$$(R) \rightarrow Cu^{2+} + 2e^- \rightarrow Cu$$

$$(L) \rightarrow 2AgCl + 2e^- \rightarrow 2Ag^+ + 2Cl^-$$

$$E_{cell} = E^\circ_{Cu} - E^\circ_{AgCl} - \frac{0.0592}{2}\big[[\log(a_{Cu})$$

$$-\log(a_{Cu^{2+}})] - [\log(Cl^-)^2$$

$$-\log(AgCl)]\big]$$

$$\Rightarrow E_{cell} = 0.337 - 0.220 - 0.0296\big[-\log(a_{Cu^{2+}})$$

$$-2\log(a_{Cl^{2+}})\big]$$

$$= 0.117 - 0.0296[0.632 - 2(-0.327)]$$

$$= 0.079\,volts$$

$$E_{cell} = 0.079\,volts$$

2.13 Reference Electrodes

2.13.1 Hydrogen Electrode

The hydrogen electrode is used as a reference for electrode potential measurements. Theoretically, it is the most important electrode for use in aqueous solutions. The reversible hydrogen electrode in a solution of hydrogen ions at unit activity exhibits a potential, which is assumed to be zero at all temperatures.

The electrode consists of a platinum wire immersed in a solution (Fig. 2.10) containing hydrogen ions and saturated with hydrogen gas. Platinum is immersed completely in aqueous-arsenic free hydrochloric acid, and hydrogen gas free from oxygen and carbon monoxide is bubbled to the platinum surface. Slowly, the air is displaced by hydrogen and the reversible potential is achieved. Unfortunately, this electrode has some drawbacks. First, the reversibility of hydrogen electrode cannot be maintained in oxidizing media. Second, if a current is withdrawn from the electrode, the electrode acts as an anode because of the ionization of gas molecules. Also, the electrode is fragile and delicate to handle.

The electrode potential for hydrogen E_{H_2} can be determined as follows:

$$2H^+ + 2e \rightleftarrows H_2 \tag{2.65}$$

$$E_{H^+/H_2} = E^\circ_{H^+/H_2} + \frac{RT}{nF}\log\frac{(a_{H^+})^2}{(p_{H_2})} \tag{2.66}$$

where a_{H^+} is activity of hydrogen ions, and p_{H_2} is hydrogen partial pressure.

At one atmosphere pressure (p_{H_2}), $a_{H_2} = 1$, and $E^\circ_{H^+/H_2} = 0$ by definition. Therefore,

$$E_{H^+/H_2} = 0.059\log(a_{H^+}) \tag{2.67}$$
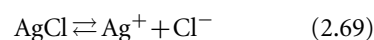
or in terms of pH,

$$E_{H^+/H_2} = -0.059\,pH \tag{2.68}$$

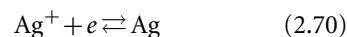### 2.13.2 Silver–Silver Chloride Electrode

This electrode is composed of a silver wire coated with silver chloride and immersed in a solution of chloride ions (Fig. 2.12).

The chloride equilibrium is given by:
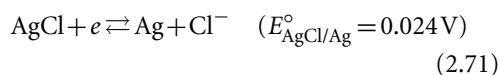
$$AgCl \rightleftarrows Ag^+ + Cl^- \tag{2.69}$$

Two other reactions involve a dynamic equilibrium between deposition and dissolution of silver together with solubility equilibrium between silver chloride and its ions.

The metallic silver reaches equilibrium with silver ions according to the following reaction:

$$Ag^+ + e \rightleftarrows Ag \tag{2.70}$$

The overall electrode reaction is, therefore, given by:

$$AgCl + e \rightleftarrows Ag + Cl^- \quad (E^\circ_{AgCl/Ag} = 0.024\,V) \tag{2.71}$$

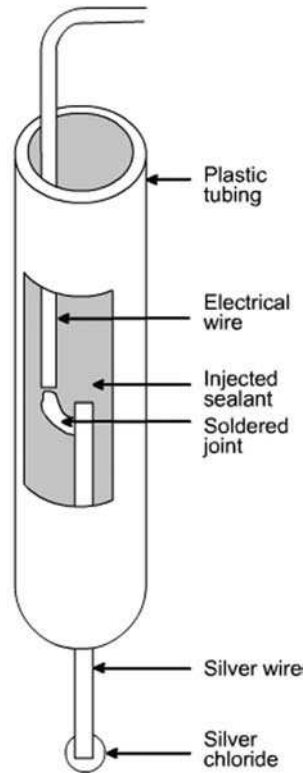**Figure 2.12** Silver–Silver chloride reference electrode

