

# Introduction to Electroanalytical Chemistry!

(chapter 13--ECA)

Potentiometry: measure voltage of galvanic cell--and relate  $E_{\text{cell}}$  to concentration/activity of given analyte  
 $E_{\text{cell}}$  related to “desire” for electrons to flow--between two electrodes--working and reference but no reactions actually take place!!

Amperometric/Voltammetric: Apply external voltage to electrochemical cell (electrolyte cell) and measure current response---if current flows---reduction reaction takes place at one electrode, and oxidation at other!!

Can also use both methods as detection systems for titrations---using chelating agents, or redox titrants!

All electrochemistry is based on Redox reactions ( $\text{Ox} + n\text{e}^- \rightleftharpoons \text{Red}$ )!--species gains electrons (reduction) and species lose electrons (oxidation)

Electric charge-(q) is measured in coulombs (C)

a single charge has  $1.602 \times 10^{-19} \text{ C}$  ; 1 mole of charge has  
 $(1.602 \times 10^{-19} \text{ C}) \times (6.022 \times 10^{23} \text{ mol}^{-1}) = 9.649 \times 10^4 \text{ C/mol} = F =$   
**Faraday's constant!**

Faraday's law: moles reacted =  $q/nF$  ; n = number of electrons in  
or  $q = nF(\text{moles reacted})$  reaction!

Current is proportional to moles reacted for electrochemical reaction:

current = amperes =  $1 \text{ C/sec}$  ;

What would be current required to reduce  $\text{Sn}^{+4} + 2 \text{ e}^- \text{ ----} \rightarrow \text{Sn}^{+2}$   
at a platinum electrode as a rate of  $4.24 \text{ mmol/h}$ ?

What would be rate per second?  $4.24 / 3600 = 1.18 \times 10^{-6} \text{ mol/sec}$   
current =  $\text{C/s} = q/\text{sec} = (1.18 \times 10^{-6} \text{ mol/sec}) \times n \times F (\text{C/mol}) =$   
 $= 0.227 \text{ A (amps)}$

## Voltage and work----

Electrical potential difference---difference in charge between two points!---this potential difference is a measure of the work required to bring (move) electrons from one point to the other!-----

has units of Volts (V)

and work done or needed to be done has units of Joules (J)

$$\text{joules (work)} = E \text{ (volts)} \times q \text{ (charge)}$$

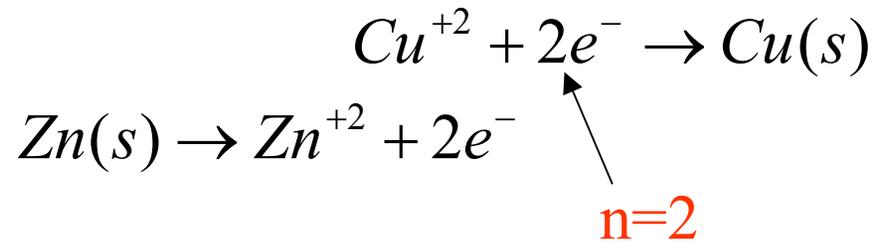
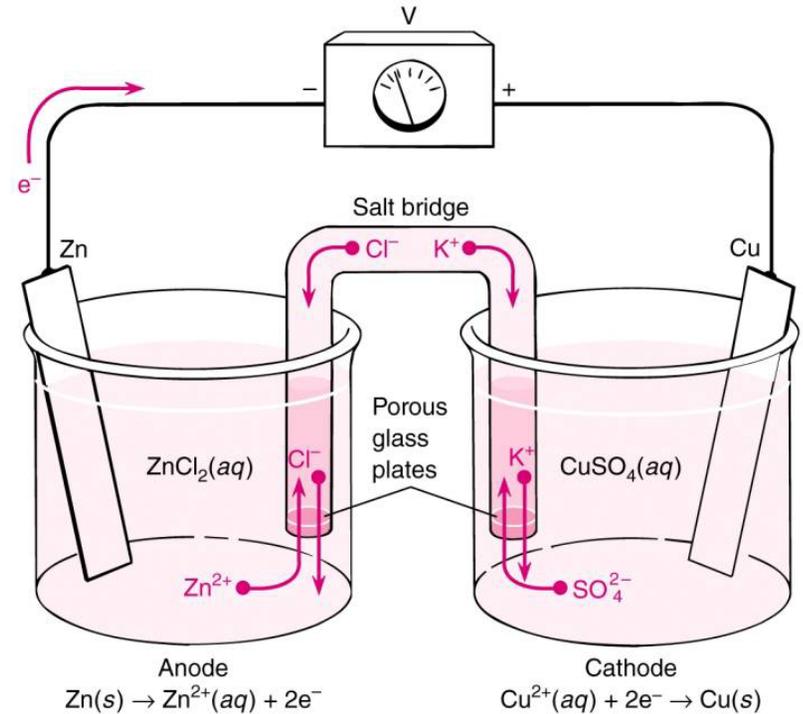
One joule of energy is used to move one coulomb of charge between two points that differ by 1 volt!

therefore-- 1 volt = joules/C

In potentiometry---we measure the desire for charge to flow from one electrode to another (we don't actually let the charge flow)---charge will only want to flow if there is a voltage difference!

# ... and more definitions

- Cathode: surface where electrons are donated to atoms or molecules, where reduction occurs
- Anode: surface where electrons are accepted from atoms or molecules, where oxidation occurs
- Electrochemical Cell: reduction at a cathode and oxidation at an anode are separated into two compartments connected by an external circuit so that electrons will flow (current) through the circuit
- Galvanic Cell: a battery, electrochemical cell that has spontaneous electron flow, capable of doing work



$$E_{cell} = E_{cathode} - E_{anode}$$

# Cell Potential, Current Flow

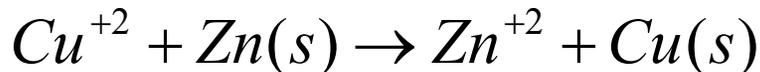
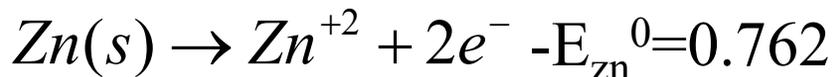
- Cell Potential,  $E_{cell}$

