

Electrodes and Potentiometry

Relating concentration to electrode potential

Class 1: Reversible metal/metal ion (ion exchanging metals bathed in electrolytes containing their own ions), for example Ag/Ag⁺.

Class 2: Reversible metal/metal ion with salt of the metal ion and excess anion X⁻, e.g. Ag/AgX/X⁻.

Class 3: Reversible metal/metal salt or soluble complex/second metal salt or complex and excess second cation, e.g. Pb/Pboxalate/Coaxalate/Ca²⁺, Hg/HgEDTA²⁻/CaEDTA²⁻/Ca²⁺.

http://www.iupac.org/publications/analytical_compendium/Cha08sec31.pdf

Faradic current: The current that is flowing through an electrochemical cell and is causing (or is caused by) chemical reactions (charge transfer) occurring at the electrode surfaces.

Classification of electrode types

Electrodes as half cells for electroanalytical techniques involve redox reactions (electrodes of zeroth, 1st, 2nd and 3rd kind).

Class 0: Inert metals used in oxidation-reduction electrolytic cells. Ideal inert materials exchange electrons reversibly with the electrolyte components and are not subject to oxidation or corrosion themselves, i.e., "ideally" polarizable electrodes.

At a *gas-electrode* one component of the redox couple is in the gaseous state.

Ion-selective electrodes (ISEs) based on thin films or selective membranes as recognitive elements, are equivalent to other half-cells.

Chemically modified electrodes (CME) form a separate group.

Capacitive current: The current flowing through an electrochemical cell that is charging/discharging the electrical double layer capacitance. This current does not involve any chemical reactions (charge transfer), it only causes accumulation (or removal) of electrical charges on the electrode and in the electrolyte solution near the electrode. There is always some capacitive current flowing when the potential of an electrode is changing, and the capacitive current is generally zero when the potential is constant.

Also called "non-faradaic" or "double-layer" current. Capacitive current can also flow at constant potential if the capacitance of the electrode is changing for some reason, e.g., change of electrode area or temperature.

Non-polarizable electrode: An electrode that is not easily polarizable. That is, the potential of the electrode will not change significantly from its equilibrium potential with the application of even a large current density. The reason for this behavior is that the electrode reaction is inherently fast (has a large exchange current density).

Polarizable electrode: An electrode that is easily polarizable. That is, the potential of the electrode will change significantly from its equilibrium potential with the application of even a small current density. The reason for this behavior is that the electrode reaction is inherently slow (has a small exchange current density).

An electrode with an applied potential different from the equilibrium potential of its red-ox system is a polarized electrode.

<http://www.corrosion-doctors.org/Dictionary/Dictionary-C.htm>

Overpotential: The difference in the electrode potential of an electrode between its equilibrium potential and its operating potential when a current is flowing. It represents the extra energy (an energy loss appearing as heat) to force the electrode reaction to proceed at a required rate

The operating potential of an anode is always more positive than its equilibrium potential.

The operating potential of a cathode is always more negative than its equilibrium potential.

Electrochemical Cells

Electrochemical cells are made up of at least two electrodes. The cell voltage E_{cell} is the difference of the electrode potentials of the two electrodes E_{el} .

During operation (short circuited), oxidation occurs at one electrode and reduction at the other.

The E_{el} is related to the concentration of the redox species involved in the electrode half reaction by the Nernst Equation.

Short circuit: Flow of electrons at electrodes, from one electrode to the other (spontaneously or otherwise).

Open circuit: No flow of electrons at the electrode interfaces.

Measurement of cell voltage with a potentiometer or high-impedance voltmeter; simply cell with the terminal disconnected.

Electrode potential (in general); Nernst equation for electrode calculates the propensity for a reduction reaction to occur when species are at a given set of concentrations. It is a measure of the *reducibility* of the species in solution

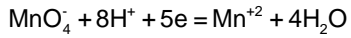
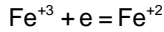
$$\begin{aligned} E_{half rxn} &= E_{el} = E_{el}^0 - \frac{RT}{nF} \ln(Q)_{el} \\ E_{rxn} &= E_{cell} = E_{cell}^0 - \frac{RT}{nF} \ln(Q)_{cell} \end{aligned}$$

Q_{el} = reaction quotient, half electrode reaction written as a reduction.

$$\text{oxidized} + \dots + ne = \text{reduced} + \dots$$

$$E_{el} = E_{el}^0 - \frac{RT}{nF} \ln \left\{ \frac{a_{reduced}^p \dots}{a_{oxidized}^q \dots} \right\} \quad Q_{el}$$

Use Nernst equation.



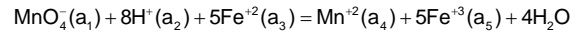
$$E_{\text{Fe}^{+3}/\text{Fe}^{+2}} = E_{\text{Fe}^{+3}/\text{Fe}^{+2}}^0 - \frac{RT}{F} \ln \frac{a_{\text{Fe}^{+2}}}{a_{\text{Fe}^{+3}}}$$

$$E_{\text{MnO}_4^-/\text{Mn}^{+2}} = E_{\text{MnO}_4^-/\text{Mn}^{+2}}^0 - \frac{RT}{5F} \ln \frac{a_{\text{Mn}^{+2}}}{a_{\text{MnO}_4^-} a_{\text{H}^+}^8}$$

E_{cell} measures the propensity of a reaction, where the species are at any nonstandard conditions.

$$E_{\text{rxn}} = E_{\text{cell}} = E_{\text{cell}}^0 - \frac{RT}{nF} \ln(Q)_{\text{cell}}$$

e.g.



$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{RT}{5F} \ln \left(\frac{a_{\text{Mn}^{+2}} a_{\text{Fe}^{+3}}^5}{a_{\text{MnO}_4^-} a_{\text{H}^+}^8 a_{\text{Fe}^{+2}}^5} \right)$$

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{RT}{5F} \ln \left(\frac{a_4 a_5^5}{a_1 a_2^8 a_3^5} \right)$$

Potentiometry

Electrode potential is related to the activities of electroactive species – indicator/test electrodes.

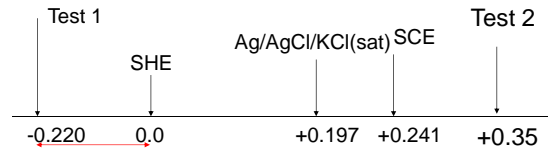
$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{RT}{nF} \ln \left(\frac{a_4 a_5^5}{a_1 a_2^8 a_3^5} \right)$$

Potentiometry relies on the measurement of 'test electrode' potential E_{el} , via E_{cell} to measure concentration or concentration variation. The electrode system is designed so that the conc. of species of interest is the variable and conc. all other are constant.

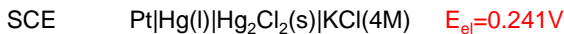
Practically electrode potentials are measured against a reference electrode not vs. SHE.

