Simple Applications of Potential Difference Measurements p139

3.6.1 The experimental determination of i. Standard Potentials and ii. Mean Activity Coefficients

i. Standard Potential

Consider a two-electrode system containing a hydrogen and silver-silver chloride electrodes:

$$\mathrm{Pt} \mid \mathrm{H_2} \mid \mathrm{HCl} \mid \mathrm{AgCl} \mid \mathrm{Ag}$$

The potentials of the hydrogen and silver-silver-chloride electrodes are given as follows:

$$E^{\mathrm{H_2|H^+}} = E^{0,\mathrm{H_2|H^+}} + \frac{RT}{F} \ln a_{\mathrm{H_3O^+}}$$

$$E^{\mathrm{Cl^-|AgCl|Ag}} = E^{0,\mathrm{Cl^-|AgCl|Ag}} - \frac{RT}{F} \ln a_{\mathrm{Cl^-}}$$

By placing both hydrogen and silver-silver chloride electrodes in the same solution, we measure *emf*, E^{M}

$$\begin{aligned} E^{\mathrm{M}} &= E^{0,\mathrm{Cl^-|AgCl|Ag}} - E^{0,\mathrm{H_2|H^+}} \\ &= E^{0,\mathrm{Cl^-|AgCl|Ag}} - E^{0,\mathrm{H_2|H^+}} - \frac{RT}{F} \ln a_{\mathrm{Cl^-}} \cdot a_{\mathrm{H_3O^+}} \end{aligned}$$

Knowing by definition that $E^{0,\mathrm{H_2/H^+}} = 0$, then we get:

$$E^{\mathrm{M}} = E^{0,\mathrm{Cl^-|AgCl|Ag}} - \frac{RT}{F} \ln a_{\mathrm{Cl^-}} \cdot a_{\mathrm{H_3O^+}}$$

Next invoke definition of mean activity

From definition of mean activity: $a^2_{\pm}{}^{\mathbf{HCl}} = a_{H3O+}\, a_{Cl-}$ so

$$E^{M} = E^{0,Cl^{-}|AgCl|Ag} - \frac{2RT}{F}\ln a_{\pm}^{HCl} \qquad \mathbf{3.160}$$

At the same time: $a_{\pm}{}^{HCl} = \gamma_{\pm}{}^{HCl}\; m_{HCl}/m^{0}$ so

$$E^{M} + 0.05136\ln m_{HCl} = E^{0,Cl^{-}|AgCl|Ag} - 0.05136\ln\gamma_{\pm}^{HCl} \qquad \textbf{Eqn. 3.161}$$

According to equation 2.77 (the Debye-Huckel limiting law) $\mathbf{ln}\ \gamma_{\pm} = -1.172\,|z^{+}z^{-}|\,\sqrt{\mathbf{I}}$ where $\mathbf{I} = ½\,\Sigma\, z_i^{2}\,(m_i/m^{0})$ and $m^{0} = 1$ *mol/kg* of solvent, so $\mathbf{ln}\ \gamma_{\pm} \cong (m/m^{0})^{½}$

So, $\gamma_{\pm}{}^{HCl}$ drops from 3.161, since $\gamma_{\pm}{}^{HCl}$ goes to 0 as $\sqrt{m/m^{0}}$ goes to 0, when plotting

$$\overbrace{E^{M} + 0.05136\ln(m_{HCl}/m^{0})}\ \text{vs}\ \underbrace{\sqrt{m_{HCl}/m^{0}}}$$

as in Fig 3.29 yields the standard potential, $E^{0,Cl^{-}|AgCl|Ag}$, as the intercept, which is 0.2224 V versus SHE .

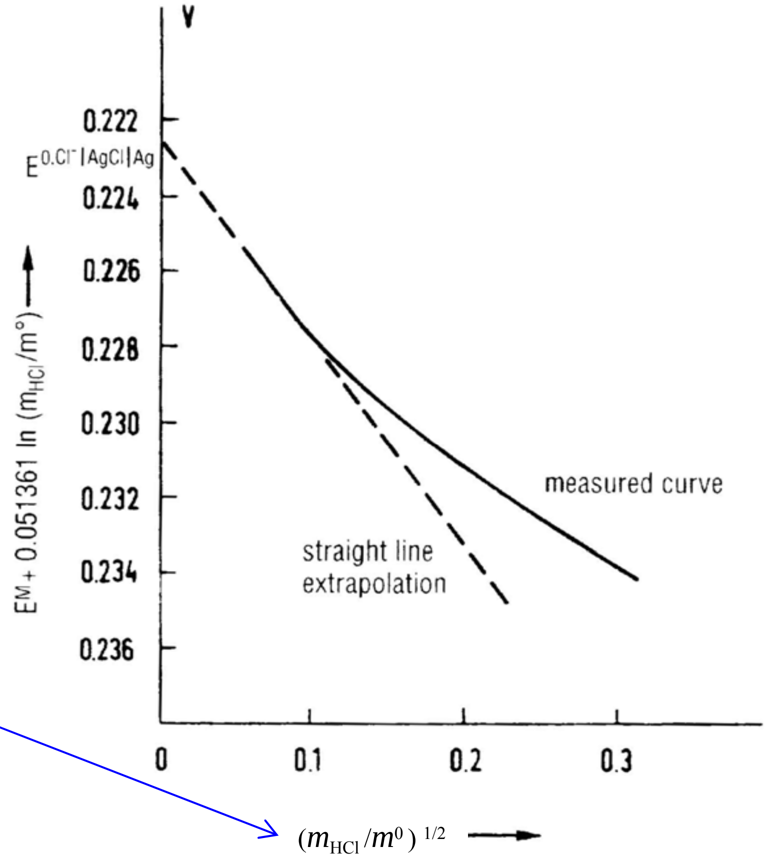


Fig 3.29 The determination of the standard potential of the silver-silver chloride electrode

