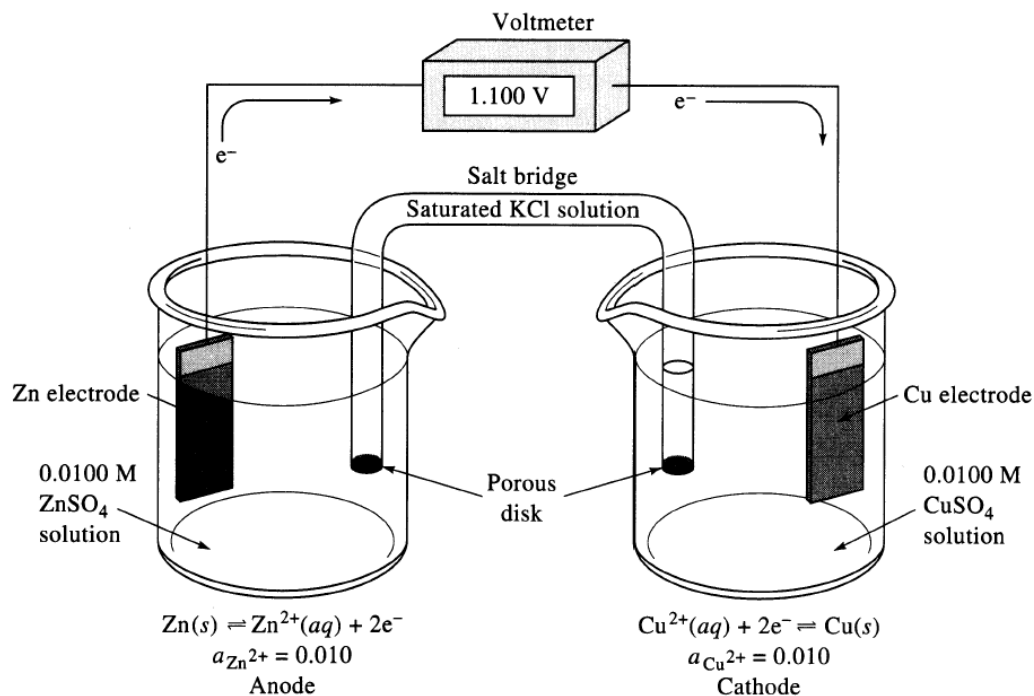# C.) Electrochemical Cell:

1) Basic Set-up:

a) Two electrodes

b) electrolytes solution

c) external connection between electrodes (wire)

d) internal connection via contact with a common solution or by different solutions connected by a <u>salt bridge</u>.

<u>salt bridge</u> – acts to isolate two halves of electrochemical cell while allowing migration of ions and current flow.

- usually consists of a tube filled with potassium chloride
- separate species to prevent direct chemical reactions

Voltmeter

1.100 V

Salt bridge
Saturated KCl solution

Zn electrode

Cu electrode

0.0100 M
ZnSO$_4$
solution

Porous
disk

0.0100 M
CuSO$_4$
solution

$Zn(s) \rightleftharpoons Zn^{2+}(aq) + 2e^-$
$a_{Zn^{2+}} = 0.010$
Anode

$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$
$a_{Cu^{2+}} = 0.010$
Cathode

2) Flow of current (charge) in cell:

a) electrons (e⁻) within wires between two electrodes

b) ions within solution of each ½ cell (anions & cations) and through salt bridge

c) electrochemical reactions at electrode
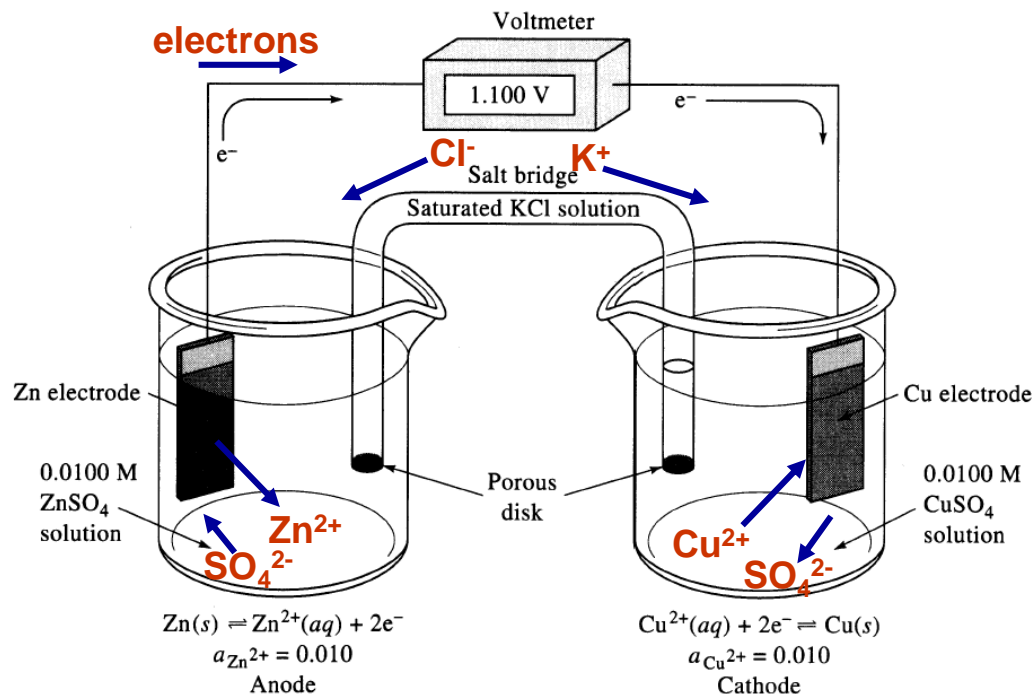
At Cu electrode: $Cu^{2+} + 2e^- \leftrightarrow Cu(s)$ → *reduction* – gain of e^- net <u>decrease</u> in charge of species

At Zn electrode: $Zn(s) \leftrightarrow Zn^{2+} + 2e^-$ → *oxidation* – loss of e^- net <u>increase</u> in charge of species

3) Net Reaction in Cell – *sum of reactions occurring in the two ½ cells*

$$Zn(s) \leftrightarrow Zn^{2+} + 2e^-$$

$$\underline{Cu^{2+} + 2e^- \leftrightarrow Cu(s)}$$

$$Cu^{2+} + Zn(s) \leftrightarrow \quad Zn^{2+} + Cu(s)$$
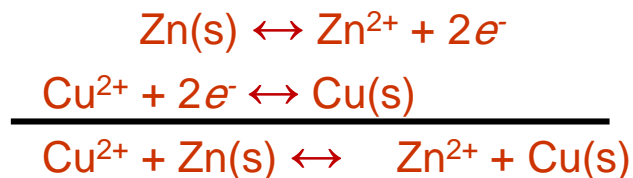
<u>Potential of overall cell</u> = measure of the tendency of this reaction to proceed to equilibrium

at equilibrium, potential (E_{cell}) = 0

∴ Larger the potential, the further the reaction is from equilibrium and the greater the driving force that exists

