Chapter 2

Electroanalytical methods

Electroanalytical methods

- Electrogravimetry
- Coulometry
- Potentiometry
- Voltammetry

Potentiometry

- Fundamentals of potentiometry
- Reference electrodes
- Indicator and ion selective electrodes
- Instrumentation and measurement of cell electromotive force (e.m.f)

Fundamentals of potentiometry

When a metal is immersed in a solution containing its own ions, the potential difference is established between the metal and the solution

$$\mathbf{Ox} + \mathbf{ne} \rightleftharpoons \mathbf{Red}$$

$$\varphi = \varphi^{\theta} + \frac{RT}{nF} \ln \frac{a_0}{a_R}$$

Fundamentals of potentiometry

$$M^{n+} + ne = M$$

$$\varphi = \varphi^{\circ} + (RT/nF)\ \ln \alpha_{M^{n+}}$$

Nernst equation

Fundamentals of potentiometry

Indicator electrode

+

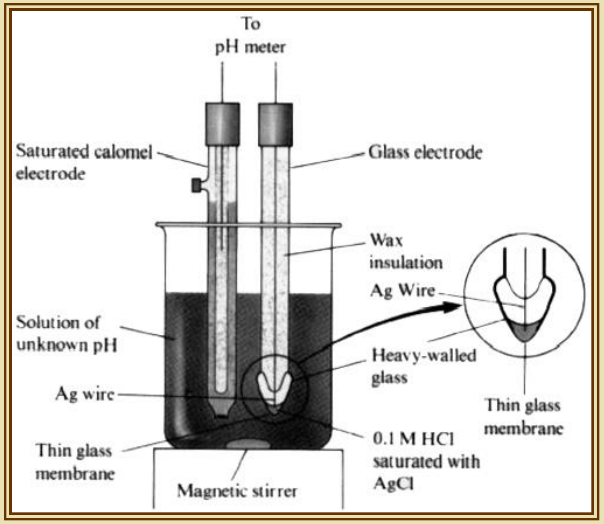
Reference electrode

+

Solution

↓

Cell



Fundamentals of potentiometry

M | M $^{n+}$ || reference electrode

$$E = \varphi_{(+)} - \varphi_{(-)} + \varphi_L$$

Liquid junction potential

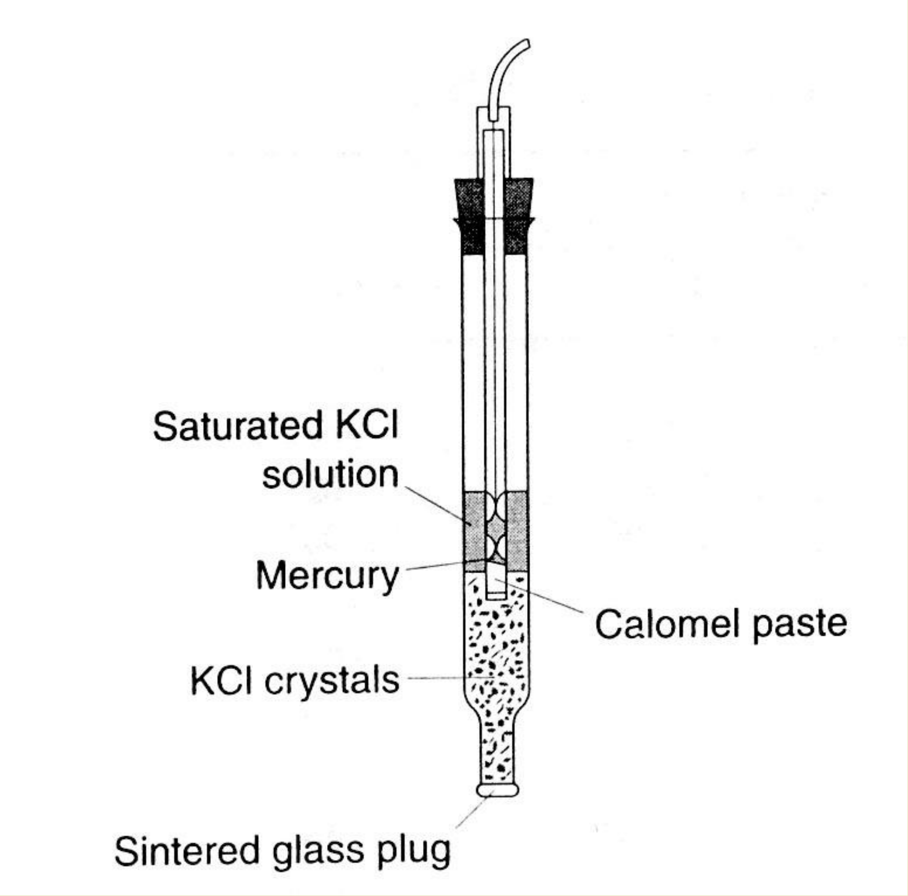
$$E = \varphi_{(+)} - \varphi_{(-)}$$

$$= \varphi_r - \varphi^\circ - (RT/nF) \ln \alpha_{Mn+}$$

Reference electrodes

- **Hydrogen electrode**
- **Calomel electrode**
- **Silver – silver chloride electrode**

