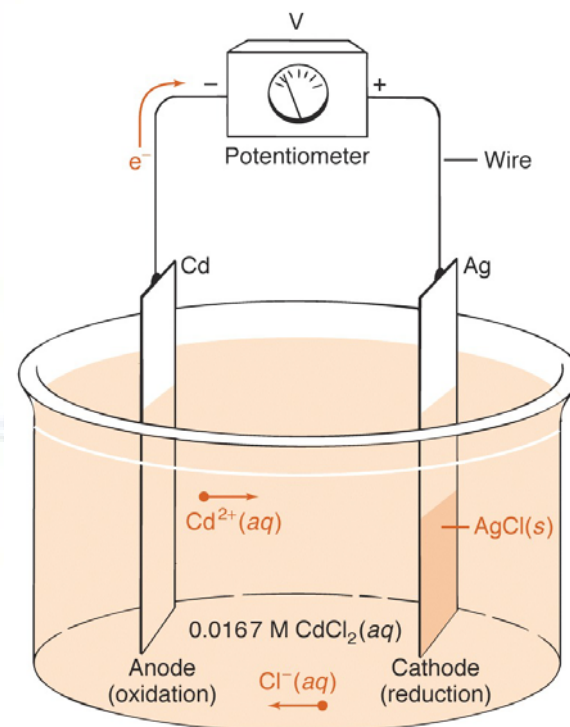# Electrochemical Potential

- Electrode potentials express the driving force for oxidation or reduction
  - A negative electrode potential describes a material easier to oxidize  compared to chemical species with a more positive potential
  - A positive electrode potential describes a material easier to reduce.
- This is given by electromotive force or potential, "E" with units of volts
- Electrochemical potential express the possibility of the redox reaction, but does not express the kinetic of the reaction!

# Electrode potential

- Redox reaction energy creates measurable electrochemical potential determined by the thermodynamics & related equilibria of the reaction

- Requires complete circuit to compare the voltage between electrodes.

- Can not measure the voltage of half a cell, requires 2 electrodes

- placed in an electrolytic medium. For ex., voltmeter reads 0.46 V in:
Cu | CuSO4(0.1 M) | AgSO4(0.1 M) | Ag

# Galvanic Cells

- Converting chemical energy into electric energy by using spontaneous chemical reaction.

- Reduction - cathode:
$2AgCl\ (s) + 2e \rightleftarrows 2Ag\ (s) + 2Cl^-\ (aq)$

- Oxidation - Anode:
$Cd\ (s) \rightleftarrows Cd^{2+}\ (aq) + 2e$

- Total reaction:
**$Cd\ (s) + 2AgCl \rightleftarrows Cd^{2+}(aq) + 2Ag(s) + 2Cl^-(aq)$**



$e^-$ — Potentiometer — Wire
Cd — Ag
$Cd^{2+}(aq)$ — $AgCl(s)$
0.0167 M $CdCl_2(aq)$
Anode (oxidation) — $Cl^-(aq)$ — Cathode (reduction)

# Electrochemical cells

- **Electrochemical Cells** involve separate redox reactions, ne-transfer from reactants to electrodes (or visa-versa) via an electrical conductor
- Components of electrochemical cells:
  - an anode, the electrode at which oxidation occurs,
  - a cathode , the electrode at which reduction occurs,
  - a metal wire, connecting anode and cathode through a load,
  - a medium with ions (usual a solution) separating anode & cathode
- allows ion transfer (conduction) between electrodes
- Cell potential difference between cathode & anode redox half reactions:
  - Ecell = Ecathode - Eanode
- The standard electrode potential is for half-reaction with all reactants & products "x" at unit activity, ax. For example:
  - E°cathode = Ecathode( aA =aB= 1); E°anode = Eanode( aC=aD= 1)

# Notation of electrochemical reactions

- | phase boundary; || salt bridge (two phases)