ii. Mean Activity Coefficients

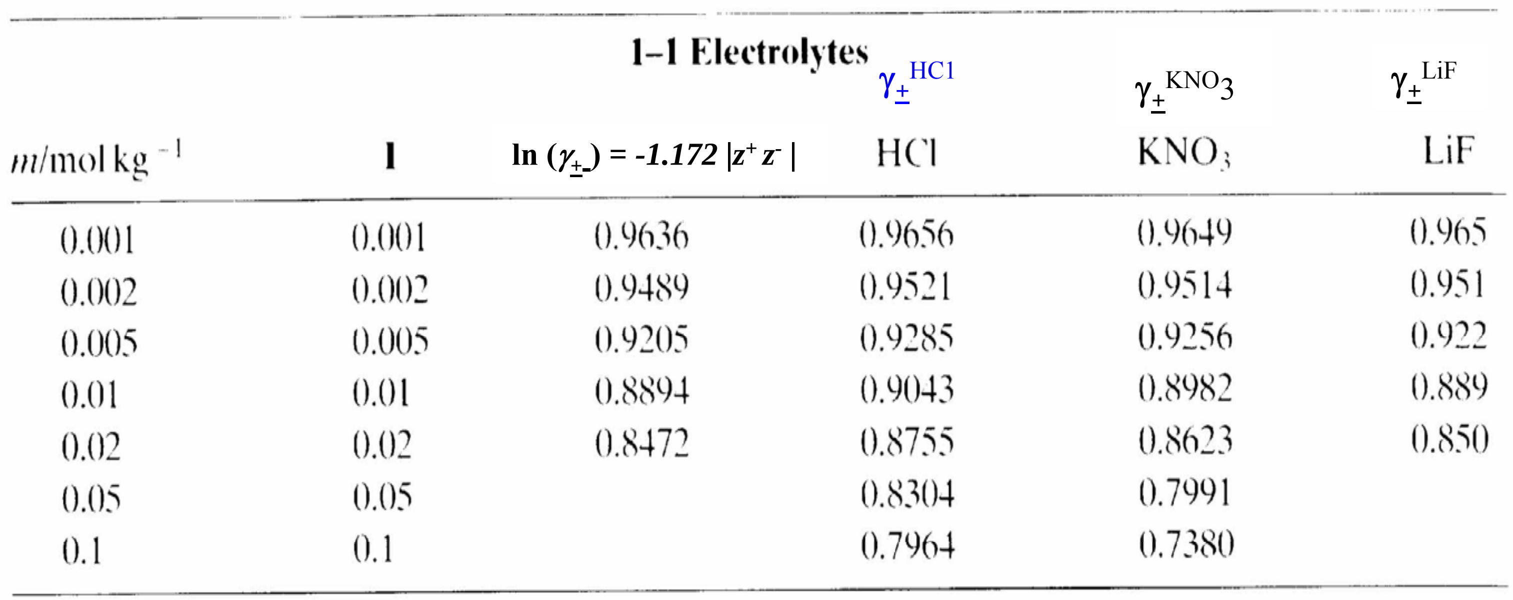
Mean activity coefficients can be determined similar to E^0 by rearranging 3.161 which gives eqn. 3.162 :

$$0.05136 \ln \gamma_{\pm}^{HCl} = E^{0,Cl^-|AgCl|Ag} - E^{M} - 0.05136\, ln(m_{HCl}/m^{0}) \qquad \text{Eqn. 3.162}$$

and using $E^{0,Cl^-/AgCl/Ag}$, which has just been determined, the measurements of EMF allows calculation of the mean activity coefficient, $\gamma_{\pm}^{HCl}$.

The resultant values of $\gamma_{\pm}^{HCl}$ as a function of m are given in Table 2.10, below.

Table 2.10 : Calculated and experimental values of $\gamma_{\pm}$ as a function of concentration (m and **I**)



		1–1 Electrolytes	$\gamma_{\pm}^{HCl}$	$\gamma_{\pm}^{KNO_3}$	$\gamma_{\pm}^{LiF}$
m/mol kg^{-1}	**I**	**ln ($\gamma_{\pm}$) = -1.172 $\|z^+ z^-\|$**	HCl	KNO_3	LiF
0.001	0.001	0.9636	0.9656	0.9649	0.965
0.002	0.002	0.9489	0.9521	0.9514	0.951
0.005	0.005	0.9205	0.9285	0.9256	0.922
0.01	0.01	0.8894	0.9043	0.8982	0.889
0.02	0.02	0.8472	0.8755	0.8623	0.850
0.05	0.05		0.8304	0.7991	
0.1	0.1		0.7964	0.7380	

Recall:

ln ($\gamma_{\pm}$) = -1.172 $|z^+ z^-|$ $\sqrt{\mathbf{I}}$ and I = ½ Σ z_i^2 (m_i/m^0) and m^0 = 1 *mol/kg* of solvent so $\gamma_{\pm} \approx \sqrt{m/m^0}$

3.6.2 Solubility Products of Slightly Soluble Salts

The electrode potential equation for AgCl permits to determine the solubility product:

$$\frac{RT}{F}\ln K_{\mathrm{s}}^{\mathrm{AgCl}} = E^{0,\mathrm{Cl}^-|\mathrm{AgCl}|\mathrm{Ag}} - E^{0,\mathrm{Ag}^+|\mathrm{Ag}}$$

Knowing thermodynamically that:

$$E^{0,\mathrm{Cl}^-|\mathrm{AgCl}|\mathrm{Ag}} = 0.2224\ \mathrm{V\ vs\ SHE\ and}\ E^{0,\mathrm{Ag}^+|\mathrm{Ag}} = 0.7996\ \mathrm{V\ vs\ SHE}$$

Substituting, yields: $K_s^{AgCl} = 1.78 \cdot 10^{-10}$

3.6.3 Determining of the Ionic Product of Water

The ionic product of water Kw is defined as $K_w = a_{H30^+} \cdot a_{OH-}$

If we use a cell made of a hydrogen half cell and silver/silver chloride half cell, then we get:

$$\mathrm{Pt} \mid \mathrm{H_2}(p = 1\ \mathrm{atm.}) \mid \mathrm{KOH}(a_{OH^-}).\mathrm{KCl}(a_{Cl^-}) \mid \mathrm{AgCl} \mid \mathrm{Ag}$$