Calomel electrode



Calomel electrode

$Hg \mid Hg_2Cl_2,\ KCl(xM) \|$

$Hg_2Cl_2(s) + 2e \rightleftharpoons 2Hg(l) + 2Cl^-$

Electrode potential

$$\varphi = \varphi^\circ_{Hg_2Cl_2/Hg} + (RT/nF)\ \ln (1/\alpha_{Cl}{}^{-2})$$

$$= \varphi^\circ_{Hg_2Cl_2/Hg} - 0.059\ \lg \alpha_{Cl^-}$$

Silver – silver chloride electrode

Ag│AgCl，KCl(xM)‖

$AgCl(s) + e \rightleftharpoons Ag(s) + Cl^-$

Electrode potential

$$\varphi = \varphi°_{AgCl/Ag} + (RT/nF) \ln (1/\alpha_{Cl^-})$$

$$= \varphi°_{AgCl/Ag} - 0.059 \lg \alpha_{Cl^-}$$

Indicator and ion selective electrodes

Indicator electrode

---The potential depends on the activity of a particular ionic species which it is desired to quantify

Indicator and ion selective electrodes

- Electrode of the first kind
- Electrode of the second kind
- Inert electrode

}

Metal electrode

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- The glass electrode
- Crystalline membrane electrode
- Biochemical electrode

}

Membrane electrode

Indicator and ion selective electrodes

Electrode of the first kind

---The ion to be determined is directly involved in the electrode reaction

Metal M immersed in a solution of **M^{n+} ion**

$$\varphi = \varphi^{\circ}_{M^{n+}/M} + (RT/nF)\ln \alpha_{M^{n+}}$$

Indicator and ion selective electrodes

Electrode of the second kind

Silver – silver chloride electrode

--- coating a silver wire with silver choloride

$$AgCl(s) + e \rightleftharpoons Ag(s) + Cl^-$$

$$\varphi = \varphi^\circ_{AgCl/Ag} + (RT/nF)\ \ln (1/\alpha_{Cl^-})$$

$$= \varphi^\circ_{AgCl/Ag} - 0.059\ \lg \alpha_{Cl^-}$$

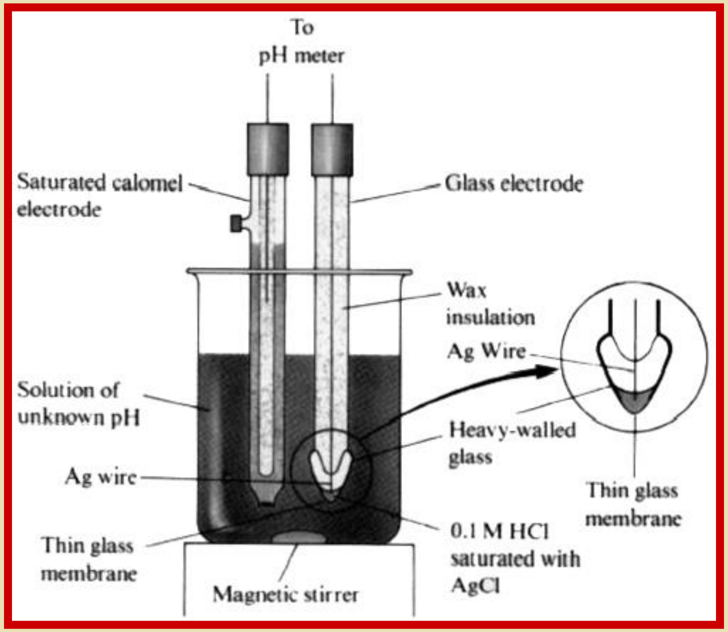
Inert electrode

---An inert electrode (Pt) is place in a system containing both an oxidizing agent and its reduction product

$$Fe^{3+} + e \rightleftharpoons Fe^{2+}$$

$$\varphi = \varphi^{\circ}_{Fe^{3+}/Fe^{2+}} + (RT/nF)\ \ln\left(\alpha_{Fe}^{3+} / \alpha_{Fe}^{2+}\right)$$