$$E_{cell} = E_{cathode} - E_{anode}$$



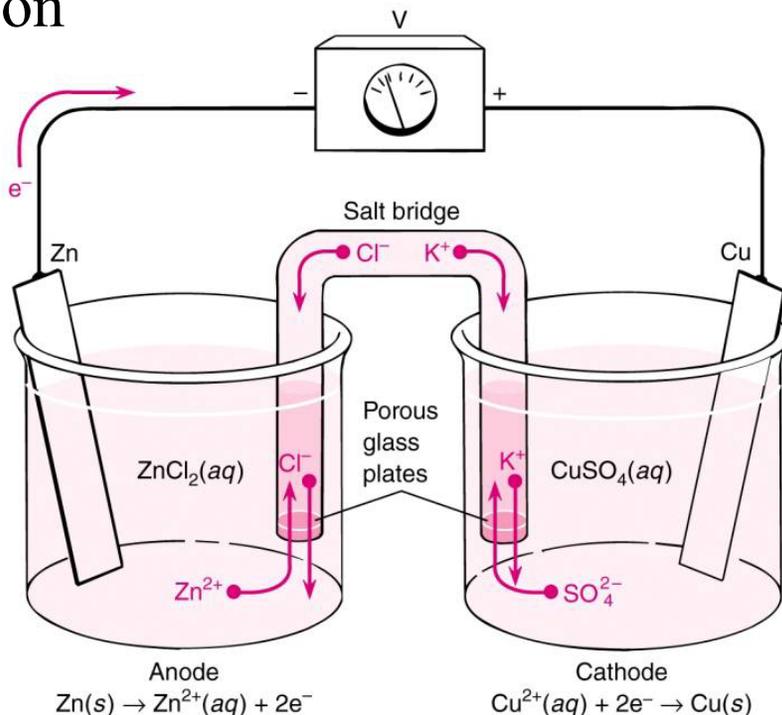
std. reduction potentials

$$E_{Cu}^0 = 0.339$$

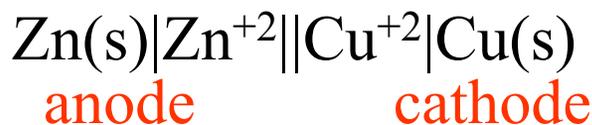


$$E_{cell} = 1.101 V$$

cell rxn



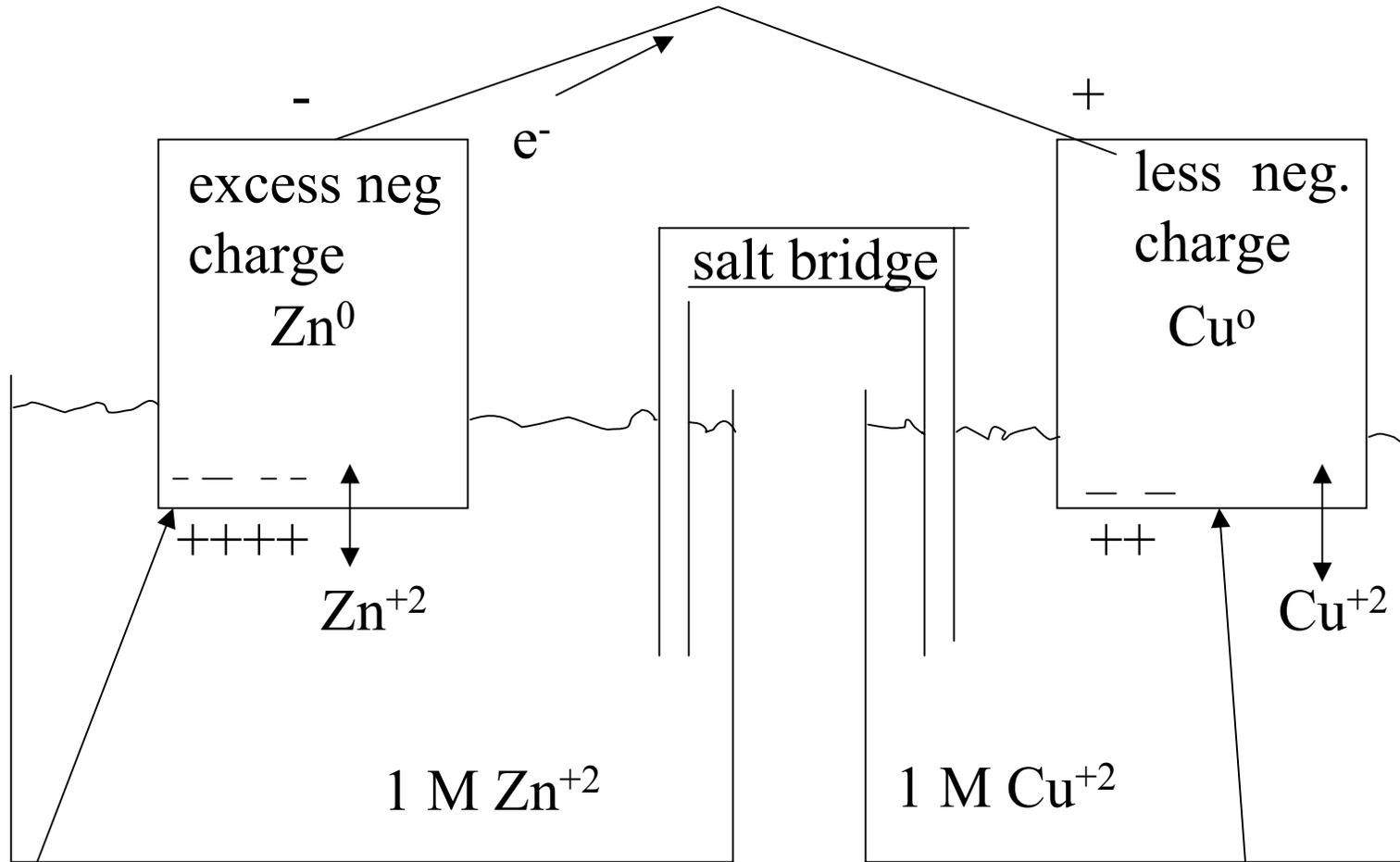
- If the cell potential is positive the cell is galvanic.
- Current will flow spontaneously.
- Cell line notation



| phase boundary

|| salt bridge

What does  $E^0$  value for each half-cell reaction really mean?