- Cd (s)|CdCl$_2$(aq)|AgCl (s)|Ag(s)
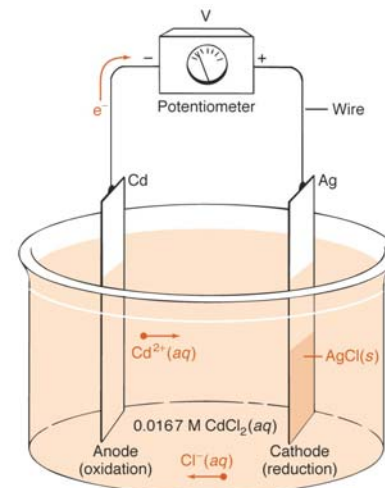


- Cd(s)|Cd(NO$_3$)$_2$ (aq)||AgNO$_3$ (aq)|Ag(s) How about without salt bridge?
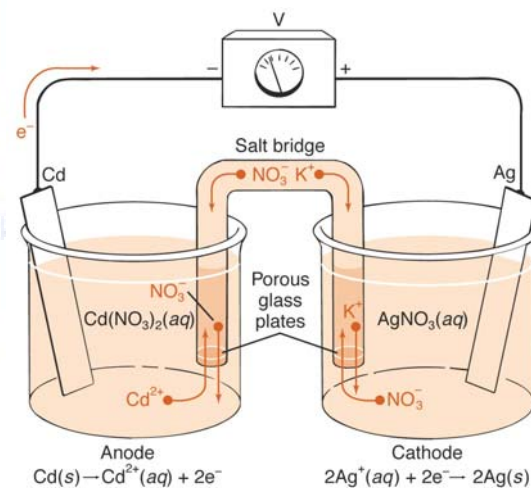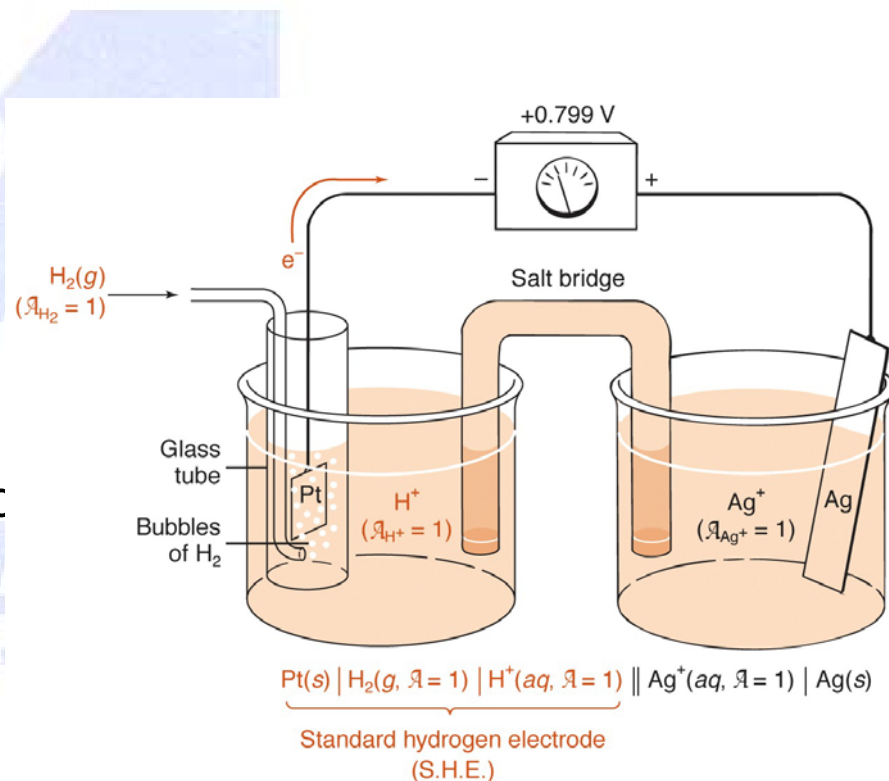
# Standard Electrode Potentials

- Standard electrode potential, "**E°**", when each of the chemical species participating in a redox process are at standard state and unit activity

  - No absolute point of reference about for an electrode potential scale

  - One half-cell has been arbitrarily defined as $E \equiv$ 0.0000 volt. Reference is a hydrogen-platinum half-cell containing unit activities, called the "**Standard Hydrogen Electrode**"

  - All other electrode or rest potentials are reported compared to SHE

# Standard Potential

- "Standard Hydrogen Electrode" :
  Pt,H2(pressure = 1 atm) |
  H+(activity = 1) (the "SHE" or
  Normal Hydrogen Potential
  "NHE")SHE describes:
  $2H^+$ (aq) + 2e- $\rightarrow$ $H_2$ (gas)
  E° = 0 V

- All other electrode or rest
  potentials are reported compared
  to SHE

  e.g.

  $Ag^+$ + e $\rightarrow$ Ag          E°=0.799V



+0.799 V

Salt bridge

$H_2(g)$
$(\mathcal{A}_{H_2} = 1)$

$e^-$

Glass tube

Pt

Bubbles of $H_2$

$H^+$
$(\mathcal{A}_{H^+} = 1)$

$Ag^+$
$(\mathcal{A}_{Ag^+} = 1)$

Ag

$Pt(s) \mid H_2(g, \mathcal{A} = 1) \mid H^+(aq, \mathcal{A} = 1) \parallel Ag^+(aq, \mathcal{A} = 1) \mid Ag(s)$

Standard hydrogen electrode
(S.H.E.)