The measured EMF of this cell, E^M, is given by

$$\begin{aligned} E^M &= E^{Cl^-|AgCl|Ag} - E^{H^+|H_2} \\ &= E^{0,Cl^-|AgCl|Ag} - \frac{RT}{F}\ln a_{Cl^-} - \frac{RT}{F}\ln a_{H_3O^+} \end{aligned}$$

Expressing a_{H30^+} in terms of K_w ($a_{H3O^+} = K_w\, a_{OH^-}$) and transforming the above equation we get:

$$\underbrace{\frac{F}{RT}\cdot\left(E^M - E^{0,Cl^-|AgCl|Ag}\right) + ln\left\{\frac{(m_{Cl^-}/m^0)}{(m_{OH^-}/m^0)}\right\}} \qquad 3.171$$

$$= -\ln K_w - \underbrace{\ln \cancel{\frac{\gamma_{Cl^-}}{\gamma_{OH^-}}}}$$

Plotting E^M (LHS of eqn. 3.171) as a function of the ionic strength I, (where $I = \frac{1}{2}\Sigma z_i^2(m_i/m^0)$) yields $\ln K_w$ as the intercept.

This is so, because as I goes to zero, the ratio of $\gamma_{Cl^-}/\gamma_{OH^-}$ goes to1 so ln ($\gamma_{Cl^-}/\gamma_{OH^-}$) goes to 0 (that is, I goes to zero, as the molality of Cl^- and OH^- decrease, as was done in slide 2).

When this extrapolation is evaluated, the solution of eqn. 3.171 is then the anti-ln of the intercept , which is $K_w = 1.008 \times 10^{-14}$

3.6.4 Dissociation Constants of Weak Acids, K_a^{HA} (the "Harned Cell")

The dissociation constants of a number of weak acids may he obtained from cells in which

- the hydrogen ions of the hydrogen electrode are supplied by dissociation of the weak acid, HA and
- the chloride ion molality determines the potential of the silver-silver chloride electrode potential.

$$\mathrm{Pt} \mid \mathrm{H_2}(p = 1\ \mathrm{atm.}) \mid \mathrm{HA, NaA, NaCl} \mid \mathrm{AgCl} \mid \mathrm{Ag} \qquad \text{Eqn. 3.172}$$

The measured *emf* of this cell is given by Eqn. 3.173:

$$\begin{aligned} E^{\mathrm{M}} &= E^{\mathrm{Cl^-|AgCl|Ag}} - E^{H^+|H_2} \\ &= E^{0,\mathrm{Cl^-|AgCl|Ag}} - \frac{RT}{F} \ln a_{H^+} \cdot a_{\mathrm{Cl^-}} \\ &= E^{0,\mathrm{Cl^-|AgCl|Ag}} - \frac{RT}{F} \ln\{\gamma_{\mathrm{H}^+} \cdot \gamma_{\mathrm{Cl^-}} \cdot (m_{\mathrm{H^+}}/m^0)(m_{\mathrm{Cl^-}}/m^0)\} \end{aligned} \qquad \text{Eqn. 3.173}$$

From the definition of the acid dissociation constant, K_a^{HA}

$$K_{\mathrm{a}}^{\mathrm{HA}} = \frac{\gamma_{\mathrm{H^+}} \cdot \gamma_{A^-} \cdot (m_{\mathrm{H^+}}/m^0)(m_{\mathrm{A^-}}/m^0)}{[\gamma_{\mathrm{HA}} \cdot (m_{\mathrm{HA}}/m^0)]} \qquad \text{Eqn. 3.174}$$

we can rearrange eqn. 3.173 to get eqn. 3.175:

$$\begin{aligned} E^{\mathrm{M}} &= E^{0,\mathrm{Cl^-|AgCl|Ag}} + \frac{RT}{F} \ln\left\{\frac{(m_{\mathrm{HA}}/m^0)\cdot(m_{\mathrm{NaCl}}/m^0)}{(m_{\mathrm{NaA}}/m^0)}\right\} \\ &- \frac{RT}{F} \ln K_{\mathrm{a}}^{\mathrm{HA}} - \frac{RT}{F} \ln\{\gamma_{\mathrm{Cl^-}} \cdot \gamma_{\mathrm{HA}}/\gamma_{\mathrm{A^-}}\} \end{aligned} \qquad \text{Eqn. 3.175}$$

neglect

where we assume $m_{\mathrm{A^-}} = m_{\mathrm{NA}} + m_{\mathrm{H^+}} \cong m_{\mathrm{NA}}$ and m_{HA} is the molality of the HA as it was initially added.
The "Harned cell" is this cell and plotting of E^{M} as a function of the ionic strength I and extrapolating to I→ 0 gives K_a^{HA}

e.g., for acetic acid at 0.05 molal and ignoring γ's we get $K_a^{\mathrm{HA}} = 1.729$
and extrapolating to I→ 0 gives the fairly accurate value of $K_a^{\mathrm{HA}} = 1.754\ 10^{-5}$

3.6.5 The Determination of the Thermodynamic State Functions

$\Delta_r G^0$, $\Delta_r H^0$ and $\Delta_r S^0$ and Equilibrium Constant, K_{eq}

We know that the connection between the standard tree energy $\Delta_r G^0$ of a reaction and the *emf* of a galvanic cell undergoing this reaction with all species in their standard states is:

$$\Delta_r G^0 = -nFE^0$$

Eqn. 3.5 now 3.176

In a similar way, the entropy change for a chemical reaction max be obtained from the *emf* value of the galvanic cell with the same overall cell reaction from the equation:

$$\Delta_r S^0 = nF \cdot \left(\frac{\partial E^0}{\partial T} \right)_p$$

Since $\Delta G = \Delta H - T\Delta S$, then the standard enthalpy, $\Delta_r H^0$, could be written as follows:

$$\Delta_r H^0 = -nF \left\{ E^0 - T \left(\frac{\partial E^0}{\partial T} \right)_p \right\}$$

Finally, the thermodynamic equilibrium constant. of a chemical reaction can also be determined from the *emf* of the corresponding electrochemical cell, since:

$$\Delta G^0 = -RT \ln K_{eq} \qquad \text{or} \qquad K_{eq} = \exp\left\{ \frac{nFE^0}{RT} \right\}$$