Ref Electrode || Test Electrode

Such measurements can be expressed in the SHE scale.

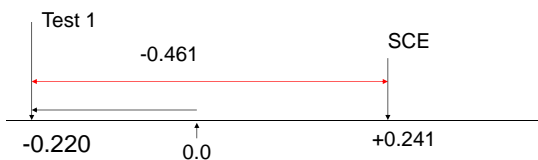


Such measurements can be expressed in the SHE scale.

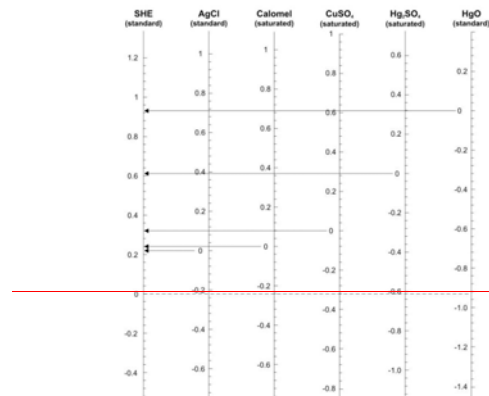


If E_{test} vs SCE = -0.461

$$E_{\text{test}} - (+0.241) = -0.461; \quad E_{\text{test}} = -0.461 - (-0.241) = -0.220$$

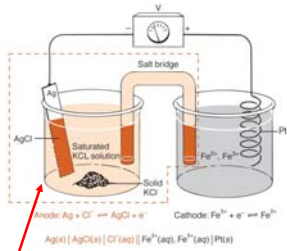


Conversion Between Reference Electrodes

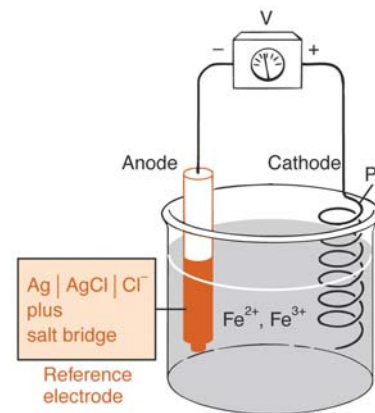
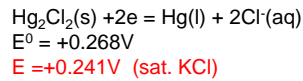
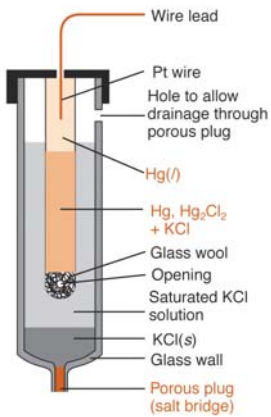
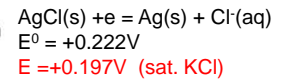
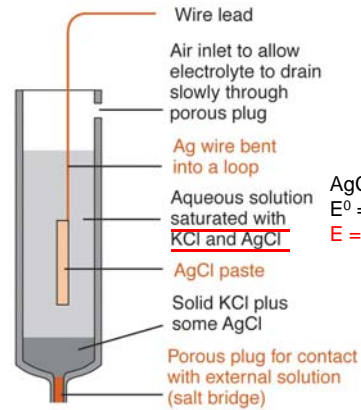


<http://www.corrosion-doctors.org/References/Pot-scales.htm>

$$E_{el} = E_{Fe^{2+}/Fe^{3+}}^0 - \frac{0.05916}{1} \log \frac{a_{Fe^{2+}}}{a_{Fe^{3+}}}$$



Reference electrode: electrode of which potential is constant (composition constant).



Junction Potential:

Two dissimilar phases brought to contact results in a charge separation.

- Metal1/metal2
- Metal/solution
- Solution1/solution2

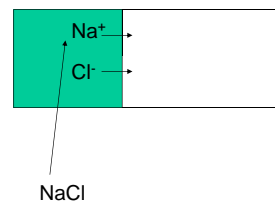
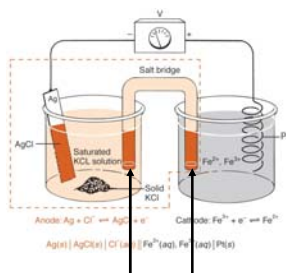


Table 15-1 Mobilities of ions in water at 25°C

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 ₃ CO ₂ ⁻	4.24×10^{-8}

^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) = m²(s · V)⁻¹.

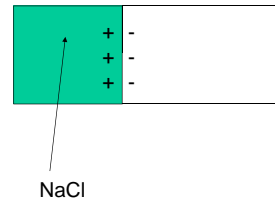
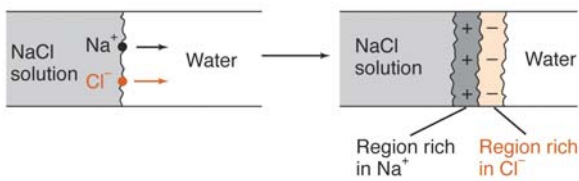
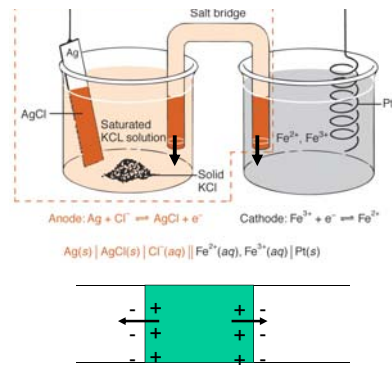


Table 15-2 Liquid junction potentials at 25°C

Junction	Potential (mV)
0.1 M NaCl 0.1 M KCl	-6.4
0.1 M NaCl 3.5 M KCl	-0.2
1 M NaCl 3.5 M KCl	-1.9
0.1 M HCl 0.1 M KCl	+27
0.1 M HCl 3.5 M KCl	+3.1

NOTE: A positive sign means that the right side of the junction becomes positive with respect to the left side.

Salt Bridge minimizes the net effect due to junction potentials



Electrode potential is related to the activities of species – indicator/test electrodes.

$$\left. \begin{aligned}
 E_{el} &= E_{Ag^+/Ag}^0 - \frac{0.05916}{1} \log \frac{1}{a_{Ag^+}} \\
 E_{el} &= E_{AgCl/Ag}^0 - \frac{0.05916}{1} \log a_{Cl^-} \\
 E_{el} &= E_{PbF_2/Pb}^0 - \frac{0.05916}{2} \log a_{F^-}^2
 \end{aligned} \right\} \text{Redox electrodes}$$

Ion-selective electrode (ISE)

An ISE is a transducer which converts the activity of a *specific ion dissolved in a solution* into an electrical potential which can be measured by a high impedance voltmeter (pH meter).

The voltage is theoretically dependent on the logarithm of the ionic activity, according to the Nernst Equation.

The sensing part of the electrode is usually made as an ion-specific membrane, and coupled to a external reference electrode (combination electrode).

