Potentiometric Electrode
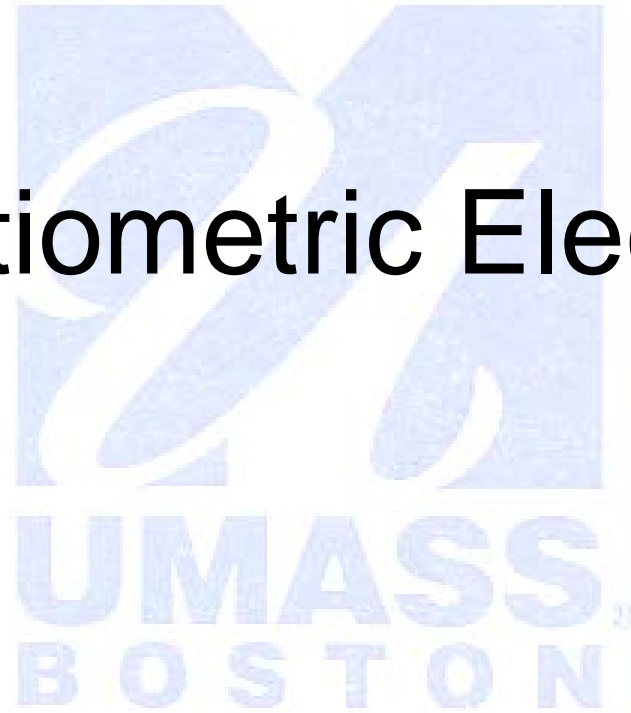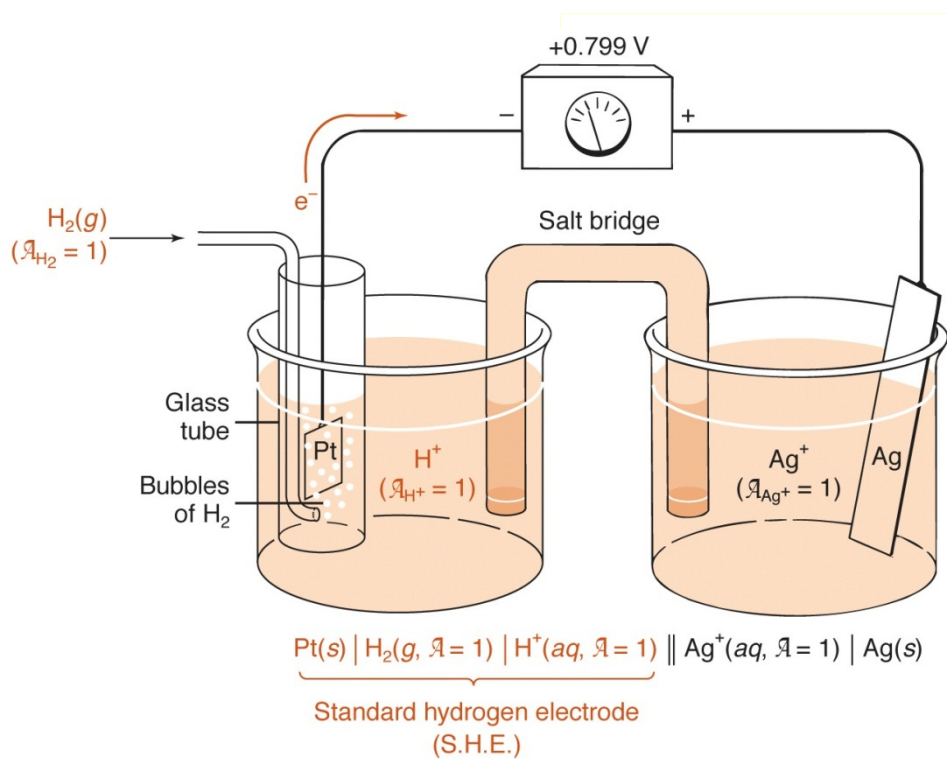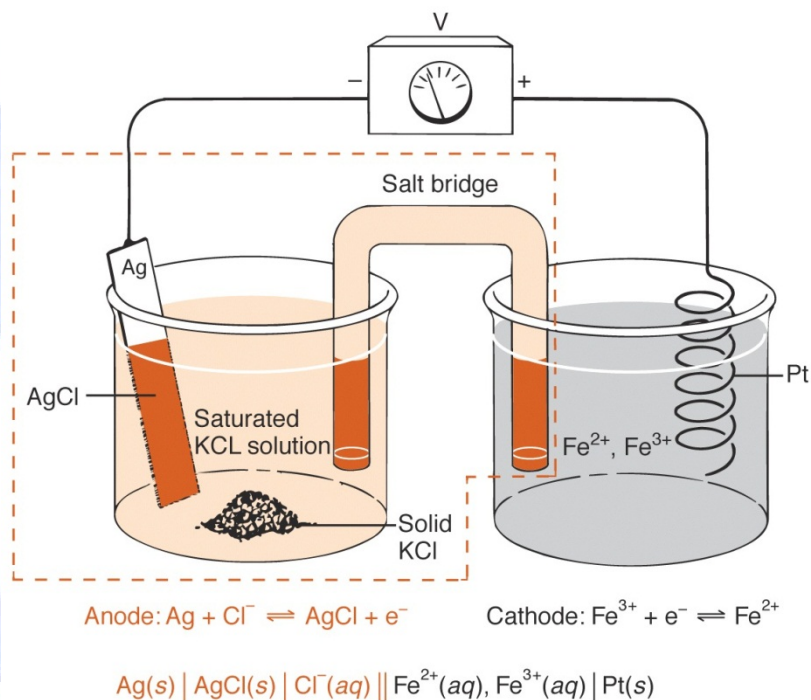
Reference Electrode
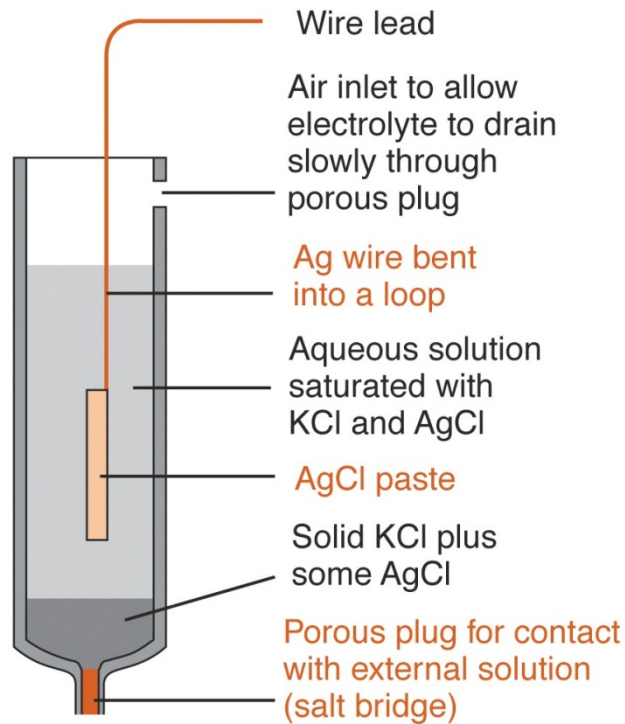

Standard Hydrogen Electrode
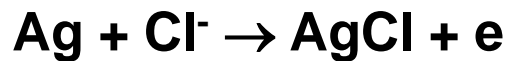
Ag/AgCl reference electrode