4) Types of Cells:

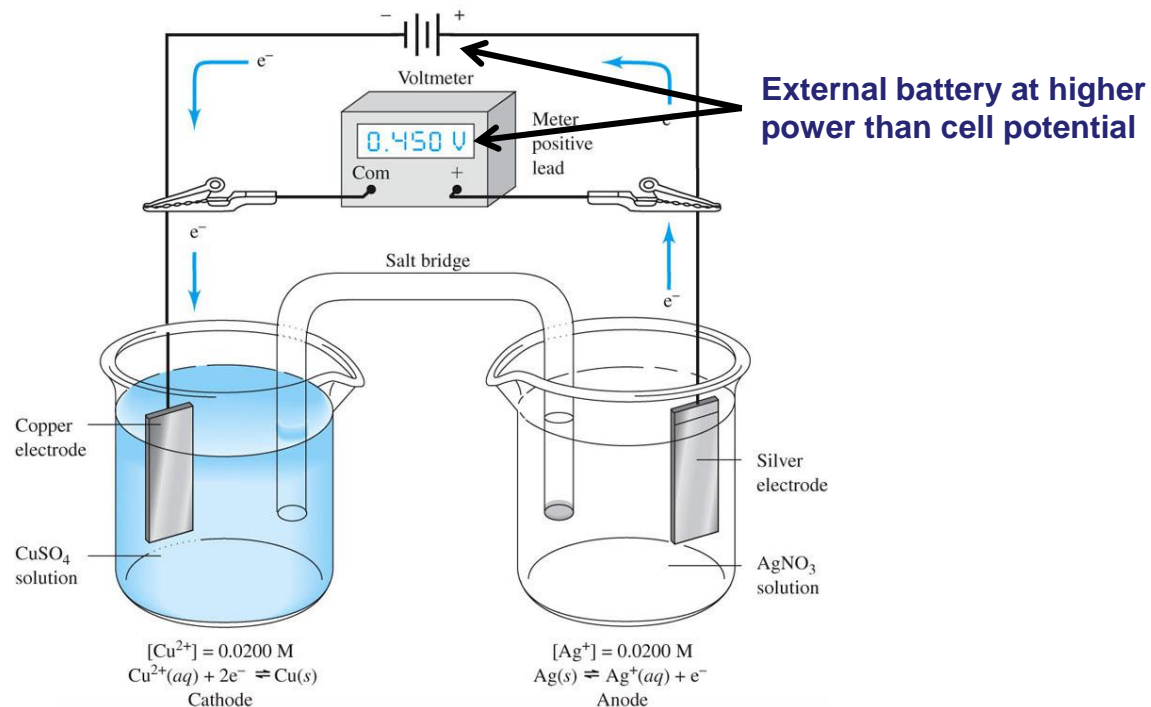Galvanic Cells (or voltaic cell) – reaction occurs naturally

- positive potential (E_{cell} = +)

- exothermic → produces energy
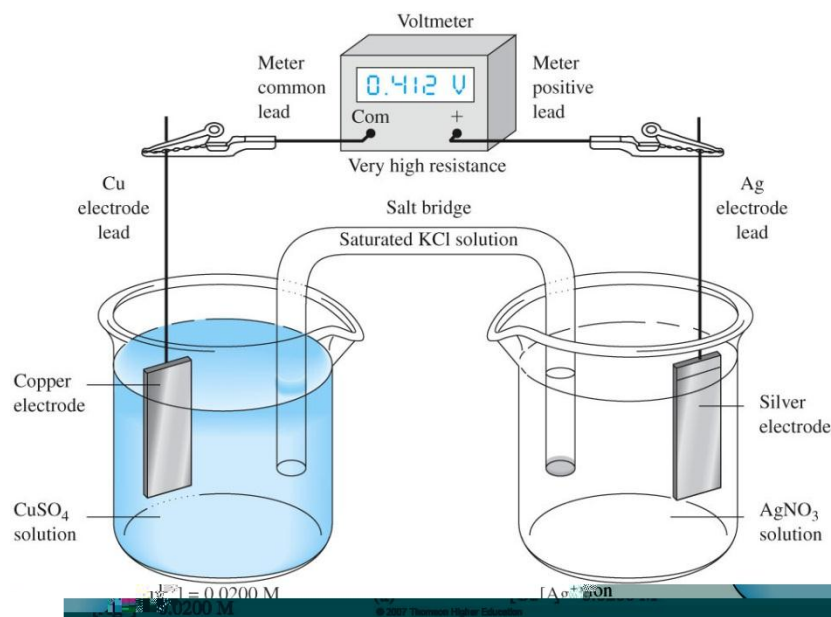
Galvanic Cell

Electrolytic Cells – reaction does not occur naturally, requires external
stimulus (energy) to occur
- negative potential (E_{cell} = -)
- endothermic → requires energy

**External battery at higher
power than cell potential**

Voltmeter

0.450 V

Meter
positive
lead

Com   +

Salt bridge

Copper
electrode

Silver
electrode

$CuSO_4$
solution

$AgNO_3$
solution

$[Cu^{2+}]$ = 0.0200 M
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$
Cathode

$[Ag^+]$ = 0.0200 M
$Ag(s) \rightleftharpoons Ag^+(aq) + e^-$
Anode

Electrolytic Cell

Chemically Reversible Cell – a cell in which reversing the direction of the
current simply reverses the chemical reaction