The glass electrode



The glass electrode

Composition

- SiO_2 72% + Na_2O 22% + CaO 6%
- SiO_2 63% + Li_2O 28% + Cs_2O 2% + BaO 4% + La_2O_3 3%

The glass electrode

Theory

--- Ion exchange process

$$\varphi_{glass} = K + (RT/nF)\ \ln \alpha_{H^+}$$

$$= K' - 0.059\ pH$$

The glass electrode

properties

- Can be used in the presence of strong oxidants and reductants
- Can be used in viscous media
- Can be used in the presence of proteins

The glass electrode

properties

- High resistance
- Acid error and alkaline error

Crystalline membrane electrode

composition

Crystal of lanthanum fluoride

+

0.1 mol/L NaF – 0.1 mol/L NaCl

+

Silver – silver chloride electrode

↓

Lanthanum fluoride eletrode

Crystalline membrane electrode

Theory

Lattice defect

$$\varphi_{membrane} = K - (RT/nF)\ln \alpha_{F^-}$$

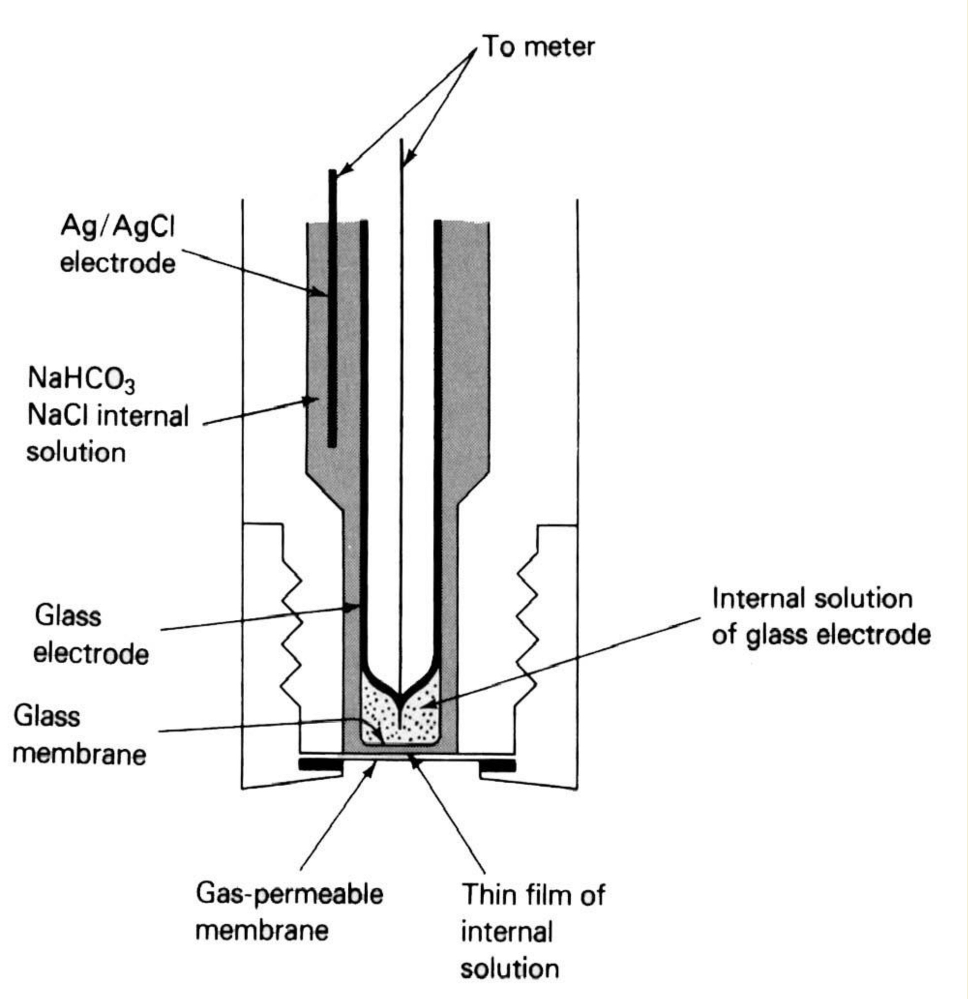
$$= K - 0.059 \lg \alpha_{F^-}$$

Crystalline membrane electrode

properties

- Detection limit ~ 10^{-7} mol/L
- Interference ~ OH^-
- pH range ~ 5 - 6

Gas – sensing electrode



NH_3 – NH_4Cl

CO_2 – $NaHCO_3$

NO_2 –$NaNO_2$

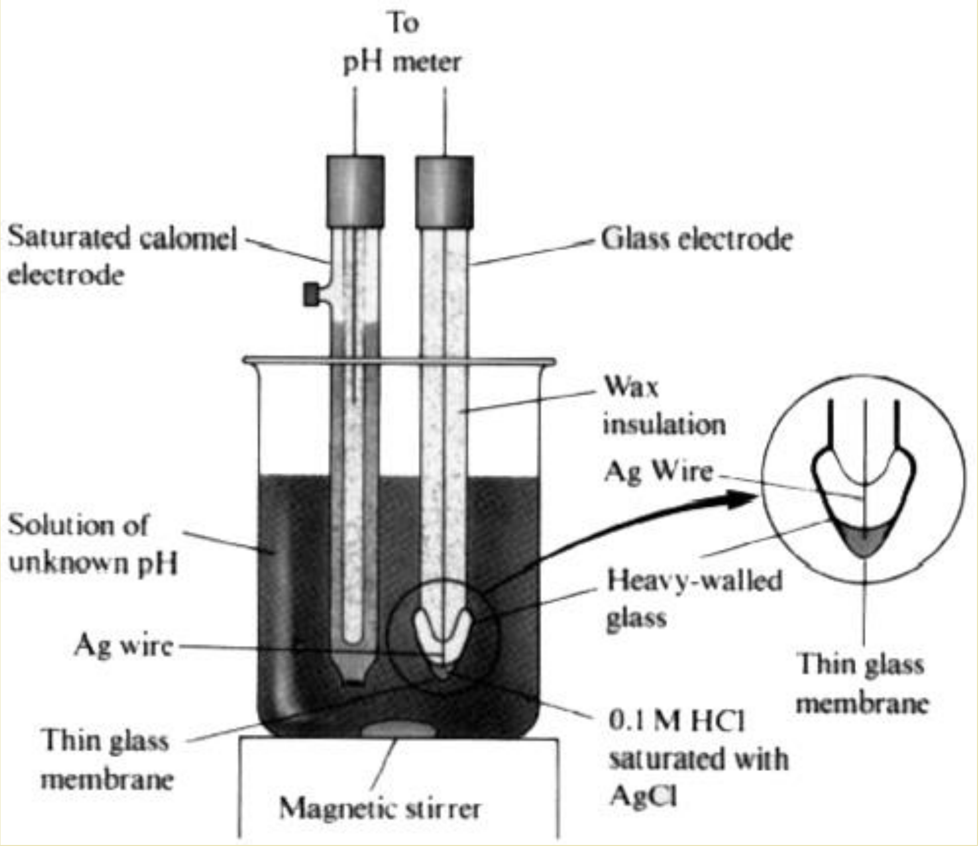
Biochemical electrode

Urea electrode

$$CO(NH_2)_2 + H_2O + 2H^+ \xrightarrow{\text{urease}} 2NH_4^+ + CO_2$$

