Potentiometry---Measure equilibrium EMF of galvanic cell--relate measured EMF to concentration of analyte---
-Can also have non-equilibrium potentiometry---where EMF observed is steady-state value--due to ion fluxes (ion-exchange) or simultaneous redox reactions at same electrode surface (so-called mixed potentials) (examples, polyion sensors, oxygen sensors based on corrosion, etc.)

-Always a two electrode system

-Measure EMF accurately (no loading), as $E_{WE} - E_{ref}$

-Types of Working Electrodes
  -electrode of first kind ($M^0/M^{n+}$)
  -electrode of second kind ($Ag/AgCl_{(s)}$)
  -inert metal electrode (Pt) to measure Redox potential
  -membrane electrodes--pH, Na, Ca, Cl, etc.
  -gas sensors--working and reference house behind gas permeable membrane (usually)
  -ISFETs and coated wire electrodes
General advantages of potentiometry:

- not kinetic measurement--not usually dependent on mass transfer--don’t worry about diffusion layer thickness, m values, electrode area, etc.--

- non-destructive to sample---no electrolysis reaction make EMF measurement with essentially zero current flowing through electrodes--

very inexpensive---just need FET based amplifier-

**Important point**--always measure $E_{\text{cell}} = E_{\text{WE}} - E_{\text{ref}}$

If $E_{\text{cell}}$ is negative----then $\Delta G$ is $+$; cell would discharge if allowed to (short circuit) but working electrode would be anode and reference would be cathode----

But we don’t care which electrode would be cathode or which would be anode---since we never allow the cell to discharge---only measure EMF which tells you the desire for cell discharge to occur!

$E_{\text{cell}}$ can be negative for analytical purposes---who cares---as long as potential is stable and reproducible.
-measuring $E_{\text{cell}}$ requires the ability to measure the difference in electron density ($q^m$) (or energy) between the metal leads of the two electrodes

-Potentials at each electrode develop as a result of the summation of all the potential differences at the interfaces of all the phases in the electrochemical cell

3-things to remember:

- potentials only develop as a result of processes that take place at phase boundaries

- if a phase has excess charge---mobile charge carriers will move in such a way so that the charge is distributed over the entire boundary of the phase--

brining a unit of positive charge into phase from any point in space requires the same amount of work, no matter where you bring the positive charge into material
The amount of excess charge in a phase to change its galvani potential is not very much---e.g., to change potential of Hg drop that is 0.5 mm in radius by 1 volt, requires $5 \times 10^{-14}$ coulombs- or $5 \times 10^{-19}$ moles---of a singly charged species.

Excess charge in given phase occurs in electrochem. as a result of equilibria at interfaces between a series of conductive phases (both electronic and ionic conductive phases)

For two phases in equilibrium---if $S$ is species in equilibrium between $\alpha$ and $\beta$ phases---

\[ \alpha \quad \beta \]
\[ \quad S \quad \]

at equilibrium, the chemical potential of species $S$ is equal in each phase
\[ \mu^\alpha_S = \mu^\beta_S = \text{chemical potential} \]

\[ \mu^\alpha_S = \mu^{o(\alpha)}_S + RT \ln a^\alpha_S \]
\[ \mu^{o(\alpha)}_S + RT \ln a^\alpha_S = \mu^{o(\beta)}_S + RT \ln a^\beta_S \]
\[ \mu^{o(\beta)}_S - \mu^{o(\alpha)}_S = \Delta \mu^o_S = -RT \ln(a^\alpha_S/a^\beta_S) \]
\[ \Delta G^o = -RT \ln K \quad ; \quad \text{or } K = e^{-\Delta G_0/RT} \]

K is the partition coefficient of species S

If species S is charged---then equilibrium between two phases is only achieved when the sum of both the chemical and electrical potentials are equal in both phases!!