Reference electrode

- Reversible and obey Nernst equation
- Exhibit a potential that is constant with time
- Return to its original potential after being subjected to small currents (high exchange current)
- Little change in potential with temperature
- Behave as an ideal nonpolarizable electrode

Configuration of a typical reference electrode

Wire lead

Air inlet to allow electrolyte to drain slowly through porous plug

Ag wire bent into a loop

Aqueous solution saturated with KCl and AgCl

AgCl paste

Solid KCl plus some AgCl

Porous plug for contact with external solution (salt bridge)

Silver-Silver Oxide Reference Electrode:

Ag + Cl$^-$ $\rightarrow$ AgCl + e

Configuration of a typical reference electrode

Wire lead

Pt wire

Hole to allow drainage through porous plug

Hg(l)

Hg, Hg_2Cl_2 + KCl

Glass wool

Opening

Saturated KCl solution

KCl(s)

Glass wall

Porous plug (salt bridge)

Electrical lead

Inner tube containing a paste of Hg, Hg_2Cl_2, and saturated KCl

Saturated KCl

Small hole

Fritted disk (or asbestos thread)

Ground glass sleeve

Calomel Reference Electrode:

$$Hg_2Cl_2 \text{ (s)} + 2e \rightarrow 2Hg \text{ (l)} + 2Cl^-$$

Properties of Umass Boston

Voltage conversions between different reference electrode
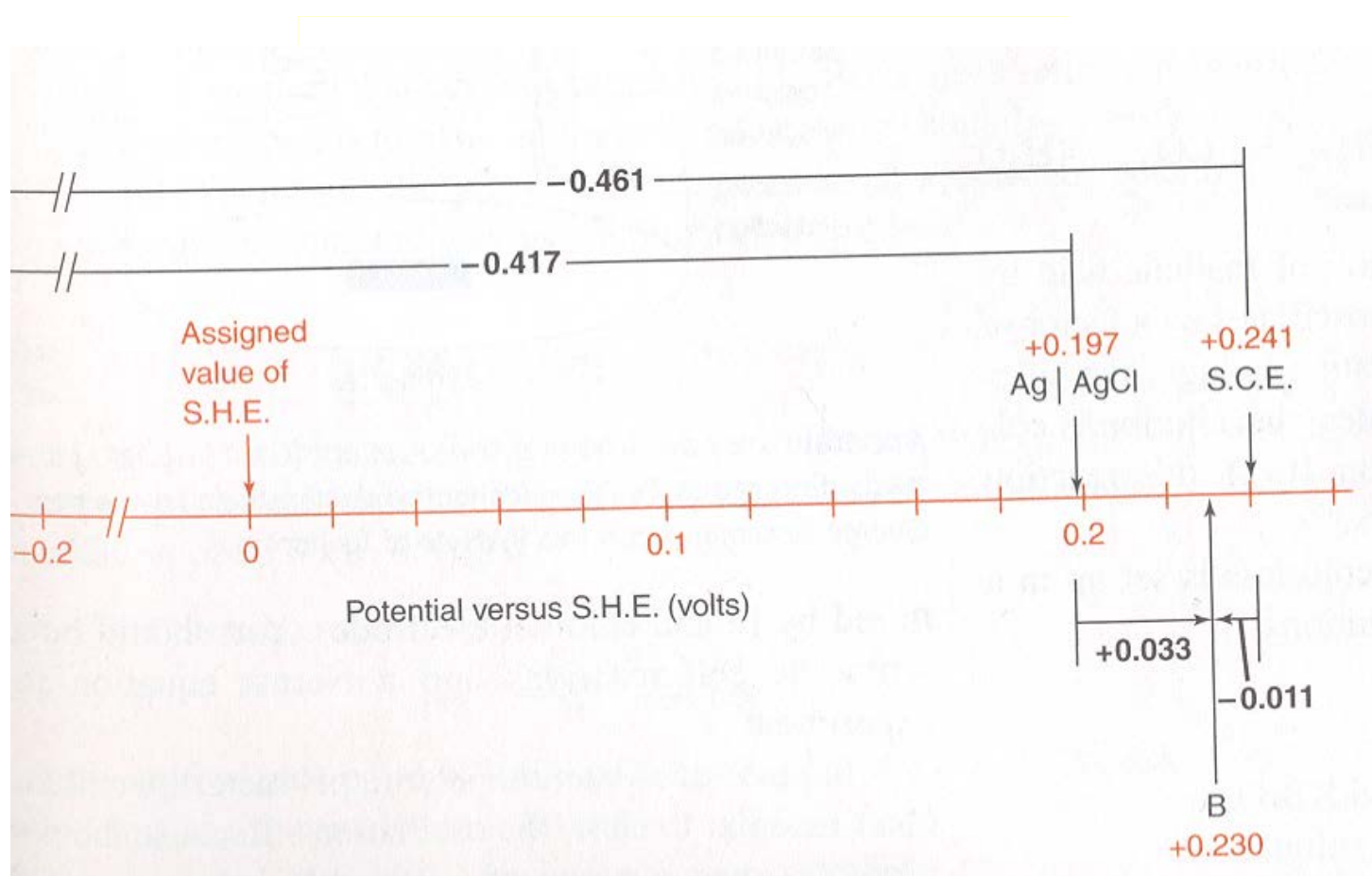
Liquid Junction Potential

- Due to the concentration gradient
  - Difference on chemical potential
  - Difference on the mobility of ions
- NOT a equilibrium process, but when it react steady state, can be treated as a constant

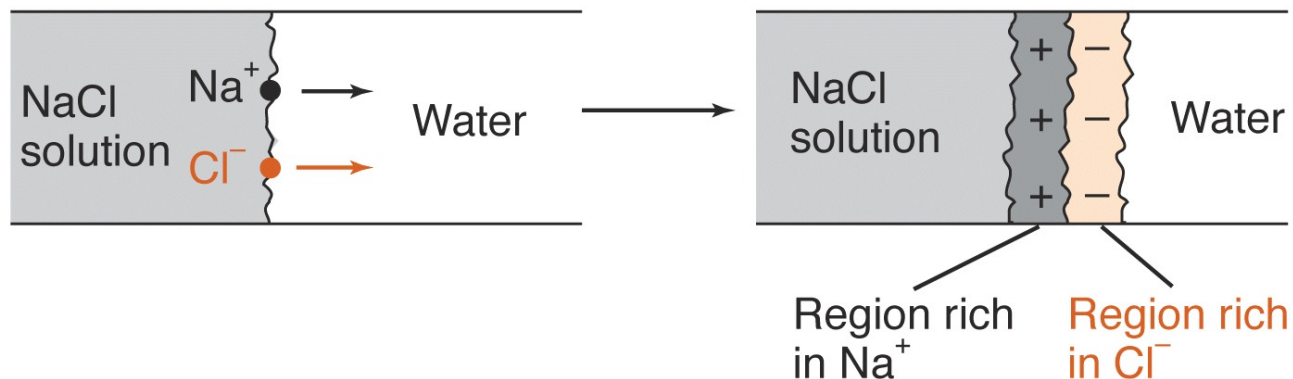KCl is normally used in the salt bridge to minimize the junction potential due to the fact that K^+ and Cl^+ have similar mobility