Ion Selective Electrodes

$$E_{el} = k + \frac{0.05916}{z} \log a_{X^z}$$

Charge with sign

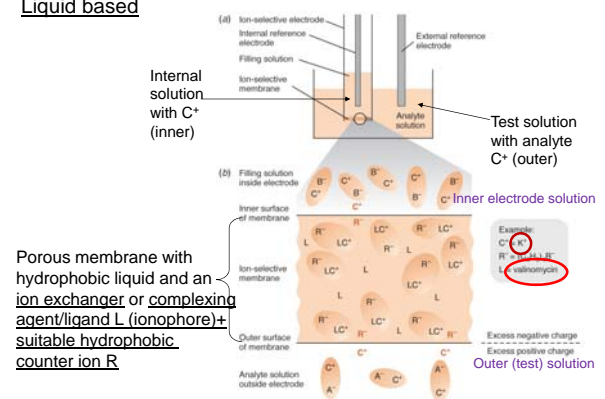
Nernstian behaviour

All electrodes are activity sensors, not concentration sensors.

Types of ion-selective membrane

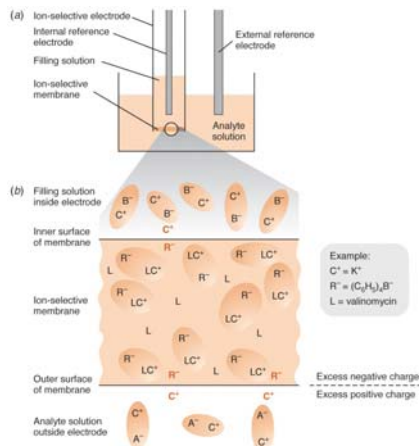
- Ion selective (exchange) membranes
- Glass membranes
- Crystalline membranes
- Compound electrodes
- Enzyme electrodes

Ion selective membranes for C⁺ (ions) Liquid based

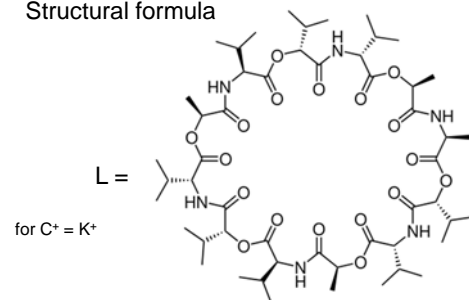


Porous membrane with hydrophobic liquid and an ion exchanger or complexing agent/ligand L (ionophore) + suitable hydrophobic counter ion R

a. Ion selective (exchange) membranes



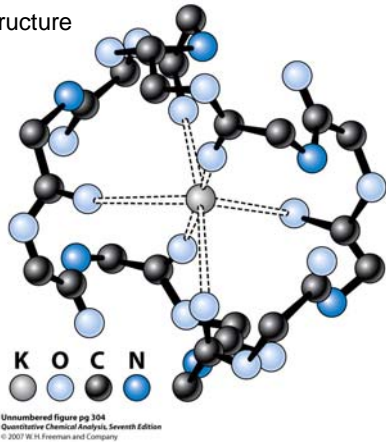
Structural formula



Valinomycin

<http://www.biochem.arizona.edu/classes/bioc62/462a/NOTES/LIPIDS/valin.html>

3D - Structure



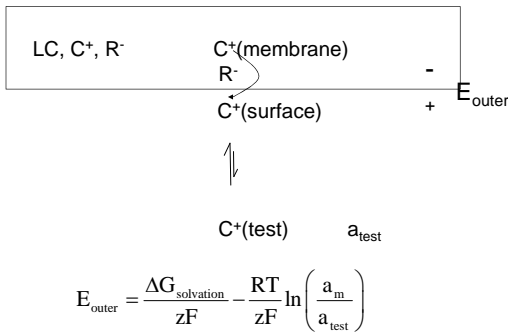
Ionophore (Ligand) L; counter ion R⁻
specific ion C⁺

Hydrophobic membrane

The ligand L is such it has a very high affinity for C⁺ ion.

This L⁻ + C⁺ = LC $K \gg 0$, not for other ions (Selectivity)

excess Un-complexed C in membrane



Free Energy changes:

$$\Delta G = \Delta G_{\text{solvation}} - RT \ln \left(\frac{a_m}{a_{\text{test}}} \right) + (-zFE_{\text{outer}})$$

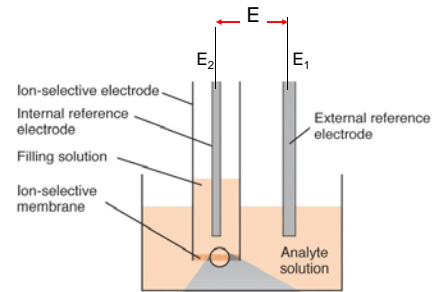
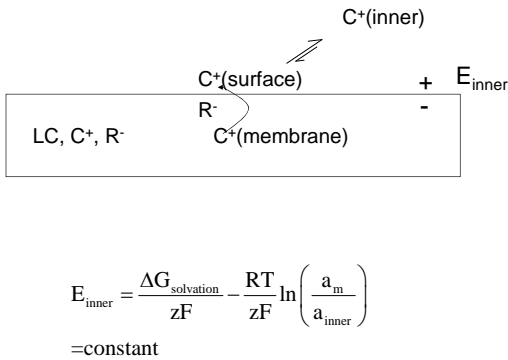
Accounts for the free energy change when species of varying activity diffuse

Free energy change due to charge imbalance

At equilibrium;

$$\Delta G = \Delta G_{\text{solvation}} - RT \ln \left(\frac{a_m}{a_{\text{test}}} \right) + (-zFE_{\text{outer}}) = 0$$

Upon rearrangement: $E_{\text{outer}} = \frac{\Delta G_{\text{solvation}}}{zF} - \frac{RT}{zF} \ln \left(\frac{a_m}{a_{\text{test}}} \right)$



$$E_2 \quad E_{\text{inner}} \quad E_{\text{outer}} \quad E_1$$

$$\text{Ref}_{\text{int}} / \text{C}^+(a_{\text{inner}}) / \text{C}^+(a_m) / \text{C}^+(\text{test}) / \text{Ref}_{\text{ext}}$$

$$E = (E_1 - E_2) + (E_{\text{outer}} - E_{\text{inner}})$$

$$E = E_{\text{outer}} - E_{\text{inner}} = \frac{\Delta G_{\text{solvation}}}{zF} - \frac{RT}{zF} \ln \left(\frac{a_m}{a_{\text{test}}} \right) - E_{\text{inner}}$$

All terms except a_{test} are constant for a given electrode configuration

$$E = k + \frac{RT}{zF} \ln(a_{\text{test}})$$

$$E = k + \frac{0.05916}{z_C} \log a_C$$

z_C = charge on the ion (with sign)