E.g., of $\Delta_r G^0$, $\Delta_r H^0$ and $\Delta_r S^0$ and Equilibrium Constant, K_{eq} …from the Daniell Cell

As a clear example for determining state functions from electrochemical measurements, consider the Daniell Cell:

$$\mathrm{Zn} \mid \mathrm{Zn}^{2+}(\mathrm{aq.}) \parallel \mathrm{Cu}^{2+}(\mathrm{aq.}) \mid \mathrm{Cu}$$

for which the corresponding electrode reactions are:

$$\begin{array}{lll} \mathrm{Cu}^{2+} + 2\,\mathrm{e}^- & \rightarrow & \mathrm{Cu}^0 \\ \mathrm{Zn}^0 & \rightarrow & \mathrm{Zn}^{2+} + 2\,\mathrm{e}^- \\ \hline \mathrm{Cu}^{2+} + \mathrm{Zn}^0 & \rightarrow & \mathrm{Cu}^0 + \mathrm{Zn}^{2+} \end{array}$$

Knowing the standard *emf* value for the overall reaction (1.103 V) we can calculate:

$$\Delta_r G^0 = -2 \cdot 96485 \cdot 1.103 = -212.846\,\mathrm{kJ\,mol^{-1}}$$

The temperature dependence of the standard *EMF* of the Daniell cell in the temperature region near 25^{0}C we measure -0.83 . 10^{-4} $\mathrm{VK^{-1}}$ that yields for the entropy:

$$\Delta_r S^0 = 2 \cdot 96485 \cdot (-0.83 \cdot 10^{-4}) = -16.02\,\mathrm{J\,K^{-1}\,mol^{-1}}$$

Following the formula presented before we find for the enthalpy:

$$\Delta_r H^0 = \Delta_r G^0 + 298 \cdot \Delta_r S^0 = -212846 - 4774 = -217620\,\mathrm{J\,mol^{-1}}$$

According to the previously presented formula we also do the equilibrium constant:

$$K_{eq} = \exp\left\{\frac{2 \cdot 96485 \cdot 1.103}{8.314 \cdot 298}\right\} = 2.041 \cdot 10^{37}$$

3.6.6 pH Measurement with a Hydrogen Electrode

We know already that the electrode reaction of a simple hydrogen electrode is:

$$H_3O^+ + e^- \rightleftharpoons \frac{1}{2} H_2 + H_2O$$

For the hydrogen equilibrium potential at p = 1 atm:

$$E^{H^+|H_2} = \frac{RT}{F} \ln a_{H_3O^+} \text{ vs SHE}$$
$$\equiv -0.0591 \text{ pH vs SHE at } 298 \text{ K}$$

Definition …. pH ≡ $-\log_{10} a_{H3O^+}$

To determine the pH of an unknown solution, the hydrogen electrode must be combined with a suitable reference electrode:

$$\text{Hg} \mid \text{Hg}_2\text{Cl}_2 \mid \text{KCl(sat.)} \parallel \text{solution of pH} = \text{pH}_x \mid \text{H}_2 \mid \text{Pt}$$

The *emf* of this cell is :

$$E^M = E^{H^+|H_2} - E^{SCE} + \Delta\varphi_{diff}$$
$$= -0.0591 \text{ pH}_x - E^{SCE} + \Delta\varphi_{diff}$$

where:

$$\text{pH}_x = -\frac{E^M + E^{SCE} - \Delta\varphi_{diff}}{0.0591}$$

and $\Delta \varphi_{diff}$ is the potential that forms at the junction of the dissimilar two cells.