Electrochemical potential-- \( \mu_i^\alpha = \mu_i^\beta \)

\[ \tilde{\mu}_i^\alpha = \mu_i^\alpha + z_i F \phi^\alpha = \tilde{\mu}_i^\beta = \mu_i^\beta + z_i F \phi^\beta \]

Substitute for \( \mu_i^\alpha = \mu_i^{o(\alpha)} + RT \ln a_i^\alpha \)
\[ \mu_i^\beta = \mu_i^{o(\beta)} + RT \ln a_i^\beta \]
\[ \mu_i^{o(\alpha)} + RT \ln a_i^\alpha + z_i F \phi^\alpha = \mu_i^{o(\beta)} + RT \ln a_i^\beta + z_i F \phi^\beta \]
solve for interfacial potential difference---

\[
\phi^\alpha - \phi^\beta = \frac{\mu^\beta_i - \mu^\alpha_i}{z_i F} + \frac{RT}{z_i F} \ln \frac{a_i^\beta}{a_i^\alpha}
\]

suppose \( \alpha \) phase is pure \( \text{Ag}^0 \) and \( \beta \) is solution containing a given activity of \( \text{Ag}^+ \)

silver ions are
fixed in lattice
with mobile free
electrons

in this case \( e^- \) can’t leave
metal--since reduction
of silver ion leads to solid
metal

\( \text{Ag}^+ \) go back and forth across interface---at same
rate when electrochemical potential is at equilibrium--
but to establish this equilibrium, some small number
of \( \text{Ag}^+ \) leave metal---creating separation of charge
-excess silver ions that leave metal are held in double layer region---separation of charge prevents any further loss of Ag⁺ since into double layer region since excess negative potential builds on metal--preventing any more charge separation!---

\[
\phi_{Ag} - \phi_{Soln} = \frac{\mu_{Ag+}^{\text{(soln)}} - \mu_{Ag+}^{\text{(metal)}}}{z_i F} + \frac{RT}{z_i F} \ln \frac{a_{Ag+}^{\text{solution}}}{a_{Ag+}^{\text{metal}}}
\]

difference in energy for silver ion being in solution--hydrated, or being in reduced state within metal phase!

\[
E_{Ag} = E^o + \frac{RT}{z_i F} \ln a_{Ag+}^{\text{soln}}
\]

\[
\Delta G^o = -zFE^o = -RT \ln K \ ; \ E^o = \frac{RT}{zF} \ln K
\]

\(E^o\) tells you the the chemical affinity of metal ion for electrons, or single ion partition coefficient if one phase is solution and other is organic phase, etc.----more positive \(E^o\) for Ag vs. Cu tells us that equilibrium constant for Ag⁺ reduction is more favorable than for Cu²⁺ reduction.
In the case of the Ag electrode; increasing the silver ion activity in solution will reduce the number of excess free electrons in metal---making the potential difference between metal and solution less negative---or more positive. ----This happens almost instantly when increase in Ag$^+$ is added to solution, provided that the concentration is high enough to yield reasonable rate of charge transfer at interface---

**exchange current** = cathodic and anodic currents that equal each other at interface of electrode at equilibrium. ---no bulk reaction---no gradient of species----since rate of reduction = rate of oxidation at equilibrium.

For redox electrodes, like platinum, in contact with Ox and Red (e.g., NHE)----potential across interface is dictated by electrochemical potential of electrons-in each phase----if Ox is present, and little Red, than solution phase has greater affinity for electrons--and surface of Pt becomes more + charged, due to loss of some electrons to Ox species at interface---

$\mu_{e^-} = -F\phi$ for each phase
Can only measure excess charge on electrode if we have second electrode in contact with same phase---the reference electrode----which effectively allows you to measure the potential difference---

Can be NHE as reference----but not used for analytical work--too complex in that hydrogen gas is needed

Four common reference electrodes---

Ag/AgCl, Hg/Hg\textsubscript{2}Cl\textsubscript{2}, Hg/Hg\textsubscript{2}SO\textsubscript{4} and Ag/Ag\textsuperscript{+}

---
-the silver/silver ion reference electrode is often use for electrochemical measurements in non-aqueous phases since you can make solutions of AgClO\textsubscript{4} in several organic solvents including acetonitrile!

Use electrodes of second kind, like Ag/AgCl or Calomel, since it is easier to keep anion activity constant---then cations---have reservoir of cation in the insoluble salt--and the free activity of cation in solution is controlled by the solubility product $K_{sp}$
for Ag/AgCl; Ksp is approx. $10^{-10}$ (value is highly temperature dependent---causes hysteresis effect when temperature of cells are changed---slow to re-equilibrate!

Will derive key equations on black-board!!-

Also----Pt/Ox-red electrode can be used as reference in certain special circumstances----Ross pH electrode

$$I_3^- + 2\text{ e} \quad <------- > \quad 3\text{ I}^-$$

since both forms of redox species soluble---don’t have to wait long for $E_{cell}$ to stabilize after temperature changes