electrical potential difference at interface-- magnitude depends on equil. const for  $Zn + 2e^- \rightleftharpoons Zn^0$

potential at this interface-- due to  $Cu^{+2} + 2e^- \rightleftharpoons Cu^0$

# Thermodynamic Free Energy

- Laws of Thermodynamics define the work done by a system as Gibbs Free Energy

$$Q = (a_{\text{Cu}^0} a_{\text{Zn}^{+2}}) / (a_{\text{Cu}^{+2}} a_{\text{Zn}^0})$$

$$F = 9.65 \times 10^4 \text{ C/mol}$$

$$E_{\text{cell}}^0 \quad \Delta G \equiv \Delta H - T \cdot \Delta S$$

$$\Delta G \equiv \text{work} = E \cdot q$$

$$\Delta G = \Delta G^0 + RT \ln(Q)$$

$$\Delta G = -nFE_{\text{cell}}$$

**Nernst Equation:**

at standard conditions:

$$E_{\text{cell}} = E^0 - \frac{RT}{nF} \ln Q$$

$$\Delta G^0 = -nFE_{\text{cell}}^0$$

$$E_{\text{cell}} = E^0 - \frac{0.0592}{n} \log Q$$

R (in joules/°K-mol)  
2.3-ln--> log conv.; 25°C

- exothermic reactions (spontaneous) e.g. galvanic:  $\Delta G < 0$

when  $E_{\text{cell}} > 0$

- endothermic reactions (not spontaneous):

$$\Delta G > 0 \quad E_{\text{cell}} < 0$$

actual conc. or activities of species present

# $E^0$ relationship to $K$ for overall electrochemical cell rxn

- $Q$  = product to reactant ratio:
  - in Zn/Cu electrode system-- soluble species at the anode divided by the soluble species at the cathode
- At equilibrium:
  - no current flow
  - $E_{\text{cell}} = 0$
  - $Q = K$  (equilibrium constant)
- Calculated (or measured)  $E^0_{\text{cell}} = E^0_{\text{cathode}} - E^0_{\text{anode}}$ 
  - can be used to predict

$$\Delta G = \Delta G^0 + RT \ln(Q)$$

$$\Delta G = 0 = \Delta G^0 + RT \ln(K)$$

$$\Delta G^0 = -RT \ln(K)$$

$$\Delta G^0 = -nFE^0_{\text{cell}}$$

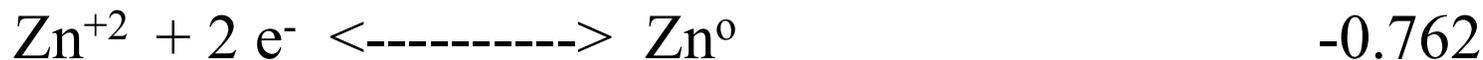
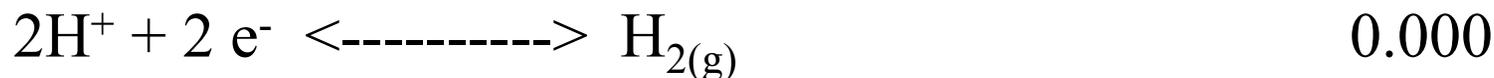
$E^0_{\text{cell}}$

$$E^0 = \frac{RT}{nF} \ln(K)$$

← equilib. const. for rxn:



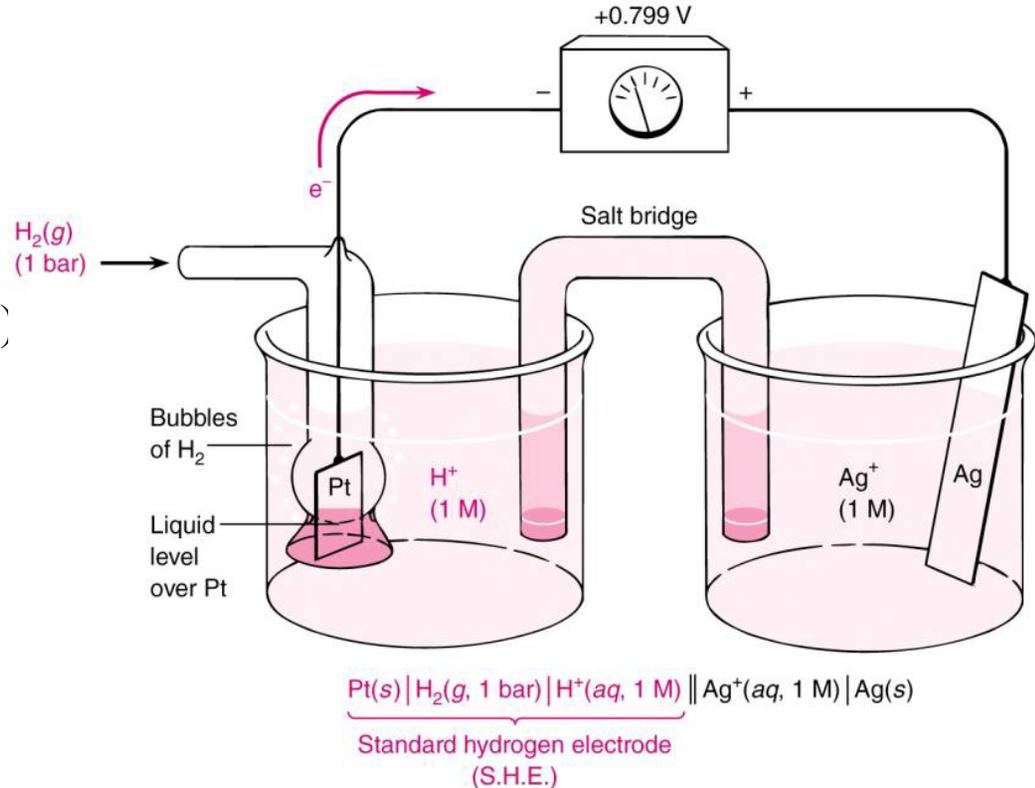
# $E^{\circ}$ values for half-cell rxns--written as reduction reactions!