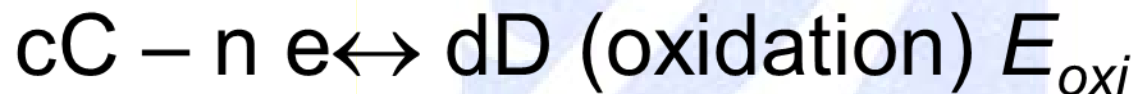| Ion	Mobility $[m^2/(s \cdot V)]^a$
H^+	36.30×10^{-8}
Rb^+	7.92×10^{-8}
K^+	7.62×10^{-8}
NH_4^+	7.61×10^{-8}
La^{3+}	7.21×10^{-8}
Ba^{2+}	6.59×10^{-8}
Ag^+	6.42×10^{-8}
Ca^{2+}	6.12×10^{-8}
Cu^{2+}	5.56×10^{-8}
Na^+	5.19×10^{-8}
Li^+	4.01×10^{-8}
OH^-	20.50×10^{-8}
$Fe(CN)_6^{4-}$	11.45×10^{-8}
$Fe(CN)_6^{3-}$	10.47×10^{-8}
SO_4^{2-}	8.27×10^{-8}
Br^-	8.13×10^{-8}
I^-	7.96×10^{-8}
Cl^-	7.91×10^{-8}
NO_3^-	7.40×10^{-8}
ClO_4^-	7.05×10^{-8}
F^-	5.70×10^{-8}
HCO_3^-	4.61×10^{-8}
$CH_3CO_2^-$	4.24×10^{-8}

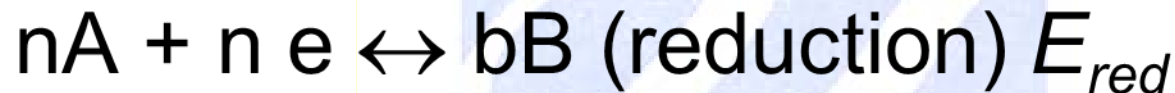**Table 15-1** Mobilities of ions in water at 25°C

a. The mobility of an ion is the terminal velocity that the particle achieves in an electric field of 1 V/m. Mobility = velocity/field. The units of mobility are therefore $(m/s)/(V/m) = m^2/(s \cdot V)$.

Thermodynamics

- Under the conditions of constant P and T
$(\triangle G)_{T,P} = -W_{non\text{-}expansion} = -nF\triangle E$
  Chemical energy   Electric Energy
$(\triangle G = \sum \mu_I$; μ is the chemical potential$)$

- For Reaction $aA + cC \leftrightarrow bB + dD$
$\triangle G = \triangle G^o + RTln([B]^b[D]^d/[A]^a[c]^c)$
$-nF\triangle E = -nF\triangle E^o + RTln([B]^b[D]^d/[A]^a[c]^c)$
$\triangle E = \triangle E^o - (RT/nF)ln\ ([B]^b[D]^d/[A]^a[c]^c)$
Nernst Equation

Nernst Equation

- Reaction $aA + cC \leftrightarrow bB + dD$ Can divided into

  $nA + n\ e \leftrightarrow bB$ (reduction) E_{red}

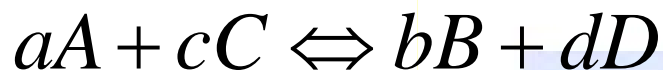 $cC - n\ e \leftrightarrow dD$ (oxidation) E_{oxi}

  $$E_{red} = E_{red}{}^0 - (RT/nF)\ln ([B]^b/[A]^a)$$

  $$E_{oxi} = E_{oxi}{}^0 - (RT/nF)\ln ([D]^d/[c]^c)$$

- $E = E^o - \dfrac{0.059}{n}\ln\dfrac{[B]^b}{[A]^a}$ *(when T=298.15K*

  or 25 degree

Equilibrium Constant

$$aA + cC \Leftrightarrow bB + dD$$

$$\Delta G = \Delta G^o + RT \ln(\frac{[B]^b [D]^d}{[A]^a [C]^c}) = \Delta G^o + RT \ln K$$

$$at \quad equilibrium: \quad \Delta G = 0$$

$$\Delta G^o = -RT \ln K = -nFE^o$$

$$E^o = \frac{RT}{nF} \ln K$$

Oxidation/reduction power

| Table 14-1 | Ordered redox potentials |

Oxidizing agent	Reducing agent	$E°$ (V)
$F_2(g) + 2e^- \rightleftharpoons 2F^-$		2.890
$O_3(g) + 2H^+ + 2e^- \rightleftharpoons O_2(g) + H_2O$		2.075
⋮		
$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$		1.507
⋮		
$Ag^+ + e^- \rightleftharpoons Ag(s)$		0.799
⋮		
$Cu^{2+} + 2e^- \rightleftharpoons Cu(s)$		0.339
⋮		
$2H^+ + 2e^- \rightleftharpoons H_2(g)$		0.000
⋮		
$Cd^{2+} + 2e^- \rightleftharpoons Cd(s)$		−0.402
⋮		
$K^+ + e^- \rightleftharpoons K(s)$		−2.936
$Li^+ + e^- \rightleftharpoons Li(s)$		−3.040

Oxidizing power increases ↑

Reducing power increases ↓

The system for Potentiometric methods

- Reference Electrode
  - Maintains a fixed potential
- Indicator electrode
  - Response to analyte activity
- Potential measuring device
  - Volt meter with high input impedance.
- E(cell)=E(indicator)-E(reference)+E(junction)

  E (cell)=Klog[ion]

Redox Electrode

- Electrochemically inert electrode e.g. Pt, Ag, Au, carbon etc.

- Function as an electrocatalyst and conductor for the redox reaction

- $Fe(CN)_6^{3-} + e \Leftrightarrow Fe(CN)_6^{4-}$

Indicator electrode

- Metal electrode – first kind

  e.g. Cu (Solid) $\Leftrightarrow$ Cu^{2+} (aqueous) + 2e

  $E = E^o - RT/nF \ln(1/[Cu^{2+}])$

- Not very selective

  Cu^{2+} $\Leftrightarrow$ Cu^{+}

  Cu^{2+} + I^{-} + e $\Leftrightarrow$ CuI (solid) etc
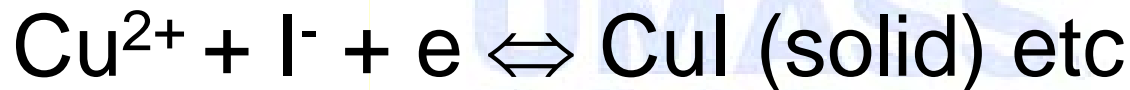
Indicator electrode

- Second kind: ions forms a precipitate and stable complex ion on metal
  $$AgCl\ (s) + e \Leftrightarrow Ag\ (s) + Cl^-$$
  $$E = 0.222 - 0.0591 \log[Cl]$$

- Good selectivity

- Microelectrode array for multiple detections

External Contact

10% Ag_2S in Graphite Epoxy

Ag^+ sensor

Encapsulated Electrode

shielded individually addressable

T^c Hg^{2+} Pb^{2+} As^{5+} Cd^{2+} H^+ Cr^{3+} O^{2-} As^{3+} Fe^{3+} Cr^{6+} S^{2-} etc.