The electrode potential, $E_{Ag/AgCl}$, is given by:

$$E_{Ag/Cl} = E^{\circ}_{Ag/AgCl} + \frac{RT}{nF} \ln \frac{a_{AgCl}}{a_{Ag} \times a_{Cl^-}} \quad (2.72)$$

$$a_{Ag} = 1$$
$$a_{AgCl} = 1$$

Therefore,

$$E_{Ag/Cl} = E^{\circ}_{Ag/AgCl} - \left(\frac{2.303 RT}{F}\right) \log a_{Cl^-} \quad (2.73)$$

or

$$E_{Ag/Cl} = E^{\circ}_{Ag/AgCl} - 0.0592 \log a_{Cl^-} \quad (2.74)$$

The equation holds at 25°C. It can also be written in the following form:

$$E_{Ag/AgCl} = 0.224 - 0.0592 \log a_{Cl^-} \quad (2.75)$$

At low concentration $\log a_{Cl^-}$ can be replaced by pH as Cl^- is provided by HCl acid, $[Cl^-] = [H^+]$ and hence $-\log a_{Cl^-}$ can be replaced by $-\log[H^+]$. Therefore,

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

Hence,

$$E_{Ag/AgCl} = 0.224 - 0.0592 \, pH \quad (2.76)$$

The following are the values of $E_{Ag/AgCl}$ for different HCl concentrations:

| Concentration (M)	Electrode potential (volts)
0.1	0.28
0.01	0.34
0.001	0.40

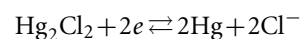### 2.13.3 THE CALOMEL ELECTRODE

It is the most commonly used reference electrode. It has a constant and reproducible potential. The electrode basically consists of a platinum wire dipped into pure mercury which rests in a paste of mercurous chloride and mercury. The paste is in contact with a solution of potassium chloride which acts as a salt bridge to the other half of the cell (Fig. 2.13).

The most commonly used concentrations of KCl are 0.1 N, 1.0 N and 3.5 N and saturated KCl. The saturated calomel is used when the liquid junction potential is to be kept low. The potential of electrode at 25°C is 0.241 V in saturated KCl solution.

Mercurous chloride is slightly soluble, and it is in equilibrium with mercurous ions according to:

$$Hg^+ + e = Hg$$
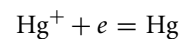
The overall equilibrium is expressed by:

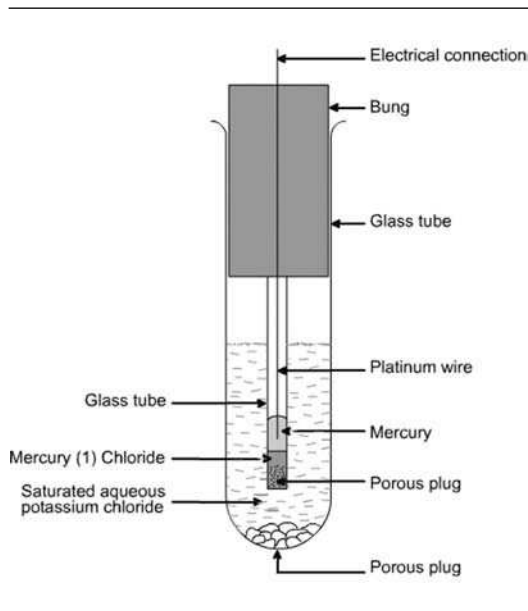$$Hg_2Cl_2 + 2e \rightleftharpoons 2Hg + 2Cl^-$$

Figure 2.13 A saturated calomel reference electrode

The mercurous chloride and mercury are at unit activity. Therefore, the electrode potential can be written as:

$$E_{Calomel} = E° + \frac{RT}{2F} \ln \left(\frac{1}{a_{Cl^-}} \right)$$

or $\qquad E_{Calomel} = E° - \dfrac{0.0592}{2} \log a_{Cl^-}$

The value of $E°$ for the half cell reaction of calomel electrode is 0.267 V. Thus, the electrode potential becomes:

$$E_{Calomel} = 0.267 - \frac{0.0592}{2} \log \left(a_{Cl^-} \right)$$

Electrode Potentials of Calomel Electrode
(Standard hydrogen electrode taken as reference)

