That is the transport number of chloride ion is 0.505

Potentiometric Titrations

We have discussed the potentiometer earlier. The potentiometer is used, as we stated, for the determination of cell e.m.f. The voltmeter which measures the potential cannot be used because it draws current whereas a potentiometer works in a reversible system. The potentiometer is used for:

acid / base titration , complexometric titration , redox titration, precipitation titration etc.

A titration is a process of following the course of a chemical reaction in solution by taking a definite aliquot of one of the reactant solution and adding measured volumes of the second reactant solution from a burette; the equivalence point of the reaction is ascertained by change of colour of a suitable indicator or by measuring some physical property such as the e.m.f. (potentiometric titration), conductance (conductometric titration), absorption (spectrophotometric titration), etc.

A derivative potentiometric titration is a titration that involves measuring, recording and computing the first derivative of the potential of a single indicator electrode with respect to the volume or otherwise added amount of reagent.

a) **Acid-Base titration** : For this type of titration we can use a pH meter, which directly measures the pH of a solution. It draws very little current.. A glass membrane electrode is an ion selective membrane electrode. The potential of glass electrode (E_G) responds to hydrogen ion concentration. The Nernst equation for the glass electrode can be written as

$$E_G = E_G^0 + k \log a_{H^+} = E_G^0 - k.pH \quad (162)$$

where k is a constant.

$$E_{\text{cell}} = E_G - E_{\text{ref}} = E_G^0 - E_{\text{ref}} - k.pH = (E_G^0 - E_{\text{ref}}) - k.pH \quad (163)$$

As E_G^0 and E_{ref} are constant quantities, the E_{cell} is linearly related to pH. That is glass electrode can be easily used to determine the pH of a given solution. . The pH meter is calibrated by using a buffer solution whose pH is known. The pH meters are generally equipped with a combination electrode which has a pH electrode and a reference electrode.(Ag, AgCl electrode combined in one unit).

Glass of the glass electrode is made by cooling a molten mixture of SiO_2 and metal oxides. The electrodes reversible with respect to metal ions like Na^+ , K^+ , Li^+ , etc. by changing the ratio of the metal oxides to SiO_2 . An insoluble crystal (insoluble in water), e.g., LaF_3 which has significant ionic conductivity in contact with a F^- solution can be directly used as an electrode for fluoride ion activity.

A titration can be done by using a pH meter between HCl solution and Na_2CO_3 solution. In the given Na_2CO_3 solution, the combined electrode is placed and we can read the pH from the pH meter. Then HCl solution can be added in aliquots and after

thorough stirring, the pH can be read. A graph of pH vs volume of HCl added can be plotted. A graph of the following type will be obtained (Fig. 6)

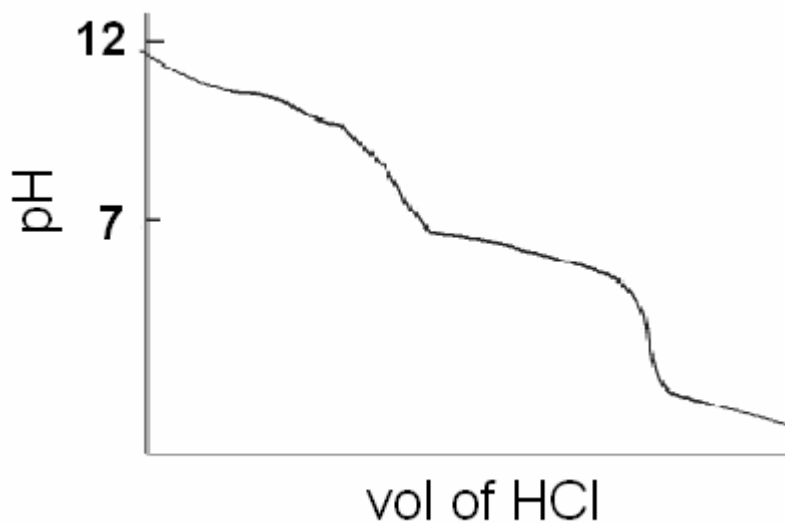


Figure 6 : Potentiometric titration curve pH vs. volume of HCl

This data can also be plotted in the following way where the first derivative can be plotted against the volume of HCl which will look as is shown in Figure 7. The two maxima indicate the first and the second (final) neutralization volume. The chemical reactions for the first and the second peaks are