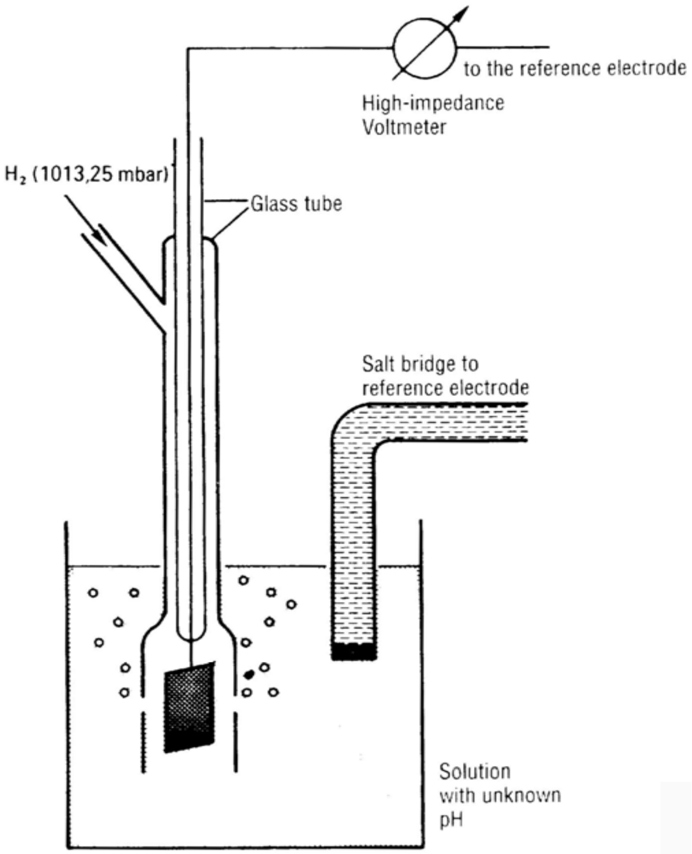


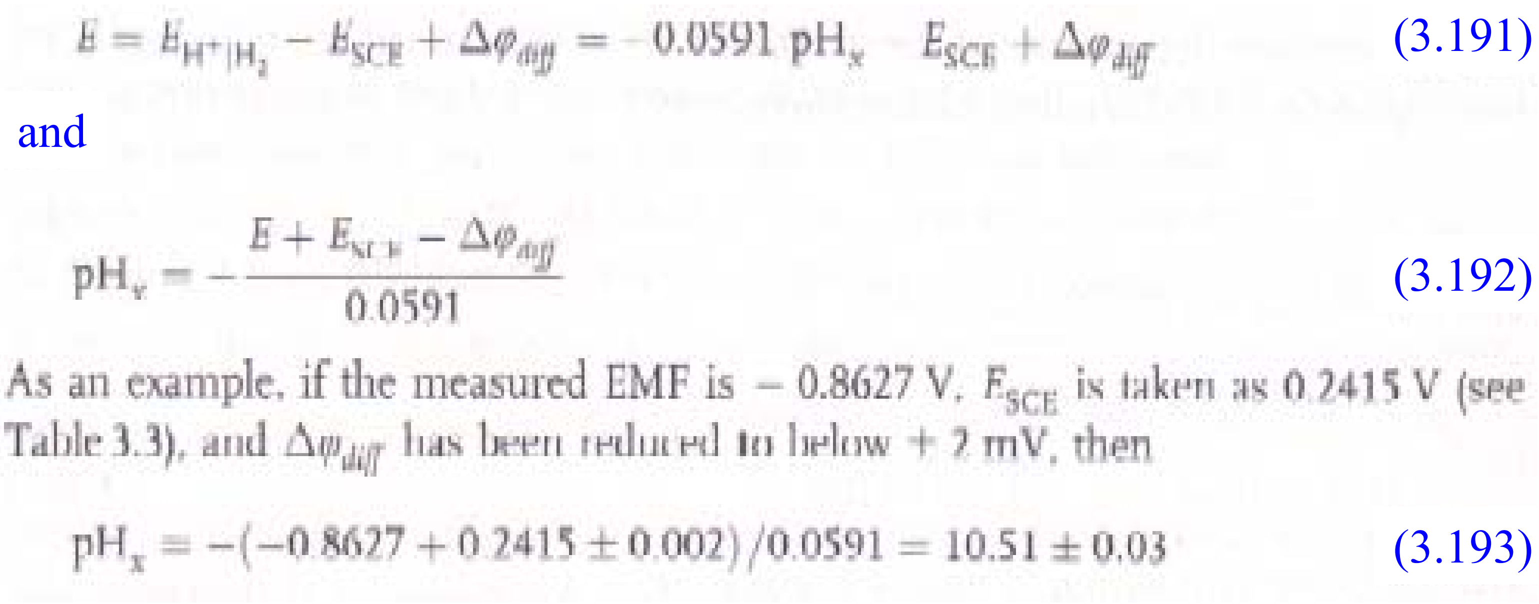
Fig 3.30 Measurement of pH with a hydrogen electrode

As an example, for the cell

$$Hg|Hg_2Cl_2|KCl(sat.)||\text{solution of } pH = pH_x|H_2|Pt \qquad \text{Cell 3.190}$$

the measured *emf* of the above cell is -0.8627 V. E^{SCE} is 0.2415 V (where SCE is the saturated calomel reference electrode whose half cell is $Hg|Hg_2Cl_2|KCl_{sat}$). Finally the accuracy of the measurement has been reduced to below ±2 mV. Calculate the pH.

The *emf* of cell 3.190 is



$$E = E_{H^+|H_2} - E_{SCE} + \Delta\varphi_{diff} = -0.0591\,pH_x - E_{SCE} + \Delta\varphi_{diff} \qquad (3.191)$$

and

$$pH_x = -\frac{E + E_{SCE} - \Delta\varphi_{diff}}{0.0591} \qquad (3.192)$$

As an example, if the measured EMF is − 0.8627 V, E_{SCE} is taken as 0.2415 V (see Table 3.3), and $\Delta\varphi_{diff}$ has been reduced to below ± 2 mV, then

$$pH_x = -(-0.8627 + 0.2415 \pm 0.002)/0.0591 = 10.51 \pm 0.03 \qquad (3.193)$$

3.6.7 pH Measurement with a Glass Electrode

If a glass surface (e.g. formed from SiO_2-CaO-Na_2O glass, i.e., “soda glass”) is immersed in water, some of the cations bound in the silica network are exchanged with H_3O^+ ions in a thin hydrated layer at the surface. This “swelling” is complete in 1 or 2 days. The ion-exchange layer is 5 to 500 nm thick and is called the Haugaard Layer (HL).

If the HL is now brought into contact with an aqueous solution containing H_30^+ ions, *a of* (H_30^+) and μ of (H_30^+) will be different in the glass and aqueous phases. H_30^+ redistributes so electrochemical potentials in the HL and solution (sol) phases are equal as below

$$\begin{aligned}\tilde{\mu}^{HL}_{H_3O^+} = \tilde{\mu}^{sol}_{H_3O^+} &= \mu^{0\dagger\,HL}_{H_3O^+} + RT\ln a^{HL}_{H_3O^+} + F\varphi^{HL} \\ &= \mu^{0\dagger\,sol}_{H_3O^+} + RT\ln a^{sol}_{H_3O^+} + F\varphi^{sol}\end{aligned} \qquad 3.203$$

If $$\mu^{0\dagger\,HL}_{H_3O^+} = \mu^{0\dagger\,sol}_{H_3O^+}$$

Then the potential difference in the HL and sol layers, $\Delta\varphi$, is :

$$\Delta\varphi = \varphi^{sol} - \varphi^{HL} = \frac{RT}{F}\ln\left\{\frac{a^{HL}_{H_3O^+}}{a^{sol}_{H_3O^+}}\right\} \qquad 3.204$$