Ag^+ Br^- REF I^- Cl^- etc.
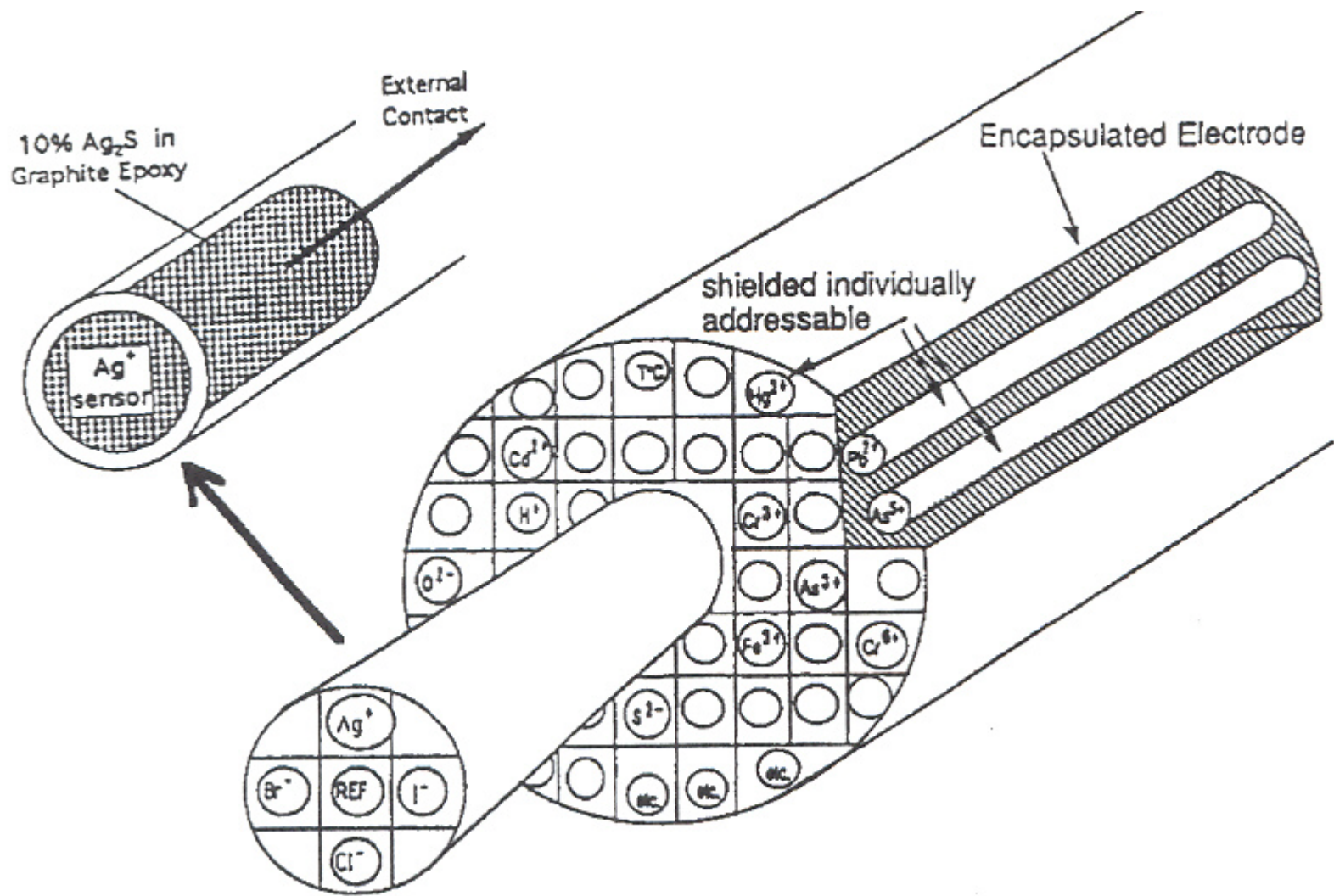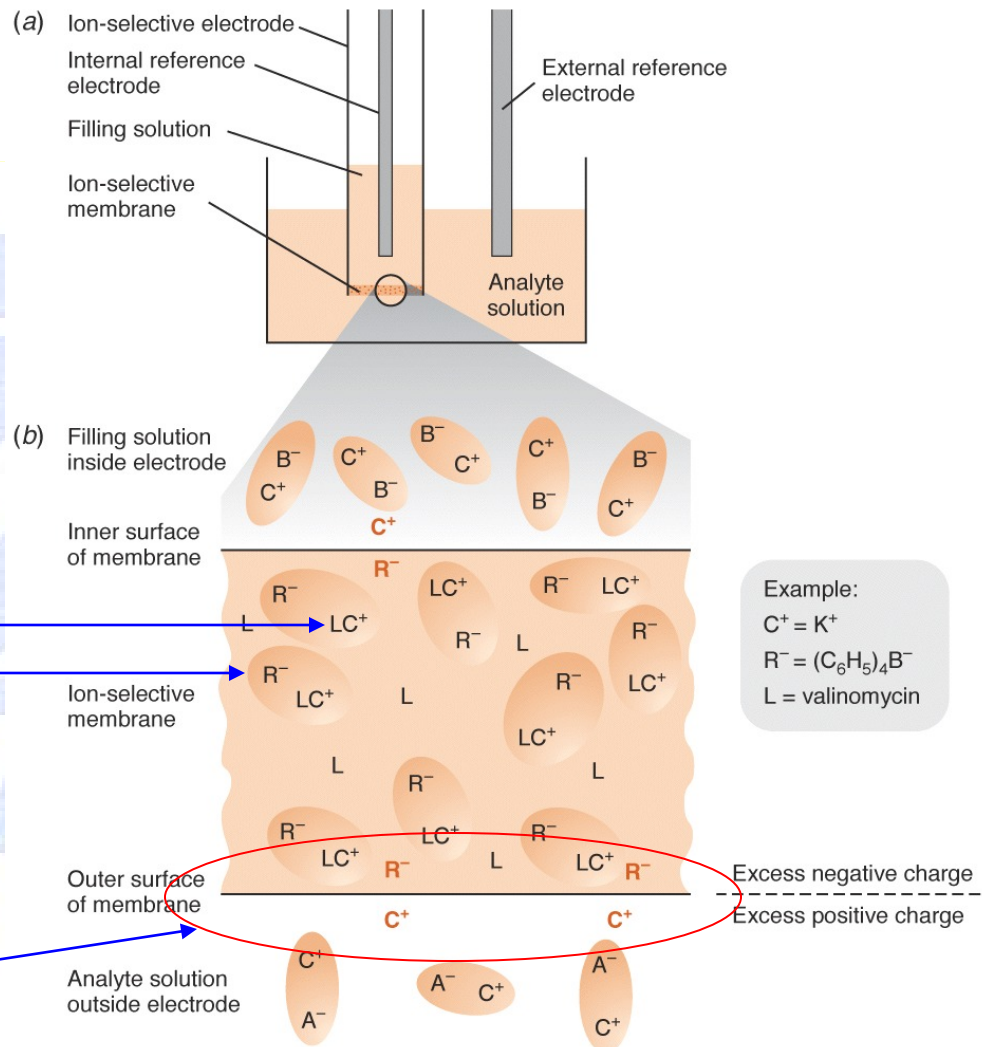
Ion selective membranes Electrode

- Is capable of binding only the intended ion.
- Minimal solubility.
- Electrical conductivity through ionic migration.
- Selective reactivity:
  selectively binding with target ion, three types of binding, ion-exchange, crystallization and complexation.