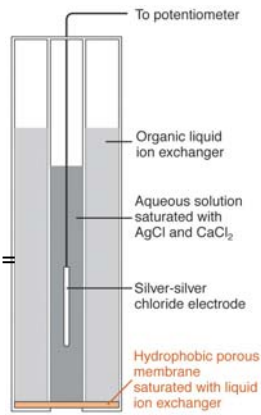
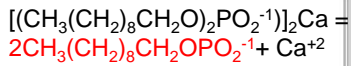
$$E = k + \beta \frac{0.05916}{z_C} \log a_C$$

Electromotive efficiency, $>0.98, =1$

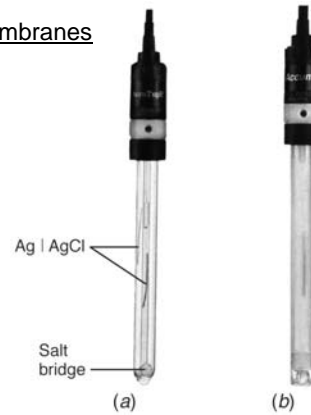
Example Ca - ISE

$$E = k + \beta \frac{0.05916}{2} \log a_{\text{Ca}^{+2}}$$

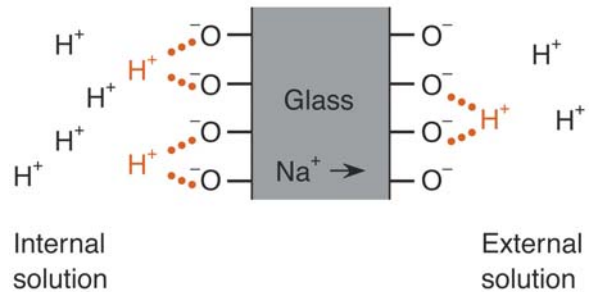
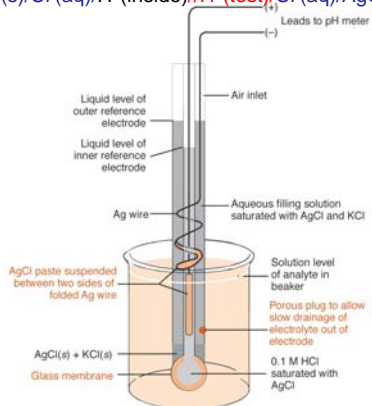
Calcium didecylphosphate



Glass membranes



$\text{Ag(s)}/\text{AgCl(s)}/\text{Cl}^-(\text{aq})/\text{H}^+(\text{inside})//\text{H}^+(\text{test})/\text{Cl}^-(\text{aq})/\text{AgCl(aq)}/\text{Ag(s)}$



Ag(s)/AgCl(s)/Cl⁻(aq)/H⁺(inside)//H⁺(test)/Cl⁻(aq)/AgCl(aq)/Ag(s)

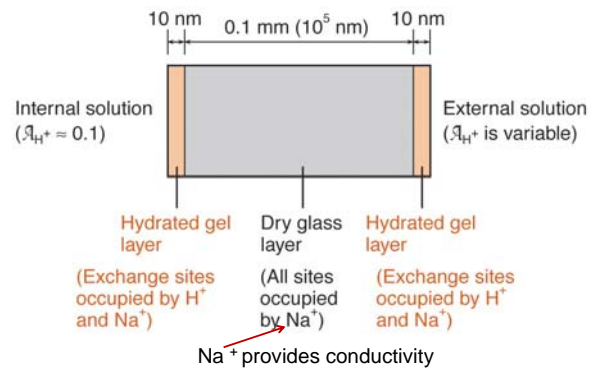
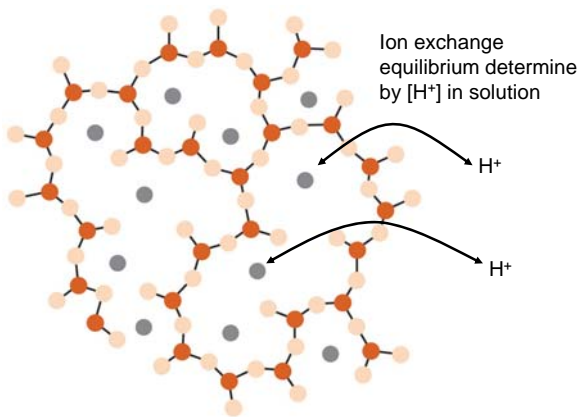
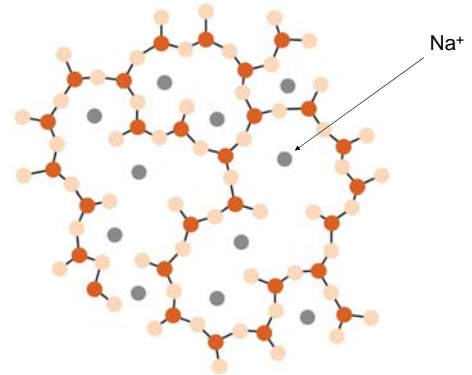
$$E = k + \beta \cdot 0.0592 \log a_{H^+}$$

$$E = k - \beta \cdot 0.0592 \text{ pH}$$

↑
Electromotive efficiency, $\beta > 0.98, \approx 1$

Calibration determines k and β

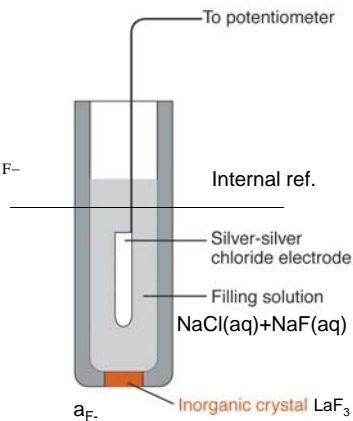
Non-crystalline nature of glass



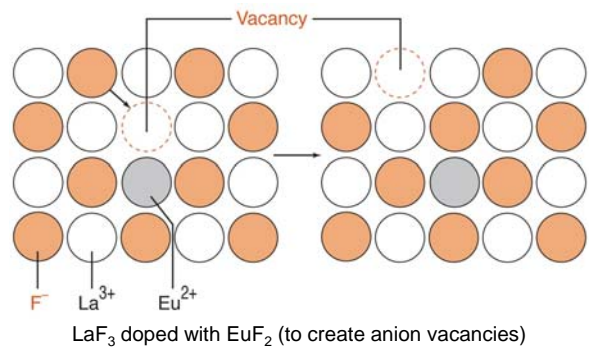
Crystalline membranes

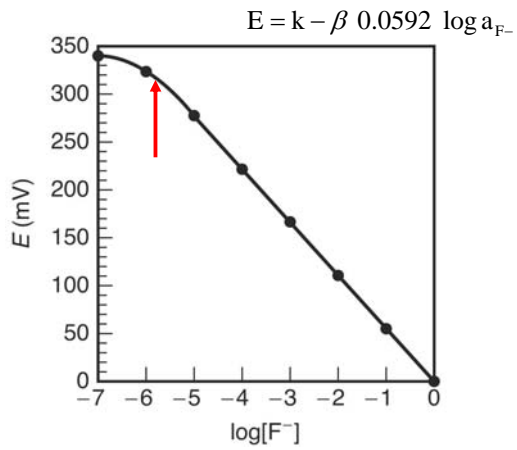
Fluoride ISE

$$E = k - \beta \cdot 0.0592 \log a_{F^-}$$



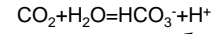
Conductance within crystal because of ions jumping into vacant sites