5) *Electrodes:*

a) <u>Cathode</u> – electrode where *reduction* occurs

<u>Anode</u> – electrode where *oxidation* occurs
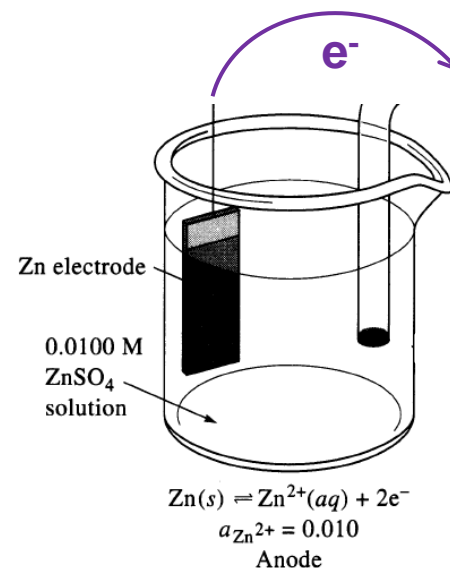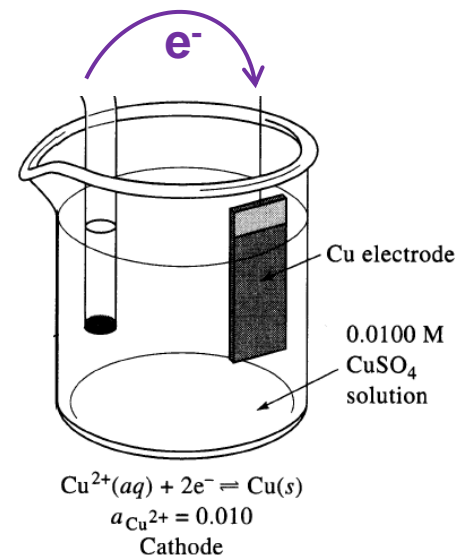
b) Examples of cathode ½ reactions:

$$Cu^{2+} + 2e^- \longleftrightarrow Cu(s)$$

$$Fe^{3+} + e^- \longleftrightarrow Fe^{2+}$$

$$AgCl(s) + e^- \longleftrightarrow Ag(s) + Cl^-$$

- e^- supplied by electrical current via electrode
- species (products/reactants) can both be in solution (Fe^{3+}/Fe^{2+}) solids or coated on electrodes (AgCl(s)/Ag(s) or combination ($Cu^{2+}/Cu(s)$)

Cu electrode

0.0100 M
$CuSO_4$
solution

$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$
$a_{Cu^{2+}} = 0.010$
Cathode

c) Examples of anode ½ reactions:

$$Cu(s) \longleftrightarrow Cu^{2+} + 2e^-$$

$$Fe^{2+} \longleftrightarrow Fe^{3+} + e^-$$

$$Ag(s) + Cl^- \longleftrightarrow AgCl(s) + e^-$$

- e^- is taken up by electrode into electrical circuit

Zn electrode

0.0100 M
$ZnSO_4$
solution

$Zn(s) \rightleftharpoons Zn^{2+}(aq) + 2e^-$
$a_{Zn^{2+}} = 0.010$
Anode

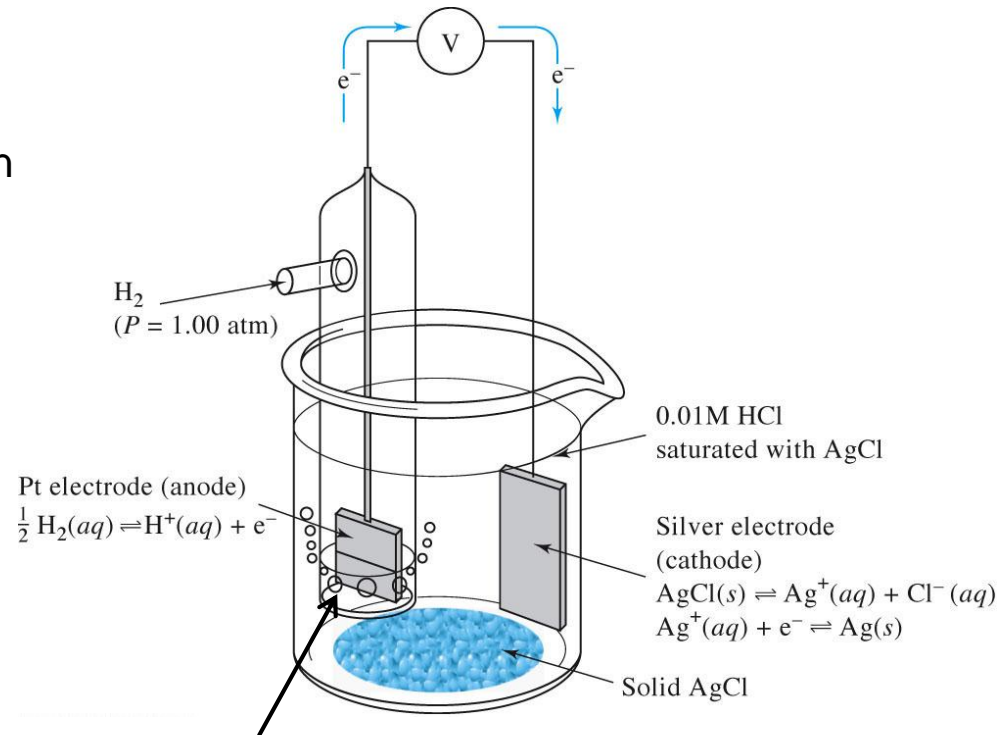d) <u>Liquid junctions</u> – interface between two solutions with different components or concentrations

The phase boundary between an electrode and its solution is called an **interface**.