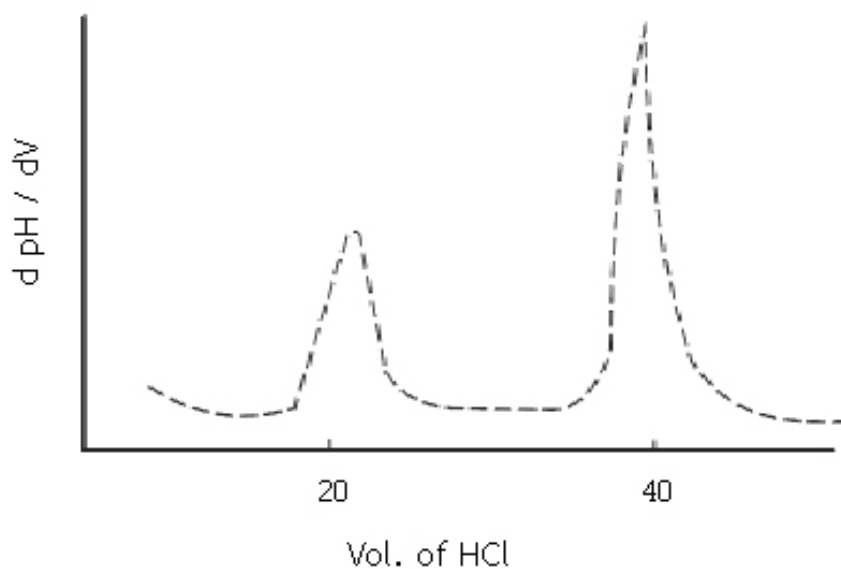
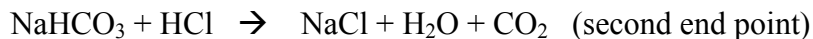


Figure 7 : The potentiometric derivative plot. The change in pH per unit volume of HCl vs Volume of HCl solution.



Due to the evolution of CO_2 at second end point of titration, there is some drift in the pH meter value

Complexometric titration : Ethylene diamine tetraacetic acid (EDTA) sodium salt can be used to determine Cu^{2+} by potentiometric titration. The indicator electrode is mercury coated Ag electrode and a reference electrode. A buffer of pH 5.8 is generally used. To copper solution one drop of Hg-EDTA solution and buffer solution is added. Then EDTA is added in aliquots. A plot of potential vs. volume will indicate the end point of the titration and hence concentration of copper in solution (Figure 8).

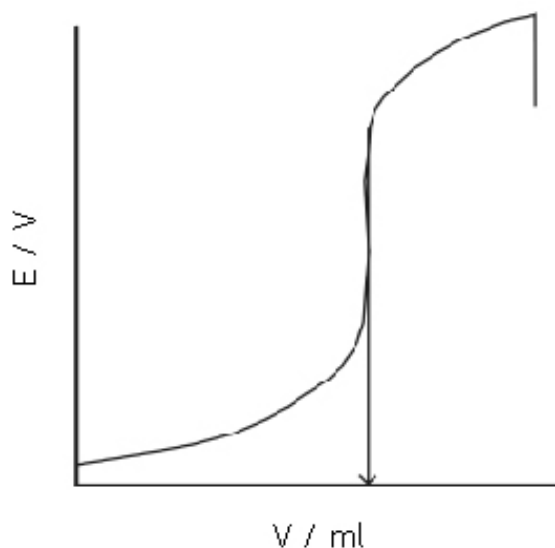


Figure 8 : Plot of experimental Emf vs volume of EDTA solution

The end-point at which the gradient of the titration curve is maximum, is more precisely obtained by the differential plot. The ratio dE/dV for the change dE produced on addition of a small volume (dV) of the titrant is plotted against V (Figure 9).