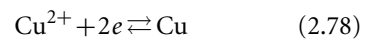| Electrode	Potential (volts)
Hg/Hg$_2$Cl$_2$/KCl (Sat.)	0.2444
Hg/Hg$_2$Cl$_2$/KCl (1.0 N)	0.289
Hg/Hg$_2$Cl$_2$/KCl (0.1 N)/Salt Bridge	0.3356

2.13.4 COPPER–COPPER SULFATE ELECTRODE

This is a reference electrode which is easy, robust and stable. It is used mainly in cathodic protection measurements, such as the measurement of pipe-to-soil potential. It has a lower accuracy than other electrodes used for laboratory work. It consists of copper metal placed in a solution containing copper sulfate and copper sulfate crystals placed in a non-conducting holder with a porous plug (Fig. 2.14). The copper sulfate crystals maintain the solution at a fixed ion concentration. Necessary contact with the earth is made through the porous plug. It is easily recharged when it becomes contaminated.

The equation for the copper–copper sulfate electrode potential is given by:

$$E°_{Cu-CuSO_4} = 0.316 + 0.0009(25°C) \, volts \quad (2.77)$$

The reaction of the Cu–CuSO$_4$ half cell is

$$Cu^{2+} + 2e \rightleftarrows Cu \quad (2.78)$$

and the electrode potential:

$$E_{Cu^{2+}/Cu} = E_{Cu^{2+}/Cu} + \frac{0.0592}{2} \log a_{(Cu^{2+})} \quad (2.79)$$

where

$a_{(Cu^{2+})}$ = activity of copper which is unity,
$E°_{Cu}$ = 0.34 V at 25°C.

A saturated solution of 1.47 M CuSO$_4$ at 25°C is used.

$a_{Cu^{2+}}$ = [Molarity (M) × Activity coefficient γ]
$a_{Cu^{2+}}$ = 1.47 × 0.037 (γ is found from the table of activity coefficients – Table 2.3)

So, $a_{Cu^{2+}} = 0.051$

Substituting in the above equation we obtain

$$E_{Cu^{2+}/Cu} = 0.34 + \frac{0.0592}{2} \log(0.051) \quad (2.80)$$

$$E_{Cu^{2+}/Cu} = 0.30 \, volts \quad (2.81)$$

$E_{Cu^{2+}/Cu} = 0.316 + 0.009$ (T°C) volts, as seen earlier in this section (equation (2.77)).

Table 2.3 Activity coefficients of strong electrolytes (M = molality)

M	0.001	0.002	0.005	0.01	0.02	0.05	0.1	0.2	0.5	1.0	2.0	3.0	4.0
HCl	0.966	0.952	0.928	0.904	0.875	0.830	0.796	0.767	0.758	0.809	1.01	1.32	1.76
HNO_3	0.965	0.951	0.927	0.902	0.871	0.823	0.785	0.748	0.715	0.720	1.17	0.876	0.982
H_2SO_4	0.830	0.757	0.639	0.544	0.453	0.340	0.265	0.209	0.154	0.130	0.124	0.141	0.171
NaOH	–	–	–	–	–	0.82	–	0.73	0.69	0.68	0.70	0.77	0.89
KOH	–	–	0.92	0.90	0.86	0.82	0.80	–	0.73	0.76	0.89	1.08	1.35
$AgNO_3$	–	–	0.92	0.90	0.86	0.79	0.72	0.64	0.51	0.40	0.28	–	–
$Al(NO_3)_3$	–	–	–	–	–	–	0.20	0.16	0.14	0.19	0.45	1.0	1.2
$BaCl_2$	0.88	–	0.77	0.72	–	0.56	0.49	0.44	0.39	0.39	0.44	–	–
$CaCl_2$	0.89	0.85	0.785	0.725	0.66	0.57	0.515	0.48	0.52	0.71	–	–	–
$Ca(NO_3)_3$	0.88	0.84	0.77	0.71	0.64	0.54	0.48	0.42	0.38	0.35	0.35	0.37	0.42
$CdCl_2$	0.76	0.68	0.57	0.47	0.38	0.28	0.21	0.15	0.09	0.06	–	–	–
$CdSO_4$	0.73	0.64	0.50	0.40	0.31	0.21	0.17	0.11	0.067	0.045	0.035	0.036	–
CsCl	–	–	0.92	0.90	0.86	0.79	0.75	0.69	0.60	0.54	0.49	0.48	0.47
$CuCl_2$	0.89	0.85	0.78	0.72	0.66	0.58	0.52	0.47	0.42	0.43	0.51	0.59	–
$CuSO_4$	0.74	–	0.53	0.41	0.31	0.21	0.16	0.11	0.068	0.47	–	–	–
$FeCl_2$	0.89	0.86	0.80	0.75	0.70	0.62	0.58	0.55	0.59	0.67	–	–	–
$In_2(SO_4)_3$	–	–	–	0.142	0.092	0.054	0.035	0.022	–	–	–	–	–
KF	–	0.96	0.95	0.93	0.92	0.88	0.85	0.81	0.74	0.71	0.70	–	–
KCl	0.965	0.952	0.927	0.901	–	0.815	0.769	0.719	0.651	0.606	0.576	0.571	0.579
KBr	0.965	0.952	0.927	0.903	0.872	0.822	0.777	0.728	0.665	0.625	0.602	0.603	0.622
KI	0.965	0.951	0.927	0.905	0.88	0.84	0.80	0.76	0.71	0.68	0.69	0.72	0.75
$K_4Fe(CN)_6$	–	–	–	–	–	0.19	0.14	0.11	0.067	–	–	–	–
K_2SO_4	0.89	–	0.78	0.71	0.64	0.52	0.43	0.36	–	–	–	–	–
LiCl	0.963	0.948	0.921	0.89	0.86	0.82	0.78	0.75	0.73	0.76	0.91	1.18	1.46
LiBr	0.966	0.954	0.932	0.909	0.882	0.842	0.810	0.784	0.783	0.848	1.06	1.35	–
LiI	–	–	–	–	–	–	0.81	0.80	0.81	0.89	1.19	1.70	–