Small potentials may develop at junction that affect overall cell potential

Voltmeter

1.100 V

e⁻

e⁻

Salt bridge
Saturated KCl solution

Zn electrode

Cu electrode

0.0100 M
ZnSO$_4$
solution

Liquid Junction

0.0100 M
CuSO$_4$
solution

$Zn(s) \rightleftharpoons Zn^{2+}(aq) + 2e^-$
$a_{Zn^{2+}} = 0.010$
Anode

$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$
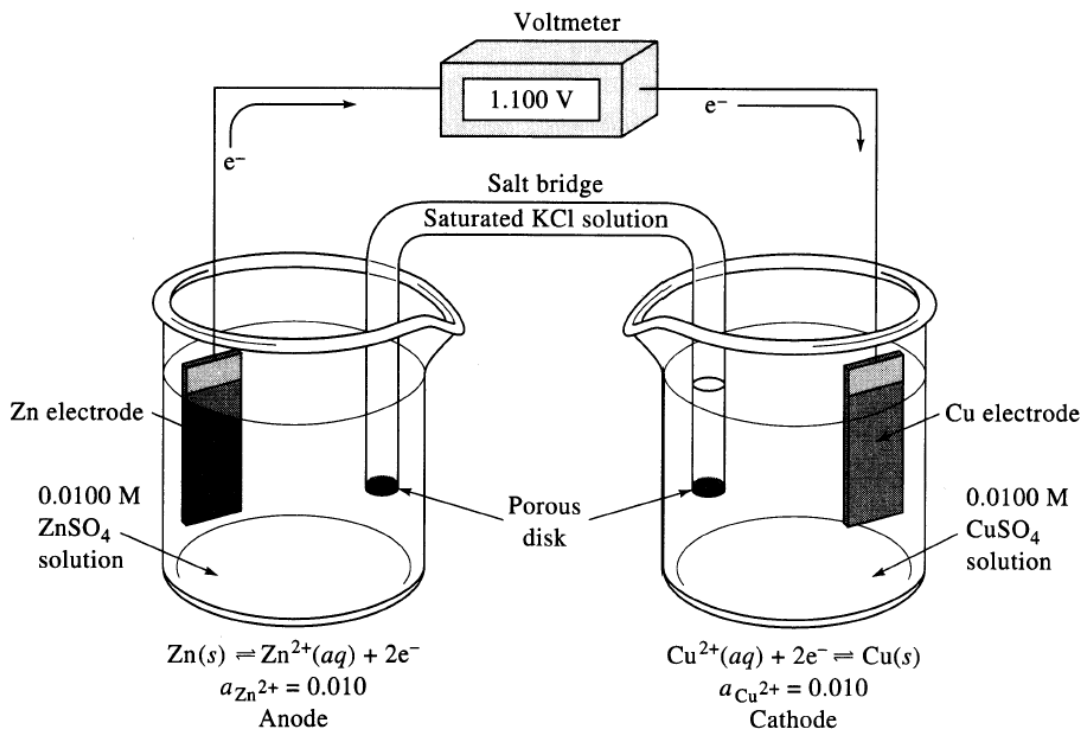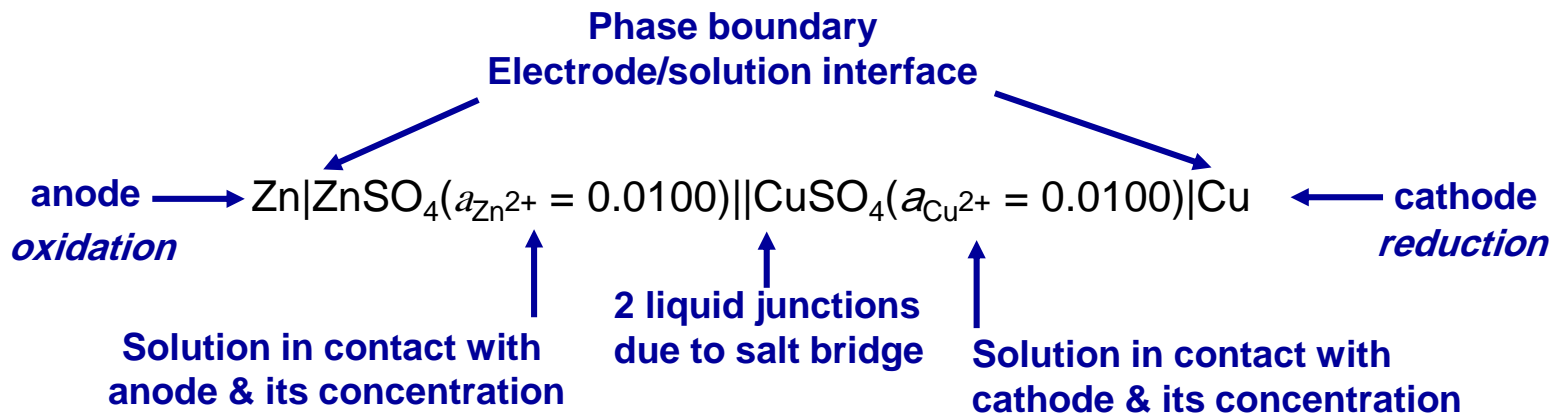$a_{Cu^{2+}} = 0.010$
Cathode
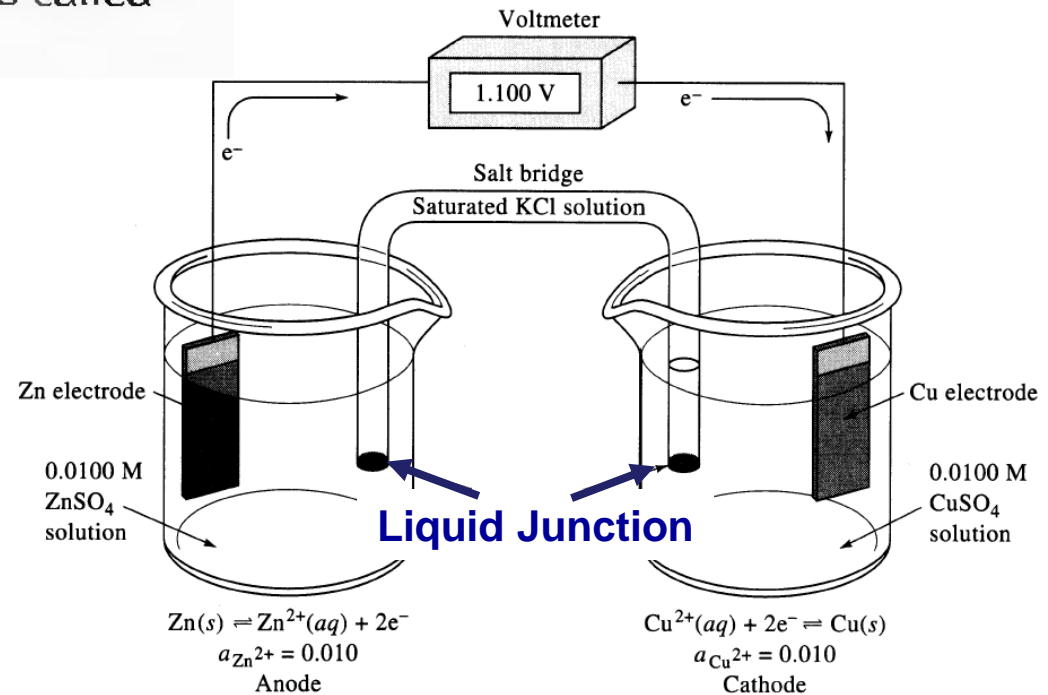
Galvanic cell *without* liquid junction

- Two species have high potential for reaction, but the reaction is slow
- mix two species directly into common solution
- not common

H$_2$
($P = 1.00$ atm)

0.01M HCl
saturated with AgCl

Pt electrode (anode)
$\frac{1}{2}$ H$_2$(aq) $\rightleftharpoons$ H$^+$(aq) + e$^-$

Silver electrode
(cathode)
AgCl(s) $\rightleftharpoons$ Ag$^+$(aq) + Cl$^-$(aq)
Ag$^+$(aq) + e$^-$ $\rightleftharpoons$ Ag(s)