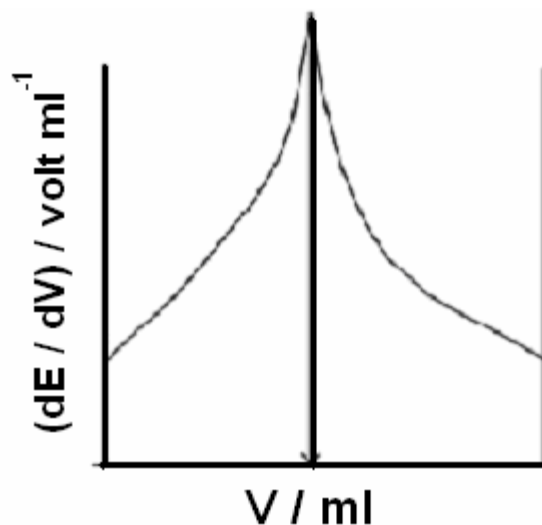
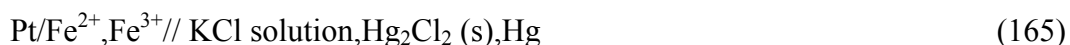


Figure 9 : Differential plot of change in emf per unit volume of added titrant vs volume of titrant for end point determination.

$$\frac{dE}{dV} = \lim_{V \rightarrow 0} \left(\frac{dE}{dV} \right) \quad (164)$$

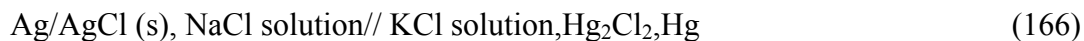
Titration with very dilute solutions is desirable.

Redox titration : A definite volume of a solution containing Fe^{2+} ions with traces of Fe^{3+} is taken in a beaker and the acidity of the solution is maintained by addition of required amount of HCl solution. A Pt wire is dipped to obtain a $\text{Fe}^{2+}/\text{Fe}^{3+}$ electrode whose potential will change with change in the concentration of the ions. This indicator electrode is then combined through a KCl salt bridge with a calomel electrode to set up the cell



A standard solution of ceric sulphate is then added in aliquots to the Fe^{2+} solution and the emf of the cell is measured after each addition. The reaction is $\text{Fe}^{2+} + \text{Ce}^{4+} \rightarrow \text{Fe}^{3+} + \text{Ce}^{3+}$ Takes place. The end point can be obtained from a suitable plot as for other titrations mentioned above.

Precipitation titration : An Ag, AgCl electrode is dipped in a definite volume of, say, NaCl solution and it is then combined with a calomel electrode of definite potential through a salt bridge. Therefore the following cell is set up

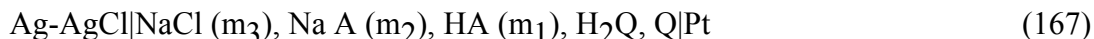


A standard AgNO_3 solution is then gradually added in small volumes and the corresponding emf of the cell is determined. The chemical reaction is



A suitable plot is made to determine the end point.

Ionization constant of acids : A cell of the following type can be used in the determination of ionisation constant of an acid



where HA is a weak acid; H_2Q and Q are hydroquinone and quinone respectively. From the e.m.f. data, the pK_a value of the weak acid can be computed.

Potentiometric titrations are useful for coloured solutions and very dilute solutions where coloured indicator titrations can not be done

Polarisation, Overpotential and Hydrogen Overvoltage : Most of the systems that we have mentioned herebefore are reversible in nature and the Nernst's eqn. can be easily used. In these cases the rate of the forward reaction and the rate of the backward reaction are almost same and the cell reactions are very very slow. However there are many situations where the rate of reaction is reasonably fast e.g. the electrolysis and the corresponding electrolytic cell or some electrochemical cell where the reaction is faster.