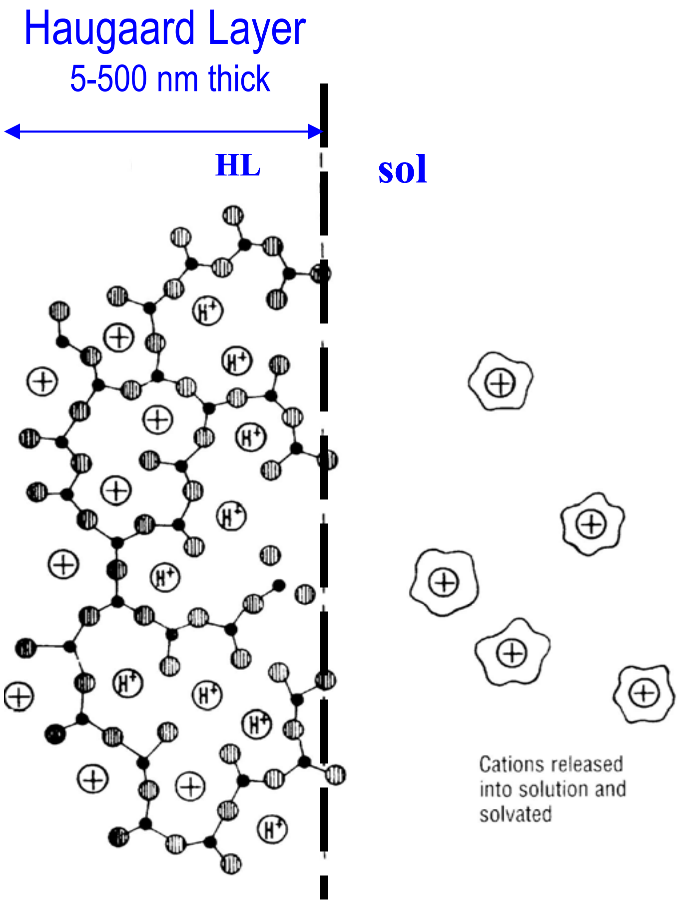


Fig. 3.31 Schematic representation of the exchange of cations for protons in the surface region (HL) of a glass membrane.

- shaded circles are oxygen,
- solid circles are silicon,
- circles with + charges (cations),
  - unsolvated cations in the HL glass (left)
  - solvated cations in solution (right).

So from 3.204 we see that $\Delta\varphi$ changes 59.1 mV for every decade change in H_3O^+ in solution, since the HL is solid (its *a* = constant; which leads to an asymmetry factor discussed next).

Determination of pH

Fig 3.32 shows a thin glass membrane (of thickness about 0.5 mm) with swollen layers on both side separates

- solution of unknown pH, II
- from a second solution, I, whose pH is assumed constant

Equilibrium between the 2 faces leads to

$$\Delta\varphi_0\ \text{(I-II)} = \frac{RT}{F}\ln\left\{\frac{a_{\mathrm{H_3O^+}}(\mathrm{HL.\,I})}{a_{\mathrm{H_3O^+}}(\mathrm{I})}\right\} - \frac{RT}{F}\ln\left\{\frac{a_{\mathrm{H_3O^+}}(\mathrm{HL.\,II})}{a_{\mathrm{H_3O^+}}(\mathrm{II})}\right\}$$

Putting $\log_{10} a_{\mathrm{H_3O^+}}(\mathrm{I}) = -\mathrm{pH_I}$ and $\log_{10} a_{\mathrm{H_3O^+}}(\mathrm{II}) = -\mathrm{pH_{II}}$

$$\Delta\varphi_0\ \text{(I-II)} = \frac{RT}{F}\ln\left\{\frac{a_{\mathrm{H_3O^+}}(\mathrm{HL.\,I})}{a_{\mathrm{H_3O^+}}(\mathrm{HL.\,II})}\right\} + 0.0591(\mathrm{pH_I} - \mathrm{pH_{II}})$$

Eqn.3.206

The asymmetry potential is

$$\frac{RT}{F}\ln\left\{\frac{a_{\mathrm{H_3O^+}}(\mathrm{HL.\,I})}{a_{\mathrm{H_3O^+}}(\mathrm{HL.\,II})}\right\}$$

and is due to stresses and in inhomogeneities in the glass.

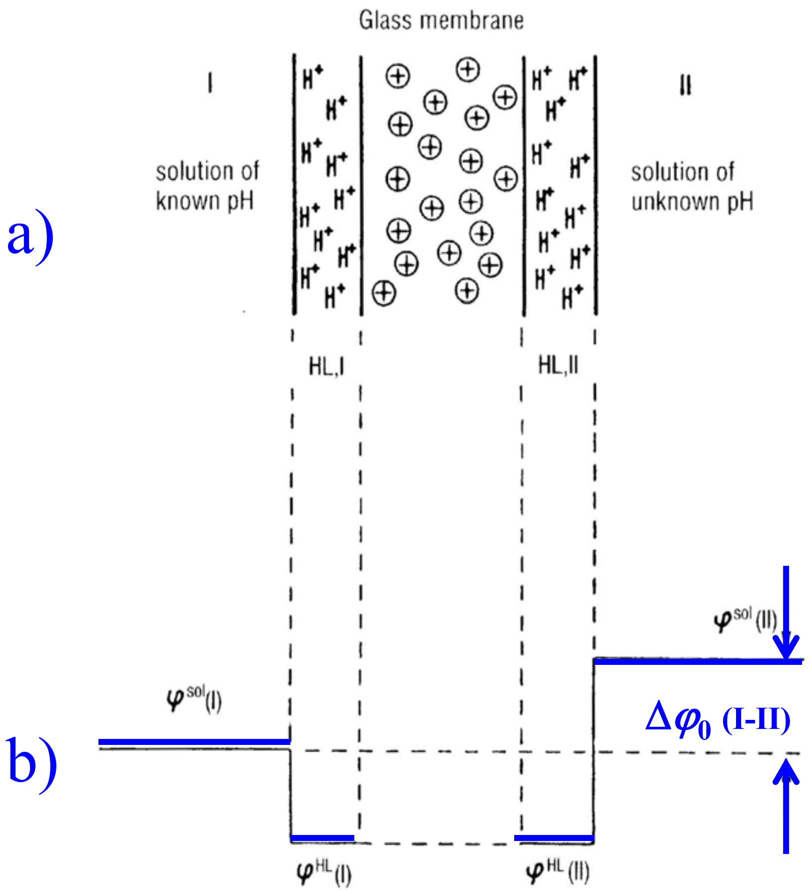


Fig 3.32 Operation of the glass electrode:

a) schematic representation of a glass membrane between two solutions of different pH. HL I and HL II are the Haugaard layers at the two membrane surfaces

b) potential variation through the membrane.