Solid AgCl

Bubble Hydrogen into a solution of AgCl

e) Representation of Cells: by convention start with anode on left

**Phase boundary
Electrode/solution interface**

anode $\longrightarrow$ $Zn|ZnSO_4(a_{Zn^{2+}} = 0.0100)||CuSO_4(a_{Cu^{2+}} = 0.0100)|Cu$ $\longleftarrow$ **cathode**
oxidation *reduction*

**Solution in contact with
anode & its concentration**

**2 liquid junctions
due to salt bridge**

**Solution in contact with
cathode & its concentration**

Voltmeter

1.100 V

e^-

e^-

Salt bridge
Saturated KCl solution

Zn electrode

Cu electrode

0.0100 M
ZnSO$_4$
solution

Porous
disk

0.0100 M
CuSO$_4$
solution

$Zn(s) \rightleftharpoons Zn^{2+}(aq) + 2e^-$
$a_{Zn^{2+}} = 0.010$
Anode

$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$
$a_{Cu^{2+}} = 0.010$
Cathode

f) Electrode Potentials

1) for convenience, represent overall reaction in cell as two ½ reactions

  i. one at anode & other at cathode

  ii. each ½ reaction has certain potential associated with it

  iii. by convention, write both ½ reactions as reduction:

$$Cu^{2+} + 2e^- \leftrightarrow Cu(s) \quad (E_{cathode})$$

$$Zn^{2+} + 2e^- \leftrightarrow Zn(s) \quad (-E_{anode})$$

  iv. potential of cell is then defined as:

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

TABLE 22-1 Standard Electrode Potentials

Reaction	E^0 at 25°C, V
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl_2$	+1.359
$O_2(g) + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.229
$Br_2(aq) + 2e^- \rightleftharpoons 2Br_2$	+1.087
$Br_2(l) + 2e^- \rightleftharpoons 2Br_2$	+1.065
$Ag^+ + e^- \rightleftharpoons Ag(s)$	+0.799
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0.771
$I_3^- + 2e^- \rightleftharpoons 3I^-$	+0.536
$Cu^{2+} + 2e^- \rightleftharpoons Cu(s)$	+0.337
$Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2Hg(l) + 2Cl_2$	+0.268
$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl_2$	+0.222
$Ag(S_2O_3)_2^{3-} + e^- \rightleftharpoons Ag(s) + 2S_2O_3^{2-}$	+0.010
$2H^+ + 2e^- \rightleftharpoons H_2(g)$	0.000
$AgI(s) + e^- \rightleftharpoons Ag(s) + I_2$	−0.151
$PbSO_4(s) + 2e^- \rightleftharpoons Pb(s) + SO_4^{2-}$	−0.350
$Cd^{2+} + 2e^- \rightleftharpoons Cd(s)$	−0.403
$Zn^{2+} + 2e^- \rightleftharpoons Zn(s)$	−0.763

2) – can not measure potential of just one electrode.
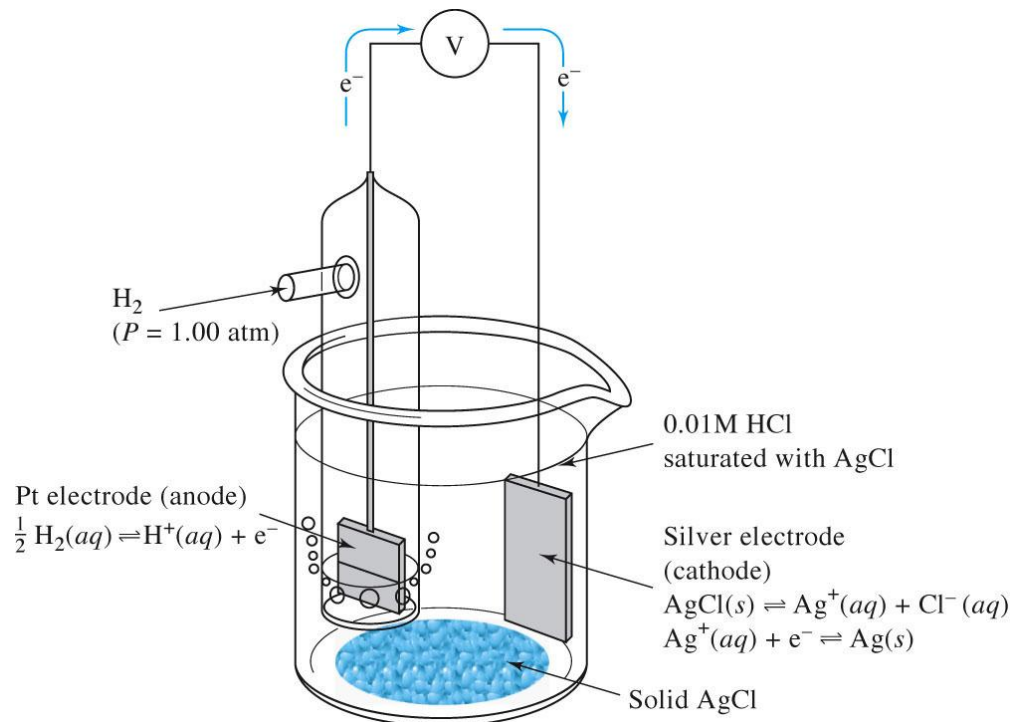   i. need to compare to another electrode
    ii. determine potential of all ½ cell reactions vs. a *common* reference electrode
    iii. reference electrode – *standard hydrogen electrode* (SHE)