species at top of table are strong oxidizing agents (more easily reduced; species at bottom are strong reducing agents---(easily oxidized))

# Measuring $E^0$

- Standard potentials means all conditions are “standard”:  
 $a_1=1$ ; 25 °C; 1 atm
- The anode: 1 atm  $H_2$  (g) is bubbled over Pt electrode,  $H_2$  is oxidized (NHE)
  - standard half-reactions are written as reductions (cathodic)
  - $H^+ + e^- \rightarrow 1/2 H_2$  (g)
- The cathode: the reduction of some metal  $M^+$  (activity=1)
  - metal precipitates on the electrode
  - $Ag^+ + e^- \rightarrow Ag(s)$
- Assumption: concentration of all analytes ( $H^+$ ,  $M^+$ ) remain constant



- Standard Hydrogen Electrode, S.H.E. (or NHE)  $E^0=0.0$  V (by convention)
- $Ag^+$ ,  $Ag(s)$  standard reduction potential equals the measured  $E_{cell}$ ,  $E^0=0.799$  V

$$E_{cell} = E_{cathode} - E_{anode}$$

$$E_{cell}^0 = 0.799 \text{ V} = E_{cathode}^0 - 0$$

If we know  $E^0$  values---we can always calculate the  $E_{\text{elect}}$  for each of the two half-cell electrodes; Use Nernst equation for each half cell reaction!

for general 1/2 cell rxn:  $\text{Ox} + ne^- \rightleftharpoons \text{Red}$

$$E_{\text{elect}} = E^0 - 0.0592 \log (a_{\text{prod}}/a_{\text{react}}) = E^0 + 0.0592 \log (a_{\text{ox}}/a_{\text{red}})$$

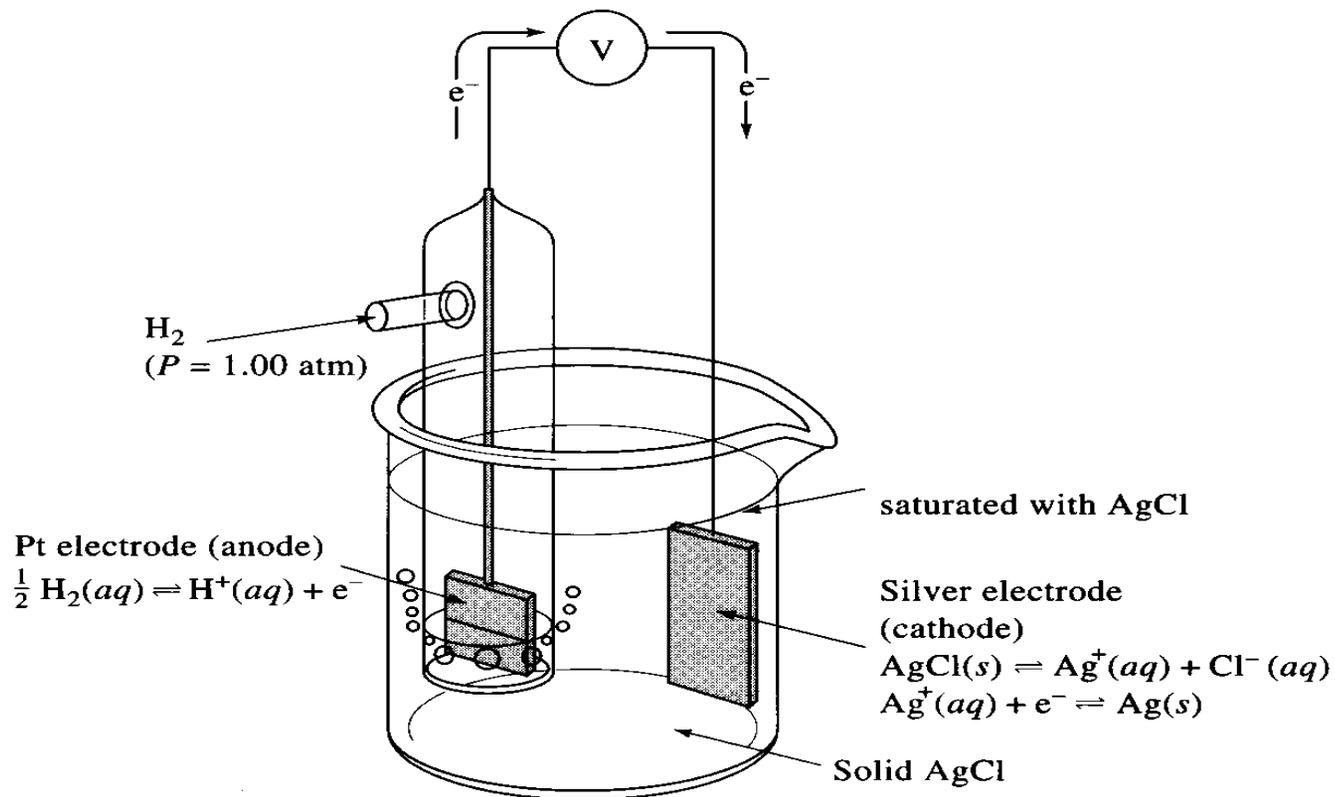
**Then to calculate cell potential---**

$$E_{\text{cell}} = E_{\text{cath}} - E_{\text{anode}} \quad (\text{use Nernst equation to calculate potential of each electrode})$$

What is  $E_{\text{cell}}$  for following galvanic cell:

**Pt,  $\text{H}_2$  (1 atm) /  $\text{H}^+$  (a=0.1 M),  $\text{Cl}^-$  (a=0.1M),  $\text{AgCl}_{(s)}$  / Ag**

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = E_{\text{cath}} - E_{\text{anode}} = E_{\text{Ag/AgCl}} - E_{\text{H}^+/\text{H}_2(\text{pt})}$$