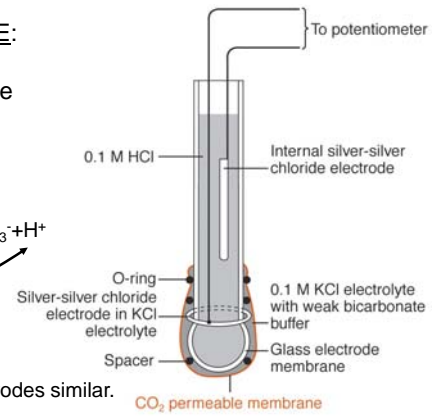
Compound ISE:

CO₂ - electrode



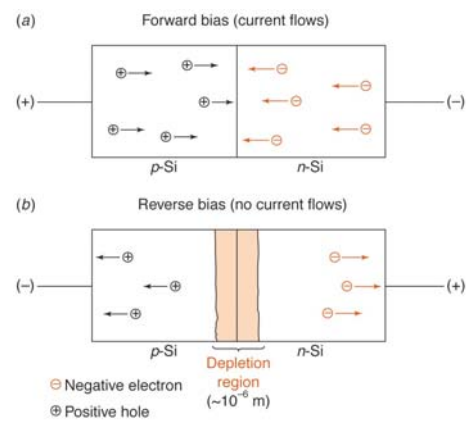
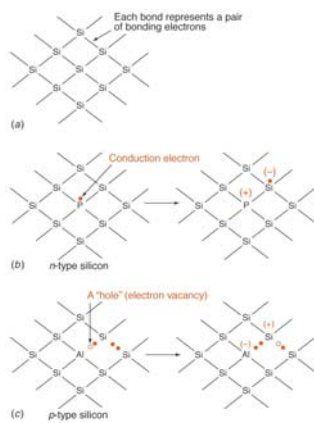
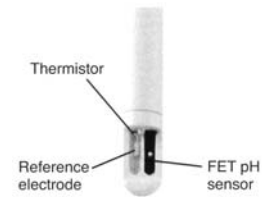
$P_{CO_2} \leftrightarrow pH$

NH₃, SO₂ electrodes similar.

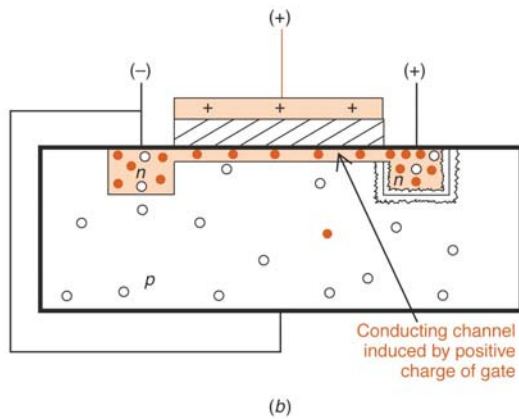
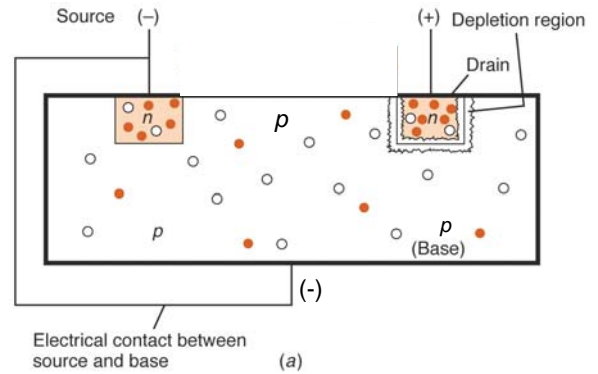


ISFET

Ion-sensitive field effect transistor measures ion concentrations in solution.



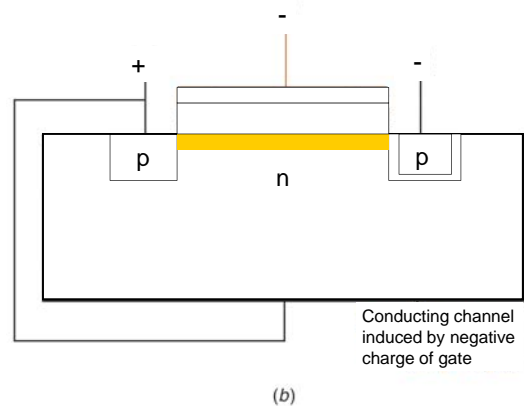
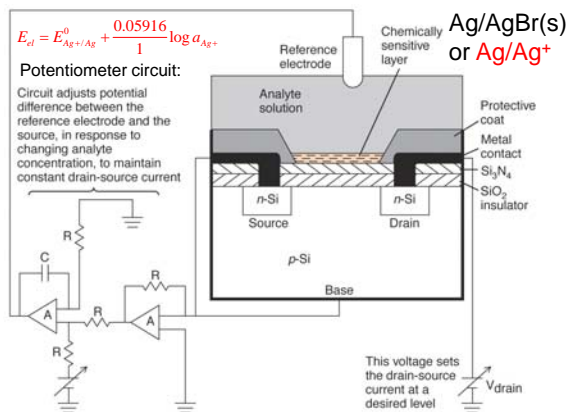
p type and n type semiconductors are made from a common base material with different concentrations of p sites and n sites.

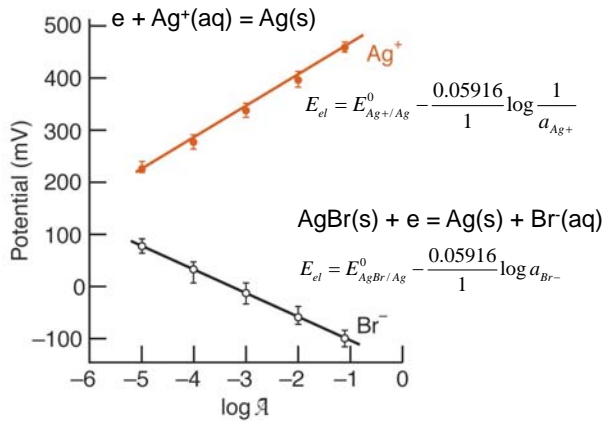


ISFET

Here, the electrode associated with the “test solution” serves as the gate. A voltage developed at the gate due to ions ‘controls’ the gate, thereby sensing the ion concentration.

The current through the conducting channel of the transistor will change in accordance with the potential created at the chemically sensitive layer (electrode). The potential at the electrode is dependent of the activity/concentration of the ions via Nernst relationship.