L is call ionophone, which is a ligand, only binds with C⁺. L is soluble in the membrane but insoluble in aqueous solution, so it will stay in the membrane

R⁻ is hydrophobic organic species, which is hardly soluble in water, so will stay inside the membrane

There are sufficient amount of C⁺ inside membrane and excess amount of L, so almost all C⁺ is attached with L. The concentration of C⁺ inside the membrane is constant. Why?

Very little amount of C⁺ diffuse out of the membrane and leave R⁺ behind. The space charge region will be created, the potential field is against the diffusion of C⁺. When it becomes equilibrium, a potential different will be created at the interface, which is proportional to the concentration of C⁺ in the solution.

(a) Ion-selective electrode
Internal reference electrode
Filling solution
Ion-selective membrane
External reference electrode
Analyte solution

(b) Filling solution inside electrode
Inner surface of membrane
Ion-selective membrane
Outer surface of membrane
Analyte solution outside electrode
Excess negative charge
Excess positive charge

Example:
$C^+ = K^+$
$R^- = (C_6H_5)_4B^-$
L = valinomycin

Thermodynamics for ion selective membrane

$at \quad the \quad outer \quad \operatorname{int} erface$

$$\Delta G = \Delta G_{solvation} - RT \ln(\frac{C_m}{C_o})$$

$at \quad equilibrium \quad \Delta G = -nFE_{out}$

$$\Delta G_{solvation} - RT \ln(\frac{C_m}{C_o}) + (-nFE_{out}) = 0 \; So \quad E_{out} = \frac{\Delta G_{solvation}}{nF} - (\frac{RT}{nF}) \ln(\frac{C_m}{C_o})$$

$$E = E_{outer} - E_{inner} = \frac{\Delta G_{solvation}}{nF} - (\frac{RT}{nF}) \ln(\frac{C_m}{C_o}) - E_{inner}$$

$$E = \frac{\Delta G_{solvation}}{nF} + (\frac{RT}{nF}) \ln(C_o) - (\frac{RT}{nF}) \ln(C_m) - E_{inner} \quad So \quad \boxed{E = Const + (\frac{RT}{nF}) \ln(C_m)}$$
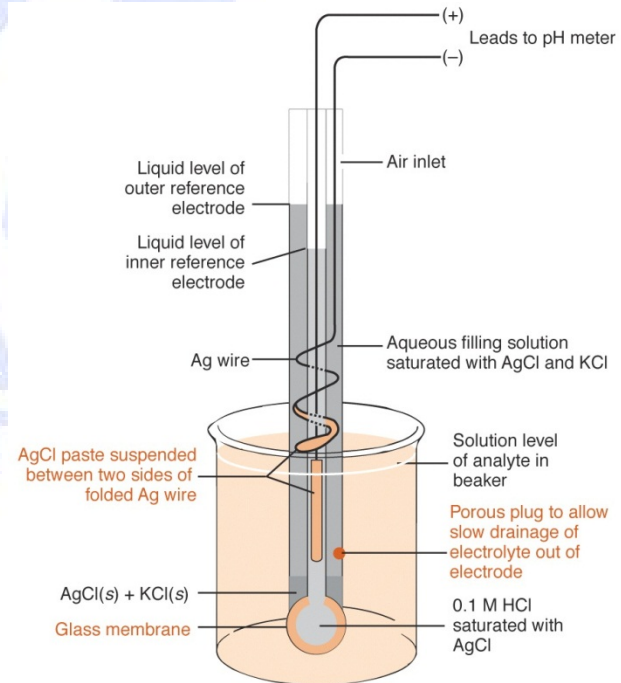
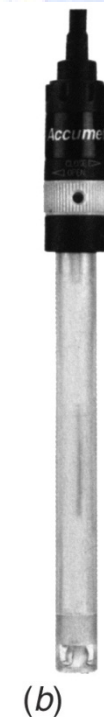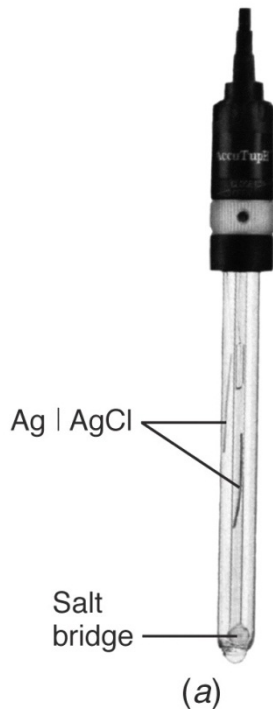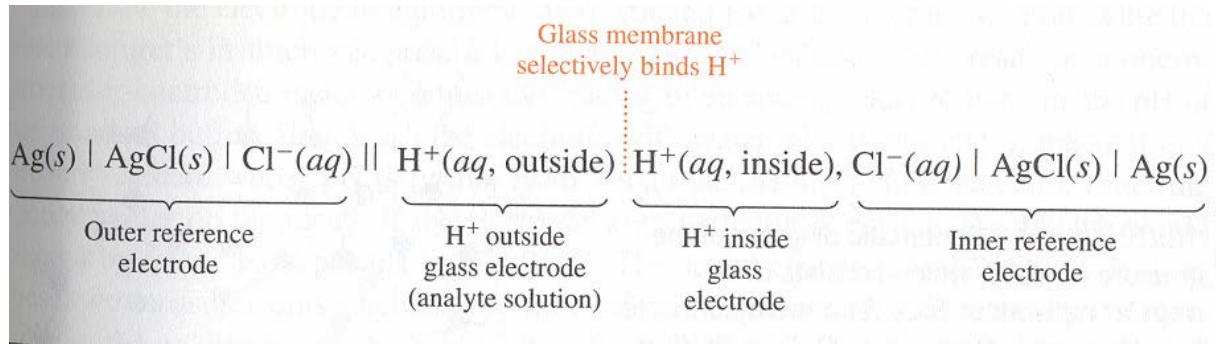# Configuration of ion selective membrane electrodes
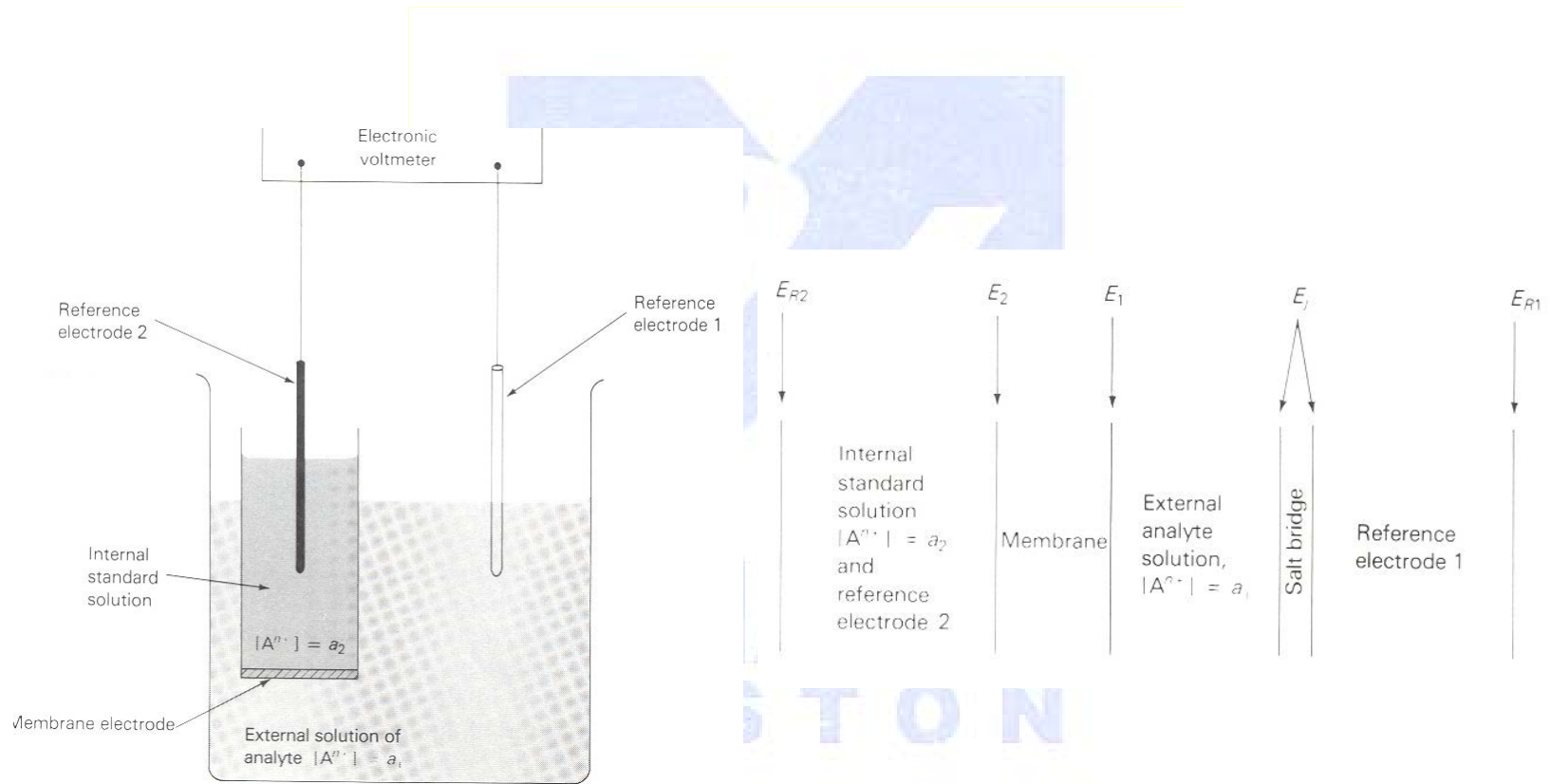
Requirement of indicator electrode