**Pt,  $\text{H}_2$  (1 atm) /  $\text{H}^+$  (a=0.1 M),  $\text{Cl}^-$  (a=0.1M),  $\text{AgCl}_{(s)}$  / Ag**

$$E_{\text{Ag}/\text{AgCl}} = E^{\circ}_{\text{Ag}/\text{AgCl}} + 0.0592 \log (a_{\text{AgCl(s)}} / a_{\text{Cl}^-} a_{\text{Ag}^+})$$

$$= 0.222 \text{ V} + 0.0592 \log (1 / 0.1 (1))$$

$$= 0.222 \text{ V} + 0.0592 \log (10) = 0.281 \text{ V or } 281 \text{ mV}$$

unit activity (solids)!

$$E_{\text{H}^+/\text{H}_2} = E^{\circ}_{\text{H}^+/\text{H}_2} + (0.0592/2) \log (a_{\text{H}^+}^2 / P_{\text{H}_2})$$

$$= 0.000 \text{ V} + 0.0592 \log (0.1 / 1)$$

$$= -0.0592 \text{ V}$$

2 values from  
 $2 \text{ H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2$   
 but these cancel out because  
 of how you treat exponents  
 in log term!

**Therefore:  $E_{\text{cell}} = 0.281 \text{ V} - (-0.059 \text{ V}) = 0.340 \text{ V or } 340 \text{ mV}$**

What would be  $E_{\text{cell}}$  if you had 0.001 M HCl (assume activities = [ ])?

$$E_{\text{Ag}/\text{AgCl}} = 0.222 + 0.0592 \log (1 / 0.001 (1)) = 0.400 \text{ V or } 400 \text{ mV}$$

$$E_{\text{H}^+/\text{H}_2} = 0.000 + 0.0592 \log (0.001 / 1) = -0.178 \text{ V or } -178 \text{ mV}$$

$$E_{\text{cell}} = 0.400 - (-0.178) = 0.578 \text{ V}$$

note that as pH increases in this cell---voltage gets more positive---  
Indeed, this S.H.E/sample, AgCl(s)/Ag cell was the cell used by  
**Roger Bates** at NBS (now NIST) to assign the pH ( $-\log a_{\text{H}^+}$ ) in the  
buffer standards that we now use to calibrate pH electrodes!

He added constant amount of NaCl salt to each potential buffer  
---so that the  $E_{\text{Ag}/\text{AgCl}}$  would not change very much---(he also  
calculated activity coeff. for chloride so he could plug in the true  
activity of chloride ion for potential of Ag/AgCl electrode

$$E_{\text{cell}} = E_{\text{Ag}/\text{AgCl}} - (E_{\text{SHE}}^0 + 0.0592 \log (a_{\text{H}^+}) - 0.0592 \log (P_{\text{H}_2(\text{g})}))$$

$$\log (a_{\text{H}^+}) = (E_{\text{cell}} - E_{\text{Ag}/\text{AgCl}}) / 0.0592$$

$E^0$  values--for given redox reactions---and be calculated based on simultaneous equilibrium reactions----true for **Electrodes of Second Kind** (e.g., Ag/AgCl); **Electrode of first kind** (M/M<sup>n+</sup>) in solution that is saturated with insoluble salt of M<sup>n+</sup>.

potential of elect. of 1st kind  $E_{\text{elect}} = E^0_{\text{M}^{n+}/\text{M}(\text{o})} + (0.0592/n) \log(a_{\text{M}^{n+}})$



$$E_{\text{Ag}} = E^0_{\text{Ag}^+/\text{Ag}(\text{o})} + 0.0592 \log (a_{\text{Ag}^+} / a_{\text{Ag}(\text{o})}) = 0.799 \text{ V} + 0.0592 \log (a_{\text{Ag}^+})$$

$$\text{but } K_{\text{sp}}(\text{AgCl}) = a_{\text{Ag}^+} a_{\text{Cl}^-} ; a_{\text{Ag}^+} = K_{\text{sp}} / a_{\text{Cl}^-} \quad K_{\text{sp}} = 1.8 \times 10^{-10}$$

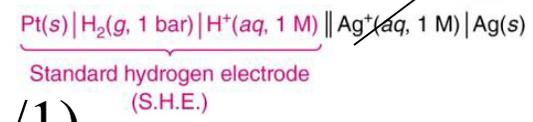
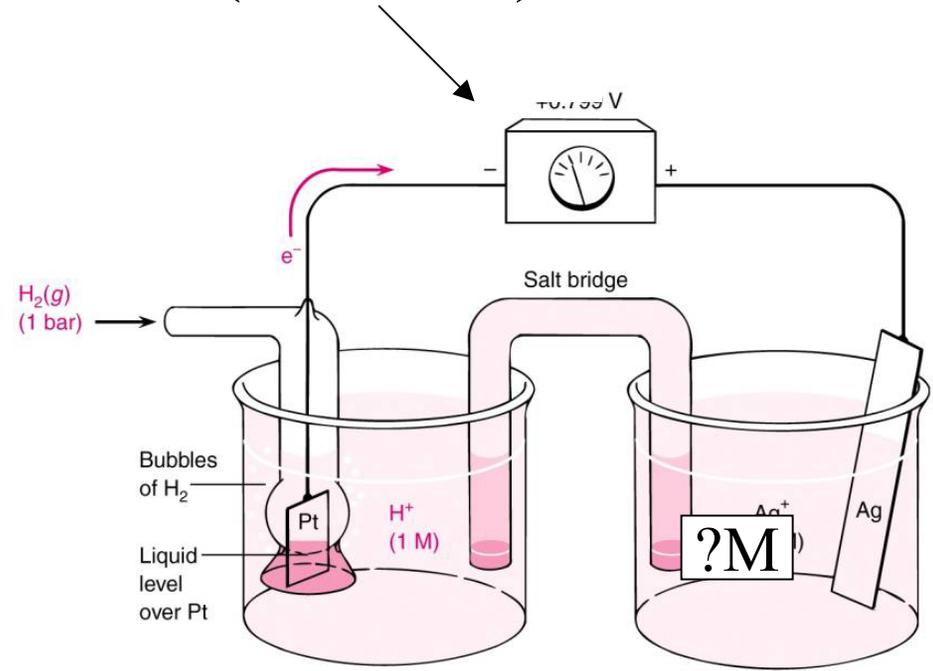
$$E_{\text{Ag}} = 0.799 + 0.0592 \log (K_{\text{sp}} / a_{\text{Cl}^-})$$

$$E_{\text{Ag}/\text{AgCl}} = 0.799 + 0.0592 \log K_{\text{sp}} - 0.0592 \log a_{\text{Cl}^-}$$

$$E_{\text{Ag}/\text{AgCl}} = \mathbf{0.222 - 0.0592 \log a_{\text{Cl}^-}} \quad \leftarrow \text{elect. responds to Cl}^-$$