|													
LiNO$_3$	0.966	0.953	0.930	0.904	0.878	0.834	0.798	0.765	0.743	0.76	0.84	0.9	–
MgCl$_2$	–	–	–	–	–	–	0.56	0.53	0.52	0.62	1.05	2.1	–
MgSO$_4$	–	–	–	0.40	0.32	0.22	0.18	0.13	0.088	0.064	0.055	0.064	–
NiSO$_4$	–	–	–	–	–	–	0.18	0.13	0.075	0.051	0.041	–	–
NH$_4$Cl	0.961	0.944	0.911	0.88	0.84	0.79	0.74	0.69	0.62	0.57	–	–	–
NH$_4$Br	0.964	0.949	0.901	0.87	0.83	0.78	0.73	0.68	0.62	0.57	–	–	–
NH$_4$NO$_3$	0.959	0.942	0.912	0.88	0.84	0.78	0.73	0.66	0.56	0.47	–	–	–
(NH$_4$)$_2$SO$_4$	0.874	0.821	0.726	0.67	0.59	0.48	0.40	0.32	0.22	0.16	–	–	–
NaF	–	–	0.93	0.90	0.87	0.81	0.75	0.69	0.62	–	–	–	–
NaCl	0.966	0.953	0.929	0.904	0.875	0.823	0.780	0.730	0.68	0.66	0.67	0.71	0.78
NaBr	0.966	0.955	0.934	0.914	0.887	0.844	0.800	0.740	0.695	0.686	0.734	0.826	0.934
NaI	0.97	0.96	0.94	0.91	0.89	0.86	0.83	0.81	0.78	0.80	0.95	–	–
NaNO$_3$	0.966	0.953	0.93	0.90	0.87	0.82	0.77	0.70	0.62	0.55	0.48	0.44	0.41
Na$_2$SO$_4$	0.887	0.847	0.778	0.714	0.641	0.53	0.45	0.36	0.27	0.20	–	–	–
NaClO$_4$	0.97	0.95	0.93	0.90	0.87	0.82	0.77	0.72	0.64	0.58	–	–	–
PbCl$_2$	0.86	0.80	0.70	0.61	0.50	–	–	–	–	–	–	–	–
Pb(NO$_3$)$_2$	0.88	0.84	0.76	0.69	0.60	0.46	0.37	0.27	0.17	0.11	–	–	–
RbCl	–	–	0.93	0.90	–	–	0.76	0.71	0.63	0.58	0.54	0.54	0.54
RbAc	–	–	–	–	–	–	0.73	0.65	0.52	0.42	–	–	–
TlNO$_3$	–	–	–	–	–	0.77	0.70	0.60	–	–	–	–	–
TlClO$_4$	–	–	–	–	–	0.79	0.73	0.65	0.53	–	–	–	–
TlAc	–	–	–	–	–	0.80	0.74	0.68	0.59	0.51	0.44	0.40	0.38
ZnCl$_2$	0.88	0.84	0.77	0.71	0.64	0.56	0.50	0.45	0.38	0.33	–	–	–
ZnSO$_4$	0.70	0.61	0.48	0.39	–	–	0.15	0.11	0.065	0.045	0.036	0.04	–
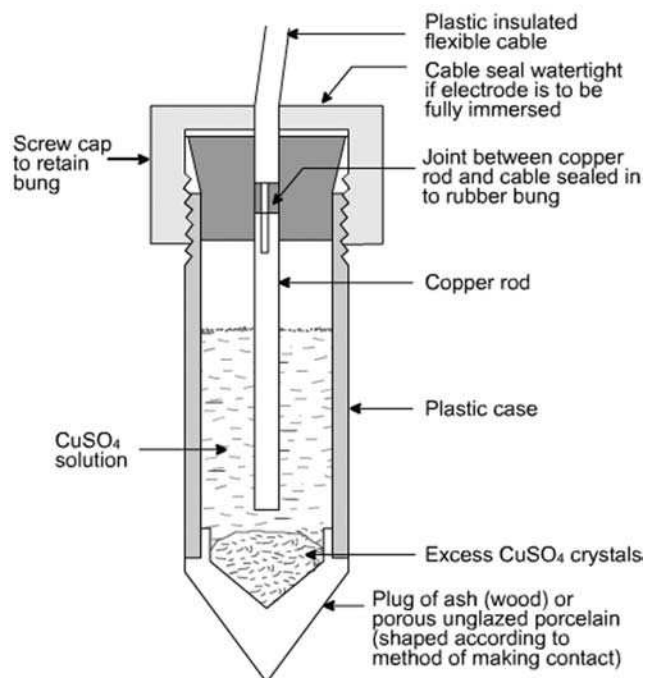
Figure 2.14   Reference copper–copper sulfate electrode