Instrumentation

Determination of pH



Determination of pH

Glass electrode | Solution X || SCE

$$E = \varphi_{SCE} - \varphi_{glass}$$

$$= \varphi_{SCE} - (\varphi^{\circ}_{AgCl\,/\,Ag} + K + (RT/nF)\ \ln \alpha_{H+})$$

$$E = K' + (2.303\ RT\ /F)\ pH$$

Determination of pH

$$E_x = K'_x + (2.303\ RT/F)\ pH_x$$

$$E_s = K'_s + (2.303\ RT/F)\ pH_s$$

$$K'_x = K'_s$$

$$\boxed{pH_x = pH_s + (E_x - E_s)\ F/2.303RT}$$

--- **Operational definition**

Determination of pH

pH standard solution (25 C°)

Solution	0.05 M potassium hydrogenphthalate	0.025 M KH_2PO_4 0.025 M Na_2HPO_4	0.01 M Borax
pH	4.004	6.864	9.182

Determination of fluoride

$$\varphi_{membrane} = K \pm (0.059/n) \lg \alpha$$

- **Calibration curve**
- **Standard addition**

Determination of fluoride

Calibration curve

- Standard solutions
- Total ionic strength adjustment buffer(TISAB)
  - NaCl — Ionic strength
  - NaAc - HAc — pH
  - Sodium citrate — Interferenc
e

Determination of fluoride

Standard addition

$$E_1 = k_c + k \log y_1 C_1$$

$$E_2 = k_c + k \log y_1 (V_1C_1 + V_2C_s)/(V_1 + V_2)$$

$$E_2 - E_1 = k \log (V_1C_1 + V_2C_s)/ C_1(V_1 + V_2)$$

$$C_1 = C_s/(10^{\Delta E/k}(1+V_1/V_2) - V_1/V_2)$$

The end