# Determining Analyte Concentration from measured $E_{\text{cell}}$ value (0.682 V)

- Left: Anode, oxidation of  $\text{H}_2$ 
  - S.H.E. standard conditions
  - $E_A = 0.0 \text{ V}$
- Right: Cathode, reduction of  $\text{Ag}^+$ , unknown concentration
  - $E^0 = 0.799 \text{ V}$  (at standard conditions)
- $E_{\text{cell}} = E_C - E_A = 0.682 \text{ V}$ 
  - initial cell voltage measured
  - What is  $[\text{Ag}^+]$  (assume activity equals concentration)



(1/1)

$$0.682 = E_{\text{Ag}} - E_{\text{SHE}}$$

$$= (0.799 + 0.0592 \log a_{\text{Ag}^+}) - (0.000 + 0.0592 \log (a_{\text{H}^+} / P_{\text{H}_2}))$$

Therefore:  $\log a_{\text{Ag}^+} = (0.682 - 0.799) / 0.0592$

$$a_{\text{Ag}^+} = 0.0106 \text{ M}$$

In potentiometric methods---we always use galvanic cell in which one of the electrodes has constant half-cell potential (called **reference electrode**).

The second electrode is called the **working** or **indicator** electrode!

We don't really care whether the cell potential is + or - --and we don't really care which electrode would be anode and which would be cathode if the galvanic cell were to discharge!!

Who cares?---we are only using the  $E_{\text{cell}}$  value to detect some analyte species, or indirectly detect some analyte (via titration, etc.).

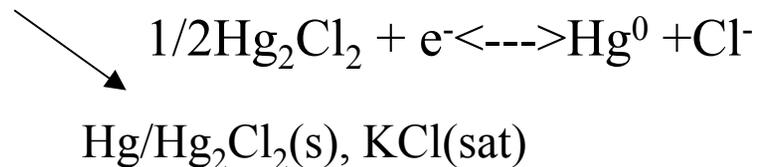
We never let cell discharge---we measure voltage under essentially zero current conditions---so there is no real cathode or anode!!

Hence--- $E_{\text{cell}} = E_{\text{ind}} - E_{\text{ref}} = E_{\text{working}} - E_{\text{ref}} = E_{+} - E_{-}$

  
+ and - here refer to which  
jack in meter you connect to !

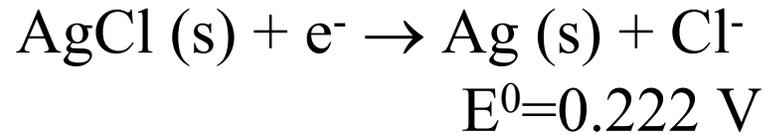
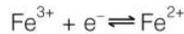
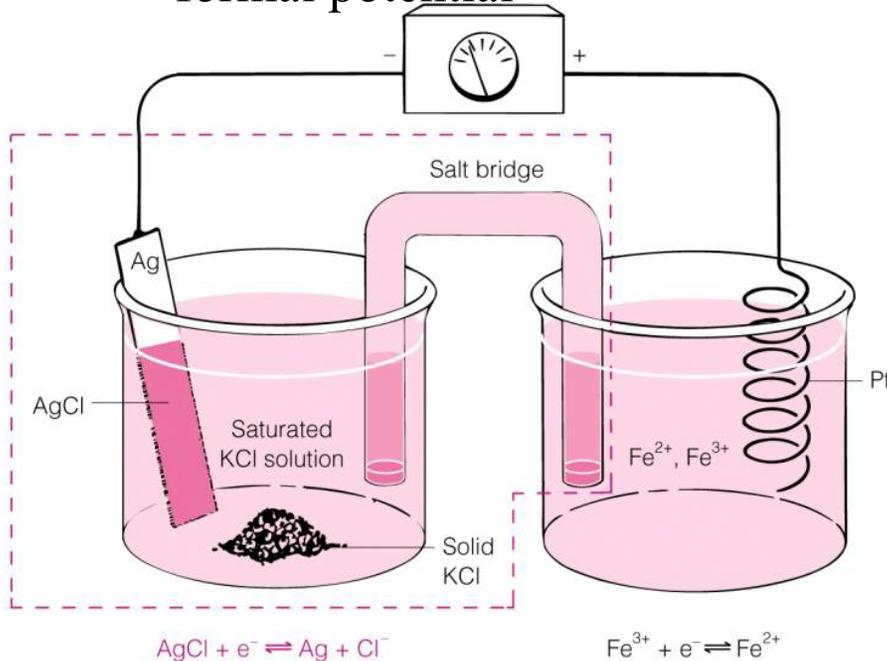
# Types of Electrodes

- **Indicator Electrode/Working Electrode:** sensitive to analyte concentration/activity---gives the analytical signal
  - Inert metal Pt (or Au) are typically used to measure redox potentials (ox + ne<sup>-</sup> <-----> red);  $E_{\text{elect.}} = E^{\circ}_{\text{ox/red}} + (0.0592/n) \log (a_{\text{ox}} / a_{\text{red}})$
  - Such electrodes also used in voltammetry and amperometry, where analyte comes to surface and is either oxidized or reduced (controlled by potential applied to electrode (electrolytic cell)!
  - electrodes of **first kind** (e.g., Ag<sup>0</sup> to measure silver ion activity, Cu<sup>0</sup> to monitor copper ion activity via potentiometry!
  - **Ion-Selective Membrane Electrodes**----pH, K<sup>+</sup>, Ca<sup>+2</sup>, etc.
- **Reference Electrodes:** electrode with a known stable, half-cell potential, completes the electrochemical cell so the analyte can be measured at the indicator or working electrode-- E<sub>ref</sub> not affected by sample composition!
  - Examples: 1) S.H.E., 2) Ag/AgCl 3) Calomel



# Ag/AgCl Reference Electrode

- formal potential



Silver chloride salt is spread onto the Ag (metal) electrode as a paste.