The following is the conversion table for important reference electrodes (Table 2.4):

Table 2.4   Conversion table for important reference electrodes

Potential *vs*		
Hydrogen (mV)	Copper–copper sulfate (mV)	Silver chloride (mV)
−400	−84	−170
−425	−109	−203
−450	−134	−228
−470	−159	−253
−500	−184	−278
−525	−209	−303
−550	−234	−320
−575	−259	−353
−600	−284	−370
−625	−309	−403
−650	−334	−428

Conversion of $Cu/CuSO_4$ electrode potential into Ag/AgCl and hydrogen electrode potentials is expressed by the following equations:

(a) emf (*vs* $Cu/CuSO_4$) = emf (*vs* Ag/AgCl) − 50 mV
(b) emf (*vs* $Cu/CuSO_4$) = emf (*vs* H_2/H^+) − 316 mV

The conversion table for reference electrodes is shown in Table 2.4.

Illustrative Problem 2.14
Convert −0.900 V (on SCE, Sat.) to the SHE scale.

Solution:

$$-0.900\,\text{V (on SCE, Sat.)} = -0.900 + 0.242\,\text{V (on SHE)}$$

$$= -0.658\,\text{V (on SHE)}$$

Illustrative Problem 2.15
Convert −0.916 V (on SCE. 1.0 N) to the SHE scale.

Solution:

$$-0.916\,V \text{ (on SCE, }1.0\,N) = -0.916 + 0.280\,V$$
$$\text{(on SHE)}$$
$$= -0.636\,V \text{ (on SHE)}$$

Illustrative Problem 2.16
What is the potential on SHE scale, for an electrode which is at a potential of $-0.920\,V$ relative to a Ag/AgCl reference in $0.01\,N$ KCl at $25°C$.