- **Sensitivity**

- **Selectivity**
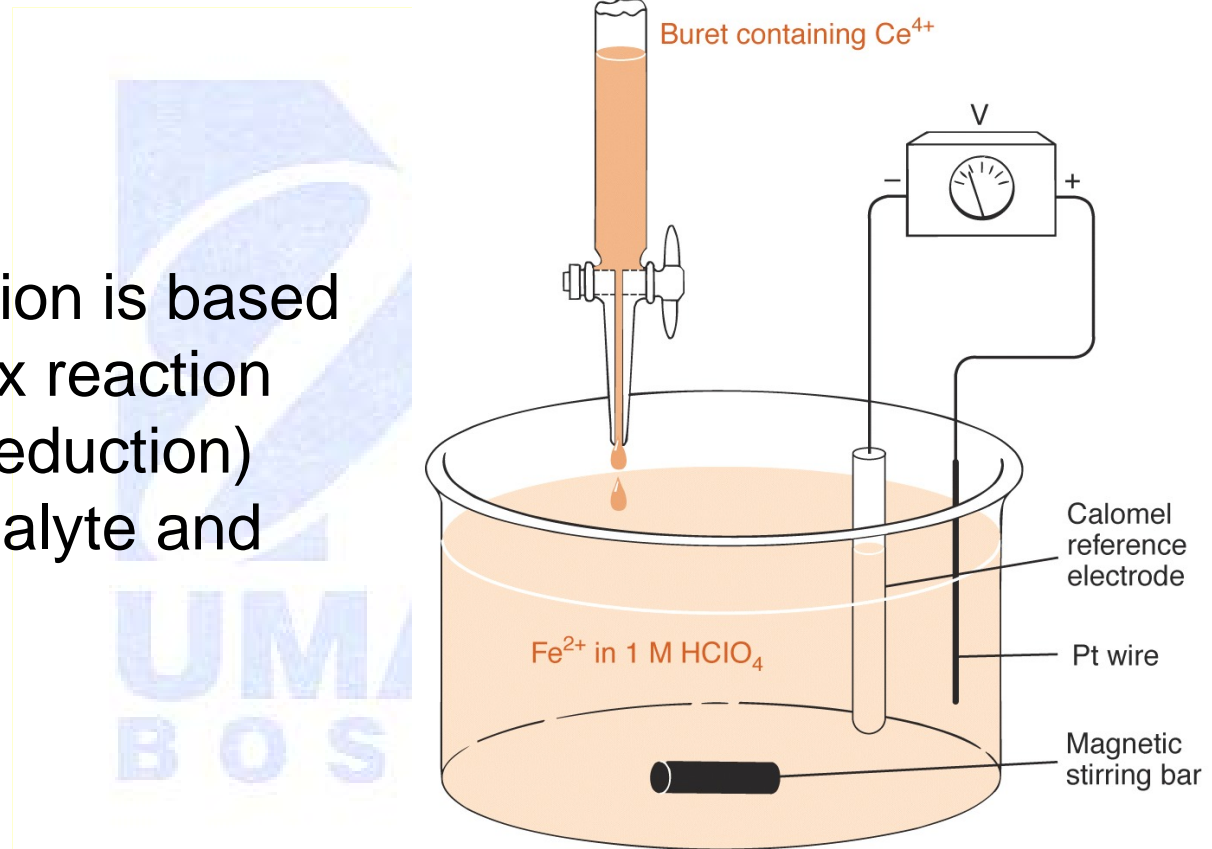 - **K=response to X/response to A**

pH Electrode – an example

$$\underbrace{Ag(s) \mid AgCl(s) \mid Cl^-(aq)}_{\substack{\text{Outer reference} \\ \text{electrode}}} \parallel \underbrace{H^+(aq, \text{outside})}_{\substack{\text{H}^+ \text{ outside} \\ \text{glass electrode} \\ \text{(analyte solution)}}} \vdots \underbrace{H^+(aq, \text{inside}),}_{\substack{\text{H}^+ \text{ inside} \\ \text{glass} \\ \text{electrode}}} Cl^-(aq) \mid AgCl(s) \mid Ag(s)}_{\substack{\text{Inner reference} \\ \text{electrode}}}$$

Glass membrane selectively binds H^+

Ag | AgCl

Salt bridge

(a)

Accumet

(b)

(+) Leads to pH meter (−)

Air inlet

Liquid level of outer reference electrode

Liquid level of inner reference electrode

Ag wire

AgCl paste suspended between two sides of folded Ag wire

Aqueous filling solution saturated with AgCl and KCl

Solution level of analyte in beaker

Porous plug to allow slow drainage of electrolyte out of electrode

AgCl(s) + KCl(s)

Glass membrane

0.1 M HCl saturated with AgCl

UMASS

Glass membrane – a ion selective membrane

10 nm   0.1 mm (10^5 nm)   10 nm

Internal solution ($\mathcal{A}_{H^+} \approx 0.1$)