First, the asymmetry potential is determined by measuring $\Delta\varphi_0$ (I-II) with identical reference electrodes and solutions on each side of the membrane so $\Delta\varphi_0$ (I-II) = $\Delta\varphi_{as}$
Second, when the membrane separates a standard pH and a solution with different pH, since $\Delta\varphi_{as}$ is known, measuring $\Delta\varphi$(I-II) can be used to find the unknown pH using eqn.3.206

Since $\Delta\varphi_{as} = \frac{RT}{F} \ln \left\{ \frac{a_{H_3O^+}(\mathrm{HL.\,I})}{a_{H_3O^+}(\mathrm{HL.\,II})} \right\}$ eqn. 3.206 can be rewritten as

$$\Delta\varphi_0\ (\text{I-II}) = \Delta\varphi_{as} + 0.0591\ (\mathrm{pH}_{\mathrm{I}} - \mathrm{pH}_{\mathrm{II}}) \qquad \text{Eqn. 3.206}$$

A silver/silver chloride electrode (SSE) with solution I (a buffer of pH=7 with KCl) is on one side of a glass electrode between a solution II connected by a salt bridge to a SCE. This cell is written

Hg |Hg_2Cl_2 |KCl(satd) || solution (II) | glass | solution (I), KCl | AgCl |Ag

So the EMF of the cell (EMF = E^{cell} = V^{cell}) is

$$\mathrm{EMF} = E^{\text{cell}} = E^0_{\text{SSE}} - E^0_{\text{SCE}} + \Delta\varphi_0\ (\text{I-II})$$

$$E^{\text{cell}} = E^0_{\text{SSE}} - E^0_{\text{SCE}} + \Delta\varphi_{as} + 0.0591\ (\mathrm{pH}_{\mathrm{I}} - \mathrm{pH}_{\mathrm{II}}) \qquad \textbf{Eqn. 3.207}$$

Now set $E^{\text{cell}} = E_S$ for solution II of standard buffer and $E^{\text{cell}} = E_x$ for solution II of an unknown and subtract E_S by E_x. Assume $\Delta\varphi_{as}$ is constant in each solution so $\Delta\varphi_{as}$ subtracts out. Solve for pH_x to get equation 3.208

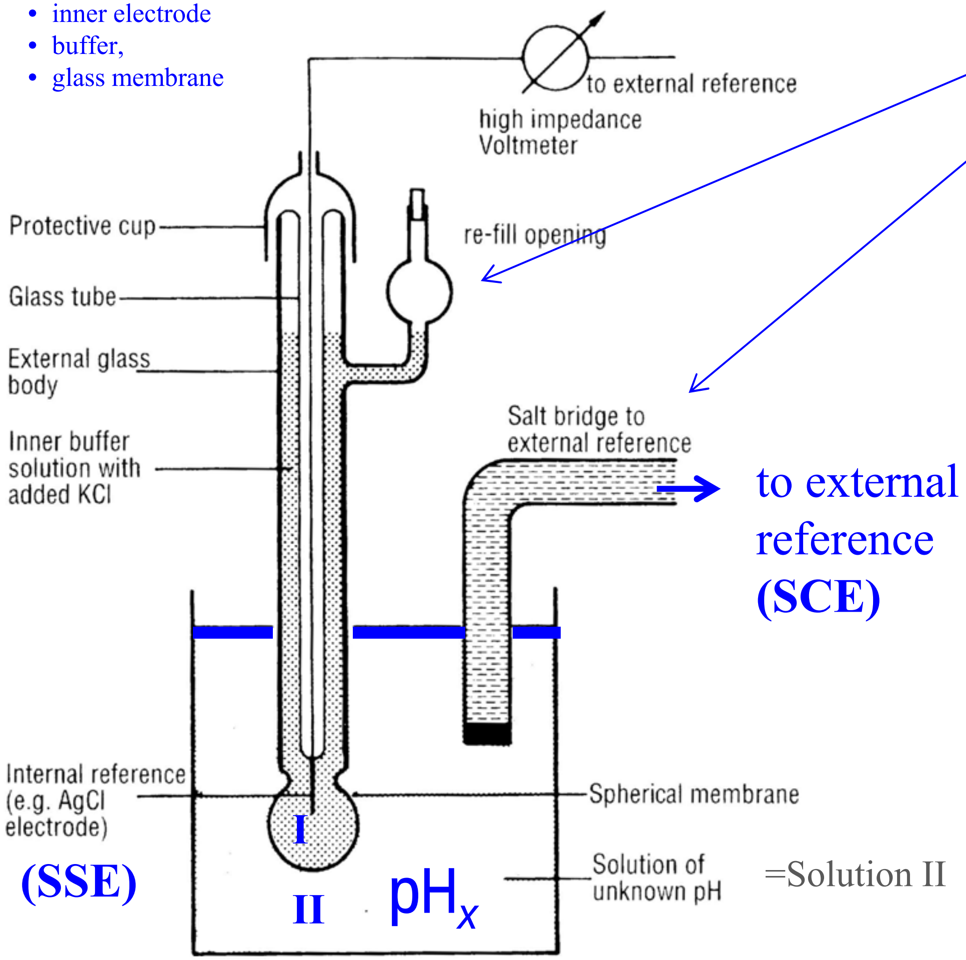
$$\mathbf{pH}_{x,\mathrm{II}} = \mathbf{pH}_{S,\mathrm{II}} + (E_S - E_x) / 0.0591 \qquad \textbf{Eqn. 3.208}$$

which is the process used to solve for pH in a pH meter.

This is why you have to calibrate a pH meter with standards, so the pH meter can set E_S !!!