Solution:
Cell reaction: $AgCl + e \rightarrow Ag + Cl^-$ from equation (2.63)
Cell potential: $E_{Ag^+/Ag} = 0.22 + 0.059 \log\left[\dfrac{1}{a_{Cl^-}}\right]$
or

$$E_{Ag^+/Ag} = -0.222 - 0.059 \log\left[a_{Cl^-}\right]$$
$$a_{Cl^-} = [\gamma_\pm]\left[Cl^-\right] = (0.901)(0.01)$$

where

$\gamma_\pm$ = activity coefficient for chloride ions
$\gamma_\pm$ = 0.901
Cl^- = concentration of chloride ions
Cl^- = 0.01 N
a_{Cl^-} = 9×10^{-3}
$E_{Ag^+/Ag}$ = $-0.222 - 0.059 \log\left[9 \times 10^{-3}\right]$

$$E_{Ag^+/Ag} = 0.343\,V \text{ with respect to SHE.}$$

Therefore,

$$-0.920\,V \text{ (on Ag/AgCl)} = (-0.920 + 0.343)\,V$$
$$= -0.577\,V$$
$$\text{(with respect to SHE)}$$

Illustrative Problem 2.17
The following reduction reactions are given:

(a) $O_2 + 2H_2O + 4e = 4OH^-$
(b) $O_2 + 4H^+ + 4e = 2H_2O$

Show that the single electrode potential for each reaction at $25°C$ has the same potential dependence.

Solution:
For reaction (a):

$$E_{O_2/OH^-} = E°_{O_2/OH^-} + \frac{0.0592}{4}\left[\log P_{O_2}\right.$$
$$\left. - \log a^4_{OH^-}\right]$$
$$E_{O_2/OH^-} = 0.401 + \frac{0.0592}{4}\log P_{O_2}$$
$$- 0.0592\log a_{OH^-}$$

Replacing $\log a_{OH^-} = pH - 14$ in the above equation:

$$E_{O_2/OH^-} = 0.401 - 0.0592[pH - 14]$$
$$+ 0.0592\log P_{O_2}$$
$$E_{O_2/OH^-} = 1.23 - 0.0592\,pH + \frac{0.059}{4}\log P_{O_2}$$

For reaction (b):

$$E_{O_2/H_2O} = E°_{O_2/H_2O} + \frac{0.0592}{4}\left[\log P_{O_2} + \log a^4_{H^+}\right]$$
$$E_{O_2/H_2O} = 1.23 + 0.0592\log a_{H^+} + \frac{0.0592}{4}\log P_{O_2}$$
$$E_{O_2/H_2O} = 1.23 - 0.0592\,pH + \frac{0.0592}{4}\log P_{O_2}$$

2.13.5 EMF and Galvanic Series

Table 2.1 gives the standard electrode potentials of metals with reference to standard hydrogen electrode (SHE) which is arbitrarily defined as zero. Potentials between metals are determined by taking the absolute difference between their standard potentials. The determination of standard electrode potential is shown Fig. 2.15.

As shown above, the electrode potential of two different metals in an electrode can be compared. Each metal in contact with an electrolyte of its ion forms a half cell. The most practical method of obtaining reliable and consistent value of relative electrode potential is to compare the value of each half cell with a common reference electrode.
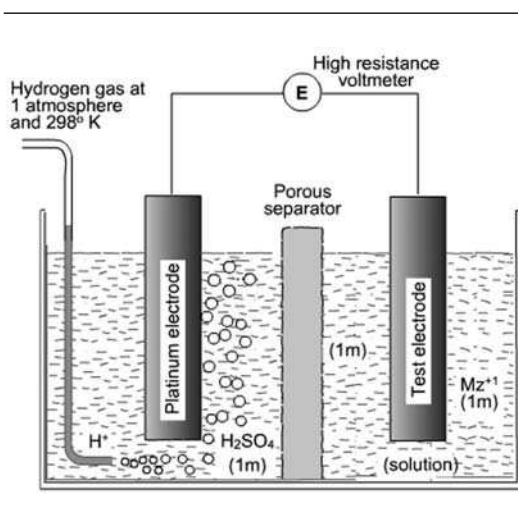
Figure 2.15   Method of determination of standard electrode potential

This common electrode is the standard hydrogen electrode which consists of a platinum wire platinized by electrolysis surrounded by a solution having a H^+ ion activity of $(a_{H^+} = 1)$ of one and enveloped in a hydrogen gas at 1 atmosphere pressure. The potential of the hydrogen electrode is given by:

$$Pt(s)|H_2(1\,atm)|H^+(a_{H^+}=1), E=0\,V$$
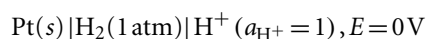
The electrode potential of all metals is compared with the standard hydrogen electrode and it is called the standard electrode potential $(E°)$. Between two metals, such as zinc and aluminum, aluminum is more active than zinc $[E_{Al}° = -1.66\,V, E_{Zn}° = -0.763\,V]$. A metal with a more negative potential has a higher tendency to corrode (dissolve) than a metal with a less negative potential, although kinetic factors may intervene.