External solution ($\mathcal{A}_{H^+}$ is variable)

Hydrated gel layer

Dry glass layer

Hydrated gel layer

(Exchange sites occupied by H^+ and Na^+)

(All sites occupied by Na^+)

(Exchange sites occupied by H^+ and Na^+)

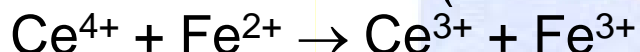Internal solution

External solution
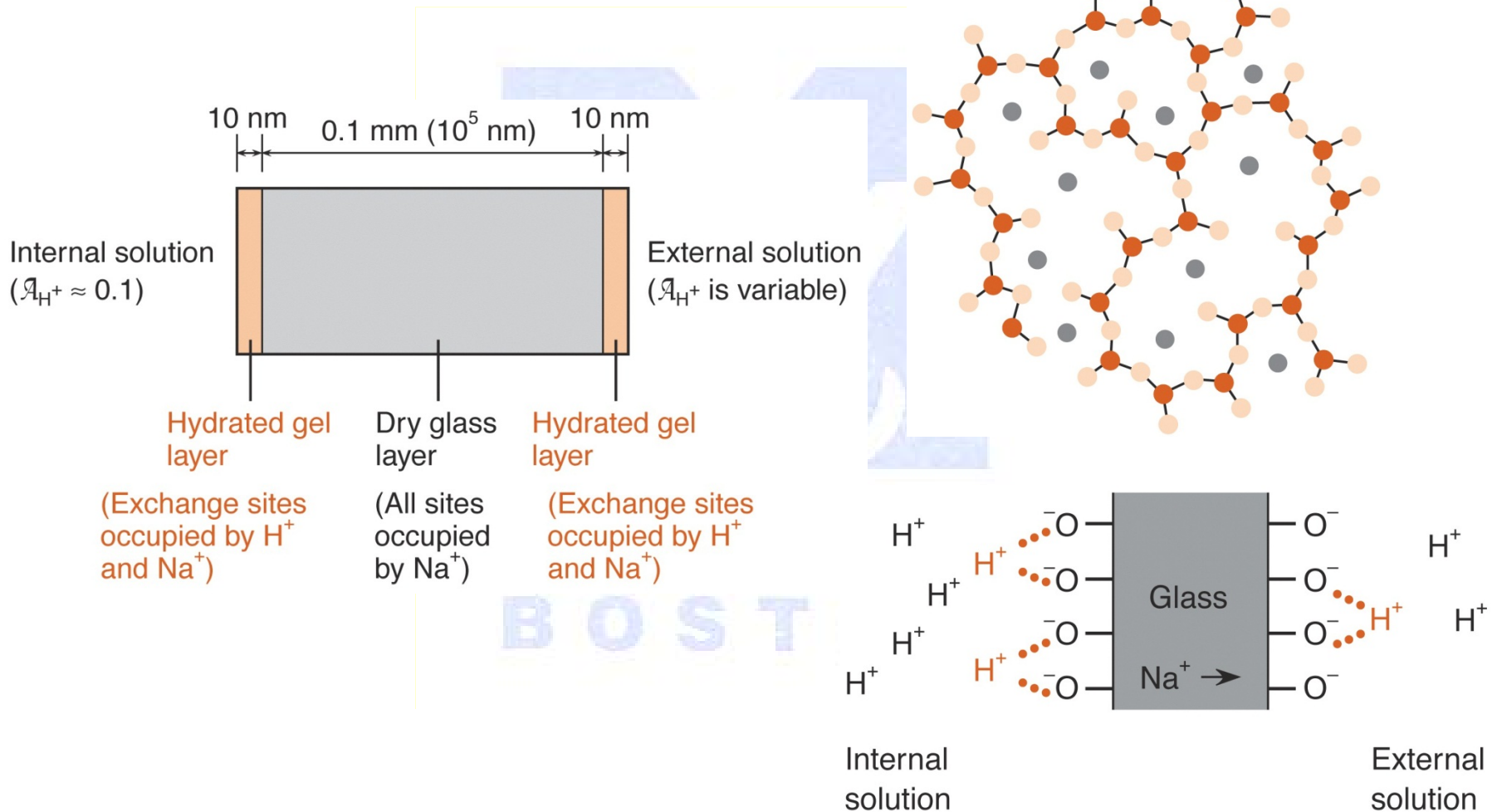
Redox Titration

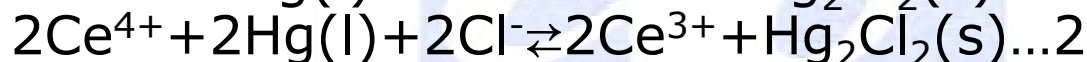- Redox titration is based on the redox reaction (oxidation-reduction) between analyte and titrant.

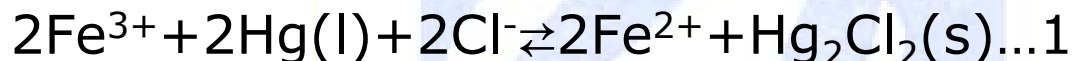Buret containing Ce^{4+}

V

− +

Calomel reference electrode

Pt wire

Magnetic stirring bar

Fe^{2+} in 1 M $HClO_4$

Electrochemical reactions

- Two electrochemical reactions
  - Titration reaction: (titrate ferrous with ceric)
    $Ce^{4+} + Fe^{2+} \rightarrow Ce^{3+} + Fe^{3+}$
  - Indication reaction: (determine end point)
    Reference (calomel): $2Hg(l)+2Cl^- \rightleftarrows Hg_2Cl_2+2e$
    Indicator 1 half reaction: $Fe^{3+}+e \rightleftarrows Fe^{2+}$
    Indicator 2 half reaction: $Ce^{4+}+e \rightleftarrows Ce^{3+}$

    $2Fe^{3+}+2Hg(l)+2Cl^- \rightleftarrows 2Fe^{2+}+Hg_2Cl_2(s)...1$
    $2Ce^{4+}+2Hg(l)+2Cl^- \rightleftarrows 2Ce^{3+}+Hg_2Cl_2(s)...2$
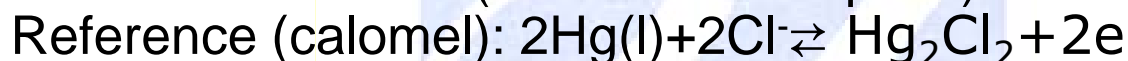
    $E_1=E^o-(RT/nF)\ln([Fe^{2+}]^2/[Fe^{3+}]^2[Cl^-]^2)$
    $E_2=E^o-(RT/nF)\ln([Ce^{3+}]^2/[Ce^{4+}]^2[Cl^-]^2)$

    $E_1 = E_2 =$ constant $-$ constant $\ln([Fe^{2+}]^2/[Fe^{3+}]^2)$
    $=$ constant $-$ constant $\ln([Ce^{3+}]^2/[Ce^{4+}]^2)$

Different reaction!!