Glass electrode:

- inner electrode
- buffer,
- glass membrane



$$E = E^{0,\mathrm{SSE}} - E^{\mathrm{SCE}} + \Delta\varphi_0(I\text{–}II)$$

$$= E^{0,\mathrm{SSE}} - E^{\mathrm{SCE}} + \Delta\varphi_{\mathrm{as}} + 0.0591(\mathrm{pH_I} - \mathrm{pH_{II}})$$

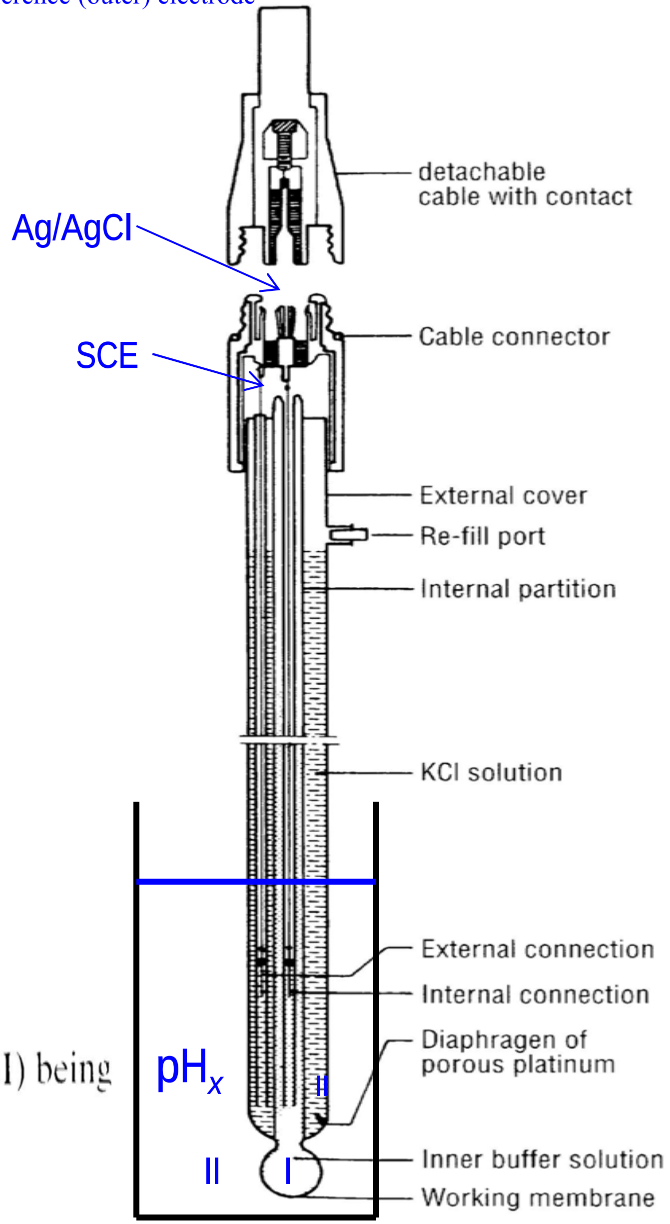
If $E = E_s$ for solution (II) being a standard buffer and $E = E_x$ for solution (II) being the unknown, it follows once again that

$$\mathrm{pH}_x = \mathrm{pH}_s + \frac{E_s - E_x}{0.0591}$$

Eqn. 3.208

Combination pH electrode

- a glass (inner) electrode and
- reference (outer) electrode



3.6.8 The Principle of Potentiometric Titrations

If. during a chemical reaction, there is a change in the activity of an ion i which can be sensed through the change in potential of a suitable electrode, then the progress of the reaction can be followed through this potential change.

1) Acid – Base Titration … pH electrode

By addition of alkali to an acid substrate, the potential difference measured will decrease at the rate of 59.1 mV per decade lowering in H_30^+ activity. As long as the acid is in excess, the pH will vary only slightly with addition of base; however, near the equivalence point. a_{H3O}+ falls very rapidly, and the potential difference also falls rapidly before leveling out again in excess base

2) Cl^- determination by Ag^+ addition "Precipitation Titration"

At the beginning of the titration, the concentration of silver in solution will, in effect. be determined by the solubilitv product of silver chloride, and. at the end-point, the Ag concentration will rise very rapidly as the last of the chloride is precipitated.

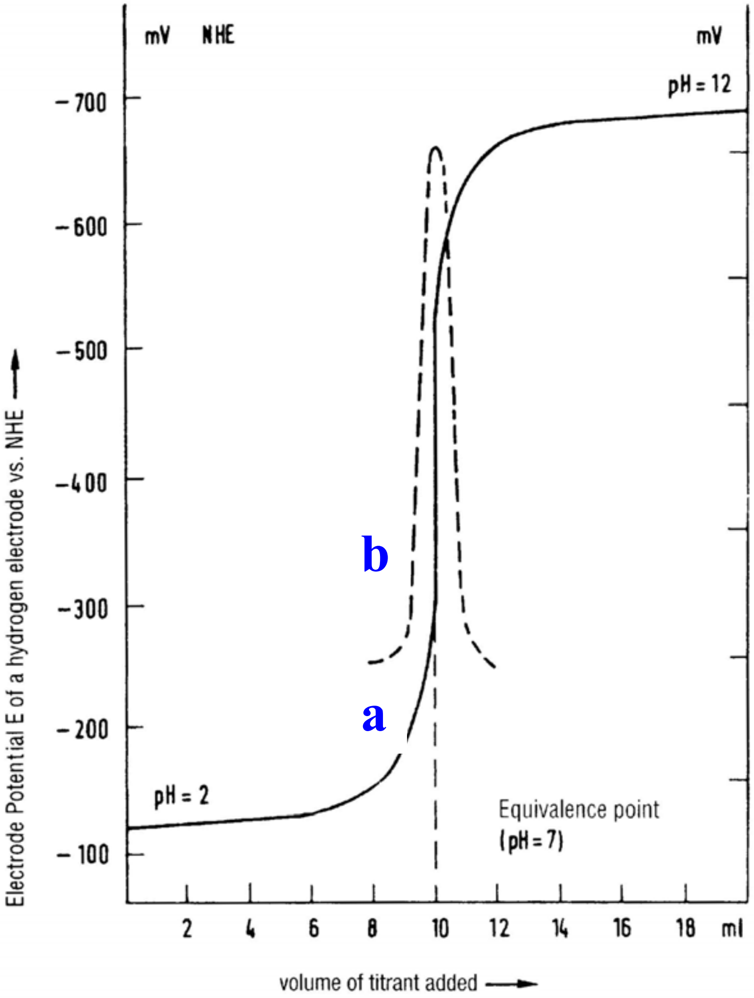


Fig 3.35 Potentiometric acid-base titration:
a. Strong acid titrated with strong base;
b. Differential potential change.

Advantage Potentiometric Titrations

….can be done in turbid and colored solution where optical endpoints are not practical.