If the potential of a metal is less than hydrogen potential, reduction rather than oxidation takes place (electrons are gained), $M^+ + e \rightarrow M$. Metals which correspond to relatively lower standard potentials $E°$ are called *active metals* and metals which corresponds to relatively higher standard potential or less negative potentials are called *noble metals.*

Cu, Ag, Au are examples of noble metals, whereas K, Li and Mg are between iron

$(E_{Fe}° = -0.443\,V)$ and zinc $(E_{Zn}° = -0.763\,V)$; zinc is more active than iron. Between copper $(E_{Cu}° = +0.334\,V)$ and silver $(+0.80\,V)$, Ag is more noble than copper. If the electrode reactions occurring on different metals at room temperature are arranged in accordance with the value of standard potentials, an electrochemical series at 25°C is obtained (Table 2.1).

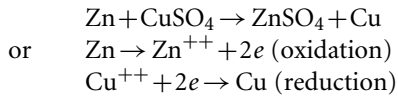## 2.13.6 SUMMARY OF CHARACTERISTICS OF EMF SERIES (TABLE 2.1)

(1) Metals with large positive potentials are called '*noble*' metals because they do not dissolve easily. Examples are copper, silver, gold, etc. The potential of a noble metal is preceded by a positive $(+)$ sign.
(2) The electrode potentials are thermodynamic quantities and have little relevance to potential of metals in solution encountered in service.
(3) The emf series lists only the electrode potentials of metals and not alloys. Alloys are not considered in the emf series.
(4) The emf series is based on pure metals. The more active metals, such as Na, Mg, Al, Zn are called '*active metals.*'
(5) Alloys are not considered in the emf series.
(6) From the reversible electrode potential in the standard emf series of metals, it is possible to predict whether a particular metal will spontaneously dissolve.
(7) It gives an indication of how active the metal is but does not necessarily predict corrosion accurately for reason to be explained later in the next chapter.

2.13.7 APPLICATION OF EMF SERIES

Following are useful applications of emf series:

(1) A less electropositive metal would displace a more electropositive metal from one of its salts in aqueous solution. For instance, if a rod of zinc is placed in a solution of copper

sulfate, zinc would dissolve in the solution and copper would be discharged:

$$Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$$

or $\quad Zn \rightarrow Zn^{++} + 2e \text{ (oxidation)}$
$\quad\quad Cu^{++} + 2e \rightarrow Cu \text{ (reduction)}$

Consequently, copper will deposit on the zinc rod.

(2) Electrode potentials indicate also the tendency of cations in aqueous solutions to be reduced at a cathode. For example, silver ions are reduced more readily than cupric ions, because silver is more electropositive.

(3) Metal ions above hydrogen are more readily reduced than the hydrogen ions with 100% efficiency.

(4) The metals in the series with high positive potentials are recognized as metals with good corrosion resistance. They show a little tendency to pass from a metallic state to an ionic state. Conversely, metals with high negative potentials show a tendency to corrode, but whether they corrode or not would depend on other factors also. For instance, iron has a potential of -0.440 V and indicates tendency to corrode, but if it develops a film of oxide it would not remain active, and hence, it would not corrode. This effect is used in formulating stainless steels, which are covered by an invisible oxide film.

(5) The metal with a more negative potential is generally the anode, and the metal with a less negative potential, the cathode. If zinc and aluminum are coupled, aluminum would become the anode $(E^\circ_{Al} = -1.67V)$ and zinc $(E^\circ_{Zn} = -0.763V)$ the cathode. It may be expected that in the presence of metals which are more negative than hydrogen in the emf series, hydrogen reduction would be the preferred process. That is, however, not always the case. Metals as negative as zinc $(E^\circ_{Zn} = -0.763\,V)$ can be plated from an acid solution without liberation of hydrogen. In the case of aluminum, however, hydrogen evolution would be the preferred process, and, therefore, aluminum is deposited by electrolysis of a non-aqueous melt in order not to give any chance for the liberation of hydrogen which may enter the metal and cause its embrittlement. The emf series is also useful for the electrolytic refining of the metals.

2.13.8 LIMITATIONS OF EMF SERIES

The following are the obvious limitations of the EMF series:

(1) The emf series lists only pure metals which have only a limited use in engineering applications. Alloys are of major interest to engineers rather than pure metals.