Increased contact speeds up the response of the electrode

$$K_{\text{sp}}^{\text{AgCl}} = 1.8 \times 10^{-10}$$

$$\text{KCl}(\text{sat}, 25\text{C}) = 26.22 \text{ wt\%}$$

$$= 3.518 \text{ M}$$

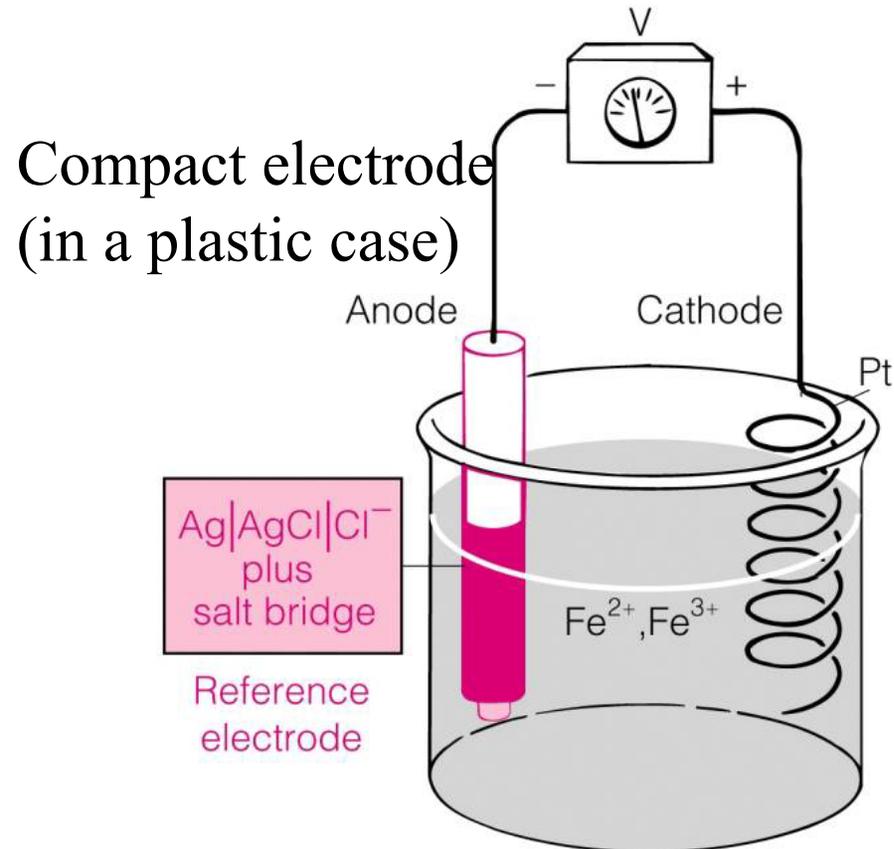
formal

potential

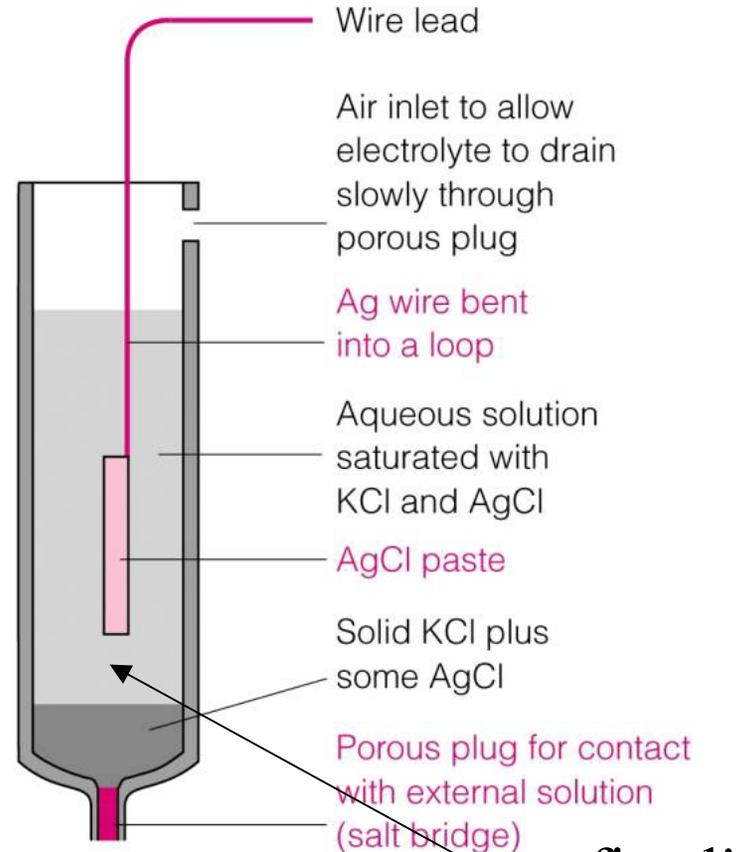
$$\rightarrow \underline{E_{\text{ref}}(\text{KCl, sat}) = 0.197 \text{ V}}$$

KCl saturated solution  
[Cl<sup>-</sup>] is constant

# Compact Electrodes



salt bridge essential  
allows flow of K<sup>+</sup> (or Cl<sup>-</sup>) out  
maintains electroneutrality

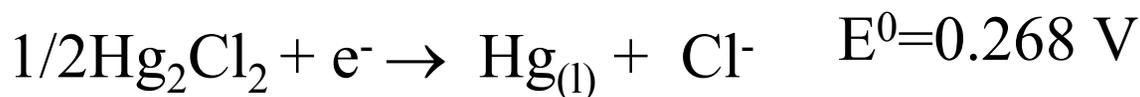


fixed!