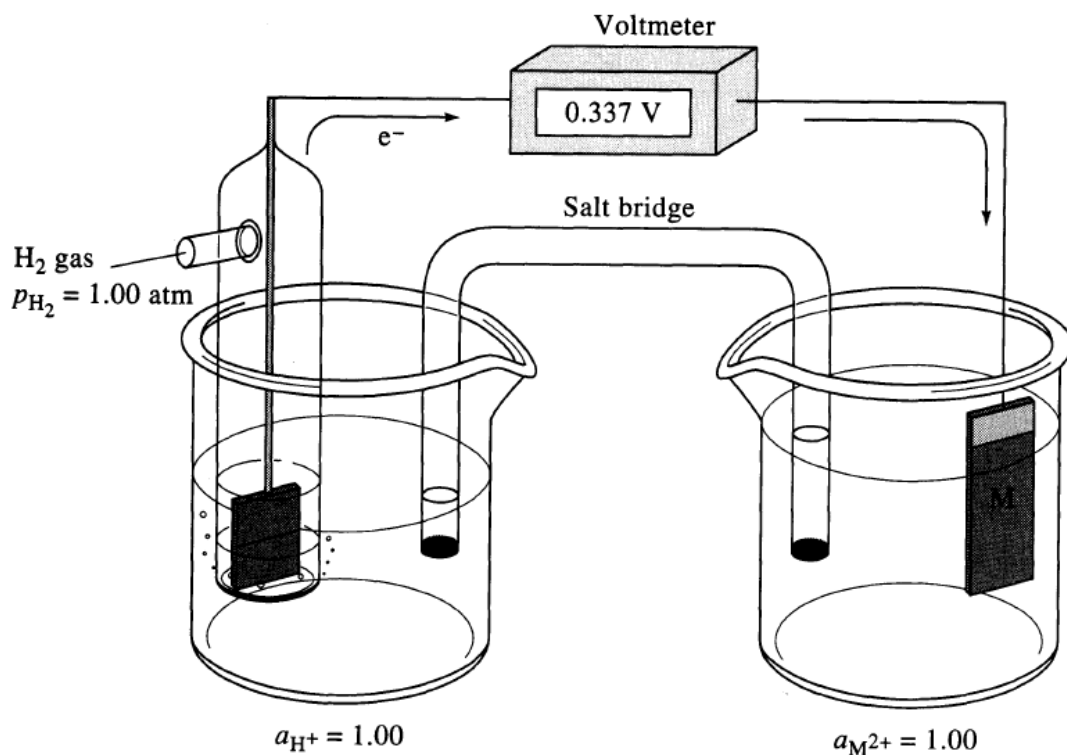$$Pt, H_2(p \text{ atm})|H+(a_{H+} = x)$$

$$2H^+ + 2e^- \longleftrightarrow H_2(g)$$

stream of H_2 keeps surface at electrode saturated with $H_2(g)$

note: potential affected by pH, [H⁺], used as an early pH indicator, also dependent on P_{H2}

H_2
$(P = 1.00 \text{ atm})$

0.01M HCl
saturated with AgCl

Pt electrode (anode)
$\frac{1}{2} H_2(aq) \rightleftharpoons H^+(aq) + e^-$

Silver electrode
(cathode)
$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$

Solid AgCl

By convention, E_{SHE} = 0.0 V at [H$^+$] = 1M, P_{H2} = 1 atm and at all temperatures.

Voltmeter

0.337 V

e^-

Salt bridge

H$_2$ gas
p_{H_2} = 1.00 atm

a_{H^+} = 1.00

$a_{M^{2+}}$ = 1.00

Potentials of other electrodes are compared to SHE using electrode in question as cathode and SHE as anode:

$$M^{n+} + ne^- \longleftrightarrow M(s)$$
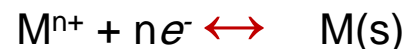
$$E_{cell} = E_{cathode} - E_{anode}$$
$$E_{cell} = E_{cathode} - E_{SHE}$$

By definition:

$$E_{cell} = E_{cathode} - 0$$
$$E_{cell} = E_{cathode}$$

E_{cell} is related to the free energy of the reaction ΔG by

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

(18-6)

<u>Standard Electrode Potential (E^o)</u> : measured E_{cell} when all species in solution or gas has an activity of 1.00

<u>Activity (a)</u> : *proportional* to molar concentration

$$a_x = \gamma_x[X]$$

where:

γ_x is the activity coefficient of solute X

[X] is the molar concentration of solute X

If E^o is "+", it indicates that the reaction:

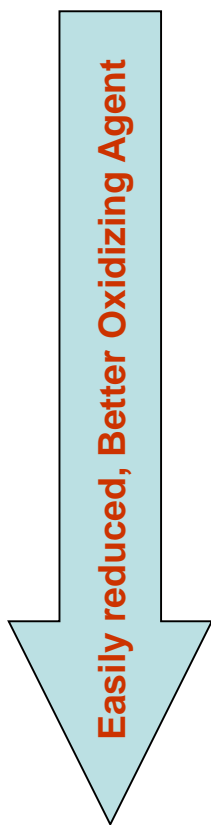$$M^{n+} + n/2H_2(g) \longleftrightarrow M(s) + nH^+$$

is favored or spontaneous.

M^{n+} is readily <u>reduced</u> by $H_2(g)$ $\therefore$ M^{n+} is better e^- acceptor or <u>oxidizing agent.</u>
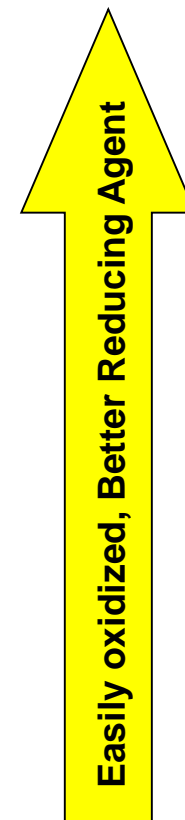
If E^o is "-", it indicates that the reaction is not favored or spontaneous and requires energy to proceed

M(s) is readily <u>oxidized</u> by H^+ $\therefore$ M(s) is better e^- donor or <u>reducing agent.</u>

As E^o increases → oxidizing ability of ½ cell reaction increases

Reaction at Interface	Half-cell Potential (E^o)
$Al^{3+} + 3e^- \rightarrow Al$	-1.706 V
$Zn^{2+} + 2e^- \rightarrow Zn$	-0.763 V
$Cr^{3+} + 3e^- \rightarrow Cr$	-0.744
$Fe^{2+} + 2e^- \rightarrow Fe$	-0.409V
$Cd^{2+} + 2e^- \rightarrow Cd$	-0.401 V
$Ni^{2+} + 2e^- \rightarrow Ni$	-0.230 V
$Pb^{2+} + 2e^- \rightarrow Pb$	-0.126 V
$2H^+ + 2e^- \rightarrow H_2$	0.00 V
$AgCl + e^- \rightarrow Ag + Cl^-$	+0.223 V
$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	+0.268 V
$Cu^{2+} + 2e^- \rightarrow Cu$	+0.340 V
$Ag^+ + e^- \rightarrow Ag$	+0.799 V
$Au^+ + e^- \rightarrow Au$	+1.680 V

Easily reduced, Better Oxidizing Agent

Easily oxidized, Better Reducing Agent

Nernst Equation

Values of $E_{electrodes}$ can also be calculated at other concentrations (activities) of species

Consider the reversible half-reaction

$$a\mathrm{A} + b\mathrm{B} + \cdots + ne^- \rightleftharpoons c\mathrm{C} + d\mathrm{D} + \cdots \qquad (18\text{-}10)$$

$$E = E^0 - \frac{RT}{nF} \ln \frac{[\mathrm{C}]^c[\mathrm{D}]^d \cdots}{[\mathrm{A}]^a[\mathrm{B}]^b \cdots} \qquad (18\text{-}11)$$

where:

   R = ideal gas constant (8.316 J mol^{-1} K^{-1})

   T = absolute temperature (K)

   n = number of electrons in process

   F = Faraday's constant (96487 C mol^{-1})

At room Temperature,

Also, using $\log_{10}$:

$$E = E^0 - \frac{0.0592}{n} \log \frac{[C]^c [D]^d \cdots}{[A]^a [B]^b \cdots} \qquad (18\text{-}12)$$

If know E^o, allows $E_{electrode}$ to be calculated under non-standard conditions.