Limitations of available materials limits the responses of ISE's solely to the desired ion.

Generally at higher concentration regions ISE's follow the ideal equation but at very low concentrations the interferences *from other ions, j*, come into prominence (which of course are present at all concentrations but negligible at higher concentrations).

$$E = k + \beta \frac{0.05916}{z_A} \log a_A$$

$$E = k + \frac{0.05916}{z_A} \log [a_A + \sum_j k_{A,j} a_j^{z_A/z_j}]$$

Potentiometric selectivity coefficient:

Principal ion sensed = A, interfering ion = X

Coefficient, $k_{A,X}$, which defines the ability of an ion-selective electrode to distinguish a particular ion A from another (X). It is evaluated by following the response of the ion-selective electrode in mixed solutions of the primary ion, A, and interfering ion, X (fixed interference method) or less desirable, in separate solutions of A and X (separate solution method).

The activities of the primary ion, A, and the interfering ion, X, at which $k_{A,X}$ is determined should always be specified.

The smaller the value of $k_{A,X}$ pot the greater the electrode's preference for the principal ion, A.

Selectivity Ratio

$$k_{A,X} = \frac{\text{response to X}}{\text{response to A}}$$

Value of $k_{A,X}$ determines the extent of interference.

For every ISE the $k_{A,X}$ values for interfering ions X are made available by the manufacturers.

Nikolski Eiseman Equation :

An extension of the Nernst equation which relates the electrode potential to the activity of *all the contributing ions*, A, X, Y, .. to the ISE potential in the sample (i.e. all interfering ions).

It is the same as the Nernst type equation but with $\log a_A$ replaced by;

$$\log [a_A + k_{A,X}(a_X)^{z_A/z_X} + k_{A,Y}(a_Y)^{z_A/z_Y} + \dots]$$

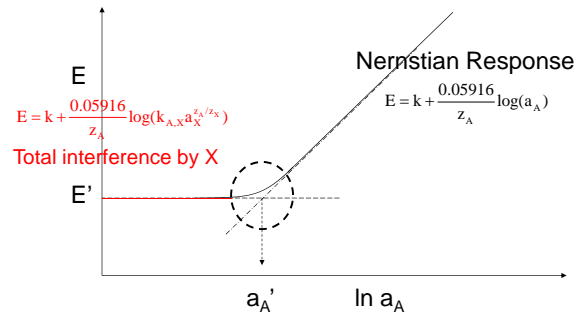
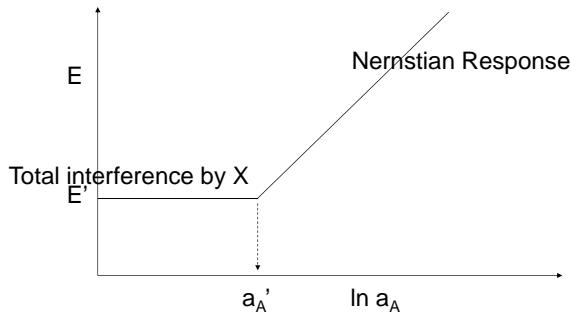
$$E = k + \frac{0.05916}{z_A} \log [a_A + \sum_j k_{A,j} a_j^{z_A/z_j}]$$

↑
=0, ideally

Determination of selectivity ratio:

Run a series of measurements of E in solutions where the activity of the interferent X is known, a_X , and held constant, but activity of A systematically changed.

Plot E vs $\ln(a_A)$.



Applied to the point of intersection;

E' interpretable as if A alone is present or X alone is present.

$$E' = k + \frac{0.05916}{z_A} \log[a'_A]$$

$$E' = k + \frac{0.05916}{z_A} \log[k_{A,X} a_X^{z_A/z_X}]$$

$$a'_A = k_{A,X} a_X^{z_A/z_X}$$

$$k_{A,X} = \frac{a'_A}{a_X^{z_A/z_X}}$$

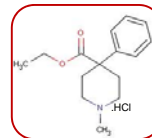
Table 15-5 Properties of solid-state ion-selective electrodes

Ion	Concentration range (M)	Membrane material	pH range	Interfering species
F ⁻	10 ⁻⁶ -1	LaF ₃	5-8	OH ⁻ (0.1 M)
Cl ⁻	10 ⁻⁴ -1	AgCl	2-11	CN ⁻ , S ²⁻ , I ⁻ , S ₂ O ₃ ²⁻ , Br ⁻
Br ⁻	10 ⁻⁵ -1	AgBr	2-12	CN ⁻ , S ²⁻ , I ⁻
I ⁻	10 ⁻⁶ -1	AgI	3-12	S ²⁻
SCN ⁻	10 ⁻⁵ -1	AgSCN	2-12	S ²⁻ , I ⁻ , CN ⁻ , Br ⁻ , S ₂ O ₃ ²⁻
CN ⁻	10 ⁻⁶ -10 ⁻²	AgI	11-13	S ²⁻ , I ⁻
S ²⁻	10 ⁻⁵ -1	Ag ₂ S	13-14	

Table 15-6 Properties of liquid-based ion-selective electrodes

Ion	Concentration range (M)	Carrier	Solvent for carrier	pH range	Interfering species
Ca ²⁺	10 ⁻⁵ -1	Calcium didecylphosphate	Diethylphenylphosphonate	6-10	Zn ²⁺ , Pb ²⁺ , Fe ²⁺ , Cu ²⁺
K ⁺	10 ⁻⁶ -1	Valinomycin	Diethylsebacate	4-9	Rb ⁺ , Cs ⁺ , NH ₄ ⁺
NO ₃ ⁻	10 ⁻⁵ -1	Tridodecylhexadecylammonium nitrate	Octyl-2-nitrophenyl ether	3-8	ClO ₄ ⁻ , I ⁻ , ClO ₃ ⁻ , Br ⁻ , HS ⁻ , CN ⁻
ClO ₄ ⁻	10 ⁻⁵ -1	Tris(substituted 1,10-phenanthroline) iron(II) perchlorate	4-10	I ⁻ , NO ₃ ⁻ , Br ⁻	
BF ₄ ⁻	10 ⁻⁵ -1	Tris(substituted 1,10-phenanthroline) nickel(II) tetrafluoroborate	2-12	NO ₃ ⁻	

Table II. Potentiometric selective coefficients K_{ij}^{pot} for the pethidine selective electrode.