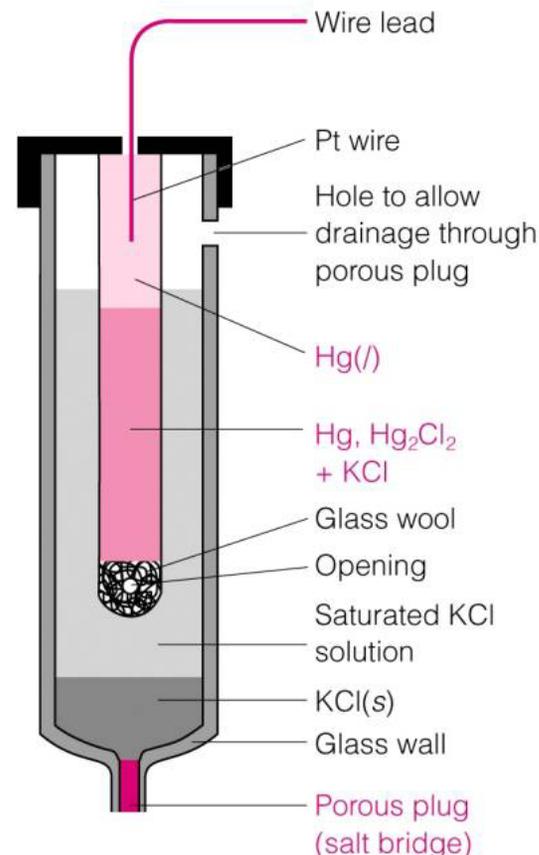
$$E_{\text{ref}} = E^{\circ}_{\text{Ag/AgCl}} - 0.0592 \log a_{\text{Cl}^-}$$

# Calomel Reference Electrode

- Calomel electrode uses Hg
- Abbreviated, S.C.E. (when electrolyte is Sat'd KCl)
  - Disadvantage, Hg is toxic
  - Advantage, Hg is a liquid, fast response, and easy to clean (Hg, contaminate salts precipitate out)

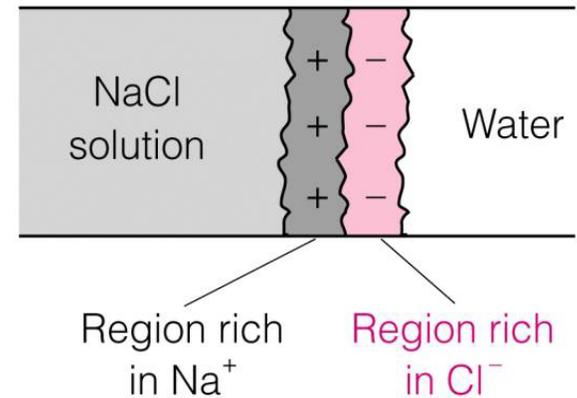
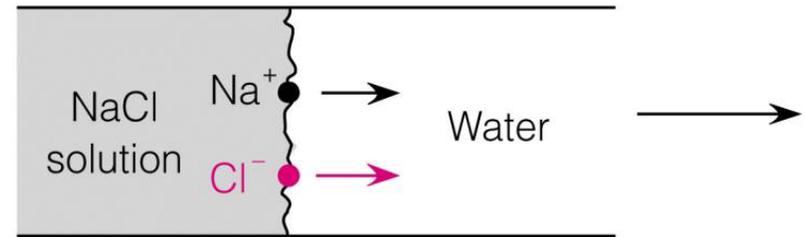


$$E_{\text{ref}}(\text{Hg}/\text{Hg}_2\text{Cl}_{2(s)}, \text{KCl (sat'd)}) = 0.241 \text{ V}$$



# Boundary Layers and Junction Potentials

- Ions diffuse from a region of high ionic strength to a region of lower ionic strength
- Ions will migrate (diffuse) at different rates, depending on their relative charge and size, ( $z/r$ )
- Creates regions with higher net negative charge and regions of higher net positive charge at the interface (or junction)
- The difference in local charge represents some work ( $\Delta G$  free energy), or chemical potential, called a junction potential

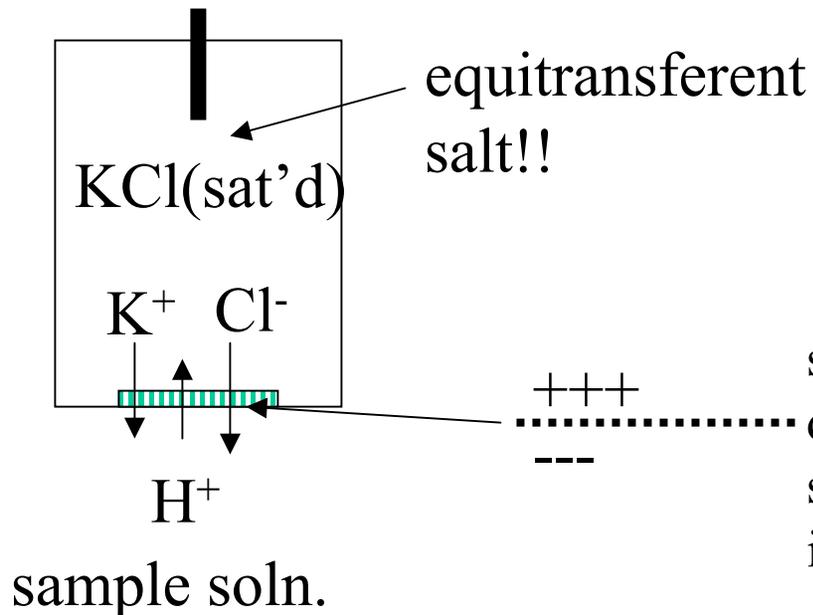


All reference electrodes that have their own electrolyte to keep the ion activity constant to yield a fixed half-cell potential----have one additional potential that is not considered when calculating voltage via the Nernst eqn.!

This is call Liquid Junction Potential ( $E_j$ )!

It occurs that the interface between the electrolyte solution of the reference electrode, and the sample solution!---

It is due to the different mobilities (diffusion rates) of ions that the interface of the two solutions!



we will ignore junction potentials---but they can cause large errors when sample is very acidic or basic to to high mobility of H<sup>+</sup> and OH<sup>-</sup> !!

small voltage difference between solutions due to different rates of ionic diffusion

++++

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**double junction reference electrodes!**---used when you want to prevent leakage of KCl (if you were measuring  $K^+$  or  $Cl^-$ ---would not want these species to leak into sample and change conc.)