Note: If all activity (concentrations) values = 1, $E_{electrode} = E^o$

Once have $E_{cathode}$ & $-E_{anode}$ by above procedure, can also get E_{cell}:

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

may need to also include junction potential, etc., but good first approximation

EXAMPLE 18-2

Typical half-cell reactions and their corresponding Nernst expressions follow.

(1) $Zn^{2+} + 2e^- \rightleftharpoons Zn(s)$ $E = E^0 - \dfrac{0.0592}{2} \log \dfrac{1}{[Zn^{2+}]}$

No term for elemental zinc is included in the logarithmic term because it is a pure second phase (solid). Thus, the electrode potential varies linearly with the logarithm of the reciprocal of the zinc ion concentration.

(2) $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}(s)$ $E = E^0 - \dfrac{0.0592}{1} \log \dfrac{[Fe^{2+}]}{[Fe^{3+}]}$

The potential for this couple can be measured with an inert metallic electrode immersed in a solution containing both iron species. The potential depends on the logarithm of the ratio between the molar concentrations of these ions.

(3) $2H^+ + 2e^- \rightleftharpoons H_2(g)$ $E = E^0 - \dfrac{0.0592}{2} \log \dfrac{P_{H_2}}{[H^+]^2}$

In this example, p_{H_2} is the partial pressure of hydrogen (in atmospheres) at the surface of the electrode. Usually, its value will be the same as atmospheric pressure.

(4) $MnO_4^- + 5e^- + 8H^+ \rightleftharpoons Mn^{2+} + 4H_2O$

$$E = E^0 - \dfrac{0.0592}{5} \log \dfrac{[Mn^{2+}]}{[MnO_4^-][H^+]^8}$$
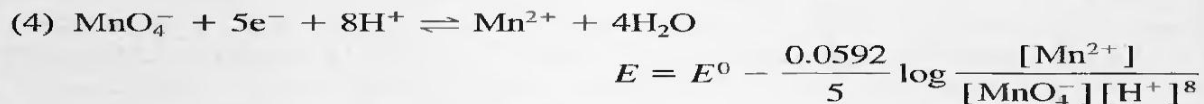
In this situation, the potential depends not only on the concentrations of the manganese species but also on the pH of the solution.

(5) $AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-$ $E = E^0 - \dfrac{0.0592}{1} \log [Cl^-]$

This half-reaction describes the behavior of a silver electrode immersed in a chloride solution that is *saturated* with AgCl. To ensure this condition, an excess of the solid AgCl must always be present. Note that this electrode reaction is the sum of the following two reactions:

$$AgCl(s) \rightleftharpoons Ag^+ + Cl^-$$

$$Ag^+ + e^- \rightleftharpoons Ag(s)$$

Note also that the electrode potential is independent of the amount of AgCl present as long as there is at least some present to keep the solution saturated.

EXAMPLE 18-3

Calculate the electrode potential of a silver electrode immersed in a 0.0500 M solution of NaCl using (a) $E^0_{Ag^+/Ag} = 0.799$ V and (b) $E^0_{AgCl/Ag} = 0.222$ V.

(a) $Ag^+ + e^- \rightleftharpoons Ag(s)$ $E^0_{Ag^+/Ag} = +0.799$ V

The Ag^+ concentration of this solution is given by

$$[Ag^+] = \frac{K_{sp}}{[Cl^-]} = \frac{1.82 \times 10^{-10}}{0.0500} = 3.64 \times 10^{-9} \text{ M}$$

Substituting into the Nernst expression gives

$$E = 0.799 - 0.0592 \log \frac{1}{3.64 \times 10^{-9}} = 0.299 \text{ V}$$

(b) Here we may write

$$E = 0.222 - 0.0592 \log [Cl^-] = 0.222 - 0.0592 \log 0.0500$$
$$= 0.299 \text{ V}$$

Limitations in the Use of Standard Electrode Potentials (E^o):

a.) E^O based on unit *activities* not *concentrations*

- activity = concentration only in dilute solutions
- at higher concentrations need to determine and use activity
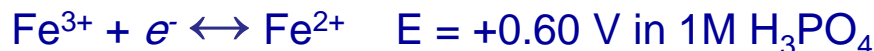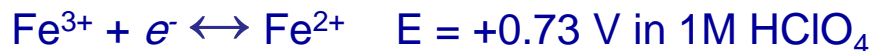
$$a_X = \gamma_X[X]$$

- example:

$$Fe^{3+} + e^- \longleftrightarrow Fe^{2+} \quad E^0 = +0.771 \text{ V}$$
but E at 1M is +0.732 V, since $\gamma < 1$

- problem if γ not known from calculations or previous experimental studies

b.) Side Reactions can Affect E^o apparent:

- example:

$$Fe^{3+} + e^- \longleftrightarrow Fe^{2+} \quad E = +0.73 \text{ V in 1M } HClO_4$$

$$Fe^{3+} + e^- \longleftrightarrow Fe^{2+} \quad E = +0.70 \text{ V in 1M } HCl$$

$$Fe^{3+} + e^- \longleftrightarrow Fe^{2+} \quad E = +0.60 \text{ V in 1M } H_3PO_4$$

reason: Fe^{2+} & Fe^{3+} form different complexes with Cl^- & PO_4^- that affects net activity of Fe^{2+} and Fe^{3+} in solution

Formal Potential (E^f or E$^{o'}$):

A **formal potential** is the electrode potential when the ratio of **analytical concentrations** of reactants and products of a half-reaction is exactly 1.00 and the molar concentrations of any other solutes are specified.

8.) Reaction Rates:

- some E^o ½ reactions listed in tables have been determined by calculations from *equilibrium* measurements rather than actual measurements of the ½ cell in an electrode system.