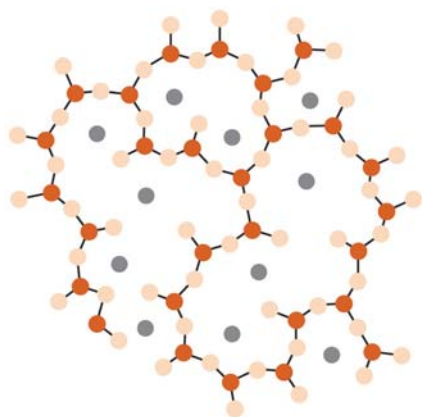
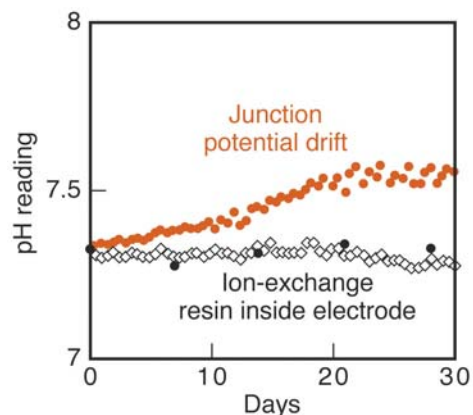
Interference	K_{ij}^{pot}	Interference	K_{ij}^{pot}
CaCl ₂	3.47×10 ⁻³	Cinchonine	1.62
MgSO ₄	5.05×10 ⁻³	Procaine	0.52
K ₂ C ₂ O ₄	7.16×10 ⁻³	Caffeine	2.95×10 ⁻²
(NH ₄) ₂ SO ₄	2.43×10 ⁻³	Acetophenetidine	0.17
NaHSO ₄	0.17	Theobromine	3.27×10 ⁻²
Na ₂ CO ₃	3.86×10 ⁻³	Theophylline	9.64×10 ⁻²
Na ₂ SO ₃	5.04×10 ⁻³	8-hydroxyquinoline	5.89×10 ⁻²
Hg(NO ₃) ₂	1.88×10 ⁻³	Diazepam	4.71×10 ⁻²
KNO ₃	2.94×10 ⁻²	DL-Alanine	0.49
H ₂ C ₂ O ₄	4.76×10 ⁻²	Cystein	0.74
Na ₂ S ₂ O ₃	1.79×10 ⁻³	Benzoic acid	0.32
V _{iso}	4.36×10 ⁻²	Berberine	3.65×10 ⁻²
V _{iso}	1.96×10 ⁻²	Picric acid	0.54
Sodium citrate	1.77×10 ⁻²	Fentanyl	4.61
Morphine HCl	4.16×10 ⁻²	Thebaine	2.58
Anisodamine	5.93		

pH Electrodes - other issues:

Accuracy of standards limits the accuracy of calibration and hence the accuracy of measurements. (true for all ISE)

Junction potential – arises if the ionic concentrations on either side of 'junction' is dissimilar. Calibration accounts for it but not if 'test' solution ionic composition is different to that of the 'calibration standard'.

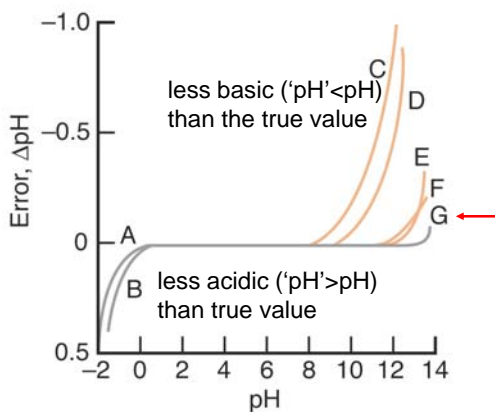
Junction potential drift – Ag/AgCl(s)/KCl (satd) reference KCl is saturated with AgCl as well; AgCl_4^{-3} , AgCl_3^{-2} . As KCl solution dilutes in 'test' region, AgCl ppts drifting 'pH'.



Alkaline (sodium) error – At low $[\text{H}^+]$ (highly basic) and in the presence of high $[\text{Na}^+]$ the electrode responds to Na^+ leading to an *apparent lower pH* than what it is.

$$E = k + \frac{0.05916}{1} \log[a_{\text{H}^+} + k_{\text{H}^+, \text{Na}^+} a_{\text{Na}^+}]$$

Acid error – At high $[\text{H}^+]$ and the hydration layer sites saturates with H^+ and would not respond to $[\text{H}^+]$ changes leading to an *apparent higher pH* than what it is.



Equilibration time – response of electrodes to changing environments are not instantaneous. there is a finite 'response time'.

Differential hydration of glass on either sides leads to asymmetry potential – (the potential developed across the glass membrane with identical solutions on both sides; term used when comparing glass electrode potential in $\text{pH} = 7$ buffer).

Calibration temperature and measurement temperature must be the same.

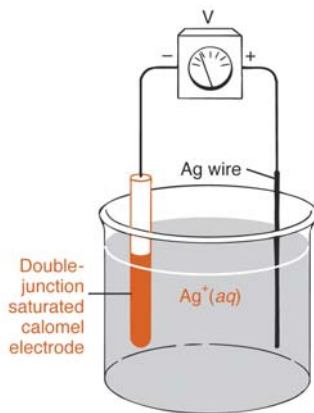
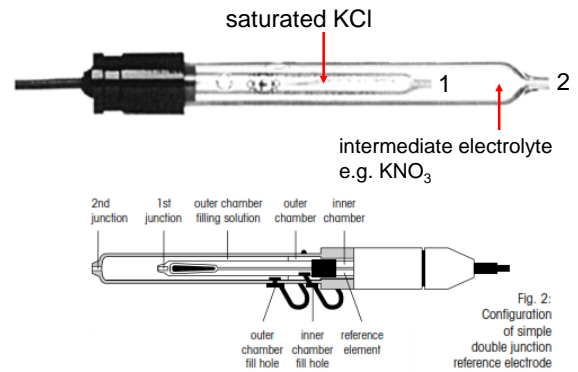
A double junction reference electrode minimizes contamination of the 'test' solution by KCl.

Often, Cl⁻ (from KCl) is the electrolyte in reference electrode. A small amount of KCl flow through the junction produces a significant [Cl⁻] in the test solution.

A double junction reference has two junctions. The first separates the reference electrode from an intermediate solution. This solution is then isolated from the test solution by a second junction.

The intermediate solution is generally less conductive than KCl; the impedance of a double junction reference is higher than that of a single junction electrode.

Double junction reference electrode.



Often the 'test' solution ionic composition is different to that of the 'calibration standard'.