The Shape of the titration curve

- Before the equivalent Point:
  Added Ce^{4+} will react with Fe^{2+} to form Fe^{3+} and Ce^{3+}. The indication potential on Pt electrode can be calculated by
  $E=0.526-0.059\log[Fe^{2+}]/[Fe^{3+}]$
  when $[Fe^{3+}]=[Fe^{2+}]$; $E=E^o$ (half way)

- At equivalent point: Stoichiometry amount of Fe^{2+} react with Ce^{4+}, so $[Fe^{3+}]=[Ce^{3+}]$ and $[Ce^{4+}]=[Fe^{2+}]$, combine them with $E_1=E_2$, one should get E=0.99 V (end point potential)

- After the equivalent point: the potential can be calculated from $2Ce^{4+}+2Hg(l)+2Cl^-$ $\rightleftarrows 2Ce^{3+}+Hg_2Cl_2(s)$, since there will be excess amount of Ce^{4+} in the solution

Equivalence point
(inflection point)

$E = E_+ - E_-$
$= E^0 (Fe^{3+} \mid Fe^{2+})$
$- E$ (S.C.E.)

$\frac{1}{2}V_e$

Potential (V versus S.C.E.)

V_{Ce4+} (mL)
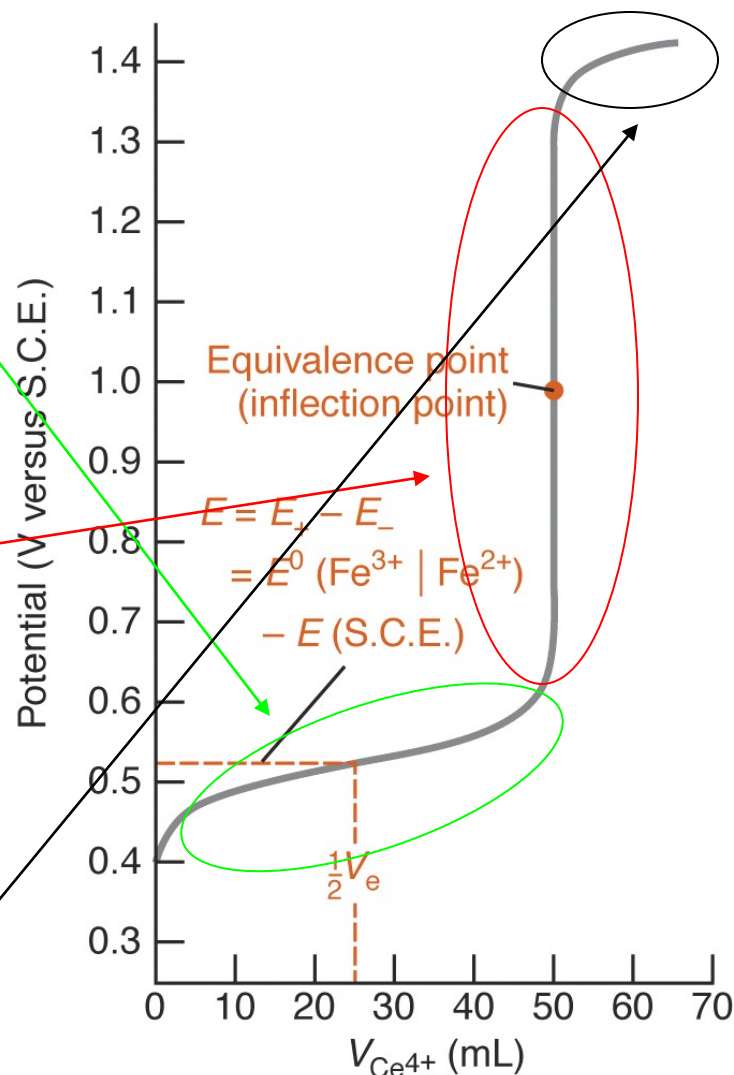
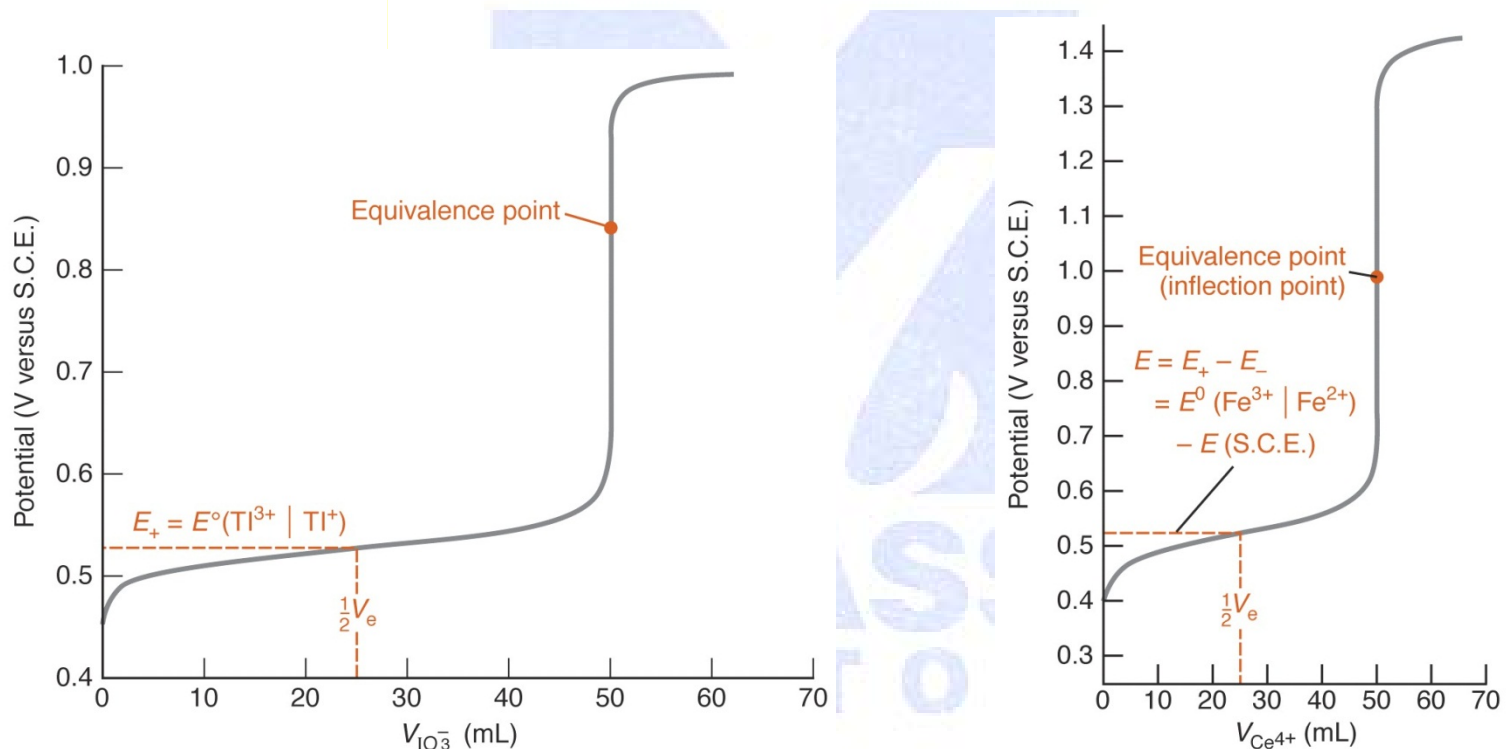# Dilution factor

- The indication potential is determined by the ratio of the redox couple e.g. E_1 =constant- constant $\ln([Fe^{2+}]^2/[Fe^3+]^2)$
- The shape of the titration curve will be independent of dilution

Position of the end point

- The position of the end point is related to the reaction stoichiometry

- Since the potential change near the end point is so steep, the position of end point will not introduce much error