# Voltage conversions between different reference electrode
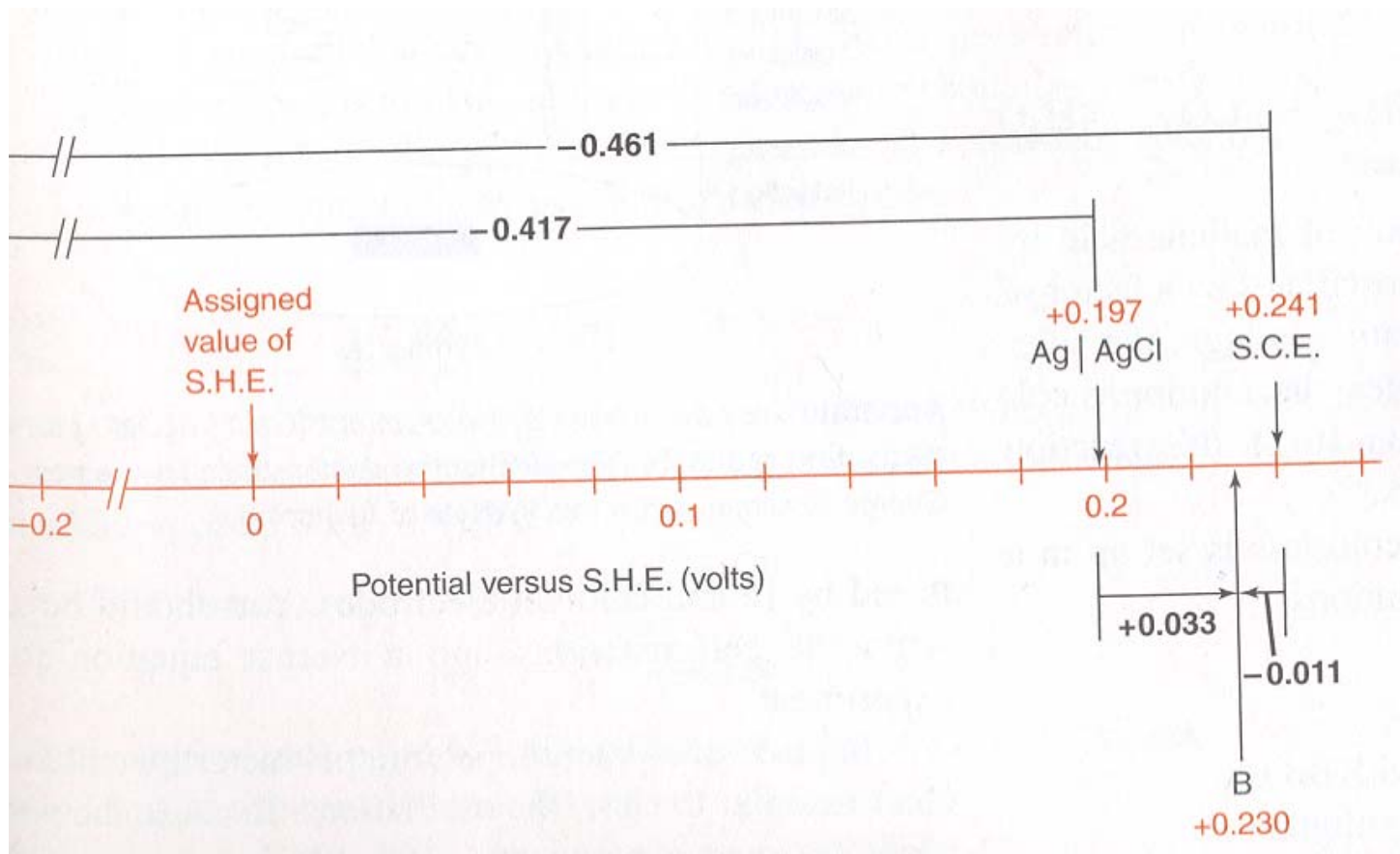
# Thermodynamics

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

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

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# Thermodynamics

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

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

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

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

# Direction of the reaction

- The second law of thermodynamics: $\Delta G=-nF\Delta E<0$ or $\Delta E=(E_+ - E_-) >0$, the reaction is spontaneous.

- A reaction is spontaneous if $\Delta G$ is negative and E is positive.

- Equilibrium
    - Equilibrium with in each half cell: the electrode potential is no long change.
    - Equilibrium between two half cell, the cell voltage = 0

# 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]

# 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