To negate this error when [X] measured using an X-ISE standard addition method is used; single addition method:



Start $V_0, c_x \rightarrow E_1$
 Add V_s of conc. $c_s \rightarrow E_2$
 Measure E each time

Single addition method:

$$E = k + \frac{0.05916}{z_C} \log a_c$$

k includes E_{ref} , junction potentials

$$E_1 = k + S \log a_x$$

$$E_2 = k + S \log \frac{V_0 a_x + V_s a_s}{V_0 + V_s}$$

$$E_2 - E_1 = k + S \log \frac{V_0 a_x + V_s a_s}{V_0 + V_s} - k - S \log a_x$$

$$= S \log \frac{V_0 a_x + V_s a_s}{V_0 + V_s} \frac{1}{a_x}$$

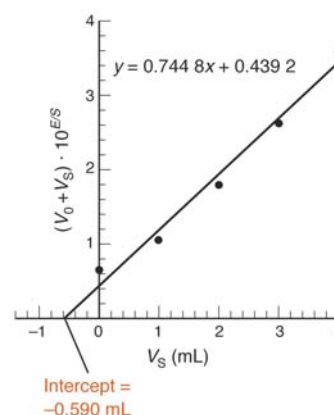
$$= S \log \frac{V_0 c_x + V_s c_s}{V_0 + V_s} \frac{1}{c_x}$$

Graphical Method:

$$E = k + S \log \frac{V_0 a_x + V_s a_s}{V_0 + V_s}$$

Rearrangement;

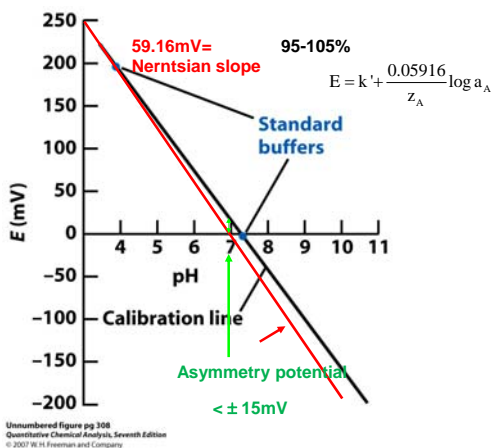
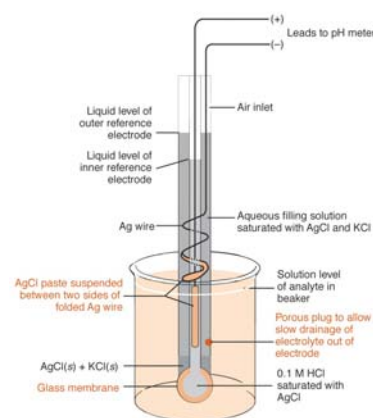
$$\underbrace{(V_0 + V_s) 10^{\frac{E}{S}}}_{\substack{\uparrow \\ \text{X-intercept} = -\frac{V_0 c_x}{c_s}}} = 10^{\frac{k}{S}} V_0 c_x + 10^{\frac{k}{S}} V_s c_s$$



Potentiometry

Relating concentration to electrode potential.

Measuring potential without drawing a current from the electrochemical (Galvanic) cell.



Asymmetry potential

For an ideal pH electrode the potential difference between the reference and measuring electrode is 0mV at pH 7. As the ideal electrode doesn't exist the deviation of a few mV at pH 7 that is found with real electrodes is called the asymmetry potential.

It is a measure of the performance of the reference electrode - if the asymmetry potential > ± 15mV, it is indicative of problems with the reference electrode such as contaminated electrolyte or reference element poisoning.

Sample Ionic Strength – The total ionic strength of a sample affects the activity coefficient of ions and that it is important that this factor stay constant throughout the calibration and at the measurement stage.

It is accomplished by the addition of an ionic strength adjuster (TISAB). Adjusted μ is large, compared to the ionic strength of the sample. TISAB increases the ionic strength of the solution making the ionic strength practically a constant. It makes the linear correlation between the $\log C_{\text{analyte}}$ and the measured voltage.

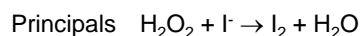
$$E = k' + \frac{0.05916}{z_A} \log C_A$$

Use a separate reference and measuring electrode with an auxiliary salt bridge containing a non-aqueous electrolyte filling solution.

Or a standard pH electrode may be used providing the following steps are performed:

Select an electrode with a low resistance membrane and a free flowing diaphragm.

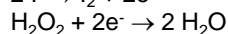
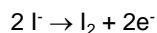
Use an electrode containing a non-aqueous filling solution (e. g. saturated LiCl in ethanol for non-polar solvents or LiCl in glacial acetic Acid for polar solvents).



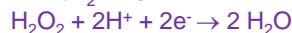
I^- (ON changes; $-1 \rightarrow 0$).

O (ON changes; $-1 \rightarrow -2$).

ΔON



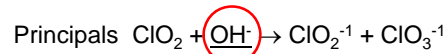
'CB'



CB +MB



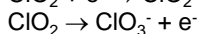
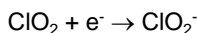
Overall



$\text{ClO}_2 \rightarrow \text{ClO}_2^-$ (Cl ON changes; $4 \rightarrow 3$).

$\text{ClO}_2 \rightarrow \text{ClO}_3^-$ (Cl ON changes; $4 \rightarrow 5$).

ΔON



'CB'



CB +MB



Overall

pH Measurement in Non-aqueous Liquids

The pH scale is defined in terms of a_{H^+} in aqueous solution and is not strictly applicable to pH measurement in non-aqueous systems.

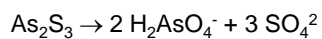
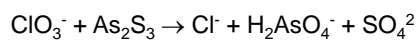
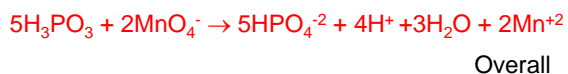
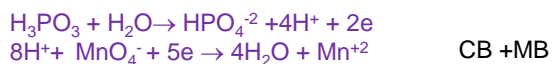
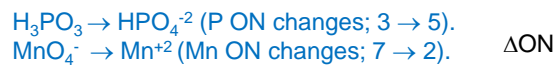
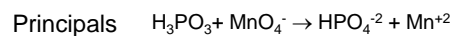
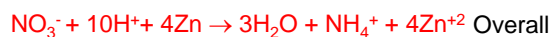
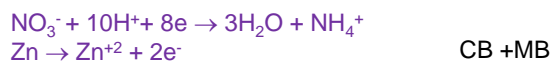
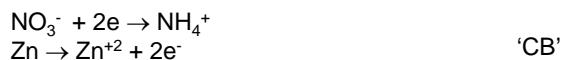
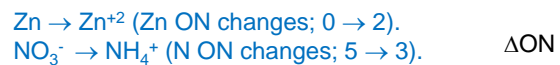
The low ionic strength and low conductivity of some non-aqueous solvents result in high noise or drift.

The glass membrane of the pH electrode may get dehydrated from immersion in the non-aqueous solvent losing its ability to respond to H^+ ions.

Soak the electrode in the non-aqueous solvent for ten minutes after standardization and before use in the sample.

Between successive measurements, the electrode should be rinsed with the non-aqueous solvent.

If the reading begins to drift after considerable time in a non-aqueous solvent, rehydrated the pH glass bulb by immersing in an aqueous buffer.



Potassium dichromate solution in dilute sulfuric acid oxidizes ethanol to ethanoic acid, CH_3COOH .

Potassium dichromate solution in dilute sulfuric acid oxidizes ethanol to acetaldehyde.

Hypochlorite (OCl^-) ion is a powerful oxidizing agent under basic conditions; I^- to yield iodine and chloride ion.