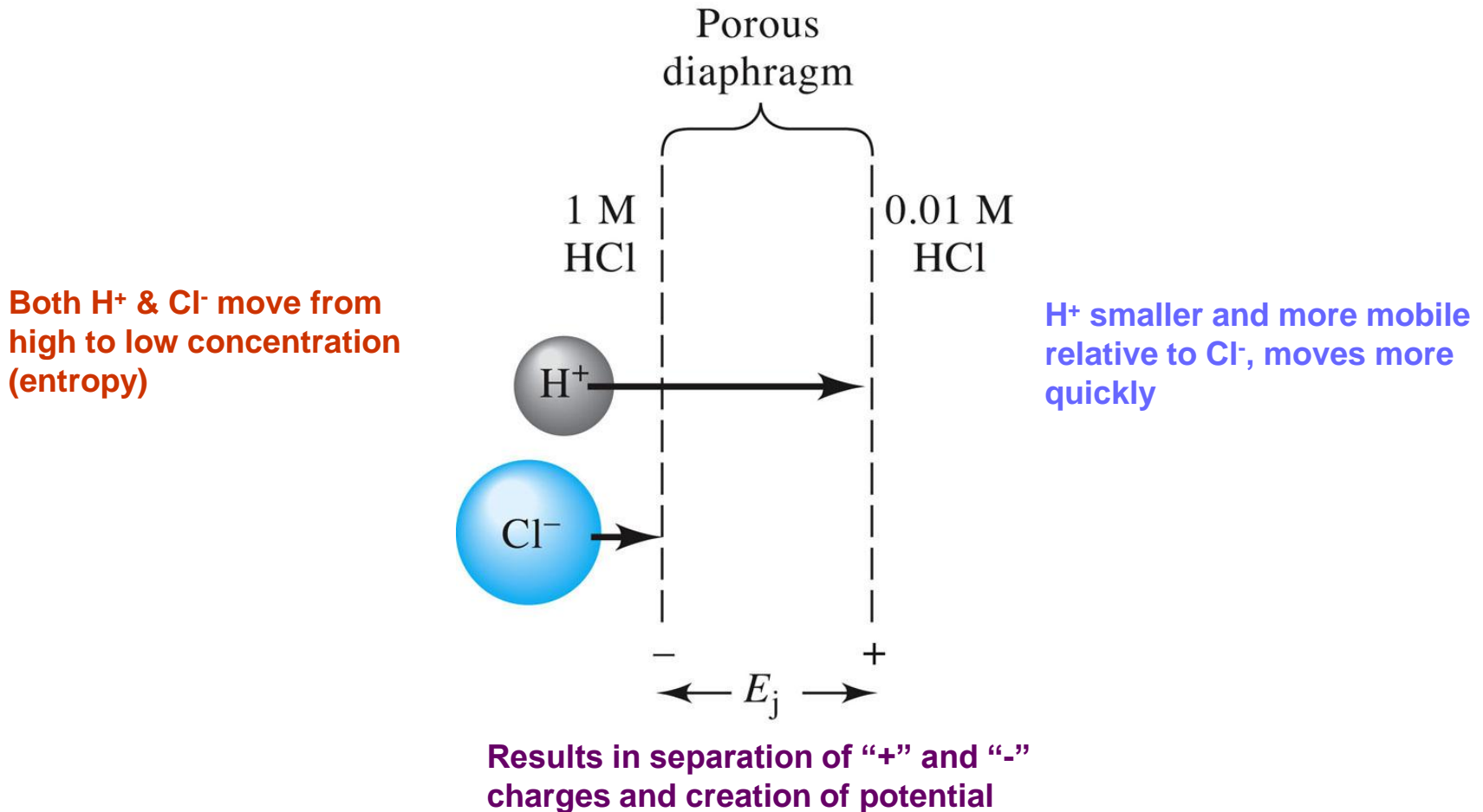$$e.g. \ 2CO_2 + 2H^+ + 2e^- \leftrightarrow H_2C_2O_4 \quad E^0 = -0.49 \ V$$

- *problem*

② reaction is slow and difficult to see in practice

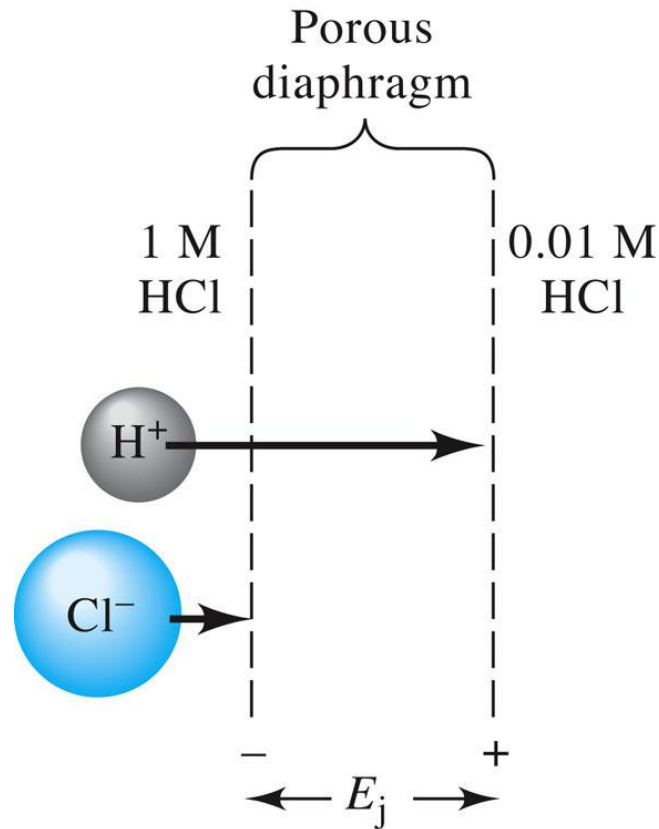② thermodynamics vs. kinetics

② no suitable electrode

- potentially useful for computational purposes

Liquid Junction Potential

- potential that develops whenever two electrolytes of different ionic composition come into contact
- due to the unequal distribution of cations & anions across a boundary as a result of the differences in rates at which ions migrate.

Porous diaphragm

1 M HCl | 0.01 M HCl

H^+

Cl^-

$\xleftarrow{\hspace{1cm}} E_j \xrightarrow{\hspace{1cm}}$

−   +

Both H^+ & Cl^- move from high to low concentration (entropy)

H^+ smaller and more mobile relative to Cl^-, moves more quickly

Results in separation of "+" and "-" charges and creation of potential

Note: **Equilibrium condition soon develops**

- junction potential can be ≥ 30 mV

- can decrease the junction potential by using salt bridge containing
  concentrated electrolyte

    ② best if mobility of ions are ~ equal

    ② 4 M KCl or KNO_3

    ② decrease junction potential to ≤ few mV