In case of an electrolysis process a storage battery can be used as an external source of electrical energy. When hydrochloric acid solution is electrolysed, platinum electrodes are generally used as anode and cathode. A variable resistance is added in the circuit so that the voltage (E) can be varied. Now one can change the voltage and the corresponding current (I) can be read from the ammeter. A current – voltage curve can be plotted which looks like

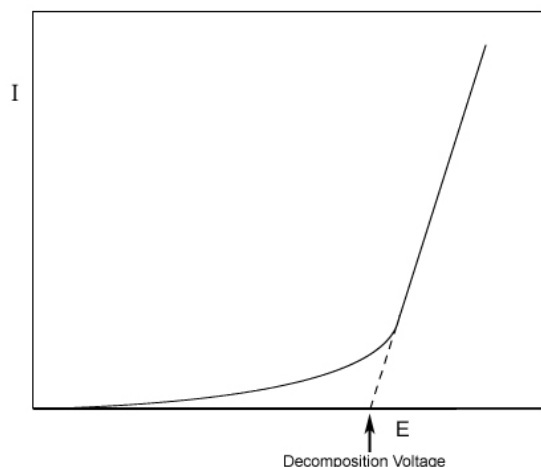
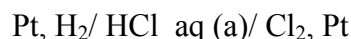


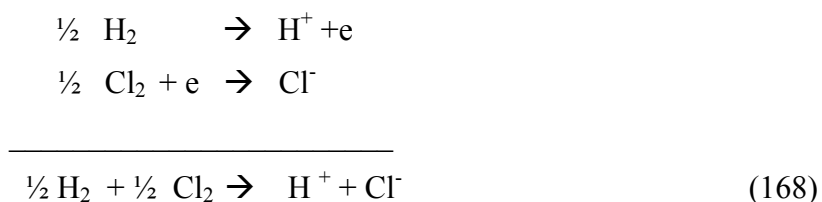
Figure 10: Determination of Decomposition Voltage. Plot of current (I) vs voltage (E)

It may be noted from the figure that the current does not increase much as the voltage increases up to a threshold voltage, E . Thereafter a small increase in voltage increases the current to a large extent. This threshold voltage is called **Decomposition Voltage** or **Decomposition Potential** (Fig. 10). The current I , that is plotted, is generally the current per unit area of the electrode i.e. current density. It is also obvious from the above figure that there is always a small amount of current in the system. This current is called the **diffusion current**.

Decomposition potential hence can be defined as the smallest voltage which should be applied so that the electrolysis occurs. In an aqueous HCl solution if two platinum electrodes are placed in contact with an external source a small amount of current passes and the hydrogen and chlorine are evolved at the cathode and anode respectively. Due to the presence of hydrogen and chlorine as well as HCl solution a chemical cell is formed. The cell can be written as



Which will have an emf working in opposition to external source. The reversible emf of this cell can easily be calculated. The emf is a function of the concentration of HCl solution. The cell reaction of the above cell is



Electrolysis of HCl solution means $\text{HCl} \rightarrow \frac{1}{2} \text{H}_2 + \frac{1}{2} \text{Cl}_2$. Therefore it is obvious that the electrolysis process is just the reverse of the reaction shown in eqn. 168. Therefore electrolysis will start when external emf is just above the cell emf. This is the decomposition potential. That is decomposition potential is either equal to or more than the reversible back emf of a cell. The cell is however formed by the minute amount of electrolysis and the discharge of H^+ and Cl^- on the respective electrodes. The electrodes are called **polarized electrodes** and the phenomenon is **polarization**. The hydrogen and chlorine so produced remain adsorbed on the surface of the platinum electrode. At the decomposition potential these gases are evolved and come out of the system in the form of bubbles.

In addition to the above there is something more happening in a cell. In a nonequilibrium process one finds that the calculated e.m.f value is always different from the experimental value. This is ascribed to two different phenomena a) **concentration polarization** and b) **overvoltage**.

Concentration Polarization : This happens because of the concentration gradient in the electrolyte medium in the cell. To explain let us take the example of electrolysis of CuSO_4 solution. Cu^{2+} will be deposited on the negative electrode. However the concentration of the Cu^{2+} will be very low just near the electrode because the ion is deposited on the electrode. However as we go away from the electrode towards bulk solution, the concentration increases and there is a concentration gradient. This in effect resembles a series of concentration cell and hence there will be a back emf. This is known as concentration polarization. However such polarization can most often be reduced to a negligible value by vigorous stirring. Moreover higher the temperature of the system lower will be the concentration polarization.