(2) The electrode potential has little relevance to potentials of metals in solutions, in which the potential of interest is the corrosion potential and not the electrode potential of the metal.

(3) The position of metals in the emf series is determined by the equilibrium potential of the metal with the concentration of ions at unit activity. Prediction about galvanic coupling can only be made when the two metals forming the galvanic couple have their ionic activities at unity. If the above conditions are not met, accurate prediction of galvanic conversion by emf series would not be possible. The activity of ions in equilibrium with a given metal vary with environment and, therefore, accurate predictions of galvanic corrosion are not generally possible.

(4) The emf series predicts the tendency to corrode but it cannot predict whether corrosion would actually take place. For instance, on the basis of some negative potential, iron shows tendency to corrode, however, if it develops a passive film in some environment it would not corrode.

(5) The emf series cannot always predict the effect of environment. For instance, in food cans, the polarity of tin may be critical. The potential of iron $(E^\circ_{Fe} = -0.44)$ is more negative than the potential of tin $(E^\circ_{Sn} = -0.1369)$. However, in the presence of certain type of foods in food cans, tin can become active to iron. Such a change cannot be predicted by emf series.

The effect of film formation on the tendency of the metal to passivate solution cannot be predicted by emf series. For instance, titanium and aluminum are more negative than iron. However, in certain environments they form a film which makes their potential less active than iron. The effect of film formation on the tendency of the metals to corrode is kinetic and cannot be predicted by the thermodynamic emf series.

2.13.9 IR Drop (Ohmic Drop)

The *IR* drop is the ohmic voltage that results from the electric current flow in ionic electrolytes, such as dilute acids, salt water, etc. When the reference electrode for measurement of potential is placed in the electrolyte, an electrolytic resistance exists along the line between the test and the reference electrode. Because the current flows through an electrolyte resistance an ohmic voltage drop is also automatically included in the measurement of potential.

$$E = E_{test} - E_{reference}$$

IR drop (ohmic drop) is an unwanted quality which must be eliminated to obtain an accurate potential measurement. By Ohm's Law, $E = IR$.

The IR drop in a flash light battery, for instance, contribute to the internal resistance. For any measurement, the reference electrode is placed closed to the working electrode, if this is not done the measurement would be inaccurate as it would include an IR drop. This is because the potential which is measured will always include the potential difference across the electrolyte which is between the reference and working electrode. As *E* is measured as *IR*, the potential is called *IR* drop. The *IR* contribution must be subtracted to obtain the current emf of the cell.

2.13.9.1 Methods to Remove IR Drop

a. Extrapolation Method

The emf is measured with the reference electrode placed as close to the working electrode as
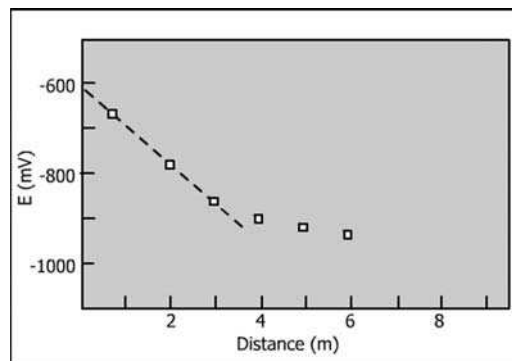

Figure 2.16   Extrapolation method

possible in the electrolyte. The electrode is moved at definite intervals of distance and potential (*E*) is measured. Emf is plotted as a function of distance and the curve is extrapolated to zero distance: Fig. 2.16. This method is applicable in electrolytes of high resistance, such as soils.

b. Current Interruption Method

When there is no current flow there cannot be any *IR* drop. However, when a current is flowing *IR* drop is included in the measurement. At a certain time, *t*, the current is interrupted so that $I = 0$, hence *IR* is also zero. The test electrode, therefore, shows a potential free from *IR* drop. Hence current interruption provides a good method for measurement of *IR* free cell potential. Unfortunately, depolarization may also occur when the current is interrupted. If the system is depolarized it is too negative at the anode area and too positive at the cathode. Various types of commercial electronic interrupters are available. The current can be interrupted by as much as 10 milliseconds of each half second. The potential must be read quickly, at the instant of interruption, by a fast response voltmeter such as an oscilloscope.

2.13.10 Galvanic Series

Having examined the limitations of the emf series, the question arises, is there a better way to predict