Due to concentration polarization there is an increase in the resistance to solvent flow and that reduces the permeate flux. This is inherent in all membrane filtration processes. In this type of case the water flux increases with the increase of the applied pressure. It is also true that with the increase of the particle size, the water flux also increases but with the increase in particle concentration water flux decreases.

Overvoltage : Overvoltage or overpotential is generally represented by the symbol (η). This is defined as the amount of deviation of the potential of an electrode from its equilibrium value required to cause a given current to flow through the electrode. The overpotential η is the sum of the η_{act} , η_{conc} and IR where η_{act} , η_{conc} and IR are activation overpotential, concentration overpotential and ohmic drop respectively. The activation overpotential is very important at small polarization currents and voltages. It is a part of the well known Butler – Volmer equation which describes charge transfer kinetics of electrochemical processes. However the Butler – Volmer equation is beyond the scope of the present chapter. The concentration overpotential describes mass transport limitations associated with electrochemical processes. It is very important at large polarization current or voltage. Overvoltage phenomenon is present in almost all electrolytic processes. However for metal deposition the overvoltage is tremendously low whereas for gas evolution the overvoltage is high and is of great importance. It should be noted though that the magnitude of overvoltage is a function of the evolved gas as well as the solid electrode material. The overvoltage that hydrogen shows on many metals are of some significance and in the Table 3 below some of these values are shown

Table 3 : Hydrogen overvoltage of metals

Metal	<u>current density , amp cm⁻²</u>		
	0	0.01	0.10
Platinized Platinum	0.005	0.035	0.055
Gold	0.02	0.56	0.77

Iron	0.079	0.56	0.82
Smooth Platinum	0.09		0.39
Nickel	0.21	0.652	0.88
Lead	0.64	1.08	1.21
Mercury	0.77	1.11	1.20
Silver	0.14	0.76	0.89

It should be noted that for platinized platinum at low current density the hydrogen overvoltage is very low, that is there is no back emf whereas for smooth platinum the overvoltage values are much higher. Hence platinized platinum electrodes are used in the conductivity cell and not the smooth platinum electrodes. It should be noted that metals with high adsorptive power, in general, have low overvoltage. Pressure also has an effect on overvoltage and as it increases the overvoltage decreases. However oxygen gas shows reasonably high overvoltage even with platinized platinum electrodes. Overvoltage can be measured reasonably easily by an assembly of equipments shown below

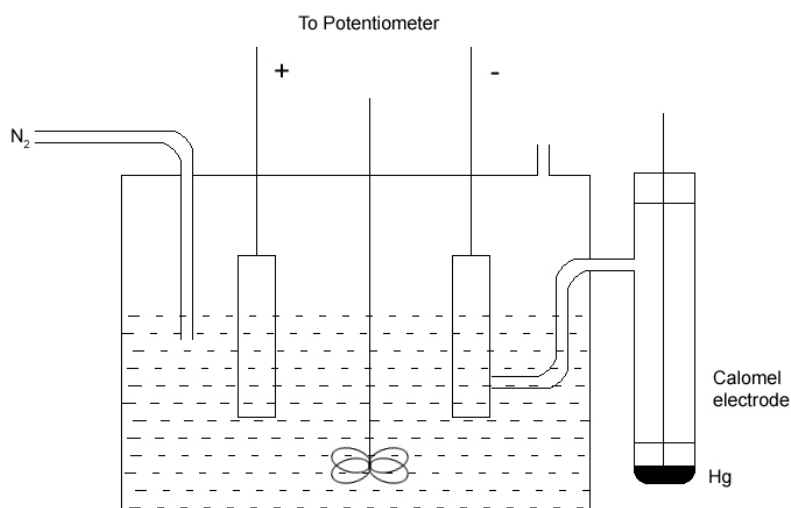


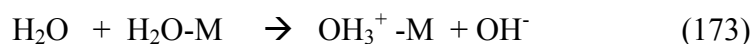
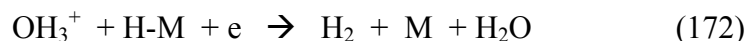
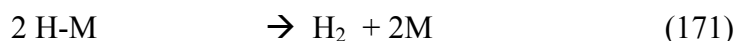
Figure 11 : Measurement of Overvoltage

The negative electrode and the reference calomel electrode are kept very near to each other to minimize the IR drop (Figure 11). The overvoltage η is related to current density (I) by the following relation

$$\eta = a + b \log I \quad (169)$$

where a and b are two constants. This equation is known as Tafel equation and can be easily derived from the Butler – Volmer equation though Tafel equation was originally suggested as an empirical one.

The mechanism of the hydrogen gas evolution in an electrolysis process is well known. However the rate determining step i.e. the slowest step in the mechanism is still now a bit controversial. However one of the followings is probably the slowest step



and on this basis the Tafel equation can be deduced.

Corrosion :

Corrosion can be defined as the deterioration of the intrinsic properties of a material, particularly of a metal. This is in general due to the reaction of the material with the environment. Corrosion is fundamentally an electrochemical process. It involves

- a) a spot in the metal(anode) which is adjacent to a cathodic site. Both anode and cathode should be in contact to the electrolyte solution.
- b) The oxidizing agent in a corrosion reaction is almost always an electrolyte. It must be able to reach the surface of a cathodic region.
- c) The electrolyte solution may be sea water, fresh water, monolayers of water, rain, humidity or snow. Electrolyte is almost always present.

This anodic and cathodic states can form by

- 1) contact with dissimilar metals e.g. connecting iron with brass, Sn, Mg etc.
- 2) dissimilar grain domains on a single metal will have the anodic and cathodic character i.e. if one of the grain is cathodic the other will be anodic
- 3) a metal is stretched i.e. bent, dented or deformed will be found to have the strained region as anode whereas the unstrained region will be cathode. The energy needed to produce the strain is responsible for its anodic behavior
- 4) impurities in metals show cathodic behavior. The pure metal state behaves as anode. Graphite is a common impurity in copper tube (used in plumbing) and behaves as cathode

- 5) any system where there can be a condition whereby one part is having less oxygen than the other will behave as an anode. The part where there is more oxygen will behave as cathode. A concentration cell can therefore show corrosion.

The pH of the solution plays an important role in the corrosion of metal. However that is not the only property of the solvent which is important. The knowledge of whether the environment is aerated or not, whether there are organic materials in the system or not is required for understanding about the status of the material. This whole thing can be represented by a potential/pH diagram which is known as the **Pourbaix diagram**. It has predominant ion boundaries and can be read as a phase diagram.

Prevention of corrosion : Prevention of corrosion is very important in the economy of any country. Billions of rupees are lost per month, all over the world, due to destruction of metals due to corrosion. Hence prevention of corrosion is important both from economic and scientific point of views. Corrosion can be prevented by

- a) by coating the metal surface by paint
- b) by coating the metal surface by some non conducting material e.g. polymer
- c) by coating the material with a passive metal. For example in the tin can, the tin corrodes, forms a monomolecular oxide and this oxide forms a coating and thereby tin is prevented from getting corroded. Tin coating on iron prevents iron corrosion. However scratching of the coat will corrode iron very rapidly
- d) a sacrificial anode is also quite often used to stop corrosion. Here a more anodic metal is attached to the metal which in that case behaves as a cathode. Hence the more anodic metal is sacrificed to protect the metal. Hence it is called sacrificial anode e.g. Zn and Fe. Zn is more anodic than Fe and will be preferentially oxidized. Zn is also (sometimes Mg) sacrificed to protect ship hull from corrosion. Similarly Zn (or Mg) is placed besides pipeline for protection. Copper tubes are sometimes corroded due to water. Copper corrosion is least in between pH 7-9. Hence sometimes NaOH is added to water to bring the pH in the 7-9 region so that copper does not corrode.
- e) Some soy based biodegradable patented products are available in the market which provides corrosion prevention.